3.01
Boron-containing Rings Ligated to Metals

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3.01.1 Background

Metal complexes of boron ring systems form an extensive area of research that overlaps with and connects three large fields: organometallic chemistry, organic heterocycles, and the metallacarboranes. This area of chemistry was already well developed prior to 1993, as summarized by Herberich in COMC (1995);[1] since then it has been extensively investigated and expanded with the discovery of new ring ligands and synthetic routes, novel molecular architectures, and applications in synthesis, especially catalysis.[2] In general, the most important advances during this period fall into one or more of these categories, and encompass a variety of five- to eight-membered ring systems that are coordinated to a range of main group and transition metals. Figure 1 presents a selection of the more important ring ligands, represented as neutral and/or anionic species. This chapter is concerned with metal complexes, and will not, in

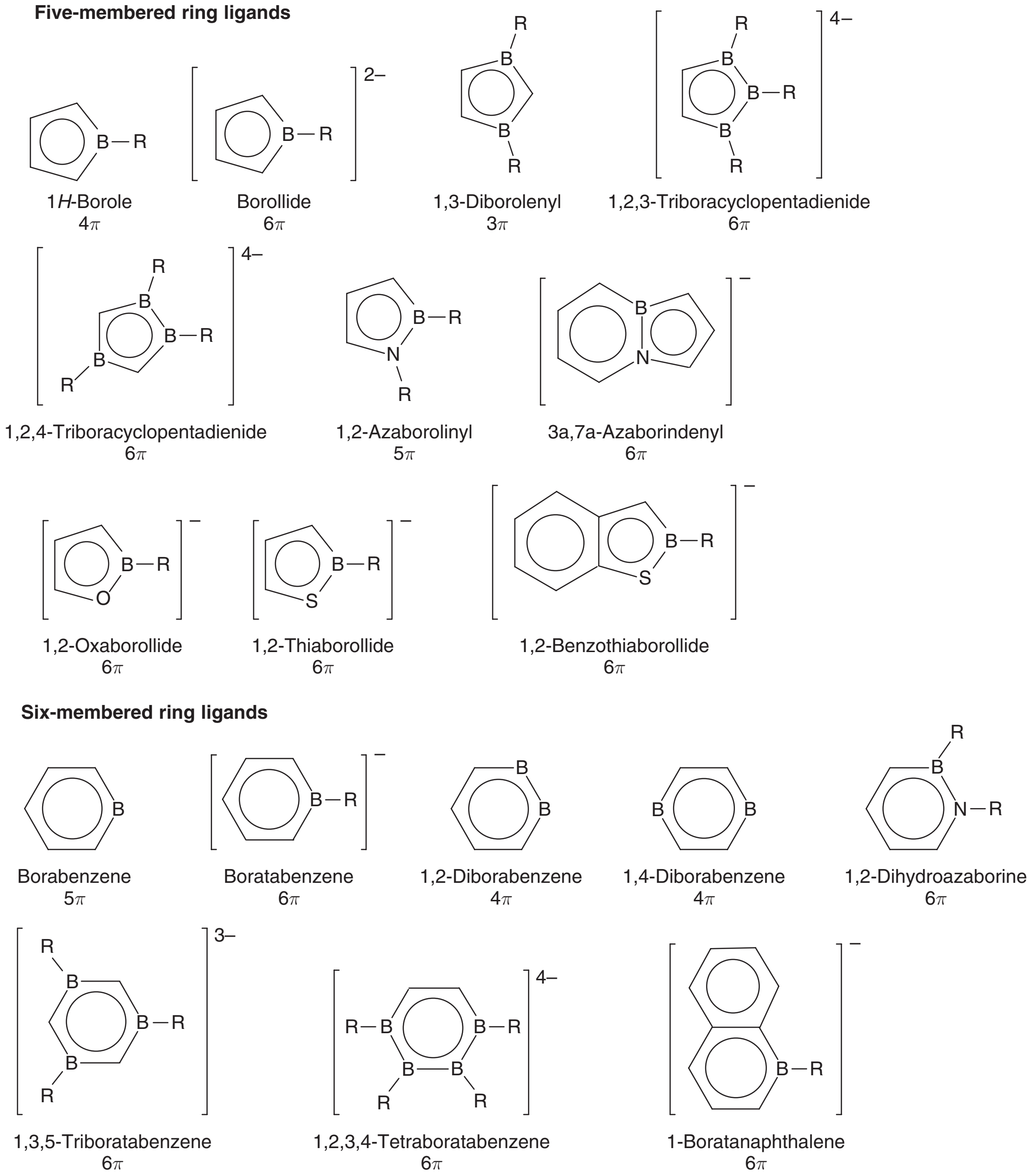


Figure 1 Ring ligands. Reproduced with permission from the American Chemical Society.

general, cover the synthesis and nonmetal chemistry of the ligands *per se*; in most cases, references dealing with those aspects can be found in the references cited herein.

3.01.2 Complexes of C_4B Rings

3.01.2.1 Mononuclear and Dinuclear Complexes of C_4B Rings (Double-Decker and Triple-Decker Sandwiches)

The chemistry of metal–borole and metal–borollide sandwich compounds has been significantly advanced since the publication of COMC (1995) (see Table 1). Herberich and his group have prepared a variety of novel complexes of planar C_4B ligands including (i) multinuclear heterometallic systems containing Re–Hg, Re–Cu, Re–Ag, Re–Au, and Fe–Pt bonds;[3] (ii) CN-bridged chains;[4] (iii) Fe–Au heterometallic complexes;[5] (iv) intramolecular Fe–H–B hydrogen-bonded species that reversibly rearrange to Fe–H–C systems;[6] and (v) several types of triple-decker sandwich complexes involving Co, Rh, Mn, Ru, and Li.[7–12] Compounds **1–5** are representative.

Table 1 Complexes of C_4B rings 1993–2005

Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Mononuclear C_4B ring complexes (double-decker sandwiches)		
Lithium		
$[(Et_2O)\mathbf{Li}]_2[H_6(C_6H_{12}-C_6H_4)(CMe_3)C_{12}B-C_6H_3(C_6H_{12}-C_6H_4)]$ 9-borafluorene complex	S, X, H, B, C	19
Tantalum		
$Cp^*R_2\mathbf{Ta}[H_4C_4B-N(CHMe_2)_2]$ ($R = Me$, $MeC{=}NAr$, H_2PMe_3, Cl_2, $ClMe$)	S, X	13
$(Me_3P)Me_3\mathbf{Ta}[H_4C_4B-N(CHMe_2)_2]$	S, H, C	21
$[\eta^5-H_4C_4B-N(CHMe_2)_2]\mathbf{Ta}[\eta^2-MeCN(C_6H_3Me_2)-(\eta^3-C_6H_3Me_2)NCHCH_2C(Me)N(C_6H_3Me_2)]$	S, X, H, C	21
$Cp^*Me_2\mathbf{Ta}(H_4C_4B-Me)$	S, X	15
$Cp^*Me_2\mathbf{Ta}[H_4C_4B-N(CHMe_2)_2]$	S	15
$Cp^*(PMe_3)_2\mathbf{Ta}(H_4C_4B-R)$ [$R = N(CHMe_2)_2$, Me]	S, X(Me)	15
$Cp^*(PMe_3)H_2\mathbf{Ta}(H_4C_4B-R)$ [$R = N(CHMe_2)_2$, Me]	S	15
$Cl_3\mathbf{Ta}[H_4C_4B-N(CHMe_2)_2]$	S, X, H, C, IR	16
$[H_4C_4B-N(CHMe_2)_2]\mathbf{Ta}Cl_2[C(SiMe_3)_2H]$	S, X, H, C, IR	16
$Cl_2(R_2C_6H_3-N{=})\mathbf{Ta}[H_4C_4B-N(CHMe_2)H]$	S, X, H, C, IR	16
$Cl_3(OCMe_2CH_2CMe{=}O)\mathbf{Ta}[H_4C_4B-N(CHMe_2)H]$	S, X, H, C, IR	16
Other $\mathbf{Ta}(H_4C_4B-R)$ complexes		16
Zirconium and Hafnium		
$Cp^*\mathbf{M}[Me_4C_4B-N(CHMe_2)_2](\mu-Cl)_2Li(OEt_2)_2$ ($\mathbf{M} = \mathbf{Zr}, \mathbf{Hf}$)	S, X(Zr)	18
$Cp^*\mathbf{M}[Me_4C_4B-NH(CHMe_2)_2](Cl)_2$ ($M = Zr$, Hf)	S, X(Zr)	18
$Cp^*ClL\mathbf{M}[H_5C_5B-N(CHMe_2)_2]$ ($\mathbf{M} = Zr$, Hf; $L = RO$, RS; $R = Me, C_6H_2Me_3$)	S, H, C, IR	18a
$Cp^*Cl(Me_3SiC{\equiv}C)\mathbf{Hf}[H_5C_5B-N(CHMe_2)_2]$	S, X, H, C, IR	18a
$Cp^*(Me_3SiC{\equiv}C)_2\mathbf{Hf}[H_5C_5B-N(CHMe_2)_2]$	S, X, H, C, IR	18a
$Cp^*ClL\mathbf{M}[H_5C_5B-N(CHMe_2)_2]$ ($\mathbf{M} = Zr$, Hf; $L = NMe_2H$, PMe_3)	S, X(PMe_3), H, C, IR	18a
$Cp^*(Me_3P)Cl\mathbf{Hf}[H_5C_5B-N(CHMe_2)_2]$	S, X, H, C, IR	18a
$Cp^*R_2\mathbf{Zr}[H_4C_4B-N(CHMe_2)_2]$ ($R = Me$, $C{\equiv}C-C_6H_4Me$, $C{\equiv}C-CMe_3$, CH_2Ph)	S, H, C	17
$Cp^*I\mathbf{Zr}[H_4C_4B-N(CHMe_2)_2]$	S, H, C	17
$Cp^*(C_3H_7)\mathbf{M}[H_4C_4B-N(CHMe_2)_2]$ ($\mathbf{M} = \mathbf{Zr}, \mathbf{Hf}$)	S, X(Hf), H, C, UV	17
$Cp^*(C_3H_7)(L)\mathbf{Hf}[H_4C_4B-N(CHMe_2)_2]$ ($L = CO$, PMe_3, NC_5H_5)	S, X(CO), H, C, I	17
$Cp^*(PMe_3)(H)\mathbf{Hf}[H_4C_4B-N(CHMe_2)_2]$	S, H	17
$[1,3-C_5H_3(SiMe_3)_2](Et_2O)(C_6F_5)\mathbf{Zr}(H_4C_4B-R)$ ($R = H$, Me)	S, X, H, F, ethylene polymerization catalysis	14a

(*Continued*)

Table 1 (Continued)

Compound[a]	*Information*[b]	*References*
[1,3-$C_5H_3(SiMe_3)_2$](R′CN)(C_6F_5)**Zr**(3-RH_3C_4B–C_6F_5) (R = H, Me; R′ = Me, CMe_3)	S, X(H, CMe_3), H, B, C, F	14
[1,3-$C_5H_3(SiMe_3)_2$]($(Me_3CNC)_2$)(C_6F_5)**Zr**(3-RH_3C_4B–C_6F_5) (R = H, Me)	S, H, B, C, F	14
[1,3-$C_5H_3(SiMe_3)_2$](Me_3CNC)(C_6F_5–C═N–CMe_3)**Zr**(3-RH_3C_4B–C_6F_5) (R = H, Me)	S, X(H), H, B, C, F	14
Rhenium		
$(CO)_3$(H_4C_4B–Ph)**Re**—HgCl	S, H, C, IR, MS	3
$(CO)_3$(H_4C_4B–Ph)**Re**—L [L = $Cu(PPh_3)_2$, $AgPPh_3$, $AuPPh_3$]	S, H, C, IR, MS	3
Iron		
$(CO)_3$**Fe**($Me_2H_2C_4B$–Ph)	S, H, B, C, IR, MS	6
Cp**Fe**(H_4C_4B–Ph)	S, E, ESR	6
$(Me_3CNC)_3$**Fe**(H_4C_4B–Ph)	S, H, B, C, IR, MS	6
(η^4-C_5H_6)(CO)**Fe**($Me_2H_2C_4B$–Ph)	S, H, B, C, IR, MS	6
(η^4-C_5H_6)(Me_3CNC)**Fe**($Me_2H_2C_4B$–Ph)	S, H, B, C, IR, MS	6
(η^5-C_5H_4R'')**Fe**($R_2R'_2C_4B$–Ph) (R″ = H, Me; R′ = H, Me, CH_2═$CH(CH_2)_4$, $(CH_2)_2CHCH_2$; R = H, Me)	S, X(H, Me, Me; Me, Me, H), H, B, C, IR, E, MS	6
(H_4C_4B–Ph)**Fe**$(CO)_2$CN—Pt(CN)$(PEt_3)_2$ (four isomers)	S, X, H, C, P, Pt, IR, UV	4
[$(Ph_3P)_2Au_2$]$(CO)_2$**Fe**(H_4C_4B–Ph)	S, X, H, B, C, P, IR	5
{[$(Ph_3P)_3Au_3$]$(CO)_2$**Fe**(H_4C_4B–Ph)}$^+$ PF_6^-	S, X (wide-angle scattering), H, B, C, P, IR	5
(Ph_3P)H$(CO)_2$**Fe**(H_4C_4B–Ph)	S, H, P, IR	5
Cobalt		
Cp**Co**(H_4C_4BR) (R = H, Me)	He photoelectron (Me)	7
Rhodium		
Cp**Rh**(H_4C_4BR) (R = H, Me)	He photoelectron (Me)	7
(H_4C_4BR)**RhI**(H_4C_4BR) (R = Ph, Me)	S, H, B, C, MS	24
py_2**IRh**(H_4C_4B–Ph)	S, H, B, C, IR	8
(bpy)**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
$(MeCN)_2$**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
$(CO)_2$**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
$(Ph_3P)_2$**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
[$Fe(C_5H_4PPh_2)_2$]**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
(norbornadiene)**IRh**(H_4C_4B–Ph)	S, H, B, C, IR, MS	8
$(MeCN)_3$**Rh**(H_4C_4B–Ph)$^+$ BF_4^-	S, H, B, C, MS	9
$(py)_3$**Rh**(H_4C_4B–Ph)$^+$ BF_4^-	S, H, B, C, MS	9
$(C_6Me_3R_3)_3$**Rh**(H_4C_4B–Ph)$^+$ BF_4^- (R = H, Me)	S, H, B, C, MS	9
Dinuclear C_4B complexes (triple-decker sandwiches and dimers)		
Lithium		
[$(Me_2N)_2C_2H_4$]**Li**[(C_4H_4)H_2C_4B–NR_2]**Li**[(C_4H_4)H_2C_4B–NR_2] (R = Me, Et)	S, X, H, B, C	10
(tmeda)**Li**(2,5-$Ph_2H_2C_4B$–NMe_2)**Li**(tmeda)	S, X, H, B, C, Li	11
Zirconium		
Cp′$(C_6F_5)_2$**Zr**[H_4C_4B–$CH_2(CH)_3B(C_6F_5)_3$]**Zr**Cp′ (Zr–F) [Cp′ = $C_5H_4SiMe_3$, C_5H_4Me, C_5H_5, 1,3-$C_5H_3(SiMe_3)_2$]	S, H, B, C, F, ethylene polymerization catalysis	14, 22
[1,3-$C_5H_3(SiMe_3)_2$]$(C_6F_5)_2$**Zr**[H_4C_4B–$CH_2(CH)_3B(C_6F_5)_3$] **Zr**[1,3-$C_5H_3(SiMe_3)_2$] (Zr–F)	X	22
Tantalum		
Me_4**Ta**[H_4C_4B–N($CHMe_2$)]**Ta**Me_2[H_4C_4B–N($CHMe_2$)]	S, X, H, C	21
	S, H, C, IR	16
Manganese		
$(CO)_3$**Mn**(H_4C_4BMe)Mn$(CO)_3$	S, He photoelectron	12
$(CO)_3$**Mn**(H_4C_4BMe)Co(H_4C_4BMe)	S, He photoelectron	12
Ruthenium		
Cp***Ru**(Me_4C_4B-6-$CHMeCH_2Me$)RuCp*	S, X, H, B, IR, MS	23

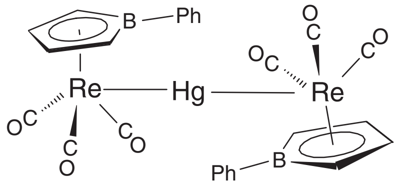
(Continued)

Table 1 (Continued)

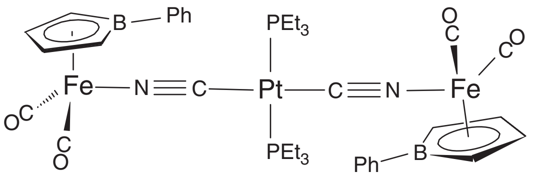
Compound[a]	*Information*[b]	*References*
Cobalt		
(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)	He photoelectron (Me)	7
(CO)$_3$**Mn**(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)	S, He photoelectron	12
Rhodium		
(H$_4$C$_4$BMe)**Rh**(H$_4$C$_4$BMe)**Rh**(H$_4$C$_4$BMe)	He photoelectron (Me)	7
(H$_4$C$_4$BR)**Rh**(H$_4$C$_4$BR)**Rh**(H$_4$C$_4$BR) (R = Ph, Me)	reaction with I$_2$ → cubane clusters	24
(μ-Ph$_2$PCH$_2$PPh$_2$)I$_2$**Rh**(H$_4$C$_4$B–Ph)**Rh**(H$_4$C$_4$B–Ph)	S, H, B, C, IR, MS	8
Cp***Rh**(μ-I)$_3$**Rh**(H$_4$C$_4$B–Ph)	S, X, H, B, C, IR, MS	8
Multinuclear complexes and extended systems		
[(H$_4$C$_4$B–Ph)(CO)$_3$**Re**]$_2$**Pd**$_2$	S, X, H, IR, MS	25
[(CO)$_3$(H$_4$C$_4$B–Ph)**Re**]$_2$Hg	S, X, H, C, IR, MS	3
trans-(NC$_5$H$_4$Me)$_2$Pt-[**Fe**(CO)$_2$H(H$_4$C$_4$B–Ph)]$_2$	S, X, H, IR, MS	3
Rh$_4$(H$_4$C$_4$BR)$_4$(μ-I)$_4$ (R = Ph, Me)	S, H, B, C, MS	24
[pyI**Rh**(H$_4$C$_4$B–Ph)]$_2$ (*cis* + *trans* isomers)	S, H, B, C, IR, MS	8
[(CO)I**Rh**(H$_4$C$_4$B–Ph)]$_2$ (*cis* + *trans* isomers)	S, H, B, C, IR, MS	8
[**Rh**(H$_4$C$_4$B–Ph)$^+$ BF$_4$$^-$]$_x$	S, H, B, C, wide-angle X-ray scattering	9
(H$_4$C$_4$B–Ph)**Rh**(μ-I)$_3$**Rh**(H$_4$C$_4$B–Ph)**Rh**(H$_4$C$_4$B–Ph)	S, X, H, B, C	9
Theoretical studies		
Molecular and electronic structure calculations		
(CO)$_3$**Mn**(H$_4$C$_4$BMe)**Mn**(CO)$_3$	INDO (Me); *ab initio*	12
(CO)$_3$**Mn**(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)	INDO (Me); *ab initio*	12
Cp**Co**(H$_4$C$_4$BR) (R = H, Me)	INDO (Me); *ab initio* (H)	7
Cp**Rh**(H$_4$C$_4$BR) (R = H, Me)	INDO (Me); *ab initio* (H)	7
(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)**Co**(H$_4$C$_4$BMe)	INDO (Me); *ab initio*	7
(H$_4$C$_4$BMe)**Rh**(H$_4$C$_4$BMe)**Rh**(H$_4$C$_4$BMe)	INDO (Me); *ab initio*	7

[a] Metals coordinated to C$_4$B rings are shown in boldface.

[b] Legend: S = synthesis, X = X-ray diffraction, H = ^{1}H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^{7}Li NMR, Pt = ^{195}Pt NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.



1[3]



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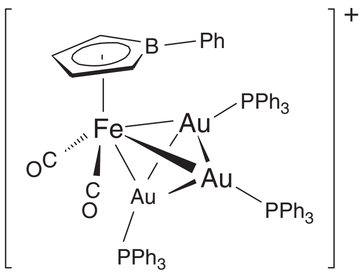
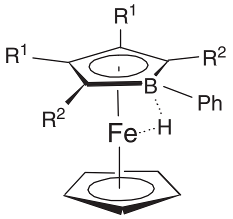
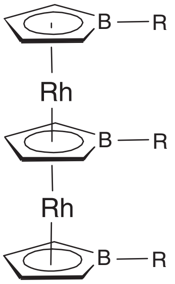


3[5]



R^1, R^2 = H, Me

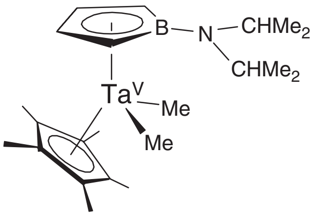
4[6]



R = H, Me

5[7]

The use of metal–borollide complexes as homogeneous Ziegler–Natta catalysts for ethylene polymerization has been explored by Bazan and co-workers[13] and by Bochmann *et al.*[14,14a] Thus, $Cp^*Me_2Ta[H_4C_4B–N(CHMe_2)_2]$ **6** mimics zirconocene in promoting the polymerization of C_2H_4 at 1 atm and 25 °C in the presence of methylaluminoxane (MAO).[13] The mononuclear and dinuclear dizirconium complexes **7** and **8** similarly polymerize ethylene when used with $AlMe_3$ or MAO.[14,14a]



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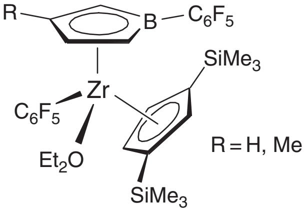
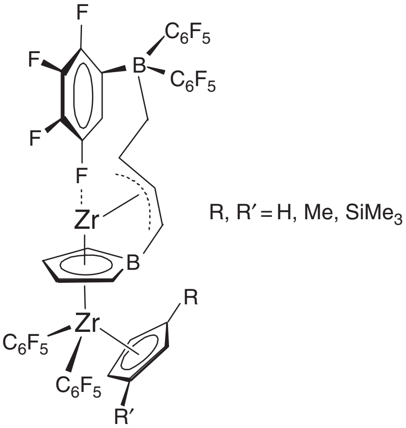
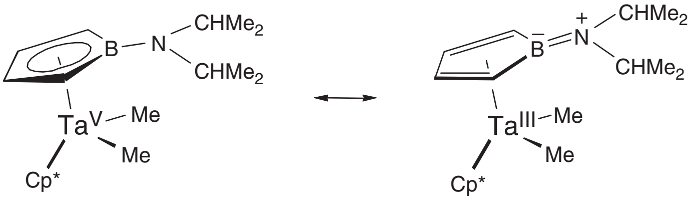


7



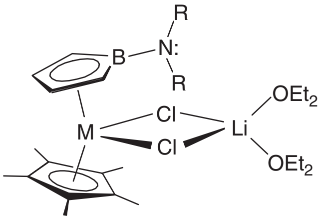
8

Aspects of borole complex reactivity have been studied in detail, including the behavior of tantalum sandwiches bearing alkyl ligands on the metal.[15–17] Complexes such as **6** are best regarded as resonance hybrids where strong B–N π-overlap lowers the formal oxidation state of the metal:[15,16]



6

Aminoborollide complexes of zirconium and hafnium that incorporate both Lewis acid and Lewis base sites have been explored.[18,18a] In molecules such as **9**, the amine nitrogen carries an electron lone pair while the d^0 metal center is acidic:

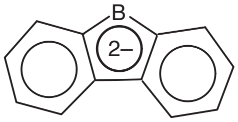


M = Zr, Hf; R = $CHMe_2$

9

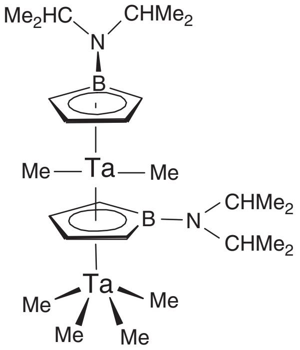
Amphoteric molecules of this type, where the acidic and basic sites are relatively close to each other but cannot interact directly, can heterolytically cleave H–X and C–X bonds where X is a halide, alkoxide, amide, alcohol, thiol, trimethylsilyl, or alkyl group.[18,18a] The ability to effect changes in the reactivity of borollide complexes by adjusting metal oxidation states and ligands allows fine-tuning of catalytic and other properties, which in turn advances the application of these compounds in synthesis.

A tricyclic aromatic system closely related to borole, 9-boratafluorene, might be expected to form η^5-coordinated transition metal sandwich complexes, but so far only the lithium complex has been characterized.[19] Monohapto aluminum adducts of neutral 9-borafluorene, in which Al is bound only to the boron atom, have been prepared.[20]

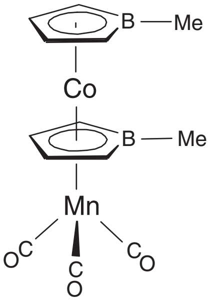


9-boratafluoreneide

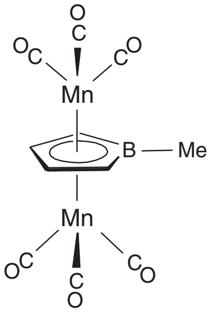
Triple-decker complexes incorporating borole or borollide ring ligands, a well-developed area prior to 1993, have been explored further in recent years (e.g., 5 and 10–12);[10–12,14,21] in most cases, the structures shown have been established crystallographically. Benzoborollide $[H_4C_6(CH)_2B\text{–}R]^{2-}$ rings coordinate (tmeda)Li^+ units to both faces of the five-membered C_4B ring to form triple-decker structures.[10,11] Treatment of $Li_2[C_4H_4B\text{–}N(CHMe_2)_2]$ with Me_3TaCl_2 afforded the extremely electron-deficient (24 electron (24e)) triple-decker **10**,[21] while the curious dizirconium complexes **8** were generated from $(C_5H_3RR')Zr(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$ and $B(C_6F_5)_3$, a process in which all three C_6F_5 ligands were transferred to the metal reagent.[14,22] In combination with MAO, compounds of type **8** (R = H, R′ = H, Me, or $SiMe_3$; R, R′ = $SiMe_3$) catalyze the polymerization of ethylene at 60 °C and 1 atm.



10[16, 21]



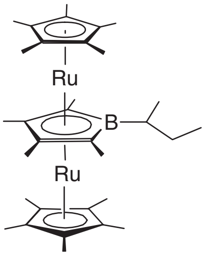
11[12]



12[12]

The electronic structures of the hetero- and homobimetallic triple-deckers **11** and **12** were investigated by photoelectron spectroscopy and intermediate neglect of differential overlap (INDO) molecular orbital (MO) calculations, which revealed that the metal–borole interaction is stronger in the dimanganese system **12** than in **11**, owing to better Mn–borole versus Co–borole orbital overlap.[12]

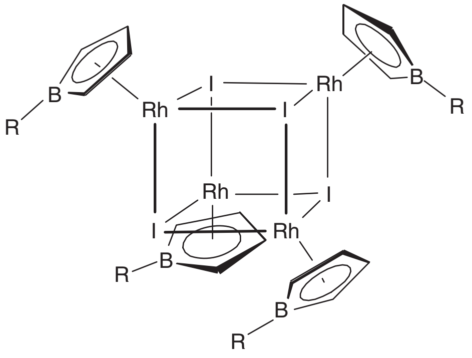
While metal–C_4B ring complexes are usually synthesized from existing borole or borollide ligands, the diruthenium triple-decker **13** (which can also be described as an Ru_2C_4B seven-vertex *closo*-metallacarborane) was serendipitously obtained as a minor product (6% yield) of the reaction of the ruthenaborane *nido*-1,2-$Cp^*{}_2H_2Ru_2B_3H_7$ with 2-butyne at 85 °C;[23] the remaining products were open-cage *nido*-$Ru_2C_2B_2$ clusters.



13

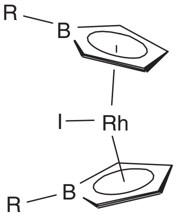
3.01.2.2 Multinuclear C_4B Ring Complexes, Clusters, and Extended Systems

Dirhodium triple-decker sandwiches such as **5** react with I_2 to generate Rh_4I_4 heterocubane clusters, for example, **14**, together with bis(borole)iodorhodium complexes, **15**;[8,24] the latter species undergo rapid ring rotation.[24] As shown by Herberich, the heterocubane clusters exhibit interesting chemical reactivity, for example, exchanging RhI(C_4H_4B–R) fragments rapidly on the NMR timescale. Treatment of **14** (R = Ph) with Lewis bases L (L = pyridine, CO, phosphines, etc.) afforded mononuclear or dinuclear products, for example, **16 and 17**;[8] the dinuclear species undergoes *cis–trans* interconversion at a rate dependent on the Lewis base.



14

R = Me, Ph



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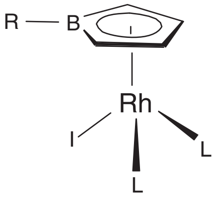

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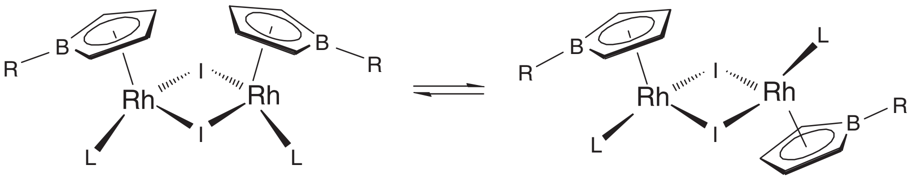
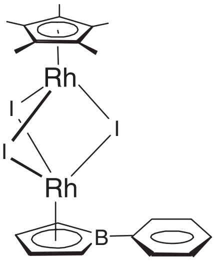


17

Reaction of the heterocubane cluster **14** (R = Ph) with $(Cp^*RhI_2)_2$, a reagent that functions both as a Lewis acid (the metal center) and a Lewis base (the iodide ligands), generates the dirhodium complex **18**.[8] Complex **14** also adds to 1,1-bis(diphenylphosphinoferrocene) to form the cyclic species **19**.[8]



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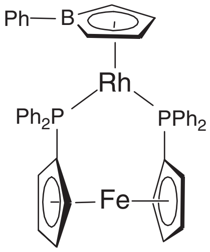
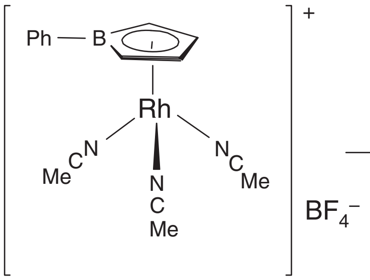
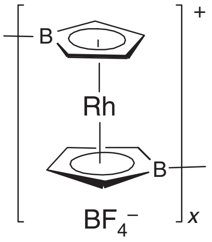


19

In yet another facet of heterocubane chemistry, **14** (R = Ph) has been found to react with Ag^+ in acetonitrile to form the salt $(MeCN)_3Rh(C_4H_4B\text{-}Ph)^+$ BF_4^- **20**, which in turn combines with arenes to generate $(arene)Rh(C_4H_4B\text{-}Ph)^+$ BF_4^- products.[9] Under vacuum, **20** loses MeCN to form the polymer **21**, the phenyl group migrating to the Rh center of a different fragment.

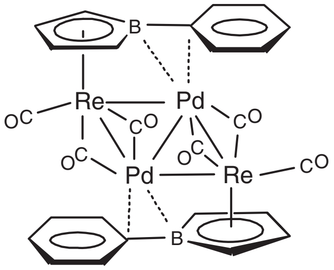


20



21

The first mixed metal borole cluster 22, which contains a planar Re$_2$Pd$_2$ array, was prepared via reaction of the [(η^5-H$_4$C$_4$B–Ph)Re(CO)$_3$]$^-$ anion with PdCl$_2$(NCPh)$_2$.[25] In this electron-deficient system, the Pd atoms are formally 14e centers, stabilized by metal–metal binding with each other and with the Re atoms.



22

3.01.3 Complexes of C$_3$B$_2$ (Diborolyl) Rings

3.01.3.1 C$_3$B$_2$ Ring Double-decker Sandwiches

The pioneering work of Siebert and co-workers on metal–C$_3$B$_2$ sandwich complexes, dating back to the 1960s, has continued through the 1990s and has opened up significant new aspects of this chemistry (see Table 2).[26,27] One contribution is the finding that the shape of the diborolyl ligand, normally planar, can be altered by manipulation of

Table 2 Complexes of C$_3$B$_2$ (1,3-diborolenyl) rings 1993–2005

Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Mononuclear C$_3$B$_2$ complexes (double-decker sandwiches)		
Iron		
Cp***Fe**[(CHMe$_2$)$_2$MeC$_3$B$_2$Et$_2$]	S, X, H, B, C, MS	28
Cp**Fe**(R$_2$MeC$_3$B$_2$Et$_2$) (R = Et, CHMe$_2$)	S, X(CHMe$_2$), H, B(CHMe$_2$), C(CHMe$_2$), E(CHMe$_2$), MS	29
Cp**Fe**[(CHMe$_2$)$_2$MeC$_3$B$_2$Et$_2$]$^-$	ESR	29
Cp***Ru**(R$_2$MeC$_3$B$_2$Et$_2$)	S, H, B, C, MS	29
[Cp***Ru**(R$_2$MeC$_3$B$_2$Et$_2$)]$^-$ (R = Et, CHMe$_2$)	ESR	29
Cp***Ru**[Et$_2$MeC$_3$B$_2$(CMe$_3$)$_2$]	S, H, B, C, E, MS	29
Cp*(CO)**Ru**(Et$_2$MeC$_3$B$_2$EtR) (R = Et, CMe$_3$)	S, X(CMe$_3$), H, B, C, MS	29
Ruthenium		
Cp*(Me$_3$CNC)**Ru**(R$_2$R′C$_3$B$_2$R″$_2$) (R, R′, R″ = Me, Et, Bu, CH$_2$SiMe$_3$)	S, X(Et, Et, Me; Et, Me, Me), H, B, C, MS	30
Cp*H$_2$**Ru**(R$_2$R′C$_3$B$_2$R″$_2$) (R, R′, R″ = Me, Et, Bu, CH$_2$SiMe$_3$)	S, H, B, C, MS	30
Cp***Ru**(R$_2$R′C$_3$B$_2$R″$_2$) (R, R′, R″ = Me, Et, Bu, CH$_2$SiMe$_3$)	S, H, B, C, MS	30
Cp***Ru**(=S)(Me$_3$C$_3$B$_2$Me$_2$)	S, H, B, C, MS	36

(*Continued*)

Table 2 (Continued)

Compound[a]	*Information*[b]	*References*
Cp***Ru**(PR$_2$R′)(Me$_3$C$_3$B$_2$Me$_2$) (R = H, Me; R′ = H, Ph, Me)	S, H, B, C, MS	36
Cp***Ru**(Me$_3$C$_3$B$_2$Me$_2$)$_2$(CS$_2$)$_2$	S, H, B, C, MS	36
Cobalt		
Cp***Co**(MeEt$_2$HC$_3$B$_2$Et$_2$)	S, H, B, C, MS	37
Cp**Co**[*cyclo*-(CH$_2$)$_6$MeHC$_3$B$_2$Me$_2$]	S, X, H, B, C, MS	31
(CO)$_3$**Co**[*cyclo*-(CH$_2$)$_6$MeC$_3$B$_2$Me$_2$]	S, X, H, B, C, MS	31
Rhodium		
(C$_6$H$_5$R)**Rh**(R′$_2$R″C$_3$B$_2$R‴) (R = Me, H; R′ = Me, Et; R″ = Me, CMe$_3$; R‴ = mesCH$_2$, Me, H)	S, X(Me, Me, Me, mesCH$_2$; Me, Et, Me, Me; Me, Me, CMe$_3$, H; H, Et, Me, Me), H, B, C, MS	32
Nickel		
(C$_8$H$_{12}$)**Ni**[*cyclo*-(CH$_2$)$_6$MeHC$_3$B$_2$Me$_2$]	S, X, H, B, C, MS	31
Cp**Ni**[*cyclo*-(CH$_2$)$_6$MeHC$_3$B$_2$Me$_2$]	S, X, H, B, C, MS	31
(C$_8$H$_{12}$)**Ni**[Et$_2$(Me$_2$CH)C$_3$B$_2$Me$_2$]	S, H, B, C, MS	33
(C$_8$H$_{12}$)**Ni**[(H$_4$C$_4$)Ni(C$_8$H$_{12}$)(R$_2$CH)C$_3$B$_2$Me$_2$] (R = Me, (CH$_2$)$_2$)	S, X[CH$_2$)$_2$], H, B, C, MS	33
Platinum		
(C$_8$H$_{12}$)**Pt**[(H$_4$C$_4$)Pt(C$_8$H$_{12}$)(R$_2$CH)C$_3$B$_2$Me$_2$] (R = Me, (CH$_2$)$_2$)	S, X(Me), H, B, C, MS	33
Dinuclear C$_3$B$_2$ complexes (triple-decker sandwiches and related clusters)		
Iron		
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Fe**(5-Me-2,3,5-C$_3$B$_7$H$_9$)	S, X, H, B, MS	41
Ruthenium		
Cp$^*_2$**Ru**$_2$H(R$_2$MeC$_3$B$_2$Me$_2$) (R = Me, Et)	S, H, B, C, MS	29
Cp***Ru**(Me$_3$C$_3$B$_2$Me$_2$)**Rh**(Et$_2$C$_2$B$_4$H$_4$)	S, H, B, C, MS	39
Cp***Ru**(Me$_3$C$_3$B$_2$Me$_2$)**Rh**(C$_2$B$_9$H$_{11}$)	S, H, B, MS	39
Cp***Ru**(Me$_3$C$_3$B$_2$Me$_2$)**Rh**(MeC$_3$B$_7$H$_9$) (Two isomers)	S, X, H, B, C, MS	39
Cp$^*_2$**Ru**$_2$(Me$_3$C$_3$B$_2$Me$_2$)H (adjacent Ru centers)	S, X, H, B, C, MS	36
Cobalt		
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(C$_2$B$_5$H$_7$)	S, H, B, MS	40
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(C$_2$B$_7$H$_9$) (Three isomers)	S, X(1,10), H, B, C, MS	40
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(C$_2$B$_9$H$_{11}$)	S, X, H, B, E, MS	38
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(5-Me-2,3,5-C$_3$B$_7$H$_9$)	S, X, MS	41
Cp**Co**[(CH$_2$=CMe)(CHMe$_2$)RC$_3$B$_2$Me$_2$]**Co**Cp (R = Me, MeC=CH$_2$, CHMe$_2$)	S, H, E, MS	37
{Cp**Co**[(CH$_2$=CMe)(CHMe$_2$)RC$_3$B$_2$Me$_2$]**Co**Cp}$^+$ (R = Me, MeC=CH$_2$, CHMe$_2$)	S, X(MeC=CH$_2$, CHMe$_2$), H, B, C, MS	37
Cp**Co**[(H$_4$C$_4$)RC$_3$B$_2$Me$_2$]**Co**Cp (R = Me, MeC=CH$_2$, CHMe$_2$, CMe$_2$C$_5$H$_5$CoCp)	S, X(CHMe$_2$, CMe$_2$C$_5$H$_5$CoCp), H, E, MS	37
{Cp**Co**[(H$_4$C$_4$)(CHMe$_2$)C$_3$B$_2$Me$_2$]**Co**Cp}$^+$	S, H, B, C, MS	37
Cp**Co**[(H$_4$C$_4$)RC$_3$B$_2$Me$_2$]**Co**Cp (R = *cyclo*-C$_5$H$_7$, *cyclo*-C$_5$H$_9$)	S, X, H, MS	37
{Cp**Co**[(H$_4$C$_4$)RC$_3$B$_2$Me$_2$]**Co**Cp}$^+$ (R = *cyclo*-C$_5$H$_7$, *cyclo*-C$_5$H$_9$)	S, H, B, C, MS	37
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(B$_9$H$_{13}$)	S, H, B, C, MS	42
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(SB$_9$H$_9$)	S, H, B, MS	42
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(S$_2$B$_9$H$_9$)	S, H, B, MS	42
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Co**(S$_2$B$_6$H$_8$)	S, X, H, B, C, MS	42
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Fe**(5-Me-2,3,5-C$_3$B$_7$H$_9$)	S, X, H, B, MS	41
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Rh**(C$_2$B$_7$H$_9$)	S, H, B, MS	40
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Ni**(8-Me-2,3,5-C$_3$B$_7$H$_9$)	S, X, H, B, MS	41
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Ni**(C$_2$B$_9$H$_{11}$)	S, X, H, E, MS	38
Rhodium		
(Me$_2$RC$_3$B$_2$Me$_2$)**Rh**(Me$_2$RC$_3$B$_2$Me$_2$)**Rh**(C$_6$H$_5$Me) (R = Me, mesCH$_2$)	S, MS	32
Cp**Co**(MeEt$_2$C$_3$B$_2$Et$_2$)**Rh**(C$_2$B$_7$H$_9$)	S, H, B, MS	40
Cp***Ru**(Me$_3$C$_3$B$_2$Me$_2$)**Rh**(Et$_2$C$_2$B$_4$H$_4$)	S, H, B, C, MS	39

(Continued)

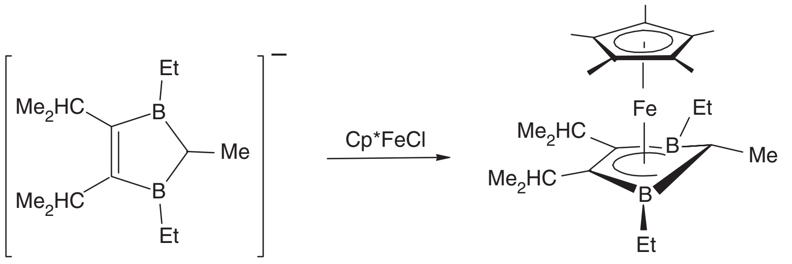
Table 2 (Continued)

Compound[a]	*Information*[b]	*References*
$Cp^*\mathbf{Ru}(Me_3C_3B_2Me_2)\mathbf{Rh}(C_2B_9H_{11})$	S, H, B, MS	39
$Cp^*\mathbf{Ru}(Me_3C_3B_2Me_2)\mathbf{Rh}(MeC_3B_7H_9)$ (Two isomers)	S, X, H, B, C, MS	39
Nickel		
$(C_3H_5)\mathbf{Ni}(RR'R''C_3B_2Me_2)\mathbf{Ni}(C_6H_{10})$ (C_6H_{10} = 1,5-hexadiene; R = Me, Bu, Hep; R′ = Me, n-C_3H_7, n-C_4H_9; R″ = H, Me, Hep, iHex)	S, H, B, C, MS	44
$Cp\mathbf{Co}(MeEt_2C_3B_2Et_2)\mathbf{Ni}(C_2B_9H_{11})$	S, X, H, E, MS	38
$Cp\mathbf{Co}(MeEt_2C_3B_2Et_2)\mathbf{Ni}(8\text{-}Me\text{-}2,3,5\text{-}C_3B_7H_9)$	S, X, H, B, MS	41
Trinuclear C_3B_2 complexes (tetradecker sandwiches)		
Cobalt		
$[Cp\mathbf{Co}(MeEt_2C_3B_2Et_2)]_2\mathbf{Ni}$	S, H, E, MS	38
Rhodium		
$(Et_2MeC_3B_2Me_2)\mathbf{Rh}(Et_2MeC_3B_2Me_2)\mathbf{Rh}(Et_2MeC_3B_2Me_2)\mathbf{Rh}$-$(C_6H_5Me)$	S, MS	32
Nickel		
$[Cp\mathbf{Co}(MeEt_2C_3B_2Et_2)]_2\mathbf{Ni}$	S, H, E, MS	38
$\{Cp\mathbf{Ni}[(H_4C_4)MeC_3B_2Me_2]\}_2\mathbf{Ni}$	S, X, H	43
$[Cp\mathbf{Ni}(HEt_2HC_3B_2R_2)]_2\mathbf{Ni}$ (R = H, Me)	S, X(H), H, B, IR(H), MS(H)	43
Tetranuclear C_3B_2 complexes (pentadecker sandwiches)		
$[Cp^*\mathbf{Ru}(Me_3C_3B_2Me_2)\mathbf{Ru}Cl]_2$	S, H, B, C, MS	30, 39
Polydecker sandwiches		
$[(RR'R''C_3B_2Me_2)\mathbf{Ni}](RR'R''C_3B_2Me_2)_n\mathbf{Ni}(RR'R''C_3B_2Me_2)$	S, EXAFS, thermogravimetry, differential calorimetry, electrical conductivity	44
Theoretical studies		
Molecular and electronic structure calculations		
Triple-decker sandwiches		
$Cp\mathbf{Fe}(C_3B_2H_5)$	Extended Hückel	29
$Cp\mathbf{Ni}(H_3C_3B_2H_2)\mathbf{Ni}Cp$	Fenske–Hall	43
Tetradecker sandwiches		
$[Cp\mathbf{Ni}(H_3C_3B_2H_2)]_2\mathbf{Ni}$	Fenske–Hall	43

[a] Metals coordinated to C_2B_3 rings are shown in boldface.

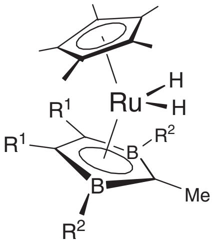
[b] Legend: S = synthesis, X = X-ray diffraction, H = ^{1}H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^{7}Li NMR, Pt = ^{195}Pt NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.

the metal electron count. Thus, in complex 23 which contains a formally 16e iron center, the ring is strongly bent out of planarity with a dihedral angle of 41°.[28] This pronounced folding, and the position of the *exo*-methyl group on the unique ring carbon atom, suggest sp^3 hybridization on that carbon; ESR studies and EHMO calculations show that the folding is a consequence of metal interaction with the C–B bonds.[29,30] Stabilization of this 16e sandwich is attributed to release of electron density by the methyl groups on the Cp^* ligand. Based on the resemblance of its ^{11}B NMR spectra to that of 23, the ruthenium analog of 23 was deduced to have a similarly folded C_3B_2 ligand.[29]



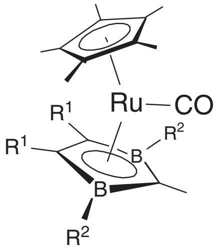
23

Oxidative addition of hydrogen to mononuclear Cp*Ru–diborolyl complexes formed the dihydride species **24**, which could not be isolated, and readily lose H_2 in vacuum;[30] detailed variable-temperature NMR studies were unable to distinguish between the possible classical $Ru(H)_2$ and non-classical $Ru(H_2)$ structures. Acetonitrile, CO, and other electron donors add similarly and in some cases reversibly, leading to bent structures such as **25**.[29,30]



R1, R2 = H, Me

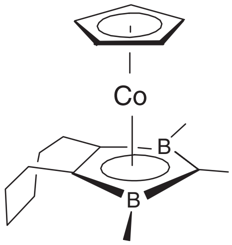
24



R1, R2 = H, Me

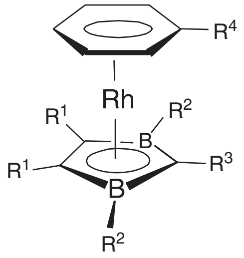
25

Reaction of cyclooctyne with $(I_2B)_2CHMe$ formed a 4,5-cyclooctadiiododiborole, which was methylated with $AlMe_3$ and the product treated with nickel or cobalt reagents to give complexes of type **26**.[31]



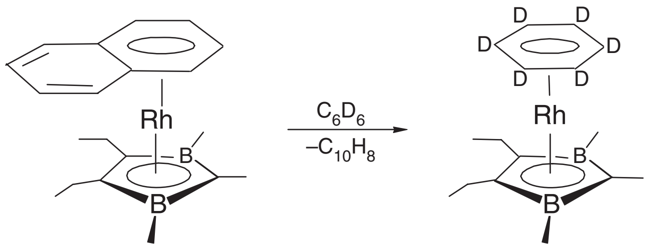
26

(Arene)metal(diborolyl) sandwiches, for example, **27**, have been synthesized from $[(C_2H_4)_2RhCl]_2$ and diborole derivatives.[32] In general, the arene ligands in these complexes are labile on heating, as shown by the displacement of naphthalene from **28** by benzene-d_6 to give **29**; this lability leads to stacking with the formation of triple-decker sandwich complexes.[32]



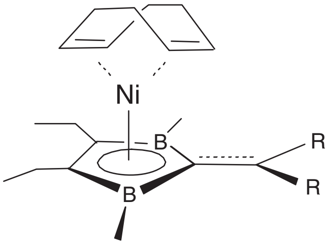
R1 = Me, Et
R2 = Me, CMe3
R3 = H, Me, MesCH2
R4 = H, Me

27

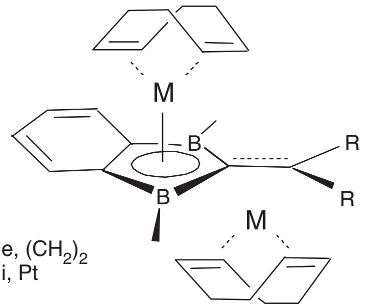


28 **29**

Novel double-deckers illustrated by **30 and 31** have been generated from 1,4-diborapentafulvene ligands.[33] In **31** a second metal center is coordinated to the B═C bond of the fulvene moiety.



30

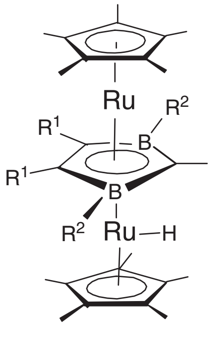


R = Me, $(CH_2)_2$
M = Ni, Pt

31

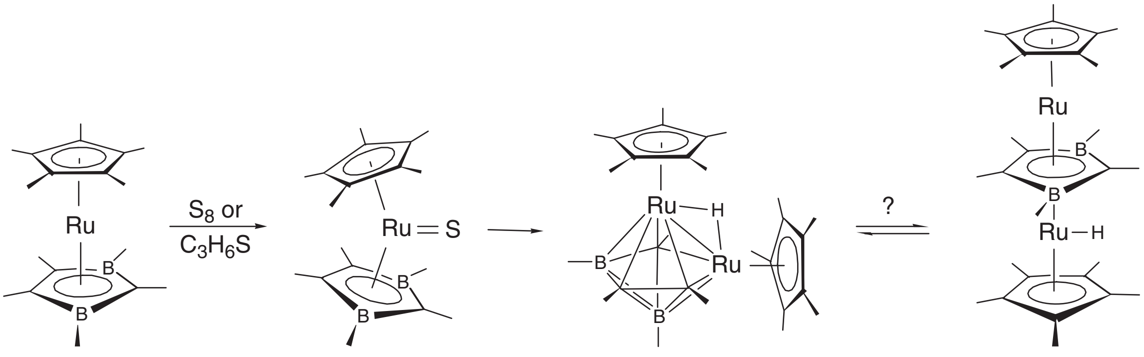
3.01.3.2 C_3B_2 Ring Triple-decker Sandwiches and Dimers

Addition of Cp*RuH to monuclear complexes $Cp^*Ru(MeR^1C_3B_2R_2)$ (analogous to **23**) afforded the 30e triple-decker **32**.[29] Complexes such as **32** can be equivalently represented as seven-vertex pentagonal bipyramidal $Ru_2C_3B_2$ metallacarborane clusters, suggesting that isomers of such clusters should exist in which one or both metal atoms occupy equatorial vertices (as is found in dicarbon metallacarboranes[34,35]). Compounds of this type have, in fact, been observed; thus, addition of sulfur to the mononuclear complex **33** generated **34**, which on standing in hexane solution at −20 °C gave the diruthenium cluster **35** having an Ru–H–Ru bridging hydrogen, whose structure was established by X-ray crystallography.[36] One might expect that **35** could undergo polyhedral rearrangement on heating to form **36**, a process well known in $M_2C_2B_3$ clusters,[34,35] but unfortunately **35** decomposes above 80 °C.[36] Sulfur can also be introduced into the ring to create heterocyclic metal complexes, as is discussed in Section 3.01.9.4.



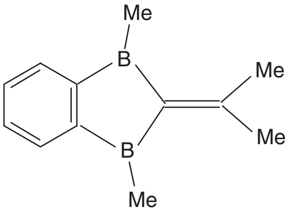
R^1, R^2 = H, Me

32

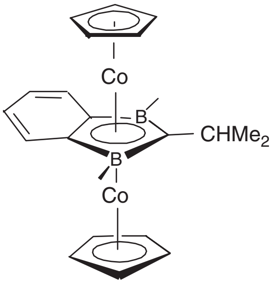


33 **34** **35** **36**

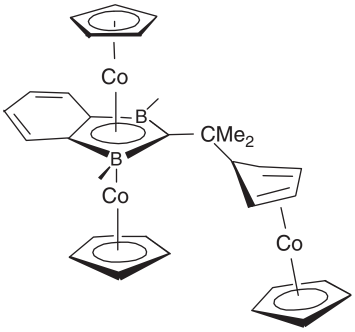
Paramagnetic 31e dicobalt triple-deckers, for example, $CpCo(Et_2MeC_3B_2Et_2)CoCp^*$, have been prepared from bis(1,3-diborole) double-decker sandwiches and $Cp^*Co(C_2H_2)_2$.[37] Reaction of the latter reagent with benzo-1,3-diborafulvene derivatives such as **37** afforded triple-deckers **38** and **39** whose electronic structures have been investigated in detail.[37]



37

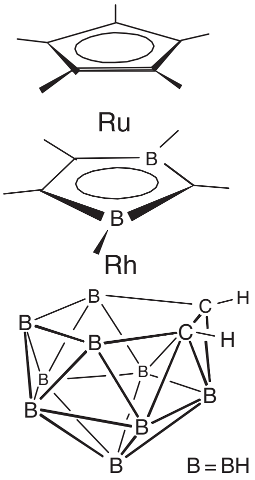


38

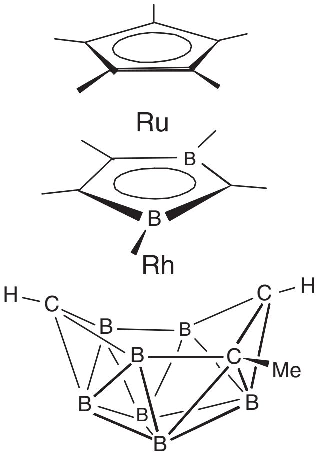


39

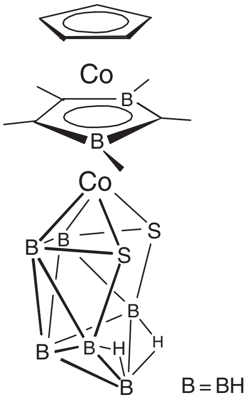
Hybrid sandwich complexes containing both C_3B_2 and C_2B_n (carborane) ligands bound to a common metal center have been known since 1989, as triple-deckers incorporating C_2B_3 or C_2B_4 units together with C_3B_2 rings.[35] In the period since the publication of COMC (1995), hybrids involving larger 11- and 10-vertex carborane ligands have been prepared, as in **40** and **41**.[38–41] A variant on this theme is provided by the diborolyl–thiaboranyl cluster **42** and related complexes.[42]



40



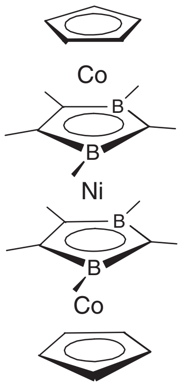
41



42

3.01.3.3 C_3B_2 Ring Tetradecker and Pentadecker Sandwiches

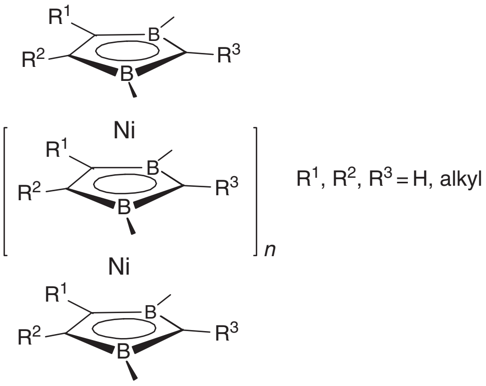
While triple-decker complexes are ubiquitous in chemistry, covalently bound molecular sandwiches having more than three decks with the metals linearly aligned are, at this writing, restricted to complexes incorporating C_3B_2 or C_2B_3 planar rings. Soluble molecular sandwiches as large as hexadeckers have been characterized (see Section 3.01.4.4). Since 1993, several new diborolyl Ni–Ni–Ni and Co–Ni–Co tetradeckers **43** have been reported,[38,43] with structural characterization of the latter.[43] A Cl_2-bridged "pentadecker" complex has also been prepared.[39]



43

3.01.3.4 Polydecker C_3B_2 Ring Sandwiches

Semiconducting black polymers characterized as **44** have been prepared via slow heating of triple-decker (allyl)nickel diborolyl triple-decker complexes.[44] EXAFS studies reveal an Ni–Ni distance of 3.35 Å and a powder conductivity of ca. 10^{-2} S·cm^{-1}. When doped with iodine or oxygen, the conductivity of these polymers decreases.



44

3.01.4 Complexes of C_2B_3 (Triboracyclopentadienyl [Carborane]) Rings

Cyclic ligands containing more boron than carbon atoms, such as C_2B_3, bear a close relationship to the C_3B_2 and C_4B ring derivatives described in the two preceding sections, yet there are major differences in their preparative routes and reaction chemistry. Borole and diborolyl derivatives in general are stable organoboron compounds, usually prepared via boronation of organic precursors, and exist both as free species and as ligands in metal complexes. In contrast, planar carborane (C_2B_3) rings, are, with very rare exceptions, known only as covalently bound metal η^5-complexes (MC_2B_3 or $M_2C_2B_3$ metallacarborane clusters), and are obtained by the extraction of the apex boron from seven-vertex MC_2B_4 cages.[35] The metal–C_2B_3 clusters (Table 3) conceptually link the metal sandwich complexes of the organoboron heterocycles with the metallacarboranes, and have features common to both. In this chapter, only compounds containing planar C_2B_3 rings coordinated to metal centers are covered; metallacarborane systems involving C_2B_4 or larger ligands are treated in a separate chapter.

The preparation of small metallacarboranes having MC_2B_4, MC_2B_3, or $M_2C_2B_3$ cores has been extensively developed by Grimes and co-workers since the early 1970s,[35,45–50] and more recently by Hosmane *et al.* for MC_2B_4 systems[51] (see Chapter 3.05). Metal complexes of planar C_2B_3 ring ligands are of interest as building-block units for

Table 3 Complexes of C_2B_3 rings 1993–2005

Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Mononuclear 2,3-C_2B_3 complexes (double-decker sandwiches)		
Iron		
$Cp^{*}\mathbf{Fe}(Et_2C_2B_3H_5)$	S, H, IR, MS	52
$(\eta^6\text{-}C_6Me_6)\mathbf{Fe}(Et_2C_2B_3H_4)\text{-}5\text{-}C{\equiv}CH$	S, H, B, C, IR, MS	53
Ruthenium		
$(\eta^5\text{-}CHMe_2C_6H_4Me)\mathbf{Ru}(Et_2C_2B_3H_4\text{-}5\text{-}Cl)$	S, H, C, MS	74
Cobalt		
$Cp\mathbf{Co}(Et_2C_2B_3H_3\text{-}4\text{-}X\text{-}6\text{-}Y)$ (X = Br, Y = I; X = Br, Y = H; X = I, Y = H)	S, H, B, C, IR, MS	52
$Cp\mathbf{Co}(Et_2C_2B_3H_3\text{-}4,6\text{-}X_2)$ (X = Br, I)	S, H, B, C, IR, MS	52
$Cp\mathbf{Co}(Et_2C_2B_3H_4\text{-}5\text{-}X)$ (X = Cl, Br, I)	S, H, B, C, MS	52
	E(Cl)	61
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_5)$	E	54
$Cp_2\mathbf{Co}^+$ [*nido*, *closo*-$(Et_2C_2B_3H_4\text{-}5\text{-}R)\mathbf{Co}(Et_2C_2B_4H_4)]^-$ (R = H, Me) cobaltocenium salts	S, H, B, IR	67
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4)\text{-}5\text{-}X$ (X = H, Br)	Cytotoxic/antitumor activity	68
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_3)\text{-}4,6\text{-}I_2$	Cytotoxic/antitumor activity	68
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_3)\text{-}4,6\text{-}X_2$ (X = Cl, Br)	NaH/Me_2CBrNO_2 → *closo*-$Cp^{*}Co(Et_2C_2B_3X_2Br)$ oxidative cage closure	63
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4)\text{-}5\text{-}R$ (R = NMe_2, $OCMe_3$)	S, H, B, C, IR, MS	56
R = $C{\equiv}CH$, $C{\equiv}CSiMe_3$	S, H, B, C, IR, MS	54, 58
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_3)\text{-}4,6\text{-}(C{\equiv}CSiMe_3)_2$	S, H, B, C, IR, MS	72
$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4\text{-}5\text{-}C{\equiv}C)]_2$	S, H, B, C, IR, UV, MS	54
Other $Cp^{*}\mathbf{Co}(Et_2C_2B_3H_5)$ B-substituted derivatives		75
Other (hydrocarbon)$\mathbf{Co}(Et_2C_2B_3)$ derivatives		55, 57
$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4)]_2$	S, X, H, B, UV, MS	59
$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_3)]_2$ (bent isomer)	S, X, H, B, IR, UV	64
$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_3)]_2$ (planar isomer)	S, X, H, B	64
$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4)]_2$ (B–B connected)	S, H, B	64
$(\eta^5\text{-}C_5H_4I)\mathbf{Co}(Et_2C_2B_3H_5)$	S, H, B, C, IR, MS	57
$[\eta^5\text{-}C_5H_4C(O)Cl]\mathbf{Co}(Et_2C_2B_3H_5)$	S, H, B, C, IR, MS	60
$(Et_2C_2B_4H_4)\mathbf{Co}H(Et_2C_2B_3H_4Me)$	S, H, B, UV, MS	75
$(Et_2C_2B_4H_4)\mathbf{Co}H(Et_2C_2B_3H_4\text{-}5\text{-}n\text{-}C_4H_9)$	S, H	65
Iridium		
$Cp^{*}\mathbf{Ir}(Et_2C_2B_3H_4\text{-}4\text{-}R)$ (R = H, Cl)	S, H, B, IR, MS	66a
$Cp^{*}\mathbf{Ir}(Et_2C_2B_3H_4\text{-}5\text{-}Cl)$	S, H, IR, MS	66a
Dinuclear 2,3-C_2B_3 complexes (triple-decker sandwiches)		
Iron		
$[Cp^{*}\mathbf{Fe}(Et_2C_2B_3H_2\text{-}5\text{-}X)\mathbf{Co}Cp^{*}]^n$ (n = +1, 0, −1, −2; X = H, Cl, Br)	S, H(correlated)(X = H), E, ESR, IR, MS, Mössbauer (X = H)	70
$[Cp^{*}\mathbf{Fe}(Et_2C_2B_3H_3)\mathbf{Co}Cp]^n$ (n = 0, −1, −2)	S, H(correlated), E, ESR, IR, MS	70
Ruthenium		
$(\eta^6\text{-}MeC_6H_4CHMe_2)\mathbf{Ru}(Et_2C_2B_3H_2Me)\mathbf{Co}H(Et_2C_2B_3H_5)$	S, H, B, UV, MS	75
$(\eta^6\text{-}MeC_6H_4CHMe_2)\mathbf{Ru}(Et_2C_2B_3H_2Me)\mathbf{Co}(Et_2C_2B_3H_5)$	S, UV, ESR, MS	75
$Cp^{*}H\mathbf{Ru}(Et_2C_2B_3H_3)\mathbf{Co}Cp^{*}$	S, H, C, IR, UV, MS	73
Molybdenum		
$(CO)_4\mathbf{Mo}(Et_2C_2B_3H_3)\mathbf{Co}Cp^{*}$	S, X, H, B, C, IR, UV, MS	76
$(CO)_4\mathbf{Mo}(Et_2C_2B_3H_2\text{-}5\text{-}CH_2Ph)\mathbf{Co}Cp^{*}$	S, X, H, IR, UV, E, MS	76
Tungsten		
$(CO)_4\mathbf{W}(Et_2C_2B_3H_2\text{-}5\text{-}R)\mathbf{Co}Cp^{*}$ (R = H, CH_2Ph)	S, X(H,CH_2Ph), H, B(R = H), C(R = H), IR, UV, E(CH_2Ph)	76
$(CO)_4\mathbf{W}(Et_2C_2B_3H_3)\mathbf{Co}Cp^{*}$	Cytotoxic/antitumor activity	68

(Continued)

Table 3 (Continued)

Compound[a]	*Information*[b]	*References*
Tantalum		
$CpCl_2\mathbf{Ta}(Et_2C_2B_3H_3)\mathbf{Co}Cp^*$	S, X, H, B, C, IR, E, UV, MS	79
$CpCl_2\mathbf{Ta}(Et_2C_2B_3Br_3)\mathbf{Co}Cp^*$	S, X, H, B, C, MS	80
$CpCl_2\mathbf{Ta}(Et_2C_2B_3HI_2)\mathbf{Co}Cp^*$	S, H, B, MS	79, 80
$CpLL'\mathbf{Ta}(Et_2C_2B_3H_3)\mathbf{Co}Cp^*$ (L = Me, CH_2Ph; L′ = Cl, Me, CH_2Ph, CH_2CMe_3)	S, X(Me_2, CH_2Ph; Cl), H, B, C, IR, UV, MS	79
Niobium		
$CpCl_2\mathbf{Nb}(Et_2C_2B_3H_3)\mathbf{Co}Cp^*$	S, H, B, C, IR, UV, E, MS	79
Cobalt		
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}H(Et_2C_2B_3H_5)$	S, X, H, B, UV, MS	75
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}(Et_2C_2B_3H_5)$	S, UV, ESR, MS	75
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}H_n(Et_2C_2B_3H_5)$ ($n = 0,1$)	S, UV, MS	78
$Cp\mathbf{Co}(Et_2C_2B_3Br_3)\mathbf{Co}Cp$	S, H, B, C, MS	52
$Cp^*\mathbf{Co}(C_2B_3H_5)\mathbf{Co}Cp^*$	X, H(correlated)	70
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Co}Cp^*$	S, X, H, B, C, E	70
$Cp^*\mathbf{Co}[Et_2C_2B_3H\text{-}4,6\text{-}(C{\equiv}CH)_2]\mathbf{Co}Cp^*$	S, H, B, C, IR, UV, MS	72
$Cp^*\mathbf{Co}[Et_2C_2B_3H_2\text{-}5\text{-}C{\equiv}CSiMe_3]\mathbf{Co}Cp^*$	S, H, B, C, IR, UV, E, MS	54
$Cp^*\mathbf{Co}[Et_2C_2B_3H_2\text{-}5\text{-}C{\equiv}CSiMe_3]\mathbf{Co}Cp^{*n}$ ($n = 0, 1, -1$)	IR(spectroelectrochem), UV, E	72
$[Cp^*\mathbf{Co}(R_2C_2B_3H_3)\mathbf{Co}Cp^*]^n$ ($n = +1, 0, -1$; R = H, Me, Et)	S, X(Et; n = 0, −1), E(Et), H(correlated), B (Et), C	70
$[Cp\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Co}Cp^*]^n$ ($n = 0, -1$)	S, X(n = 0), H(correlated), B	64, 70
$(\eta^5\text{-}NC_4Me_4)\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Co}(\eta^5\text{-}NC_4Me_4)$	X	77
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}H_n(Et_2C_2B_4H_4)$ ($n = 0,1$)	S, H, UV, MS	78
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}H(Et_2C_2B_4H_4)$	S, H, B, UV, MS	75
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Co}(Et_2C_2B_4H_4)$ ($\mathbf{M} = \mathbf{Co}H$, $\mathbf{Co}$)	S, ESR, UV, MS	75
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Mo}(CO)_4$	S, X, H, B, C, IR, UV, MS	76
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2\text{-}5\text{-}CH_2Ph)\mathbf{Mo}(CO)_4$	S, X, H, IR, UV, E, MS	76
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2\text{-}5\text{-}R)\mathbf{W}(CO)_4$ (R = H, CH_2Ph)	S, X(H,CH_2Ph), H, B(R = H), C(R = H), IR, UV, E(CH_2Ph)	76
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{W}(CO)_4$	Cytotoxic/antitumor activity	68
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Nb}CpCl_2$	S, H, B, C, IR, E, UV, MS	79
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Ta}Cl_2Cp$	S, X, H, B, C, IR, E, UV, MS	79
$Cp^*\mathbf{Co}(Et_2C_2B_3Br_3)\mathbf{Ta}Cl_2Cp$	S, X, H, B, C, MS	80
$Cp^*\mathbf{Co}(Et_2C_2B_3HI_2)\mathbf{Ta}Cl_2Cp$	S, H, B, MS	79, 80
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Ta}CpLL'$ (L = Me, CH_2Ph; L′ = Cl, Me, CH_2Ph, CH_2CMe_3)	S, X(Me_2, CH_2Ph; Cl), H, B, C, IR, UV, MS	79
$[Cp^*\mathbf{Co}(Et_2C_2B_3H_2\text{-}5\text{-}X)\mathbf{Fe}(Cp^*)]^n$ ($n = +1, 0, -1, -2$; X = H, Cl, Br)	S, H(correlated)(X = H), E, ESR, IR, MS, Mössbauer (X = H)	70
$[Cp\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Fe}Cp^*]^n$ ($n = 0, -1, -2$)	S, H(correlated), E, ESR, IR, MS	70
$Cp^*\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Ru}HCp^*$	S, H, C, IR, UV, MS	73
$(Et_2C_2B_3H_5)\mathbf{Co}H(Et_2C_2B_3H_2Me)\mathbf{Ru}(\eta^6\text{-}MeC_6H_4CHMe_2)$	S, H, B, UV, MS	75
$(Et_2C_2B_3H_5)\mathbf{Co}(Et_2C_2B_3H_2Me)\mathbf{Ru}(\eta^6\text{-}MeC_6H_4CHMe_2)$	S, H, B, UV, MS	75
$Cp^*\mathbf{Co}(Et_2C_2B_3H_4\text{-}4\text{-}Cl)\mathbf{Ir}Cp^*$	S, H, B, UV, MS	66a
$Cp^*\mathbf{Co}(Et_2C_2B_3Me_3)\mathbf{Ni}(Et_2C_2B_4H_4)$	S, H, B, UV, MS	75
Other $\mathbf{Co}(C_2B_3)\mathbf{M}$ triple-decker complexes		72
Iridium		
$Cp^*\mathbf{Ir}(Et_2C_2B_3H_4\text{-}4\text{-}Cl)\mathbf{Co}Cp^*$	S, H, B, UV, MS	66a
$Cp^*\mathbf{Ir}(Et_2C_2B_3H_4\text{-}4\text{-}Cl)\mathbf{Ir}Cp^*$	S, X(Ir), H, B, IR, UV, MS	66a
Nickel		
$(Et_2C_2B_4H_4)\mathbf{Ni}(Et_2C_2B_3Me_3)\mathbf{Co}Cp^*$	S, H, B, UV, MS	75
Trinuclear 2,3-C_2B_3 complexes (tetradecker sandwiches)		
Molybdenum		
$[Cp^*\mathbf{Co}(Et_2C_2B_3H_3)]_2\mathbf{Mo}(CO)_2$	S, X, H, B, C, IR, E, UV	76
Ruthenium		
$Cp^*\mathbf{Co}(Et_2C_2B_3H_2\text{-}5\text{-}Cl)\mathbf{Ru}(Et_2C_2B_3H\text{-}4,5\text{-}Cl_2)\mathbf{Co}Cp^*$	E, ESR	84
$[(\eta^6\text{-}MeC_6H_4CHMe_2)\mathbf{Ru}(Et_2C_2B_3H_2\text{-}5\text{-}X)]_2\mathbf{Co}$ (X = Me, Cl)	S, X(Me), H, IR, UV, MS	74

(Continued)

Table 3 (Continued)

Compound[a]	*Information*[b]	*References*
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$H$_2$-5-Cl)]$_2$**Co**H	S, H, C, IR, UV, MS	74
(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$H$_2$-5-Me)**Co**(Et$_2$C$_2$B$_3$H$_2$-5-Et)**Ru**(η^6-MeC$_6$H$_4$CHMe$_2$)	S, X, IR, UV, MS	74
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$Me$_3$)]$_2$**Co**	S, IR, UV, MS	74
Other Ru tetradecker sandwiches		74
Cobalt		
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_3$H$_5$)	S, UV, ESR, MS	75
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_4$H$_4$)	S, UV, ESR, MS	75
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Ni**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_4$H$_4$)	S, H, B, UV, MS	75
[Cp***Co**(Et$_2$C$_2$B$_3$H$_2$-5-X)]$_2$**Co** [X = H, Me, Cl, Br, C(O)Me, CH$_2$C≡CMe]	E	84
[Cp***Co**(Et$_2$C$_2$B$_3$H$_3$)]$_2$**Mo**(CO)$_2$	S, X, H, B, C, IR, E, UV	76
[Cp***Co**(Et$_2$C$_2$B$_3$H$_2$-5-R)]$_2$**Fe**H (R = Me, Cl)	S, UV, ESR, MS, oxidative fusion → Co$_2$C$_4$B$_8$ clusters	83
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)CoCp*	S, H, UV, MS	66a
[Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-R)]$_2$**Rh**H (R = H, Cl)	S, X(Cl), H, B, C, IR, UV, MS	82
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)CoCp*	S, H, UV, MS	66a
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)IrCp*	S, H, UV, MS	66a
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)CoCp*	S, H, UV, MS	66a
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)CoCp*	S, H, UV, MS	66a
[Cp***Co**(Et$_2$C$_2$B$_3$H-4,5-Cl$_2$)]$_2$**Ni**	S, H, B, C, E, Ms	84
[Cp***Co**(Et$_2$C$_2$B$_3$FCl$_2$)]$_2$**Ni**	S(electrochem), H, F, E, MS	84
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$-5-Cl)**Ru**(Et$_2$C$_2$B$_3$H-4,5-Cl$_2$)**CoCp***	E, ESR	84
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$H$_2$-5-X)]$_2$**Co** (X = Me, Cl)	S, X(Me), H, IR, UV, MS	74
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$H$_2$-5-Cl)]$_2$**Co**H	S, H, C, IR, UV, MS	74
(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$H$_2$-5-Me)**Co**(Et$_2$C$_2$B$_3$H$_2$-5-Et)**Ru**(η^6-MeC$_6$H$_4$CHMe$_2$)	S, X, IR, UV, MS	74
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$Me$_3$)]$_2$**Co**	S, IR, UV, MS	74
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**IrCp**	S, H, UV, MS	66a
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**CoCp***	S, H, UV, MS	66a
[Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-R)]$_2$**Rh**H (R = H, Cl)	S, X(Cl), H, B, C, IR, UV, MS	82
Rhodium		
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**IrCp**	S, H, UV, MS	66a
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**CoCp***	S, H, UV, MS	66a
[Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-R)]$_2$**Rh**H (R = H, Cl)	S, X(Cl), H, B, C, IR, UV, MS	82
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**IrCp***	S, H, UV, MS	66a
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**CoCp***	S, H, UV, MS	66a
Iridium		
Cp***Co**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**CoCp***	S, H, UV, MS	66a
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**IrCp***	S, H, UV, MS	66a
Cp***Ir**(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**Rh**H(Et$_2$C$_2$B$_3$H$_4$-5-Cl)**CoCp***	S, H, UV, MS	66a
Nickel		
[Cp***Co**(Et$_2$C$_2$B$_3$H-4,5-Cl$_2$)]$_2$**Ni**	S, H, B, C, E, Ms	84
[Cp***Co**(Et$_2$C$_2$B$_3$FCl$_2$)]$_2$**Ni**	S(electrochem), H, F, E, MS	84
[(η^6-MeC$_6$H$_4$CHMe$_2$)**Ru**(Et$_2$C$_2$B$_3$Me$_3$)]$_2$**Ni**	S, IR, UV, MS	74
Tetranuclear 2,3-C$_2$B$_3$ complexes (pentadecker sandwiches)		
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_3$H$_3$)**Co**(Et$_2$C$_2$B$_3$H$_3$)**CoCp***	S, UV, ESR, MS	85
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_3$H$_3$)**Co**H$_n$(Et$_2$C$_2$B$_3$H$_2$Me)**CoCp*** (n = 0,1)	S, H, B, UV, ESR (n = 0), MS	85
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$Me)**Co**H(Et$_2$C$_2$B$_3$H$_3$)**Ni**(Et$_2$C$_2$B$_3$H$_2$Me)**CoCp***	S, H, UV, ESR, MS	85
Pentanuclear 2,3-C$_2$B$_3$ complexes (hexadecker sandwiches)		
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$-5-Me)**Co**H$_n$(Et$_2$C$_2$B$_3$H$_3$)**Co**(Et$_2$C$_2$B$_3$H$_3$)**Co**(Et$_2$C$_2$B$_3$H$_2$-5-Me)**CoCp*** (n = 0,1)	S, X(n = 1), H, UV, ESR, MS	78,85
Cp***Co**(Et$_2$C$_2$B$_3$H$_2$-5-Me)**Co**H(Et$_2$C$_2$B$_3$H$_3$)**Co**(Et$_2$C$_2$B$_3$H$_3$)**Co**H(Et$_2$C$_2$B$_3$H$_2$-5-Me)**CoCp***	S, X, UV, ESR, MS	85

(Continued)

Table 3 (Continued)

Compound[a]	*Information*[b]	*References*
$Cp^{*}\mathbf{Co}(Et_2C_2B_3H_2\text{-}5\text{-}Me)\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Pt}(Et_2C_2B_3H_3)\mathbf{Co}(Et_2C_2B_3H_3)\mathbf{Co}Cp^{*}$	S, UV, ESR, MS	85
Other $Co(C_2B_3)$-containing hexadecker sandwiches		85
Linked sandwiches and multisandwich assemblies		
Molybdenum		
$[(Et_2C_2B_3H_5)\mathbf{Mo}(CO)_2]_2(\mu\text{-}Br)_2$	S, H, B, IR, UV	76
Cobalt		
$[(Et_2C_2B_3H_5)\mathbf{Co}(\eta^5C_5Me_4{-}C{\equiv}C)]_2$	S, H, MS	55
$[(\text{-}CH_2C_5Me_4)\mathbf{Co}(Et_2C_2B_3H_4\text{-}5\text{-}X)]_2$ (X = H, Cl, Br, I)	S, H, B, UV, MS	59
1,3-$[Cp^{*}\mathbf{Co}(2',3'\text{-}Et_2C_2B_3H_3)\mathbf{Co}(\eta^5\text{-}C_5H_4)]_2$-5-(*nido*-$Et_2C_2B_3H_5)\mathbf{Co}(\eta^5\text{-}C_5H_4)C_6H_3$	S, H, B, C, IR, UV, MS	57
1,4-$(Et_2C_2B_3H_5)\mathbf{Co}(\eta^5\text{-}C_5Me_4{-}C{\equiv}C)]_2C_6H_4$ (phenylene-bridged)	S, X, H, B, C, MS	55
nido-$(Et_2C_2B_3H_3\text{-}4\text{-}R\text{-}5\text{-}R')\mathbf{Co}(C_5Me_4)\text{-}C_6H_4\text{-}(C_5Me_4)\mathbf{Co}[(Et_2C_2B_3H_3\text{-}4\text{-}R''\text{-}5\text{-}R''')$ (R, R′, R″, R‴ = H, Cl, Br, Me) phenylene-bridged	S, H, B	87
[*nido*-$(Et_2C_2B_3H_4R)CoL]_2(C_6H_4)L\mathbf{Co}(Et_2C_2B_3H_2R)\text{-}\mathbf{M}(Et_2C_2B_3H_2R)\mathbf{Co}L]_n(C_6H_4)$ ($n = 1, 3, 5$; $L = \eta^5\text{-}C_5Me_4$; **M** = **Co**, **Ni**; R = Cl, Me)	E	61
nido-, *closo*-$\mathbf{M}[(Et_2C_2B_3H\text{-}4\text{-}R\text{-}5\text{-}R')\mathbf{Co}(C_5Me_4)\text{-}C_6H_4\text{-}(C_5Me_4)\mathbf{Co}(Et_2C_2B_3H_4\text{-}R'')]_2$ (R, R′, R″ = H, Cl, Me; **M** = **Co**, **Co**H, **Ni**) phenylene-bridged	S, X(Co); R,R′ = Cl; R″ = H), H, B, UV, MS(FAB)	87
nido-, *closo*-$[(Et_2C_2B_3H_4Cl)\mathbf{Co}(C_5Me_4)]_2[(C_5Me_4)\mathbf{Co}\text{-}(Et_2C_2B_3H_2Cl)\mathbf{Co}(Et_2C_2B_3H_2Cl)\mathbf{Co}(C_5Me_4)]_3(C_6H_4)_4$ phenylene-bridged	S, MS(FAB)	87
Other *nido*-$\mathbf{Co}C_2B_3$ phenylene-bridged complexes		87
1,3,5-$[(2',3'\text{-}Et_2C_2B_3H_3)\mathbf{Co}(\eta^5\text{-}C_5H_4)]_3C_6H_3$ benzene-centered	S, X, H, B, C, IR, UV, MS E	57 72
1,3,5-$[Cp^{*}\mathbf{Co}(Et_2C_2B_3H_4\text{-}5\text{-}C{\equiv}C)]_3C_6H_3$ benzene-centered	S, H, B, C, IR, UV, MS	54, 58
1,3,5-$[Cp^{*}_2\mathbf{Co}_2(2',3'\text{-}Et_2C_2B_3H_2\text{-}5\text{-}C{\equiv}C)]_3C_6H_3$ benzene-centered tris(triple-decker sandwich)	S, X, H, B, C, IR, UV, E, MS	58, 54
Other *nido*-$\mathbf{Co}C_2B_3$ benzene-centered complexes		55
[*nido*-$(Et_2C_2B_3H_4\text{-}5\text{-}Me)\mathbf{Co}(\eta^5\text{-}C_5H_4)]_2$ fulvalene-bridged	S, H, B	87
nido-, *closo*-$[(Et_2C_2B_3H_4\text{-}5\text{-}Me)\mathbf{Co}(\eta^5\text{-}C_5H_4)_2Co_3(Et_2C_2B_3H_2\text{-}5\text{-}Me)_2(\eta^5\text{-}C_5H_4)]_2$ fulvalene-bridged	S, H, UV, MS(FAB)	87
DAB-dendrimer-$\{[(\eta^5\text{-}C_5H_4NHC(O))]\mathbf{Co}(Et_2C_2B_3H_5)\}_n$ ($n = 16, 32$)	S, H, B, C, IR, UV, E, MS	60
$[(Et_2C_2B_4H_4)\mathbf{Co}(Et_2C_2B_3H_3\text{-}5\text{-}n\text{-}C_4H_9)\mathbf{Ru}]_4$	S, X, H, MS	65
Theoretical studies		
Molecular and electronic structure calculations		
$CpCo(2,3\text{-}C_2B_3H_5)CoCp$	Extended Hückel	72

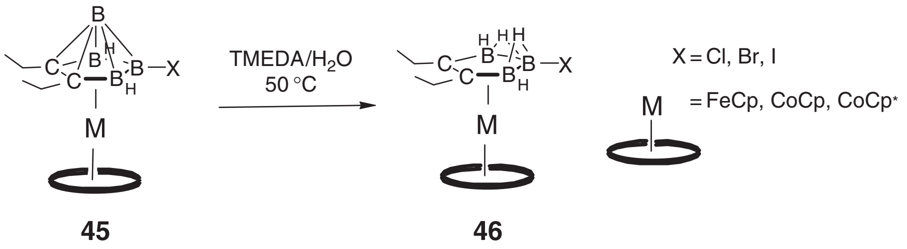
[a] Metals coordinated to C_4B rings are shown in boldface.

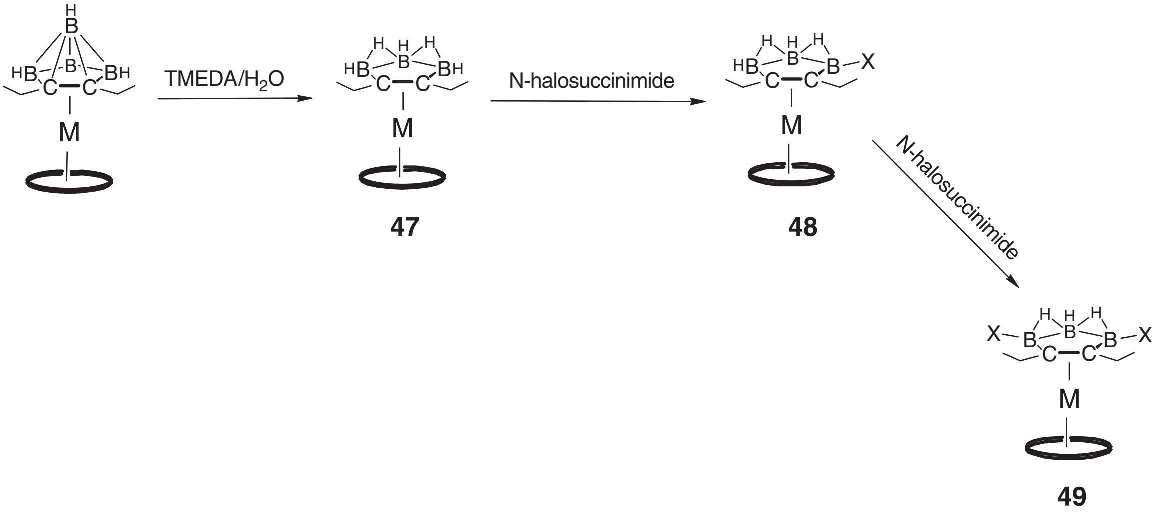
[b] Legend: S = synthesis, X = X-ray diffraction, H = ^{1}H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^{7}Li NMR, Pt = ^{195}Pt NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.

constructing extended systems having tunable electronic properties. As discussed below, these are of two general types: multidecker stacks consisting of parallel C_2B_3 rings coordinated to face-bonded metal atoms, and covalently linked arrays in which small metallacarborane clusters are linked by hydrocarbon chains or rings.

3.01.4.1 C_2B_3 Ring Double-decker Sandwiches

One approach to the synthesis of linked MC_2B_4 or MC_2B_3 metallacarboranes is via B-substituted derivatives containing reactive substituents such as halogens or alkynyl. Following earlier work,[34] systematic methods for regiospecific halogenation[52] and introduction of alkynyl groups[53,54] have been published. These methods allow selective syntheses of C_2B_3 complexes that are functionalized at the middle boron [B(5)] or the end borons [B(4,6)] (see **45–49**).[52]

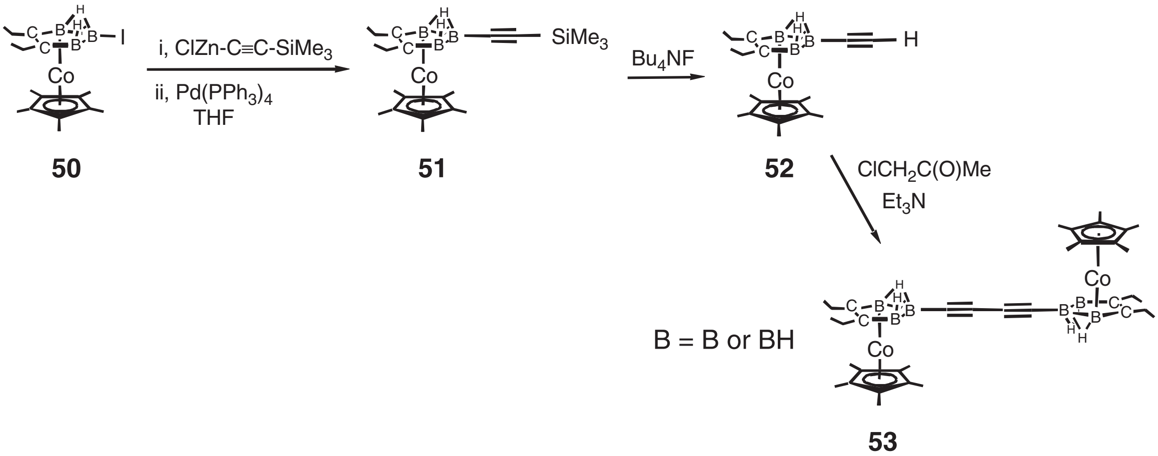


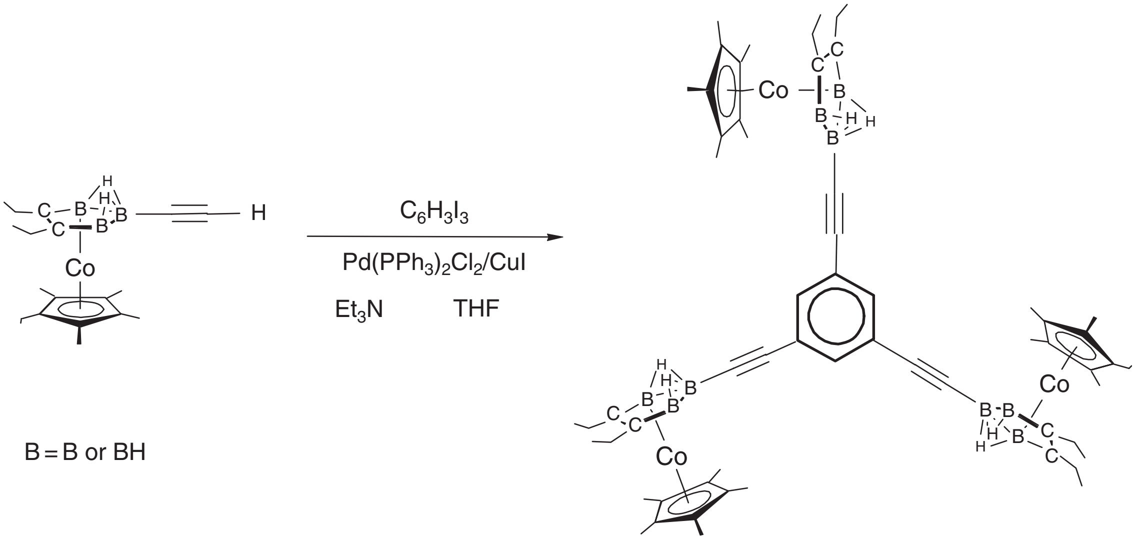


The B-halogenated derivatives, in turn, allow direct introduction of alkynyl and other functional groups; desilylation and linkage affords dimers linked by dialkynyl chains:[54,55]

Other B-substituted derivatives of metal–$\mathrm{C_2B_3}$ complexes have been prepared by reducing $\mathrm{Co^{III}C_2B_4}$ clusters to 19e $\mathrm{Co^{II}}$ species that, in turn, undergo radical reactions with electrophiles and nucleophiles. The $\mathrm{MC_2B_4}$ clusters obtained have OH, OR, or $\mathrm{NH_2}$ substituents on the center equatorial boron [B(5)]; removal of the apex BH affords the corresponding metal–$\mathrm{C_2B_3}$ complexes.[56]

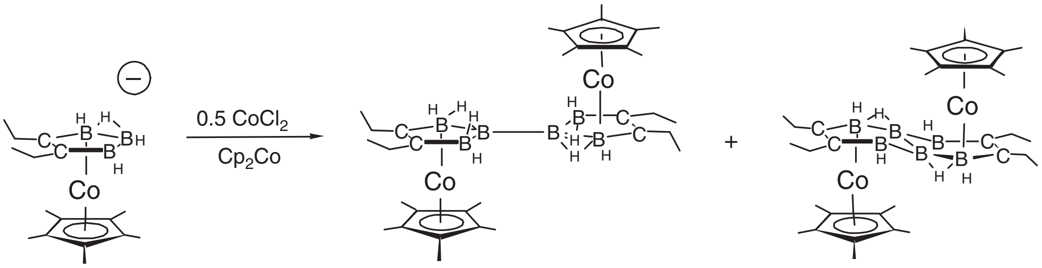
Species functionalized at boron, such as 50–53, have also been prepared from the corresponding $\mathrm{MC_2B_4}$ *closo* clusters via the removal of the apex BH unit (decapitation) with TMEDA.[54–57] The same approach has been employed to link $\mathrm{CoC_2B_3}$ units to benzene or other arenes:[55,58] As shown in the following subsection, di- and trinuclear complexes such as 53 and 54 are easily converted to multi-triple-decker sandwich systems.



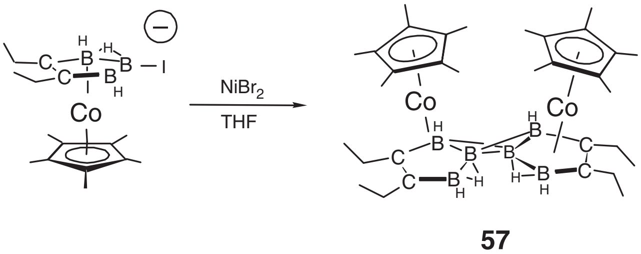


54

Other modes of linkage of metal–C_2B_3 complexes have been demonstrated. For example, metal-promoted connection of monomeric species yielded dimers connected by a single B–B bond **55** or in more complex fashion **56–58** as revealed by X-ray crystallography.[59] Other polymetallacarborane assemblies that incorporate planar C_2B_3 end rings have been constructed by linking metal-bound cyclopentadienyl ligands.[57]



55 **56**



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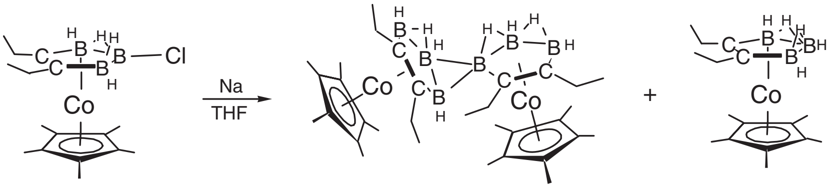
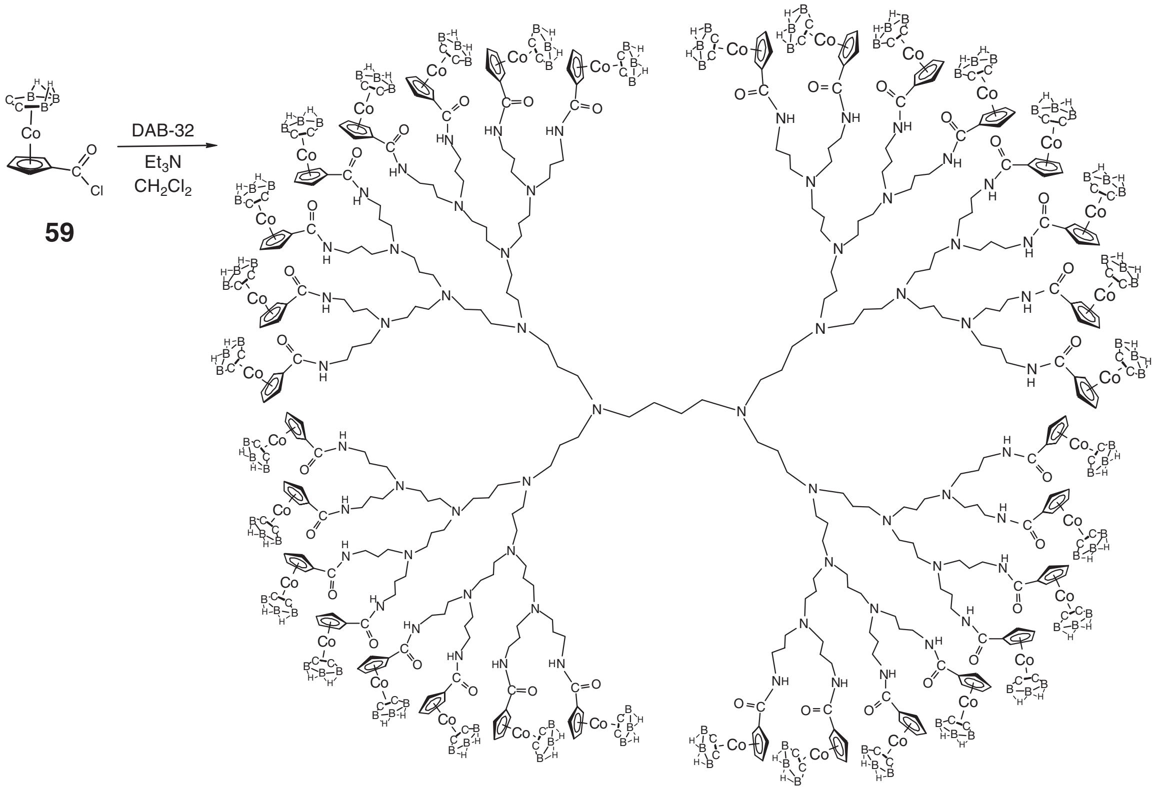


58

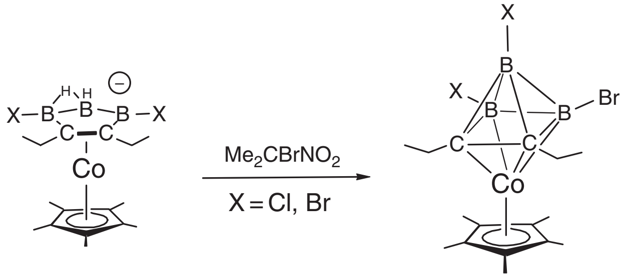
Organic functional groups can also be placed on the Cp ligands in $CpMC_2B_3$ complexes, e.g., **59**,[60] and this approach has been exploited to generate metallodendrimers such as **60** [DAB-32 = diaminobutane-dend$(NH_2)_{32}$].[60]



59

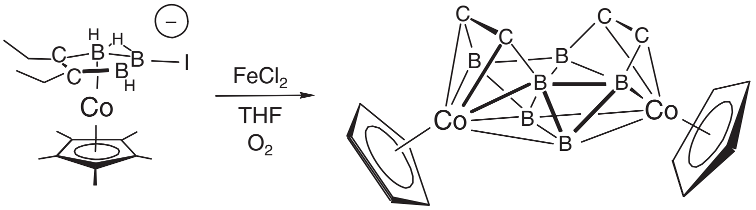
60

The electrochemical[54,61] and chemical redox behavior of metal–C_2B_3 complexes has been studied in detail. The oxidation of $[Cp^*Co(Et_2C_2B_3H_3X_2)]^-$ anions to the *closo*-$Cp^*Co(Et_2C_2B_3X_2Br)$ products **61**, predicted from electron-counting theory,[62,62a] provided the first experimental demonstration of a *nido–closo* conversion in a six-vertex cluster system.[63] The process shown is reversible; reduction of **61** (X = Br) with lithium naphthaleneide regenerated the open CoC_2B_3 cluster.[63]



61

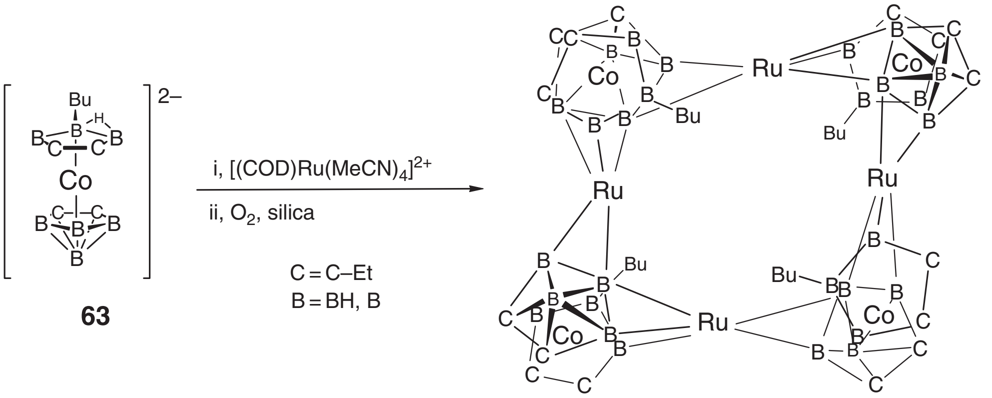
Metal-promoted fusion or linkage of anionic CoC_2B_3 complexes affords exceedingly rich and varied chemistry. Thus, $FeCl_2$-promoted oxidative face-to-face fusion gave $Co_2C_4B_6$ clusters **62**. With $NiBr_2$, the product was a B–B linked dimer **57** as noted above, while CoX_2 (X = Cl, Br, I) generated tetradecker sandwich products (see Section 3.01.4.3).[64]



B = B–H
C = C–Et

62

Oxidative fusion of the *nido*-, *closo*-cobaltacarborane **63**, which has both C_2B_3 and C_2B_4 ligands, yielded the Ru_4Co_4 tetramer **64** whose structure was confirmed crystallographically.[65]

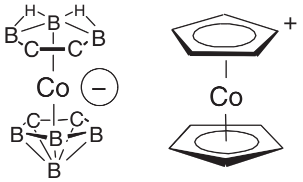


C = C–Et
B = BH, B

63

64

The extensively developed chemistry of cobalt–C_2B_3 complexes has been extended to the remaining cobalt group metals. Following an earlier preparation of $Cp^*Rh(Et_2C_2B_3H_5)$,[66] the iridium analogs $Cp^*Ir(Et_2C_2B_3H_4–X)$ (X = H, Cl) have been synthesized[66a] and used to construct mixed metal cobalt group tetradecker sandwiches (see below). Mixed sandwich cobaltocenium–metallacarborane salts **65** have been prepared and characterized.[67]



C = C–C_2H_5
B = BH

65

Several metal complexes of planar C_2B_3 ligands have been shown to have significant cytotoxicity against lymphoma and leukemia cells in both cultures and solid tumors.[68]

3.01.4.2 C_2B_3 Ring Triple-decker Sandwiches

The study of isolable, robust transition metal multidecker sandwiches began with the synthesis and isolation of isomeric $CpCo(RR'C_2B_3H_3)CoCp$ complexes, which were the first examples of neutral, air-stable triple-decker compounds.[69] Extensive development of this area continued through the period covered by COMC (1982) and COMC (1995), and more recently has been extended in new directions, as is apparent from the compounds listed in Table 3. These studies include detailed electronic probes, new structural modes such as sandwiches endcapped by open C_2B_3 rings and linked triple-deckers, and the synthesis of extended chains. Paramagnetic triple-deckers such as the $Fe^{III}Co^{III}$ species **66**, whose NMR spectra are ordinarily uninformative because the signals are shifted over very broad ranges of frequencies, have been characterized by NMR methods in which the neutral paramagnetic species are gradually reduced and/or oxidized to diamagnetic anions or cations, allowing the paramagnetic spectra to be interpreted via correlation diagrams.[70,71] This is illustrated in Figure 2, where the ^1H NMR signals of neutral paramagnetic $Cp^*Fe(Et_2C_2B_3H_3)CoCp^*$ (29 ve) vary from ca. +20 to −10 ppm; on stepwise reduction to the diamagnetic 30 ve monoanion via exposure of the solution to a potassium mirror, the signals are compressed to a much smaller range, and are readily assigned to the ethyl (A,C), $FeCp^*$ (D), and $CoCp^*$ (B) protons. Further reduction of the anion, or oxidation of the neutral complex, yields the paramagnetic dianion and the paramagnetic monocation, respectively. The slopes of the correlations are proportional to the degree to which the various proton environments are influenced by the addition or subtraction of electron density to the complex. Thus, it is clear that in the $Fe^{III}Co^{III}$ neutral species the unpaired electron resides mainly on Fe, whereas in the $Fe^{II}Co^{II}$ dianion it is primarily located on

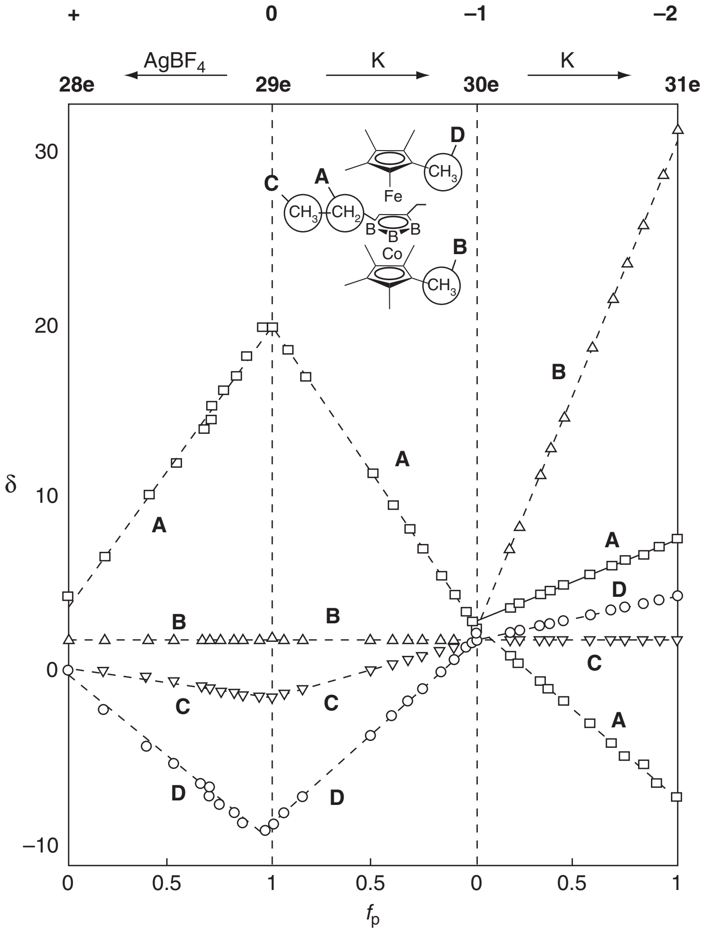
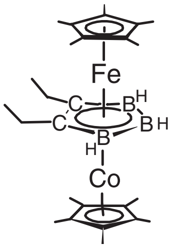


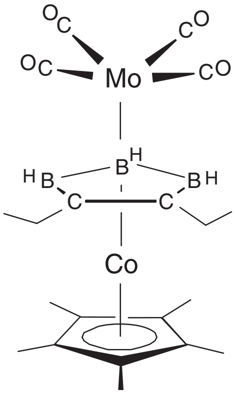
Figure 2 Correlation diagram for ^1H NMR spectra of $Cp^*Fe(Et_2C_2B_3H_3)CoCp^*$ in $CDCl_3$ (for the oxidation) and THF-d_8 (for the reductions), showing δ plotted vs. mole fraction of the paramagnetic component (f_p).[70] Reproduced with permission of the American Chemical Society.

the cobalt center.[70] ESR, Mössbauer, and electrochemical data further illuminate the electronic structures of this and other related multidecker complexes.[70]



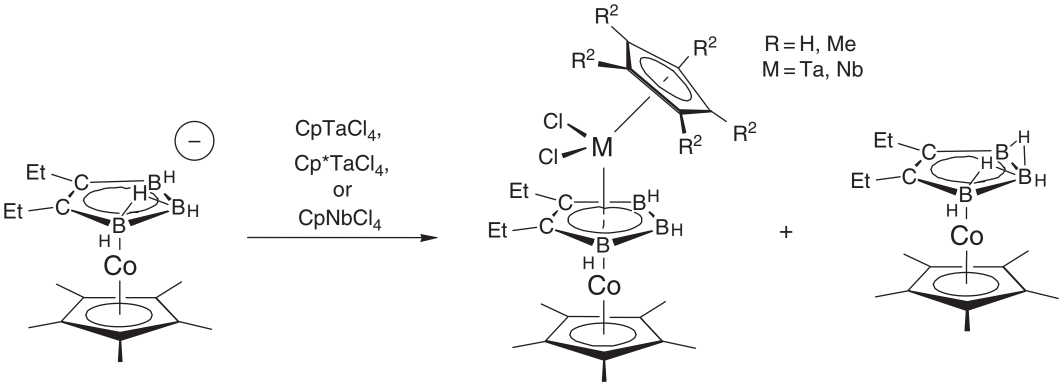
66

Methods for introducing functional groups into Co(C_2B_3)M triple-deckers, important in many synthetic strategies for constructing multicage oligomers and polymers (Section 3.01.4.5), have been developed with the synthesis of B-alkynyl and B-halo derivatives.[52,54,72] Hydridometal triple-deckers have also been synthesized.[73] Carborane-bridged triple-decker and larger carborane sandwich complexes that have arene,[74,75] CO,[76] pyrrolyl,[77] or other groups as end ligands have been prepared and characterized (see Table 3); complex **67** is typical.[76]



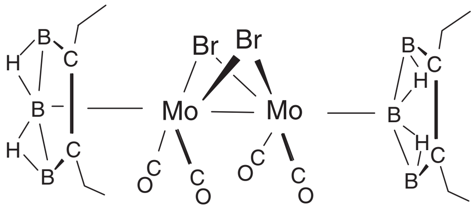
67

Triple-decker sandwiches that are capped at one or both ends by C_2B_3 rings are important synthons for the construction of larger stacks via coordination to metal ions (see the following subsection), and many of these have been synthesized and their reactivity investigated.[75,78] Bent triple-deckers such as **68**[79,80] that resemble bent metallocene complexes have been prepared, structurally characterized, and shown to be amenable to the introduction of halo- and organosubsitutuents at boron.[80]



68

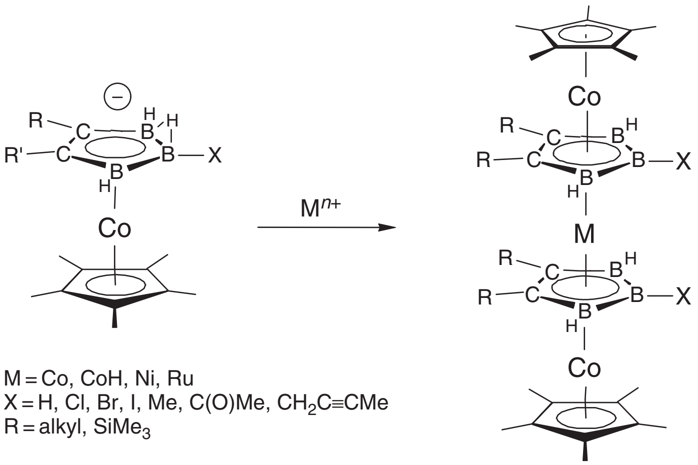
Triple-decker sandwiches of type **69** containing central metal–metal linkages and having C_2B_3 or C_2B_4 end ligands have been synthesized.[76]



69

3.01.4.3 C_2B_3 Ring Tetradecker Sandwiches

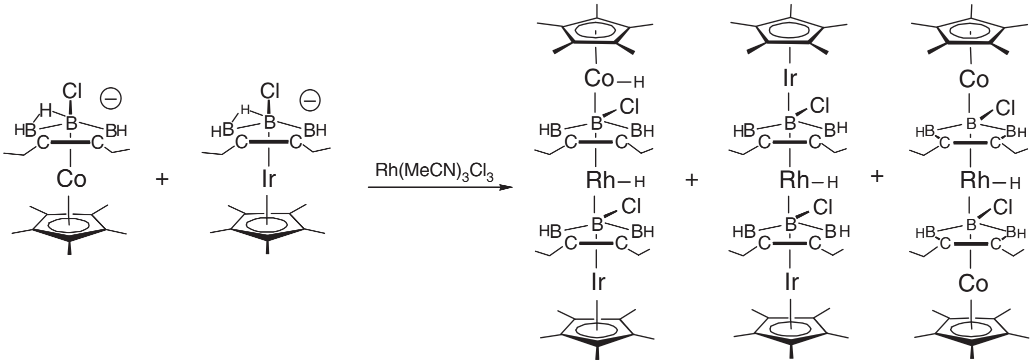
During the 1990s, rational methods for the construction of C_2B_3-bridged tetradecker and larger sandwiches were developed in the author's group. In these syntheses, anionic stacks having an open C_2B_3 end ring are face-bonded to a central metal ion **70**.[66a,81,82]



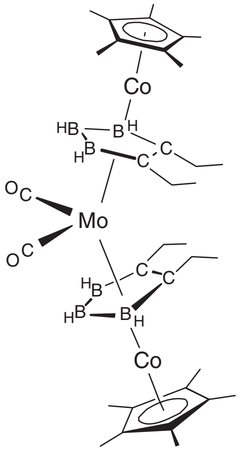
M = Co, CoH, Ni, Ru
X = H, Cl, Br, I, Me, C(O)Me, $CH_2C{\equiv}CMe$
R = alkyl, $SiMe_3$

70

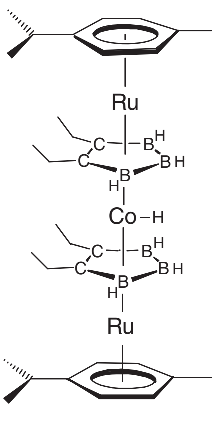
Heterotrimetallic sandwiches involving all three cobalt group metals **71–73** have been prepared and isolated:[66a] other tetradecker types synthesized recently include bent,[76] arene-endcapped,[74] and C_2B_3-endcapped[75] sandwiches **74–76**.



71 **72** **73**



74



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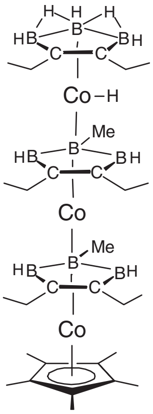
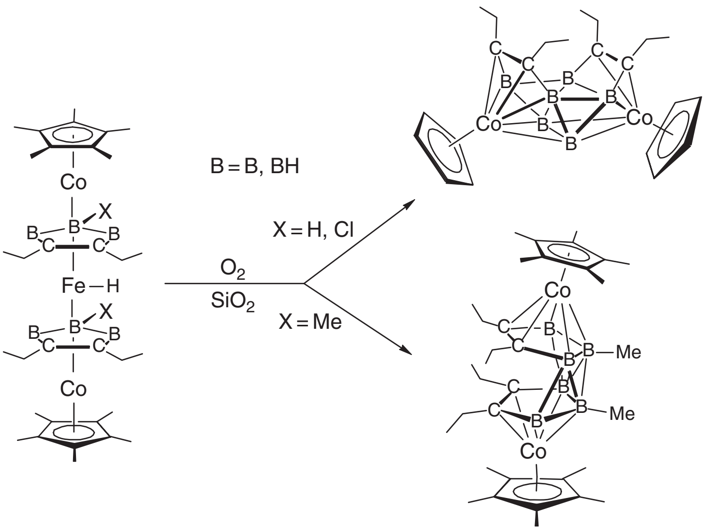


76

Iron-centered tetradecker sandwiches, when in contact with oxygen on silica, undergo oxidative fusion with ejection of iron to generate 12-vertex $Co_2C_4B_8$ clusters.[83] The cluster geometry, however, depends on the nature of the substituent X at B(3) in the iron sandwich. When X = H or Cl, the isolated species are of type **62**, also obtained directly from CoC_2B_3 complexes as described in Section 3.01.4.1;[64] when X = Me, the cluster produced is **77**.[84]



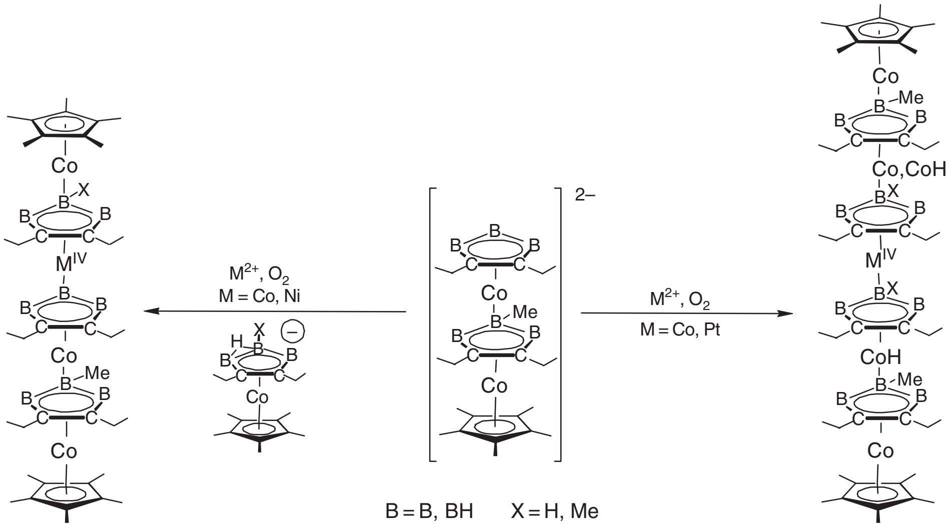
62

77

The electronic properties of C_2B_3-bridged tetradecker (and larger) sandwich complexes have been examined via electrochemical, ESR, and other methods. In general, it was found that in paramagnetic species the unpaired electron(s) are largely delocalized over the three metal centers.[84]

3.01.4.4 C_2B_3 Ring Pentadecker and Hexadecker Sandwiches

Covalently bonded sandwiches having five or six decks **78, 79** have been constructed via the reactions of C_2B_3-endcapped anions with transition metal cations:[78,85] the hexadeckers vary in metal composition, in the nature of the substituents on boron (X), in the number of protonated metal centers, and in the number of electrons associated with the metals. Some of these complexes are diamagnetic, but most are paramagnetic with one or two unpaired electrons, in most cases extensively delocalized over the stack as shown by ESR and electrochemical studies.[85]

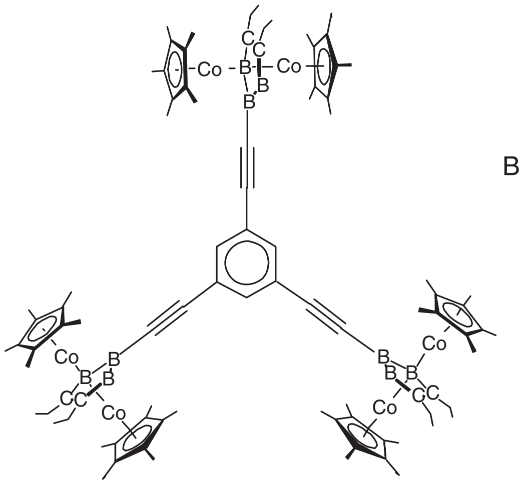


78

79

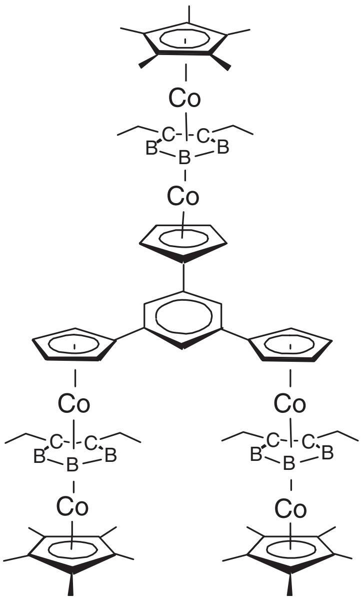
3.01.4.5 C_2B_3 Ring Multisandwich Assemblies

The general air stability, solubility in hydrocarbons, and electronic properties of the C_2B_3-bridged multidecker sandwich complexes (e.g., 80, 81) suggest possible nanoelectronic applications including, for example, conducting or semiconducting polymers that can be tailored to have specified combinations of properties.[45,46,48,86] Oligomers and polymers of several different architectural types have been constructed and characterized, in some of which the individual sandwich or cluster units are directly linked via the B–B or C–C bonds, while others are connected by alkenyl, alkynyl, thionyl, or other connecting groups. In the fulvalene-bridged oligomer 82,[87] electrochemical data suggest extensive electron delocalization through the entire chain,[88] while in 83, whose bridging phenylene rings are tilted out of the Cp ring planes, there is little communication between the individual tetradecker stacks.[61] Some insight into the electronic properties of poly(multidecker sandwich) complexes such as 80 and related systems has been gained through detailed electrochemical, UV–visible, and theoretical studies.[72]

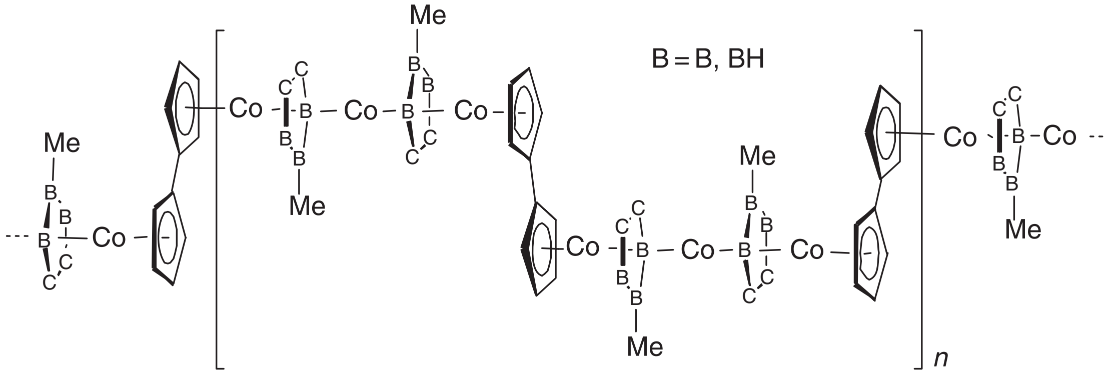


80[54,58]

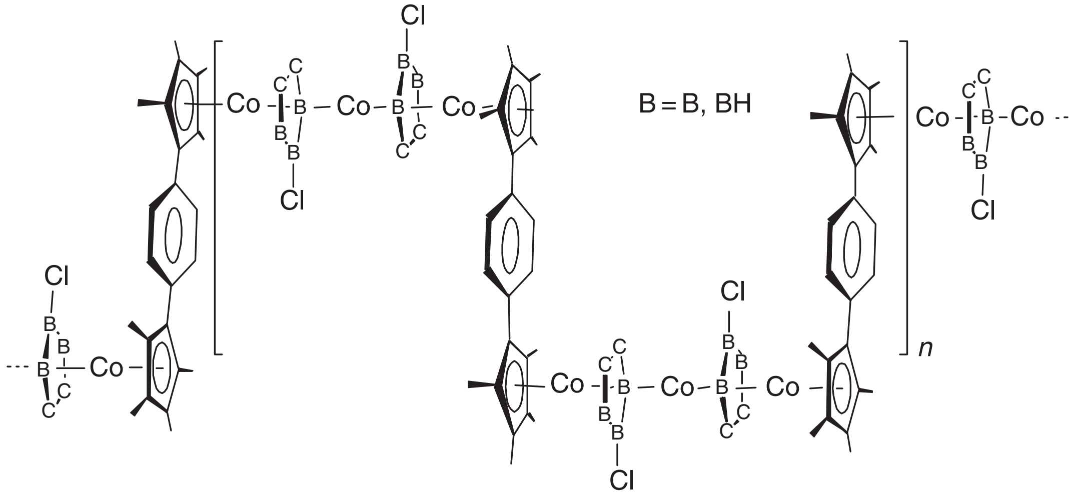
B = BH



81[57]



82[87]



83[87]

3.01.5 Complexes of C_5B (Borabenzene and Boratabenzene) Rings

The formal addition of H^-, or more generally R^-, to neutral, 5π-electron H_5C_5B (borabenzene, Figure 1) affords $H_5C_5BR^-$ (boratabenzene) anions, which feature 6π-electron planar rings and are electronically analogous to cyclopentadieneide ion; indeed, $Fe(H_5C_5B–Me)_2$ resembles ferrocene in its chemical properties.[89] Like $C_5H_5^-$, boratabenzene ligands face-bond to metal ions to form stable molecular sandwich complexes (Table 4), and thus have attracted attention as potentially valuable alternatives to metallocene-based catalysts for ethylene polymerization and in other applications.[89,90] In the interval since the publication of COMC (1995), the field has expanded markedly

Table 4 Complexes of C_5B, C_6B, and C_7B rings 1993–2005

Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Mononuclear C_5B complexes (double-decker sandwiches)		
Lithium		
$Li(OC_4H_8)^+\ Li(H_5C_5BH)_2^-$	S, X, H, B, C	125
$[Me_2N(CH_2)_3NMe_2]\mathbf{Li}^+\ (H_5C_5B–NR_2)^-$ (R = Me, Et)	S, X(Me)	91
(tmeda)$\mathbf{Li}^+\ (Me_3H_8C_{10}B–NMe_2)^-$ chiral α-pinene boratabenzene	S, X, H, B, C, Li	122
(tmeda)$\mathbf{Li}^+\ (Me_3H_8C_{10}B–Me)^-$ pinene-fused dihydroborinine	S, X, H, B, C	123

(*Continued*)

Table 4 (Continued)

Compound[a]	*Information*[b]	*References*
$(18\text{-crown-}6)\mathbf{K}^+(H_5C_5B{-}NPh_2)^-$ (B–N π-bonding stronger than B–P π-bonding)	S, X	112
$(18\text{-crown-}6)\mathbf{K}^+(H_5C_5B{-}PPh_2)^-$ (B–P π-bonding stronger than B–P π-bonding)	S, X	112
$(tmeda)\mathbf{Li}^+(H_9C_{13}B{-}Ph)^-$ 9-boraanthracene complex	S, X, H, B, C	107
Sodium		
$\mathbf{Na}^+(H_5C_5B{-}CH{=}CH{-}C_6H_4{-}CH{=}CHPh)^-$ boratastilbene complex	S, UV	130
$\mathbf{Na}_2{}^+\ [(H_5C_5B{-}CH{=}CH)_2C_6H_4]^{2-}$ boratastilbene complex	S, X, UV	130
Scandium		
$[\mathbf{Sc}(H_5C_5B{-}Me)_2]_2(\mu\text{-}Cl)_2$	S, X, H, B, C	120
$[\mathbf{Sc}(3,5\text{-}Me_2H_3C_5B{-}NMe_2)_2]_2(\mu\text{-}Cl)_2$	S, X, H, B, C	120
$Cl\mathbf{Sc}[3,5\text{-}Me_2H_3C_5B\text{-}N(SiMe_3)_2]_2$	S, X, H, B, C	120
$Ph_2(C_4H_8O)\mathbf{Sc}(H_5C_5B{-}Ph)$	S, X, H, B, C	98
$Ph(C_4H_8O)\mathbf{Sc}(H_5C_5B{-}Ph)_2$	S, H, B, C	98
Titanium		
$Cl_3\mathbf{Ti}(H_5C_5B{-}Me)$	S, X, H, B, C, E, MS	119
cyclo-$(Cl_2\mathbf{M})N(C\mathbf{Me}_3)SiMe_2[H_4C_5B{-}N(CHMe_2)_2]$ $(\mathbf{M} = \mathbf{Zr}, \mathbf{Ti})$ constrained-geometry catalysts for C_2H_4 polymerization	S, X(Zr), H, B, C	109
$[(Me_3Si)_2N]_2\mathbf{Ti}^{III}(H_5C_5B{-}Ph)$	S, X, IR	118
$(H_7C_7B{-}Me)\mathbf{Ti}(H_5C_5B{-}Me)$	S, X, H, B, C, IR	144
(*bicyclo*-$H_8C_9B{-}Me)\mathbf{Ti}(H_5C_5B{-}Me)$	S, H, B, C, IR	144
$[H_6(Me_3Si)C_7B{-}Me]\mathbf{Ti}(H_5C_5B{-}Me)$	S, X, H, B, C, IR	144
Zirconium		
$Cl_3\mathbf{Zr}(H_5C_5B{-}Me)$	S, H, B, C, MS	119
$Cl_2\mathbf{Zr}(H_5C_5B{-}Me)_2$	S, X, H, B, C, E, MS	119
$Cp^*Cl_2\mathbf{Zr}(H_5C_5B{-}Me)$	S, X, H, B, C, E, MS	119
(*cyclo*-$RC{=}C{=}C{=}CR)\mathbf{Zr}(H_5C_5B{-}X)_2$ $[X = N(CHMe_2), Ph)]$	S, X, H, C	114
$(H_9C_9B{-}Ph)\mathbf{Zr}(H_5C_5B{-}Ph)$ boratanaphthalene	S, X, H, C	114
$Cl_2\mathbf{Zr}(H_5C_5B)_2(\mu\text{-}MeNCH_2CH_2NMe)$ (chiral) barrier to conformational equilibrium	S, X, H, C	115
$Cl_2\mathbf{Zr}(H_5C_5B{-}OEt)_2$ catalyst for conversion of C_2H_4 to 1-alkenes)	S, X	99
$Cl_2\mathbf{Zr}(p\text{-}RH_4C_5B{-}Y)_2$ $[R = H, Y = N(CHMe_2)_2;\ R = H, Y = Ph;\ R = CMe_3, Y = Ph]$ catalysts for oligomerization of C_2H_4 in the presence of MAO	X(CMe$_3$,Ph), H, B, C, MS	100
$Cp^*Cl_2\mathbf{Zr}[H_5C_5B{-}N(CHMe_2)_2]$ catalyst for polymerization of C_2H_4 in the presence of MAO	S, X	103
$Cl_2\mathbf{Zr}[H_5C_5B{-}N(CHMe_2)_2]_2$ catalyst for polymerization of C_2H_4 in the presence of MAO	S, X	103
$Me_2\mathbf{Zr}[H_5C_5B{-}N(CHMe_2)_2]_2$ catalyst for polymerization of C_2H_4 in the presence of MAO	S	103
$X_2\mathbf{Zr}[{-}H_4C_5B{-}N(CHMe_2)_2](\mu\text{-}CH_2CH_2)$ $(X = Cl, Me)$ catalyst for polymerization of alkenes in the presence of MAO	S, X(Me), H, B, C, MS	106
$Cl_2\mathbf{Zr}[{-}H_4C_5B{-}N(CHMe_2)_2](\mu\text{-}SiMe_2)$ catalyst for polymerization of alkenes in the presence of MAO	S, H, B, C, MS	106
$Cl_2\mathbf{Zr}[{-}H_4C_5B{-}N(CHMe_2)_2](\mu\text{-}CMe_2)$ catalyst for polymerization of alkenes in the presence of MAO	S, X, H, B, C, MS	106
$Cl_2\mathbf{Zr}$(*exo*/*exo*-$Me_3H_8C_{10}B{-}X)$ $(X = NMe_2, OMe, Me)$ chiral pinene-fused boratabenzene complexes	S, X(NMe$_2$), H, B, C, MS	124
$Me_2\mathbf{Zr}$(*exo*/*exo*-$Me_3H_8C_{10}B\text{-}NMe_2)$ chiral pinene-fused boratabenzene complexes	S, H, B, C, MS	124
$Cp^*Me_2\mathbf{Zr}(H_5C_5B{-}R)$ $(R = NMe_2, OEt, Ph)$	S, H, B, C, E(OEt)	113
$Cp^*Me[MeB(C_6F_5)_3]\mathbf{Zr}(H_5C_5B{-}R)$ $(R = NMe_2, OEt, Ph)$	S, X(NMe$_2$, Ph), H(var. temp., NMe$_2$, Ph), B, C, F	113
$Cp^*(CO)_2\mathbf{Zr}(H_5C_5B{-}R)$ $(R = NMe_2, OEt, Me, Ph)$	S, H, B, C, IR	113

(Continued)

Table 4 (Continued)

Compound[a]	*Information*[b]	*References*
$(CO)_2\mathbf{Zr}(H_5C_5B–R)_2$ (R = NMe_2, OEt, Me, Ph)	S, H, B, C, IR	113
$Cl_2\mathbf{Zr}(H_5C_5B–R)_2$ (R = NMe_2, Me)	S, E	113
$Cl_2\mathbf{Zr}(H_5C_5B–OR)_2$ (R = *cyclo*-C_6H_{13}, Ph, CH_2Ph) catalyst for oligomerization of C_2H_4 in the presence of MAO	S, X(Ph), H, B, C	105
$Cl_2\mathbf{Zr}(H_5C_5B\text{-}OR)_2(\mu\text{-}cyclo\text{-}C_6H_{10})$	S, X, H, B, C	105
$Cl_2\mathbf{Zr}(H_5C_5B\text{-}O\text{-})(\mu\text{-binap})$ catalyst for oligomerization of C_2H_4 in the presence of MAO	S, H, B, C	105
$Cp^*Cl_2\mathbf{Zr}(H_5C_5B–Me)$	S, X, H, B, C	105
$Cp^*Cl_2\mathbf{Zr}(H_5C_5B–OEt\cdot AlMe_3)$	S, X, H, B, C	105
$Cl_2\mathbf{Zr}(H_5C_5B–R)_2$ (R = Me, Ph) catalyst for oligomerization of C_2H_4 in the presence of MAO	S	105
$Cp^*Cl_2\mathbf{Zr}(H_5C_5B–Me)$	S, H, B, C, MS	119
$Cp^*Cl_2\mathbf{Zr}(H_5C_5B–Ph)$ catalyst for polymerization of C_2H_4 in the presence of MAO	S, H, B, C	107
$Cl_2\mathbf{Zr}(H_5C_5B–R)_2$ (R = Ph, OEt) catalyst for conversion of C_2H_4 to branched polyolefins in the presence of MAO		104
$Cp^*\mathbf{Zr}(H_7C_9B–R)$ [R = NEt_2, $N(CHMe_2)_2$] boratanaphthalene	S, $X(CHMe_2)_2$, H, B, C, MS	116
$Cp^*Me_2\mathbf{Zr}(H_9C_{13}B–Ph)$ 9-boraanthracene	S, H, B, C	107
$Cp^*Cl_2\mathbf{Zr}(H_9C_{13}B–Ph)$ 9-boraanthracene catalyst for polymerization of C_2H_4 in the presence of MAO	S, X, H, B, C	107
$(PhCH_2)_3\mathbf{Zr}(H_5C_5B–CH_2Ph)$	S, H, B, C	98
$(PhCH_2)_2\mathbf{Zr}(H_5C_5B–CH_2Ph)_2$ catalyst for polymerization of C_2H_4 in the presence of MAO or $B(C_6F_5)_3$,	S, H, B, C	98
$(Me_2N)_3\mathbf{Zr}(H_5C_5B–NMe_2)$	S, X, H, B, C	98
Hafnium		
$Cl_3\mathbf{Hf}(H_5C_5B–Me)$	S, H, B, C, MS	119
$Cl_2\mathbf{Hf}(H_5C_5B–Me)_2$	S, H, B, C, MS	119
$(PhCH_2)_3\mathbf{Hf}(H_5C_5B–CH_2Ph)$	S, X, H, B, C	98
Tantalum		
$(Ph_3H_4C_4)Me_2\mathbf{Ta}(H_5C_5B–Me)$	S, X, H, C	117
$(C_4H_6)Cp^*\mathbf{Ta}[H_5C_5B–N(CHMe_2)_2]$	S, X, H, C	117
Chromium		
$(CO)_3\mathbf{Cr}[(SiMe_3)H_4C_5B–(oxazoline)]$ single stereoisomer	S, X, H	126
$\mathbf{Cr}(H_5C_5B–R)_2$ (R = Me, NMe_2, Ph) co-catalysts for C_2H_4 polymerization with MAO or $B(C_6F_5)_3$	S, X(Me, NMe_2), H, IR	102
$Cl_2(Me_3P)\mathbf{Cr}(H_5C_5B–Me)$ co-catalysts for C_2H_4 polymerization with MAO or $B(C_6F_5)_3$	S, X, H, IR	102
$[Me\mathbf{Cr}(H_5C_5B–Me)]_2(\mu\text{-}Cl)_2$ (R = Me, NMe_2, Ph) co-catalysts for C_2H_4 polymerization with MAO or $B(C_6F_5)_3$	S, X, H, IR	102
$(H_5C_5N)R_2\mathbf{Cr}(H_5C_5B–R)$ (R = Ph, Me) co-catalysts for C_2H_4 polymerization with MAO or $B(C_6F_5)_3$	S, X, H, B, IR	102
$L_2(Me_3P)\mathbf{Cr}(H_5C_5B–R)$ (L = Me, Ph) co-catalysts for C_2H_4 polymerization with MAO or $B(C_6F_5)_3$	S, X, H, B	101
$[MeB(C_6F_5)_3]^+$ $[Me(Me_3P)_2\mathbf{Cr}(H_5C_5B–Me)]^-$	S, X, H, B	101
Manganese		
$(CO)_3\mathbf{Mn}[H_5C_5B–NRR']$ (R, R′ = $CHMe_2)_2$; R = Me, R′ = Bz) B–N bond rotation studied	S, X(Me, Bz), H (var. temp), B, C, MS	111
$(CO)_3\mathbf{Mn}(Me_3H_8C_{10}B–NMe_2)$ chiral pinene-fused boratabenzene complex	S, H, B, C, MS	124
Iron		
$(C_6Me_6)\mathbf{Fe}(H_5C_5B–R)$ (R = Me, Ph, NEt_2)	S, X(Me), H, ESR, E, MS	127
$(\eta^5\text{-}C_6Me_7)\mathbf{Fe}(H_5C_5B–R)$ (R = Me, Ph, NEt_2)	S, H, B, C, E	127
$(\eta^5\text{-}C_6Me_6H)\mathbf{Fe}(H_5C_5B–R)$	S, H	127
$(C_6Me_6)\mathbf{Fe}(H_5C_5B–OH)$	S, H, ESR, E, MS	127
$[(C_6Me_6)Fe(H_5C_5B–R)]^+$ (R = Me, Ph, NEt_2, OH)	S, X(Me), H, B, C, IR, E	127

(Continued)

Table 4 (Continued)

Compound[a]	*Information*[b]	*References*
$(\mathrm{C_6Me_6})\mathbf{Fe}(\eta^5\text{-}\mathrm{H_5MeC_5B{-}Ph})$ (Three isomers)	S, H, B, C, IR, E	127
$(\mathrm{C_6Me_6})\mathbf{Fe}(\eta^5\text{-}\mathrm{H_6C_5B{-}Ph})$ (Two isomers)	S, H, B, C, IR	127
$\mathbf{Fe}(\mathrm{H_5C_5B})_2(\mu\text{-}\mathrm{MeNCH_2CH_2NMe})$ (chiral) barrier to conformational equilibrium	S, X, H, C	115
$\mathbf{Fe}[\mathrm{H_5C_5B{-}NRR'}]_2$ (R, R′ = $\mathrm{CHMe_2}$; R = Me, R′ = Bz) B–N bond rotation studied	S, H (var. temp), B, C, MS	111
$\mathrm{Cp^*}\mathbf{Fe}$(*exo*/*endo*-$\mathrm{Me_3H_8C_{10}B{-}X}$) (X = $\mathrm{NMe_2}$, OMe, Me) chiral pinene-fused boratabenzene complexes	S, X(*exo*-$\mathrm{NMe_2}$), H, B, C, MS	124
Ruthenium		
$\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_5C_5B{-}R})$ (R = $\mathrm{NMe_2}$, OMe, Me)	S, H, B, C	131
$\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_5C_5B{-}Me})$	S, H, B, C, E, MS	132
$\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_7C_9B{-}Me})$ boratanaphthalene	S, X, H, B, C, MS	116
Rhodium		
$[\mathrm{Cp^*}\mathbf{Rh}(\mathrm{H_5C_5B{-}Me})]^+$	S, H, C	131
$(\mathrm{C_2H_4})_2\mathbf{Rh}(\mathrm{H_5C_5B{-}R})$ (R = Ph, $\mathrm{NMe_2}$)	S, X, H, catalysis of (*cyclo*-$\mathrm{C_2Me_4OBO}$) to (*cyclo*-$\mathrm{C_2Me_4OB\{(CH_2)_7Me\}O}$)	110
Germanium		
$\mathbf{Ge}(\mathrm{H_5C_5B{-}Me})_2$	S, H, B, C, MS	121
Tin		
$\mathbf{Sn}(\mathrm{H_5C_5B{-}Me})_2$	S, H, B, C, MS	121
Lead		
$\mathbf{Pb}(\mathrm{H_5C_5B{-}Me})_2$	S, X, H, B, C, Pb, MS	121
$\mathbf{Pb}(\mathrm{H_5C_5B{-}Me})_2\cdot\mathrm{L}$ (L = tmeda, bipyridyl)	S, X(bipyr), H, B, C, Pb, MS	121
Dinuclear C_5B complexes (triple-decker sandwiches and dimers)		
Iron		
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Fe}\mathrm{Cp^*}]^+$	S, X, B, E, UV, MS	132
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{M}\mathrm{Cp^*}]^+$ (**M** = **Ru**, **Rh**, **Ir**)	S, B, E, UV, MS	132
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{M}\mathrm{Cp^*}]^{2+}$ (**M** = **Rh**, **Ir**)	S, H, C	132
Ruthenium		
$[\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_5C_5B{-}Me})\mathbf{Ru}\mathrm{Cp^*}]^+$	S, X, H, B, C	131
$[\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_5C_5B{-}Me})\mathbf{Rh}\mathrm{Cp^*}]^{2+}$	S, H, B, C	131
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Ru}\mathrm{Cp^*}]^+$	S, B, E, UV, MS	132
$\mathrm{Cp^*}\mathbf{Ru}[\mathrm{H_5C_5B{-}C{\equiv}C(C_5H_4)FeCp}]^+$ nonlinear optics application	S, X, H, C, IR, UV, E, hyper-Rayleigh scattering	20
Cobalt		
$1,4\text{-}[\mathrm{Cp}\mathbf{Co}(\mathrm{H_5C_5B})]_2\mathrm{C_6H_4}$ (phenylene-linked)	S, X, H, B, C, IR, E, MAG	128
Rhodium		
$[(\mathrm{C_8H_{12}})\mathbf{Rh}(\mathrm{H_5C_5B{-}Me})\mathbf{Rh}(\mathrm{C_8H_{12}})]^+$	S, X, B, H	132
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Rh}\mathrm{Cp^*}]^+$	S, B, E, UV, MS	132
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Rh}\mathrm{Cp^*}]^{2+}$	S, H, C	132
$[\mathrm{Cp^*}\mathbf{Ru}(\mathrm{H_5C_5B{-}Me})\mathbf{Rh}\mathrm{Cp^*}]^{2+}$	S, H, B, C	131
$\mathrm{Cp^*}\mathbf{Rh}[\mathrm{H_5C_5B{-}C{\equiv}C(C_5H_4)}\mathbf{Fe}\mathrm{Cp}]^+$ nonlinear optics application	S, X(Rh), H, C, IR, UV, E, hyper-Rayleigh scattering	20
Iridium		
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Ir}\mathrm{Cp^*}]^+$	S, B, E, UV, MS	132
$[\mathrm{Cp^*}\mathbf{Fe}(\mathrm{H_5C_5B{-}Me})\mathbf{Ir}\mathrm{Cp^*}]^{2+}$	S, H, C	132
$\mathrm{Cp^*}\mathbf{Ir}[\mathrm{H_5C_5B{-}C{\equiv}C(C_5H_4)FeCp}]^+$ nonlinear optics application	S, X(Rh), H, C, IR, UV, E, hyper-Rayleigh scattering	20
C_6B complexes		
Molybdenum		
$(\mathrm{H_6C_6B{-}R})\mathbf{Mo}(\mathrm{CO})_3$ [R = H, OMe, OH, $\mathrm{N(CHMe_2)_2}$, $\mathrm{N(CH_2)_5}$, $\mathrm{N(C_6H_{11})_2}$, $\mathrm{NMeCH_2Ph}$, $\mathrm{O_{1/2}}$] borepin complexes	S, X[$\mathrm{N(CHMe_2)_2}$], H, B, C, IR, MS	142

(Continued)

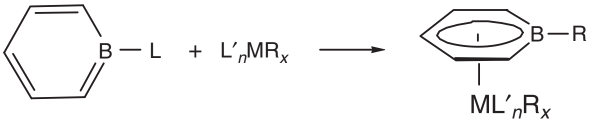
Table 4 (Continued)

Compound[a]	*Information*[b]	*References*
C_7B complexes		
(H_7C_7B–Me)**Ti**(H_5C_5B–Me)	S, X, H, B, C, IR	144
[$H_6(Me_3Si)C_7B$–Me]**Ti**(H_5C_5B–Me)	S, X, H, B, C, IR	144
Theoretical studies		
Catalytic activity calculations		
$[(\eta^6\text{-}H_5C_5B)\text{-}CMe_2\text{-}(\eta^6\text{-}C_6H_5)M^{II}(HC{=}CH)_2]^+$ (M = Zr, Hf)	Conversion of C_2H_4 to linear α-olefins, C_2H_4 trimerization (DFT)	108

[a] Metals coordinated to C_nB rings are shown in boldface.

[b] Legend: S = synthesis, X = X-ray diffraction, H = ^{1}H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^{7}Li NMR, Pt = ^{195}Pt NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.

through contributions from Herberich, Ashe, Bazan, Fu, and others. A significant advance during this period was the discovery of a more efficient route to borabenzene derivatives that utilizes metal-promoted electrocyclic ring closure of 2,4-pentadienylborane intermediates.[91–93] An earlier method, involving the hydrostannation of 1,4-pentadiynes to form stannacyclohexadienes that are converted to boratabenzenes on reaction with boron halides, has been extended to generate a variety of new $H_5C_5BR^-$ derivatives[89,94–97] that are available as ligands in metal sandwich complexes. Bazan and co-workers have found that boratabenzene complexes can be generated from base-substituted borabenzene precursors via intramolecular nucleophilic substitution:[98]



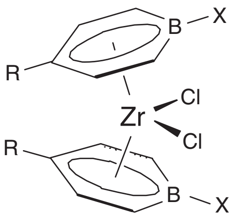
L = PMe_3, C_5H_5N

R = Ph, CH_2Ph

M = Sc, Zr, Hf

3.01.5.1 C_5B Ring Double-decker Sandwiches

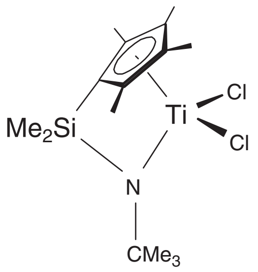
Considerable effort has been directed to the study of early transition metal boratabenzene complexes in catalysis. Bazan has explored $Cl_2Zr(H_5C_5B–R)_2$ sandwiches **84** as co-catalysts with MAO in the conversion of ethylene to 1-alkenes.[98–102] The catalytic properties of these complexes toward C_2H_4 in the presence of MAO can be tuned by varying the substituent X on boron. Thus, when X is $N(CHMe_2)_2$, the product is high molecular weight polyethylene;[100,103] more electrophilic substituents promote faster β-hydrogen elimination, leading to 1-alkenes and dimers thereof.[100] A different approach employing **84**-type complexes in combination with silicon-bridged titanium species **85** as co-catalysts with MAO converts ethylene to branched polyolefins.[104] The catalytic activity of B-alkoxy and B-aryloxy derivatives of type **84** (with MAO) toward ethylene varies considerably with the choice of X; 1-alkenes are the predominant products, but when the two X groups are replaced by a 1,2-*trans*-cyclohexanediol bridge, polyethylene is generated.[105] Other zirconium–boratabenzene complexes that have been explored as olefin polymerization co-catalysts with MAO include bridged[106] and borataanthracene[107] derivatives **86, 87**.



X = Ph, $N(CHMe_2)_2$

R = H, CMe_3

84



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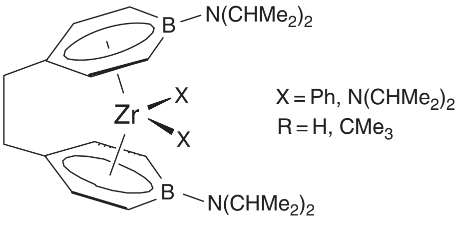
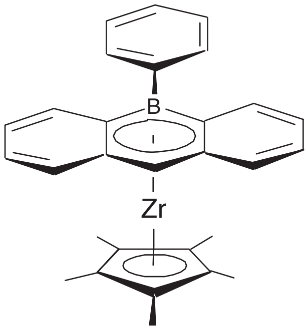


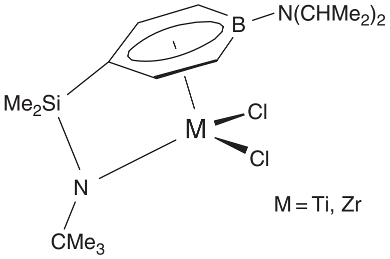
86[106]



87[107]

The activity of CMe_2-bridged Zr(II) and Hf(II) boratabenzene cationic complexes toward ethylene trimerization has been explored computationally using a gradient-corrected DFT approach; the Zr species was calculated to be a highly efficient catalyst, exceeding the efficiency of the corresponding Cp system.[108]

Constrained-geometry catalysts for C_2H_4 polymerization 88 that are counterparts of well-known *ansa*-metallocene systems have been prepared and shown to be active, in combination with MAO, toward polymerization of ethylene; the product is almost entirely polyethylene, with ca. 1% of 1-octene obtained. The titanium complex was found to be four times as active as the zirconium species.[109]



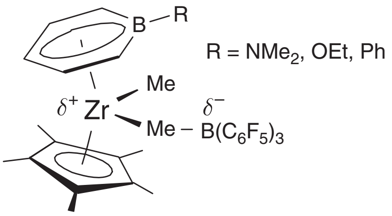
88

Late transition metal boratabenzene complexes can catalyze C–H activation; thus, the bis(ethylene)rhodium derivatives $(H_5C_5B\text{–}R)Rh(C_2H_4)_2$ (R = Ph, NMe_2) promote boration of alkanes faster than does the Cp^* analog $Cp^*Rh(C_2H_4)_2$, although the boratabenzene compounds are thermally less stable.[110]

The molecular and electronic structures and bonding interactions in boratabenzene–transition metal sandwich complexes have been explored in detail. The rate of exocyclic B–N bond rotation in B-amino manganese and iron complexes has been measured via variable-temperature NMR spectroscopy, and was found to be strongly influenced by the electron-withdrawing power of the metal.[111] Thus, in $(CO)_3Mn(H_5C_5B\text{–}NMeCH_2Ph)$, NMR and X-ray diffraction data show that the B–N binding is much stronger than the B–Mn interaction. A crystallographic study comparing P–B and N–B π-bonding in phosphido- and amidoboratabenzene salts revealed that the B–N interaction is significantly stronger,[112] a finding that correlates with their respective chemical reactivities.

Bazan and co-workers have probed the electron-donating abilities of various boratabenzenes as ligands in zwitterionic zirconium complexes 89 which undergo ion-pair dissociation/recombination in solution, and in dicarbonyl sandwiches 90, 91.[113] In this study, changes in electron density at the metal as a function of the boron substituent were measured via variable-temperature NMR, electrochemical, infrared (IR), and crystallographic evidence, and applied to the tuning of boratabenzene catalysts for olefin polymerization. As in other studies, the authors concluded that this "tunability" in boratabenzene complexes confers the advantage of greater versatility than that of standard metallocene catalysts.

The bis(trimethylphosphino)zirconium complex 92 undergoes unusual reactions with alkynes.[114] With diynes, metallocyclic products 93 are formed, whereas acetylene affords 94 whose nonplanar boratanaphthalene ligand is coordinated to Zr via both C_5B rings. In 94 the bridgehead carbon is close to Zr (2.39 Å) and is presumably bound to it, making this carbon atom pentacoordinate.[89,114] Ashe and co-workers have prepared chiral bis(boratabenzene) iron and zirconium complexes in which the two boron atoms are linked by $MeNCH_2CH_2NMe$ chains, and determined the barrier to the interconversion of the enantiomers, which is higher than that of the Cp analogs.[115]



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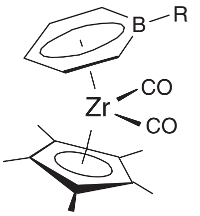

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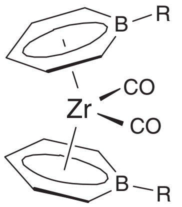

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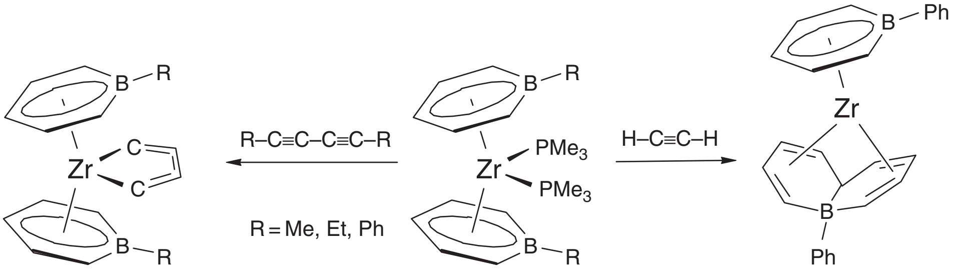
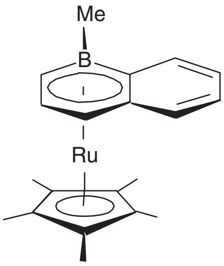


93 **92** **94**

Boratanaphthalene complexes of ruthenium and zirconium 95, 96 have been synthesized by Ashe and co-workers.[116] In 96 the binding of the metal to the C_5B ring is unsymmetrical, with very long Zr–B and Zr–bridgehead carbon distances suggesting little or no bonding interaction. In related work, (tribenzyldimethane)Ta(boratabenzene) complexes that are counterparts of well-known Cp systems have been synthesized and structurally characterized.[117] The Cp–boratabenzene analogy has also been pursued in the preparation of Ti(III) complexes such as $[(Me_3Si)_2N]_2Ti^{III}(H_5C_5B\text{–}Ph)$, which is inactive in promoting C_2H_4 polymerization.[118]



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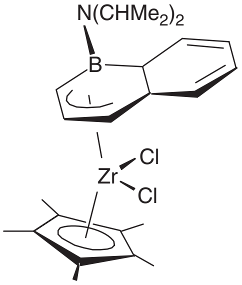
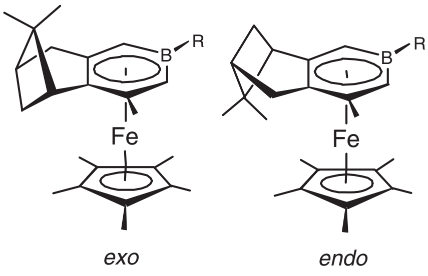


96

Since 1993 a number of advances in boratabenzene–metal chemistry have been reported from Herberich's laboratory. Complexes of the type $Cl_3M(H_5C_5BMe)$ and $CpCl_2M(H_5C_5BMe)$ (M = Ti, Zr, Hf) were prepared from the metal tetrachlorides and MCl_3Cp reagents, respectively,[119] while monomeric and dimeric scandium–boratabenzene complexes were obtained from $ScCl_3$ and $Li(H_5C_5B\text{–}R)$ salts [$R = N(SiMe_3)_2$ or NMe_2].[120] Extension of this field to the *p*-block elements has been accomplished with the synthesis and characterization of the species $M(H_5C_5BMe)_2$ (M = Ge, Sn, Pb), all of which have bent-sandwich structures.[121]

Metal complexes of pinene-fused boratabenzene ligands, analogous to chiral metallocenes that have found application in catalysis and enantioselective synthesis, have been prepared.[122–124] With late transition metals such as Mn and Fe, the complexes are obtained as mixtures of diastereomers (e.g., 97) with the sterically less congested *exo* form predominating, but the bis(ligand) Zr complex 98 was obtained as the pure *exo*,*exo* product.[124] A lithium bis(1-H-boratabenzene) sandwich[125] and an enantiomerically pure Li complex have also been synthesized.[122] In a different approach, Fu *et al.* prepared a planar-chiral Lewis acid complex **99** as a single stereoisomer.[126]



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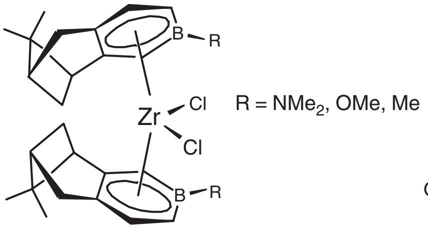

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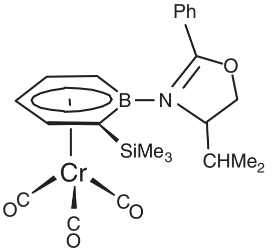
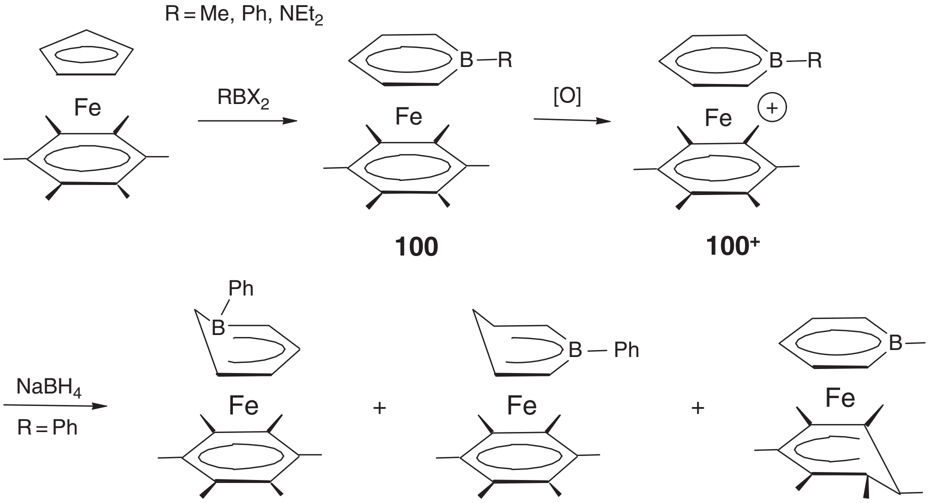


99

The electronic structure of boratabenzene complexes has been a focus of interest. A family of electron-rich 19-valence electron iron sandwiches (e.g., **100**) was prepared via reaction of CpFe(arene) complexes with organic halides and oxidized to their 18e diamagnetic cations.[127] The structures of the cations are markedly different from the neutral species, with the arene ligand adopting, for example, a boat conformation in **100** and an inverted boat conformation in the cation **100**$^+$. This finding illustrates the effect of the "extra" electron in paramagnetic **100**, which appears from ESR data to occupy a predominantly metallic antibonding $a''(3d_{xz})$ orbital. On treatment with $NaBH_4$, the B-phenylated cation undergoes hydride addition, forming (η^5-H_6C_5B–Ph)Fe(η^6-C_6Me_6) isomers **101, 102** and (η^6-H_5C_5B-Ph)Fe(η^5-C_6Me_6H) **103**.[127]



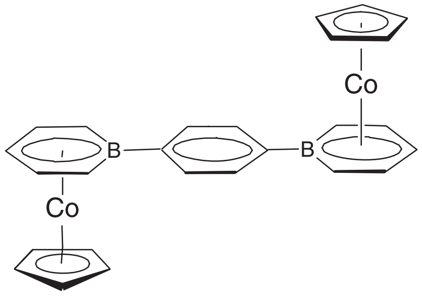
100 **100**$^+$

101 **102** **103**

3.01.5.2 C$_5$B Ring Dinuclear Complexes (Triple-decker Sandwiches and Dimers)

The electronic and magnetic properties of bridged dimetallic complexes such as **104** and **105** have been explored. Oxidation of the Co^{II}–Co^{II} phenylene-bridged species **104** affords the mixed valence Co^{II}–Co^{III} complex and the diamagnetic Co^{III}–Co^{III} dication.[128] Magnetic, IR, and electrochemical evidence on neutral **104** indicates weak Co–Co interaction.

The ethynyl-linked complexes **105** were prepared and explored as potential building blocks for nonlinear optical (NLO) materials.[129] Spectroscopic and cyclic voltammetry data indicate a small but real interaction between the ferrocenyl donor group and the borabenzene unit, increasing in the order Ru < Ir < Rh. Hyper-Rayleigh scattering revealed small values for the first hyperpolarizability β, which increases in the same order.



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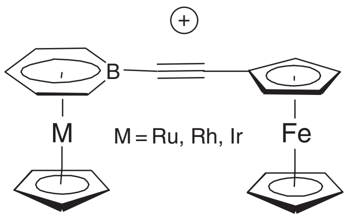
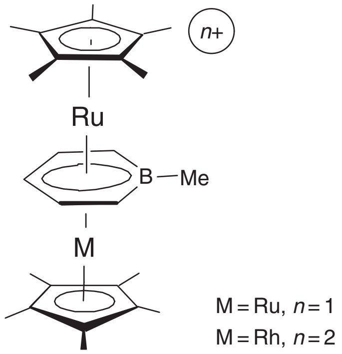


105

Related to these dimetallic systems, though not involving transition metals, are the boratastilbene complexes such as $Na^+[H_5C_5B{-}CH{=}CH{-}C_6H_4{-}CH{=}CHPh]^-$ (isoelectronic with distyrylbenzene chromophores) that show aggregation-dependent photophysics. In nonpolar solvents, they form tightly bound ion pairs that are poorly luminescent, but in polar solvents, or when the counter ions are encapsulated in crown ethers, strong emission is observed as a result of intramolecular charge transfer.[130]

Boratabenzene-bridged multidecker sandwiches are few in number, all prepared in the Herberich group. Stacking reactions of $Cp^*Ru(H_5C_5BMe)$ with electrophilic metal reagents gave complexes **106 and 107**:[131,132] interestingly, some of the stacking processes are reversible—that is, the triple-deckers can be degraded to double-deckers—suggesting that boratabenzene ligands may be undergoing transfer reactions.



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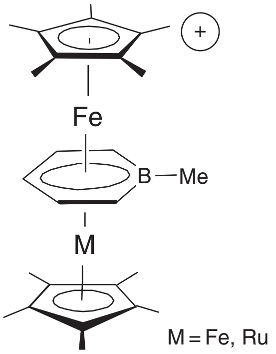


107

3.01.6 Complexes of C_4B_2 Rings

Planar diborabenzene and other ligands containing C_4B_2 rings form η^6-bound metal complexes (Table 5), many of them prepared and characterized by Siebert and co-workers.

Table 5 Complexes of C_4B_2, C_3B_3, and C_2B_4 rings 1993–2005

Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Dinuclear 1,4-diboracyclohexadienene complexes		
Cp**Ni**(η^6-$H_2Me_2C_4B_2Me_2$)**Ni**Cp (triple-decker)	S, H, B, E, MS	133
Mononuclear diboranaphthalene and related complexes		
Iron		
(MeC_6H_5)**Fe**(η^6-$H_8C_{12}B_2Me_2$) (9,10-diboraanthracene)	S, X, H, B, C, ESR, E, MS	137

(*Continued*)

Table 5 (Continued)

Compound[a]	*Information*[b]	*References*
Ruthenium		
(CO)$_3$**Ru**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, E, MS	137
Cobalt		
Cp**Co**[η^6-H$_5$(SiMe$_3$)C$_8$B$_2$(CMe$_3$)$_2$] (1,3-diboranaphthalene)	S, X, H, B, C, MS	135
Cp***Co**[η^6-H$_4$(Me$_4$C$_2$)C$_8$B$_2$Me$_2$] (1,4-diboradodecatetraene)	S, H, B, C, MS	136
Cp**Co**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, ESR, E, MS	137
Nickel		
(η^4-C$_8$H$_{12}$)**Ni**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, MS	137
[(Ph$_2$P)$_2$C$_2$H$_4$]**Ni**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, P, MS	138
(η^6-H$_8$C$_{12}$B$_2$Me$_2$)**Ni**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, H, B, MS	138
Palladium		
(η^4-C$_8$H$_{12}$)**Pd**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, MS	138
Platinium		
(η^4-C$_8$H$_{12}$)**Pt**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, X, H, B, C, MS	138
Rhodium		
Cp**Rh**[η^6-H$_4$(Me$_4$C$_2$)C$_8$B$_2$Me$_2$] (1,4-diboradodecatetraene)	S, X, H, B, C, MS	136
Cp**Rh**(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene)	S, H, B, C, MS	138
Dinuclear diboranaphthalene and related complexes		
Lithium		
[C$_2$H$_4$(Me$_2$N)$_2$]**Li**[η^6-H$_6$C$_8$B$_2$(NMe$_2$)$_2$]**Li**[(Me$_2$N)$_2$C$_2$H$_4$] (2,3-diboranaphthalene triple-decker)	S, X, H, B	134
Iron		
Cp**Fe**[η^6-H$_5$(SiMe$_3$)C$_8$B$_2$(CMe$_3$)$_2$]**Fe**Cp (1,3-diboranaphthalene triple-decker)	S, X, H, B, C, MS	135
Cp**Fe**(η^6-H$_8$C$_{12}$B$_2$Me$_2$)**Fe**Cp (9,10-diboraanthracene triple-decker)	S, X, H, B, C, MS	138
Cobalt		
Cp**Co**[η^6,η^4-H$_5$(SiMe$_3$)C$_8$B$_2$(CMe$_3$)$_2$]**Co**Cp (1,3-diboranaphthalene staggered triple-decker)	S, H, B, C, MS	135
Cp***Co**[η^6,η^4-H$_4$(Me$_4$C$_2$)C$_8$B$_2$Me$_2$]**Co**Cp* (1,4-diboradodecatetraene staggered triple-decker)	S, B, E, MS	136
Cp**Co**[η^6-H$_4$(Me$_2$CH)(MeC$=$CH$_2$)C$_8$B$_2$Me$_2$]**Co**Cp (1,4-diboranaphthalene triple-decker)	S, B, E, MS	136
Cp**Co**(η^6-H$_8$C$_{12}$B$_2$Me$_2$)**Cr**(CO)$_3$ (9,10-diboraanthracene staggered triple-decker)	S, H, B, C, IR, MS	137
Cp**Co**(η^6-H$_8$C$_{12}$B$_2$Me$_2$)**Co**Cp (9,10-diboraanthracene triple-decker)	S, H, B, C, MS	138
Nickel		
(η^3-RC$_3$H$_4$)**Ni**(η^6-H$_8$C$_{12}$B$_2$Me$_2$)**Ni**(η^3-RC$_3$H$_4$) (R = H, Me) (9,10-diboraanthracene triple-decker)	S, X(H), H, B, C, MS	138
Triboratabenzene complexes		
Cp**Co**[η^6-1,3,5-(CHMe$_2$)Me$_2$C$_3$B$_3$Me$_3$]**Co**Cp	S, X, H, B, C, E, MS	139
{Cp**Co**[η^6-1,3,5-(CHMe$_2$)Me$_2$C$_3$B$_3$Me$_3$]**Co**Cp}$^+$	S, H, B, C, MS	139
(η^4-C$_8$H$_{12}$)**Pt**[η^5-1,3,5-(CHMe$_2$)Me$_2$HC$_3$B$_3$Me$_3$]	S, X, H, B, C, MS	139
Tetraboratabenzene complexes		
Cp**Co**[η^6-*cyclo*-(CH$_2$)$_3$C$_2$B$_4$H$_4$]CoCp	S, X, H, B, MS	140
Multinuclear complexes and extended systems		
Cp$^*_3$**Co**$_3$(η^6-H$_8$C$_{12}$B$_2$Me$_2$) (9,10-diboraanthracene trinuclear sandwich)	S, X, H, B, C, MS	138
Theoretical studies		
Molecular and electronic structure calculations		
(CO)$_3$**Fe**(η^6-H$_6$C$_8$B$_2$H$_2$) (1,4-diboranaphthalene)	Extended Hückel	134a
Cp**Fe**(η^6-H$_6$C$_8$B$_2$H$_2$)**Fe**Cp (1,4-diboranaphthalene triple-decker)	Extended Hückel	134a

(*Continued*)

Table 5 (Continued)

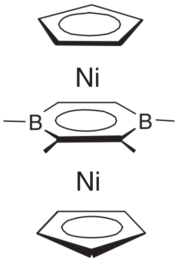
Compound[a]	*Information*[b]	*References*
$(CO)_3$**Fe**$(\eta^6,\eta^4\text{-}H_6C_8B_2H_2)Fe(CO)_3$ (1,4-diboranaphthalene staggered triple-decker)	Extended Hückel	134a
$(CO)_3$**Fe**$(\eta^6,\eta^4\text{-}H_6C_8B_2H_2)Fe(CO)_2$ (1,4-diboranaphthalene twin double-decker)	Extended Hückel	134a

[a] Metals coordinated to C_mB_n rings are shown in boldface.

[b] Legend: S = synthesis, X = X-ray diffraction, H = ^1H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^7Li NMR, Pt = ^{195}Pt NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.

3.01.6.1 Diboracyclohexadiene Complexes

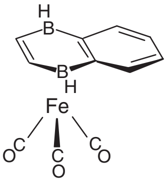
The dinickel triple-decker **108**, a diamagnetic 34 ve sandwich, undergoes electrochemical oxidation to form a stable cation; upon 1e reduction, it is degraded to the double-decker anion $CpNi(1,4\text{-}Me_2H_2C_4B_2Me_2)^-$ and CpNi.[133]



108

3.01.6.2 Diboranaphthalene and Related Complexes

An extended Hückel MO investigation of 1,4-dihydrodiboranaphthalene double- and triple-decker sandwiches[134] (e.g., **109** and **110**) supports a description of these as 18 and 30 ve complexes, respectively.[134a] 1,3-dihydro-1,3-diboranaphthalene complexes of cobalt and iron **111–113** have been synthesized and crystallographically characterized.[135] Metal complexes of the 1,4-diboratetralene ligand **114, 115** have also been prepared.[136]



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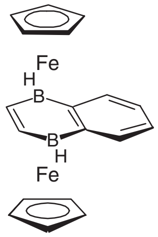

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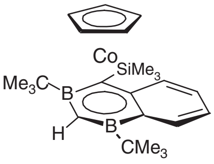

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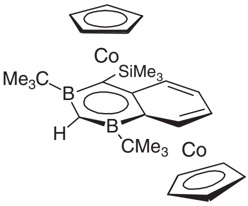

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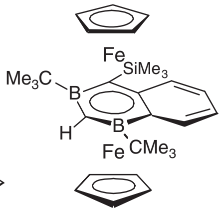

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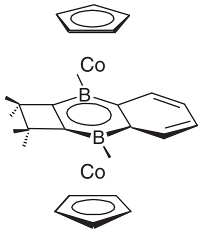

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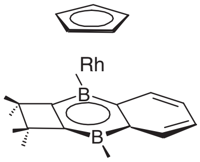
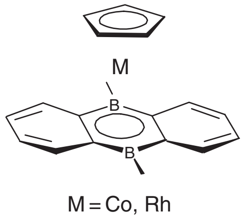


115

Derivatives of the closely related heterocycle 9,10-diboraanthracene react with transition metal fragments such as CpCo, $Ru(CO)_3$, and $Ni(C_8H_{12})$ to form stable sandwich complexes such as **116–119** that illustrate the versatility of this ligand system.[137,138]



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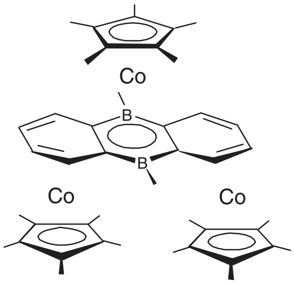

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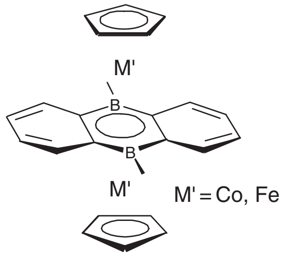

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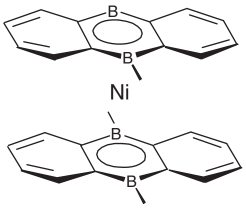
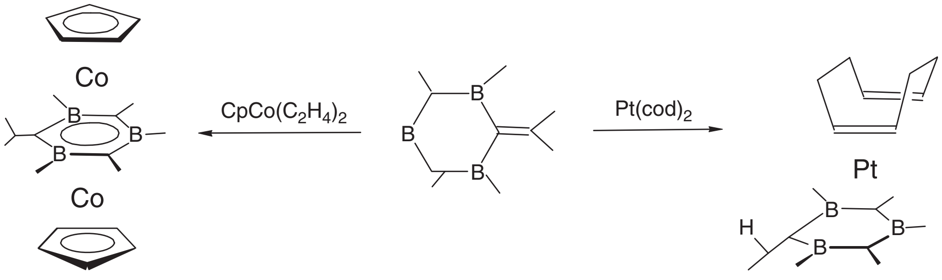


119

3.01.7 Complexes of C_3B_3 and C_2B_4 Rings

3.01.7.1 Triboratabenzene Complexes

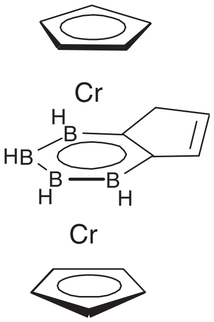
Formal replacement of three carbon atoms in benzene with three B^- ions affords the planar triboratabenzene trianion (Figure 1), whose only known complex is the triple-decker sandwich **120** reported in 1995.[139] This compound was obtained by the reaction of a cyclic isopropylidene with $CoCo(C_2H_4)_2$; treatment of the same organoborane with $Pt(cod)_2$ gave an asymmetrically coordinated platinum complex **121** containing a nonplanar C_3B_3 ring ligand.



120 **121**

3.01.7.2 Tetraboratabenzene Complexes

Serendipitous insertion of $C_5H_5^-$ into the metallaborane $Cp^*_2Cr_2B_4H_8$ gave the triple-decker sandwich **122** in low yield.[140] This compound can be described as an eight-vertex $Cr_2C_2B_4$ *closo*-metallacarborane cluster, and its preparation is notable as one of the few examples of metallacarborane synthesis from a metallaborane precursor (rather than by the usual metal insertion into a carborane), an approach first demonstrated by Grimes and co-workers in the 1970s.[34,141,141a]

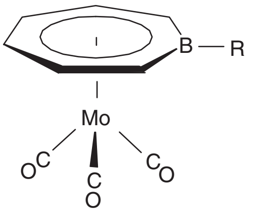


122

3.01.8 Complexes of C_6B, C_5B_2, and C_7B Rings

3.01.8.1 Borepine Complexes

In recent work, Ashe *et al.* have prepared a series of molybdenum tricarbonyl complexes of $C_6H_6B–R$ ligands.[142] X-ray diffraction data on $[H_6C_6B–N(CHMe_2)_2]Mo(CO)_3$ **123** revealed that the metal is coordinated to the six ring carbons but not to boron.

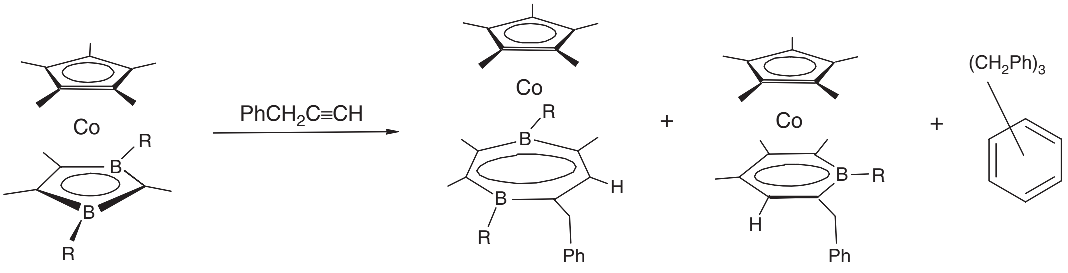


R = H, OMe, OH, $N(CHMe_2)_2$, $N(CH_2)_5$, $N(C_6H_{11})_2$, $NMeCH_2Ph$, $O_{1/2}$

123

3.01.8.2 4-Borataborepine Complexes

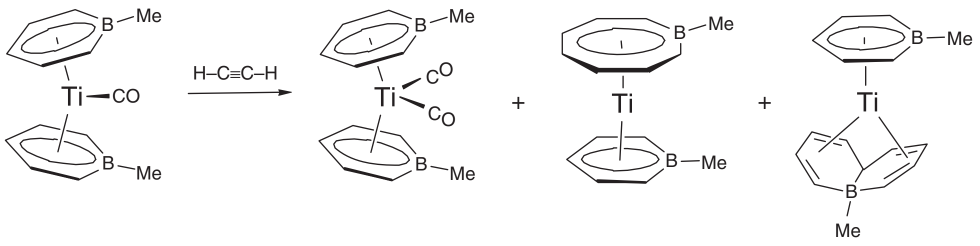
Ruthenium–borataborepine derivatives **124**, which incorporate a seven-membered C_5B_2 borataborepine heterocycle, have been obtained via the insertion of terminal alkynes into $Cp^*Ru(1,3\text{-}Me_3C_3B_2R_2)$, where R is Me or CH_2SiMe_3.[143] Other products isolated were the boratabenzene complex **125** and a benzene derivative.



124 **125**

3.01.8.3 Boratacyclooctatetraene Complexes

A boron-containing analog of cyclooctatetraenide dianion ($C_8H_8^{2-}$), the $C_7H_7BMe^{3-}$ trianion, has been obtained via acetylene insertion into the boratabenzene ring, affording complex **126** and other products, e.g., **127**.[144]



126 **127**

3.01.9 Complexes of Heterocyclic Ligands

As rich and varied as the chemistry of boron–carbon heterocycles is, its versatility is extended considerably by the introduction of additional elements as ring heteroatoms (Table 6). At this writing, development in this area has involved primarily N- and S-containing rings, but examples of P- and O-containing boron heterocycles are also known.

Table 6 Complexes of $C_mB_nX_p$ heterocyclic ring ligands 1993–2005

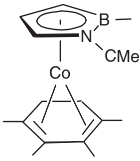
Compound[a]	*Information*[b]	*References*
Synthesis and characterization		
Complexes of nitrogen-containing rings		
$Li^+[(CMe_3)\mathbf{N}H_3C_3B{-}R]^-$ [$R = N(CHMe_2)_2$, $O(CMe_3)$, H, $C{\equiv}CPh$, PPh_2] 1,2-azaborolyl complexes		147
$(CO)_2IFe[(CMe_3)\mathbf{N}H_3C_3B{-}Cl]$ 1,2-azaborolyl complex	S, E	145
$CpFe[(CMe_3)\mathbf{N}H_3C_3B{-}R]$ ($R = Cl$, Otf, NMe_2, OMe, C_4H_9, SBn, F, allyl, H, PPh_2) 1,2-azaborolyl complexes	S, E	145
$(\eta^6\text{-}C_6R_4H_4)Co[(CMe_3)\mathbf{N}H_3C_3B{-}Me]$ (R = H, Me, Et, pr) 1,2-azaborolyl complexes	S, H(2d), B, C, MS	146
$(C_4R_4)Co[(CMe_3)\mathbf{N}H_3C_3B{-}Me]$ (R = Ph, Et, pr) 1,2-azaborolyl complexes	S, H(2d), B, C, MS	146
$Cp^*Ru(\eta^6\text{-}\mathbf{N}H_4C_4B{-}Ph)$ catalyst for acylation of benzyl alcohol by phenyl ethyl ketone)	S, X, H, B, C, MS	151
$(CO)_3Mo[(CMe_3)\mathbf{N}H_4C_4B{-}Me]$ azaborine complex	S, X, H, B, C, IR, MS	150
$(CO)_3Cr(Me\mathbf{N}H_4C_4B{-}Ph]$ azaborine complex	S, X, H, B, C, IR, MS	150
$(C_8H_{12})Rh[(CMe_3)\mathbf{N}H_3C_3B{-}N(CHMe_2)_2]$ 1,2-azaborolyl	S, X	147
$(CO)_3(SnMe_3)Cr[(CMe_3)\mathbf{N}H_3C_3B{-}R]$ [$R = N(CHMe_2)_2$, $O(CMe_3)$, H, $C{\equiv}CPh$, PPh_2] 1,2-azaborolyl complexes	S	147
$CpCl_2Zr[(CMe_3)\mathbf{N}H_3C_3B{-}R]$ [$R = N(CHMe_2)_2$, $O(CMe_3)$, H, $C{\equiv}CPh$, PPh_2] 1,2-azaborolyl complexes	S	147
$Cp^*Cl_2Zr[H_3C_3B\mathbf{N}C_4H_4]$ azaborindenyl complex	S, X, H, B, C	149
$Cp^*Cl_2Zr[H_3C_3B\mathbf{N}C_4H_6]$ dihydroazaborindenyl complex	S, X, H, B, C	149
Complexes of phosphorus-containing rings		
$Cp^*Ru(H\mathbf{P}Me_3C_3B_2Me_2)$	S, H, B, C, MS	36
$Cp^*Ru(\mathbf{P}^tBuMe_3C_4B_2Me_2)$	S, H, B, C, MS	36
$Cp^*_2Ru_2(H\mathbf{P}Me_3C_3B_2Me_2)$ (triple-decker sandwich)	S, H, B, C, MS	36
$(CO)_3Mn[H_2Me_2C_4\mathbf{P}B{-}N(CHMe_2)_2]$	S, X, H, B, C, P	152
$Cp^*Ru[H_2Me_2C_4\mathbf{P}B{-}N(CHMe_2)_2]$	S, X, H, B, C, P	152
Complexes of oxygen-containing rings		
$Cp^*Ru[\mathbf{O}H_3C_3B{-}N(CHMe_2)_2]$ 1,2-oxaborolide	S, X, H, B, C, MS	153
$(CO)_3Mn[\mathbf{O}H_3C_3B{-}N(CHMe_2)_2]$ 1,2-oxaborolide	S, X, H, B, C, MS	153
Complexes of sulfur-containing rings		
$Cp^*M[\mathbf{S}H_3C_3B{-}N(CHMe_2)_2]$ (M = Ru, $ZrCl_2$) thiaborolide complexes	S, X(Ru), H, B, C, MS	155
$(H_4C_5)Cl_2Zr[\mathbf{S}H_3C_3B{-}N(CHMe_2)_2](\mu\text{-}SiMe_2)$ thiaborolide complex	S, X(Ru), H, B, C, MS	155
$(CO)_3Mo(\mathbf{S}H_4C_4B{-}Me)$	S, X, H, B, C, MS	158
$Cp^*M[\mathbf{S}H_3C_3B{-}N(CHMe_2)_2]$ (M = Ru, $ZrCl_2$)	S, X(Ru), H, B(Ru), C, MS	154
$Cp^*Cl_2Zr[\mathbf{S}C_2(C_4H_4)CHB{-}N(ipr)_2]$	S, H, B, C, MS	156
$Cp^*Ru[\mathbf{S}C_2(C_4H_4)CHB{-}N(ipr)_2]$	S, X, H, B, C, MS	156
$Cp^*Ru(2,3,5\text{-}\mathbf{S}Me_3C_3B_2Me_2)$	S, H, B, C, MS	36
$[Cp^*Ru(\mathbf{S}Me_3C_4)]_2(\mu\text{-}MeBO)_2$	S, X, H, B, C, MS	36
$Li^+[\mathbf{S}H_5C_7B{-}N(CHMe_2)_2]^-$ benzothiaborolide complex	S, H, B, C, MS	157
$Cp^*Ru[\mathbf{S}H_5C_7B{-}N(CHMe_2)_2]$ benzothiaborolide complex	S, X, H, B, C, MS	157

[a] Metals coordinated to $C_mB_nX_p$ rings are shown in boldface.

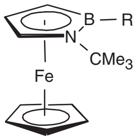
[b] Legend: S = synthesis, X = X-ray diffraction, H = ^{1}H NMR, B = ^{11}B NMR, C = ^{13}C NMR, F = ^{19}F NMR, P = ^{31}P NMR, Li = ^{7}Li NMR, Pt = ^{195}Pt NMR, 2d = two-dimensional NMR, IR = infrared data, MS = mass spectroscopic data, UV = UV–visible data, E = electrochemical data, ESR = electron spin resonance data.

3.01.9.1 Complexes of Nitrogen-containing Rings

The five-membered azaborolyl ring $H_3C_3BHNH^-$, a 6π-electron donor that is isoelectronic with $C_5H_5^-$, forms stable metal sandwich complexes analogous to metallocenes;[145–148] compounds **128–131** are typical. From measured oxidation potentials in B-nucleophile substituted derivatives **129**, it was shown that the 1,2-azaborolyl ligand is more electron-rich than cyclopentadienyl.[145] A particularly useful approach to the synthesis of azaborolyl and azaborine (C_4BN ring) complexes has been developed by Ashe and Fang, based on ring-closing metathesis on vinyl or allyl aminoboranes to form initially azaboracycloalkenes which are then converted to the aromatic heterocycles.[148]

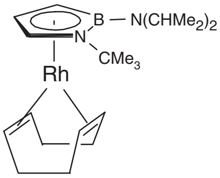


128[146]

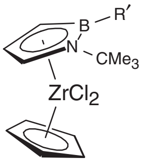


129[145]

R = H, Bu, OMe, NMe$_2$, F, allyl, PPh$_2$, SBn



130[147]

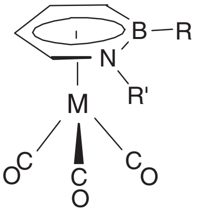


131[147,148]

R′ = H, N(CHMe$_2$)$_2$, OCMe$_3$, C≡CPh, PPh$_2$

Zirconium complexes of a new five-membered BN heterocycle, the 3a,7a-azaborindenyl ligand (Figure 1), have been reported.[149]

Substitution of BH and NH for two adjacent CH units in benzene yields the isoelectronic and isostructural analog 1,2-dihydroazaborine (Figure 1). Until recent years, very few metal sandwich complexes of this ligand were known, but since 1993 this area has seen increasing interest. Ashe has developed an efficient route to the ligand and its complexes, based on a carbenoid ring expansion of lithium 1,2-azaborolides which affords the free dihydroazaborine; this in turn can be complexed to chromium or molybdenum tricarbonyl fragments **132**.[150] X-ray diffraction studies established that in each case the metal is bound to all six ring atoms.



M = Cr, Mo

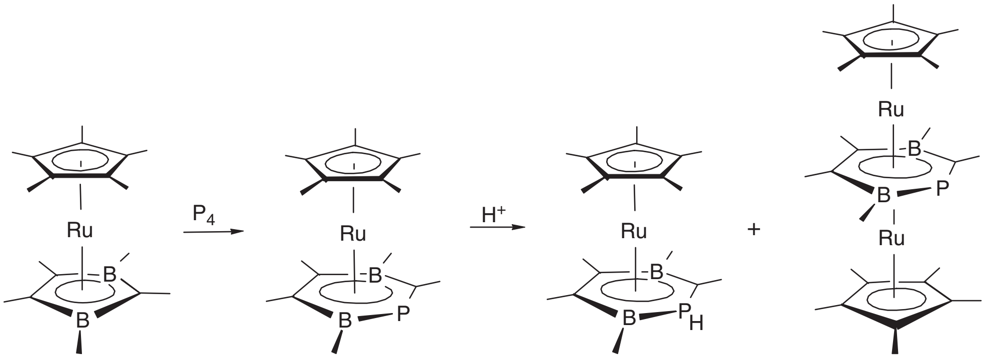
R, R' = H, Me, CMe$_3$, Ph

132

The "bare nitrogen" analog of dihydroazaborine, where the R′ substituent on N is effectively replaced by an electron pair, is the azaboratabenzene anion $H_4C_4BRN^-$. The synthesis of this ligand and a ruthenium sandwich complex Cp*Ru(H_4C_4BPhN) that is catalytically active in the acylation of benzyl alcohol have been reported.[151]

3.01.9.2 Complexes of Phosphorus-containing Rings

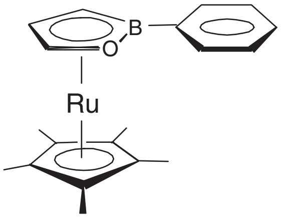
Phosphoratabenzene complexes of the type LM[$H_2Me_2C_4PB$–N(CHMe$_2$)$_2$] (L = (CO)$_3$Mn or Cp*Ru) have been prepared by Ashe *et al.*[152] Double- and triple-decker sandwiches **133–135** were obtained by Siebert and co-workers from the reaction of the diborole complex **33** (Section 3.01.3.2) with elemental phosphorus.[36] The structures of these complexes have not yet been confirmed crystallographically, and the proposed triple-decker **135** has been seen only in the mass spectrum of **134**.



33 **133** **134** **135**

3.01.9.3 Complexes of Oxygen-containing Rings

The 1,2-oxaborolide anion (Figure 1), an analog of furan, has been prepared by two different routes and sandwich complexes with ruthenium and manganese **136, 137** have been characterized.[153] Comparison of IR stretching frequencies suggests that oxaborolide is a weaker electron donor and better electron acceptor than cyclopentadienyl.



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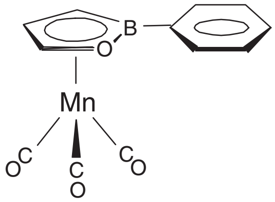
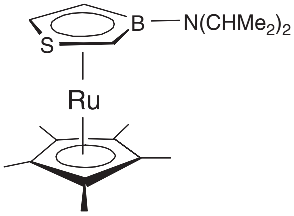


137

3.01.9.4 Complexes of Sulfur-containing Rings

The thiaborolide anions $H_3C_3BRS^-$, isoelectronic with thiophene (H_4C_4S), form transition metal sandwich complexes such as **138** and **139**, which incorporate the 1,3-thiaborolide ligand in which the ring heteroatoms are separated.[154] The zirconium complex in the presence of MAO catalyzes the polymerization of ethylene. The isomeric 1,2-thiaborolide ligand is also known, as are several metal complexes **140, 141**.[155] The closely related benzothiaborolide ion, a heterocyclic analog of indenyl, has also been prepared in two isomeric forms, several metal complexes of which have been characterized **142, 143**.[156,157] X-ray diffraction and spectroscopic evidence indicate that the thiaborolide rings are η^5-bound aromatic ligands.[157]



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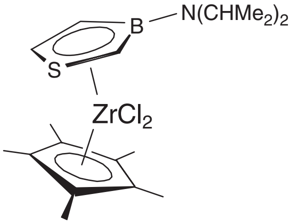

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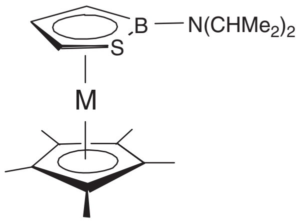
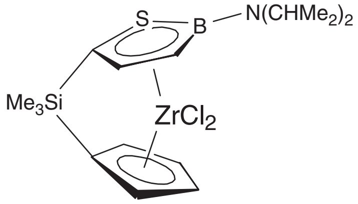
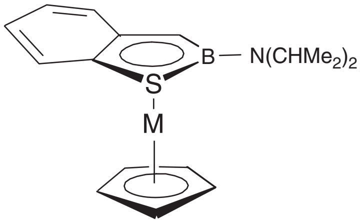


M = Ru, ZrCl$_2$

140

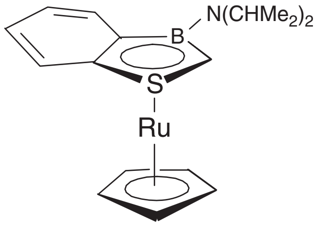


141



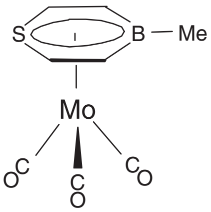
M = Ru, ZrCl$_2$

142



143

Few examples have been reported of metals coordinated to six-membered boron–sulfur heterocycles. Ashe *et al.* prepared 4-methyl-1,4-thiaborin (SC_4H_4BMe) which forms a stable molybdenum tricarbonyl sandwich complex **144**.[158] In Siebert's laboratory, the reaction of the diborolyl complex **33** (Section 3.01.3.2) with COS afforded the dinuclear complex **145** whose structure was determined crystallographically.[36] Other products, not involving boron–sulfur heterocycles and hence outside the scope of this discussion, were obtained via the treatment of **33** with different sulfur reagents such as CS_2.[36]



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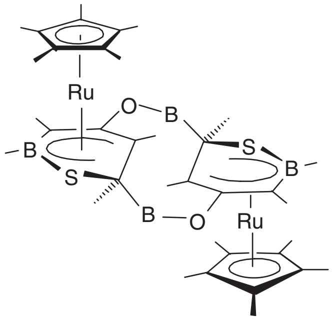

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3.02
Polyhedral Carboranes

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3.02.1 Introduction

This chapter concerns carboranes (carbaboranes), which are boron clusters with at least one carbon atom as part of the polyhedral cage. Published studies on carboranes before 1981 were reviewed in COMC (1982) and between 1982 and 1992 in COMC (1995). The present review covers the period of 1992 to early 2005. Unlike in previous chapters, boron hydrides with organic substituents attached to a boron atom, organopolyboron hydrides, are not discussed in this chapter. Borane clusters containing at least one non-carbon atom as part of the cage framework are reviewed in Chapters 3.03, 3.04 and 3.05 of this volume.

3.02.2 General Literature Reviews

Articles on carboranes are found in annual reports covering carboranes and their metal complexes,[1–8] and boron chemistry.[9–19] Accounts on specialized aspects of carborane chemistry include: carboranes for boron neutron capture therapy (BNCT) and other medicinal applications,[20–27] weakly coordinating carborane anions,[28,29] syntheses of small carboranes[30] and their group I metal complexes,[31] use of icosahedral carboranes in supramolecular chemistry,[32–34] "camouflaged" carboranes,[35] the interesting mercuracarborands (macrocycles containing carborane and mercury),[36] cyclopentadienyl carboranes,[37] hydrogen bonding in carboranes,[38] carboranes for molecular rods[39] and liquid crystals,[40] carborane anions with group I metals,[41] carbon insertion into carboranes,[42] geometrical patterns of carboranes[43] and carboranes refined by *ab initio* computations.[44] In addition, a recent survey on carboranes entitled "from small organoboranes to carboranes" has included valuable discussions on the structural relationships between ring and cage C_xB_y systems.[45] Several books and conference proceedings contain accounts of specialized carborane research.[46–50]

3.02.3 *Ab Initio* Computations

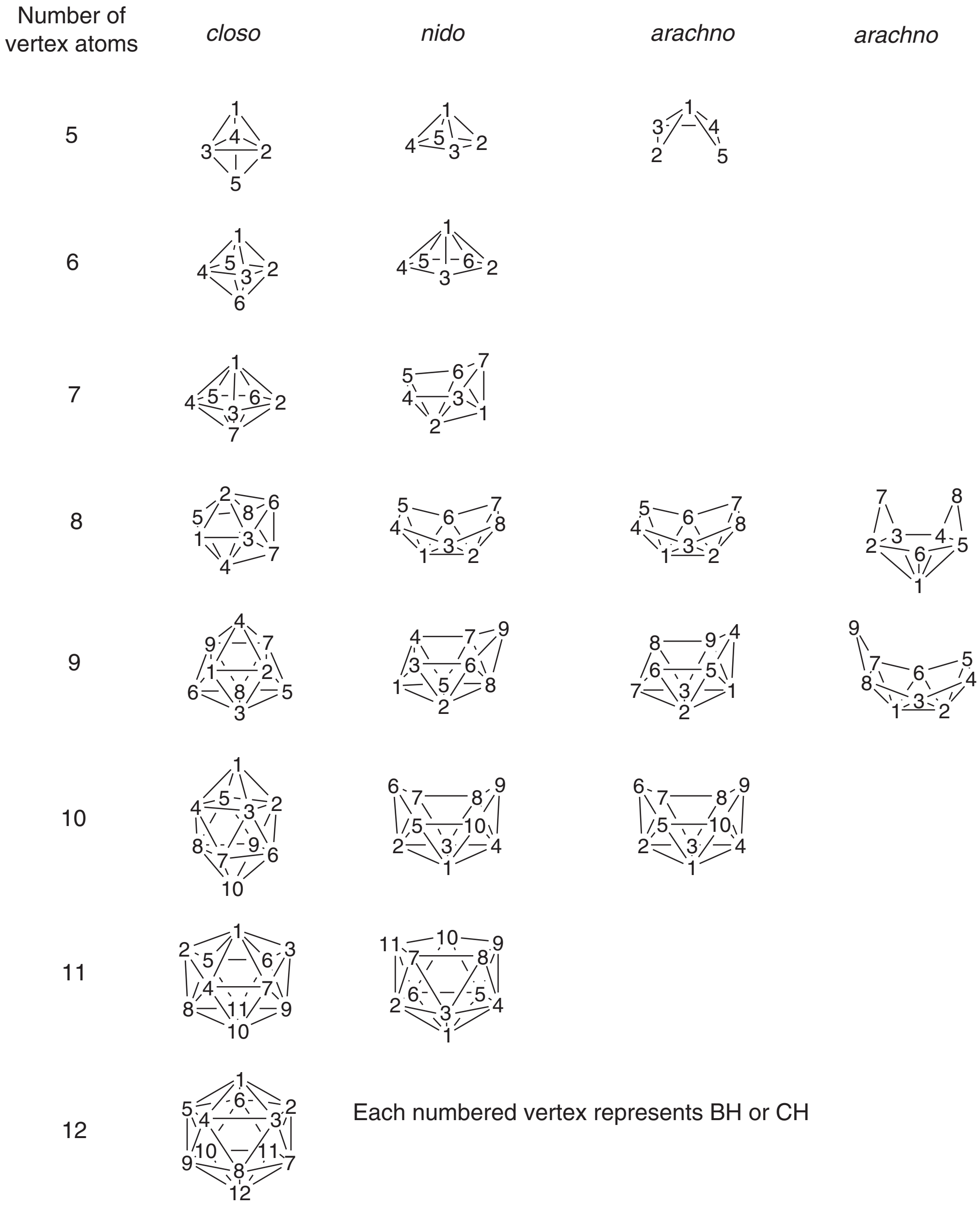
The impact of *ab initio*/NMR computations on carborane chemistry research has been enormous in the last 15 years. Optimized geometries of carboranes from *ab initio* computations are remarkably accurate at the MP2/6-31G* level of theory when compared with experimental structures of carboranes determined by X-ray crystallography.[51,52] GIAO or IGLO ^{11}B NMR shifts computed from an optimized geometry are generally within an error of 2 ppm compared to observed ^{11}B NMR shifts of a carborane sample – if the correct geometry is found.[51–57] This is remarkable given that the range of the observed boron chemical shifts for carboranes is between +30 and −60 ppm. Experimental ^{13}C and, to a lesser extent, ^{1}H NMR data can also be compared with computed NMR shifts for confirmation of the correct geometry for the carborane studied.[51–53,58,59]

Ab initio computations, particularly at MP2 and (the computationally less intensive) B3LYP levels of theory, have been largely responsible for the rapid progress in carborane structural research, permitting the determination of the molecular geometry of a novel carborane from solution-state NMR data where X-ray diffraction could not be used (such as those in trace amounts or for which suitable crystals could not be obtained). Earlier proposed geometries[56,57,60–64] or ^{11}B chemical shifts[65,66] of some carboranes were corrected with the aid of these computations.[44]

Ab initio computations have so far proved to be reliable structural tools for neutral carboranes and their anions. They have been used to predict the carborane geometries for six-vertex, eight-vertex, and 11-vertex *nido*-carboranes,[67–69] and for 5–12 vertex *closo*-carboranes.[70,71] However, carborane anions in the presence of a group I metal cation may form ion-pair anions with one cation tightly bound to the carborane anion (see Chapter 3.03).[72,73] Even computations on a salt with a carborane anion in a non-coordinating solvent would need to include the cation for computed shifts that tally with observed NMR data.[74]

3.02.4 Geometrical Pattern for Subicosahedral Carboranes

Figure 1 shows the known experimental geometries of carboranes. For discussion of *closo*-, *nido*-, and *arachno*-electron counts and their expected geometries, see COMC (1982) 5.4.2.2 and 5.4.2.3. *Arachno*-six- and seven-vertex geometries are not known experimentally for carboranes.



Each numbered vertex represents BH or CH

Figure 1 Experimental geometries of carboranes.

Only in two cases, the eight- and nine-vertex *arachno*-species shown in Figure 1, have alternative geometries been found for species of the same formula type (electron count).[44,75]

3.02.5 Syntheses of Subicosahedral and Icosahedral Carboranes

3.02.5.1 From Polyboranes and Alkynes

The vast majority of known carboranes synthesized in the literature are derivatives of *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$. They were synthesized from the reaction of decaborane, $B_{10}H_{14}$, with suitable alkynes in the presence of a suitable

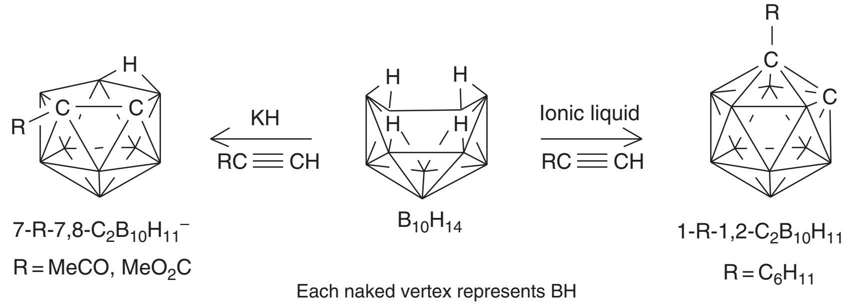


Figure 2 Syntheses of dicarbaboranes.

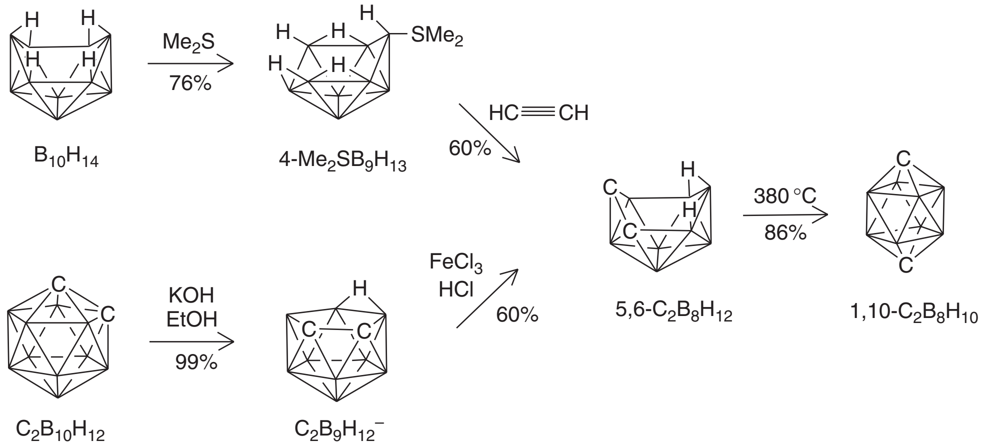


Figure 3 Syntheses of 5,6-$C_2B_8H_{12}$ and 1,10-$C_2B_8H_{10}$.

ligand such as acetonitrile or dialkylsulfide (COMC (1982) 5.4.2.6.1 and COMC (1995) 6.2.4.1). Alkylalkynes generally give low yields of the desired alkyl carborane whereas alkynes with electron-withdrawing groups give good yields of the desired carborane.[76] A recent development using ionic liquids instead of acetonitrile or dialkylsulfide has shown a remarkable improvement in the yield (91%) of the hexyl carborane with a reaction time of only 7 min from octyne and decaborane in a two-phase mixture of an ionic liquid and toluene (Figure 2, cage C without a substituent attached is assumed as CH throughout unless otherwise stated).[77] This is an exciting development as the high yielding procedure appears to be general for a variety of alkynes.

The *nido*-carborane anion, 7,8-$C_2B_9H_{12}^-$, and derivatives are generally formed by deboronating *ortho*-carboranes with suitable bases (COMC (1982) 5.4.2.6.6) but a direct route to two derivatives of the anion has been developed in good yields from decaborane and polarized alkynes.[78]

nido-5,6-$C_2B_8H_{12}$ is synthesized via deboronation of the *ortho*-carborane cage[79] but can also be made in similar yields from 4-$Me_2SB_9H_{13}$ and ethyne (Figure 3).[80] While the cage-deboronation route is preferred for the parent carborane, the yields are much higher for C-substituted derivatives of 5,6-$C_2B_8H_{12}$ from the alkyne route than from the cage-dismantling route. The *nido*-carborane is a useful precursor to 10-vertex *closo*-dicarbaboranes and a high yield multigram scale procedure from 5,6-$C_2B_8H_{12}$ to 1,10-$C_2B_8H_{10}$ was recently reported.[81]

3.02.5.2 From Polyboranes and Carbenes

A route to $CB_{11}H_{12}^-$ from $B_{11}H_{14}^-$ was achieved by carbene insertion using base and chloroform (Figure 4).[82] However, while yields of 40% were reported for gram scale syntheses, this reaction proved to be poorly reproducible and multigram scale syntheses gave reduced yields (10–20%).[83] Unlike $B_{10}H_{14}$, the 11-vertex borane anion $B_{11}H_{14}^-$ can be generated from relatively inexpensive and commercially available boron starting materials in about 50% yields.

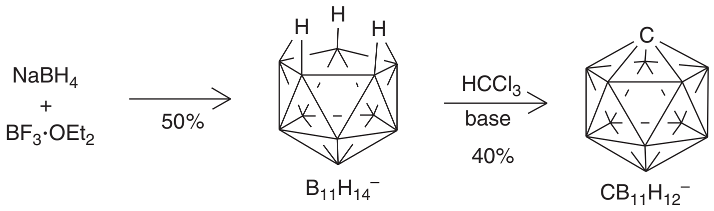


Figure 4 Synthesis of carborane anion, $CB_{11}H_{12}^-$, by carbene insertion.

Thus, further refinement of this route to the carborane anion $CB_{11}H_{12}^-$ from $B_{11}H_{14}^-$ would represent a significant advance in opening up $CB_{11}H_{12}^-$ chemistry.

Aryl derivatives, 1-Ar-1-$CB_{11}H_{11}^-$, were made in 30–40% yields from $B_{11}H_{14}^-$ and arylhalocarbenes (generated from substituted benzal chlorides).[83] A carbene insertion route to 7-$CB_{10}H_{13}^-$ was also reported for the reaction of $B_{10}H_{14}$ with CH_2Br_2 and NaH in 25% yield.[84,85]

3.02.5.3 From Polyboranes and Aldehydes

While alkynes, nitriles, and isocyanides have long been known to insert a cage carbon into polyboranes (COMC (1982) 5.4.2.6.1 and 5.4.2.6.2), the use of aldehydes to insert a cage carbon was first reported by Bernd Brellochs in 1997 (Figure 5).[86] Good yields of 10-vertex monocarbaboranes were obtained from $B_{10}H_{14}$ with KOH and many aldehydes and this reaction was thus coined the "Brellochs reaction."[87]

The Brellochs reaction represents a significant breakthrough in monocarbaborane chemistry, the exploration of which was previously limited by multistep routes. For example, the important carborane anion $CB_{11}H_{12}^-$ can now be made in two steps with an overall yield of 66%.[88] Its synthesis previously required three steps involving undesirable compounds such as hydrogen cyanide, dimethylsulfate, and trialkylamine. (COMC (1982) 5.4.2.6.2) The *arachno*-carborane

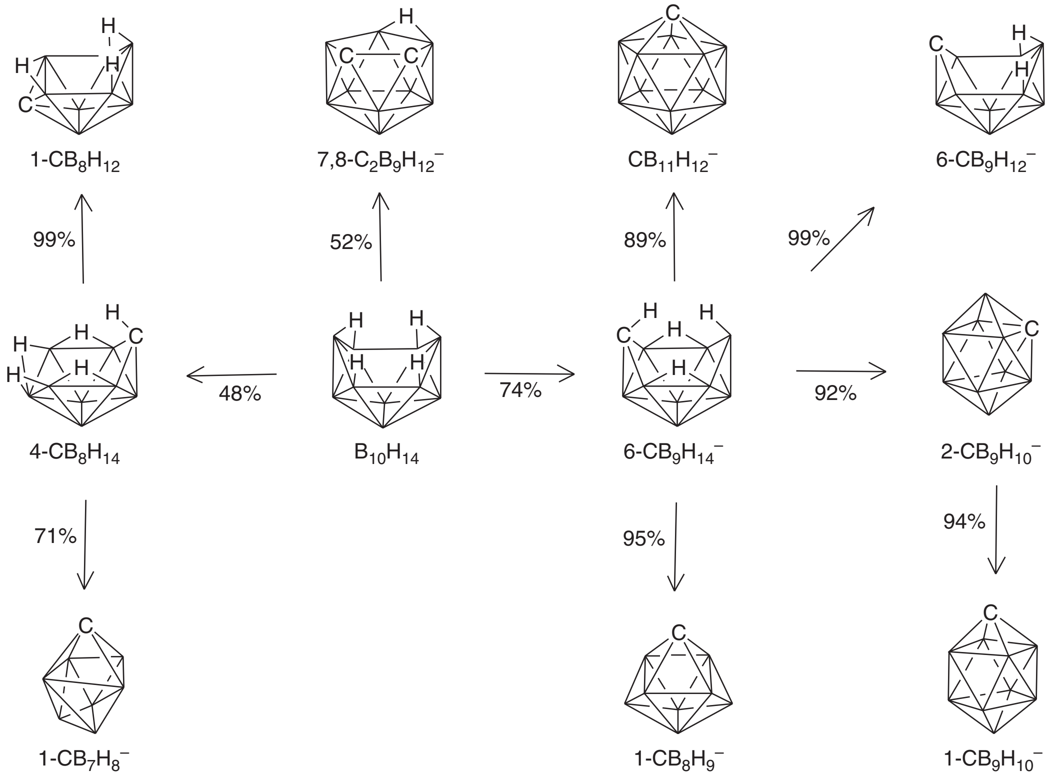


Figure 5 Important carboranes accessible from $B_{10}H_{14}$ via the Brellochs reaction.

4-CB_8H_{14}, previously made from *ortho*-carborane in three steps with an overall yield of 45%,[89] can now be made in a one-pot procedure from $B_{10}H_{14}$ with 48% yield.[90] The well-known *nido*-7,8-$C_2B_9H_{12}^-$ anion can be formed from $B_{10}H_{14}$ with HCHO in 52% yield.[91]

While the parent carboranes can be made from formaldehyde and decaborane, carboranes with substituents at the cage carbon can easily be synthesized from the appropriate aldehyde. For example, benzaldehyde and $B_{10}H_{14}$ give the *nido*-6-Ph-6-$CB_9H_{11}^-$ anion in 94% yield.[92] The phenyl carborane formed is *nido*- not *arachno*- but subsequent carborane products can be made using similar reagents as for the parent *arachno*-6-$CB_9H_{14}^-$.[93]

3.02.5.4 Syntheses of Small Carboranes

The search for high yield routes to small parent or C-substituted carboranes is a challenge since the seemingly limitless supply of hazardous pentaborane, B_5H_9, has been destroyed in the United States.[30] (COMC (1982) 5.4.2.6.1) High yield multigram syntheses of 2,3-Et_2-2,3-$C_2B_4H_6$ and 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_6$ from pentaborane with EtCCEt and $Me_3SiCCSiMe_3$ therefore will not be possible after existing laboratory stocks of B_5H_9 are depleted. *nido*-2,3-$C_2B_4H_8$ can be obtained on a gram scale by a seven-step synthesis from *ortho*-carborane with six deboronation steps but it is time consuming and expensive.[75]

Reasonable amounts of small carboranes, however, can be formed as polyalkyl derivatives from alkynyl(diethyl)-boranes and alkylboranes. Derivatives of *arachno*-1-CB_4H_{10} were characterized—and their structures confirmed—for the first time in 1994.[61,94,95] One satisfactory route to these derivatives is from the reaction of $Me_2Si(CCMe)_2$ with Et_2BH (actually a mixture of ethylboranes in which $Et_4B_2H_2$ is a main component) yielding about 55% of *arachno*-2,5-$Me_2SiHCEt$-1,2,3,4,5-Et_5-1-CB_4H_3.[94] A route to a variety of small carboranes, not just the *arachno*-carborane, uses Et_2BCCMe and Et_2BH (Figure 6). This reaction can be tuned to give gram quantities of *closo*-Et_5-1,5-C_2B_3,[96] *nido*-Et_6-2,4-$C_2B_4H_2$,[97] and *arachno*-2,5-Et_2BCEt-1,2,3,4,5-Et_5-1-CB_4H_3.[96]

3.02.6 Tricarbaboranes

The number of known tricarbaboranes has rapidly grown in the last 15 years. Ten-vertex tricarbaboranes were made by monocarbon insertion into dicarbaboranes using alkynes, nitriles, or isocyanides.[42] From the 4,6-$C_2B_7H_{12}^-$ anion, *arachno*-5,6,7-$C_3B_7H_{13}$ derivatives were obtained with alkynes[78,98] and a *nido*-5,6,9-$C_3B_7H_{10}^-$ derivative with acetonitrile (Figure 7).[99,100]

The 11-vertex *nido*-carborane anion, 7,8,10-$C_3B_8H_{11}^-$ or derivatives, can be synthesized via two different routes from dicarbaboranes (Figure 7).[101–105] Protonation of 7-Me-7,8,10-$C_3B_8H_{10}^-$ gives 2-Me-2,7,10-$C_3B_8H_{11}$ as the cage undergoes rearrangement to accommodate the bridging proton.[106] The open faces of the 11-vertex *nido*-tricarborane anions are isolobal to the cyclopentadienyl anion, $C_5H_5^-$.

3.02.7 *hypho*-Carboranes

A few *hypho*-carboranes have been reported in the last decade namely, 7,8-$C_2B_6H_{13}^-$ the "helmet" anion,[107] *exo*-5-R_3N-4,9-$C_2B_7H_{13}$ (R = Me or Et),[107] 9-$(NCCH_2)$-7,8,9-$C_3B_6H_{12}^-$,[78] *endo*-7-(Ph_2HP)-8-R-7,8-$C_2B_6H_{11}$ (R = H or Me),[108] and 7,9-$((NC)_2C)_2$-7,8-$C_2B_7H_{12}^-$.[109] They all have a common cage framework where the six-vertex all-boron *nido*-type pentagonal pyramidal cage has two non-adjacent CH_2 bridges and three bridging hydrogens around the perimeter (Figure 8).

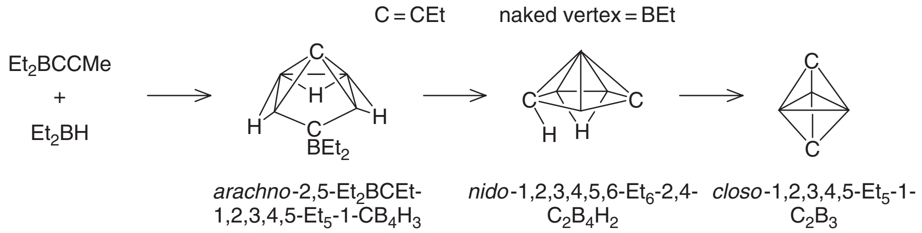


Figure 6 Syntheses of small carboranes from organoboranes.

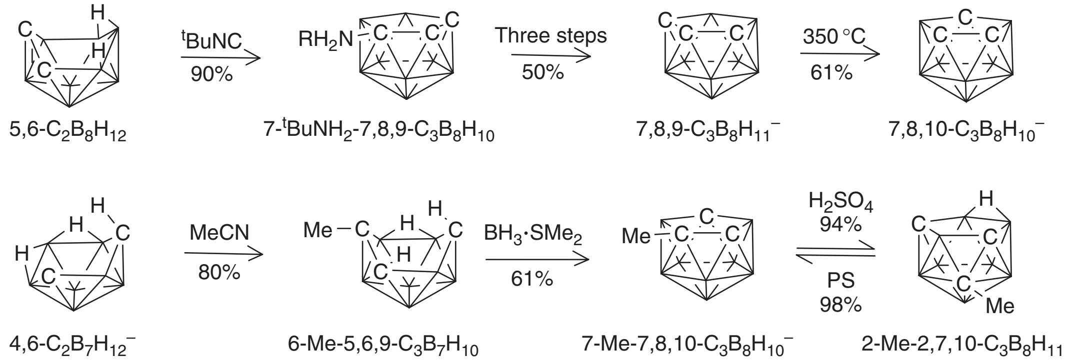


Figure 7 Syntheses of 11-vertex-*nido*-tricarbaboranes.

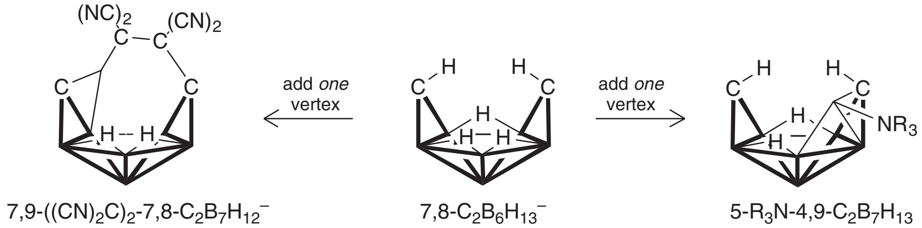


Figure 8 All known *hypho*-carboranes have a common C_2B_6 cage framework.

3.02.8 Carborane Radicals and Cations

Carborane radicals and cations are rare. Two radicals have been generated from polymethylated derivatives of the icosahedral $CB_{11}H_{12}^-$ anion. Chemical (PbO_2/CF_3CO_2H) or electrochemical oxidation of the permethylated anion, $CB_{11}Me_{12}^-$, gave a stable crystalline free radical, $CB_{11}Me_{12}^{\cdot}$, which has been structurally characterized by X-ray crystallography.[110] It is the first isolated neutral metal-free odd-electron boron cluster, stable to air for days and sublimable under reduced pressure. It is a strong oxidizing agent. The second example is the $HCB_{11}Me_{11}^{\cdot}$ radical briefly reported as a reactant.[111]

Two carborane cations, *nido*-2,3,4,5,6-$Me_5C_5BBr^+$ and the tentatively proposed *arachno*-$MeC_2BH_7^+$, were reported. The identity and pyramidal structure of the pentacarbaborane cation was determined by X-ray crystallography.[112] The small *arachno*-carborane was detected on the basis of *ab initio* computations and ^{11}B NMR data in the mixture from reaction of the 2-propyl cation with diborane.[113] Two neutral adducts based on the pentacarbaborane cation, *nido*-2,3,4,5,6-$Me_5C_5BBRCl_2$ (R = Cl or $SiCl_3$), were made from $Me_5C_5SiMe_3$ or $(Me_5C_5)_2Si$ with B_2Cl_4, respectively.[114] The BCl_3 adduct was structurally characterized by X-ray crystallography.

3.02.9 Subicosahedral Carboranes in Detail

3.02.9.1 Four-vertex Carboranes

***nido*-2-CB_3H_7:** The smallest *nido*-carborane 1,3,4-$^tBu_3$-2-CB_3H_4 was made in 90% yield from the anion $B_4H_3{}^tBu_4^-$ with MeI in THF.[115]

3.02.9.2 Five-vertex Carboranes

***closo*-1-$CB_4H_5^-$:** The carborane anion, 1-Me_3Si-3,4-Dur_2-2,5-$(Me_3SiCH_2)_2$-1-CB_4^- (Dur = 2,3,5,6-tetramethylphenyl), was made in 87% yield from the non-carborane 5-Cl-1-Me_3Si-3,4-Dur_2-2,5-$(Me_3SiCH_2)_2$-1-CB_4 with Li in Et_2O.[116] It was structurally characterized by an X-ray diffraction study.

Table 1 Synthetic routes to *arachno*-1-CB_4H_{10} derivatives

Derivatives of 1-CB_4H_{10}	*Starting materials*	*Solvent, temp, yield*
2(3)-Me-1-Me-	B_4H_{10}, $H_2C{=}C{=}CH_2$	70 °C, 10%[122]
2,5-H_2C-1-Me-	B_4H_{10}, MeCCH	70 °C, 2%[123]
2,5-MeHC-	B_4H_{10}, MeCCH	70 °C[123]
2,5-MeHC-1-Me-	B_4H_{10}, MeCCMe	70 °C, 4%[123]
2,5-H_2C-1-Et-	B_4H_{10}, EtCCH	70 °C, 2%[123]
2,5-EtHC-	B_4H_{10}, EtCCH	70 °C[123]
2,5-(1,2-C_6H_4)-1-^{i}Pr-	$C_6H_4(BCl)_2C{=}CMe_2$, $LiBH_4$, $HBF_4{\cdot}OEt_2$	THF, pentane, 36%[95]
2,5-(1,2-C_6H_4)-1-$(CH_2)_4$CH-	$C_6H_4(BCl)_2C{=}C(CH_2)_4$, $LiBH_4$, $HBF_4{\cdot}OEt_2$	THF, pentane, 45%[95]
2,5-Et(Me_2SiH)C-1,2,3,4,5-Et_5-	Et_2BH, $Me_2Si(CCMe)_2$	61%[94]
2,5-Et(Me_3Si)C-1,2,3,4,5-Et_5-	Et_2BH, $Me_3SiCCMe$, Et_2BCCMe	33%[124]
2,5-MeHC-1,2,3,4,5-Et_5-	Et_2BH, $Et_2BCH{=}CH_2$, Et_2BCCMe	52%[124]
2,5-MeHC-2,3,4,5-Et_4-	Et_2BH, $Et_2BCH{=}CH_2$, $(Et_2B)_3CH$	45%[124]
2,5-(Et_2B)HC-2,3,4,5-Et_4-	Et_2BH, $(Et_2B)_3CH$	[124]
2,5-Et(Et_2B)C-1,2,3,4,5-Et_5-	Et_2BH, Et_2BCCMe	23%[96]

***closo*-1-CB_4H_6:** The reaction of $HBF_4{\cdot}OMe_2$ with the anion 1-Me_3Si-3,4-Dur_2-2,5-$(Me_3SiCH_2)_2$-1-CB_4^- gave 1-Me_3Si-3,4-Dur_2-2,5-$(Me_3SiCH_2)_2$-1-CB_4H which has been identified in the solid state by X-ray diffraction.[116]

***closo*-1,5-$C_2B_3H_5$:** Parent *closo*-1,5-$C_2B_3H_5$ and its 2-methyl and 2,3-dimethyl derivatives were made in low yields from high energy flash reactions of diborane, triborane carbonyl (B_3H_7CO), and tetraborane with alkynes (ethyne, propyne, and 2-butyne).[62,117] 1,2,3,4,5-Et_5-1,5-C_2B_3 was formed from tetraethyldiborane Et_2BH and Et_2BCCMe at 150 °C (see Figure 6).[96] Heating ^{t}Bu$CH_2C(BR_2)_3$ (R = Cl or Me) at 170 °C for 2 h gave 1,5-(^{t}Bu$CH_2)_2$-2,3,4-R_3-1,5-C_2B_3.[118] These three persubstituted derivatives were all structurally characterized by X-ray crystallography.[96,118,119] Heating $(Me_3Si)_2C(BDur)_2C{=}BN(SiMe_3)_2$ gave 1,5-$(Me_3Si)_2$-2,3-Dur_2-4-$(Me_3Si)_2$N-1,5-C_2B_3.[120]

***nido*-1,2-$C_2B_3H_7$:** No derivatives of *nido*-1,2-$C_2B_3H_7$ are presently known. The parent carborane *nido*-1,2-$C_2B_3H_7$ was obtained in 25% yield from tetraborane B_4H_{10} and ethyne at 70 °C.[121] It was structurally characterized by gas-phase electron diffraction and microwave spectroscopy.

***arachno*-1-CB_4H_{10}:** There are many routes to *arachno*-1-CB_4H_{10} derivatives listed in Table 1 (see Figure 6).

***arachno*-1-$CB_4H_9^-$:** Deprotonation of 2,5-(1,2-C_6H_4)-1-^{i}Pr-1-CB_4H_7 gave the anion 2,5-(1,2-C_6H_4)-1-^{i}Pr-1-$CB_4H_6^-$.[95]

3.02.9.3 Six-vertex Carboranes

***closo*-1,2-$C_2B_4H_6$:** The C-trimethylsilyl derivatives of *closo*-1-Me_3Si-2-R-1,2-$C_2B_4H_4$ were made from the dianions 2-Me_3Si-3-R-1,2-$C_2B_4H_4^{2-}$ with $NiCl_2$. The yields were 64%,[125] 69%,[125] 27–59%,[125–127] 40–54%,[125,127] and 4%[127] for R = Bu, ^{t}Bu, Me_3Si, Me, and H, respectively. The trisubstituted derivative 4-^{i}Bu-1,2-$(Me_3Si)_2$-1,2-$C_2B_4H_3$ was made by the same procedure from 5-^{i}Bu-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_3^{2-}$ in 12% yield.[128] Two derivatives were characterized by X-ray crystallography, 1,2-$(Me_3Si)_2$-1,2-$C_2B_4H_4$ and 1-Me_3Si-2-Me-1,2-$C_2B_4H_4$,[129–131] the former also by gas-phase electron diffraction.[129]

***closo*-1,6-$C_2B_4H_6$:** Three 1-Me_3Si-2-R-1,2-$C_2B_4H_4$ derivatives (R = Bu, ^{t}Bu, and Me_3Si) were rearranged at 250 °C for 5 h to their more thermally stable 1,6 isomers in 72–76% yields.[125,129] 1,6-$(Me_3Si)_2$-1,6-$C_2B_4H_4$ was structurally characterized by gas-phase electron diffraction and low-temperature X-ray crystallography.[129] The perethyl derivative, 1,2,3,4,5,6-Et_6-1,6-C_2B_4, was formed from the anion 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H^-$ with iodine or Et_2BCl.[132]

***nido*-2,3-$C_2B_4H_8$:** Several derivatives of *nido*-2,3-$C_2B_4H_8$ have been synthesized as shown in Table 2. The reaction of 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_6$ with MeI gave 5-Me-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5$ in 75% yield.[128] The trisubstituted compound 5-R-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5$ (R = $Me_2SiClCH_2$, Me, and ^{i}Bu) derivatives were made from 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5^-$ with $Me_2SiClCH_2Cl$, CF_3SO_3Me, and ^{i}BuBr, respectively, in high yields.[128,133] 4-Me-5-^{i}Bu-2-Me_3Si-2,3-$C_2B_4H_5$ was obtained from 5-^{i}Bu-2-Me_3Si-2,3-$C_2B_4H_5^-$ and CF_3SO_3Me in 52% yield.[128]

***nido*-2,3-$C_2B_4H_7^-$:** Several alkali metal salts have been made from C-trimethylsilyl derivatives of *nido*-2,3-$C_2B_4H_8$ by deprotonation with BuLi or NaH with THF or TMEDA in high yields.[127,128,137] Salts that have been structurally characterized are 2-Me_3Si-3-Me-2,3-$C_2B_4H_5^-$ $Na(TMEDA)_2^+$,[138] 5-^{i}Bu-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4^-Na(THF)^+$,[128]

Table 2 Synthetic routes to *nido*-2,3-$C_2B_4H_8$ derivatives

2,3-$C_2B_4H_8$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	2,3-$C_2B_5H_7$, TMEDA	H_2O, 77%
2-Me-	MeB_5H_8, MeCCH	230 °C, 7%[134]
2-Me-	B_4H_{10}, MeCCH	50–70 °C, 4%[135]
5-Et-	B_4H_{10}, HCCH	50–70 °C, 2%[121,135]
1,2-Me_2-	MeB_5H_8, MeCCH	230 °C, 6%[134]
2,4-Me_2-	B_4H_{10}, HCCH	50–70 °C, 2%[121,135]
2,3-Et_2-	B_5H_9, EtCCEt, NEt_3	THF, 47%[136]
2-Ph-	B_5H_9, PhCCH, NEt_3	THF, 20%[136]
2,3-Ph_2-	B_5H_9, PhCCPh, NEt_3	THF, 21%[136]
2-Me_3Si-3-Bu-	B_5H_9, Me_3SiCCBu	140 °C, 3 d, 33%[125]
2-Me_3Si-3-^{t}Bu-	B_5H_9, Me_3SiCC^{t}Bu	140 °C, 3 d, 45%[125]
2,4(5,6)-Me_2-	MeB_5H_8, MeCCH	230 °C, 12%[134]
2-Et-3-Me-	MeB_5H_8, EtCCMe	190 °C, 10%[134]
2-Et-3,4-Me-	B_4H_{10}, MeCCH	50–70 °C, 1%[135]
2-Et-3,1(4,5,6)-Me_2-	MeB_5H_8, EtCCMe	190 °C, 9%[134]

(2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5^-$)$_2$Li$(TMEDA)_2^+$,Li^+,[139] 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5^-$Li$(TMEDA)_2^+$,[137] 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5^-$Na(THF),$^+$[127] and 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5^-$Na$(TMEDA)^+$.[127] In some salts the cations are coordinated to the anions in the solid state.

***nido*-2,3-$C_2B_4H_6^{2-}$:** Various alkali metal salts of the *nido*-2,3-$C_2B_4H_6^{2-}$ derivatives were synthesized in high yields from their respective anions or neutral analogs.[73,127,138] X-ray analysis of the dianion 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4^{2-}$ with two Li$(TMEDA)^+$ cations reveals one lithium atom closely bound to the open face and the other bridging the two boron-attached hydrogen atoms.[127]

***nido*-2,4-$C_2B_4H_8$:** Only one derivative of *nido*-2,4-$C_2B_4H_8$ is known, the hexaethyl derivative, 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H_2$, obtained in 31% yield from *arachno*-2,5-Et(Et_2B)C-1,2,3,4,5-Et_5-1-CB_4H_3 at 85 °C (see Figure 6).[97] It is also accessible in 87% yield by protonation of its anion.[132]

***nido*-2,4-$C_2B_4H_7^-$:** Many derivatives of the *nido*-2,4-$C_2B_4H_7^-$ anion are known. Preparation involved reduction of 1,2-$(Me_3Si)_2$-1,2-$C_2B_4H_4$, protonation of the dianions 2,4-$(Me_3Si)_2$-2,4-$C_2B_4H_4^{2-}$,[72] addition[54] of $LiNMe_2$ to 2,4-$C_2B_5H_7$, and deprotonation of 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H_2$.[97] The salts, 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H^-$ Na^+[97] and 2,4-$(Me_3Si)_2$-2,4-$C_2B_4H_5^-$Na(THF)$(TMEDA)^+$,[72] were structurally characterized by X-ray diffraction.

***nido*-2,4-$C_2B_4H_6^{2-}$:** The *nido*-dianion 2,4-$(Me_3Si)_2$-2,4-$C_2B_4H_4^{2-}$ was formed from reduction of *closo*-1,2-$(Me_3Si)_2$-1,2-$C_2B_4H_4$ with lithium in 90–93% yields.[140] Two Li$(THF)^+$ and Li$(TMEDA)^+$ salts of 2,4-$(Me_3Si)_2$-2,4-$C_2B_4H_4^{2-}$ were structurally characterized. The 1,2,3,4,5,6-Et_6-2,4-C_2B_4 dianion was made from the anion 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H^-$ with BuLi.[141]

***nido*-2,3,4-$C_3B_3H_7$:** The parent *nido*-2,3,4-$C_3B_3H_7$ (characterized for the first time in 1996) and its methyl derivatives were formed by the gas-phase reactions of B_4H_{10} with enynes, $H_2C{=}CHCCH$ and $H_2C{=}CHCCMe$, at 70 °C.[142] The derivative 2-Me-2,3,4-$C_3B_3H_7$ was made from the gas-phase reaction of B_4H_{10} and ethyne at 50 °C (COMC (1982) 5.4.2.6.1).[135] An unusual derivative 5,6-$MeCH_2$-2(3)-Me-1,3(2),5,6-Et_4-2,3,4-C_3B_3H with a bridging Et moiety was produced in low yield from Et_2BH and Et_2BCCMe in the presence of Me_3SnCl.[143]

***nido*-2,3,5-$C_3B_3H_7$:** All reported alkyl derivatives of *nido*-2,3,5-$C_3B_3H_7$ were obtained from Et_2BH with unsaturated organoboranes. 2,3-^{i}Pr$_2$-1,4,5,6-Et_4-2,3,5-C_3B_3H and 2,3-^{i}Pr$_2$-1,4,5,6-Et_4-2,3,5-C_3B_3H were made in 39% yields from $(Me_2C{=}C)_2(BMe)_2CHMe$ and $(Me_2C{=}C)_2(BEt)_2CHMe$, respectively, with Et_2BH.[144] 5-^{i}Pr-1,2,3-Et_3-4,6-Me_2-2,3,5-C_3B_3H and 5-^{i}Pr-1,2,3,4,6-Et_5-2,3,5-C_3B_3H were similarly produced using $Et_2C_2(BMe)_2C{=}CMe_2$ and $Et_2C_2(BEt)_2C{=}CMe_2$ with Et_2BH, respectively. All these alkyl derivatives give monoanions of type 2,3,5-$C_3B_3H_6^-$ on deprotonation by NaH, BuLi, Na, and Li. 5-^{t}BuCH$_2$-1,2,3-Et_3-4,6-Me_2-2,3,5-C_3B_3H is formed from $Et_2C_2(BMe)_2C{=}CH^t$Bu with Et_2BH. 2-Me-1,4,5,6-Et_4-2,3,5-$C_3B_3H_2$ is generated in low yield from the reaction of $Et_2BCCBEt_2$ with Et_2BH in the presence of Me_3SnCl.[143] 5-CH_2BEt-1,4,6-Et_3-2,3,5-$C_3B_3H_2$ with an unusual bridging moiety at C5 was obtained in low yield from $Et_2BCCBEt_2$ and Et_2BH at 80 °C.[145]

***nido*-2,3,4,5-$C_4B_2H_6$:** Table 3 lists the many synthetic methods reported for *nido*-2,3,4,5-$C_4B_2H_6$ derivatives (COMC (1982) 5.4.2.6.8).

Many structures were also published: 5-$Fe_2(CO)_6$SN-1,2,3,4,5-Me_5-2,3,4,5-C_4B_2,[153] 1,6-I_2-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] 6-PhCC-1-I-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] 6-PhCC-1-Me_3SiCC-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] 6-Cp$(CO)_2$Fe-1-

Table 3 Synthetic routes to *nido*-2,3,4,5-$C_4B_2H_6$ derivatives

Derivatives of 2,3,4,5-$C_4B_2H_6$	*Starting materials*	*Solvent, temp, yield*
3-Me-	B_4H_{10}, $H_2C{=}CMeCCH$	70 °C, 3%[142]
1,2,3,4,5,6-Et_6-	$Et_2C_2(BEt)_2O$	Heat[146]
6-Br-1,3,4-Et_3-	$(HC{=}C(BEt_2)EtC{=}CH)_2Sn$, BBr_3	4%[147]
1,6-Cl_2-2,5-R_2-3,4-Et_2-	$(RC{=}C(BEt_2)EtC{=}CR)_2Sn$, BCl_3	[148]
1,6-Br_2-2,5-R_2-3,4-Et_2-	$(RC{=}C(BEt_2)EtC{=}CR)_2Sn$, BBr_3	>90%[148]
1,6-I_2-2,5-R_2-3,4-Et_2-	$(RC{=}C(BEt_2)EtC{=}CR)_2Sn$, BI_3	>90%[148]
1,6-Me_2-2,5-Pr_2-3,4-Et_2-	$(PrC{=}C(BEt_2)EtC{=}CPr)_2Sn$, $MeBBr_2$	[148]
1,6-Mes_2-2,3-(CH=CHCH=CH)-4-Me_3Si-	$Ph(Me_3Si)C{=}C(BMesCl)_2$, Mg	Et_2O, 74%[149]
1,6-I_2-2,3,4,5-Et_4-	EtCCEt, NaK alloy, BI_3	66%[150]
1,6-I_2-2,3,4,5-Et_4-	EtCCEt, $Et(I_2B)C{=}C(BI_2)Et$	53%[150]
1,6-I_2-2,3,4,5-Me_4-	MeCCMe, NaK alloy, BI_3	15%[150]
1,6-I_2-2,3,4,5-Ph_4-	PhCCPh, NaK alloy, BI_3	5%[150]
4(5)-^tBu-2,3-Et_2-1,6-Me_2-	$Et_2C_2(BMe)_2C{=}CH^tBu$	[151]
2,4-$^iPr_2$-3,5-$(H_2C{=}CMe)_2$-1,6-Cl_2-	$(Me_2C{=}C)_2(BCl)_2(C{=}CMe_2)_2$	UV[152]
2,4-$^iPr_2$-3,5-$(H_2C{=}CMe)_2$-1,6-Me_2-	$(Me_2C{=}C)_2(BMe)_2(C{=}CMe_2)_2$	UV[152]

I-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] 6-$(CO)_6Co_2PhC_2$-1-I-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] 6-(1,2-$HCB_{10}H_{10}C$)-1-I-2,3,4,5-Et_4-2,3,4,5-C_4B_2,[150] and 1,6-Mes_2-2,3-(CH=CHCH=CH)-4-Me_3Si-2,3,4,5-C_4B_2H.[149]

***nido*-2,3,4,5,6-$C_5BH_6^+$:** As discussed in the cationic carborane section, two related *nido*-pentacarbaborane adducts 1-Cl_3B-2,3,4,5,6-Me_6-2,3,4,5,6-C_5B (53% yield) and 1-$(Cl_3Si)Cl_2B$-2,3,4,5,6-Me_6-2,3,4,5,6-C_5B were obtained.[114] The BCl_3 adduct and the known cation 1-Br-2,3,4,5,6-Me_6-2,3,4,5,6-C_5B^+ were structurally determined by X-ray diffraction.[112,114]

3.02.9.4 Seven-vertex Carboranes

***closo*-2-$CB_6H_7^-$:** The parent anion, 2-$CB_6H_7^-$, was produced in only 6% yield from 4-CB_8H_{14} with NEt_3 in refluxing toluene in the presence of air (see Figure 5).[154] The C-phenyl anion, 2-Ph-2-$CB_6H_6^-$, was formed in low yields from 1-Ph-1-CB_8H_{11} or 1-Ph-1-CB_8H_{13} with NEt_3 in refluxing toluene.[93,155] The anion, 2-$CB_6H_7^-$, reacts with iodine and NEt_3 in CH_2Cl_2 to give 4,5-I_2-2-$CB_6H_5^-$ in 93% yield.[154] The salts Et_4N^+ 2-Ph-2-$CB_6H_6^-$ and Ph_4P^+4,5-I_2-2-$CB_6H_5^-$ were structurally determined by X-ray crystallography.[93,154]

***closo*-2,3-$C_2B_5H_7$:** The identity of the parent carborane *closo*-2,3-$C_2B_5H_7$, unlike its long-known and more thermodynamically stable isomer 2,4-$C_2B_5H_7$ (COMC (1982) 5.4.2.6.1), was only confirmed for the first time in 1996.[60,75] It was made from 4,5-$C_2B_6H_{10}$ in 54% yield by passing through a hot tube at 350 °C and from 7-MeCH=CMe-4,5-$C_2B_6H_9$ in 35% yield by heating to 110 °C in dodecane.[75]

***closo*-2,4-$C_2B_5H_7$:** The parent carborane *closo*-2,4-$C_2B_5H_7$ was made from the high energy flash reactions of diborane and tetraborane with ethyne in low yields.[117] 2,3-Me_2-2,4-$C_2B_5H_5$ was formed as a minor product in the reaction of 2-MeB_5H_8 with propyne at 230 °C. The hexaethyl derivatives, 1,2,3,4,5,6-Et_6-2,4-C_2B_5H and 1-Br-2,3,4,5,6,7-Et_6-2,4-C_2B_5, were made in 39% and 5% yields, respectively, from BBr_3 and the anion 1,2,3,4,5,6-Et_6-2,4-$C_2B_4H^-$ in toluene.[132]

***nido*-4,5-$C_2B_5H_8^-$:** *nido*-4,5-$C_2B_5H_8^-$ was prepared from the reaction of 2,3-$C_2B_5H_7$ with $LiEt_3BH$ in THF.[75] The adducts, 7-TMEDA-4,5-$C_2B_5H_7$ and 7-Me_3PCH_2-4,5-Et_2-4,5-$C_2B_5H_5$, were made from the reactions of 2,3-$C_2B_5H_7$ and 2,3-Et_2-2,3-$C_2B_5H_5$ with TMEDA and $Me_3P{=}CH_2$, respectively.[75,156] The latter adduct was structurally characterized by X-ray crystallography.[156]

3.02.9.5 Eight-vertex Carboranes

***closo*-1-$CB_7H_8^-$:** Several synthetic routes to the parent anion 1-$CB_7H_8^-$ and its C-phenyl analog were reported (see Figure 5).[90,93,154,157,158] The reaction of 1-$CB_7H_8^-$ with a slight excess of iodine in CH_2Cl_2 gave 7-I-1-$CB_7H_7^-$ and 7,8-I_2-1-$CB_7H_6^-$ anions in 73% and 27% yields, respectively.[157] Crystal structures of the salts Ph_4P^+7,8-I_2-1-$CB_7H_6^-$, Ph_4P^+7-I-1-$CB_7H_7^-$, and Et_4N^+1-Ph-1-$CB_7H_7^-$ were determined experimentally.[93,157,158]

***nido*-4,5-$C_2B_6H_{10}$:** Acidification of the salt K^+4,5-$C_2B_6H_9^-$ with HCl in pentane gave 70% yield of *nido*-4,5-$C_2B_6H_{10}$.[75,159]

***nido*-3,5-$C_2B_6H_9^-$:** The anion *nido*-3,5-$C_2B_6H_9^-$ was prepared from *closo*-1,7-$C_2B_6H_8$ with LiH in THF.[160] The related adduct *nido*-6-Me_3N-3,5-$C_2B_6H_8$ was formed from *closo*-1,7-$C_2B_6H_8$ with NMe_3.

***nido*-4,5-$C_2B_6H_9^-$:** The anion *nido*-4,5-$C_2B_6H_9^-$ was formed in high yield (97%) from *arachno*-4,5-$C_2B_7H_{13}$ with KH in THF then MeCN.[75,159] The anion was structurally characterized as its Bu_4N^+ salt.[159] The monosubstituted derivatives, 7-PhHC═CH-, 7-MeHC═CMe-, and 7-C_6H_{13}-4,5-$C_2B_6H_8^-$, were generated from 4,5-$C_2B_6H_{10}$ with PhCCH, MeCCMe, and $C_4H_9CH{=}CH_2$, respectively, in the presence of proton sponge (PS) in 41–83% yields.[75] The salt PSH^+7-*cis*-MeHC═CMe-4,5-$C_2B_6H_8^-$ was structurally determined by an X-ray study.[75]

***nido*-5,6,7,8-$C_4B_4H_8$:** 1,2,3,4-Et_4-5,6,7,8-$C_4B_4H_4$ was formed in 12% yield from $Et_2BCCBEt_2$ and Et_2BH[145,161] and structurally characterized by X-ray crystallography.[145] The tetraiodo derivative, 1,2,3,4-I_4-5,6,7,8-Et_4-5,6,7,8-C_4B_4, was made in 29% yield from $Et(I_2B)C{=}C(BI_2)Et$ with NaK alloy.[162] In the presence of oxygen, the complexes Cp(2,3-Et_2-2,3-$C_2B_4H_4$)TaMeCR═RMe (R═Me, Et, and Ph) gave 5,6-R_2-7,8-Et_2-5,6,7,8-$C_4B_4H_4$ in 30–36% yields.[163]

***arachno*-4,5-$C_2B_6H_{11}^-$:** The reaction of *nido*-4,5-$C_2B_6H_9^-$ with MeLi and PS in THF gave *arachno*-7-Me-4,5-$C_2B_6H_{10}^-$.[75]

***arachno*-4,5-$C_2B_6H_{10}^{2-}$:** The dianion 4,5-$C_2B_6H_{10}^{2-}$ was reported to be formed from *arachno*-4,5-$C_2B_6H_{11}^-$ and lithium.[75]

***arachno*-4,8-$C_2B_6H_{11}^-$:** From 1,6-$C_2B_7H_9$ and "dry" Bu_4NF in THF, the *arachno*-4,8-$C_2B_6H_{11}^-$ anion was identified.

***hypho*-7,8-$C_2B_6H_{13}^-$:** The "helmet" anion *hypho*-7,8-$C_2B_6H_{13}^-$ (Figure 8) was prepared in 61% yield from 4,5-$C_2B_7H_{13}$ and NaCN.[107] The bridging derivative, 7,8-NCCH-7,8-$C_2B_6H_{11}^-$, was formed from 4-$NCCH_2$-4,6-$C_2B_7H_{12}$ and NH_4OH in 63% yield and structurally determined by X-ray crystallography.[78] The reaction of 4,6-$C_2B_7H_{13}$ with NaH and Ph_2PCl gave the adduct 7-Ph_2HP-7,8-$C_2B_6H_{12}$.[108] With MeI present in the latter reaction, the adduct 7-Ph_2HP-8-Me-7,8-$C_2B_6H_{11}$ was obtained in 38% yield. These two adducts were structurally determined by X-ray diffraction analyses.

3.02.9.6 Nine-vertex Carboranes

***closo*-4-$CB_8H_9^-$:** The structures of Ph_3PMe^+4-$CB_8H_9^-$ and Et_4N^+4-Ph-4-$CB_8H_8^-$ were determined by X-ray crystallography. Several synthetic routes to the parent and its C-phenyl derivatives have been described (see Figure 5).[90,92,93,154,164,165]

***nido*-1-CB_8H_{12}:** The parent anion *nido*-1-CB_8H_{12} was formed in 99% yield by heating 4-CB_8H_{14} at 200 °C for 6 h.[90] The C-phenyl derivative was obtained in 78% yield from 4-Ph-4-CB_8H_{13} in refluxing toluene.[93]

***arachno*-4-CB_8H_{14}:** A crystal structure was determined for 6-uro-4-CB_8H_{12} (uro = urotropine, $(CH_2)_4N_4$) by X-ray analysis.[166] Table 4 lists the many reported routes to *arachno*-4-CB_8H_{14} and derivatives.

***arachno*-4-$CB_8H_{13}^-$:** The structure of its PSH^+ salt was determined experimentally.[89]

***arachno*-4-$CB_8H_{12}^{2-}$:** The dianion was generated from 4-CB_8H_{14} with NaH and MeCN in 44% yield.[167]

***arachno*-5-$CB_8H_{13}^-$:** From 1-CB_8H_{12} with NMe_3, NEt_3, and C_9H_7N, respectively, the adducts 4-Me_3N-, 4-Et_3N-, and 4-C_9H_7N-5-CB_8H_{12} were formed.[165] The molecular structure of 4-Et_3N-5-CB_8H_{12} was confirmed by X-ray crystallography.

Table 4 Synthetic routes to *arachno*-4-CB_8H_{14} derivatives

4-CB_8H_{14} and derivatives	*Starting materials*	*Solvent, temp, yield*
	$B_{10}H_{14}$, NaOH, CH_2O, $FeCl_3$, HCl	Hexane, H_2O, 48%[90]
	$B_{10}H_{14}$, NaOH, CH_2O, HCHO, HCl	Hexane, H_2O, 50%[90]
	9-Me_2S-6,9-(HO)BCH_2-6-CB_9H_{11}	Hexane, H_2O, 24 h, 75%[89]
6-Me_3N-	7,9-$C_2B_{10}H_{13}^-$, NMe_3	H_2O, CH_2Cl_2, 3 h, 91%[166]
6-Me_3N-	9-*endo*-Me-8-Me_3N-6-CB_9H_{12}, NMe_3	H_2O, CH_2Cl_2, EtOH, 87%[166]
6-Me_2S-	7,9-$C_2B_{10}H_{13}^-$, SMe_2, $HO_2C(CH_2)_2CO_2H$	H_2O, 2 d, 31%[166]
6-py-	7,9-$C_2B_{10}H_{13}^-$, py	H_2O, 4 d, 63%[166]
6-uro-	7,9-$C_2B_{10}H_{13}^-$, uro, $HO_2C(CH_2)_2CO_2H$	H_2O, 3 d, 27%[166]
4-Ph-	6-Ph-6-$CB_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 78%[93,158]
4-Ph-	6-Ph-6-$CB_9H_{11}^-$, BH_3.THF, $FeCl_3$	22%[93,158]
6,6′-uro-	7,9-$C_2B_{10}H_{13}^-$, uro, $HO_2C(CH_2)_2CO_2H$	H_2O, 3 d, 16%[166]

***arachno*-4,5-$C_2B_7H_{12}^-$:** Deprotonation of 4,5-$C_2B_7H_{13}$ with aqueous Na_2CO_3 gave the anion *arachno*-4,5-$C_2B_7H_{12}^-$ in 92% yield.[107] The adduct, 6-MeNC-4,5-$C_2B_7H_{11}$, was synthesized from 4,5-$C_2B_7H_{13}$ with methyl isocyanide in CH_2Cl_2 in low yield.

***arachno*-4,6-$C_2B_7H_{13}$:** Acidification of 4-NCCH═CH-4,6-$C_2B_7H_{11}^-$ gave *arachno*-4-NCCH═CH-4,6-$C_2B_7H_{12}$ in 63% yield.[78] The compound 4-*endo*-NCCH$_2$CH$_2$-4,6-$C_2B_7H_{12}$ was produced quantitatively from the reaction of 4,6-$C_2B_7H_{12}^-$ with H_2C═CHCN and structurally determined by X-ray diffraction.[109] The reactions of 4,6-$C_2B_7H_{13}$ with alkenes using $H_2PtCl_6 \cdot 6H_2O$, $PdBr_2$, or $PtBr_2$ as catalyst gave 5-alkyl or 5-alkenyl derivatives.[168] Crystal structures of 5-Et-4,6-$C_2B_7H_{12}$, 5-MeCH═CH-4,6-$C_2B_7H_{12}$, and 5-PhCH═CH-4,6-$C_2B_7H_{12}$ were obtained.

***arachno*-4,6-$C_2B_7H_{12}^-$:** The anion 4-NCCH═CH-4,6-$C_2B_7H_{11}^-$ was formed in 82% yield from 4,6-$C_2B_7H_{13}$ and HCCCN in THF.[78]

***arachno*-7,8-$C_2B_7H_{12}^-$:** The anion *arachno*-7,8-$C_2B_7H_{12}^-$, with the less stable geometry as found in *n*-B_9H_{15}, was made from the reaction of the *nido*-anion 4,5-$C_2B_6H_9^-$ with $BH_3 \cdot$THF in 98% yield and structurally characterized as its PSH$^+$ salt.[75]

***hypho*-4,9-$C_2B_7H_{14}^-$:** *arachno*-4,5-$C_2B_7H_{13}$ with tertiary amines R_3N gave the adducts *hypho*-5-R_3N-4,9-$C_2B_7H_{13}$ (R = Me and Et) in 41–55% yields (Figure 8).[107]

***hypho*-7,8-$C_2B_7H_{14}^-$:** The reaction of 4,6-$C_2B_7H_{12}^-$ with $(NC)_2C$═$C(CN)_2$ in DME gave the *hypho*-7,9-$(CN)_2CC(CN)_2$-7,8-$C_2B_7H_{12}^-$ anion in 40% yield.[109] This *hypho*-anion was structurally characterized by X-ray crystallography (Figure 8).

3.02.9.7 Ten-vertex Carboranes

***closo*-1-$CB_9H_{10}^-$:** Table 5 lists the reported syntheses of 1-$CB_9H_{10}^-$ and derivatives (see Figure 5, COMC (1982) 5.4.2.6.3).

There have been many halogenation reactions of 1-$CB_9H_{10}^-$ and its derivatives to form anions with B-halogen bonds (F, Cl, Br, and I).[88,93,177–181] The hydroxyl derivative 6-HO-1-Ph-1-$CB_9H_8^-$ was made from 1-Ph-1-$CB_9H_9^-$

Table 5 Synthetic routes to *closo*-1-$CB_9H_{10}^-$ derivatives

1-$CB_9H_{10}^-$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	2-$CB_9H_{10}^-$	DME, reflux, 18 h, 92%[169] 94%[88]
	6-$CB_9H_{14}^-$	220 °C, 35%[164]
	6-$CB_9H_{12}^-$	220 °C, 3%[164]
	6-Me_3N-6-CB_9H_{11}, piperidine	70 °C, 3 d, 68%[170]
6-Me-	9,10-CH_2-7-$CB_{10}H_{11}^-$, KNC_4H_4	THF, 55%[171]
6-Me-	9,10-CH_2-7-$CB_{10}H_{11}^-$, KNC_4Me_4	THF, 55%[171]
6-Et-	9,10-MeCH-7-$CB_{10}H_{12}^-$, KNC_4H_4	THF, 30%[171]
6-CH_2Ph-	9,10-PhCH-7-$CB_{10}H_{12}^-$, KNC_4H_4	THF, 45%[171]
1-HO_2C-	2-HO_2C-2-$CB_9H_9^-$	MeCN, reflux, 18 h, 94%[172]
1-H_3N^+-	6-H_3N-6-CB_9H_{11}, $NaBH_4$, $Et_3N \cdot BH_3$	THF, 200 °C, 75%[173]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$	200 °C, 5%[93]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$, $BH_3 \cdot NEt_3$	210 °C, 25%[92,93]
1-Ph-	2-Ph-2-$CB_9H_9^-$	DME, reflux, 18 h, 94%[93,169]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$, Na	THF, 74%[93]
1-(2′-C_4H_3S)-	$B_{10}H_{14}$, 4-(2-C_4H_3S)CHO, NaOH, I_2	EtOH, MeOH, reflux, 76%[174]
1-(4-$H_2NC_6H_4$)-	$B_{10}H_{14}$, 4-$H_2NC_6H_4$CHO, NaOH, I_2	EtOH, MeOH, reflux, 78%[174] 48%[175]
1-(4-BrC_6H_4)-	2-(4-BrC_6H_4)-2-$CB_9H_9^-$	EtOH, reflux, 16 h, 95%[174]
1-(4-$HO_2CC_6H_4$)-	2-(4-$HO_2CC_6H_4$)-2-$CB_9H_9^-$	MeCN, reflux, 18 h, 94%[172]
1-(4-$HOCH_2C_6H_4$)-	2-(4-$HOCH_2C_6H_4$)-2-$CB_9H_9^-$	MeCN, reflux, 18 h, 94%[172]
1-Me-6-Et-	7-Me-9,10-MeCH-7-$CB_{10}H_{11}^-$, KNC_4H_4	THF, 47%[171]
6-(4-$PhCH_2C_5H_4N)^+$-1-Ph-	6-Ph-6-$CB_9H_{11}^-$, $FeCl_3$, 4-$PhCH_2C_5H_4N$	$CHCl_3$, reflux, 55%[176]
10-Cl-1-Ph-	7-Cl-2-Ph-2-$CB_9H_8^-$	DME, heat[93]
6-Cl-1-Ph-	7-Cl-2-Ph-2-$CB_9H_8^-$	DME, heat[93]
10-Br-1-Ph-	7-Br-2-Ph-2-$CB_9H_8^-$	DME, heat[93]
10-I-1-Ph-	7-I-2-Ph-2-$CB_9H_8^-$	DME, heat, 44%[93]
6-Br-1-Ph-	7-Br-2-Ph-2-$CB_9H_8^-$	DME, heat[93]
6-I-1-Ph-	7-I-2-Ph-2-$CB_9H_8^-$	DME, heat[93]

Table 6 Structures of *closo*-1-$CB_9H_{10}^-$ derivatives determined experimentally

1-$CB_9H_{10}^-$ and derivatives	*Cation M^+*	*References*
	Ag^+	183
	$(C_5Me_5)_2Ir_2Cl_3^+$	170
1-HO_2C-	Et_4N^+	172
1-$HOCH_2$-	Et_4N^+	172
1-Ph-	$(^tBuC_3H_3N)_3ZnCl^+$	184
1-Ph-	Et_4N^+	92,93
1-(4-$HO_2CC_6H_4$)-	Et_4N^+	172
1-(4-$N_2C_6H_4$)-$^+$		175
1-(4-$H_2NC_6H_4$-4-$N{=}NC_6H_4$)-	Et_4N^+	175
1-(4-$Me_2C{=}NHC_6H_4$)-$^+$	Et_2O	175
1-(4-(2,4-$(O_2N)_2$)$C_6H_3NHN{=}CHC_6H_4$)-	Et_4N^+	172
1-(2,4-$(O_2N)_2C_6H_3$)$NHN{=}CH$-	Et_4N^+	172
1-(4-BrC_6H_4)-	Bu_4N^+	174
1-Me_3N-$^+$		173
6-(4-$PhCH_2C_5H_4N$)$^+$-1-Ph-		176
6-HO-1-Ph-	Et_4N^+	93
6,8-F_2-	$Ag(C_6H_6)_2^+$	177
10-MeCONH-6,7,8,9-F_4-	Ph_4P^+	181
1-$PhCH_2$-2,3,4,5,6,7,8,9,10-Cl_9-	$PhCH_2NMe_3^+$	182
6,7,8,9,10-Br_5-	$(^tBuC_3H_3N)_3ZnCl^+$	184
6,7,8,9,10-Br_5-	$Ag(PhMe)^+$	183
6,7,8,9,10-Br_5-	Cs^+	88
2,3,4,5,6,7,8,9,10-Br_9-	$Ag(C_6H_6)^+$	182
2,3,4,5,6,7,8,9,10-Br_9-	1.5 $Ag_3(C_6H_6)_2^+$ 0.5 NO_3^- 0.5 THF	182
2,3,4,5,6,7,8,9,10-Br_9-	$H_9O_4^+$	185
2,3,4,5,6,7,8,9,10-Br_9-	Cs^+, 0.5 H_2O	182
6,8,10-Br_3-1-Ph-	Et_4N^+	93
6,7,8,9,10-Br_5-1-(4-BrC_6H_4)-	Et_4N^+	93
6,7,8,9-(4-MeC_6H_4)$_4$-10-I-1-Ph-	0.5 $((4\text{-}MeC_6H_4)_3P)_4Pd_2I_2^{2+}$	93,179
6,7,8,9,10-I_5-1-Ph-	Et_4N^+	93
1,1′-$C_6H_4NHCOC_6H_4CONHC_6H_4$-	2 Et_4N^+	176

with $KMnO_4$ and H_2SO_4 in 42% yield.[93] 1-$PhCH_2$-2,3,4,5,6,7,8,9,10-Cl_9-1-CB_9^- was made from the nonachloro anion with BuLi and benzylbromide in 95% yield.[182] The many structural studies on 1-$CB_9H_{10}^-$ derivatives are listed in Table 6.

***closo*-2-$CB_9H_{10}^-$:** Syntheses of 2-$CB_9H_{10}^-$ and derivatives generally used *nido*-$CB_9H_{12}^-$ or *arachno*-6-$CB_9H_{14}^-$ precursors with hydroxide ion and iodine (see Figure 5).[88,93,169,172,174,186] The 7-X-2-Ph-2-$CB_9H_8^-$ anions (X = Cl, Br, I) were made from the reaction of the 2-Ph-2-$CB_9H_9^-$ anion in acetonitrile with the corresponding N-halogenosuccinimides in 85–90% yields.[93] Four Et_4N^+ salts of 2-HO_2C-, 2-Ph-, 2-(4-$HO_2CC_6H_4$)-2-$CB_9H_9^-$, and 7-Br-2-Ph-2-$CB_9H_8^-$ were determined by X-ray crystallography.[93,169,172,186]

***nido*-6-$CB_9H_{12}^-$:** Table 7 summarizes the methods used for *nido*-6-$CB_9H_{12}^-$ and its derivatives (Figure 5). Et_4N^+ salts of 6-Ph-6-$CB_9H_{11}^-$ and 6-(4-$HO_2CC_6H_4$)-6-$CB_9H_{11}^-$ were characterized by X-ray studies.[93,172]

***arachno*-6-$CB_9H_{14}^-$:** Synthetic procedures to the *arachno*-6-$CB_9H_{14}^-$ anion and its derivatives are listed in Table 8 (Figure 5).

***closo*-1,2-$C_2B_8H_{10}$:** The carborane 1,2-Ph_2-1,2-$C_2B_8H_8$ was obtained in 36% yield from the reaction of $B_9H_{13}{\cdot}SMe_2$ with PhCCPh in toluene.[80] Similarly, 1-(4-BrC_6H_4)-2-C_5H_{11}-1,2-$C_2B_8H_8$ was formed from $B_9H_{13}{\cdot}SMe_2$ with 4-$BrC_6H_4CCC_5H_{11}$ in 30% yield.[187] The known parent *closo*-1,2-$C_2B_8H_{10}$ was structurally determined by gas-phase electron diffraction.[188]

***closo*-1,6-$C_2B_8H_{10}$:** The parent carborane *closo*-1,6-$C_2B_8H_{10}$ was made in 30–35% yields from the dianion 6,9-$C_2B_8H_{10}^{2-}$ with $CuCl_2$.[189]

***closo*-1,10-$C_2B_8H_{10}$:** Synthetic routes to *closo*-1,10-$C_2B_8H_{10}$ and derivatives are listed in Table 9 (see Figure 3). Several C-substituted derivatives were made from metallation of the C–H bond with butyllithium followed by carbon dioxide,[187,190] alkyl halides,[190,193] or silyl chlorides.[191] Transmetallation with copper permits self-coupling[191] or coupling with bromoalkynes[192,193] and iodoarenes[187] to give C-substituted derivatives. 1,10-$(NC)_2$-1,10-$C_2B_8H_8$,

Table 7 Synthetic routes to *nido*-6-$CB_9H_{12}^-$ derivatives

6-$CB_9H_{12}^-$ and derivatives	Starting materials	Solvent, temp, yield
	$CB_9H_{14}^-$	220 °C, 5%[164]
	$CB_9H_{14}^-$, Et_3N, I_2	CH_2Cl_2, 100%[90]
6-Ph-	$B_{10}H_{14}$, PhCHO, KOH	EtOH, H_2O, 64–94%[93]
6-(4-MeC_6H_4)-	$B_{10}H_{14}$, 4-MeC_6H_4CHO, KOH	EtOH, H_2O, 65%[93]
6-(4-BrC_6H_4)-	$B_{10}H_{14}$, 4-BrC_6H_4CHO, KOH	EtOH, H_2O, 69%[93,176]
6-(4-$HO_2CC_6H_4$)-	$B_{10}H_{14}$, 4-$HO_2CC_6H_4CHO$, KOH	H_2O, 62%[172,186]
6-(4-$HOCH_2C_6H_4$)-	$B_{10}H_{14}$, 1,4-$(CHO)_2C_6H_4$, KOH	H_2O, 58%[172]
6-(4-$MeCONHC_6H_4$)-	$B_{10}H_{14}$, 4-$MeCONHC_6H_4CHO$, NaOH	H_2O, EtOH, 64%[174]
9-Me-8-Me_3N-	9-*endo*-Me-8-Me_3N-6-CB_9H_{12}, HCl	Me_2CO, 70%[166]
9-Me-8-HO-	7,9-$C_2B_{10}H_{13}^-$	Me_2CO, 80%[166]

Table 8 Synthetic routes to *arachno*-6-$CB_9H_{14}^-$ derivatives

6-$CB_9H_{14}^-$ and derivatives	Starting materials	Solvent, temp, yield
	$B_{10}H_{14}$, HCHO, NaOH	H_2O, hexane, 56%[90]
	$B_{10}H_{14}$, HCHO, NaOH	H_2O, 44%[164]
	$B_{10}H_{14}$, HCHO, KOH	H_2O, MeOH, 74%[88]
6-HO_2C-	$B_{10}H_{14}$, 4-$HO_2CCHO(OH_2)$, KOH	H_2O, 53%[172,186]
6-(2-$MeOC_6H_4$)-	$B_{10}H_{14}$, 2-$MeOC_6H_4CHO$, NaOH	H_2O, EtOH, 53%[174]
9-*endo*-Me-8-Me_3N-$^+$	7,9-$C_2B_{10}H_{13}^-$, NMe_3	H_2O, EtOH, 1 h, 76%[166]
9-Me_2S^+-6,9-(HO)BCH_2-	7,9-$C_2B_{10}H_{13}^-$, SMe_2, HCl	H_2O, 77%[89]

Table 9 Synthetic routes to *closo*-1,10-$C_2B_8H_{10}$ derivatives

1,10-$C_2B_8H_{10}$ and derivatives	Starting materials	Solvent, temp, yield
	5,6-$C_2B_8H_{12}$	380 °C, 86%[81]
	6,9-$C_2B_8H_{10}^{2-}$, $CuCl_2$	CH_2Cl_2, 350 °C, 35%[189]
	1,12-$C_2B_{10}H_{12}$, KOH	Tetraglyme, 2%[52]
2-HO-	1,12-$C_2B_{10}H_{12}$, KOH	Tetraglyme, 4%[52]
1-(4-BrC_6H_4)-10-C_5H_{11}-	$B_9H_{13}\cdot SMe_2$, 4-$BrC_6H_4CCC_5H_{11}$	Toluene, 350 °C, 23%[187]
1-C_5H_{11}-	$B_9H_{13}\cdot SMe_2$, $C_5H_{11}CCH$	Toluene, 330 °C, 23%[187]
1-C_6H_{13}-	5(6)-C_6H_{13}-5,6-$C_2B_8H_{11}$	260 °C, 35%[187]

1,10-$(Me_3SiCC)_2$-1,10-$C_2B_8H_8$, and the two-cage carboranes 1,10′-$(C_5H_{11}CC)_2$- and 1,10′-$(C_7H_{15})_2$-10-(1′-1′,10′-CB_8H_8C)-1,10-$C_2B_8H_8$ were structurally characterized.[192,193]

***nido*-5,6-$C_2B_8H_{12}$:** Several synthetic routes to *nido*-5,6-$C_2B_8H_{12}$ and its C-substituted derivatives reported are listed in Table 10 (see Figure 3).

***nido*-5,6,9-$C_3B_7H_{11}$:** Protonation of the 6-Me-5,6,9-$C_3B_7H_9^-$ anion or 7-Me-5,7,14,12-$C_3NB_8H_{11}$ gave 6-Me-5,6,9-$C_3B_7H_{10}$ in 40–42% yield.[99,194,195]

***nido*-5,6,9-$C_3B_7H_{10}^-$:** The reaction of 4,6-$C_2B_7H_{13}$ with NaH/LiH and MeCN gave the anion *nido*-6-Me-5,6,9-$C_3B_7H_9^-$ in 80–85% yields (Figure 7).[99,100,194] The crystal structure of the salt $Li(NCMe)_2^+$6-Me-5,6,9-$C_3B_7H_9^-$ was determined.[100]

***nido*-5,6,10-$C_3B_7H_{11}$:** The reaction of 4,5-$C_2B_7H_{13}$ with $HCCCO_2Me$ in the presence of PS gave 6-MeO_2CCH_2-5,6,10-$C_3B_7H_{10}$ in 39% yield.[98] 6-MeO_2CCH_2-5,6,10-$C_3B_7H_{10}$ and butyllithium gave 6-MeO_2CCH_2-5(10)-Bu-5,6,10-$C_3B_7H_9$.

***arachno*-5,6-$C_2B_8H_{13}^-$:** The anion 9-CN-5,6-$C_2B_8H_{12}^-$ was made from 5,6-$C_2B_8H_{12}$ and NaCN in 45–48% yields.[103] The reactions of 5,6-$C_2B_8H_{12}$ with ammonia and $PrNH_2$ in CH_2Cl_2 gave the adducts, 9-H_3N- and 9-PrH_2N-5,6-$C_2B_8H_{12}$, respectively, in moderate yields.[196]

Table 10 Synthetic routes to *nido*-5,6-$C_2B_8H_{12}$ derivatives

5,6-$C_2B_8H_{12}$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	$B_9H_{13}\cdot SMe_2$, HCCH	Toluene, reflux, 53–60%[80]
	7,8-$C_2B_9H_{12}^-$, $FeCl_3$, HCl	H_2O, hexane, 60%[79]
5-Me-	7-Me-7,8-$C_2B_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 9%[79]
6-Me-	7-Me-7,8-$C_2B_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 27%[79]
5(6)-C_6H_{11}-	7-C_6H_{11}-7,8-$C_2B_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 10%[187]
5(6)-C_6H_{11}-	7-C_6H_{11}-7,8-$C_2B_9H_{12}$, SO_2	Hexane, 16%[187]
5,6-Me_2-	$B_9H_{13}\cdot SMe_2$, MeCCMe,	Toluene, reflux, 85%[80]
5,6-Me_2-	7,8-Me_2-7,8-$C_2B_9H_{10}^-$, $FeCl_3$, HCl	H_2O, hexane, 32%[79]
5-Ph-	7-Ph-7,8-$C_2B_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 5%[79]
6-Ph-	7-Ph-7,8-$C_2B_9H_{11}^-$, $FeCl_3$, HCl	H_2O, hexane, 10%[79]
6-Ph-	$B_9H_{13}\cdot SMe_2$, PhCCH,	Toluene, reflux, 52%[80]
5,6-Ph_2-	$B_9H_{13}\cdot SMe_2$, PhCCPh,	Toluene, reflux, 52%[80]
5,6-Ph_2-	7,8-Ph_2-7,8-$C_2B_9H_{10}^-$, $FeCl_3$, HCl	H_2O, hexane, 12%[79]

***arachno*-5,10-$C_2B_8H_{13}^-$:** Adducts 6-Et_3N- and 6-Bu_3N-5,10-$C_2B_8H_{12}$ were formed from the reactions of 5,6-$C_2B_8H_{12}$ with Et_3N and Bu_3N, respectively.[196] The adduct 6-Et_3N-5,10-$C_2B_8H_{12}$ was structurally characterized by X-ray diffraction. The parent anion *arachno*-5,10-$C_2B_8H_{13}^-$ was made from the 6-Et_3N-5,10-$C_2B_8H_{12}$ adduct with Na in THF in 22–31% yields or from 10,7,8-$SC_2B_8H_{10}$ with Na in 19% yield.

***arachno*-5,6,7-$C_3B_7H_{13}$:** From *arachno*-4,6-$C_2B_7H_{12}^-$ with HCCCN, $HCCCO_2Me$, and HCCCOMe, the tricarbaboranes 6-$NCCH_2$-, 6-MeO_2CCH_2-, and 6-$MeCOCH_2$-5,6,7-$C_3B_7H_{12}$, respectively, were formed in good yields (Figure 7).[78,197] A one-pot reaction from 4,6-$C_2B_7H_{13}$, $HCCCO_2Me$, and PS gave 6-MeO_2CCH_2-5,6,7-$C_3B_7H_{12}$ in 64% yield.[98] The *arachno*-carboranes 6-$NCCH_2$-5,6,7-$C_3B_7H_{12}$ and 6-MeO_2CCH_2-5,6,7-$C_3B_7H_{12}$ were structurally determined.[78,197]

***arachno*-5,6,7-$C_3B_7H_{12}^-$:** Deprotonation of 6-$NCCH_2$-5,6,7-$C_3B_7H_{12}$ with KH in THF or PS in CH_2Cl_2 produced the anion 6-$NCCH_2$-5,6,7-$C_3B_7H_{11}^-$ in 57–81% yields.[78,98]

***arachno*-5,6,9-$C_3B_7H_{13}$:** The reaction of the *nido*-anion, 7,8,10-$C_3B_8H_{11}^-$, with Me_3N, HCl, and $FeCl_3$ in aqueous ethanol produced *arachno*-5,6,9-$C_3B_7H_{13}$ in 55% yield.[102,198] An unusual intramolecular carbon insertion took place in the deprotonation of 4-$NCCH_2CH_2$-4,6-$C_2B_7H_{12}$ followed by acidification to give 6,9-CH_2CH_2-5,6,9-$C_3B_7H_{11}$.[109]

***arachno*-5,6,10-$C_3B_7H_{13}$:** The reaction of 6-MeO_2CCH_2-5,6,10-$C_3B_7H_{10}$ and butyllithium gave 6-MeO_2CCH_2-5(10)-Bu-5,6,10-$C_3B_7H_{11}$.

***arachno*-5,6,8,10-$C_4B_6H_{12}$:** *arachno*-6,9-HC═CH-5,6,8,10-$C_4B_6H_{10}$ was formed in low yield from *nido*-4,5-$C_2B_7H_{13}$ with ethyne and PS at 120 °C.[199]

3.02.9.8 Eleven-vertex Carboranes

***Closo*-2-$CB_{10}H_{11}^-$:** Syntheses of *closo*-2-$CB_{10}H_{11}^-$ are listed in Table 11 (Figure 5). The salt Et_4N^+2-Ph-2-$CB_{10}H_{10}^-$ and the zwitterion 2-Me-3-Ph_3PMeCH-2-$CB_{10}H_{10}$ were structurally determined.[93,158,200]

***closo*-2,3-$C_2B_9H_{11}$:** The known parent *closo*-2,3-$C_2B_9H_{11}$ (see COMC (1982) 5.4.2.6.3) was made by acidification of the anions 7,9-$C_2B_9H_{12}^-$ and 10-EtO-7,9-$C_2B_9H_{11}^-$ in high yields.[59] Several C- and B-substituted derivatives of *closo*-2,3-$C_2B_9H_{11}$ were also made by adding acid to the derivatives of 7,9-$C_2B_9H_{12}^-$. The "camouflaged" carborane 1,4,5,6,7,8,9,10,11-Me_9-2,3-$C_2B_9H_2$ was formed from the anion 1,2,4,5,6,9,10,11-Me_8-7,8-$C_2B_9H_3^-$ with SiO_2, MeI, and $AlCl_3$.[243] The parent *closo*-$C_2B_9H_{11}$ was structurally determined by gas-phase electron diffraction.[303]

Table 11 Synthetic routes to *closo*-2-$CB_{10}H_{11}^-$ derivatives

2-$CB_{10}H_{11}^-$ and derivatives	*Starting materials*	*Solvent, temp, yield*
2-Ph-	7-Ph-7-$CB_{10}H_{12}^-$, I_2, OH^-	H_2O, 65%[93,158]
2-Me_3N^+-	7-Me_3N-7-$CB_{10}H_{11}^-$, I_2	CH_2Cl_2, 79%[201]
2-Me_3N^+-	7-Me_3N-7-$CB_{10}H_{12}$, NaI	CH_2Cl_2, H_2O, electrochemical, 95%[201]
2-Me_3N^+-	7-Me_3N-7-$CB_{10}H_{11}^-$, I_2	MeCN[85]
2-Me_3N^+-3-I-	4-I-7-Me_3N-7-$CB_{10}H_{10}^-$, I_2	$MeCN/CH_2Cl_2$, 81%[201]
2-Me-3-Ph_3PMeCH-$^+$	7-Me-9,10-MeCH-7-$CB_{10}H_{10}^-$, $(Ph_3P)_2PdCl_2$	EtOH, 4%[200]

Table 12 Synthetic routes to *nido*-7-$CB_{10}H_{13}^-$ derivatives

7-$CB_{10}H_{13}^-$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	$CB_9H_{12}^-$	220 °C, 20%[164]
	$B_{10}H_{14}$, NaH, CH_2Br_2	THF, 25%[84]
7-Ph-	6-Ph-6-$CB_9H_{11}^-$	200 °C, 22%[92,93]
7-Ph-	6-Ph-6-$CB_9H_{11}^-$, BH_3·THF, $FeCl_3$	$C_2H_4Cl_2$, 40%[92,93,158]
7-^{t}BuNH_2-$^+$	$B_{10}H_{14}$, ^{t}BuNC	Benzene, 90%[205]
7-$C_6H_{11}NH_2$-$^+$	$B_{10}H_{14}$, *cyclo*-$C_6H_{11}NC$	Benzene, 92%[85]
2-Me_2S^+-7-$PhCH_2NH$-11-$(Me_3Si)_2C{=}CH$	5-Me_2S-6-$(Me_3Si)_2C{=}CH$-$B_{10}H_{11}$, PhNC	Benzene, 60%[206]
2-Me_2S^+-7-BuNH-11-$(Me_3Si)_2C{=}CH$	5-Me_2S-6-$(Me_3Si)_2C{=}CH$-$B_{10}H_{11}$, BuNC	Benzene, 40%[206]
2-Me_2S^+-7-^{t}BuNH-11-$(Me_3Si)_2C{=}CH$-	5-Me_2S-6-$(Me_3Si)_2C{=}CH$-$B_{10}H_{11}$, ^{t}BuNC	Benzene, 48%[206]
2-Me_2S^+-7-$PhCH_2NH$-11-$Bu(Me_3Si)C{=}CH$-	5-Me_2S-6-$Bu(Me_3Si)C{=}CH$-$B_{10}H_{11}$, BuNC	Benzene, 61%[206]

Table 13 Structures of *nido*-7-$CB_{10}H_{13}^-$ derivatives determined experimentally

7-$CB_{10}H_{13}^-$ and derivatives	*Cation, M^+*	*References*
	Cs^+	207
7-Ph-	Et_4N^+	93
4-MeS-7-Ph-	Et_4N^+	93
7-^{t}BuNH-	$PhCH_2NEt_3^+$	205
7-^{t}BuMeNH-$^+$		85
7-$C_6H_{11}Me_2N$-$^+$		85
7-Me-8-EtO-9-Ph_3PMeCH-$^+$		200

***nido*-7-$CB_{10}H_{13}^-$:** Reported procedures for syntheses of *nido*-7-$CB_{10}H_{13}^-$ and derivatives are listed in Table 12. B-Chlorination, B-bromination, and B-iodination of the zwitterion 7-Me_3N-7-$CB_{10}H_{12}$ have been reported.[201,202] Derivatives containing B–S bonds were also made from 7-Ph-7-$CB_{10}H_{12}^-$ and 7-Me_3N-7-$CB_{10}H_{12}$.[93,203,204] Several structures were determined experimentally and are summarized in Table 13.

***nido*-7,8-$C_2B_9H_{13}$:** The parent *nido*-7,8-$C_2B_9H_{13}$ was made in 70% yield from deboronation of *ortho*-carborane followed by acidification with H_3PO_4.[208] Acidification of 7-C_6H_{11}-7,8-$C_2B_9H_{11}^-$, 7,8-$(PhCH_2)_2$-7,8-$C_2B_9H_{10}^-$, and 1,2,4,5,6,9,10,11-Me_8-7,8-$C_2B_9H_4^-$ gave 7-C_6H_{11}-7,8-$C_2B_9H_{12}$, 7,8-$(PhCH_2)_2$-7,8-$C_2B_9H_{11}$, and 1,2,4,5,6,9,10,11-Me_8-7,8-$C_2B_9H_5$, respectively.[187,219,243]

***nido*-2,7-$C_2B_9H_{12}^-$:** Compound 11-Me-2,7-$C_2B_9H_{11}^-$ was observed in the reaction mixture of 11-Me-2,7-$C_2B_9H_{12}$ and aqueous cesium hydroxide.[59]

***nido*-2,7-$C_2B_9H_{13}$:** Compound 11-Me-2,7-$C_2B_9H_{12}$ was isolated on a multigram scale from the double deprotonation of 7,8-$C_2B_9H_{13}$ with BuLi followed by MeI and then acidification.[59]

***nido*-2,8-$C_2B_9H_{13}$:** 7-Me-2,8-$C_2B_9H_{12}$ was made from the deprotonation of 7,9-$C_2B_9H_{12}^-$ with BuLi followed by MeI and then acid.[59]

***nido*-7,8-$C_2B_9H_{12}^-$:** This anion and many derivatives are generally formed from the deboronation reactions of 1,2-$C_2B_{10}H_{12}$ and derivatives (COMC (1982) 5.4.2.6.6 and COMC (1995) 6.2.4.6). Deboronating reagents used include KOH in MeOH[209–219] or EtOH,[220–242] KOEt,[243] piperidine,[237,238,244–249] pyrrolidine,[210,242,250–252] pyridine,[253,254] ^{i}Pr_2NEt,[255] wet Bu_4NF,[210,234,239,256–265] KF,[209,266] CsF,[267] $HNP(NMe_2)_3$,[268] K_2CO_3,[252] $NaHCO_3$,[269] NaOCN,[270] NaOPh,[271] N_2H_4,[234,272] NH_4OH,[273] wet dimethylsulfoxide (DMSO),[274,275] wet hexamethylphosphoramide (HMPA),[275] wet DMF,[275] $Me_3NH{\cdot}HF_2$,[264] $PhCH_2NMe_3F$,[264] K,[218] Na,[219] $K(NC_4H_4)$,[276] $HNMe_2$,[277] Et_3N,[265] Me_2NCOCl,[274] water,[278] $MeCO_2H$,[279,280] H_2O_2,[281] EtOH,[282,283] and MeOH.[278,284]

There are other routes to *nido*-7,8-$C_2B_9H_{12}^-$ and derivatives. Decaborane, $B_{10}H_{14}$, with HCHO, MeCOCCH, or MeOCOCCH under basic conditions gives 7,8-$C_2B_9H_{12}^-$, 7-MeCO-7,8-$C_2B_9H_{11}^-$, or 7-MeOCO-7,8-$C_2B_9H_{11}^-$, respectively (Figure 2).[78,91] The parent anion 7,8-$C_2B_9H_{12}^-$ can also be generated from 6-$CB_9H_{14}^-$ with KOH and HCHO or from 7,9-$C_2B_{10}H_{13}^-$ with H_2O_2 in high yields.[91,285] The anion 9-Me-7,8-$C_2B_9H_{11}^-$ is formed from deprotonation of 11-Me-2,7-$C_2B_9H_{12}$.[59] The dimethylsulfide adduct, 9-Me_2S-7,8-$C_2B_9H_{11}$, is made from 7,9-

Table 14 Structures of *nido*-7,8-$C_2B_9H_{12}^-$ derivatives determined experimentally by X-ray crystallography unless stated otherwise with C(7)–C(8) bond lengths listed where possible

7,8-$C_2B_9H_{12}^-$ and derivatives	*Cation/anion*	*C7–C8 bond length, solvate*
	K^+	1.5576(15)[249]
	$(Me_2N)_3PNH_2^+$	1.555(2)[268]
	PSH^+	1.564(3)[295]
	$0.5((Me_2N)_3PNH)_2((Me_2N)_3PNH_2)_2B_2O^{2+}$	1.580(7)[268]
	PSH^+	1.570(4)[295] (neutron diffraction)
7-Me_2NCH_2-	Me_4N^+	1.53(2)[215]
7-$MeOCH_2$-	$PhCH_2NMe_3^+$	1.544(8)[230]
7-MeCO-	PPN^+	1.570(4)[78]
7-$C_6H_4(CO)_2N(CH_2)_2$-	Bu_4N^+	1.561(3)[234]
7-$O_2CC_6H_4(CO)NH(CH_2)_2$-$^-$	$2Me_3NH^+$	1.568(3)[234]
7,8-$(HOCH_2CH_2)_2$-	$K(18C6)^+$	1.585(3)[218]
7,8-$(MeOCH_2CH_2)_2$-	Me_3NH^+	1.574(3)[218]
7,8-$[(O_2C_{12}H_8)_2N_3P_3OCH_2]_2$-	Et_3NH^+	1.569(3)[265]
7-$(O_2C_{12}H_8)_2N_3P_3(O^-)OCH_2$-8-$EtOCH_2$-	$2Et_3NH^+$	1.585(10)[265]
7,8-Ph_2-	$PhCH_2NMe_3^+$	1.602(3)[296]
7,8-Ph_2-	Et_3NH^+	1.590(5)[296]
7-PhCC-8-Ph-	Ph_4P^+	1.600(7), 1.582(7)[297]
7-PhCC-8-Ph-	Bu_4N^+	1.608(15)[298]
7,8-$(Ph_2P)_2$-	Me_4N^+	1.61(2) EtOH[248]
7-$H_3B^iPr_2P$-8-Me-	Bu_4N^+	1.592(3), 1.594(3)[299]
7-$Ph_2P(=O)$-8-Ph-	Bu_4N^+	1.592(11)[246]
7-Ph_2P-8-^iPrS-	Me_4N^+	1.607(4)[226]
7-$(C_5H_5NCH_2^+)$-		1.562(2)[253]
7-$H_3N^+(CH_2)_3$-		1.569(2)[234]
7,8-$(C_5H_5NCH_2^+)_2$-	$CF_3SO_3^-$	1.592(3)[253]
7-$^iPr_2PH^+$-8-Me-		1.598(2)[246]
7,8-PPh_2O-H-OPh_2P^+-		1.609(5)[281]
7,7′-(1,4-$C_6H_4NMeCONMe$-1,4-C_6H_4)-	Bu_4N^+	Not determined[260]
B-substituted derivatives		
1,2,4,5,6,9,10,11-Me_8-	PPN^+	1.522(11)[243]
3-Et-7,8-Ph_2-	Et_3NH^+	1.602(3)[231]
3-I-	Me_3NH^+	1.555(13)[227]
9-I-	Me_3NH^+	1.540(16), 1.57(3)[294]
5-I-7,8-Ph_2-	$PhCH_2NMe_3^+$	1.609(10)[231]
9,11-I_2-	Me_3NH^+	1.547(6)[294]
10-$(C_4H_8O)^+$-7,8-$(PhCH_2)_2$-		1.583(5)[219]
10-Me_2S^+-		1.547(4)[289]
10-$(CH_2)_4S^+$-		1.546(5)[289]
11-Me_2S^+-7-Ph-		1.557(11)[290]
10-Me_2S^+-7,8-Ph_2-		1.609(8)[291]

$C_2B_{10}H_{13}^-$ with Me_2S and $FeCl_3$ in 71% yield.[285] Structures of *nido*-7,8-$C_2B_9H_{12}^-$ and derivatives determined experimentally are listed in Table 14.

9-Alkyl derivatives are made from the reaction of 7,8-$C_2B_9H_{12}^-$ with sodium followed by an alkyl halide[286,287] or by formaldehyde with dialkylsulfides and acid.[288] The dialkylsulfide adducts, 10-R_2S-7,8-$C_2B_9H_{11}$, were formed from the corresponding 7,8-$C_2B_9H_{12}^-$ derivative with R_2S, acid, and MeCHO.[288–291] 9-Chloro, bromo, and iodo derivatives were obtained from the reaction of the anion with halosuccinimides, bromine, iodine, or sodium iodide.[242,292–294] The anion 10-HO-7,8-$C_2B_9H_{11}^-$ and the zwitterion 10-Et_2O-7,8-$C_2B_9H_{11}$ were made in 47% and 22% yields, respectively, from 7,8-$C_2B_9H_{12}^-$ with acid and MeCHO.[288]

***nido*-7,9-$C_2B_9H_{12}^-$:** This anion and many derivatives are generally formed by deboronation reactions of 1,7-$C_2B_{10}H_{12}$ and derivatives but reaction conditions required are more severe than for deboronation of 1,2-$C_2B_{10}H_{12}$ and derivatives (COMC (1982) 5.4.2.6.6 and COMC (1995) 6.2.4.6). Deboronating agents used have included piperidine,[52,259] KOH in EtOH,[52,259,302] BuOH[300] or Et_2O,[212] wet Bu_4NF,[250,257–259,263,264,301,302] and CsF.[267]

Table 15 Synthetic routes to *nido*-7,8,10-$C_3B_8H_{11}^-$ derivatives

7,8,10-$C_3B_8H_{11}^-$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	7,8,9-$C_3B_8H_{11}^-$	350 °C, 65%[102,104]
7-Me-	7-Me-2,7,10-$C_3B_8H_{11}$, PS	CH_2Cl_2, 98%[106]
7-Me-	6-Me-5,6,9-$C_3B_7H_9^-$, Me_2SBH_2Br	CH_2Cl_2, 61%[105]
7-$PhCH_2$-	6-$PhCH_2$-5,6,9-$C_3B_7H_9^-$, Me_2SBH_2Br	CH_2Cl_2, 56%[105]
7-$PhCH_2$-	7-$PhCH_2$-2,7,10-$C_3B_8H_{11}$, PS	CH_2Cl_2, 97%[106]
10-Me_3N-$^+$	7-Me_3N-7,8,9-$C_3B_8H_{10}$	350 °C, 97%[102,104]

Table 16 Synthetic routes to *nido*-7,8,9-$C_3B_8H_{11}^-$ derivatives

nido-*7,8,9-$C_3B_8H_{11}^-$ derivatives*	*Starting materials*	*Solvent, temp, yield*
7-H_2N-	5,6-$C_2B_8H_{12}$, NaCN	Hexane, H_2O, 30%[101,103]
7-^{t}BuMeHN-$^+$	5,6-$C_2B_8H_{12}$, NaH, ^{t}BuNC, Me_2SO_4	DME, 47%[103]
7-^{t}BuH_2N-$^+$	5,6-$C_2B_8H_{12}$, ^{t}BuNC	Benzene, 15%[103]
7-Me_3N-$^+$	5,6-$C_2B_8H_{12}$, NaCN, NaOH, Me_2SO_4	Hexane, H_2O, 27%[101,103]
7-^{t}BuH_2N-$^+$	5,6-$C_2B_8H_{12}$, NaH, ^{t}BuNC, HCl	THF, DME, 53%[101,103]
7-^{t}BuH_2N-$^+$	5,6-$C_2B_8H_{12}$, NaH, ^{t}BuNC, HCl	Et_2O, CH_2Cl_2, MeCN, 90%[308]

The 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$ anion was made by thermal cage rearrangement of 7,8-Ph_2-7,8-$C_2B_9H_{10}^-$ anion at 300–350 °C.[257,302] The anions 10-F-7,9-(4-FC_6H_4)$_2$-7,9-$C_2B_9H_{10}^-$ and B-Me-7,9-$C_2B_9H_{10}^-$ were produced from their corresponding *closo*-2,3-$C_2B_9H_{11}$ derivatives with $NaBH_4$.[59] The anion, 8-$HCCCH_2$-7,9-$C_2B_9H_{11}^-$, resulted in 90% yield from the cage rearrangement of 7,8-$C_2B_9H_{12}^-$ with Na and $HCCCH_2Br$.[286] Methylation at the 10 position of the 7,9-$C_2B_9H_{12}^-$ anion was achieved with butyllithium and methyl iodide.[59]

The molecular structures of the salts PSH^+7,9-$C_2B_9H_{12}^-$, Bu_4N^+10-HO-7,9-Ph_2-7,9-$C_2B_9H_9^-$, and Et_3NH^+3-EtO-7,9-Ph_2-7,9-$C_2B_9H_9^-$ were determined by X-ray diffraction studies.[52,302]

***nido*-2,9-$C_2B_9H_{13}$:** This carborane (COMC (1995) 6.2.4.6) was synthesized in 45% yield from 1,12-$C_2B_{10}H_{12}$ with KOH in refluxing toluene and tetraglyme followed by acid.[52] Its molecular structure was determined by gas-phase electron diffraction.[303]

***nido*-2,9-$C_2B_9H_{12}^-$:** The molecular structure of the anion as its PSH^+ salt was determined by X-ray crystallography.[52]

***nido*-7,8-$C_2B_9H_{11}^{2-}$:** The dianion was formed from $C_2B_9H_{13}$ or [Me_3NH]7,8-$C_2B_9H_{12}$ with BuLi, NaH, or KH.[73,208,304–306] The anions of type 9-L-7,8-$C_2B_9H_{10}^-$ were also obtained by deprotonation of the adducts 9-L-7,8-$C_2B_9H_{11}$ (L=Me_2S, Me_3N, and C_5H_5N).[306] The salts $Na_2(THF)_3^{2+}$7,8-$C_2B_9H_{11}^{2-}$, 2Li$(THF)_2^+$ 7,8-$C_2B_9H_{11}^{2-}$, 9-Me_2S-7,8-$C_2B_9H_{10}^-$ $Li_2(THF)_4^+$, 9-Me_2S-7,8-$C_2B_9H_{10}^-$Na$(THF)_2^+$, 9-Me_3N-7,8-$C_2B_9H_{10}^-$Na$(THF)_2^+$, and 9-C_5H_5N-7,8-$C_2B_9H_{10}^-$Na$(THF)_2^+$ were structurally determined by X-ray crystallography.[306]

***nido*-7,9-$C_2B_9H_{11}^{2-}$:** The dianion was made from [Me_3NH]7,9-$C_2B_9H_{12}$ with BuLi.[73]

***nido*-2,9-$C_2B_9H_{11}^{2-}$:** The carborane 2,9-$C_2B_9H_{13}$ with BuLi produced the salt $Li_2$2,9-$C_2B_9H_{11}$.[73]

***nido*-2,7,10-$C_3B_8H_{12}$:** Protonation of 7-$PhCH_2$-7,8,10-$C_3B_8H_{10}^-$ and 7-Me-7,8,10-$C_3B_8H_{10}^-$ gave 2-$PhCH_2$-2,7,10-$C_3B_8H_{11}$ and 2-Me-2,7,10-$C_3B_8H_{11}$, respectively, via cage rearrangements (Figure 7).[106]

***nido*-7,8,9-$C_3B_8H_{12}$:** The reaction of 7-Me_3N-7,8,9-$C_3B_8H_{10}$ with Na and then CF_3CO_2H gave *nido*-7,8,9-$C_3B_8H_{12}$ in 60% yield.[101]

***nido*-7,8,9-$C_3B_8H_{11}^-$:** Table 16 lists the routes to *nido*-7,8,9-$C_3B_8H_{11}^-$ derivatives. The reaction of 7-^{t}BuH_2N-7,8,9-$C_3B_8H_{10}$ with NaH and MeI in DME gave the B-methyl derivatives 10-Me-7-^{t}BuMe_2N-7,8,9-$C_3B_8H_9$ and 10,11-Me-7-^{t}BuMe_2N-7,8,9-$C_3B_8H_8$ in low yields.[104] The salt PSH^+ 8-^{t}BuNH-7,8,9-$C_3B_8H_{10}^-$ and the zwitterion 7-^{t}BuNHMe-7,8,9-$C_3B_8H_{10}$ were characterized by X-ray crystallography.[103,307]

***nido*-7,8,10-$C_3B_8H_{11}^-$:** The synthetic procedures for *nido*-7,8,10-$C_3B_8H_{11}^-$ and derivatives are listed in Table 15 (Figure 7). Two structures were determined by X-ray crystallography, the salt PPN^+7-$PhCH_2$-7,8,10-$C_3B_8H_{10}^-$ and the zwitterion 10-Me_3N-7,8,10-$C_3B_8H_{10}$.[102,104,105]

3.02.10 Deboronating Agents for Icosahedral Carboranes

Cage-deboronation (also labeled degradation, deboration, decapitation) reactions of *ortho*-carborane (1,2-$C_2B_{10}H_{12}$) and derivatives continue to use alcoholic potassium hydroxide in many cases (COMC (1982) 5.4.2.6.6 and COMC (1995) 6.2.4.6). Amines such as piperidine, pyrrolidine, and pyridine are alternative, sometimes more suitable, deboronating agents. Piperidine, for example, is much less likely to cleave C–P bonds in the deboronation of carboranes containing a cage C–P bond than alcoholic KOH.[248] An adduct from the reaction of *ortho*-carborane with $(Me_2N)_3P{=}NH$ was structurally characterized and appears to represent the first stage of the deboronation process.[268]

A new deboronating agent for icosahedral carboranes, "dry" tetrabutylammonium fluoride (TBAF), was found to degrade some small carboranes, *ortho*- and *meta*-carborane(COMC (1995) 6.2.4.6).[55] As it was clear that water plays a part in the process, this reagent in its wet form was used to deboronate a large number of *meta*-carborane derivatives.[257–259,264] Wet TBAF proved to be superior to alcoholic potassium hydroxide for effective deboronation of *meta*-carboranes as the latter method requires more forcing conditions for complete conversion and gives alkoxy carborane anions as side products.[52,300,302]

Ortho-carboranes are particularly susceptible to deboronation if the substituents at the cage carbons are strongly electron-withdrawing. If the substituent contains an amino group, it can self-degrade.[278,284] There are now many examples of facile cage deboronation of such compounds with DMSO,[275] methanol,[284] water,[278] and acids.[280]

3.02.11 Derivatization of Icosahedral Carboranes

This area has been very active as might be expected given the commercial availability of the parent icosahedral carboranes. Monosubstitution of the dicarbaboranes via the usual metallation route can be problematic, with disubstituted carboranes often present as side products (COMC (1982) 5.4.2.7.5). An elegant route for the synthesis of monoalkyl-*ortho*-carboranes involves the use of a bulky silyl group, ^{t}BuMe$_2$Si-, as a protecting group.[309–311] The protecting group is easily removed with TBAF. This method has been used very successfully in the formation of carboracycles where two or more cages form rings with -CH_2RCH_2- links.[312–314] High yield synthesis of the *ortho*-carborane monothiol, 1-HS-1,2-$C_2B_{10}H_{11}$, was achieved using dimethoxyethane as the solvent[315] whereas a high yield procedure for the preparation of 1-Me_3Si-1,2-$C_2B_9H_{11}$ employs high dilution conditions.[316] The general syntheses of 1-aryl-*ortho*-carboranes from *ortho*-carborane do not give diaryl products.[317]

While C–C bond formation via metallation and alkyl or aryl halides is well known (COMC (1982) 5.4.2.7.5), the C–C bond formation with TBAF and aldehyde, enones, or enals is new (Figure 9).[318] Carboranyl groups can actually be used as protecting groups for aldehydes and ketones due to the facile cleavage of the cage C–C(OH) bond with

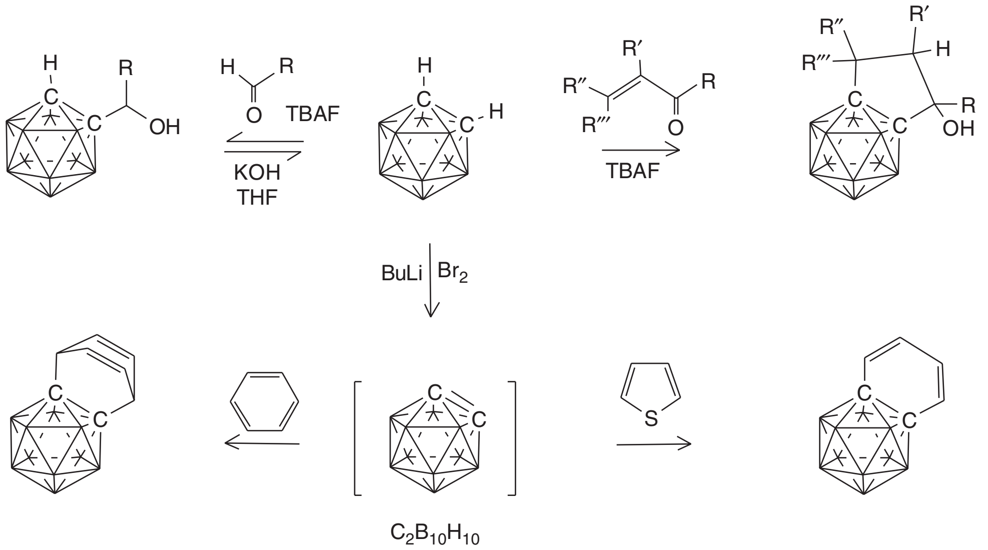


Figure 9 Alternative C–C bond formation in *ortho*-carboranes.

base.[319] Reaction of *ortho*-carborane with BuLi and Br_2 gives the 1,2-dehydro-*ortho*-carborane as an intermediate *in situ*. This benzyne-like carborane reacts with thiophenes, aromatics, alkynes, and dienes to form carboranes with unsaturated substituents at the cage carbons.[320,321]

3.02.12 Icosahedral Carboranes in Detail

3.02.12.1 $CB_{11}H_{12}^-$ and Derivatives

Interest in these compounds—mainly for use as weakly coordinating anions—has grown rapidly in the last decade. Many synthetic routes to $CB_{11}H_{12}^-$ and its derivatives are shown in Table 17 (Figures 4 and 5). The structures of $CB_{11}H_{12}^-$ and its derivatives determined experimentally are summarized in Table 18. The table shows one column for cations where the anions are regarded as discrete entities within the crystal lattice and the other for cations where the anions are viewed as a fragment of a molecule or polymer in the solid state.

The C–H bond in $CB_{11}H_{12}^-$ and related anions can be metallated by butyllithium and then converted into C-substituted anions with aldehydes, alkyl halides, Ph_3SiCl, and Ph_2PCl.[322–329] C-halogenated (F,Cl,Br, or I) derivatives are made from the C-copper derivative with $(PhSO_2)_2NF$ or the corresponding N-halosuccinimide.[330] The 1-Me-2,3,4,5,6,7,8,9,10,11,12-F_{11}-CB_{11}^- anion is made from the reaction of the corresponding F_{11} anion with

Table 17 Synthetic routes to *closo*-$CB_{11}H_{12}^-$ derivatives

$CB_{11}H_{12}^-$ and derivatives	*Starting materials*	*Solvent, temp, yield*
	6-$CB_9H_{14}^-$, $BH_3\cdot SMe_2$	$C_2H_4Cl_2$, heat 4 d, 89%[88]
	$B_{11}H_{14}^-$, NaH, $CHCl_3$, EtOH	THF, 42%[82]
	$B_{11}H_{14}^-$, CCl_3COONa	H_2O, 12%[82]
	$B_{11}H_{14}^-$, NaH, $CHBr_3$, EtOH	THF, 11%[82]
1-$H_3B\cdot H_2N$-	7-$H_3B\cdot H_2N$-7-$CB_{10}H_{12}$, $BH_3\cdot NEt_3$	200 °C 6 h, 60%[350]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$, $BH_3\cdot SMe_2$	$C_2H_4Cl_2$, heat, 92%[93]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$, $BH_3\cdot NEt_3$	210 °C, 50%[93,351]
1-Ph-	6-Ph-6-$CB_9H_{11}^-$, $BH_3\cdot THF$	THF, heat 2 d, 5%[158]
1-Ph-	$B_{11}H_{14}^-$, NaH, $PhCHCl_2$, EtOH	THF, 27%[83]
1-(4-FC_6H_4)-	$B_{11}H_{14}^-$, NaH, (4-FC_6H_4)$CHCl_2$, EtOH	THF, 29%[83]
1-(4-ClC_6H_4)-	$B_{11}H_{14}^-$, NaH, (4-ClC_6H_4)$CHCl_2$	THF, 50 °C 3 d, 43%[83]
1-(4-BrC_6H_4)-	$B_{11}H_{14}^-$, NaH, (4-BrC_6H_4)$CHCl_2$	THF, 40 °C 18 h, 30%[83]
1-(4-BrC_6H_4)-	6-(4-BrC_6H_4)-6-$CB_9H_{11}^-$, $BH_3\cdot SMe_2$	[93]
1-(4-IC_6H_4)-	$B_{11}H_{14}^-$, NaH, (4-IC_6H_4)$CHCl_2$	THF, 50 °C 3 d, 12%[83]
1-(4-PhC_6H_4)-	$B_{11}H_{14}^-$, NaH, (4-PhC_6H_4)$CHCl_2$	THF, 50 °C 1.5 d, 41%[83]
1-Me_2NH^+-	6-Me_3N-6-CB_9H_{11}, $BH_3\cdot NEt_3$	210 °C 8 h, 61%[352]
B-substituted derivatives		
2-Me_3N^+	$HNMe_3{}^+B_{11}H_{14}^-$, BuLi, $CHCl_3$	THF, 19%[82]
2-Ph-	7-$CB_{10}H_{13}^-$, BuLi, $PhBCl_2$	THF, 25%[353]
2-(4-MeC_6H_4)-	7-$CB_{10}H_{13}^-$, BuLi, 4-$MeC_6H_4BCl_2$	THF[353]
2-F-	7-$CB_{10}H_{13}^-$, BuLi, $BF_3\cdot Et_2O$	THF, 67%[353]
2-Cl-	$B_{11}H_{14}^-$, NaH, $CHCl_3$, EtOH	THF, 2%[82]
2-Br-	$B_{11}H_{14}^-$, NaH, $CHBr_3$, EtOH	THF, 29%[82]
2-EtO-	$B_{11}H_{14}^-$, NaH, $CHCl_3$, EtOH	THF, 4%[82]
2-Me_3N^+-	7-$CB_{10}H_{13}^-$, BuLi, Me_2NBCl_2, Me_2SO_4	THF, 36%[353]
2-$^iPr_2NH^+$-	7-$CB_{10}H_{13}^-$, BuLi, $^iPr_2NBCl_2$, Me_2SO_4	THF[204]
2-$Cl(CH_2)_4O$-	7-$CB_{10}H_{13}^-$, BuLi, $Me_2S\cdot BCl_3$,THF	THF, 37%[353]
1-Me_3N^+-2-Ph-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, $PhBCl_2$	THF[204]
1-Me_3N^+-2-F-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, $BF_3\cdot OEt_2$	THF[204]
1-Me_3N^+-2-$Cl(CH_2)_4O$-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, BCl_3	THF[204]
1-Me_3N^+-2-$Br(CH_2)_4O$-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, BBr_3	THF[204]
1-Me_2N-2-$CH_2NH^iPr_2{}^+$-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, $^iPr_2NBCl_2$	THF, 19%[354]
1-Me_2NH^+-2-CH_2Cl-	7-Me_3N-7-$CB_{10}H_{12}$, BuLi, Me_2NBCl_2	THF, 26%[354]
1,2-Ph_2-	7-Ph-7-$CB_{10}H_{12}^-$, BuLi, $PhBCl_2$	THF, 78%[93]
1-(4-MeC_6H_4)-2-Ph-	7-(4-MeC_6H_4)-7-$CB_{10}H_{12}^-$, BuLi, $PhBCl_2$	THF, 73%[93]
1-Me_3N-2-Ph-8-Br-$^+$	4-Br-7-Me_3N-7-$CB_{10}H_{11}$, BuLi, $PhBCl_2$	THF[201]
1-Me_3N-2-Ph-8-I-$^+$	4-I-7-Me_3N-7-$CB_{10}H_{11}$, BuLi, $PhBCl_2$	THF, 57%[201]

Table 18 Structures of *closo*-$CB_{11}H_{12}^-$ derivatives determined experimentally

$CB_{11}H_{12}^-$ *and derivatives*	*Cation* M^+ (***solvate, solvate-carborane C-H···X interaction***)	*Fragment* M^+ *in molecule or polymer* (***M-carborane interactions, solvate, solvate-carborane C-H···X interaction***)
	1-Et-3-Me-IM[355], 1-Et-2,3-Me_2-IM[355], $(C_8H_{12})Rh(THF)_2$[356], $(Ph_3P)_4Rh_2H_3Cl_2$ (***$2CH_2Cl_2$***)[357], $((^tBu_2PCH_2)_2CH_2)PtMe$[358], $(CTV)_2Ag(OH_2)$ (***2MeCN,H_2O***)[359], (HDH)Na (***CTV,3$CHCl_3$, 2C-H···Cl^-***)[360], (HDH)K (***3(TTT)Ni***)[361], (HDH)K (***3(TTT)Ni***)[361], $(CTV)_2Rb_2(OH_2)^+$ (***2DMF***)[362], $(CTV)_2K_2(OH_2)OH$ (***2DMF***)[362], $(CTV)_2Na(OH_2)_2$ (***2DMF,H_2O***)[362], $(CTV)_2Na(OH_2)_2$ (***2CF_3CH_2OH,H_2O***)[362], $(CTV)_2Cs(OH_2)_2$, (***2DMF,H_2O***)[362]	$PhCH_2Zr(C_5H_5)_2$ (***Zr-H***)[363], $MeZr(C_5H_4Me)_2$ (***Zr-H***)[363], $Me_2Zr(C_5Me_5)$ (***3Zr-H***)[363], $(C_8H_{12})Rh$ (***2Rh-H***)[356], Ph_3PAg (***3Ag-H, 3Ag-B***)[364,365], $(Ph_3P)_2Ag$ (***Ag-H***)[365], $(C_5H_5)Mo(CO)_3I\cdot Ag$ (***2Ag-H***)[366,367], $(Ph_3P)_2Rh$ (***2Rh-H, 2Rh-B***)[357], $(Cx_2P)_2Rh$ (***2Rh-H***)[368], $(C_5H_5)Mo(CO)_3$ (***Mo-H***)[367], $(C_5Me_5)Mo(CO)_3$ (***Mo-H***)[367], $Ag(MeCN)_2$ (3***Ag-H***)[369], $Ag(NCCH_2CN)_2$ (***Ag-H***)[369], $Ag_4(NC(CH_2)_2CN)_5^{3+}$ (***Ag-H***)[369]
1-Me-	1-Et-3-Me-IM[355], Ag (***C_6H_6***)[327]	
1-Et-	1-Et-3-Me-IM[355]	
1-Ph-	Et_4N (***CH_2Cl_2***)[92,93,370]	
1-(4-FC_6H_4)-	PPN[83]	
1-(4-BrC_6H_4)-	Et_4N[93]	
1-Me_2N-	Me_4N[371]	
B-substituted derivatives		
2-Br-	PPN[82]	
2-$Cl(CH_2)_4O$-	Ph_4P[353]	
12-$OC_4H_8O^+$-[347]		
12-F-		$Ag(C_6H_6)_2$ (***Ag-H,Ag-B***)[334]
12-Cl-	$((Ph_2P)_2C_2H_4)_2Pd^+$ (***3CH_2Cl_2***)[372]	
12-Br-	Cs[324], Ag (***C_6H_6***)[373]	$(C_5H_5)Mo(CO)_3$ (***Ag-Br***)[374], $(C_5H_5)Mo(CO)_3I\cdot Ag$ (***Ag-Br, CH_2Cl_2***)[374]
1,2-Ph_2	Et_4N[93]	
1-(4-MeC_6H_4)-2-Ph	Et_4N[93]	
1-Me_2N-2-$^iPr_2NHCH_2^+$[354]		
1-Me_2NH-2-$ClCH_2^+$[375]		
1-Ph-7-SMe	Et_4N[93]	
1,12-Ph_2	Et_4N[93,158]	
1-[4-(4′-$MeC_6H_4C_6H_4$)]-12-(4-MeC_6H_4)	Et_4N[93,176]	
1-Ph-12-(MeCH=CH)-	Et_4N[93]	
1-Ph-12-SMe_2-$^+$[93]		
1-Ph-12-$MeS(CH_2)_4OH$-$^+$[93]		
1-Ph-12-(MeCH=CH)-	Et_4N[93]	
1-$C_5H_{11}C((CH_2)_2)_3N^+$-12-I-[376]		
7,8,9,10,11,12-F_6-	Cation unknown[377]	
7,8,9,10,11,12-Cl_6-	Cs[88], (TPP)Fe(PhMe) (***2PhMe***)[378], $(TPP)Fe(OH_2)$ (***H_2O***)[379], $(TPP)_2Fe(OH)$ (***PhMe***)[380], 1-Et-3-Me-IM (2***C-H···Cl***)[355], 1-C_8H_{15}-3-Me-IM[355], 1-Et-2,3-Me_2-IM[355], 1-^nBu-2,3-Me_2-IM[355], Et_2OH (***Et_2O, C-H···Cl***)[381], Ph_2COH (***Ph_2CO***)[381], $PhNO_2H$ (***$PhNO_2$***)[381], Et_2OH (***H_2O***)[381], $^iPr_3Si$[382]	Et_2Al (***2Al-Cl, C-H···Cl***)[383], Ag(1,4-$Me_2C_6H_4$) (***2Ag-Cl***)[384], $(CTV)Na(OH_2)$ (***Na-Cl, CF_3CH_2OH, C-H***···π)[385], $(CTV)K(0.5CF_3CH_2OH)$ (***K-Cl***)[385], (CTV)Cs(MeCN) (***2Cs-Cl***)[385]
7,8,9,10,11,12-Br_6-	Cs[88], MeC_6H_6 (***PhMe, C-H···Br***)[386], 1,4-$Me_2C_6H_5$ (***1,4-$Me_2C_6H_4$***)[386], $MesH_2$ (***1,2-$Cl_2C_6H_4$***)[386], Me_6C_6H (***C-H···Br***)[386], H_3O (***3H_2O***)[387], C_4H_8OH (***THF, 2C-H···Br***)[381], Et_3Si[388], $^iPr_3Si$[388,389], $^tBu_3Si$[388], $^tBu_2SiMe$[388],	

(*Continued*)

Table 18 (Continued)

$CB_{11}H_{12}^{-}$ and derivatives	*Cation M^+* ***(solvate, solvate-carborane C-H···X interaction)***	*Fragment M^+ in molecule or polymer* ***(M-carborane interactions, solvate, solvate-carborane C-H···X interaction)***
	${}^{t}Bu_3Si(OH_2)$[390], Et_2Alpy_2 (***0.5C_6H_6,C-H···Br***)[391], ${}^{t}BuC{=}C(SiMe_2CH_2)_2CH_2$[392], 1-Et-3-Me-IM[355], (TPP)Fe(C_6H_6) (***3.5C_6H_6***)[378], $(C_6H_8)Rh(PPh_3)_2$ (***2CH_2Cl_2***)[368], $(Ph_3P)_4Rh_2^{+}$ (***2.78CH_2Cl_2,C-H···Br***)[357], $(C_5H_5)Mo(CO)_3(OH_2)$ (***C-H···Br***)[374,393], $(Ph_3P)_2Ir(C_2H_4)_3$ (***4$CHCl_3$***)[393], $(C_5Me_5)_3Rh_3Cl_4^{+}$ (***3CH_2Cl_2 3C-H···Br***)[394], $(1,3\text{-}TMS_2C_5H_3)_2Sm(THF)_2$ (***THF***)[395], $(1,3\text{-}TMS_2C_5H_3)_2Er(THF)_2$ (***1.25PhMe***)[395], $(CTV)Na_2(OH_2)_2(DMF)_4^{+}$ (0.5DMF, CTV, 2C-H···***Br***)[362]	Et_2Al (***2Al-Br***)[391], $Tl_2(PhMe)_2$ (***2Tl-Br, 2C-H···Br***)[396], (TPP)Fe (***Fe-Br, C-H···Br***)[379],Ag (***2Ag-Br, C-H···Br***)[384], Ph_3PAg (***3Ag-Br, 2C-H···Br***)[364,365], $(C_5H_5)Mo(CO)_3I.Ag$ (***2Ag-Br***)[367], $(Ph_3P)_2Ir$ (***2Ir-Br, PhF, C-H···Br***)[393], $(CTV)Na(OH_2)$ (***Na-Br, CF_3CH_2OH, C-H···π***)[385], $(CTV)Rb(OH_2)$ (***2Rb-Br***)[385], (CTV)Cs(MeCN) (***2Cs-Br***)[385]
7,8,9,10,11,12-I_6-	${}^{i}Pr_3Si$[382]	Ag (***2Ag-I, C_6H_6***)[384]
1-Ph-7,8,9,10,12-Br_5-	Et_4N[93]	
1-Ph-7,8,9,10,12-I_5-	Et_4N[93]	
1-Me-7,8,9,10,11,12-Cl_6-	Ag (MesH)[327]	
1-Me-7,8,9,10,11,12-Br_6-	Ag[327]	
1-Me-7,8,9,10,11,12-I_6-	Ag[327]	
1-Ph-7,8,9,10,11,12-I_6-	Et_4N[93]	
1-Ph-7,8,9,10,11-$(4\text{-}C_6H_4)_5$-12-I-	Et_4N[93]	
1-Me-2,3,4,5,7,8,9,10,11,12-Br_{10}-		$Ag(1,4\text{-}Me_2C_6H_4)$ (***4Ag-Br***)[328]
2,3,4,5,6,7,8,9,10,11,12-Me_{11}-	Ph_3C[374], Ph_3PAg[397], $(3,5\text{-}Me_2C_6H_3)_3PAg$[343], $Ph_3PAg(OEt_2)_2$[343], $(Ph_3P)_2Ag$[343], $(C_5H_5)_2Mo_2(CO)_6Cl$[374], $[(C_5H_5)Mo(CO)_3I.Ag]_6^{+}$[374], $({}^{i}Pr_3P)_6Rh_6H_{12}$[398], $({}^{i}Pr_2P)_2PtMe$[399]	Ag (***6Ag-H***)[343], Cx_3PAg (***3Ag-H***)[343], $MeZr(C_5H_5)_2$ (***Zr-H***, C_6H_5F)[400]
2,3,4,5,6,7,8,9,10,11,12-Cl_{11}-		$Ag(1,4\text{-}Me_2C_6H_4)_2$ (***2Ag-Cl, 0.5 1,4-$Me_2C_6H_4$, C-H···π***)[401]
2,3,4,5,6,7,8,9,10,11,12-Br_{11}-	Cs[328], H_7O_3[185]	Ag(MeCN)(MesH) (***2Ag-Br***)
2,3,4,5,6,7,8,9,10,11,12-I_{11}-	H_3O (Et_2O)[185]	
2,3,4,5,6-Me_5-7,8,9,10,11,12-Cl_6-	Cs[344],${}^{t}Bu$ (***CH_2Cl_2***)[402]	
2,3,4,5,6-Me_5-7,8,9,10,11,12-Br_6-	Cs[344],${}^{t}C_5H_{11}$ (***CH_2Cl_2***)[402], *c*MeC_5H_8[402], C_6H_7[344,386], Mes_3Si[403]	${}^{i}Pr$ (***C-Br***)[404]
2,3,4,5,6-Me_5-7,8,9,10,11,12-I_6-	Cs[344]	
2,3,4,5,6-$(HO)_5$-7,8,9,10,11,12-Br_6-	Ph_3PMe ($3H_2O$)[345], Ph_3PMe, H_7O_3 (***3H_2O***)[345]	
2,3,4,5,6-Cl_5-7,8,9,10,11,12-Br_6-	Me_3NH (***Me_3N,HCl,H_2O***)[401], H_3O (DMF)[185]	Ag(MesH) (***2Ag-Br, MesH, C-H···π***)[401]
2,3,4,5,6-Br_5-7,8,9,10,11,12-Cl_6-	H_3O (H_2O)[185]	Ag(MesH) (***2Ag-Cl, MesH***)[401]
2,3,4,5,6-Br_5-7,8,9,10,11,12-I_6-	Cs (***THF***)[401]	$Ag(C_5H_5N)_2$ (***2Ag-I, C_5H_5N, C-H···N***)[401]
Me_{12}-	Li (***PhMe***)[405], Na (***2C_6H_6***)[405], K (***2C_6H_6***)[405], Rb(***2C_6H_6***)[405], Cs (***2C_6H_6***)[405], Tl (***2C_6H_6***)[405], $PhMe_2NH$ (***MeOH***)[323], $1,2\text{-}(PTA)_2C_6H_4$ (***2CH_2Cl_2***)[406]	${}^{n}Bu_3Sn$ (***2Sn-C***)[407,408]
Br_{12}-	Me_3NH[328]	
$(CH_2F)_{12}$-	Ph_2EtPMe[409]	
1-Me-2,3,4,5,6,7,8,9,10,11,12-F_{11}-	$Ag(Ph_3CH)$[410]	
1-Et-2,3,4,5,6,7,8,9,10,11,12-F_{11}-	$(CO)_4Cu$[411], $(C_6H_6)Rh(CO)_2$[412], $Rh(CO)_4$[412]	
1-$C_6H_5CH_2$-2,3,4,5,6,7,8,9,10,11,12-F_{11}-		$Cu(CO)_2$ (***2Cu-C***)[411]
1-Me-2,3,4,5,6,7,8,9,10,11,12-Cl_{11}-	Me_3NH[336]	Ag (***6Ag-Cl***)[401]

(Continued)

Table 18 (Continued)

$CB_{11}H_{12}^-$ and derivatives	*Cation M^+* (***solvate, solvate-carborane C-H···X interaction***)	*Fragment M^+ in molecule or polymer* (***M-carborane interactions, solvate, solvate-carborane C-H···X interaction***)
1-Me-2,3,4,5,6,7,8,9,10,11,12-Br_{11}-	H_3O[185]	Ag (***2Ag-Br***)[328,401]
1-CuCl-2,3,4,5,6,7,8,9,10,11,12-F_{11}^-	Bu_4N[331]	
1-($Me_4C_2O_2$)B-12-(4-BrC_6H_4)-2,3,4,5,6,7,8,9,10,11-Me_{10}-	$Na(H_2O)(MeCN)$[333]	
1,1′-(2,3,4,5,6-I_5-7,8,9,10,11,12-$Br_6CB_{11})_2Ag^-$-		$Ag_3(MeCN)_4$ (***2Ag-Br,3Ag-I***)[332]
Complex anions (***interactions***)		
$Ag(CB_{11}H_6Cl_6)_2^-$ (***3Ag-Cl***)	$C_{59}N^+$ (***1,2-$Cl_2C_6H_4$, 2C-H···Cl***)[413]	
$Ag(CB_{11}H_6Br_6)_2^-$ (***3Ag-Br***)	(TPP)Fe (***4 1,4-$Me_2C_6H_4$***)[413,414]	
$Ag_2(CB_{11}H_{12})_4^{2-}$ (***2/4Ag-H,Ag-B***)	$(IMes)_2Ag$[415]	
	Complex cations (***interactions***)	
	$(C_5H_5)_2Rh_2Cl_2CB_{11}H_{12}$ (***2Rh-H***)[394]	
	$(Ph_2PCH_2)_2CH_2Pd$ (***2Pd-H, 2Pd-B***)[372]	
Radical		
Me_{12}[349]		

PPN = bis(triphenylphosphine)iminium
TPP = tetraphenylporphyrinate
IMes = 1,3-dimesitylimidazol-2-ylidene
CTV = cyclotriveratrylene
HDH = 4,7,13,16,24-hexaoxa-1,10-diazabicyclo(8.8.8)hexacosane
TTT = 5,7,12,14-tetramethyldibenzo(b,i)-1,4,8,11-tetraazacyclotetradecine
IM = imidazolium
PTA = phenothiazine.

NaOH and Me_2SO_4.[331] C-Metallated derivatives of $CB_{11}H_{12}^-$ have also been isolated where the anion is perhalogenated at the boron atoms.[331,332] The reaction of the C-lithiated anion $LiCB_{11}H_{11}^-$ with $^{i}PrOB(O_2C_6H_{12})$ gave the B–C substituted anion 1-$(C_6H_{12}O_2)$B-1-$CB_{11}H_{11}^-$.[333] Fluorination at the cage borons was achieved with F_2, F-TEDA, or HF.[178,331,334] Reagents used for chlorination of the cage borons were Cl_2, N-chlorosuccinimide, and iodine monochloride.[324,327,328,335–337] Brominations of the borons at the cage were carried out using Br_2 and N-bromosuccinimide.[93,324,327,328,330,338] Cage-iodination was achieved with iodine and iodine monochloride as reagents.[93,176,182,201,327,328,335,339–342]

Methylation at the boron atoms can be achieved with methyl triflate or methyl bromide.[180,323,333,343,344] The anion 2,3,4,5,6,7,8,9,10,11,12-Et_{11}-1-$CB_{11}H^-$ was made from $CB_{11}H_{12}^-$ and EtBr in a sealed tube at 220 °C in 92% yield.[180] The reaction of H_2O_2 with $CB_{11}H_{12}^-$ gave an anion with hydroxy groups at all cage borons.[345,346] Zwitterions of B-C_7H_6-1-$CB_{11}H_{12}$ were made from acidification of $CB_{11}H_{12}^-$ and reaction with $C_7H_6BF_4$.[342] Acidification of $CB_{11}H_{12}^-$ with sulfuric acid at 175 °C gave 12-HO-1-$CB_{11}H_{11}^-$ in 83% yield.[347] The dioxane adduct 12-OC_4H_8O-1-$CB_{11}H_{11}$ was obtained in low yield from the parent anion with Me_2SO_4 and dioxane.[347] B-sulfur derivatives of $CB_{11}H_{12}^-$ were obtained from the parent anion with alkylsulfide or sulfoxide in acid.[93,348] The reaction of the lithiated carborane with C_6F_5Br unexpectedly gave 7- and 12-C_6F_5-1-$CB_{11}H_{10}^-$ anions.[324] Oxidation of the permethylated anion, $CB_{11}Me_{12}^-$, gave the radical $CB_{11}Me_{12}^{\cdot}$.[349]

3.02.12.2 *ortho-Carborane*, 1,2-$C_2B_{10}H_{12}$, *and Derivatives*

The research field of *ortho*-carborane chemistry continues to expand rapidly mainly due to the commercial availability of *ortho*-carborane itself and the recent interest of these derivatives as agents for BNCT and other applications. Synthesis of these carboranes is still dominated by reactions of decaborane with various alkynes as shown in Table 19 (Figure 2). 3-Substituted derivatives are made by capping the *nido*-7,8-$C_2B_9H_{12}^-$ anions as listed in Table 20 (COMC (1982) 5.4.2.6.4). The many cage C–H to C–X and B–H to B–X conversions are summarized in Table 21 (COMC (1982) 5.4.2.7.5, 5.4.2.7.7, 5.4.2.7.9, 5.4.2.7.10 and COMC (1995) 6.2.5.5). The C–H bond is often metallated first to

Table 19 Synthetic routes to *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*-carborane) derivatives from decaborane and alkynes

1,2-$C_2B_{10}H_{12}$ and derivatives	*Starting materials*	*Starting alkyne*	*Solvent, temp, yield*
	$B_{10}H_{14}$, MeCN	$^{t}BuO_2CCCH$	Toluene, 52%[416]
1-C_6H_{13}-	$B_{10}H_{14}$	$C_6H_{13}CCH$	Toluene, BMIMCl, 91%[77]
1-C_7H_{15}-	$B_{10}H_{14}$, SR_2	$C_7H_{15}CCH$	Benzene, 32–38%[76]
1-RCH_2-	$B_{10}H_{14}$, MeCN	RCH_2CCH	Toluene, 25%[301]
1-RCH_2-	$B_{10}H_{12}(SEt_2)_2$	RCH_2CCH	Toluene, 28%[417]
1-RCH_2-	$B_{10}H_{14}$, MeCN	RCH_2CCH	Benzene, 10%[252]
1-^{t}Bu-	$B_{10}H_{14}$, MeCN	$^{t}BuCCH$	Toluene, 36%[418]
1-C_4H_9-	$B_{10}H_{14}$, MeCN	C_4H_9CCH	Toluene[244]
1-$MeCO_2(CH_2)_n$-	$B_{10}H_{14}$, MeCN	$MeCO_2(CH_2)_nCCH$	Toluene, 42–70%[419]
1-Me_2NCH_2-	$B_{10}H_{14}$, MeCN	Me_2NCH_2CCH	Toluene, 47%[420]
1-Me_2NCH_2-	$B_{10}H_{12}(SEt_2)_2$	Me_2NCH_2CCH	Toluene, 40%[420]
1-Me_2NCH_2-	$B_{10}H_{14}$	Me_2NCH_2CCH	Benzene, 36%[420]
1-$RR'N(CH_2)_3$-	$B_{10}H_{12}(NCMe)_2$	1-$RR'N(CH_2)_3CCH$	Benzene, 53%[421]
1-$RCONHCH_2$-	$B_{10}H_{14}$, MeCN	$RCONHCH_2CCH$	Toluene, 61–71%[422]
1-$PhMeC_8H_4NCCONMeCH_2$-	$B_{10}H_{14}$, MeCN	$PhMeC_8H_4NCCONMeCH_2CCH$	Toluene[423]
1-$C_6H_4(CO)_2NCH_2$-	$B_{10}H_{12}(NCMe)_2$	$C_6H_4(CO)_2NCH_2CCH$	Toluene, 66%[272]60%[424]
1-$C_6H_4(CO)_2N(CH_2)_3$-	$B_{10}H_{12}(NCMe)_2$	$C_6H_4(CO)_2N(CH_2)_3CCH$	Toluene, 59%[272]
1-$TsO(CH_2)_2$-	$B_{10}H_{12}(NCMe)_2$	$TsO(CH_2)_2CCH$	Toluene, 65%[272]
1-$I(CH_2)_3$-	$B_{10}H_{14}$, MeCN	$Cl(CH_2)_3CCH$	Toluene, NaI, acetone, 53%[283,425]
1-$RO(CH_2)_2$-	$B_{10}H_{14}$, MeCN	$RO(CH_2)_2CCH$	Toluene, 60%[426]
1-$RO(CH_2)_4$-	$B_{10}H_{14}$, MeCN	$RO(CH_2)_4CCH$	Toluene, 51%[426]
1-$ROCH_2$-	$B_{10}H_{14}$, MeCN	$ROCH_2CCH$	Toluene, 43–49%[427]
1-$ROCH_2$-	$B_{10}H_{14}$, Et_2S	$ROCH_2CCH$	Toluene, 36%[252]
1-$RO(CH_2)_2$-	$B_{10}H_{14}$, MeCN	$RO(CH_2)_2CCH$	Toluene, 43%[426] 61%[427]
1-$ClC_4H_8O(CH_2)_2OCH_2$-	$B_{10}H_{14}$, MeCN	$ClC_4H_8O(CH_2)_2OCH_2CCH$	MeCN, 65%[428]
1-$ArOCH_2$-	$B_{10}H_{14}$, MeCN	$ArOCH_2CCH$	MeCN, 52%[428]
1-(4-$C_2H_4S_2CC_6H_4$)OCH_2-	$B_{10}H_{14}$, MeCN	4-$(C_2H_4S_2C)C_6H_4OCH_2CCH$	MeCN, 51%[428,429] 47%[430,431]
1-$HC_6F_4OCO(CH_2)_2$-	$B_{10}H_{14}$, MeCN	$HC_6F_4OCO(CH_2)_2CCH$	50%[242]
1-(3-$C_2H_4S_2CC_6H_4$)OCH_2-	$B_{10}H_{14}$, MeCN	3-$C_2H_4S_2CC_6H_4OCH_2CCH$	MeCN, 58%[430]
1-(4-MeC_6H_4)OCH_2-	$B_{10}H_{12}(NCMe)_2$	4-$MeC_6H_4OCH_2CCH$	Toluene, 75%[270]
1-$MeO_2SOCH_2CH_2$-	$B_{10}H_{14}$, MeCN	$MeO_2SOCH_2CH_2CCH$	Benzene, 45%[432] 93%[433]
1-MeO_2SOCH_2-	$B_{10}H_{14}$, MeCN	MeO_2SOCH_2CCH	42%[432]
1-$MeOCH_2$-	$B_{10}H_{14}$, MeCN	$MeOCH_2CCH$	Benzene, 57%[230]
1-$MeOC_2H_4$-	$B_{10}H_{14}$, SMe_2	$MeOCH_2CH_2CCH$	Benzene, 5%[230]
1-(3-$NCC_6H_4OCH_2$)-	$B_{10}H_{12}(NCMe)_2$	3-$NCC_6H_4OCH_2CCH$	Toluene, 52%[434]
1-$Ph_2C{=}NCH(CN)CH_2$-	$B_{10}H_{12}(NCMe)_2$	1-$Ph_2C{=}NCH(CN)CH_2CCH$	Toluene, 36%[270,435]
1-$PhCH_2OCO(CH_2)_2$-	$B_{10}H_{12}(NCMe)_2$	$PhCH_2OCO(CH_2)_2CCH$	MeCN, 60%[436]
1-$Me_2SB_{12}H_{10}SMeCH_2$-	$B_{10}H_{14}$, MeCN	$Me_2SB_{12}H_{10}SMeCH_2CCH$	48%[437]
1-MeO_2C-	$B_{10}H_{14}$, Me_2NPh	MeO_2CCCH	Toluene, 93%[438]
1-$ROCH_2$-	$B_{10}H_{14}$, MeCN	$ROCH_2CCH$	[439]
1-$(^{t}BuOCO)_2NCH_2$-	$B_{10}H_{12}(NCMe)_2$	$(^{t}BuOCO)_2NCH_2CCH$	Benzene, 18%[440]
1-$^{t}BuOCONHCH_2$-	$B_{10}H_{12}(NCMe)_2$	$(^{t}BuOCO)_2NCH_2CCH$	Benzene, 13%[440]
1-$(^{t}BuOCO)_2N(CH_2)_3$-	$B_{10}H_{12}(NCMe)_2$	$(^{t}BuOCO)_2N(CH_2)_3CCH$	Benzene, 15%[440]
1-$(PhCH_2OCO)_2NCH_2$-	$B_{10}H_{12}(SEt_2)_2$	$(PhCH_2OCO)_2NCH_2CCH$	Toluene, 63%[440,441]
1-$(PhCH_2OCO)_2N(CH_2)_2$-	$B_{10}H_{12}(SEt_2)_2$	$(PhCH_2OCO)_2N(CH_2)_2CCH$	Toluene, 59%[440,441]
1-$PhCH_2OCH_2$-	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCH$	Toluene, 60%[442]
1-$^{i}PrH(MeO)_2C_3N_2CHCH_2$	$B_{10}H_{12}(NCMe)_2$	$^{i}PrH(MeO)_2C_3N_2CHCH_2CCH$	Toluene, 35%[443,270]
1-$BrCH_2$-	$B_{10}H_{14}$, SR_2	$BrCH_2CCH$	Benzene, 84–89%[76]
1-$BrCH_2$-	$B_{10}H_{14}$, MeCN	$BrCH_2CCH$	Toluene[244]
1,2-$(RCONHCH_2)_2$-	$B_{10}H_{14}$, MeCN	$RCONHCH_2CCCH_2NHCOR$	Toluene, 35%[422]
1-$PhCH_2OCH_2$-2-MeO_2CCH_2-	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2CO_2Me$	Toluene, 63%[442]
1-$PhCH_2OCH_2$-2-$R(CH_2)_4$-	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2OR$	Toluene, 26%[444]
1,2-$(MeO_2C)_2$-	$B_{10}H_{14}$, SR_2	MeO_2CCCCO_2Me	Benzene, 82–88%[76]
1,2-$(MeOCH_2)_2$-	$B_{10}H_{14}$, SMe_2	$MeOCH_2CCCH_2OMe$	Benzene, 73%[230]
1,2-$(PhCH_2OCH_2)_2$-	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2OCH_2Ph$	Toluene, 48%[442]
1,2-$(MeOCH_2CH_2)_2$-	$B_{10}H_{14}$, SMe_2	$MeOCH_2CH_2CCCH_2CH_2OMe$	Benzene, 5%[230]

(*Continued*)

Table 19 (Continued)

1,2-$C_2B_{10}H_{12}$ and derivatives	*Starting materials*	*Starting alkyne*	*Solvent, temp, yield*
$1-PhCH_2OCH_2-2-ROCH_2-$	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2OR$	Toluene, 43%[444] 33–37%[442]
$1-PhCH_2OCH_2-2-FCH_2-$	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2F$	Toluene, 61%[445]
$1-PhCH_2OCH_2-2-C_6H_{11}OCH_2-$	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2OC_6H_{11}$	Toluene, 50%[445]
$1-PhCH_2OCH_2-2-FC_6H_{10}OCH_2-$	$B_{10}H_{14}$, MeCN	$PhCH_2OCH_2CCCH_2OC_6H_{10}F$	Toluene, 69%[445]
$1-C_6H_4(CO)_2NCH_2-2-PhCH_2O(CH_2)_2-$	$B_{10}H_{12}(SEt_2)_2$	$C_6H_4(CO)_2NCH_2CC(CH_2)_2OCH_2Ph$	50%[446]
$1,2-Et_2-3-MeCO_2(CH_2)_6-$	$6-MeCO_2(CH_2)_6B_{10}H_{13}$	EtCCEt	Toluene, BMIMCl, 93%[77]
1-Ph-	$B_{10}H_{14}$, MeCN	PhCCH	71%[242] C_6H_6, 52%[447]
1-Ph-	$B_{10}H_{14}$, MeCN	PhCCH	Toluene, 67%[418]
1-Ar-	$B_{10}H_{14}$, MeCN	ArCCH	Toluene, 80 °C, 60%[448]
1-Ar-	$B_{10}H_{14}$, MeCN	ArCCH	Benzene[449]
1-Ar-	$B_{10}H_{14}$, Et_2S	ArCCH	Toluene[450]
$1-(4-ROCC_6H_4)-$	$B_{10}H_{14}$, Me_2NPh	$4-ROCC_6H_4CCH$	Toluene, 23–30%[438]
$1-(3-MeC_6H_4)-$	$B_{10}H_{14}$, MeCN	$3-MeC_6H_4CCH$	Benzene[449]
$1-(4-MeC_6H_4)-$	$B_{10}H_{12}(NCMe)_2$	$4-MeC_6H_4CCH$	Toluene, 70%[270]
$1-(4-Me_2NC_6H_4)-$	$B_{10}H_{14}$, MeCN	$4-Me_2NC_6H_4CCH$	[451]
$1-(4-CF_3C_6H_4)-$	$B_{10}H_{14}$, MeCN	$4-CF_3C_6H_4CCH$	[451]
$1-(4-NCC_6H_4)-$	$B_{10}H_{14}$, MeCN	$4-NCC_6H_4CCH$	Toluene, 30%[452]
$1-(4-MeSC_6H_4)-$	$B_{10}H_{14}$, MeCN	$4-MeSC_6H_4CCH$	Toluene, 58%[452]
$1-(4-MeOC_6H_4)-$	$B_{10}H_{14}$, MeCN	$4-MeOC_6H_4CCH$	Toluene, 69%[451,452] 41%[418]
$1-(4-PhOC_6H_4)-$	$B_{10}H_{12}(NCMe)_2$	$PhOC_6H_4CCH$	Toluene, 40%[271]
$1-(3-C_2H_4S_2CC_6H_4)-$	$B_{10}H_{14}$, MeCN	$3-C_2H_4S_2CC_6H_4CCH$	MeCN, 57%[430]
$1-(2'-C_4H_3S)-$	$B_{10}H_{14}$, MeCN	$(2-C_4H_3S)CCH$	Toluene, 52%[216]
$1-(2-NC_5H_4)-$	$B_{10}H_{12}(SEt_2)_2$	$2-NC_5H_4CCH$	Toluene, 28%[317]
$1-(4-Br-2-NC_5H_4)-$	$B_{10}H_{12}(SEt_2)_2$	$4-Br-2-NC_5H_4CCH$	Toluene, 32%[453]
1-Ph-2-Me-	$B_{10}H_{14}$, Me_2NPh	PhCCMe	Toluene, 68%[454]
$1-Ar-2-C_4H_9-$	$B_{10}H_{14}$, MeCN	$ArCCC_4H_9$	Toluene, 80 °C, 60%[448]
$1-Ar-2-C_8H_{17}-$	$B_{10}H_{14}$, MeCN	$ArCCC_8H_{17}$	Toluene, 80 °C, 60%[448]
1-Ar-2-Ph-	$B_{10}H_{14}$, Et_2S	ArCCPh	Toluene[450]
$1-(4-MeCO_2C_6H_4)-2-Ph-$	$B_{10}H_{12}(NCMe)_2$	$PhCCC_6H_4CO_2Me$	Toluene, 37%[271]
$1-(3-H_2NC_6H_4)-2-Ph-$	$B_{10}H_{14}$, MeCN	$3-H_2NC_6H_4CCPh$	C_6H_6, reflux, 3 d, 28%[260]
$1-(4-H_2NC_6H_4)-2-Ph-$	$B_{10}H_{14}$, MeCN	$4-H_2NC_6H_4CCPh$	C_6H_6, reflux, 3 d, 27%[260]
$1,2-(4-MeOC_6H_4)_2-$	$B_{10}H_{14}$, MeCN	$(4-MeOC_6H_4)_2C_2$	C_6H_6, 31%[455]
$1,2-(4-IC_6H_4)_2-$	$B_{10}H_{12}(SMe_2)_2$	$(4-IC_6H_4)_2C_2$	Toluene, 58%[456]
$1,2-(4-MeC_6H_4)_2-$	$B_{10}H_{14}$, Me_2NPh	$(4-MeC_6H_4)_2C_2$	80%[457]
$1,2-(4-PhOC_6H_4)_2-$	$B_{10}H_{12}(SEt_2)_2$	$(4-PhOC_6H_4)_2C_2$	Toluene, 65%[271]
$1-(4-PhOC_6H_4)-2-(4-MeCO_2C_6H_4)-$	$B_{10}H_{12}(NCMe)_2$	$PhOC_6H_4CCC_6H_4CO_2Me$	Toluene, 22%[271]
$1-(4-PhOC_6H_4)-2-(4-MeC_6H_4)-$	$B_{10}H_{12}(NCMe)_2$	$PhOC_6H_4CCC_6H_4Me$	Toluene, 23%[271]
$1-(4-PhOC_6H_4)-2-(4-BrC_6H_4)-$	$B_{10}H_{12}(NCMe)_2$	$PhOC_6H_4CCC_6H_4Br$	Toluene, 34%[271]
1-PhCC-2-Ph-	$B_{10}H_{14}$, Me_2NPh	PhCCCCPh	78%[457]
1-PhCC-2-Ph-	$B_{10}H_{12}(NCMe)_2$	PhCCCCPh	Toluene, 33%[458]
$1-PhEtC{=}C(C_6H_4OCH_2CH_2I)-$	$B_{10}H_{12}(NCMe)_2$	$PhEtC{=}C(C_6H_4OCH_2CH_2I)CCH$	Toluene, 10%[277]
$1-C_3H_5-$	$B_{10}H_{14}$, MeCN	C_3H_5CCH	Toluene, 18%[418]
$1,1'-(1,2-C_6H_4)-$	$B_{10}H_{14}$, MeCN	$1,2-(HCC)_2C_6H_4$	C_6H_6, reflux, 3 d, 10%[459,460]
$1,1'-(1,3-C_6H_4)-$	$B_{10}H_{14}$, MeCN	$1,3-(HCC)_2C_6H_4$	C_6H_6, reflux, 2 d, 44%[460]
$1,1'-(5-NO_2-1,3-C_6H_4)-$	$B_{10}H_{14}$, MeCN	$1,3-(HCC)_2-5-NO_2-C_6H_4$	C_6H_6, 12%[461]
$1,1'-(1,4-C_6H_4)-2,2'-Ph_2-$	$B_{10}H_{14}$, Et_2S	$1,4-(PhCC)_2C_6H_4$	Toluene, reflux, 80%[462]
$1,1'-(1,3-C_6H_4)-2,2'-Ph_2-$	$B_{10}H_{14}$, Et_2S	$1,3-(PhCC)_2C_6H_4$	Toluene, reflux, 75%[462]
$1,1'-CH_2C(CO_2Et)_2CH_2-$	$B_{10}H_{12}(SEt_2)_2$	$HCCCH_2C(CO_2Et)_2CH_2CCH$	Toluene, reflux, 2 d, 73%[463]
$1,1'-CH_2C(C_3H_6O_2)CH_2-$	$B_{10}H_{12}(SEt_2)_2$	$HCCCH_2C(C_3H_6O_2)_2CH_2CCH$	Toluene, reflux, 2 d, 33%[463]
$1,1'-(1,4-C_6H_4-1,4-C_6H_4)-$	$B_{10}H_{12}(SEt_2)_2$	$HCC-1,4-C_6H_4-1,4-C_6H_4CCH$	Toluene, reflux, 3 d, 83%[464]

(Continued)

Table 19 (Continued)

1,2-$C_2B_{10}H_{12}$ and derivatives	*Starting materials*	*Starting alkyne*	*Solvent, temp, yield*
1,1′-$CH_2CRR'CH_2$-2,2′-Me_2-	$B_{10}H_{12}(NCMe)_2$	$MeCCCH_2CRR'CH_2CCMe$	Toluene, 27%[270]
1,1′-$CH{=}CH$-2,2′-Ar_2-	$B_{10}H_{14}$, MeCN	$ArCCCH{=}CHCCAr$	45–80%[222]
1,1′-$(Me_2SB_{12}H_{10}SMeCH_2)_2$-	$B_{10}H_{12}(SEt_2)_2$	$HCCCH_2MeSB_{12}H_{10}SMeCH_2CCH$	MeCN, 37%[437]
1,1′-$CH_2S(CHCO_2Me)_2SCH_2$-	$B_{10}H_{12}(NMe_2Ph)_2$	$HCCCH_2S(CHCO_2Me)_2SCH_2CCH$	Toluene, 24%[465]
1,1′,1″-(1,3,5-C_6H_3)-	$B_{10}H_{12}(SEt_2)_2$	1,3,5-$(HCC)_3C_6H_3$	Toluene, reflux, 3 d, 78%[464]
1,1′,1″-(1,3,5-C_6H_3)-2,2′,2″-Ph_3-	$B_{10}H_{14}$, Et_2S	1,3,5-$(PhCC)_3C_6H_3$	Toluene, reflux, 59%[462]
1,1′-(1,4-C_6H_4)-2,1″-(1,4-C_6H_4)-	$B_{10}H_{12}(SMe_2)_2$	HCC-1,4-C_6H_4CC-1,4-C_6H_4CCH	Toluene, reflux, 38%[466]
1,1,1″,1‴-$(CH_2)_2CHCOCH(CH_2)_2$-	$B_{10}H_{14}$, MeCN	$(HCCCH_2)_2CHCOCH(CH_2CCH)_2$	Toluene, 80 °C, 3 d, 16%[467]

Table 20 Synthetic routes to *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*-carborane) derivatives from 7,8-$C_2B_9H_{12}^-$ anions

Derivatives of 1,2-$C_2B_{10}H_{12}$	*7,8-$C_2B_9H_{12}^-$ and derivatives as starting material*	*Reagents*	*Solvent, yield*
3-$Br(CH_2)_3$-		NaH, $Cl_2B(CH_2)_3Br$	THF, pentane, heptane, 30%[239]
3-${}^tBuCH{=}CH$-		NaH, $Cl_2BCH{=}CH^tBu$	Ether, 81%[468]
3-$CH_2{=}CHCH_2O$-		NaH, $Cl_2BOCH_2CH{=}CH_2$	THF, pentane, heptane, 20%[239]
1,2-Ph_2-3-Me-	7,8-Ph_2-	BuLi, $MeBBr_2$	Ether, 40–60 ether, 14%[231]
1,2-Ph_2-3-Et-	7,8-Ph_2-	BuLi, $EtBBr_2$	Ether, 40–60 ether, 33%[231]
1,2-Ph_2-3-F-	7,8-Ph_2-	BuLi, $BF_3{\cdot}OEt_2$	Ether, 40–60 ether, 32%[231]
1-Me-3-Br-	7-Me-	BuLi, BBr_3	Ether, hexane, 5 h, 62%[469]
1-Ph-3-Br-	7-Ph-	BuLi, BBr_3	Ether, hexane, 5 h, 55%[469]
3-I-		BuLi, BI_3	Hexane, 22 h, 27%[470]
3-I-		BuLi, BI_3	Toluene, 37 h, 74%[470]
1-Me-3-I-	7-Me-	BuLi, BI_3	Ether, hexane, 5 h, 71%[469]
1-Ph-3-I-	7-Ph-	BuLi, BI_3	Ether, hexane, 5 h, 52%[469]
3,6-I_2-	3-I-	BuLi, BI_3	Toluene, 52%[470]
3,9,12-I_3-	5,6-I_2-	BuLi, BI_3	Toluene, 55%[470]
3,9,12-I_3-	5,6-I_2-	BuLi, BI_3	Hexane, 36%[470]
3,6,9,12-I_4-	3,5,6-I_3-	BuLi, BI_3	Toluene, 29%[470]
3,3′-$(CH_2)_6$-		NaH,$Cl_2B(CH_2)_6BCl_2$	THF, pentane, heptane, 15%[239]
3,3′-$(CH_2)_3O$-		NaH,$Cl_2B(CH_2)_3OBCl_2$	THF, pentane, heptane, 14%[239]

C–Li using BuLi in THF or ether–benzene followed by a reagent. Several structures of *closo*-1,2-$C_2B_{10}H_{12}$ derivatives determined experimentally are summarized in Table 22.

3.02.12.3 *meta-Carborane*, 1,7-$C_2B_{10}H_{12}$, *and Derivatives*

The only reported synthesis of a *meta*-carborane derivative is by capping the 7,9-$C_2B_9H_{12}^-$ anion with NaH and $Cl_2B(CH_2)_3Br$ to form 2-$Br(CH_2)_3$-1,7-$C_2B_{10}H_{11}$ in 30% yield.[239] Many reactions of the commercially available *meta*-carborane and their derivatives have been published and only cage C–H to C–X and B–H to B–X conversions are listed in Table 23 (COMC (1982) 5.4.2.7 and COMC (1995) 6.2.5.5). Several structures of *closo*-1,7-$C_2B_{10}H_{12}$ (*meta*-carborane) derivatives have been published and interestingly a significant number of structures are macrocycles as summarized in Table 24.

3.02.12.4 *para-Carborane*, 1,12-$C_2B_{10}H_{12}$, *and Derivatives*

New syntheses of *para*-carborane, 1,12-$C_2B_{10}H_{12}$, and derivatives have not been reported in the literature in the period reviewed. However, many reactions of the commercially available *para*-carborane and their derivatives have been published and only cage C–H to C–X and B–H to B–X conversions are listed in Table 25 (COMC (1982) 5.4.2.7

Table 21 C–H to C–X and B–H to B–X conversions in *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*-carborane) derivatives

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
C–H to C–X conversion			
C–C bond formation			
1-Bu-		BuLi, BuCl	DME, 67%[315]
1-C_8H_{17}-		Na, NH_3, $C_8H_{17}Br$	83%[471]
1-$C_{18}H_{33}$-		BuLi, $C_{18}H_{33}Br$	Benzene, Et_2O, 53%[471]
1-$C_{13}H_9CH_2$-		BuLi, $C_{12}H_8C{=}CH_2$	Et_2O, toluene, 85%[472]
1-RCH_2-		BuLi, $TsOCH_2R$	473
1-$NC(CH_2)_2$-		KOH, $CH_2{=}CHCN$, DB18C6	Benzene, 49%[474]
1-$NC(CH_2)_2$-		KOH, $CH_2{=}CHCN$, DB18C6	Benzene, 31%[474]
1-$C_6H_4(CO)_2N(CH_2)_2$-		BuLi, $C_6H_4(CO)_2NCH_2CH_2Br$	DME, 81%[475]
1-$PhCH_2$-		BuLi, $PhCH_2Br$	DME, 86%[315]
1-(2′-py)CH_2-		BuLi, 2-pyCH_2Cl	Et_2O, 57–65%[221,453,476]
1-$HOCH_2$-		TBAF, HCHO	THF, 86%[318]
1-RCH(OH)-		TBAF, RCHO	THF, 86–99%[318]
1-$MeOCH_2CH_2$-		BuLi, $MeO(CH_2)_2Cl$	Et_2O, toluene, 23%[218]
1-$C_5H_5Me_2C$-		BuLi, $Me_2C{=}CC_4H_4$	C_6H_6, Et_2O, 92%[477] toluene, Et_2O, 85%[209]
1-$C_6H_4(CO)_2N(CH_2)_3$-		BuLi, $C_6H_4(CO)_2N(CH_2)_3Br$	DME, 36%[475]
1-$B_{12}H_{11}O(CH_2)_4$-$^{2-}$ $[Bu_4N^+]_2$		BuLi, $B_{12}H_{11}O(CH_2)_4^-$, Bu_4NBr	DME, 86%[478]
1-(4-NCC_6H_4)CH_2-		BuLi, 4-$NCC_6H_4CH_2Br$	THF, 70%[479]
1-(4-$MeO_2CC_6H_4$)CH(OH)-		BuLi, 4-$MeO_2CC_6H_4CHO$	THF, 95%[480]
1-(3-$CHOC_6H_4$)CH(OH)-		BuLi, 1,3-$(CHO)_2C_6H_4$	THF, 52%[480]
1-O_2NCH_2RCH-		Na, NH_3, $RCH{=}CHNO_2$	AcOH, 75–77%[481]
1-(HOC_3H_6)-		BuLi, $(CH_2)_3O$	46%[482]
1-$(PhCH_2)_2NCH_2CH_2$-		BuLi, $(PhCH_2)_2NCH_2CH_2Cl$	C_6H_6, 95%[483]
1-$(Me_3Si)_2NCH_2CH_2$-		$(Me_3Si)_2NCH_2CH_2Cl$	C_6H_6, 78%[483]
1-$CH_2{=}CHCH_2$-		NaH, $BrCH_2CH{=}CH_2$	NaI, DME, 60%[439]
1-PhCH(OTs)-		TBAFH, PhCHO, TsCl	451,484
1-ArCH(OH)-		TBAF, ArCHO	THF, 48–96%[318]
1-$(EtO)_2CHCH_2$-		BuLi, $BrCH_2CH(OEt)_2$	Benzene, 77%[485]
1-$MeCH{=}CHCH(OH)$-		TBAF, $MeCH{=}CHCHO$	THF, 63%[318]
1-$MeC({=}O)CH_2CH_2$-		TBAF, $H_2C{=}CHC({=}O)Me$, KOH	THF, 48%[318]
1-HO_2C-		BuLi, CO_2	Et_2O, 95%[486]
1-$C_{10}H_7CH(OH)$-		BuLi, $C_{10}H_7CHO$	THF, 86%[480]
1-$C_{14}H_{15}CH_2$-		BuLi, $C_{14}H_{15}CH_2Cl$	Et_2O, benzene, 88%[487]
1-$C_{14}H_{15}CH(OH)$-		BuLi, $C_{14}H_{15}CHO$	THF, 91%[487]
1-EtO_2CCH_2-		BuLi, $BrCH_2CO_2Et$	THF, 42%[479]
1,2-$(RCH_2)_2$-		Na, NH_3, RCH_2X	80–85%[471]
1-$MeHC{=}CH$-2-Me-	1-Me-	BuLi, $H_2C{=}CHCH_2Br$, KOH	Et_2O[488]
1-C_6H_{13}-2-Me-	1-Me-	BuLi, $C_6H_{13}Br$	LiI, THF, 92%[489]
1-(3-BrC_6H_4)CH_2-2-Me-	1-Me-	BuLi, 3-$BrC_6H_4CH_2Br$	DME, 65%[431]
1-(4-BrC_6H_4)CH_2-2-Me-	1-Me-	BuLi, 4-$BrC_6H_4CH_2Br$	DME, 75%[431]

(*Continued*)

Table 21 (Continued)

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-$PhCH_2$-2-Me-	1-Me-	BuLi, $PhCH_2Br$	LiI, THF,89%[489]
1-$PhCH_2$-2-Me-	1-Me-	BuLi, $PhCH_2Cl$	LiI, THF,82%[489]
1-$NC(CH_2)_2$-2-Me-	1-Me-	KOH, $CH_2{=}CHCN$, DB18C6	Benzene, 46%[474]
1-$NC(CH_2)_2$-2-$H_2C{=}CH$-	1-$H_2C{=}CH$-	KOH, $CH_2{=}CHCN$, DB18C6	Benzene, 47%[474]
1-$PhCH_2$-2-$BrCH_2$-	1-$BrCH_2$-	$^iPr_2NLi$, $PhCH_2Br$	THF, 82%[490,491]
1-Me-2-$BrCH_2$-	1-$BrCH_2$-	$^iPr_2NLi$, MeI	THF, 75%[490,491]
1-HO_2C-2-$BrCH_2$-	1-$BrCH_2$-	$^iPr_2NLi$, CO_2	THF, 76%[490,491]
1-HO_2C-2-$MeOCH_2$-	1-$MeOCH_2$-	MeLi, CO_2	Et_2O[492]
1-^nBu-2-Me-	1-Me-	BuLi, ^nBuBr	LiI, THF,88%[489]
1,2-$(HSCH_2CH_2)_2$-		BuLi, $S(CH_2)_2$	Diglyme, 64%[493]
1-PhCO-2-Me-	1-Me-	BuLi, PhCOCl	Toluene, 82%[271]
1-$CH_2{=}CHCH_2$-2-Me-	1-Me-	BuLi, $CH_2{=}CHCH_2Br$	LiI, THF,90%[489]
1-$C_{14}H_{15}CH(OH)$-2-^iPr-	1-^iPr-	BuLi, $C_{14}H_{15}CHO$	THF, 83%[487]
1,2-$(C_{14}H_{15}CH(OH))_2$-		BuLi, $C_{14}H_{15}CHO$	Et_2O, benzene, 89%[487]
1,9(12)-$(MeC_6H_4)_2$-	9-MeC_6H_4-	BuLi, CuCl, 4-$MeC_6H_4N_2BF_4$	Et_2O, THF, 33%[494]
1-RCH_2-2-Me-	1-Me-	BuLi, $ClCH_2R$	Et_2O, 76%[133]
1-$Cl(CH_2)_3$-2-R-	1-R-	BuLi, $Cl(CH_2)_3Br$	THF, 93–95%[276]
1-$CH_2{=}CH(CH_2)_2$-2-Me-	1-Me-	BuLi, $CH_2{=}CH(CH_2)_2Br$	LiI, THF, 94%[489] 74%[495]
1-$MeCH{=}CHCH_2$-2-Me-	1-Me-	BuLi, $MeCH{=}CHCH_2Br$	LiI, THF, 76%[489]
1-(4-BrC_6F_4)-2-Me-	1-Me-	BuLi, C_6F_5Br	Et_2O, 81%[496]
1,2-$(HOCH_2CH_2)_2$-		BuLi, C_2H_4O	Et_2O, Toluene, 92%[218]
1,2-$(MeOCH_2CH_2)_2$-		BuLi, $MeO(CH_2)_2Cl$	Et_2O, Toluene, 52%[218]
1-$(EtO_2C)_2CH$(3-$O_2NC_6H_4$)CH-2-^iPr-	1-^iPr-	BuLi, (3-$O_2NC_6H_4$) $CH{=}C(CO_2Et)_2$, HCl	Benzene, Et_2O, 51%[497]
1,2-$(PhNHCO)_2$-		BuLi, PhNCO	Toluene, 77%[271]
1,2-$(MeNHCO)_2$-		BuLi, MeNCO	Toluene, 65%[271]
1-$(EtO)_2CHCH_2$-2-Me-	1-Me-	BuLi, $BrCH_2CH(OEt)_2$	Benzene, 77%[485]
1,2-$(HO_2C)_2$-8,9,10,12-Et_4-	8,9,10,12-Et_4-	BuLi, CO_2	Benzene, Et_2O, 85%[238]
1,2-$(Me_2CH(OH))_2$-8,9,10,12-Et_4-	8,9,10,12-Et_4-	BuLi, Me_2CO	Benzene, Et_2O, 90%[238]
1,2-$(PhCH_2)_2$-8,9,10,12-Et_4-	8,9,10,12-Et_4-	BuLi, $PhCH_2Cl$	Benzene, Et_2O, 90%[238]
1,2-$(C_6H_4(CO)_2NCH_2)_2$-		BuLi, $C_6H_4(CO)_2NCH_2Br$	Hexane[498]
1,2-$(Me_2NCH_2)_2$-		BuLi, $H_2C{=}NMe_2I$	Toluene[284]
1-(2-HOC_6H_9)-2-Me-	1-Me-	BuLi, $C_6H_{10}O$	86%[233]
1-C_6F_5-2,1′-(1,4-C_6H_4)-2′,1″-(1,4-C_6H_4)-	1,1′-(1,4-C_6H_4)-2,1″-(1,4-C_6H_4)-	BuLi, C_6F_6	DME, 13%[466]
1-$HOCH_2$-2-$PhCH_2O$-	1-$PhCH_2O$-	TBAF, HCHO	THF, 87%[442]
1,2-$(EtO_2CCH_2)_2$-		BuLi, $BrCH_2CO_2Et$	THF, 13%[479]
1-EtO_2CCH_2-2-Me-	1-Me-	BuLi, $BrCH_2CO_2Et$	THF, 45%[479]
1-EtO_2CCH_2-2-$(PhCH_2OCH_2)_2CHOCH_2$-	1-$(PhCH_2OCH_2)_2$ $CHOCH_2$-	BuLi, $BrCH_2CO_2Et$	THF, 47%[479]
1-(4-NCC_6H_4)CH_2-2-Me-	1-Me-	BuLi, 4-$NCC_6H_4CH_2Br$	THF, 65%[479]
1-(4-NCC_6H_4)CH_2-2-$(PhCH_2OCH_2)_2CHOCH_2$-	1-$(PhCH_2OCH_2)_2$ $CHOCH_2$-	BuLi, 4-$NCC_6H_4CH_2Br$	THF, 75%[479]
1-HO_2C-2-Et_2NCH_2-	1-Et_2NCH_2-	BuLi, CO_2	C_6H_6, Et_2O, 85%[499]
1-$C_6H_{13}Me_2SiCC(CH_2)_2$-2-Me-	1-Me-	$C_6H_{13}Me_2SiCC(CH_2)_2Br$	LiI, THF,96%[489]

(Continued)

Table 21 (Continued)

Derivatives of 1,2-C$_2$B$_{10}$H$_{12}$	*1,2-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1,2-(PhCH$_2$)$_2$-		BuLi, PhCH$_2$Br	Et$_2$O, toluene, 72%[209]
1,2-((MeO)$_2$C$_6$H$_3$CH$_2$)$_2$-		BuLi, (MeO)$_2$C$_6$H$_3$CH$_2$Br	Et$_2$O, toluene, 60%[500]
1,2-(C$_{16}$H$_9$CH$_2$)$_2$-		BuLi, C$_{16}$H$_9$CH$_2$Cl	Et$_2$O, toluene, 40%[500]
1-PhCH(OTs)-2-Me-	1-Me-	TBAFH, PhCHO, TsCl	[484]
1-B$_{12}$H$_{11}$O(CH$_2$)$_4$-2-Me-$^{2-}$ [Bu$_4$N$^+$]$_2$	1-Me-	BuLi, B$_{12}$H$_{11}$O(CH$_2$)$_4$$^-$, Bu$_4$NBr	THF, 89%[478]
1-HSCH$_2$CH$_2$-2-Me-	1-Me-	BuLi, CH$_2$═CHSH	Et$_2$O, 77%[501]
1-O$_2$NCH$_2$RCH-2-^{i}Pr-	1-^{i}Pr-	Na, NH$_3$, RCH═CHNO$_2$	AcOH, 83–85%[481]
1-(PhCH$_2$)$_2$NCH$_2$CH$_2$-2-Me-	1-Me-	BuLi, (PhCH$_2$)$_2$NCH$_2$CH$_2$Cl	C$_6$H$_6$, 98%[483]
1-MeO$_2$C(NHOCO^{t}Bu)(CF$_3$)C-2-Me-		BuLi, ^{t}BuOCON═C(CF$_3$)CO$_2$Me	Et$_2$O, 89%[502]
1,2-(HO$_2$C)$_2$-		BuLi, CO$_2$	Et$_2$O, 95%[503]
1,2-(HOC$_3$H$_6$)$_2$-		BuLi, (CH$_2$)$_3$O	THF, 85%[273]
1-NC-2-Me-	1-Me-	BuLi, TsCN	Et$_2$O, 91%[504]
1-HO$_2$C-2-Me-	1-Me-	BuLi, CO$_2$	Et$_2$O, 67%[505]
1-TsOCH$_2$-2-^{i}Pr-	1-^{i}Pr-	BuLi, HCHO, TsCl	Benzene, 83%[506]
1,2,4,5,7,8,9,10,11,12-Me$_{10}$-	4,5,7,8,9,10,11,12-Me$_8$-	BuLi, MeI	Et$_2$O, 95%[243]
1-(4-MeOC$_6$H$_4$)-		BuLi, CuCl, 4-MeOC$_6$H$_4$I	DME, pyridine[451,507]
1-(4-Me$_2$NC$_6$H$_4$)-		BuLi, CuCl, 4-Me$_2$NC$_6$H$_4$I	DME, pyridine[451]
1-(4-CF$_3$C$_6$H$_4$)-		BuLi, CuCl, 4-CF$_3$C$_6$H$_4$I	DME, pyridine[451]
1-(4-O$_2$NC$_6$H$_4$)-		BuLi, CuCl, 4-O$_2$NC$_6$H$_4$I	DME, pyridine, 42%[317]
1-(3-O$_2$NC$_6$H$_4$)-		BuLi, CuCl, 3-O$_2$NC$_6$H$_4$I	DME, pyridine, 37%[317]
1-(3,6-Ar$_2$-2,4,5-C$_3$N$_3$)-		BuLi, 3,6-Ar$_2$-4-O$^-$-1,2,4-HC$_3$N$_3$$^+$, Me$_2$NCOCl	THF, 40%[274]
1-(1-Ph-1,7-CB$_{10}$H$_{10}$C-1,4-C$_6$F$_4$-)		BuLi, 1-C$_6$F$_5$-7-Ph-1,7-C$_2$B$_{10}$H$_{10}$	Et$_2$O, 56%[508]
1-(1-Ph-1,12-CB$_{10}$H$_{10}$C-1,4-C$_6$F$_4$-)		BuLi, 1-C$_6$F$_5$-12-Ph-1,12-C$_2$B$_{10}$H$_{10}$	Et$_2$O, 68%[508]
1-(1,3,5-Cl$_2$C$_3$N$_3$)-		BuLi, 1,3,5-Cl$_3$C$_3$N$_3$	THF, 59%[509]
1-(3′-py)-		BuLi, CuCl, 3-BrC$_5$H$_4$N	DME, pyridine, 33%[453]
1-NC(CH$_2$)$_2$-2-Ph-	1-Ph-	KOH, CH$_2$═CHCN, DB18C6	Benzene, 71%[474]
1-PhCO-2-Ph-	1-Ph-	BuLi, PhCOCl	Toluene, 65%[271]
1-Ar(RR′N)R″OC-2-Ph-	1-Ph-	BuLi, C$_6$H$_4$(CO)$_2$N(CH$_2$)$_2$Br	63%[510]
1-RCH$_2$-2-Ph-	1-Ph-	BuLi, ClCH$_2$R	Et$_2$O, 81%[133]
1-MeCO$_2$CH$_2$-2-Ph-	1-Ph-	BuLi, HCHO, MeCOCl	Benzene, 76%[506]
1-TsOCH$_2$-2-Ph-	1-Ph-	BuLi, HCHO, TsCl	Benzene, 95%[506]
1-EtO$_2$CCH$_2$-2-Ph-	1-Ph-	BuLi, BrCH$_2$CO$_2$Et	THF, 50%[479]
1-PhCOCH$_2$-2-Ph-	1-Ph-	BuLi, BrCH$_2$COPh	THF, 30%[479]
1-EtO$_2$CH(NO$_2$)ArCH-2-Ph-	1-Ph-	BuLi, ArCH═C(NO$_2$)CO$_2$Et, HCl	Benzene, Et$_2$O, 89–93%[497]
1-HO$_2$N═C(CO$_2$Et)ArCH	1-Ph-	BuLi, ArCH═C(NO$_2$)CO$_2$Et	Benzene, Et$_2$O, 76–94%[497]
1-(EtO$_2$C)$_2$CH(3-O$_2$NC$_6$H$_4$)CH-2-Ph-	1-Ph-	BuLi, (3-O$_2$NC$_6$H$_4$)CH═C(CO$_2$Et)$_2$, HCl	Benzene, Et$_2$O, 70%[497]
1-HO$_2$C-2-Ph-	1-Ph-	BuLi, CO$_2$	Et$_2$O, 56%[505]
1-CH$_2$═CH(CH$_2$)$_4$-2-Ph-	1-Ph-	BuLi, Br(CH$_2$)$_4$CH═CH$_2$	THF, 81%[428]

(*Continued*)

Table 21 (Continued)

Derivatives of 1,2-C$_2$B$_{10}$H$_{12}$	*1,2-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-CH$_2$OCHCH$_2$-2-Ph-	1-Ph-	BuLi, ClCH$_2$CHOCH$_2$	THF, 62%^{428}
1-NC-2-Ph-	1-Ph-	BuLi, TsCN	Et$_2$O, 87%^{504}
1-(4-NCC$_6$H$_4$)CH$_2$-2-Ph-	1-Ph-	BuLi, 4-NCC$_6$H$_4$CH$_2$Br	THF, 65%^{479}
1-^{n}Pr-2-Ar-	1-Ar-	NaH, ^{n}PrI	DMF^{449}
1-RCH$_2$-2-Ar-	1-Ar-	NaH, RCH$_2$I	DMF^{450}
1-PhCH(OTs)-2-Ar-	1-Ar-	TBAFH, PhCHO, TsCl	^{451}
1-(1,3,5-Cl$_2$C$_3$N$_3$)-2-Me-	1-Me-	BuLi, 1,3,5-Cl$_3$C$_3$N$_3$	THF, 62%^{509}
1-(2-FC$_6$H$_4$)-2-Me-	1-Me-	BuLi, (1,2-F$_2$C$_6$H$_4$)Cr(CO)$_3$	Et$_2$O^{511}
1-(2,3-Cl$_2$C$_6$H$_3$)-2-Me-	1-Me-	BuLi, (1,2-Cl$_2$C$_6$H$_4$)Cr(CO)$_3$	Et$_2$O^{511}
1-(4-BrC$_6$F$_4$)-2-^{t}Bu-	1-^{t}Bu-	BuLi, C$_6$F$_5$Br	Et$_2$O, 49%^{496}
1-(3,6-Ar$_2$-2,4,5-C$_3$N$_3$)-2-Ph-	1-Ph-	BuLi, 3,6-Ar$_2$-4-O$^-$-1,2,4-HC$_3$N$_3^+$, Me$_2$NCOCl	THF, 21–39%^{274}
1-(3,6-Ph$_2$-2-HO-2,4,5-HC$_3$N$_3$)-2-Ph-	1-Ph-	BuLi, 3,6-Ph$_2$-4-O$^-$-1,2,4-HC$_3$N$_3^+$	THF, 11%^{274}
1-(2-ArCO-3-MeCO-4-Ar-2,3,5-C$_2$N$_3$)-2-Ph-	1-Ph-	BuLi, 3,6-Ar$_2$-4-O$^-$-1,2,4-HC$_3$N$_3^+$, MeCOCl	THF, 41–67%^{274}
1-(2-ArCO-3-MeCO-4-(2-C$_4$H$_3$O)-2,3,5-C$_2$N$_3$)-2-Ph-	1-Ph-	BuLi, 3-(2-C$_4$H$_3$O)-6-Ar-4-O$^-$-1,2,4-HC$_3$N$_3^+$, MeCOCl	THF, 21%^{274}
1-Ar(RR′N)(R″O)C-2-Ph-	2-Ph-	BuLi, 1,2-C$_6$H$_4$(CO)$_2$NCH$_2$CH$_2$Br	Toluene, 63%^{510}
1-(PhCH$_2$)$_2$NCH$_2$CH$_2$-2-Ph-	1-Ph-	BuLi, (PhCH$_2$)$_2$NCH$_2$CH$_2$Cl	C$_6$H$_6$, 98%^{483}
1-PhCO-2-Ph-	1-Ph-	BuLi, PhCOCl	Et$_2$O, 62%^{505}
1,1′-(1,4-C$_6$F$_4$)-2,2′-Ph$_2$-	1-Ph-	BuLi, C$_6$F$_6$	Et$_2$O, 69%^{512}
1-(4-BrC$_6$F$_4$)-2-Ph-	1-Ph-	BuLi, C$_6$F$_5$Br	Et$_2$O, 85%^{496}
1-Ph-2-(2-C$_5$H$_4$N)-	1-(2-C$_5$H$_4$N)-	BuLi, CuCl, PhI	DME, pyridine, 72%^{317}
1,2-(2-C$_5$H$_4$N)$_2$-		BuLi, CuCl, 2-BrC$_5$H$_4$N	DME, pyridine, 80%^{317}
1-(4-NO$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 4-NO$_2$C$_6$H$_4$F	DMF, 20 min, 91%^{513}
1-(4-NO$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	KO^{t}Bu, 4-NO$_2$C$_6$H$_4$F	DMF, 40 min, 83%^{513}
1-(2-F-4-NO$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 3-NO$_2$C$_6$H$_4$F	DMF, 16 h, 12%^{513}
1-(3-HO-4-NO$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 2-NO$_2$C$_6$H$_4$F	DMF, 4 h, 5%^{513}
1-(2,4-(NO$_2$)$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 2,4-(NO$_2$)$_2$C$_6$H$_4$F	DMF, 9 h, 10%^{513}
1-(6-F-2,4-(NO$_2$)$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 2,4-(NO$_2$)$_2$C$_6$H$_4$F	DMF, 9 h, 3%^{513}
1-(2,4-(NO$_2$)$_2$C$_6$H$_4$)-2-Ph-	1-Ph-	KO^{t}Bu, 2,4-(NO$_2$)$_2$C$_6$H$_4$F	DMF, 9 h, 28%^{513}
1-(4-NCC$_6$H$_4$)-2-Ph-	1-Ph-	NaH, 4-NCC$_6$H$_4$F	DMF, 3 h, 42%^{513}
1-(4-NCC$_6$H$_4$)-2-Ph-	1-Ph-	KO^{t}Bu, 4-NCC$_6$H$_4$F	DMF, 10 h, 20%^{513}
1-(4-NO$_2$C$_6$H$_4$)-2-Ar-	1-Ar-	NaH, 4-NO$_2$C$_6$H$_4$F	DMF, 20–40 min, 63–90%^{513}
1-(4-NO$_2$C$_6$H$_4$)-2-Ar-	1-Ar-	KO^{t}Bu, 4-NO$_2$C$_6$H$_4$F	DMF, 15–40 min, 51–91%^{513}
1-(MeCH=C=CEt)-		BuLi, Br$_2$, EtCCEt	30%^{514}
1-(EtCH=C=CPr)-		BuLi, Br$_2$, PrCCPr	^{514,515}
1-(H$_2$C=C=CPh)-		BuLi, Br$_2$, MeCCPh	6%^{514,515}
1-^{n}Bu-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, ^{n}BuBr	C$_6$H$_6$/Et$_2$O, 1 d, 80%^{309,310}
1-PhCH$_2$-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, PhCH$_2$Br	C$_6$H$_6$/Et$_2$O, 1 d, 61%^{310}
1-ClCH$_2$(1,2-C$_6$H$_4$)CH$_2$-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, 1,2-(ClCH$_2$)$_2$C$_6$H$_4$	THF, 94%^{516}
1-BrCH$_2$(1,2-C$_6$H$_4$)CH$_2$-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, 1,2-(BrCH$_2$)$_2$C$_6$H$_4$	THF, 86%^{516}
1-CH$_2$=CHCH$_2$-2-^{t}BuMe$_2$Si	1-^{t}BuMe$_2$Si-	BuLi, CH$_2$=CHCH$_2$Br	C$_6$H$_6$/Et$_2$O, 1 d, 79%^{310}

(Continued)

Table 21 (Continued)

Derivatives of 1,2-C$_2$B$_{10}$H$_{12}$	*1,2-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-CH$_2$=CHCH$_2$CH$_2$-2-^{t}BuMe$_2$Si	1-^{t}BuMe$_2$Si-	BuLi, CH$_2$=CHCH$_2$CH$_2$Br	C$_6$H$_6$/Et$_2$O, 1 d, 81%[310]
1-HOCH$_2$CH$_2$CH$_2$-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, C$_3$H$_6$O	C$_6$H$_6$/Et$_2$O, 1 d, 84%[310] 95%[421]
1-Me$_3$SiCC-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, Me$_3$SiCCBr	C$_6$H$_6$/Et$_2$O, 1 d, 74%[311]
1-Me-2-^{t}BuSiMe$_2$-	1-^{t}BuMe$_2$Si-	BuLi, MeI	C$_6$H$_6$/Et$_2$O, 1 d, 86%[309]
1-MeO$_2$C-2-^{t}BuSiMe$_2$-	1-^{t}BuMe$_2$Si-	BuLi, ClCO$_2$Me	C$_6$H$_6$/Et$_2$O, 1 d, 93%[309,310]
1-(2,6-(2′-py)$_2$C$_5$H$_2$N)-2-^{t}BuSiMe$_2$-	1-^{t}BuMe$_2$Si-	BuLi, 4-Cl-2,6- (2-py)$_2$C$_5$H$_2$N	60%[282]
1-CH$_2$=CHCH$_2$-2-EtOCH$_2$O-	1-EtOCH$_2$O-	BuLi, CH$_2$=CHCH$_2$I	THF[520]
1-PhCHC$_5$H$_5$-2-HS-	1-HS	BuLi, C$_4$H$_4$C=CHPh	THF, 85%[517]
1-HO$_2$C-2-^{t}BuO$_2$CN(H)^{t}BuO$_2$CN-	1-^{t}BuO$_2$CN(H)^{t}BuO$_2$CN-	BuLi, CO$_2$	Et$_2$O, THF[518]
1-HO$_2$C-2-^{t}BuO$_2$CNH-	1-^{t}BuO$_2$CNH-	BuLi, CO$_2$	Et$_2$O, 96%[486,503]
1-HO$_2$C-3-PhCONH-	3-PhCONH-	BuLi, CO$_2$	Et$_2$O, 85%[486]
1-HO$_2$CCH$_2$-2-Me-3-RCONH-	1-Me-3-RCONH-	NaNH$_2$, BrCH$_2$CO$_2$Na	NH$_3$, 89–90%[279]
1-HO$_2$CCH$_2$-2-Ph-3-RCONH-	1-Ph-3-RCONH-	NaNH$_2$, BrCH$_2$CO$_2$Na	NH$_3$, 94%[279]
1-HO$_2$CCH$_2$-3-RCONH-	3-RCONH-	NaNH$_2$, BrCH$_2$CO$_2$Na	NH$_3$, 85–95%[279]
C–N bond formation			
1-^{t}BuO$_2$CN(H)^{t}BuO$_2$CN-		BuLi, ^{t}BuOCON=NCO$_2{}^t$Bu	84%[518]
1-N$_3$-2-Me-	1-Me-	BuLi, TosN$_3$	THF, 54%[519]
1-N$_3$-2-^{t}BuMe$_2$Si-	1-^{t}BuMe$_2$Si-	BuLi, TosN$_3$	THF, 59%[518]
C–O bond formation			
1-HO-2-^{t}Bu-	1-^{t}Bu-	BuLi, (PhCO$_2$)$_2$	Toluene, 81%[418]
1-HO-2-C$_3$H$_5$-	1-C$_3$H$_5$-	BuLi, (PhCO$_2$)$_2$	Toluene[418]
1-HO-2-(4-MeOC$_6$H$_4$)-	1-(4-MeOC$_6$H$_4$)-	BuLi, (PhCO$_2$)$_2$	Toluene, 79%[418]
1-Me$_3$SiO-		BuLi, (Me$_3$SiO)$_2$	THF, 77%[520]
1-HO-2-Ph-	1-Ph-	BuLi, (PhCO$_2$)$_2$	Toluene, 21%[521]
1-HO-2-Me$_3$Si-	1-Me$_3$Si-	BuLi, (PhCO$_2$)$_2$	Toluene, 30%[418]
C–F bond formation			
1-F-2-Ph-	1-Ph-	BuLi, NFBS	Et$_2$O, 24%[521]
C–I bond formation			
1-IPh(OAc)-2-Me$_3$Si-	1-Me$_3$Si-	BuLi, IPh(OAc)$_2$	Et$_2$O, 46%[522]
C–B bond formation			
1-IBC$_4$Et$_4$B-		BuLi, IBC$_4$Et$_4$BI	Toluene, 76%[150]
1,2-(H$_3$B)$_2$-$^{2-}$ 2Li$^+$		BuLi, Me$_3$NBH$_3$	DME, 90%[523]
1,2-(H$_2$XB)$_2$-$^{2-}$ 2Li$^+$		BuLi, Me$_3$NBH$_2$X	DME, 73–95%[523]
1-C$_9$H$_7$(^{i}Pr$_2$N)B-		BuLi, C$_9$H$_7$(^{i}Pr$_2$N)BCl, C$_5$H$_6$	Et$_2$O, toluene, 65%[524]
1-H$_3$B-2-Ph-$^-$ Li$^+$	1-Ph	BuLi, Me$_3$NBH$_3$	DME, 86%[523]
1-H$_2$XB-2-Ph-$^-$ Li$^+$	1-Ph	BuLi, Me$_3$NBH$_2$X	DME, 42–89%[523]
1-Ph$_2$B-2-Me-	1-Me-	BuLi, Ph$_2$BCl	Ether, 72%[271]
1-H$_3$B-2-Me-$^-$ Li$^+$	1-Me	BuLi, Me$_3$NBH$_3$	DME, 61%[523]
1-(HO$_2$C)H$_2$B-2-Me-$^-$ Li$^+$	1-Me	BuLi, Me$_3$NBH$_2$CO$_2$H	DME, 36%[523]
C–P bond formation			
1-^{i}Pr$_2$P-2-Me-	1-Me-	BuLi, ^{i}Pr$_2$PCl	Et$_2$O, 64%[525]
1,2-(^{i}Pr$_2$P)$_2$-		BuLi, ^{i}Pr$_2$PCl	Et$_2$O, 61%[525]
1-^{i}Pr$_2$P-2-Ph-	1-Ph-	BuLi, ^{i}Pr$_2$PCl	Et$_2$O, 85%[526]
1,2-(ClMeO(O)P)$_2$-		BuLi, MeOP(O)Cl$_2$	Ether, toluene, 43%[527]

(*Continued*)

Table 21 (Continued)

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-Ph_2P-		BuLi, Ph_2PCl	Et_2O, 53%[528] DME, 74%[315]
1-R_2P-2-Me-	1-Me-	BuLi, R_2PCl	Et_2O, toluene, 64–78%[247]
1-$C_9H_7(^iPr_2N)P$-		BuLi, $C_9H_7(^iPr_2N)PCl$, Me_3NHCl	Toluene, Et_2O, 57%[529]
1,2-$(R_2P)_2$-		BuLi, R_2PCl	Et_2O, 64–77%[247]
1,2-$(Ph_2P)_2$-8,9,10,12-Et_4-	8,9,10,12-Et_4-	BuLi, Ph_2PCl	Benzene, Et_2O, 93%[238]
1-Et_2P-		BuLi, Et_2PCl	DME, toluene, 54%[530]
1-$^iPr_2P$-		BuLi, $^iPr_2PCl$	DME, toluene, 42%[530]
1-Et_2P-2-Ph-	1-Ph-	BuLi, Et_2PCl	Et_2O, 82%[530]
1-PhPCl-2-Ph-	1-Ph-	BuLi, $PhPCl_2$	Et_2O, 15%[530] benzene, 41%[531]
1-Ph_2P-2-Me_2NCH_2-	1-Me_2NCH_2-	BuLi, Ph_2PCl	THF, 65%[532]
1-R_2P-		BuLi, R_2PCl ($R = Me,OEt,Ph$)	THF, 80–85%[533,534]
1-Ph_2P-2-Me-	1-Me-	BuLi, Ph_2PCl	Et_2O, 91%[535]
1,2-$(PhPCl)_2$-		BuLi, $PhPCl_2$	Et_2O, 56%[531]
1-PhPCl-		BuLi, $PhPCl_2$	Benzene, 60%[531]
C–S bond formation			
1,2-$(RS)_2$-		BuLi, RSSR	Et_2O, 68–71%[262]
1-HS-2-Et_2NCH_2-	1-Et_2NCH_2-	BuLi, S	C_6H_6, Et_2O, 82%[499]
1-HS-		BuLi, S	DME, 91%[315]
1-HS-2-$BrCH_2$-	1-$BrCH_2$-	$^iPr_2NLi$, S	THF, 80%[490,491]
1-RS-2-$^tBuMe_2Si$-	1-$^tBuMe_2Si$-	BuLi, RSSR	Et_2O, 78–80%[262]
1-PhS-2-Me-	1-Me-	BuLi, PhSSPh	Et_2O, 76%[536]
1,2-$(PhS)_2$-		BuLi, PhSSPh	Et_2O, 76%[537]
1,2-$(HS)_2$-8,9,10,12-Et_4-	8,9,10,12-Et_4-	BuLi, S	Benzene, Et_2O, 93%[238]
1-Ph_2P-2-RS-	1-RS-	BuLi, Ph_2PCl	Et_2O, 72–78%[226]
1-HS-2-$(2\text{-}C_5H_4N)$-	1-$(2\text{-}C_5H_4N)$-	BuLi, S	Et_2O, 85%[538]
1-HS-2-Ph-	1-Ph-	NaH, S	DME, 16%[521]
1-HS-2-Me-	1-Me-	BuLi, S	THF, 70%[226]
C–Si bond formation			
1-Me_3Si-		BuLi, Me_3SiCl	THF, 86%,[316,539,540] 96%,[418]82%[541]
1-$C_5H_5Me_2Si$-		BuLi, $C_5H_5Me_2SiCl$	Et_2O, Toluene, 79%[542,543]
1-$^tBuMe_2Si$-		BuLi, $^tBuMe_2SiCl$	C_6H_6/Et_2O, 1 d, 99%[309]
1-$C_9H_7Me_2Si$-		BuLi, $C_9H_7Me_2SiCl$	Et_2O, toluene, 77%[544]
1-$Me_4C_5Me_2Si^-$ $[Li(0.5OEt_2)]^+$		BuLi, $Me_5C_5SiMe_2Cl$	Et_2O, toluene, 82%[545]
1-$Me_2N(CH_2)_2C_9H_6Me_2Si^-$ $[Li(OEt_2)]^+$		BuLi, $Me_2N(CH_2)_2C_9H_6Me_2SiCl$	Et_2O, toluene, 79%[546]
1-$MeO(CH_2)_2C_9H_6Me_2Si^-$ $[Li(OEt_2)]^+$		BuLi, $MeO(CH_2)_2C_9H_6Me_2SiCl$	Et_2O, toluene, 88%[547]
1-$(2,6\text{-}^iPr_2C_6H_3)NHSiMe_2$-		BuLi, $2,6\text{-}^iPr_2C_6H_3NHSiMe_2Cl$	THF, 96%[551]
1-Me_3Si-2-Ph-	1-Ph-	BuLi, Me_3SiCl	Benzene, 90%[548]

(Continued)

Table 21 (Continued)

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-^{t}BuMe$_2$Si-2-Ph-	1-Ph-	BuLi, ^{t}BuMe$_2$SiCl	Benzene, 31%[549]
1-Me$_2$SiH-2-Ph-	1-Ph-	BuLi, HSiMe$_2$Cl	THF, 96%[550]
1-^{t}BuSiMe$_2$-9,12-Me$_2$-	9,12-Me$_2$-	BuLi, ^{t}BuMe$_2$SiCl	C_6H_6/Et_2O, 1 d, 99%[313]
1-^{t}BuSiMe$_2$-9,12-Ph$_2$-	9,12-Ph$_2$-	BuLi, ^{t}BuMe$_2$SiCl	THF, 98%[314]
1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	9,12-Ar$_2$-	BuLi, ^{t}BuMe$_2$SiCl	THF, 98%[314]
1-^{t}BuNHSiMe$_2$-2-Ph-	1-Ph-	BuLi, ^{t}BuNHSiMe$_2$Cl	THF, 92%[551]
1-Me$_2$SiH-2-R$_2$P-	1-R$_2$P-	BuLi, Me$_2$SiHCl	THF, 82–92%[533,534]
C–Se bond formation			
1-HSe-		BuLi, Se	DME, 40%[552]
Cyclic bond formation			
1,2-(CH$_2$)$_3$-	1-I(CH$_2$)$_3$-	RLi	THF[421]
1,2-PhCHOCH$_2$-	1-BrCH$_2$-	^{i}Pr$_2$NLi, PhCHO	THF, 80%[490,491]
1,2-Ph$_2$COCH$_2$-	1-BrCH$_2$-	^{i}Pr$_2$NLi, Ph$_2$CO	THF, 52%[490,491]
1,2-(4-BrC$_6$H$_4$)CHOCH$_2$-	1-BrCH$_2$-	^{i}Pr$_2$NLi, 4-BrC$_6$H$_4$CHO	THF, 90%[490,491]
1,2-(CH$_2$)$_5$COCH$_2$-	1-BrCH$_2$-	^{i}Pr$_2$NLi, (CH$_2$)$_5$C=O	THF, 73%[490,491]
1,2-MeC=CPh-		BuLi, Br$_2$, MeCCPh	18%[514,515]
1,2-CH(CH=CH)$_2$CH-		BuLi, Br$_2$, C$_6$H$_6$	8%
1,2-CH(C$_8$H$_6$)CH-		BuLi, Br$_2$, C$_{10}$H$_8$	15%[320]
1,2-CH=CHCH=CH-		BuLi, Br$_2$, C$_4$H$_4$S	19%[321]
1,2-CMe=CHCH=CMe-		BuLi, Br$_2$, 2,5-Me$_2$C$_4$H$_2$S	15%[321]
1,2-CRSR′CR″H-		BuLi, Br$_2$, 2,5-R$_2$C$_4$H$_2$S	14%[321]
1,2-CRR′-O-CRR′-		BuLi, Br$_2$, 2,5-R$_2$C$_4$H$_2$O	321
1,2-CROR′CR″H-		BuLi, Br$_2$, 2,5-R$_2$C$_4$H$_2$O	321
1,2-CH$_2$(1,2-C$_6$H$_4$)CH$_2$-		BuLi, 1,2-(BrCH$_2$)$_2$C$_6$H$_4$	Et$_2$O, toluene, 95%[553]
1,2-CH$_2$(C$_6$H$_4$C$_6$H$_4$)CH$_2$-		BuLi, BrCH$_2$-1,2-C$_6$H$_4$-1,2-C$_6$H$_4$CH$_2$Br	Et$_2$O, toluene, 90%[553]
1,2-CH$_2$(1,8-C$_{10}$H$_6$)CH$_2$-		BuLi, 1,8-(ClCH$_2$)$_2$C$_{10}$H$_6$	Et$_2$O, toluene, 75%[553]
1,2-RR′CCHR″CR‴(OH)-		TBAF, RR′C=CR″COR‴	THF, 40–90%[318]
1,2-RR′CCHR″CR‴(OH)-	1-Me$_3$Si-	TBAF, RR′C=CR″COR‴	THF, 35–83%[539,540]
1,2-(CH$_2$)$_2$CH(OH)-	1-HCO(CH$_2$)$_2$-	TBAF	THF, 49%[318]
1,2-(CH$_2$)$_3$CH(OH)-	1-HCO(CH$_2$)$_3$-	TBAF	THF, 99%[318]
1,2-(CH$_2$)$_4$CH(OH)-	1-HCO(CH$_2$)$_4$-	TBAF	THF, 99%[318]
1,2-(CH$_2$)$_2$CMe(OH)-	1-MeCO(CH$_2$)$_2$-	TBAF	THF, 79%[318]
1,2-(CH$_2$)$_3$CMe(OH)-	1-MeCO(CH$_2$)$_3$-	TBAF	THF, 82%[318]
1,2-Me(HO)CH(CH$_2$)$_4$-	1-MeCO(CH$_2$)$_4$-	TBAF	THF, 35%[318]
1,2-C(OSiMe$_2$^{t}Bu)RNR′(CH$_2$)$_2$-	1-^{t}BuMe$_2$Si-	BuLi, C$_6$H$_4$(CO)$_2$N(CH$_2$)$_2$Br	Benzene, Et$_2$O, 97%[234]
1,2-C(OSiMe$_2$^{t}Bu)RNR′(CH$_2$)$_3$-	1-^{t}BuMe$_2$Si-	BuLi, C$_6$H$_4$(CO)$_2$N(CH$_2$)$_3$Br	Benzene, Et$_2$O, 95%[234]
1,2-SiEt$_2$SiEt$_2$-		BuLi, Et$_2$SiClSiClEt$_2$	Et$_2$O, 53%[554]
1,2-SiMe$_2$SiMe$_2$-		BuLi, Me$_2$SiClSiClMe$_2$	THF, 35%[555]
1,2-SiMe$_2$SiMe$_2$-	1,1′-SiMe$_2$SiMe$_2$-	BuLi, (SiMe$_2$Cl)$_2$	THF, 78%[556]
Multiple cage assemblies			
1,1′-(CH$_2$RCH$_2$)-		BuLi, ClCH$_2$RCH$_2$Cl	DME, 54–64%[223]
1,1′-CH$_2$RCH$_2$-2,2′-Me$_2$-	1-Me-	BuLi, ICH$_2$RCH$_2$I	THF[244]
1,1′-(CH$_2$-2,6-C$_5$H$_3$N-CH$_2$)-2,2′-Ph$_2$-	1-Ph-	BuLi, 1,3-(ClCH$_2$)$_2$C$_6$H$_4$	Et$_2$O, 79%[557]
1,1′-COC$_6$H$_4$CO-2,2′-Me$_2$-	1-Me-	BuLi, 1,4-(ClCO)$_2$C$_6$H$_4$	Et$_2$O, 53%[271]
1,1′-CO-1,7-CB$_{10}$H$_{10}$C-CO-		BuLi, 1,7-(ClCO)$_2$-1,7-C$_2$B$_{10}$H$_{10}$	Et$_2$O[271]

(*Continued*)

Table 21 (Continued)

Derivatives of 1,2-C$_2$B$_{10}$H$_{12}$	*1,2-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1,1′,2,2′-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)$_2$-	1,1′-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)-	BuLi, 1,3-(BrCH$_2$)$_2$C$_6$H$_4$	THF, 9%[312,313]
1,1′-CH$_2$(5-Br-1,3-C$_6$H$_3$)CH$_2$-2,2′-Me$_2$-	1-Me-	BuLi, 5-Br-1,3-(BrCH$_2$)$_2$C$_6$H$_3$	LiI, THF, 63%[431,558]
1,1′-CO-1,7-CB$_{10}$H$_{10}$C-CO-2,2′-Me$_2$-	1-Me-	BuLi, 1,7-(ClCO)$_2$-1,7-C$_2$B$_{10}$H$_{10}$	Et$_2$O[271]
1,1′-(1,4-C$_6$H$_4$)-2,2′-Me$_2$-	1-Me-	BuLi, (1,4-F$_2$C$_6$H$_4$)Cr(CO)$_3$	THF, 9%[511]
1,1′-(CH$_2$RCH$_2$)-2,2′-Me$_2$-	1-Me-	BuLi, ClCH$_2$RCH$_2$Cl	DME, 68–77%[223]
1,1′-(CH$_2$RCH$_2$)-2,2′-Ph$_2$-	1-Ph-	BuLi, ClCH$_2$RCH$_2$Cl	DME, 63–72%[223]
1,1′-(1,4-C$_6$H$_4$-SO$_2$-1,4-C$_6$H$_4$)-		BuLi, ClC$_6$H$_4$SO$_2$C$_6$H$_4$Cl	DME, 56%[223]
1,1′-(1,4-C$_6$H$_4$-SO$_2$-1,4-C$_6$H$_4$)-2,2′-Me$_2$-	1-Me-	BuLi, ClC$_6$H$_4$SO$_2$C$_6$H$_4$Cl	DME, 67%[223]
1,1′-(1,4-C$_6$H$_4$-SO$_2$-1,4-C$_6$H$_4$)-2,2′-Ph$_2$-	1-Ph-	BuLi, ClC$_6$H$_4$SO$_2$C$_6$H$_4$Cl	DME, 49%[223]
1,1′-CH$_2$C$_6$H$_4$CH$_2$-2,2′-(1,3-C$_6$H$_4$)-	1,1′-(1,3-C$_6$H$_4$)-	NaH, 1,3-(BrCH$_2$)$_2$C$_6$H$_4$	77%[460]
1,1′,1″,2,2′,2″-(C$_3$H$_6$)$_3$-	1,1′-(C$_3$H$_6$CB$_{10}$H$_{10}$CC$_3$H$_6$)-	BuLi, Br(CH$_2$)$_3$Br	THF, 1 d, 74%[312,313]
1,1′,1″,1‴,2,2′,2″,2‴-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)$_4$-	1,1′-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)-	BuLi, 1,3-(BrCH$_2$)$_2$C$_6$H$_4$	THF, 38%[312,313]
1,1′-PhB-2,2′-Me$_2$-	1-Me-	BuLi, PhBCl$_2$	Et$_2$O, 64%[271]
1,1′-S$_3$-1′1-Ph$_2$-	1-Ph-	NaH, S	DME, 4%[521]
1,1′-PhP-2,2′-Ph$_2$-	1-Ph-	BuLi, PhPCl$_2$	Et$_2$O, 91%[559]
1,1′-SiMe$_2$SiMe$_2$-		BuLi, (SiMe$_2$Cl)$_2$	THF, 90%[556]
1,1′-SiMe$_2$SiMe$_2$-2,2′-Me$_2$-	1-Me-	BuLi, (SiMe$_2$Cl)$_2$	Benzene, 96%[556]
1,1′-SiMe$_2$SiMe$_2$-2,2′-Ph$_2$-	1-Ph-	BuLi, (SiMe$_2$Cl)$_2$	Benzene, 94%[556]
1,1′-(CH$_2$C$_6$H$_4$CH$_2$)-2,2′-(^{t}BuSiMe$_2$)$_2$- 74%[242,309,309,311]	1-^{t}BuSiMe$_2$-	BuLi, 1,2-(BrCH$_2$)$_2$C$_6$H$_4$	C$_6$H$_6$/Et$_2$O, 1 d,
1,1′-(CH$_2$-2,6-C$_5$H$_3$N-CH$_2$)-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, 2,6-(BrCH$_2$)$_2$C$_5$H$_3$N	C$_6$H$_6$/Et$_2$O, 30%[313]
1,1′-(C$_3$H$_6$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Me$_4$-	1-^{t}BuSiMe$_2$-9,12-Me$_2$-	BuLi, Br(CH$_2$)$_3$Br	C$_6$H$_6$/Et$_2$O, 1 d, 51%[313]
1,1′-(C$_4$H$_8$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ph$_4$-	1-^{t}BuSiMe$_2$-9,12-Ph$_2$-	BuLi, Br(CH$_2$)$_4$Br	THF, 82%[314]
1,1′-(C$_3$H$_6$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ar$_4$-	1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	BuLi, Br(CH$_2$)$_3$Br	THF, 58%[314]
1,1′-(C$_6$H$_{12}$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ar$_4$-	1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	BuLi, Br(CH$_2$)$_6$Br	THF, 81%[314]
1,1′-(C$_8$H$_{16}$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ar$_4$-	1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	BuLi, Br(CH$_2$)$_8$Br	THF, 90%[314]
1,1′-(C$_{14}$H$_{12}$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ar$_4$-	1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	BuLi, BrCH$_2$(C$_6$H$_4$C$_6$H$_4$)CH$_2$Br	THF, 80%[314]
1,1′,2,2′-(C$_8$H$_{16}$)$_2$-9,9′,12,12′-Ar$_4$-	1,1′-(C$_8$H$_{16}$)-9,9′,12,12′-Ar$_4$-	BuLi, Br(CH$_2$)$_8$Br	THF, 71%[314]
1,1′-(CH$_2$C$_5$H$_3$NCH$_2$)-2,2′-(^{t}BuSiMe$_2$)$_2$-9,9′,12,12′-Ar$_4$-	1-^{t}BuSiMe$_2$-9,12-Ar$_2$-	BuLi, 2,6-(BrCH$_2$)$_2$C$_5$H$_3$N	THF, 81%[314]
1,1′-(C$_3$H$_6$)-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, Br(CH$_2$)$_3$Br	C$_6$H$_6$/Et$_2$O, 1 d, 61%[220,310]
1,1′-(C$_4$H$_8$)-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, Br(CH$_2$)$_4$Br	C$_6$H$_6$/Et$_2$O, 1 d, 70%[220,309]
1,1′-(C$_5$H$_{10}$)-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, Br(CH$_2$)$_4$Br	C$_6$H$_6$/Et$_2$O, 1 d, 53%[220]
1,1′-C$_3$H$_6$CB$_{10}$H$_{10}$CC$_3$H$_6$-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, 1,2-(TsOC$_3$H$_6$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$	C$_6$H$_6$/Et$_2$O, 1 d, 75%[309,311]
1,1′-CH$_2$CH(C$_2$H$_4$Ph)CH$_2$-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, PhCH$_2$CH$_2$CH(CH$_2$OTs)$_2$	C$_6$H$_6$/Et$_2$O, 1 d, 75%[310]
1,1′-CH$_2$CH(C$_2$H$_4$Ph)CH$_2$-2,2′-(^{t}BuSiMe$_2$)$_2$-	1-^{t}BuSiMe$_2$-	BuLi, TsN(CH$_2$CH$_2$OTs)$_2$	C$_6$H$_6$/Et$_2$O, 1 d, 17%[220]
1,1′-SiMe$_2$CB$_8$H$_8$CSiMe$_2$-2,2′-Me$_2$-	1-BrCH$_2$-	Mg, 1,10-(Me$_2$SiCl)$_2$-1,10-C$_2$B$_8$H$_8$	THF, reflux, 6 h, 61%[560]

(Continued)

Table 21 (Continued)

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1,1′-(1,3,5-ClC_3N_3)-		BuLi, 1,3,5-$Cl_3C_3N_3$	THF, 65%[509]
1,1′-(1,3,5-ClC_3N_3)-2,2′-Me_2-	1-Me-	BuLi, 1,3,5-$Cl_3C_3N_3$	THF, 69%[509]
1-(1′-1′,2′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 18%[561]
1-(3′-1′,2′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 8%[561]
1-(4′-1′,2′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 5%[561]
1,1′,2,2′-$(PhP)_2$-		BuLi, $PhPCl_2$	Et_2O, toluene, 53%[247]
1,1′-PhP-2,2′-Me_2-	1-Me-	BuLi, $PhPCl_2$	Et_2O, 77%[247]
1,1′-Se_2-		BuLi, Se	DME, 28%[552]
1,1′,1″-(1,3,5-C_3N_3)-		BuLi, 1,3,5-$Cl_3C_3N_3$	THF, 77%[509]
1,1′,1″-(1,3,5-C_3N_3)-2,2′,2″-Me_3-	1-Me-	BuLi, 1,3,5-$Cl_3C_3N_3$	THF, 81%[509]
1,1′,1″-(1,3,5-C_3N_3)-2,2′,2″-Ph_3-	1-Ph-	BuLi, 1,3,5-$Cl_3C_3N_3$	THF, 78%[509]
1,1′,1″,1‴,2,2′,2″,2‴-$(C_3H_6)_4$-	1,1′-(C_3H_6)-	BuLi, $Br(CH_2)_3Br$	THF, 87%[312,313]
1,1′,1″,1‴,2,2′,2″,2‴-$(C_3H_6)_4$-9,9′,9″,9‴,12,12′,12″,12‴-Me_8-	1,1′-(C_3H_6)-9,9′,12,12′-Me_4-	BuLi, $Br(CH_2)_3Br$	THF, 51%[313]
1,1′,1″,1‴,2,2′,2″,2‴-$(C_4H_8)_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ph_8-	1,1′-(C_4H_8)-9,9′,12,12′-Ph_4-	BuLi, $Br(CH_2)_4Br$	THF, 79%[314]
1,1′,1″,1‴,1⁗,1⁗′,2,2′,2″,2‴,2⁗,2⁗′-$(C_4H_8)_6$-9,9′,9″,9‴,9⁗,9⁗′,12,12′,12″,12‴,12⁗,12⁗′-Ph_{12}-	1,1′-(C_4H_8)-9,9′,12,12′-Ph_4-	BuLi, $Br(CH_2)_4Br$	THF[314]
1,1′,1″,1‴,2,2′,2″,2‴-$(C_3H_6)_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ar_8-	1,1′-(C_3H_6)-9,9′,12,12′-Ar_4-	BuLi, $Br(CH_2)_3Br$	THF, 69%[314]
1,1′,1″,1‴,2,2′,2″,2‴-$(C_8H_{16})_4$-9,9′,9″,9⁗,12,12′,12″,12‴-Ar_8-	1,1′-(C_8H_{16})-9,9′,12,12′-Ar_4-	BuLi, $Br(CH_2)_8Br$	THF, 9%[314]
1,1′,1″,1‴,2,2′,2″,2‴-$(CH_2C_5H_3NCH_2)_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ar_8-	1,1′-$(CH_2C_5H_3NCH_2)$-9,9′,12,12′-Ar_4-	BuLi, 2,6-$(BrCH_2)_2C_5H_3N$	THF, 10%[314]
1,1′,1″,1‴-$Si(C_2H_4SiMe_2)_4$-2,2′,2″,2‴-Ph_4-	1-Ph-	BuLi, $Si(C_2H_4SiMe_2Cl)_4$	Et_2O, toluene, 62%[550]
B–H to B–X conversions			
B–C bond formation			
8,9,10,12-Me_4-		MeI, CF_3SO_3H	Reflux, 4 d, 65%[562]
8,9,10,12-Et_4-		EtBr, $CH_2{=}CH_2$, $AlCl_3$	238
9-$ArCH_2$-		$ArCH_2X$, $AlCl_3$	CH_2Cl_2, 85–90%[563]
9(12)-$ArCH_2$-1-^iPr-	1-^iPr-	$ArCH_2X$, $AlCl_3$	CH_2Cl_2, 78–90%[563]
4,5,7,8,9,10,11,12-Me_8-		MeI, $AlCl_3$	Reflux, 50 h, 98%[243]
4,5,7,8,9,10,11,12-Me_8-		MeI, $(CF_3SO_2)O$	60%[243]
3,4,5,7,8,9,10,11,12-Me_9-	3-Me-	MeI, $AlCl_3$	Reflux, 2 d, 98%[564]
1,4,5,7,8,9,10,11,12-Me_9-	1-Me-	MeI, $AlCl_3$	Reflux, 50 h, 98%[243]
9,10,11,12-Me_4-1-(1′-(9′,10′,11′,12′-Me_4-1′,2′-$C_2B_{10}H_7$))-	1-(1′-(1′,2′-$C_2B_{10}H_{11}$))-	MeI, $AlCl_3$	97%[243]
3-(1′-1′,2′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 8%[561]
4-(1′-1′,2′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 5%[561]
B–N bond formation			
3-H_2N-		Na, NH_3, $KMnO_4$	84%[486]
3-H_2N-		Na, NH_3, $CuCl_2$	56%[424]
3-H_2N-1-^iPr-	1-^iPr-	Na, NH_3, $CuCl_2$	80%[237]
B–Br bond formation			
4-Br-8,9,10,12-Et_4-	8,9,10,12-Et_4-	Br_2, $AlCl_3$	81%[238]

(*Continued*)

Table 21 (Continued)

Derivatives of 1,2-$C_2B_{10}H_{12}$	*1,2-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
B–I bond formation			
9-I-		ICl, $AlCl_3$	CH_2Cl_2[507]
9-I-1,2-Ph_2-	1,2-Ph_2-	I_2, HNO_3, H_2SO_4	AcOH, 72%[565]
8-I-9,12-Et_2-	9,12-Et_2-	I_2, $AlCl_3$	79%[238]
4-I-8,9,10,12-Et_4-	8,9,10,12-Et_4-	I_2, $AlCl_3$	87%[238]
9,12-I_2-		I_2, $AlCl_3$	CH_2Cl_2, 14 h, 90%[566]
9,12-I_2-		ICl, $AlCl_3$	CH_2Cl_2, 4 h, 90%[566]
9,12-I_2-		I_2, HNO_3, H_2SO_4	AcOH, 80 °C, 82%[567]
9,12-I_2-1,2-Ph_2-	1,2-Ph_2-	I_2, HNO_3, H_2SO_4	AcOH, 50 °C, 48%[231]
3,6,9-I_3-	3,6-I_2-	I_2, $AlCl_3$	CH_2Cl_2, 6 h, 88%[470]
3,6,9,12-I_4-	3,6-I_2-	I_2, $AlCl_3$	CH_2Cl_2, 34 h, 77%[470]
3,9,12-I_3-	3-I-	I_2, $AlCl_3$	CH_2Cl_2, 34 h, 65%[470]
4,5,7,8,9,10,11,12-I_8-		ICl, CF_3SO_3H	120 °C, 66%[339]
3,4,5,7,8,9,10,11,12-I_9-	3-I-	ICl, CF_3SO_3H	90 °C, 3d, 94%[564]

Table 22 Structures of *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*-carborane) derivatives determined experimentally by X-ray diffraction unless otherwise stated with cage C(1)–C(2) bond lengths listed where possible

1,2-$C_2B_{10}H_{12}$ and derivatives	*C1–C2, solvate*
	1.620(3), 1,10-$C_{12}H_8N_2$[568]
	1.629(6), 1.630(6), HMPA[569]
	$(C_6H_4(OH)CH_2)_5$, CH_2Cl_2 1.626(5)[570]
	1.622, $(CH_2C_6H_4(OMe)_2)_3$[571]
	1.624(8)[572] (electron diffraction)
Derivatives with* exo *C–C bond	
1-(HO_2C)-	1.631(2)[573]
1-(2′-py)CH_2-	1.636(3)[235], 1.622(4)[453]
1-$C_{13}H_9CH_2$-	1.652(5), 1.682(5)[472]
1-$MeOCH_2$-	1.636(9)[230]
1-$(C_{19}H_{23}O_3)COCH_2CO_2(CH_2)_2$-	1.635, H_2O[436]
1-Ph_2PCH_2-	1.614(9)[420]
1-$C_6H_4(CO)_2NCH_2$-	1.652(4)[574]
1-$C_6H_4(CO)_2N(CH)_2$-	1.648(4)[575]
1-$C_6H_4(CO)_2N(CH_2)_3$-	1.637(4)[475]
1-$(PhCH_2)_2NCH_2CH_2$-	1.614(3)[483]
1-$PhCH_2NH_2CH_2CH_2$-$^+$ Cl^-	1.637(7)[483]
1-$PhMeC_8H_4NCCONMeCH_2$-	1.638(4)[576]
1-RCH_2-	1.655(1)[283,425]
1-(3-$NCC_6H_4OCH_2$)-	1.648(2)[434]
1-$Ph_2C{=}NCH_2$-	1.620(4)[475]
1-$Me_2C{=}NH^+CH_2$- 0.25$[W_{10}O_{32}]^{4-}$	1.642(8), 0.5H_2O, Me_2CO[577]
1-$^tBuOCON(H)N^tBuO_2C$-	1.668(6)[518]
1-$MeO_2CC(NHSO_2Ph)CH_2$-	1.657(4)[502]
1-$Me_2SB_{12}H_{10}SMeCH_2$-	1.655(4)[437]
1-$ArOCH_2$-	1.61(3)[428]
1-HO_2C-2-Me-	1.6694(17)[505]

(*Continued*)

Table 22 (Continued)

1,2-C$_2$B$_{10}$H$_{12}$ and derivatives	*C1–C2, solvate*
1-HO$_2$C-2-MeOCH$_2$-	1.656(2), 1.669(2)[492]
1,2-(HO$_2$C)$_2$-	1.651(3), 1.652(2), 1.653(2), 1.660(2)[578]
1-^{t}BuOCO(NC$_4$H$_4$)C$_2$H$_4$-2-Me-	1.6749(17)[495]
1-(C$_{10}$H$_{14}$N$_2$SO$_3$)CH$_2$-2-Me-	1.689(6), CH$_2$Cl$_2$[485]
1-C$_6$H$_4$(CO)$_2$NCH$_2$-2-Me-	1.671(3)[579]
1-C$_6$H$_4$(CO)$_2$NCH$_2$-2-PhCH$_2$O(CH$_2$)$_2$-	1.684(2)[446]
1,2-(C$_6$H$_4$(CO)$_2$NCH$_2$)$_2$-	1.700(2)[498]
1,2-(HOCH$_2$CH$_2$)$_2$-	1.684(3)[218]
1,2-(CF$_3$SO$_3$CH$_2$)$_2$-	1.682(2)[253]
1-HSCH$_2$CH$_2$-2-Me-	1.670(3)[501]
1-MeCH=CH-2-Me-	1.688(2)[488]
1-CH$_2$=CHCH=CH-2-Me-	1.6829(13)[495]
1-PhEtC=C(C$_6$H$_4$OCH$_2$CH$_2$Cl)-	1.674(3), 1.657(3)[277]
1-PhCH$^-$-2-PhCH$_2$-[K(18C6)THF$^+$]	2.416(3)[580]
1-Ph-	1.649(2)[581]
1-Ph-	1.640(5)[447]
1-Ph-	1.627(8) (electron diffraction)[447]
(4-EtO$_2$CHC(CH$_2$CH$_2$)$_2$NOCC$_6$H$_4$)-	1.635(7), 1.648(7)[438]
1-(2-py)-	1.632(3)[453]
1-(4-Br-2-py)-	1.639(5)[453]
1-(3-py)-	1.663(2)[453]
1-(2,6-(2′-py)$_2$C$_5$H$_2$N)-	1.649(1)[282,283]
1-((Me$_2$N)$_2$-1,3,5-C$_3$N$_3$)-	1.609(19)[509]
1-(2-(4-MeC$_6$H$_4$)CO-3-MeCO-4-(4-MeC$_6$H$_4$)-2,3,5-C$_2$N$_3$)-2-Ph-	1.695(3)[274]
1-Ph-2-Me-	1.695(5)[454]
1-(2,3-Cl$_2$C$_6$H$_3$)-2-Me-	1.706(5)[511]
1-(4-BrC$_6$F$_4$)-2-Me-	1.712(7)[496]
1-(4-BrC$_6$F$_4$)-2-^{t}Bu-	1.761(6)[496]
1-HO$_2$C-2-Ph-	1.678(3), 1.691(3)[505]
1-HO$_2$C-2-Ph-	1.705(2), H$_2$O[505]
1-PhCO-2-Ph-	1.695(3)[505]
1-Ar(RR′N)(R″O)C-2-Ph-	1.708(5)[510]
1-PhCC-2-Ph-	1.710(2)[458]
1,2-Ph$_2$-	1.733(4), 1.720(4)[582]
1-(3,6-(4-MeC$_6$H$_4$)$_2$-2,4,5-C$_3$N$_3$)-2-Ph-	1.709(3)[274]
1-(PhNMeCONMe-1,3-C$_6$H$_4$)-2-Ph-	1.727(5)[260]
1-(PhNMeCONMe-1,4-C$_6$H$_4$)-2-Ph-	1.747(5)[260]
1-(4-O$_2$NC$_6$H$_4$)-2-(3-O$_2$NC$_6$H$_4$)-	1.717(3)[457]
1,2-(3-O$_2$NC$_6$H$_4$)$_2$-	1.724(7)[457]
1-(4-BrC$_6$F$_4$)-2-Ph-	1.743(7), 1.736(8)[496]
1-(4-Cl-6-Me$_2$N-1,3,5-C$_3$N$_3$)-2-Me-	1.662[509]
1-C$_3$H$_5$-	1.675(3)[583]
1-C$_3$H$_5$-2-CH(OH)Ph-	1.691(4)[583]
Derivatives with* exo *C–B bond	
1-C$_9$H$_7$(^{i}Pr$_2$N)B-	1.668(5)[524]
1-IBC$_4$Et$_4$B-	1.687(2), 2 1,2-C$_2$B$_{10}$H$_{12}$[150]
Derivatives with* exo *C–N bond	
2-H$_2$N-1-Ph-	1.745(3), 1.765(3), 1.774(3), 1.785(3)[521]
2-H$_2$N-1-Ph-	1.853(8), 1.818(8), HMPA[521]
Derivatives with* exo *C–O bond	
2-HO-1-Ph-	1.723(2), 0.5H$_2$O[521]
2-O$^-$-1-Ph-[Ph$_3$PCH$_2$$^+$]	2.065(7)[521]
Derivatives with* exo *C–P bond	
1-Ph$_2$P-2-Me$_2$NCH$_2$-	1.689(3)[532]
1-^{i}Pr$_2$P-2-Ph-	1.769(4)[526]
1-^{i}Pr$_2$P-2-Me-	1.731(9)[525]
1-PhPCl-2-Ph-	1.716(2)[531]

(*Continued*)

Table 22 (Continued)

1,2-$C_2B_{10}H_{12}$ and derivatives	*C1–C2, solvate*
1,2-(PhPCl)$_2$-	1.702(3)[531]
1,2-(^{i}Pr$_2$P)$_2$-	1.719(3)[525]
1-Ph$_2$P-	1.666(9)[528]
1-Ph$_2$P-2-Me-	1.702(6)[535]
1-C$_9$H$_7$(^{i}Pr$_2$N)P-	1.653(4)[529]
1-C$_9$H$_6$(^{i}Pr$_2$N)P-$^-$ [Li(DME)$_3$]$^+$	1.650(3)[529]
1-Ph$_2$P-2-Ph-	1.737(3)[247]
1,2-(PhHP)$_2$-	1.683(2)[584]
Derivatives with* exo *C–S bond	
1-(2′-C$_5$H$_4$N)S-	1.643(3)[262]
1-PhS-2-Me-	1.708(4)[536]
1-Ph$_2$P-2-^{i}PrS-	1.747(5)[226]
1-HS-2-(2-C$_5$H$_4$N)-	1.730(3)[538]
1,2-(MeS)$_2$-	1.8033(18)[585]
1,2-(PhS)$_2$-	1.798(3)[537]
1-S$^-$-2-Me- [Ph$_3$PMe$^+$]	1.792(5)[586]
1-S$^-$-2-Ph- [PSH$^+$]	1.836(5)[587]
1,2-S$_2$-$^{2-}$ [NH$_2$Me$_2$$^+$]$_2$	1.844(7)[588]
Derivative with* exo *C–Br bond	
1-Ph-2-Br-	1.692(8)[589]
Derivatives with* exo *C–Si bond	
1-(2,6-^{i}Pr$_2$C$_6$H$_3$)NHSiMe$_2$-	1.653(4)[551]
1-ClCH$_2$(1,2-C$_6$H$_4$)CH$_2$-2-^{t}BuMe$_2$Si-	1.699(2)[516]
1-BrCH$_2$(1,2-C$_6$H$_4$)CH$_2$-2-^{t}BuMe$_2$Si-	1.697(4)[516]
1-Me$_3$Si-2-Ph-	1.708(4)[548]
1-^{t}BuMe$_2$Si-2-Ph-	1.745(6)[549]
1-Ph(MeCOCH$_2$)CHSiMe$_2$-2-HOMe$_2$Si-	1.724(5)[590]
B-substituted derivatives	
3-Ph-	1.626(3)[469] 1.6225(5)[591]
3-(Me$_3$PC$_3$H$_6$)-$^+$ Br$^-$	1.625, H_2O[592]
3-Me-1,2-Ph$_2$-	1.734(3)[231]
9-Me(O)C-	1.637(2)[593]
9-NC-	1.6289(19)[593]
9-(Ph$_5$C$_6$)-	1.621(5)[594]
1,12-Ph$_2$-	Not determined[452]
9,12-Ph$_2$-	1.621(4)[314]
9,12-(4-MeOC$_6$H$_4$)$_2$-	1.612(4)[314]
9,12-(4-HOC$_6$H$_4$)$_2$-	1.625(6), Et$_2$O[314]
9,12-(4-ClC$_6$H$_4$)$_2$-	1.611(6)[314]
9,12-(4-MeCOC$_6$H$_4$)$_2$-	1.637(9)[595]
9,12-(4-FC$_6$H$_4$)$_2$-	1.621(8), 1.617(8), 1.624(9), 1.600(9)[596]
9,12-(3,5-F$_2$C$_6$H$_3$)$_2$-	1.627(6)[596]
3-CN-	1.638(4)[424]
3-CHONH-	1.632(4)[424]
3-MeOC$_{10}$H$_6$CHMeCONH-1-Me-	1.619(6), 1.621(6)[597]
9-Ph$_2$PS-	1.621(4)[598]
3-Br-1-Ph-	1.671(6)[469]
3-I-	1.624(8)[599]
9-I-1,2-Ph$_2$-	1.724(4)[565]
9,12-I$_2$-	1.626(5)[567]
9,12-I$_2$-1,2-Ph$_2$-	1.733(8)[231]
8,9,10,12-F$_4$-	1.632(1)[600]
4,5,7,8,9,10,11,12-Me$_8$-	1.635(9)[243]
3,4,5,7,8,9,10,11,12-I$_9$-	1.637(14), EtOAc[564]
1-NCC$_3$H$_6$-4,5,7,8,9,10,11,12-Me$_8$-	1.662(5)[482]
1-ClC$_3$H$_6$-4,5,7,8,9,10,11,12-Me$_8$-	1.657(7)[482]

(*Continued*)

Table 22 (Continued)

1,2-C$_2$B$_{10}$H$_{12}$ and derivatives	*C1–C2, solvate*
Cyclic carboranes	
1,2-CH(4-NCC$_6$H$_4$)OCH$_2$-	1.578(8), 1.587(8)[491]
1,2-CMe=CPh-	1.618(3)[515]
1,2-CRMeCR′Ph-	1.610(2),1.613(2)[515]
1,2-CH(1,2-C$_6$H$_4$)$_2$CH-	1.612(11)[522,541]
1,2-CH(C$_5$H$_6$)CH-	1.618(2)[522,541]
1,2-CH$_2$CH=CHCH$_2$-	1.661(1), 1.662(1)[261]
1,2-CR=CRCH=CH-	1.650(3)[321]
1,2-CH=CHCH=CH-	1.654(3), 1.647(3)[261]
1,2-CH(CH=CH)$_2$CH-	1.596[320]
1,2-CHMeCH$_2$CH(OH)-	1.621, 1.641, 1.630[318]
1,2-CH$_2$(1,2-C$_6$H$_4$)CH$_2$-	1.646(3),[553] 1.649(2)[516]
1,2-CH$_2$(1,2-C$_6$H$_4$-1,2-C$_6$H$_4$)CH$_2$-	1.667(5)[553]
1,2-(CH$_2$)$_2$S(CH$_2$)$_2$O(CH$_2$)$_2$S(CH$_2$)$_2$-	1.684(6)[493]
1,2-CH$_2$OP(O)OCH$_2$CF$_3$OCH$_2$-	1.649(3)[601]
1,2-CH(CH=CHPh)SiMe$_2$OSiMe$_2$OSiMe$_2$OSiMe$_2$(PhCH=CH)CH-	1.71(2)[602,603]
1,2-CH(CH=CHPh)SiEt$_2$SiEt$_2$(PhCH=CH)CH-	1.701(3)[554]
1,2-C(OSiMe$_2$^{t}Bu)RNR′(CH$_2$)$_2$-	1.684(4)[234]
1,2-C-N-B- link	1.717(14)[604]
1,2-SiMe$_2$SiMe$_2$-	1.706(3)[555]
1,2-SiMe$_2$O(4-NCC$_6$H$_4$)CHSiMe$_2$-	1.698(10)[590]
1,2-SiMe$_2$OC(=CPh$_2$)SiMe$_2$-	1.700(3)[590]
1,2-SiMe$_2$(Me$_3$Si)C=CPhSiMe$_2$-	1.677(6)[605]
1,2-SiMe$_2$C(=CHPh)SiMe$_2$-	1.685(4)[606]
1,2-SiMe$_2$N(CH$_2$C$_{14}$H$_9$)SiMe$_2$-	1.664(8)[607]
1,2-SiMe$_2$N(C$_9$H$_6$)SiMe$_2$-	1.680(3)[607]
1,2-SiMe$_2$PhC=CPhSiMe$_2$-	1.66(1)[602]
1,2-SiMe$_2$PhC=CHSiMe$_2$SiMe$_2$-	1.685(3)[556]
1,2-SiMe$_2$OSiMe$_2$-	1.691(4)[555]
1,2-SiMe$_2$SiMe$_2$SiMe$_2$-	1.727(5), 1.714(5)[556]
1,2-SiEt$_2$SiEt$_2$-	1.691(7)[554]
1,2-SiEt$_2$CH=CPhSiEt$_2$-	1.691(4)[554]
1,2-P(=S)Ph–S–PhP(=S)-	1.658(3)[584]
1,2-S(C=S)S-	1.632(3)[608]
[1,1′(Me$_4$C$_5$Me$_2$Si)$_2$-2,2′-(Li(OEt$_2$))$_2$-Li]$^-$ [Li(THF)$_4$]$^+$	1.592(4), 1.850(5), THF[545]
9,10,11,12-Me$_4$-1-(1′(9′,10′,11′,12′-Me$_4$-1′,2′-C$_2$B$_{10}$H$_7$))-	1.635(9)[243]
Two-cage assemblies	
1,1′-CH$_2$S(CHCO$_2$Me)$_2$SCH$_2$-	1.629(3)[465]
1,1′-(CH=CH-CH-CH-)$_2$-	1.654(2)[609]
1,1′-CH=CH-2,2′-Ph$_2$-	1.690[222]
1,1′-(1,2-C$_6$H$_4$)-	1.700(3), 1.657(3)[459,460]
1,1′-(1,4-C$_6$H$_4$-1,4-C$_6$H$_4$)-	1.634(8), 1.643(7)[464]
1,1′-(1,3-C$_6$H$_4$NHCONH-1,3-C$_6$H$_4$)-	Not determined[461]
1,1′-(1,4-C$_6$H$_4$NHCONH-1,4-C$_6$H$_4$)-	Not determined[461]
1,1′-(1,3-C$_6$H$_4$NMeCONMe-1,3-C$_6$H$_4$)-	Not determined[461]
1,1′-(1,4-C$_6$H$_4$NMeCONMe-1,4-C$_6$H$_4$)-	Not determined[461]
1,1′-(1,4-C$_6$H$_4$)-2,2′-Me$_2$-	1.684(5)[511]
1,1′-(1,3-C$_6$H$_4$NMeCONMe-1,3-C$_6$H$_4$)-2,2′-Ph$_2$-	1.719(3)[260]
1,1′-(1,4-C$_6$H$_4$NMeCONMe-1,4-C$_6$H$_4$)-2,2′-Ph$_2$-	1.728(6), 1.749(6)[260]
1,1′-(1,4-C$_6$H$_4$)-2,2′-Ph$_2$-	1.720(2)[462,610]
1,1′-(1,3-C$_6$H$_4$)-2,2′-Ph$_2$-	Not determined[462]
1,1′-(CH$_2$C$_6$H$_4$CH$_2$)-	1.645(9), 1.648(11)[311]
1,1′-(CH$_2$-2,6-C$_5$H$_3$N–CH$_2$)-2,2′-Ph$_2$-	1.711(4), 1.718(4)[557]
1,1′-(1,4-C$_6$F$_4$)-2,2′-Ph$_2$-	1.730(3)[512]
1,1′-PhP-2,2′-Me$_2$-	1.716(7), 1.675(7)[530]
1,1′-PhP-2,2′-Ph$_2$-	1.761(3), 1.780(3)[559]
1,1′-S$_3$-2,2′-Ph$_2$-	1.731, 1.734[521]
1,1′,2,2′-S$_2$BClBClS$_2$-$^{2-}$ [NH$_2$Me$_2$$^+$]$_2$	1.680(8), 1.628(10)[588]

(Continued)

Table 22 (Continued)

1,2-C$_2$B$_{10}$H$_{12}$ and derivatives	*C1–C2, solvate*
1,1′-SiMe$_2$SiMe$_2$-	1.670(3)[556]
1,1′-SiMe$_2$SiMe$_2$-2,2′-Me$_2$-	1.692(4)[556]
1,1′-(CH$_2$C$_6$H$_4$CH$_2$)-2,2′-(^{t}BuSiMe$_2$)$_2$-	1.714(6), 1.707(7)[309]
1,1′-SiMe$_2$CB$_8$H$_8$CSiMe$_2$-2,2′-Me$_2$-	1.668(6)[560]
1,1′,2,2′-(Me$_2$Si)$_2$-	1.688(5)[611]
1,1′,2,2′-(Me$_2$Si)$_2$-R-N(Me$_2$Si)$_2$-	1.674(3), 1.671(3)[602,603]
1,1′-CH$_2$(1,2-C$_6$H$_4$)CH$_2$CH$_2$(1,2-C$_6$H$_4$)CH$_2$-2,2′-(^{t}BuMe$_2$Si)$_2$-	1.694(2)[516]
1,1′-CH$_2$(1,2-C$_6$H$_4$)CH═CH(1,2-C$_6$H$_4$)CH$_2$-2,2′-(^{t}BuMe$_2$Si)$_2$-	1.702(2)[516]
1-(1′-1′,2′-C$_2$B$_{10}$H$_{11}$)-$^{2-}$ [Na$_2$(15C5)$_3$]$^{2+}$	2.418(6)[612]
1-(1′-1′,2′-C$_2$B$_{10}$H$_{11}$)-$^{2-}$ [Ph$_3$PMe]$_2^+$	2.414(4)[612,613]
1-(3′-1′,2′-C$_2$B$_{10}$H$_{11}$)-	Not determined[561]
1-(4′-1′,2′-C$_2$B$_{10}$H$_{11}$)-	1.701(11)[561]
1,1′,2,2′-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)$_2$-	1.736(9)[313]
1,1′-CH$_2$C$_6$H$_4$CH$_2$-2,2′-(1,3-C$_6$H$_4$)-	1.699, 1.709[460]
3,3′-(CH$_2$)$_6$-	1.624(7)[239]
Three-cage assemblies	
1,1′,1″-(1,3,5-C$_6$H$_3$)-2,2′,2″-Ph$_3$-	1.709(2)[462,610]
1,1′,1′,2,2′,2″-Se$_2$B(Se$_2$)BSe$_2$-$^{2-}$ [NH$_2$Me$_2$$^+$]$_2$	1.645(12), 1.661(12), 1.666(12), [NH$_2$Me$_2$]$_2$Cl$_2$[588]
1,1′-(1,4-C$_6$H$_4$)-2,1″-(1′,2′-CB$_{10}$H$_{10}$C)-2′,1″-(1,4-C$_6$H$_4$)-	1.646(9), 1.676(9), 1.732(8), MeCN[466]
1,1′,1″-P(CH$_2$)$_3$-	1.635(5)[256]
1,1′,1″-(1,3,5-C$_3$N$_3$)-2,2′,2″-Ph$_3$-	1.67(2)[509]
Four-cage assemblies	
1,1,′,1″,1‴-(CH$_2$)$_2$CHCOCH(CH$_2$)$_2$-	Not determined[467]
1,1′,1″,1″″-(1,3,5-C$_6$H$_4$-NMeCONMe-1,3,5-C$_6$H$_4$)	Not determined[461]
1,1′,2,2′-(1,4-C$_6$H$_4$-1,7-CB$_{10}$H$_{10}$C-1,4-C$_6$H$_4$)$_2$-	1.72(1), C$_6$H$_6$, 6C$_6$H$_{12}$[456]
1,1′,1″,1‴-Si(C$_2$H$_4$SiMe$_2$)$_4$-2,2′,2″,2‴-Ph$_4$-	1.694(5), 1.698(6), 1.708(6), 1.720(5)[550]
1,1′,1″,2,2′,2″-(C$_3$H$_6$)$_3$-	1.681(13), 1.678(13), MeCONMe$_2$[312]
1,1′,1″,1‴,2,2′,2″,2‴-(C$_3$H$_6$)$_4$-	1.689(10), 1.697(10)[313]
1,1′,1″,1‴,2,2′,2″,2‴-(C$_3$H$_6$)$_4$-9,9′,9″,9‴,12,12′,12″,12‴-Me$_8$-	1.680(7), 1.675(7)[313]
1,1′,1″,1‴,2,2′,2″,2‴-(CH$_2$-1,3-C$_6$H$_4$CH$_2$)$_4$-	1.664(17), Me$_2$CO[312]
1,1′,1″,1‴,2,2′,2″,2‴-(C$_4$H$_8$)$_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ph$_8$-	1.704(9), 6 dioxane[314]
1,1′,1″,1‴,2,2′,2″,2‴-(C$_3$H$_6$)$_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ar$_8$-	1.678(9), 1.653(10), 2 1,3-(MeO)$_2$C$_6$H$_3$[314]
1,1′,1″,1‴,2,2′,2″,2‴-(CH$_2$C$_5$H$_3$NCH$_2$)$_4$-9,9′,9″,9‴,12,12′,12″,12‴-Ar$_8$-	1.696(11), 1.698(12), 4 dioxane, 2H$_2$O,[314]
1,1′,1″,1‴,1″″,1″″′,2,2′,2″,2‴,2″″,2″″′-(C$_4$H$_8$)$_6$-9,9′,9″,9‴,9″″,9″″′,12,12′,12″,12‴,12″″,12″″′-Ph$_{12}$-	1.684(3), 1.686(4), 8 1,3-(MeO)$_2$C$_6$H$_3$,[314]

Table 23 C–H to C–X and B–H to B–X conversions in *closo*-1,7-C$_2$B$_{10}$H$_{12}$ (*meta*-carborane) derivatives

Derivatives of 1,7-C$_2$B$_{10}$H$_{12}$	*1,7-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
C–H to C–X conversion			
Derivatives with *exo* C–C bond			
1-RCH$_2$-		BuLi, TsOCH$_2$R	[473]
1-Me$_2$NCH$_2$-		BuLi, Me$_2$N$^+$═CH$_2$Cl$^-$	C$_6$H$_6$, Et$_2$O, 77%[499]
1-(HOC$_3$H$_6$)-		BuLi, (CH$_2$)$_3$O	65%[482]
1-HO$_2$C-		BuLi, CO$_2$	Et$_2$O, 95%[486]
1-Ph(OTs)CH-		BuLi, PhCHO, TsCl	[484]
1-RHO(R′O)C-		BuLi, MeI	THF, −10 °C, 68–98%[614]
1-C$_{14}$H$_{15}$CH(OH)-		BuLi, C$_{14}$H$_{15}$CHO	THF, 93%[487]
1-B$_{12}$H$_{11}$O(CH$_2$)$_4$-$^{2-}$ [Bu$_4$N$^+$]$_2$		BuLi, B$_{12}$H$_{11}$O(CH$_2$)$_4^-$, Bu$_4$NBr	THF, 72%[478]
1-Ph-		CuO^{t}Bu, PhI	DME, pyridine, 57%[317]

(Continued)

Table 23 (Continued)

Derivatives of 1,7-$C_2B_{10}H_{12}$	*1,7-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-Ph-		BuLi, CuCl, PhI	DME, pyridine, 45%[317]
1-(4-PhOC_6H_4)-		BuLi, CuCl, 4-PhOC_6H_4I	DME, pyridine, 89%[317]
1-(4-$O_2NC_6H_4$)-		BuLi, CuCl, 4-$O_2NC_6H_4$I	DME, pyridine, 43%[317]
1-(3-MeOC_6H_4)-		BuLi, CuCl, 3-MeOC_6H_4I	DME, pyridine, 39%[615]
1-(4-MeOC_6H_4)-		BuLi, CuCl, 4-MeOC_6H_4I	DME, pyridine, 42%[507,615]
1-(2-NC_5H_4)-		BuLi, CuCl, 2-BrC_5H_4N	DME, pyridine, 57%[616]
1,7-($C_{14}H_{15}$CH(OH))$_2$-		BuLi, $C_{14}H_{15}$CHO	Et_2O, benzene, 89%[487]
1-R′CH_2-7-RCH_2-	1-RCH_2-	BuLi, TsOCH_2R′	[473]
1-R′CH_2-7-RCH_2-	1-RCH_2-	BuLi, R′CH_2OTs	THF, 83%[617]
1,7-(Me_2NCH_2)$_2$-		BuLi, $Me_2N^+{=}CH_2Cl^-$	C_6H_6, Et_2O, 12%[499]
1,7-(HOC_3H_6)$_2$-		BuLi, $(CH_2)_3O$	THF[439]
1,7-(HO_2C)$_2$-		BuLi, CO_2	Et_2O, 95%[503]
1-HO_2C-7-$Me_2NH^+CH_2$- Cl^-	1-Me_2NCH_2-	BuLi, CO_2, HCl	C_6H_6, Et_2O, 76%[499]
1-NC-7-Me-	1-Me-	BuLi, TsCN	Et_2O, 92%[504]
1,7-(PhNHCO)$_2$-		BuLi, PhNCO	Toluene, 98%[271]
1,7-(MeNHCO)$_2$-		BuLi, MeNCO	Toluene, 72%[271]
1,7-(^{t}BuNHCO)$_2$-		BuLi, ^{t}BuNCO	Toluene, 81%[271]
1-MeS_2C-		BuLi, CuBr, CS_2, MeI	THF, LiBr 55%[618]
1-NC-7-Ph-	1-Ph-	BuLi, TsCN	Et_2O, 86%[504]
1-MeO_2C-7-(4-MeOC_6H_4)-	1-(4-MeOC_6H_4)-	BuLi, ClCO_2Me	C_6H_6/Et_2O, 82%[615]
1-MeO_2C-7-(3-MeOC_6H_4)-	1-(3-MeOC_6H_4)-	BuLi, ClCO_2Me	C_6H_6/Et_2O, 76%[615]
1-RCH_2-7-(3-MeOC_6H_4)-	1-(3-MeOC_6H_4)-	BuLi, BrCH_2R	C_6H_6/Et_2O, 52%[615]
1-RCH_2-7-(4-MeOC_6H_4)-	1-(4-MeOC_6H_4)-	BuLi, BrCH_2R	C_6H_6/Et_2O, 63%[615]
1-Ph(TsO)CH-7-Ar-	1-Ar-	BuLi, PhCHO, TsCl	[451]
1,7-Ph_2-		CuO^{t}Bu, PhI	DME, pyridine, 40%[317]
1,7-(4-ClC_6H_4)$_2$-		BuLi, CuCl, 4-ClC_6H_4I	DME, pyridine, 80%[317]
1,7-(3-ClC_6H_4)$_2$-		BuLi, CuCl, 3-ClC_6H_4I	DME, pyridine, 68%[317]
1,7-(4-$O_2NC_6H_4$)$_2$-		BuLi, CuCl, 4-$O_2NC_6H_4$I	DME, pyridine, 34%[317]
1,7-(4-PhOC_6H_4)$_2$-		BuLi, CuCl, 4-PhOC_6H_4I	DME, pyridine, 75%[317]
1,7-(4-PhOC_6H_4)$_2$-		BuLi, CuCl, 4-Ph$OC_6H_4N_2BF_4$	Et_2O, THF, 41%[317]
1,7-(3-IC_6H_4)$_2$-		BuLi, CuCl, 1,3-$I_2C_6H_4$	DME, pyridine, 14%[317]
1,7-(4-BrC_6H_4)$_2$-		BuLi, CuCl, 4-BrC_6H_4I	DME, pyridine, 65%[317]
1,7-(4-MeC_6H_4)$_2$-		BuLi, CuCl, 4-Me$C_6H_4N_2BF_4$	Et_2O, THF, 47%[317]
1,7-(4-MeC_6H_4)$_2$-		BuLi, CuCl, 4-MeC_6H_4I	DME, pyridine, 62%[317]

(Continued)

Table 23 (Continued)

Derivatives of 1,7-$C_2B_{10}H_{12}$	*1,7-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1,7-$(4\text{-}FC_6H_4)_2$-		BuLi, CuCl, 4-FC_6H_4I	DME, pyridine, 62%[256]
1,7-$(2\text{-}NC_5H_4)_2$-		BuLi, CuCl, 2-BrC_5H_4N	DME, pyridine, 79%[616]
1-F_5C_6-7-Ph-	1-Ph-	BuLi, C_6F_6	Et_2O, 19%[508]
1-Me-7-$^tBuMe_2Si$-	1-$^tBuMe_2Si$-	BuLi, MeI	C_6H_6, Et_2O, 90%[310]
1-HO_2C-7-$^tBuOCON(H)^tBuO_2CN$-	1-$^tBuOCON(H)^tBuO_2CN$-	BuLi, CO_2	Et_2O, THF[518]
1-$R'CH_2$-7-RHN-	1-RHN-	BuLi, $TsOCH_2R'$	[250,301]
Derivatives with *exo* C–N bond			
1-$^tBuO_2CN(H)$ $^tBuO_2CN$-		BuLi, $^tBuOCON{=}NCO_2{}^tBu$	Et_2O, 84%[518]
Derivatives with *exo* C–O bond			
1-HO-7-Ph-	1-Ph-	BuLi, $(PhCO_2)_2$	Toluene, Et_2O, 47%[521]
1-HO-7-$(3\text{-}MeOC_6H_4)$-	1-$(3\text{-}MeOC_6H_4)$-	BuLi, $(PhCO_2)_2$	C_6H_6, Et_2O, 44%[615]
1-HO-7-$(4\text{-}MeOC_6H_4)$-	1-$(4\text{-}MeOC_6H_4)$-	BuLi, $(PhCO_2)_2$	C_6H_6, Et_2O, 41%[615]
1-Me_3SiO-		BuLi, $(Me_3SiO)_2$	THF, 10%[520]
Derivatives with *exo* C–S bond			
1,7-$(HS)_2$-		BuLi, S	[619]
1-HS-7-Ph-	1-Ph-	Na, NH_3, $Fe(NO_3)_3.9H_2O$, S, HCl	Hexane, 78%[521]
1-HS-7-$Me_2NH^+CH_2$- Cl^-	1-Me_2NCH_2-	BuLi, S, HCl	C_6H_6, Et_2O, 42%[499]
Derivatives with *exo* C–B bond			
1,7-$(Ph_2B)_2$-		BuLi, Ph_2BCl	Ether, 82%[271]
Derivatives with *exo* C–Si bond			
1-$^tBuMe_2Si$-		$^tBuMe_2SiCl$	C_6H_6, Et_2O, 40%[310]
Multicage assemblies			
1,1′-$(1,4\text{-}C_6H_4)$-7,7′-$(4\text{-}BrC_6H_4)_2$-		BuLi, CuCl, 4-BrC_6H_4I	DME, pyridine, 5%[317]
1,1′-$(1,3\text{-}C_6H_4)$-		BuLi, CuCl, 1,3-$I_2C_6H_4$	DME, pyridine, 22%[317]
1,1′-$(1,4\text{-}C_6F_4)$-7,7′-Ph_2-	1-Ph-	BuLi, C_6F_6	Et_2O, 70%[508]
1,1′-PhB-		BuLi, $PhBCl_2$	Et_2O, 61%[271]
1,1′,1″,7,7′,7″-$(1,3\text{-}C_5H_4)_3$-		BuLi, CuCl, 1,3-$I_2C_6H_4$	DME, pyridine, 5%[317,620]
1,1′,1″,7,7′,7″-$(2,6\text{-}C_5H_3N)_3$-		BuLi, CuCl, 2,6-$Br_2C_5H_3N$	DME, pyridine, 10%[616]
1,1′,7,7′-$(CH_2\text{-}1,3\text{-}C_6H_4CH_2)_2$-		BuLi, 1,3-$(BrCH_2)_2C_6H_4$	Et_2O, 71%[314]
1,1′,7,7′-$(CH_2\text{-}1,3\text{-}C_6H_4CH_2)_2$-9,9′,12,12′-$Me_4$-	9,12-Me_2-	BuLi, 1,3-$(BrCH_2)_2C_6H_4$	Et_2O, 67%[314]
1,1′,1″,1‴,7,7′,7″,7‴-$(CH_2\text{-}1,3\text{-}C_6H_4CH_2)_4$-9,9′,12,12′-$Me_8$-	9,12-Me_2-	BuLi, 1,3-$(BrCH_2)_2C_6H_4$	Et_2O, 15%[314]
1-$BrCH_2C_5H_3NCH_2$-		BuLi, 2,6-$(BrCH_2)_2C_5H_3N$	Et_2O, 55%[314]
1,7-$(BrCH_2C_5H_3NCH_2)_2$-		BuLi, 2,6-$(BrCH_2)_2C_5H_3N$	THF, 41%[314]
1,1′-$(CH_2C_5H_3NCH_2)$-		BuLi, 1-$BrCH_2C_5H_3NCH_2$-1,7-$C_2B_{10}H_{11}$	C_6H_6/Et_2O, 62%[314]
1,1′,7,7′-$(CH_2C_5H_3NCH_2)_2$-		BuLi, 1,7-$(BrCH_2C_5H_3NCH_2)_2$-1,7-$C_2B_{10}H_{10}$	THF, 84%[314]
1,1′,7,7′-$(CH_2C_5H_3NCH_2)_2$-	1,1′-$(CH_2C_5H_3NCH_2)$-	BuLi, 2,6-$(BrCH_2)_2C_5H_3N$	THF, 58%[314]

(Continued)

Table 23 (Continued)

Derivatives of 1,7-$C_2B_{10}H_{12}$	*1,7-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1,1′,7,7′-(1,4-C_6H_4-1,2-$CB_{10}H_{10}C$-1,4-C_6H_4)$_2$-		BuLi, CuCl, 1,2-(4-IC_6H_4)$_2$-1,2-$C_2B_{10}H_{10}$	DME, pyridine, 9%[456]
1-(1′-1′,7′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 56%[561]
1-(1′-1′,7′-$CB_{10}H_{10}CCB_{10}H_{10}CCB_{10}H_{10}CH$)-		BuLi, $CuCl_2$	Et_2O, 22%[561]
B–H to B–X conversion			
4,5,6,8,9,10,11,12-Me_8-		MeI, $AlCl_3$	Reflux, 50 h, 97%[243]
9-I-		ICl, $AlCl_3$	CH_2Cl_2[507]
9,12-I_2-		I_2, $AlCl_3$	CH_2Cl_2, 7 d, 60%[566]
9,12-I_2-		ICl, $AlCl_3$	CH_2Cl_2, 4 h, 90%[566]
4,5,6,8,9,10,11,12-I_8-		ICl, CF_3SO_3H	120 °C, 50%[339]

Table 24 Structures of *closo*-1,7-$C_2B_{10}H_{12}$ (*meta*-carborane) derivatives determined experimentally by X-ray diffraction unless otherwise stated

1,7-$C_2B_{10}H_{12}$ and derivatives	*Solvate, reference*
	HMPA, 569
	Electron diffraction, 572
1-RC(OR′)OH-	614
1,7-(CH_2)$_8$-	619
1,7-Cl_2-	Electron diffraction, 621
1,7-S(CH_2)$_7$S-	619
1,7-Ph_2-	621a
9,12-Ph_2-	566
9,12-I_2-	566
Cyclic two-cage assemblies	
1,1′,7,7′-(S(CH_2)$_7$S)$_2$-	619
1,1′,7,7′-(1,3-C_6H_4-1,3-C_6H_4)$_2$-	622
1,1′,7,7′-(CH_2-1,3-C_6H_4–CH_2)$_2$-	314
1,1′,7,7′-(CH_2-2,6-C_5H_3N–CH_2)$_2$-	314
1,1′,7,7′-(1,4-C_6H_4-NMeCONMe-1,4-C_6H_4)$_2$-	623
1,1′,7,7′-(CH_2-1,3-C_6H_4-CH_2)$_2$-9,9′,12,12′-Me_4-	314
Cyclic three-cage assemblies	
1,1′,1″,7,7′,7″-(1,4-C_6H_4–NMeCONMe-1,4-C_6H_4)$_3$-	623
1,1′,1″,7,7′,7″-(1,3-C_6H_4)$_3$-	620
Cyclic four-cage assemblies	
1,1′,1″,1‴,7,7′,7″,7‴-(1,4-C_6H_4–NMeCONMe-1,4-C_6H_4)$_4$-	623
1,1′,7,7′-(1,4-C_6H_4-1,2-$CB_{10}H_{10}C$-1,4-C_6H_4)$_2$-	C_6H_6, 6C_6H_{12}, 456

and COMC (1995) 6.2.5.5). The structures of *closo*-1,12-$C_2B_{10}H_{12}$ (*para*-carborane) derivatives determined experimentally are presented in Table 26.

3.02.13 At the Icosahedral–Supraicosahedral Border

The solid-state structure of *ortho*-carborane was determined for the first time in 1996 featuring HMPA as a weak hydrogen bond adduct in the solid state.[569] The geometry of *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, is a distorted icosahedron with a bond of 1.62 Å between the cage carbons (C1–C2). This bond is remarkably elastic being elongated up to 1.85 Å

Table 25 C–H to C–X and B–H to B–X conversions in *closo*-$1,12\text{-}C_2B_{10}H_{12}$ (*para*-carborane) derivatives

Derivatives of $1,12\text{-}C_2B_{10}H_{12}$	$1,12\text{-}C_2B_{10}H_{12}$ *and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
C–H to C–X conversion			
Derivatives with *exo* C–C bond			
$1\text{-}HO_2C\text{-}$		BuLi, CO_2	Et_2O, 95%[486]
$1\text{-}HO_2C\text{-}$		BuLi, $ClCO_2Me$, NaOH, HCl	72%[191]
$1\text{-}RCH_2\text{-}$		BuLi, $TsOCH_2R$	[473]
$1\text{-}C_6H_8\text{-}$		BuLi, 3-Br-cyclohexene	THF, 80 °C[625]
$1\text{-}MeS_2C\text{-}$		BuLi, CuBr, CS_2, MeI	THF, LiBr, 67%[626]
$1\text{-}RC(OH)R'\text{-}$		BuLi, $RCOR'$	C_6H_6/Et_2O, 87%[625]
$1\text{-}CH(OEt)_2\text{-}$		BuLi, $PhOCH(OEt)_2$	C_6H_6, 80 °C, 36 h, 71%[627]
$1\text{-}Ph(TsO)CH\text{-}$		BuLi, PhCHO, TsCl	[484]
$1\text{-}B_{12}H_{11}O(CH_2)_4\text{-}^{2-}$	$2Cs^+$	BuLi, $B_{12}H_{11}O(CH_2)_4^-$, CsF	THF, 77%[478]
$1\text{-}Ph\text{-}$		BuLi, CuCl, PhI	DME, pyridine, 52%[628]
$1\text{-}Ph\text{-}$		BuLi, CuI, PhI	THF, NMP, $(Ph_3P)_2PdCl_2$, 68%[629]
$1\text{-}(2\text{-}NC_5H_4)\text{-}$		BuLi, CuCl, $2\text{-}BrC_5H_4N$	DME, pyridine, 62%[616]
$1\text{-}(3\text{-}MeOC_6H_4)\text{-}$		BuLi, CuCl, $3\text{-}MeOC_6H_4I$	DME, pyridine, 61%[630]
$1\text{-}(4\text{-}MeOC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}MeOC_6H_4I$	DME, pyridine, 79%[628], 60%[507,615]
$1\text{-}(4\text{-}O_2NC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}O_2NC_6H_4I$	DME, pyridine, 43%[628]
$1\text{-}(4\text{-}Me_2NC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}Me_2NC_6H_4I$	DME, pyridine, 82%[628]
$1\text{-}(4\text{-}F_3CC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}F_3CC_6H_4I$	DME, pyridine, 50%[628]
$1\text{-}(4\text{-}ClC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}ClC_6H_4I$	DME, pyridine[631]
$1\text{-}(4\text{-}PhOC_6H_4)\text{-}$		BuLi, CuCl, $4\text{-}PhOC_6H_4I$	DME, pyridine, 25%[317]
$1\text{-}PhC{\equiv}CC_6H_4\text{-}$		BuLi, CuI, $IC_6H_4C{\equiv}CC_6H_4I$	THF, NMP, $(Ph_3P)_2PdCl_2$, 6%[632]
$1\text{-}HO_2C\text{-}12\text{-}RCH_2\text{-}$	$1\text{-}RCH_2\text{-}$	BuLi, CO_2	THF, 68–77%[633]
$1\text{-}R'CH_2\text{-}12\text{-}RCH_2\text{-}$	$1\text{-}RCH_2\text{-}$	BuLi, $TsOCH_2R'$	[473]
$1,12\text{-}(HO_2C)_2\text{-}$		BuLi, CO_2	[503]
$1\text{-}HO(CH_2)_3\text{-}12\text{-}{}^tBuSCH_2\text{-}$	$1\text{-}{}^tBuSCH_2\text{-}$	BuLi, $(CH_2)_3O$	85%[626]
$1\text{-}MeO_2C\text{-}12\text{-}RC(OH)R'\text{-}$	$1\text{-}RC(OH)R'\text{-}$	BuLi, $ClCO_2Me$	Et_2O, 88%[625]
$1\text{-}MeO_2C\text{-}12\text{-}C_6H_8\text{-}$	$1\text{-}C_6H_8\text{-}$	BuLi, $ClCO_2Me$	Et_2O[625]
$1\text{-}HO_2C\text{-}2,3,4,5,6,7,8,9,10,11\text{-}Me_{10}\text{-}$	$2,3,4,5,6,7,8,9,10,11\text{-}Me_{10}\text{-}$	MeLi, CO_2	THF/Et_2O, 5 h, 76%[634]
$1\text{-}HOCH_2\text{-}2,3,4,5,6,7,8,9,10,11\text{-}Me_{10}\text{-}$	$2,3,4,5,6,7,8,9,10,11\text{-}Me_{10}\text{-}$	MeLi, HCHO	85%[635]
$1\text{-}MeO_2C\text{-}12\text{-}(3\text{-}MeOC_6H_4)\text{-}$	$1\text{-}(3\text{-}MeOC_6H_4)\text{-}$	BuLi, $ClCO_2Me$	C_6H_6/Et_2O, 87%[630]
$1\text{-}RCH_2\text{-}12\text{-}(3\text{-}MeOC_6H_4)\text{-}$	$1\text{-}(3\text{-}MeOC_6H_4)\text{-}$	BuLi, $BrCH_2R$	C_6H_6/Et_2O, 66%[615,630]
$1\text{-}(4\text{-}BrC_6H_4)\text{-}12\text{-}RCH_2\text{-}$	$1\text{-}RCH_2\text{-}$	BuLi, CuI, $4\text{-}BrC_6H_4I$	THF, 86%[633]
$1\text{-}Ph(TsO)CH\text{-}12\text{-}Ar$	$1\text{-}Ar$	BuLi, PhCHO, TsCl	[451]
$1,12\text{-}Ph_2\text{-}$		BuLi, CuCl, PhI	DME, pyridine, 18%[628]
$1\text{-}Ph\text{-}12\text{-}(4\text{-}ClC_6H_4)\text{-}$	$1\text{-}(4\text{-}ClC_6H_4)\text{-}$	BuLi, CuCl, PhI	DME, pyridine[631]
$1,12\text{-}(4\text{-}MeC_6H_4)_2\text{-}$		BuLi, CuCl, $4\text{-}MeC_6H_4I$	DME, pyridine, 84%[628,636]
$1,12\text{-}(4\text{-}O_2NC_6H_4)_2\text{-}$		BuLi, CuCl, $4\text{-}O_2NC_6H_4I$	DME, pyridine, 38%[628]
$1,12\text{-}(4\text{-}PhOC_6H_4)_2\text{-}$		BuLi, CuCl, $4\text{-}PhOC_6H_4I$	DME, pyridine, 78%[636]
$1\text{-}(4\text{-}O_2NC_6H_4)\text{-}12\text{-}(4\text{-}MeOC_6H_4)\text{-}$	$1\text{-}(4\text{-}MeOC_6H_4)\text{-}$	BuLi, CuCl, $4\text{-}O_2NC_6H_4I$	DME, pyridine, 71%[628]

(*Continued*)

Table 25 (Continued)

Derivatives of 1,12-C$_2$B$_{10}$H$_{12}$	*1,12-C$_2$B$_{10}$H$_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-(3,5-(F$_3$C)$_2$C$_6$H$_4$)-12-(4-MeOC$_6$H$_4$)-	1-(4-MeOC$_6$H$_4$)-	BuLi, CuCl, 3,5-(F$_3$C)$_2$C$_6$H$_4$I	DME, pyridine, 96%[628]
1-(4-O$_2$NC$_6$H$_4$)-12-(4-Me$_2$NC$_6$H$_4$)-	1-(4-Me$_2$NC$_6$H$_4$)-	BuLi, CuCl, 4-O$_2$NC$_6$H$_4$I	DME, pyridine, 69%[628]
1,12-(2-NC$_5$H$_4$)$_2$-		BuLi, CuCl, 2-BrC$_5$H$_4$N	DME, pyridine, 67%[616]
1-C$_6$F$_5$-12-Ph-	1-Ph-	BuLi, C$_6$F$_6$	Et$_2$O, 52%[508]
1,12-(Me$_3$SiC$\equiv$C)$_2$-		BuLi, CuCl, Me$_3$SiC$\equiv$CBr	DME, pyridine, 15%[637]
1,12-(Me$_3$SiC$\equiv$C)$_2$-		BuLi, CuBr, Me$_3$SiC$\equiv$CBr	Et$_2$O, 10%[638]
1-HO(CH$_2$)$_3$-12-^{t}BuMe$_2$SiO-	1-^{t}BuMe$_2$SiO-	BuLi, (CH$_2$)$_3$O	79%[639]
1-MeO$_2$C-12-(4-MeOC$_6$H$_4$)-	1-(4-MeOC$_6$H$_4$)-	BuLi, ClCO$_2$Me	C$_6$H$_6$/Et$_2$O, 91%[615]
1-RCH$_2$-12-(4-MeOC$_6$H$_4$)-	1-(4-MeOC$_6$H$_4$)-	BuLi, BrCH$_2$R	C$_6$H$_6$/Et$_2$O, 45%[615]
1,12-(HOC$_3$H$_6$)$_2$-		BuLi, (CH$_2$)$_3$O	THF[439]
1,12-(4-MeOC$_6$H$_4$)-		BuLi, CuCl, 4-MeOC$_6$H$_4$I	DME, pyridine, 60%[455]
1-RCH$_2$-12-Ph$_3$Si-	1-Ph$_3$Si-	BuLi, RCH$_2$Br	THF, 92–98%[633]
1-C$_5$H$_{11}$C$\equiv$C-12-Ph$_3$Si-	1-Ph$_3$Si-	BuLi, CuBr, C$_5$H$_{11}$C$\equiv$CBr	DME, pyridine, 97%[633]
1-Ar-12-Ph$_3$Si-	1-Ph$_3$Si-	BuLi, CuBr, ArI	DME, pyridine, 31%[633]
1,12′-(C$_7$H$_{15}$)$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C)-	1-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	BuLi, C$_7$H$_{15}$I	THF, 94%[193]
1,12′-(C$_5$H$_{11}$C$\equiv$C)$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C)-	1-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	BuLi, CuBr, C$_5$H$_{11}$C$\equiv$CBr	THF, 78%[193]
1,12′-(HO$_2$C)$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C)-	1-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	BuLi, CO$_2$, HCl	79%[191]
1-HO$_2$C-12-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	1-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	BuLi, CO$_2$, HCl	56%,[191] 41%[624]
1-HO$_2$C-12-^{t}BuOCON(H)^{t}BuO$_2$CN-	1-^{t}BuOCON(H)^{t}BuOCON-	BuLi, CO$_2$	Et$_2$O, THF[518]
Derivatives with *exo* C–N bond			
1-H$_2$N-		BuLi, MeLi, MeONH$_2$.HCl	[503]
1-^{t}BuOCON(H)^{t}BuO$_2$CON-		BuLi, ^{t}BuOCON=NCO$_2$^{t}Bu	Et$_2$O, 91%[518]
Derivatives with *exo* C–O bond			
1-HO-		BuLi, dry air	Et$_2$O, C$_6$H$_6$, 35%[639]
1-Me$_3$SiO-		BuLi, (Me$_3$SiO)$_2$	THF, 25%[520]
1-HO-12-CHO-	1-CH(OEt)$_2$-	BuLi, B(OMe)$_3$, CH$_3$CO$_3$H, CF$_3$CO$_2$H	88%[627]
1-HO-12-(3-MeOC$_6$H$_4$)-	1-(3-MeOC$_6$H$_4$)-	BuLi, (PhCO$_2$)$_2$	C$_6$H$_6$, Et$_2$O, 65%[615,630]
1-HO-12-(4-MeOC$_6$H$_4$)-	1-(4-MeOC$_6$H$_4$)-	BuLi, (PhCO$_2$)$_2$	C$_6$H$_6$, Et$_2$O, 75%[615]
Derivatives with *exo* C–S bond			
1,12-(HS)$_2$-		BuLi, S	Et$_2$O, 58%[640]
1,12-(HO$_2$S)$_2$-		BuLi, SO$_2$	THF, 88%[641]
1,12-(HO$_2$S)$_2$-		BuLi, SO$_2$, SO$_2$Cl$_2$	THF, 94%[641]
1-HO$_2$S-12-Ph$_2$MeSi-	1-Ph$_2$MeSi-	BuLi, SO$_2$	THF[641]
1-C$_4$H$_9$S-12-RCH$_2$-	1-RCH$_2$-	BuLi, C$_4$H$_9$SCl	THF, 40%[633]
Derivatives with *exo* C–F bond			
1-F-2,3,4,5,6,7,8,9,10,11-(CF$_3$)$_{10}$-	2,3,4,5,6,7,8,9,10,11-Me$_{10}$-	F$_2$, N$_2$	Freon 113, 35 °C[642]
1,12-F$_2$-2,3,4,5,6,7,8,9,10,11-(CF$_3$)$_{10}$-	2,3,4,5,6,7,8,9,10,11-Me$_{10}$-	F$_2$, N$_2$	Perfluorononane, 110 °C[642]
Derivatives with *exo* C–I bond			
1-I-12′-HO$_2$C-12-(1′-1′,12′-C$_2$B$_{10}$H$_{10}$)-	1-HO$_2$C-12-(1′-1′,12′-C$_2$B$_{10}$H$_{11}$)-	BuLi, I$_2$	31%[191]
1-I-12-HO$_2$C-	1-HO$_2$C-	BuLi, I$_2$	46%[191]

(*Continued*)

Table 25 (Continued)

Derivatives of 1,12-$C_2B_{10}H_{12}$	*1,12-$C_2B_{10}H_{12}$ and derivatives as starting material*	*Reagents*	*Solvent, temp, yield*
1-I-12-$(C_6H_{11})_3$Si-	1-$(C_6H_{11})_3$Si-	BuLi, I_2	Et_2O[643]
Derivatives with *exo* C–Si bond			
1-$(C_6H_{11})_3$Si-		BuLi, $(C_6H_{11})_3$SiCl	[643]
1-Ph_3Si-		BuLi, Ph_3SiCl	THF, 40–58%[633, 633a]
1-R_3Si-12-(1′-1′,12′-$C_2B_{10}H_{11}$)-	1-(1′-1′,12′-$C_2B_{10}H_{11}$)-	BuLi, R_3SiCl	52–79%[644]
1,1′,1″-$(RMe_2Si)_3$-12,12′,12″-(1,3,5-C_6H_4)-	1,1′,1″-(1,3,5-C_6H_4)-	${}^tBuLi$, RMe_2SiCl	Et_2O, 25–30%[629]
Multicage assemblies			
1-(1′-1′,12′-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 80%,[644] 94%,[191] 40%[624]
1-(1′-1′,12′-$CB_{10}H_{10}$C-$CB_{10}H_{10}$C-$C_2B_{10}H_{11}$)-		BuLi, $CuCl_2$	Et_2O, 16%,[644] 9%[191]
1,12‴-$(R_3Si)_2$-12-(1′-1′,12′-$CB_{10}H_{10}$C–$CB_{10}H_{10}$C–$CB_{10}H_{10}$C)-	1-R_3Si-12-(1′-1′,12′-$C_2B_{10}H_{11}$)-	BuLi, $CuCl_2$	60%[644]
1,1′-$C_6H_4C{\equiv}CC_6H_4$-		BuLi, CuI, $IC_6H_4C{\equiv}CC_6H_4I$	THF, NMP, $(Ph_3P)_2PdCl_2$, 25%[632]
1,1′-(1,3-C_6H_4)-		BuLi, CuI, 1,3-$I_2C_6H_4$	THF, NMP, $(Ph_3P)_2PdCl_2$, 61%[629]
1,1′-(1,4-C_6F_4)-12,12′-Ph_2-	1-Ph-	BuLi, C_6F_6	Et_2O, 31%[508]
1,1′,1″-(1,3,5-C_6H_4)-		BuLi, CuI, 1,3,5-$I_3C_6H_3$	THF, NMP, $(Ph_3P)_2PdCl_2$, 56%[629]
B–H to B–X conversion			
Derivatives with *exo* B–X bond			
2-I-		I_2, $AlCl_3$	[645]
2-I-		ICl, $AlCl_3$	CH_2Cl_2[507]
2,9-I_2-	2-I-	ICl, $AlCl_3$	CH_2Cl_2, 11%[646]
2,3-I_2-	2-I-	ICl, $AlCl_3$	CH_2Cl_2, 8%[646]
2,7-I_2-	2-I-	ICl, $AlCl_3$	CH_2Cl_2, 16%[646]
2,3,4,5,6,7,8,9,10,11-I_{10}-		ICl	CF_3SO_3H, 120 °C, 89%[339]
2,3,4,5,6,7,8,9,10,11-Me_{10}-		MeI, $AlCl_3$	9 d, 95%[243]
2,3,4,5,6,7,8,9,10,11-Me_{10}-		CF_3SO_3Me	CF_3SO_3H, 130 °C (sealed), 91%[634]
2,3,4,5,6,7,8,9,10,11-Me_{10}-		CF_3SO_3Me	CF_3SO_3H, reflux, 10 h, 89%[647]
1,2,3,4,5,6,7,8,9,10,11-Me_{11}-	1-Me-	CF_3SO_3Me	CF_3SO_3H, reflux, 10 h, 60%[647]
1-Br-2,3,4,5,6,7,8,9,10,11-Me_{10}-	1-Br-	CF_3SO_3Me	CF_3SO_3H, reflux, 10 h, 89%[647]
2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(4\text{-}HO_2CC_6H_4)_2$-	H_2O_2	Reflux, 35%[641]
2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(HOCH_2)_2$-	H_2O_2	Reflux, 80%[648]
1-HO_3S-2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(HO_2S)_2$-	H_2O_2	Reflux, 15%[641]
1-HO_3S-2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(HO_3S)_2$-	H_2O_2	Reflux, 25%[641]
1-HO_3S-2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1-HO_2S-	H_2O_2	Reflux, 90%[641]
1,2,3,4,5,6,7,8,9,10,11,12-Me_{12}-	1,12-Me_2-	CF_3SO_3Me	CF_3SO_3H, reflux, 20 h, 91%[647]
1,12-$(HO_3S)_2$-2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(HO_2S)_2$-	H_2O_2	Reflux, 45%[641]
1,12-$(HO_3S)_2$-2,3,4,5,6,7,8,9,10,11-$(HO)_{10}$-	1,12-$(HO_3S)_2$-	H_2O_2	Reflux, 35%[641]

Table 26 Structures of *closo*-1,12-$C_2B_{10}H_{12}$ (*para*-carborane) derivatives determined experimentally by X-ray diffraction unless otherwise stated

1,12-$C_2B_{10}H_{12}$ and derivatives	*Solvate, reference*
	HMPA, 569
	Electron diffraction, 572
1-Ph-	629
1-PhC$\equiv$CC_6H_4-	632
1,12-(HC$\equiv$C)$_2$-	637
1,12-(Me_3SiC$\equiv$C)$_2$-	638
1,12-(N$\equiv$C)$_2$-	638
1,12-(HS)$_2$-	Electron diffraction, 640
1-(4-EtOC_6F_4)-12-Ph-	508
1,12-(4-BrC_6H_4COC_6H_4OC_6H_4)$_2$-	622
1-^{t}BuOCON(H)^{t}BuO$_2$CN-12-HO$_2$C-	518
1-Ph$_3$Si-12-Me-	633a
B-substituted derivatives	
2-I-	646
2,9-(Me_3SiC$\equiv$C)$_2$-	649
2,9-Ph$_2$-	646
2,9-I$_2$-	646
2,3-I$_2$-	646
2,7-I$_2$-	646
1-C_6H_{11}NHCO-2,3,4,5,6,7,8,9,10,11-Me$_{10}$-	634
1-CH$_2$OH-2-CH$=$NOH-3,4,5,6,7,8,9,10,11-Me$_9$-	635
2,3,4,5,6,7,8,9,10,11-(HO)$_{10}$-	648
2,3,4,5,6,7,8,9,10,11-(CF$_3$)$_{10}$-	642
1,2,3,4,5,6,7,8,9,10,11,12-Me$_{12}$-	647
1,12-(CF$_3$SO$_3$CH$_2$)$_2$-2,3,4,5,6,7,8,9,10,11-Me$_{10}$-	633a
1,12-(MeO$_3$S)$_2$-2,3,4,5,6,7,8,9,10,11-(MeO)$_{10}$-	641
1,12-(HO$_3$S)$_2$-2,3,4,5,6,7,8,9,10,11-(HO)$_{10}$-	641
1,12-(NaO$_3$S)$_2$-2,3,4,5,6,7,8,9,10,11-(HO)$_{10}$-	641
1,12-(KO$_3$S)$_2$-2,3,4,5,6,7,8,9,10,11-(HO)$_{10}$-	641
1-F-2,3,4,5,6,7,8,9,10,11-(CF$_3$)$_{10}$-	642
1,12-F$_2$-2,3,4,5,6,7,8,9,10,11-(CF$_3$)$_{10}$-	642
2,3,4,5,6,7,8,9,10,11-(CHCl$_2$)$_{10}$-	650
2,3,4,5,6,7,8,9,10,11-I$_{10}$-	646
Multicage assemblies	
1,1′-(1,4-C_6H_4-CC-1,4-C_6H_4)-	632
1,1′-(1,4-C_6H_4-1,4-C_6H_4)-12,12′-Ph$_2$-	631
2,2′-C$\equiv$C–C$\equiv$C-	649
1,12′-(C_7H_{15})$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C)-	193
1,12′-(C_5H_{11}CC)$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C)-	193
2,2′-CH$_2$NONOCH$_2$-(1-CH$_2$OH-3,4,5,6,7,8,9,10,11-Me$_9$-)$_2$-	635
1,12‴-(Bu$_3$Si)$_2$-12-(1′-1′,12′-CB$_{10}$H$_{10}$C–CB$_{10}$H$_{10}$C–CB$_{10}$H$_{10}$C)-	644

with neutral π-donor substituents at one or both carbons as shown in Table 22.[521,537,585] The orientation of the substituent with respect to the C1–C2 bond also influences the C1–C2 bond length.[466,521,583,651] With substituents of type CH_2^- and O^- at one of the carbons, the C1–C2 distances are 2.42 and 2.07 Å, respectively.[521,580] The cage geometry for the anions is between a *closo*-12-vertex icosahedron and a *nido*-12-vertex open-cage geometry, that is, at the "icosahedral—supraicosahedral border."

An excellent example of this border is the reduction of bis-*ortho*-carborane, $(C_2B_{10}H_{11})_2$ (COMC (1995) 6.2.3.1 and 6.2.5.3).[612,613] A two-electron (2e) reduction gives a dianion with a geometry containing an intercage C–C double bond (Figure 10). The two extra electrons create a π-bond at the intercage C–C bond. Clearly, the *ortho*-carborane cage has an unusual capacity for accommodating a double bond with an appropriate (i.e., a π-electron donating) substituent at a cage carbon.

The C7–C8 bond in *nido*-7,8-$C_2B_9H_{12}^-$ anions shows no such capacity for elasticity with substituents at the cage carbons and reported bond lengths between 1.56 and 1.61 Å for various derivatives (Table 14).

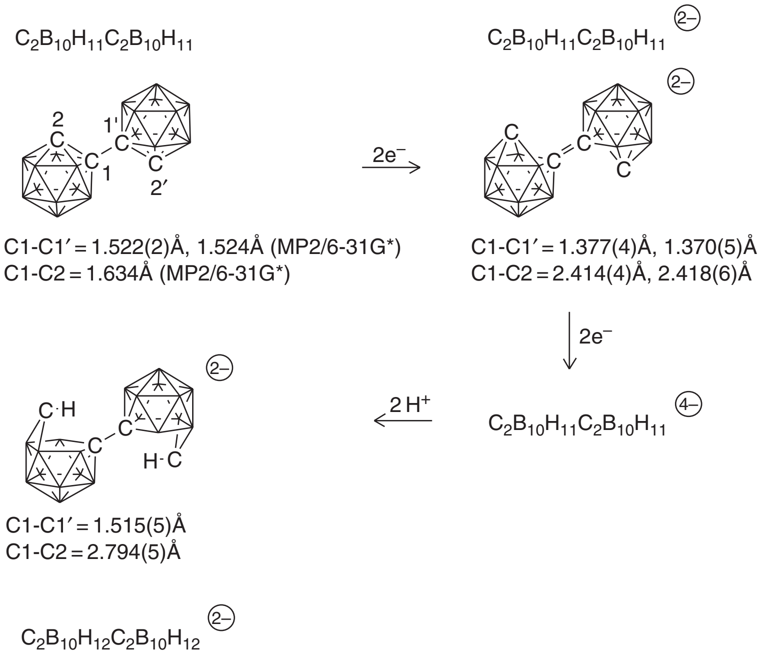


Figure 10 Reduction of biscarborane.

3.02.14 Supraicosahedral Carboranes

Closo-carboranes with 5 to 12 cage vertices have been known for several decades (Figure 1, COMC (1982) 5.4.2.2 and 5.4.2.3). However, the first report of a 13-vertex *closo*-carborane only appeared in 2003.[652] The synthesis of the first supraicosahedral *closo*-carborane was made possible using a tether linking both carbon atoms of *ortho*-carborane with 1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-1,2-$C_2B_{10}H_{10}$ as the starting carborane. This was reduced by sodium to a *nido*-C_2B_{10} dianion followed by capping the open face with $PhBCl_2$ to yield 3-Ph-1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-1,2-$C_2B_{11}H_{10}$ in 6% yield (Figure 11). The structure of the carborane determined by X-ray crystallography is a henicosahedron with a quadrilateral face rather than a docosahedron which has only triangular faces. Both geometries probably exist in solution as the NMR data are appropriate for a (fluxional) molecule with high symmetry. The docosahedron geometry of the parent carborane 1,2-$C_2B_{11}H_{13}$ is computed to be 7.4 kcal mol^{-1} higher in energy than the henicosahedron geometry. The first 14-vertex *closo*-carborane was reported in 2005.[653] A tethered carborane was also used as starting material. Lithium metal has been shown to reduce 1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-1,2-$C_2B_{10}H_{10}$ to a tetraanion.[553,654] This 4e reduction is not possible with the nontethered *ortho*-carborane. For the 14-vertex carborane, 1,2-$CH_2CH_2CH_2$-1,2-$C_2B_{10}H_{10}$ was reduced to the tetraanion with lithium and capped on both open faces with $BH_3{\cdot}SMe_2$ to give 2,3-$CH_2CH_2CH_2$-2,3-$C_2B_{12}H_{12}$ in 7% yield (Figure 11). The latter 14-vertex carborane can also be made from 1,2-$CH_2CH_2CH_2$-1,2-$C_2B_{11}H_{11}$ via sodium and $BH_3{\cdot}SMe_2$ as shown in Figure 11. The 14-vertex 2,3-isomer rearranges to the more stable 2,8-isomer on treatment with sodium and $BH_3{\cdot}SMe_2$. A crystal structure determination of 2,8-$CH_2CH_2CH_2$-2,8-$C_2B_{12}H_{12}$ revealed a bicapped hexagonal antiprism.

It is anticipated that the area of supraicosahedral carborane chemistry will expand rapidly since the materials like *ortho*-carborane needed to make these 13- and 14-vertex carboranes are commercially available.

3.02.15 An Unusual Carborane Geometry

From the reaction of the six-vertex carborane dianion 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4{}^{2-}$ with $NiCl_2$, a 12-vertex *nido*-carborane $(Me_3Si)_4C_4B_8H_8$ was isolated in 10% yield.[125,126] From X-ray data analysis, it has an unusual distorted cuboctahedral structure with four quadrilateral faces (isomer B, Figure 12). The cage carbons are as far apart from each other as possible and the isomer is termed "carbons-apart." It is fluxional in solution and the cuboctahedron geometry is suggested as an intermediate. On heating, the carborane rearranges to a more conventional and thermodynamically stable "carbons-apart" geometry, isomer A, with the cage carbons still as far apart from each other.[125]

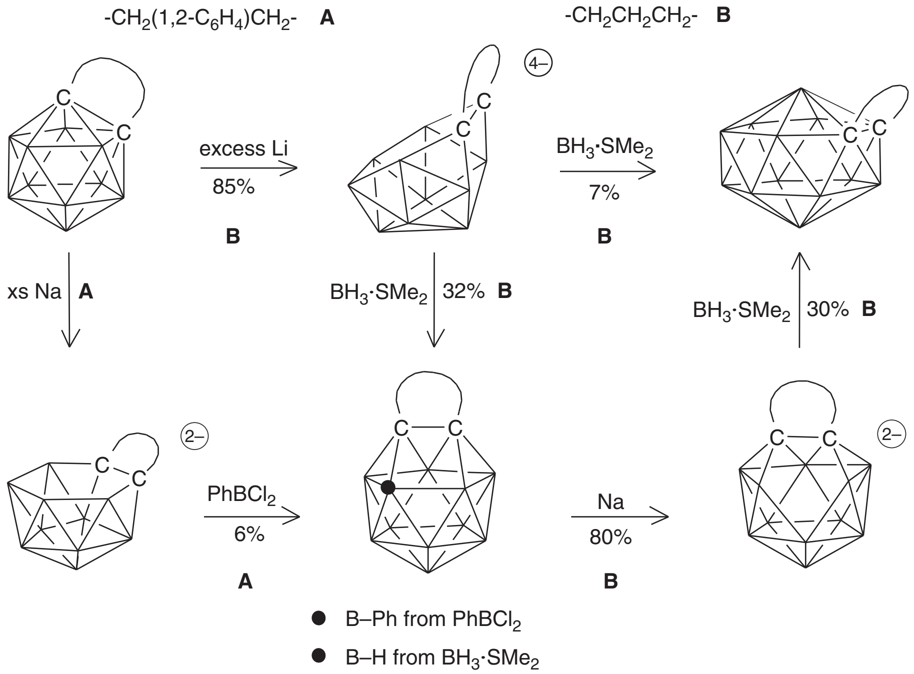


Figure 11 Syntheses of 13- and 14-vertex *closo*-carboranes.

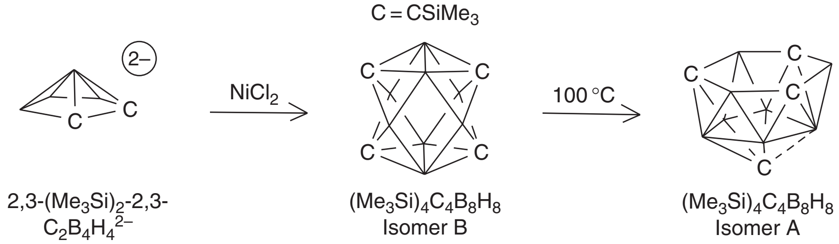


Figure 12 Synthesis of the "carbons-apart" 12-vertex *nido*-$(Me_3Si)_4C_4B_8H_8$ isomers, A and B.

3.02.16 Geometrical Pattern for Supraicosahedral Carboranes

Unlike the subicosahedral geometrical pattern, the supraicosahedral pattern is complex as shown in Figure 13 (COMC (1982) 5.4.2.7.2 and COMC (1995) 6.2.3.1, 6.2.4.4 and 6.2.5.1). For example, there are eight distinct geometries known with a *nido*-12-vertex count. This pattern is expected to expand further as the interest in 13- and 14-vertex *closo*-carboranes, which were only identified in the last three years, grows.

3.02.17 Supraicosahedral Carboranes in Detail

3.02.17.1 Eleven-vertex Carboranes

***arachno*-8-$CB_{10}H_{15}^-$ (B in Figure 13):** Protonation of the tetraanion, 1,2-CH_2(1,2-C_6H_4)CH_2-1,2-$C_2B_{10}H_{10}^{4-}$, gave 8,10-CH_2(1,2-C_6H_4)CH_2CH_2-8-$CB_{10}H_{13}^-$ structurally characterized as its K(18C6)(THF)$^+$ salt (18C6 = 18-crown-6 ether).[553] Protonation of 1,2-CH_2(1,2-$C_{10}H_6$)CH_2-1,2-$C_2B_{10}H_{10}^{4-}$ presumably yields a similar monoanion. ***arachno*-7,8,9,11-$C_4B_7H_{13}$ (A):** The reaction of *arachno*-4,5-$C_2B_7H_{13}$ with ethyne and PS at 120 °C gave 10-Me-7,11-CH_2-7,8,9,11-$C_4B_7H_{10}$ in low yield.[199]

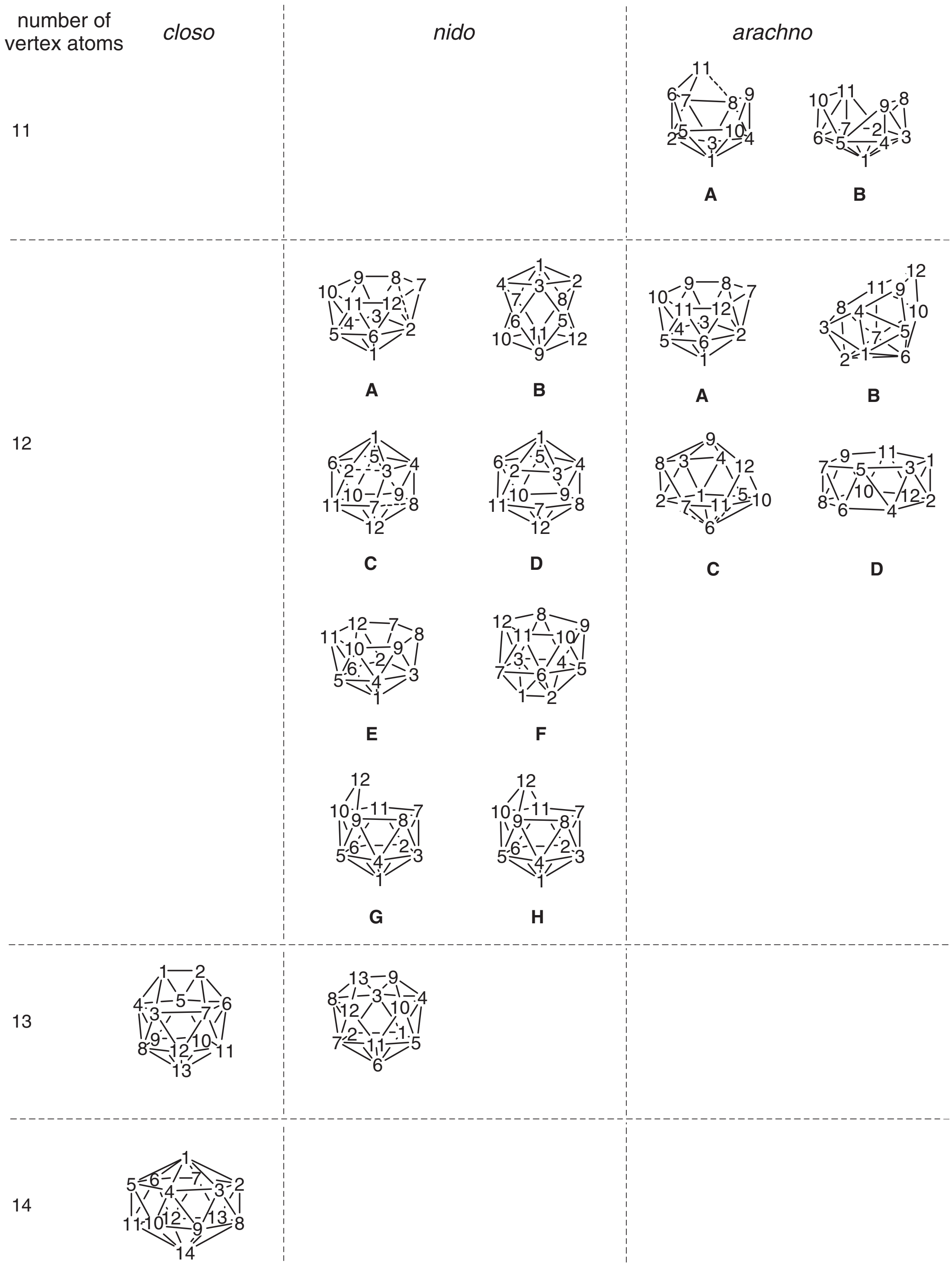


Figure 13 The supraicosahedral carborane pattern.

3.02.17.2 Twelve-vertex Carboranes

***nido*-9,10-CH$_2$-7-CB$_{10}$H$_{11}$$^-$ (G in Figure 13):** This long-known compound (COMC (1982) 5.4.2.3 and 5.4.2.4.1) has been named as *nido*-7,10- or 7,12-C$_2$B$_{10}$H$_{13}$$^-$ but it is considered here as a *nido*-CB$_{10}$ 11-vertex geometry with a bridging CH$_2$ at the B9 and B10 borons. *nido*-9,10-CH$_2$-7-CB$_{10}$H$_{11}$$^-$ and its C-methyl and C-phenyl derivatives have been made in high yield from 1,2-$C_2B_{10}H_{12}$ and its C-methyl/phenyl derivatives with Mg and iodine.[171,200,655] The two-cage version of *nido*-9,10-CH_2-7-$CB_{10}H_{11}^-$ linked via the bridging carbons was generated from the 4e reduction of biscarborane followed by water and structurally characterized as its Ph_3PMe^+ salt (Figure 10).[612] The reaction of 7-Me-9,10-MeCH-7-$CB_{10}H_{10}^-$ with $(Ph_3P)_2PdCl_2$ gave the zwitterions 5-Ph_3P-7-Me-9,10-MeCH-7-$CB_{10}H_{10}$ and 6-Ph_3P-7-Me-9,10-MeCH-7-$CB_{10}H_{10}$ which were structurally characterized by X-ray crystallography.[200]

***nido*-7,9-$C_2B_{10}H_{13}^-$ (A in Figure 13):** The reduction of 1,2-$(PhCH_2)_2$-1,2-$C_2B_{10}H_{10}$ with potassium in THF followed by the crown ether 18C6 gave the salt $K(THF)_2(18C6)^+$7,9-$(PhCH_2)_2$-7,9-$C_2B_{10}H_{11}^-$ which was structurally determined by X-ray analysis.[580] Using the same procedure on 1,2-$(HOCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ gave $K(18C6)^+$ 7,8-(OCH_2CH_2)-9-$HOCH_2CH_2$-7,9-$C_2B_{10}H_9^-$ where an OH group formed a B–O bond at the 8 position.[218] The salt Ph_3PMe^+7,9-Me_2-7,9-$C_2B_{10}H_{11}^-$ was structurally determined by X-ray crystallography.[656]

***nido*-7,9-$C_2B_{10}H_{12}^{2-}$ (A):** The parent dianion was made in quantitative yield from *ortho*-carborane with sodium in THF.[657] 1,2-$(PhCH_2)_2$-1,2-$C_2B_{10}H_{10}$ was reduced by Na or K metal to give the dianion, 7,9-$(PhCH_2)_2$-7,9-$C_2B_{10}H_{10}^{2-}$, which was structurally characterized as $Na(THF)_2^+$, $K(THF)^+$, and $K(18C6)^+$ salts by X-ray studies.[580] Reduction of 1,2-$(MeOCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with sodium gave 7,9-$(MeOCH_2CH_2)_2$-7,9-$C_2B_{10}H_{10}^{2-}$ where its $Na_2(THF)^{2+}$ salt was structurally characterized.[218] The trianions 7-$(C_5H_4)Me_2C$-7,9-$C_2B_{10}H_{11}^{3-}$ and 7-(2,6-$^iPr_2C_6H_3$)NMe_2Si-7,9-$C_2B_{10}H_{11}^{3-}$ were generated from 1-$(C_5H_5)Me_2C$-1,2-$C_2B_{10}H_{11}$ and 1-(2,6-$^iPr_2C_6H_3$)$NHMe_2Si$-1,2-$C_2B_{10}H_{11}$, respectively, with sodium in 70% yields.[210,551]

***nido*-7,8-$C_2B_{10}H_{12}^{2-}$ (E):** This anion was made with tethers keeping the two cage carbons together. From 1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-1,2-$C_2B_{10}H_{10}$ and sodium or potassium metal, the dianion 7,8-$CH_2(1,2\text{-}C_6H_4)CH_2$-7,8-$C_2B_{10}H_{10}^{2-}$ was made and structurally characterized as the $Na_2(THF)_3^{2+}$ or $K_4(18C6)_3(MeCN)_2^{4+}$ salts.[553,654,658] A second tethered dianion 7,8-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-7,8-$C_2B_{10}H_{10}^{2-}$ was similarly made by reduction of 1,2-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-1,2-$C_2B_{10}H_{10}$.[553]

***nido*-7,8-$C_2B_{10}H_{13}^-$ (E):** From the tethered carborane 1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-1,2-$C_2B_{10}H_{10}$ with Na and then $BF_3.Et_2O$, the Et_3NH^+ salt of 7,8-$CH_2(1,2\text{-}C_6H_4)CH_2$-7,8-$C_2B_{10}H_{11}^-$ was obtained in 42% yield (Figure 11).[652] This salt was structurally characterized by X-ray diffraction. With water, instead of $BF_3.Et_2O$, the $K(18C6)_2(H_2O)^+$ salt of 7,8-$CH_2(1,2\text{-}C_6H_4)CH_2$-7,8-$C_2B_{10}H_{11}^-$ was isolated and structurally characterized.[553] The anion 7,8-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-7,8-$C_2B_{10}H_{11}^-$ was made similarly with 1,2-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-1,2-$C_2B_{10}H_{10}$ as the starting carborane.

***nido*-7,8-$C_2B_{10}H_{13}^-$ (H):** The coupling of two 1-$C_9H_6Me_2Si$-1,2-$C_2B_{10}H_{11}^{2-}$ dianions by UV light gave a two-cage anion with a B–C link, 12-(1′-(1′,2′-$C_2B_{10}H_{11}$))-7,8-$C_2B_{10}H_{12}^-$.[659] (COMC (1995) 6.2.4.7). The structure of the anion was determined from $ErCl_2(THF)_5^+$ and $YCl_2(THF)_5^+$ salts. A zwitterion 12-$(Me_2N)_3P{=}NH$-7,8-$C_2B_{10}H_{12}$ was made in low yield from 1,2-$C_2B_{10}H_{12}$ with $(Me_2N)_3P{=}NH$ and structurally characterized.[268]

***nido*-3,7-$C_2B_{10}H_{12}^{2-}$ (D):** With an expanded tether, the 1,2-$CH_2(1,2\text{-}C_6H_4)_2CH_2$-1,2-$C_2B_{10}H_{12}$ gave, on reduction with lithium or sodium, the dianion 3,7-$CH_2(1,2\text{-}C_6H_4)_2CH_2$-3,7-$C_2B_{10}H_{12}^{2-}$ with a "carbons-apart" geometry.[553] The structure of the salt $Na_2(THF)_3^{2+}$3,7-$CH_2(1,2\text{-}C_6H_4)_2CH_2$-3,7-$C_2B_{10}H_{12}^{2-}$ was determined by X-ray crystallography.

***nido*-"Carbons-apart"-$C_2B_{10}H_{13}^-$:** Protonation of the dianion 3,7-$CH_2(1,2\text{-}C_6H_4)_2CH_2$-3,7-$C_2B_{10}H_{12}^{2-}$ by water gave a "carbons-apart" anion which has not been determined structurally.[553]

***nido*-8,12-$C_2B_{10}H_{13}^-$ (F):** The anions 8,12-$CH_2(1,2\text{-}C_6H_4)CH_2$-8,12-$C_2B_{10}H_{11}^-$ and 8,12-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-8,12-$C_2B_{10}H_{11}^-$ were made by heating the kinetic "carbons-adjacent" anions 7,8-$CH_2(1,2\text{-}C_6H_4)CH_2$-7,8-$C_2B_{10}H_{11}^-$ and 7,8-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-7,8-$C_2B_{10}H_{11}^-$.[553,658] The salt $K(18C6)^+$8,12-$CH_2(1,8\text{-}C_{10}H_6)CH_2$-8,12-$C_2B_{10}H_{11}^-$ was structurally characterized by X-ray crystallography. The 7,8-anion has a quadrilateral face and a six-membered open face, a mirror plane symmetry, and no unfavorable 7-coordinate borons, whereas the thermodynamically more stable 8,12-anion has no quadrilateral face, no mirror plane symmetry, a five-membered open face, and two unfavorable 7-coordinate borons.

***arachno*-9,12-$C_2B_{10}H_{12}^{4-}$ (B):** The tethered carboranes 1,2-$CH_2(1,2\text{-}C_6H_4)CH_2$-, 1,2-$CH_2(1,2\text{-}C_{10}H_6)CH_2$-, and 1,2-$CH_2CH_2CH_2$-1,2-$C_2B_{10}H_{10}$ with excess lithium gave the tetraanions 9,12-$CH_2CH_2CH_2$-, 9,12-$CH_2(1,2\text{-}C_6H_4)CH_2$-, and 9,12-$CH_2(1,2\text{-}C_{10}H_6)CH_2$-9,12-$C_2B_{10}H_{10}^{4-}$, respectively (Figure 11).[553,653,654] The salts $Li_4(THF)_5^{4+}$9,12-$CH_2CH_2CH_2$-9, 12-$C_2B_{10}H_{10}^{4-}$, $Li_4(THF)_6^{4+}$9,12-$CH_2(1,2\text{-}C_6H_4)CH_2$-9,12-$C_2B_{10}H_{10}^{4-}$, and $Li_4(THF)_4(DME)_2^{4+}$9,12-$CH_2(1,2\text{-}C_6H_4)CH_2$-9,12-$C_2B_{10}H_{10}^{4-}$ were all structurally characterized by X-ray crystallography.[553,653,654]

***arachno*-7,8-$C_2B_{10}H_{15}^-$ (A):** The reaction of $B_{10}H_{14}$ with KH and HCCCN in THF gave 8-NC-7,8-$C_2B_{10}H_{14}^-$ in 87% yield. Its PPN^+ salt was structurally determined.[78]

***nido*-"Carbons-apart"-$C_4B_8H_{12}$ (A):** Table 27 lists the reported syntheses of C-trimethylsilyl derivatives of the "carbons-apart" $C_4B_8H_{12}$ isomer A. This isomer is computed to be the most stable "carbons-apart" $C_4B_8H_{12}$ geometry and is fluxional in solution. The compound C-$(Me_3Si)_4$-$C_4B_8H_8$ reacts with Br_2, CF_3SO_3Me, and ^tBuLi to give

Table 27 Synthetic routes to trimethylsilyl derivatives of the "carbons-apart" $C_4B_8H_{12}$ isomer A

"Carbons-apart" $C_4B_8H_{12}$ derivatives	*Starting materials*	*Solvent, temp, yield*
$C\text{-}(Me_3Si)_4\text{-}$	$2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4^{2-}$, $NiCl_2$	TMEDA, benzene, 100 °C, 25%[125]
$C\text{-}(Me_3Si)_4\text{-}$	$2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4^{2-}$, $CrCl_3$, $PbCl_2$	THF, benzene, 30%[125]
$C\text{-}(Me_3Si)_4\text{-}$	$(Me_3Si)_4C_4B_8H_8$, isomer B	C_6H_6, 100 °C, 6 h, 96%[125]
$C\text{-}(Me_3Si)_2\text{-}C\text{-}Me_2\text{-}$	$2\text{-}Me_3Si\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_4^{2-}$, $NiCl_2$	Hexane, 25%[125]
$C\text{-}(Me_3Si)_2\text{-}C\text{-}Bu_2\text{-}$	$2\text{-}Me_3Si\text{-}3\text{-}Bu\text{-}2,3\text{-}C_2B_4H_4^{2-}$, $NiCl_2$	Pentane, 13%[125]
$C\text{-}(Me_3Si)_2\text{-}C\text{-}{}^tBu_2\text{-}$	$2\text{-}Me_3Si\text{-}3\text{-}{}^tBu\text{-}2,3\text{-}C_2B_4H_4^{2-}$, $NiCl_2$	Pentane, 14%[125]
$C\text{-}(Me_3Si)_2\text{-}C\text{-}Bu_2\text{-}$	$2\text{-}Me_3Si\text{-}3\text{-}Bu\text{-}2,3\text{-}C_2B_4H_5^{-}$, $NiCl_2$	Hexane, 18%[125]

B-monobromo, B-monomethyl, and B-monobutyl derivatives, respectively.[125,660] Both $1,8,10,12\text{-}(Me_3Si)_4\text{-}1,8,10,12\text{-}C_4B_8H_8$ and $7\text{-}Br\text{-}1,8,10,12\text{-}(Me_3Si)_4\text{-}1,8,10,12\text{-}C_4B_8H_7$ were structurally determined by X-ray studies.[125]

***nido*-"Carbons-apart"-$C_4B_8H_{12}$ (B):** The reaction of the dianion $2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4^{2-}$ with $NiCl_2$ in TMEDA gave $C\text{-}(Me_3Si)_4\text{-}C_4B_8H_8$ isomer B in 11% yield.[125,126] This isomer was structurally characterized by X-ray crystallography which revealed an unusual distorted cuboctahedron geometry, $2,4,10,12\text{-}(Me_3Si)_4\text{-}2,4,10,12\text{-}C_4B_8H_8$ (Figure 12). It is fluxional in solution and the fluxionality is believed to occur via a cuboctahedron geometry.[125]

***nido*-"Carbons-adjacent"-$C_4B_8H_{12}$ (C) and (D)** (see COMC (1982) 5.4.2.7.6 and COMC (1995) 6.2.3.1, 6.2.5.1): Oxidation of the monoanion $2\text{-}Me_3Si\text{-}3\text{-}Bu\text{-}2,3\text{-}C_2B_4H_5^{-}$ with $NiCl_2$ gave $C\text{-}(Me_3Si)_2\text{-}Bu_2\text{-}C_4B_8H_8$ in 41% yield and consists of two "carbons-adjacent" isomers C(37%) and D(4%).[125] Both were structurally characterized as $2,8\text{-}(Me_3Si)_2\text{-}3,7\text{-}Bu_2\text{-}2,3,7,8\text{-}C_4B_8H_8$ isomer C and $2,8\text{-}Bu_2\text{-}3,7\text{-}(Me_3Si)_2\text{-}2,3,7,8\text{-}C_4B_8H_8$ isomer D. Isomers C and D differ geometrically with the presence of a C3–C7 bond in C.

***nido*-$C_4B_8H_{12}$:** A carborane of formula $C\text{-}(Me_3Si)_2\text{-}Me_2\text{-}C_4B_8H_8$ was made in 12% yield from the reaction of $2\text{-}Me_3Si\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_4^{2-}$ with $NiCl_2$.[125] It is fluxional in solution and has been suggested to contain a six-membered C–B–C–C–C–B open face.

***arachno*-7,8,9,10-$C_4B_8H_{14}$ (A):** The reaction of $5,6\text{-}C_2B_8H_{12}$ with NaH and MeO_2CCCH gave the carborane $8\text{-}MeO_2C\text{-}7,8,9,10\text{-}C_4B_8H_{13}$ which was structurally characterized.[78]

***arachno*-"Carbons-apart"-$C_4B_8H_{13}^{-}$ (C):** Reduction of the $C\text{-}(Me_3Si)_4\text{-}C_4B_8H_8$ isomer A with lithium, sodium, and potassium gave the fluxional anion "carbons-apart" $C\text{-}(Me_3Si)_4\text{-}C_4B_8H_9^{-}$.[660,661] The crystal structure of $Li(THF)_4^{+}1,7,9,10\text{-}(Me_3Si)_4\text{-}1,7,9,10\text{-}C_4B_8H_9^{-}$ did not locate the bridging hydrogen which was suggested to be at B4 and B5 or B11 and B12.

***arachno*-"Carbons-apart"-$C_4B_8H_{12}^{2-}$ (A):** Reduction of the $C\text{-}(Me_3Si)_4\text{-}C_4B_8H_8$ isomer A with cesium gave the fluxional dianion "carbons-apart" $C_4B_8H_{12}^{2-}$.[660,662] The salt $Cs^{+}Cs(TMEDA)^{+}1,7,9,11\text{-}(Me_3Si)_4\text{-}1,7,9,11\text{-}C_4B_8H_{12}^{2-}$ was structurally determined by an X-ray analysis.

***arachno*-$C_6B_6H_{12}$ (D):** This carborane $3,4,7,8,11,12\text{-}Et_6\text{-}1,2,5,6,9,10\text{-}C_6B_6H_6$ with an unusual highly symmetrical drum-like geometry was made in low yield from $Et_2BCCBEt_2$ with Et_2BH at 80 °C.[663]

3.02.17.3 Thirteen-vertex Carboranes

***closo*-1,2-$C_2B_{11}H_{13}$:** The tethered carborane $1,2\text{-}CH_2(1,2\text{-}C_6H_4)CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ was reduced by sodium and then added with $PhBCl_2$ to give $3\text{-}Ph\text{-}1,2\text{-}CH_2(1,2\text{-}C_6H_4)CH_2\text{-}1,2\text{-}C_2B_{11}H_{10}$ in 6% yield.[652] This 13-vertex *closo*-carborane was structurally determined by X-ray crystallography (Figure 11). The reaction of $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}^{4-}$ and $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{11}H_{12}^{2-}$ with $HBBr_2.SMe_2$ gave $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{11}H_{11}$ in 32% and 12% yields, respectively.[653]

***nido*-9,13-$C_2B_{11}H_{13}^{2-}$:** $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{11}H_{11}$ was reduced by sodium to give the dianion $9,13\text{-}CH_2CH_2CH_2\text{-}9,13\text{-}C_2B_{11}H_{13}^{2-}$ in 80% yield.[653] The dianion was structurally determined as the $Na_2(THF)_4^{2+}$ salt (Figure 11).

3.02.17.4 Fourteen-vertex Carboranes

***closo*-2,3-$C_2B_{12}H_{14}$:** The reaction of $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}^{4-}$ and $1,2\text{-}CH_2CH_2CH_2\text{-}1,2\text{-}C_2B_{11}H_{12}^{2-}$ with $HBBr_2.SMe_2$ gave $2,3\text{-}CH_2CH_2CH_2\text{-}2,3\text{-}C_2B_{12}H_{12}$ in 7% and 30% yields, respectively (Figure 11).[653]

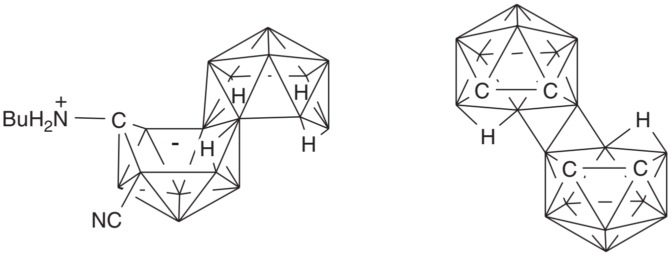


Figure 14 Structurally characterized macropolyhedral carboranes.

***closo*-2,8-$C_2B_{12}H_{14}$:** Reduction of 2,3-$CH_2CH_2CH_2$-2,3-$C_2B_{12}H_{12}$ with Na followed by $HBBr_2.SMe_2$ gave the more symmetrical isomer 2,8-$CH_2CH_2CH_2$-2,8-$C_2B_{12}H_{12}$.[653]

3.02.18 Macropolyhedral Carboranes

The first structurally characterized macropolyhedral carborane was 8-NC-9-^{t}BuNH$_2$-*anti*-9-$CB_{17}H_{18}$ synthesized in 12% yield from ^{t}BuNC and *anti*-$B_{18}H_{22}$ in benzene.[664] The molecule can be viewed as a fusion of two 10-vertex *nido*-type clusters each sharing an edge on the open face with its partner (Figure 14).

The 22-vertex carborane $C_4B_{18}H_{22}$ (COMC (1982) 5.4.2.6.7) was structurally characterized by X-ray crystallography and contains two *nido*-type 7,8-C_2B_9 clusters linked by three B–B bonds between B–B edges on their open faces.[665] It is considered to be related to the neutral 7,8-$C_2B_9H_{13}$ rather than the 7,8-$C_2B_9H_{12}^-$ anion on the basis of NMR spectroscopic and structural comparisons.[52,665]

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3.03
s- and *p*-Block Heteroboranes and Carboranes

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3.03.1 Introduction

In this chapter heteroboranes, heterocarbaboranes, and also their metal complexes are covered. On the basis of Chapter 5.6 COMC (1982) and Chapter 7 COMC (1995) the literature is reviewed.[1,2] Two recent partial review articles were published by Hosmane and co-workers.[3,4] Furthermore, in *Molecular Clusters of the Main Group Elements*, Eds. M. Driess, H. Nöth, Wiley-VCH, Weinheim, 2004, six chapters on boron cluster chemistry are presented: chapter 1, R. B. King, P. v. R. Schleyer, Theory and Concepts in Main-Group Cluster Chemistry; chapter 2.1, H. Nöth, Homonuclear Boron Clusters; chapter 2.2, D. Gabel, Y. Endo, Boron Clusters in Medical Applications; chapter 3.2, M. Hofmann, W. Siebert, B. Wrackmeyer, Carboranes: From Small Organoboranes to Clusters; chapter 3.3, L. Wesemann, N. S. Hosmane, Heteropolyboranes with the Heavier Group 14 Elements; and chapter 3.4, P. Paetzold, Borane Clusters with Group 15 and Group 16 Heteroatoms: Survey of Compounds and Structures.

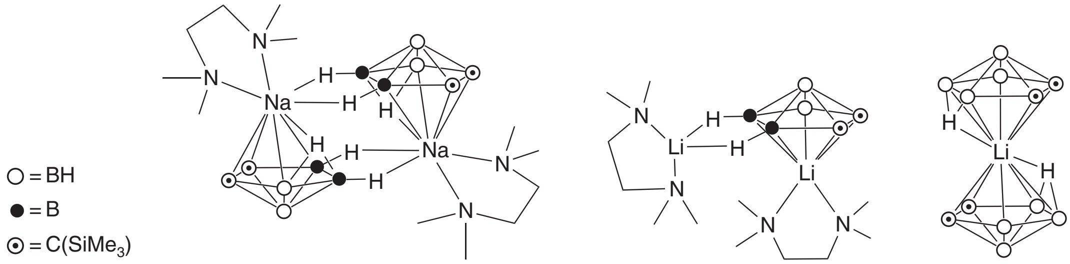
3.03.2 Derivatives Containing Group 1 Elements

Nido- and *hypho*-lithiacarbaboranes were prepared in the remarkable reaction of triboracyclobutane, triboracyclopentane, and triboracyclohexane with elemental Li. The crystal structures of the respective lithium salts exhibit contact ion pairs with the cation coordinated side-on at B–B and B–C bonds.[5–8]

Products of the deprotonation of [*nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$] with sodium hydride or *n*-butyllithium have been characterized in solution and in the solid state.[9,10]

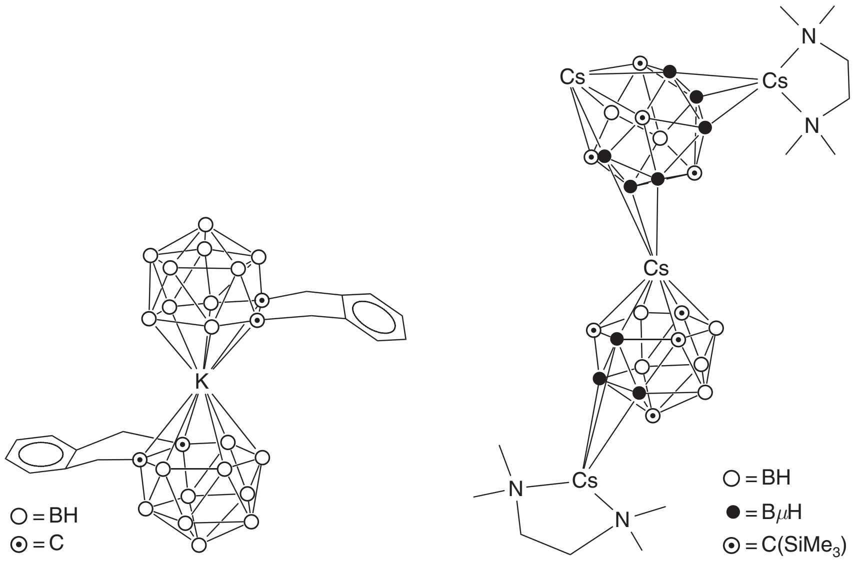
In the case of sodium hydride, only one of the acidic protons reacts with the base resulting in the isolation of the sodium salt. In the structure of the dimeric form of [*nido*-1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$] **1** found in the solid state, the sodium atom is coordinated at the dicarbaborate exhibiting two relatively short contacts: Na-C1 2.846(5), Na-C2 3.199(5), and Na-B3 3.360(7), Na-B4 3.191(7), Na-B5 2.799(6) Å (see Figure 1). In reaction with *n*-butyllithium however, the complete deprotonation of the dicarbaborane was achieved and in solution two ^{7}Li NMR signals for the dilithium salt Li_2[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$] were detected. Deduced from the X-ray crystal structure analysis, one lithium is coordinated *exo*-polyhedrally at two BH units and the other counter cation was found in an apical position of the heteroborate **2**.[9] Slow sublimation of the monodeprotonated lithium salt [Li(TMEDA)][2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$] at 160–170 °C resulted in the isolation of a lithium salt exhibiting sandwich type coordination of two dicarbaborate units [2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$] at lithium **3**.[11]

In the case of the isomeric dicarbaborane with the carbon atoms in non-adjacent positions, lithium and sodium salts of the anion $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_5]^-$ and dianion $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ were synthesized by reduction of [1,2-$(SiMe_3)_2$-*closo*-1,2-$C_2B_4H_4$]. The structures in the solid state are closely related to the arrangements found for the 2,3-C_2B_4-skeletons.[12,13]



1 **2** **3**

Figure 1 Schematic drawing of three alkali metal carbaboranes.



4 **5**

Figure 2 Schematic drawing of a sandwich potassacarbaborane and a part of a polymeric cesium carbaborate.

In order to characterize the alkali metal salts of the 11-vertex *nido*-dicarbaborates $[C_2B_9H_{11}]^{2-}$ in solution, a series of salts were synthesized and studied by NMR spectroscopy and quantum mechanical calculations. Comparison of the theoretical ^{11}B, ^{13}C, and ^{1}H NMR chemical shifts of the isomeric dianions 7,8-, 7,9-, and $[2,9\text{-}C_2B_9H_{11}]^{2-}$, and the ion pairs $[\text{ap-M-}C_2B_9H_{11}]^-$ and $M[\text{ap-M}C_2B_9H_{11}]$ with the observed data indicate that the alkali metal salts $M_2[C_2B_9H_{11}]$ exist in solution as anionic ion pairs $[\text{ap-M-}C_2B_9H_{11}]^-$ with the metal in apical position (ap) coordinated at the five-membered open face of the cluster.[14]

Reaction of 1,2-*o*-xylylene-1,2-dicarba-*closo*-dodecaborane with an excess of lithium metal in THF resulted in a four electron (4e) reduction and the formation of $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}Li_4(THF)_6]_2$. In the solid state, two lithium cations were found to coordinate in an η^6- and η^5-coordination mode at the six-membered C_2B_4 and five-membered C_2B_3 open faces of the dicarbaborate. With sodium as the reducing agent, a disodium salt $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$ was characterized as the product of the redox reaction, with a sodium cation coordinating at the C_2B_4 hexagonal open face. A potassacarbaborane sandwich of composition $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2K_3(18\text{-crown-}6)_2][(18\text{-crown-}6)K(CH_3CN)_2]$ **4** was the product of the carbaborane reaction with excess potassium and crown ether (18-crown-6) (see Figure 2).[15–18]

Complexation of cesium at a tetracarbaborane cage was achieved in the reaction of $[\textit{nido}\text{-}2,4,6,12\text{-}(SiMe_3)_4\text{-}2,4,6,12\text{-}C_4B_8H_8]$ with an excess quantity of cesium metal in THF. In the polymeric structure of the cesium salt, one cesium atom occupies an apical position above an open six-membered C_3B_3 face **5**.[19]

3.03.3 Derivatives Containing Group 2 Elements

Endo-polyhedral magnesium complexes have been synthesized and structurally characterized for the first time in the case of the six-vertex dicarbaborane clusters $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$.[20,21] Following a three-step procedure starting with the *closo*-cluster $[1,2\text{-}(SiMe_3)_2\text{-}\textit{closo}\text{-}1,2\text{-}C_2B_4H_4]$, magnesium coordination in apical position at the isomeric dicarbaborate $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ was achieved.[22] In the structure of the first barium salt of a carbaborane, coordination of the barium atoms at BH units and carbon vertices of two clusters $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ was found.[23]

Treatment of $[\textit{nido}\text{-}2,4,6,12\text{-}(SiMe_3)_4\text{-}2,4,6,12\text{-}C_4B_8H_8]$ over a period of 6 days with magnesium in THF resulted in the isolation of a magnesacarbaborane with the alkaline earth metal coordinated at a C_2B_2 unit [Mg–C 2.315(3), 2.326(9), Mg–B 2.393(12), 2.402(11) Å].[19,24]

3.03.4 Derivatives Containing Group 13 Elements

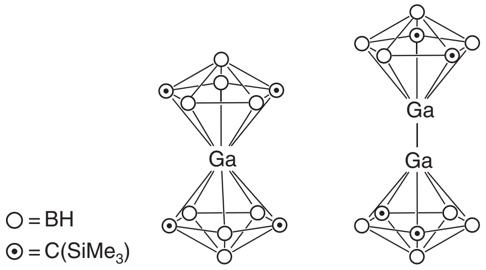
The structure and NMR spectra of the long-known bis(dicarbollid)aluminum anion were calculated by *ab initio* methods in order to compare this sandwich structure with the $[AlCp^*_2]^+$ cation.[25] The structures of tetraborane(10) derivatives $H_2MB_3H_8$ and $(CH_3)_2MB_3H_8$ (M = B, Al, Ga, In) have been investigated by *ab initio* calculations and in the case of $H_2GaB_3H_8$, $(CH_3)_2AlB_3H_8$, and $(CH_3)_2GaB_3H_8$ the molecular structure in the gas phase has been redetermined by electron diffraction. Gallium derivatives of tetraborane(10) with one or more boron atoms replaced by gallium were investigated by quantum mechanical methods.[26–28] The structure in the solid state of the extremely air sensitive dimethylindiumoctahydrotriborate was investigated by X-ray crystal structure analysis.[29] In the series of gallacarbaboranes with the dicarbaborane skeleton C_2B_4, the *commo*-clusters with adjacent and non-adjacent carbon atoms **6** were structurally characterized (see Figure 3). An example for an interestingly short Ga–Ga bond was found as the connection between the *closo*-clusters in $[1\text{-Ga-}2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$ **7**. The structure of the *closo*-indium dicarbaborane $[Me_2CH\text{-}1\text{-In-}2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]$ dimer is closely related to the isomeric 1,2,3-indadicarbaborane skeleton and exhibits also In–H–B bonds as bridging contacts.[30–33]

3.03.5 Derivatives Containing Group 14 Elements

3.03.5.1 Silaboranes and Silacarbaboranes

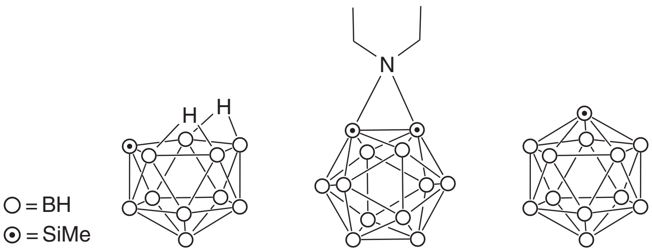
The first *arachno*-silaborane $[MeSiB_9H_{12}(NHMe_2)]$ was isolated from the reaction between bis(dimethylamino)-methylsilane and the dimethylsulfide adduct $[\textit{arachno}\text{-}B_9H_{13}(SMe_2)]$. This silaborane cluster shows decaborane geometry with the silicon vertex in position 6 of the cluster framework.[34]

The 11-vertex *nido*-silaborate cluster $[MeSiB_{10}H_{12}]^-$ **8** was synthesized either by nucleophilic degradation of the *closo*-disilaborane $[1,2\text{-}Me_2\text{-}1,2\text{-}Si_2B_{10}H_{10}]$ or by salt elimination reaction between deprotonated decaborane $[B_{10}H_{12}]^{2-}$ and dichloromethylsilane $MeSiHCl_2$ (see Figure 4).[35,36] Incorporation of tin and antimony into the silaborate skeleton was achieved after deprotonation of $[MeSiB_{10}H_{12}]^-$ and reaction with the electrophiles $SnCl_2$ or SbI_3 to give the *closo*-boranes $[Sn(MeSi)B_{10}H_{10}]^-$ and $[Sb(MeSi)B_{10}H_{10}]$.[37] As a ligand in transition metal



6 **7**

Figure 3 Gallacarbaboranes.



8 **9** **10**

Figure 4 Three schematic drawings of silaboranes.

chemistry the *nido*-silaborate was found to exhibit a variety of coordination modes. In the dinuclear iron complex $[\{HFe(MeSiB_{10}H_{10})\}_2]^{2-}$, hydrogen bridging of the Fe–Si bond was detected. Stepwise activation of two BH units and formation of two $B–NMe_2–M$ bridges were observed in the reaction of the sila-*nido*-undecaborate with the dimethylamides of tantalum and niobium ($[M(NMe_2)_5]$ M = Nb, Ta) in dihalomethane as a reacting solvent.[38–41]

ortho-Silaboranes $[Me_2Si_2B_{10}H_{10}]$ and $[Ph_2Si_2B_{10}H_{10}]$ were found to react as Lewis acids with the nucleophiles diethylamide, methoxide, oxide, and various carbanions. The nucleophiles attack the silicon vertex of the cluster. In the case of $[NEt_2]^-$ in the solid state as well as in solution, the nucleophile is coordinated in bridging position at the Si–Si edge of the cluster **9**.[42–45]

The 12-vertex *closo*-borate $[MeSiB_{11}H_{11}]^-$ **10** was synthesized in a typical cluster closure reaction with the amineborane adduct Et_3NBH_3 either from the *nido*-silaborate $[MeSiB_{10}H_{12}]^-$ or from the *arachno*-silaborane $[MeSiB_9H_{12}(NHMe_2)]$.[34,46]

Constrained-geometry heterocarbaboranes with silicon and germanium have been synthesized in moderate yield starting with the *o*-carborane derivative *closo*-1-(CH_2OH)-2-(Me)-1,2-$C_2B_{10}H_{10}$.[47]

3.03.5.2 Germaboranes and Germacarbaboranes

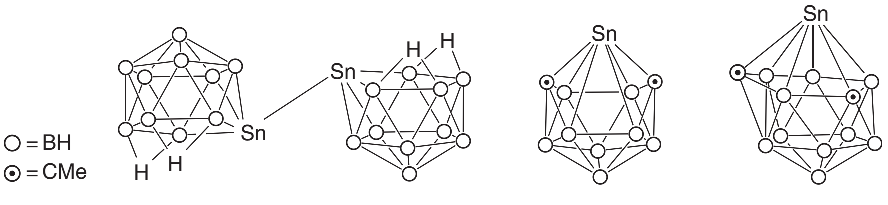
Deprotonated decaborane $Na_2B_{10}H_{12}$ was reacted with germanium diiodide to give the 11-vertex *nido*-cluster $[7\text{-}I\text{-}7\text{-}GeB_{10}H_{12}]^-$ in 75% yield. The heteroborate was characterized by two-dimensional ^{11}B–^{11}B NMR spectroscopy and by X-ray crystal structure analysis [Ge–B: 2.203(7)–2.218(7) Å].[48] Exchange of the heteroatom tin in the pentagonal bipyramid of *closo*-1-Sn-2-$(SiMe_3)$-3-R-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) against germanium was achieved in the reaction of the respective cluster with $GeCl_4$. Lewis bases attack the germacarbaborane at the germanium vertex under cluster opening.[49]

3.03.5.3 Stannaboranes and Stannacarbaboranes

Isomers of pentaborane and hexaborane derivatives $SnPh_2(B_5H_8)_2$ and $Ph_3SnB_6H_9$ were studied by ^1H, ^{11}B, ^{13}C, and ^{119}Sn NMR spectroscopy in solution and solid state structures of three isomers were also reported.[50–53]

Formation of a tin–tin bond was found in the surprising reaction product of *nido*-stannaundecaborate $[7\text{-}Br\text{-}7\text{-}SnB_{10}H_{12}]^-$ with MeLi. The linked cluster $[7,7'\text{-}(SnB_{10}H_{12})_2]^{2-}$ **11** exhibits a tin–tin bond length of 2.8886(6) Å and an ^{119}Sn NMR signal at $\delta = -336$ ppm (see Figure 5).[48] In a variety of coordination compounds, the stanna-*closo*-dodecaborate cluster $[SnB_{11}H_{11}]^{2-}$ was found to act as a ligand with a strong *trans*-influence. Activation of platinum complexes towards isonitrile insertion and hydroformylation as well as cluster formation with gold complex fragments are examples for the interesting ligand abilities of this nearly icosahedral Lewis base.[54–58]

Seven-, 11- and 13-vertex stannadicarbaboranes with naked tin atoms were isolated: the missing derivative [*closo*-1-Sn-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$] with non-adjacent carbon atoms was synthesized and structures in the solid state of adducts with nitrogen Lewis bases were determined.[59] Tin was incorporated into the framework of dicarba-*nido*-undecaborate in a classical salt elimination reaction between anhydrous $SnCl_2$ and deprotonated Na_2[*nido*-6,9-R_2-6,9-$C_2B_8H_8$] (R = H, Me, Ph) to give an 11-vertex stannadicarbaborane **12**.[60] The first supraicosahedral *p*-block metallacarbaboranes [4,1,6-*closo*-$SnC_2B_{10}H_{12}$] **13** and [1,6-Me_2-4,1,6-*closo*-$SnC_2B_{10}H_{10}$] were straightforwardly prepared starting with the 2e reduction product of *o*-carbaborane. In the solid state, tin is coordinated at four boron atoms and two non-adjacent carbon atoms. However, time-averaged C_s-symmetry of the cluster was detected in the ^{11}B NMR spectrum in solution and this dynamic behavior was further studied by density functional calculations.[61,62] Linking the cage carbon atoms together via a short bridge in *o*-carbaborane resulted after reduction with sodium and



11 **12** **13**

Figure 5 Stannaboranes and stannacarbaboranes.

reaction with $SnCl_2$ to give the carbon-adjacent 13-vertex stannadicarbaborane. Adducts of this cluster with acetonitrile, THF, and dimethoxyethane were structurally characterized.[63]

3.03.5.4 Plumbacarbaboranes

In the series of the well-investigated heterodicarbaheptaboranes, a further lead derivative was characterized with the TMEDA adduct of [1-Pb-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$].[64]

3.03.5.5 Group 14 Heteroboranes Investigated by Theoretical Methods

A series of 1,2-silaboranes [$Si_2B_nH_{n+2}$, $Si_2B_nH_n$ (n = 4,5,8,10)] and their dehydrogenosilaboryne derivatives were studied using density functional theory and compared with the results for the homologous *closo*-carbaboranes and *closo*-carbaborynes.[65,66] *Ab initio* molecular orbital (MO) calculations on a series of eight-vertex *closo*-heteroboranes [$X_2B_6H_6$ (X = SiH, GeH, SnH, PbH)] indicate that the 1,7-bisdisphenoid isomer has the lowest energy and the hexagonal bipyramidal arrangements were calculated to be energetically competitive alternatives.[67] A topographical study using electron density and molecular electrostatic potential was carried out on the silaboranes 1,5-$Si_2B_3H_5$, 1,6-$Si_2B_4H_6$, and 1,7-$Si_2B_5H_7$.[68] Five-, six-, and seven-vertex *closo*-heteroboranes [XYB_nH_n (n = 3–5, X, Y = N, CH, P, SiH)] with the heteroatom capping the n-membered borocyclic ring B_nH_n (n = 3–5) were studied by *ab initio* MO calculations. In the case of the heterocapped *closo*-heteroboranes, the ring substituents are bent toward the cap that provides the less diffuse orbitals.[69] *Ab initio* MO studies on a series of pyramidal structures [B_3H_6X (X = P, PH^+, NH^+, N, SiH)] indicate in the case of the SiH capping group that the terminal hydrogen atoms are directed away from the capping group.[70] Skeletal bonding in *closo*-heteroboranes [1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH, Y = NH_2, CH_3, H)] was discussed on the basis of theoretical investigations. The boron substituents play the key role in these clusters concerning the question on classical or non-classical bonding.[71–73] On the basis of *ab initio* studies, relative stabilities of the $Si_2B_{10}H_{12}$ isomers were presented.[74]

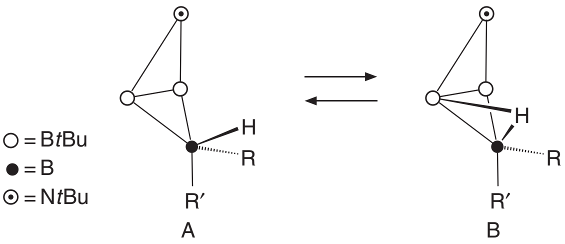
3.03.6 Derivatives Containing Group 15 Elements

3.03.6.1 Azaboranes and Azacarbaboranes

3.03.6.1.1 Three boron atoms in the skeleton

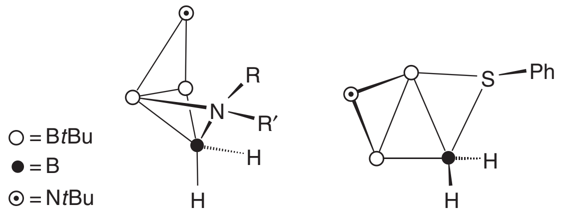
Treatment of tri-*tert*-butylazadiboriridine with Lewis acids RR′BH (R/R′ = H/H, Me/H, *t*Bu/H, CMe_2*i*Pr/H, Ph/H, *s*Bu/H, Et/Et) produced aza-*nido*-tetraborane [NB_3H*t*Bu_3RR']. In dependency on the substituents in the alkylborane RR′BH either high excess of one of the isomeric azaborane clusters (Figure 6, **14**: A, B) or a mixture of both was isolated and characterized.[75] Reaction of the azadiboriridine with dialkylboranes results in the exclusive formation of isomer B. However, a halogenated derivative of isomer A was formed in 82% yield in the reaction of the three-membered NB_2 cycle with the chloroborane $BH_2Cl(SMe_2)$.[76]

Diaza-*arachno*-pentaborane [$N_2B_3H_2$*t*Bu_3RR'] **15** clusters with an N_2B_3 skeleton were straightforwardly synthesized from a mixture of aminoboranes $H_2B{=}NRR'$ (R/R′ = Pr/H, *t*Bu/H, Me/Me, Et/Et) and tri-*tert*-butylazadiboriridine (see Figure 7).[75] Reacting substituted thiaboranes [(THF)BH_2SR] (R = Ph, Pr) with the NB_2*t*Bu_3-cyclical molecule, formation of thiaaza-*arachno*-pentaborane [SNB_3H_2*t*Bu_3R] **16** was observed. The structures of both the



14

Figure 6 Aza-*nido*-tetraborane.



15 **16**

Figure 7 Diaza-*arachno*-pentaborane and thiaaza-*arachno*-pentaborane.

diaza- and thiaazapentaborane were discussed.[75,77] Azadiborolane hydroboration with BH_3(THF) resulted to give azadicarba-*nido*-hexaborane clusters like [NC_2B_3HMe*i*Pr_2Dur_2] in good yield.[78–80]

3.03.6.1.2 Four boron atoms in the skeleton

Diaza-*nido*-hexaboranes [$N_2B_4R_4R'_2$] are the products of the fusion of rings NB_2R_2R'. The mechanism of this cluster formation was investigated and in the case of the neopentyl substituent ($R' = CH_2$*t*Bu, R = *t*Bu) a tetracyclic molecule was identified as a possible intermediate in the ring fusion reaction.[81,81a]

3.03.6.1.3 Five boron atoms in the skeleton

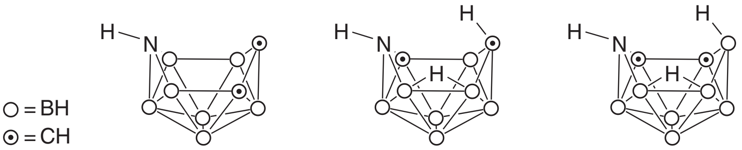
With the metathesis-driven reaction between halogenated pentaborane clusters and silylamines, the formation of new aminopentaboranes was reported. In reaction with the silylamine (*t*Bu)(Me_3Si)NH and bromopentaborane, the formation of a *hypho*-pentaborane cluster *hypho*-2,3-μ-(*tert*-butylamino)pentaborane(11) was found and the mechanism was studied in the reaction with deuterated pentaborane B_5D_9.[82] This type of *hypho*-cluster [B_5H_{10}(μ-NH*i*Pr)] was also found as the product of the hydrolysis of halogenated azanonaborane [(*i*$PrNH_2)_2B_8H_{10}$BrNH*i*Pr].[83]

3.03.6.1.4 Six boron atoms in the skeleton

A terminal methyl group was generated in the reaction of the dicarbaborane [*arachno*-4,5-$C_2B_7H_{13}$] with butyl nitrite to give [*exo*-8-CH_3-*hypho*-7,8-NCB_6H_{11}] with a yield of 5%. The *endo* isomer of this azacarbaborane is also known and was produced from [8,9-μ-NH_2-*arachno*-5,6-$C_2B_8H_{11}$] after removal of two boron vertices.[84]

3.03.6.1.5 Seven boron atoms in the skeleton

The first compounds of the 10-vertex *nido*- and *arachno*-azadicarbaborane family [*nido*-6,8,9-$C_2NB_7H_{10}$ **17**, *arachno*-6,5,9-$NC_2B_7H_{12}$ **18**, *arachno*-6,5,10-$NC_2B_7H_{12}$ **19**] were generated in reaction of butyl nitrite with the dicarbaborane [*nido*-5,6-$C_2B_8H_{12}$] or [*arachno*-4,5-$C_2B_7H_{13}$] (see Figure 8). Structures of these clusters were proposed on the basis of NMR spectroscopy and the correctness supported on the basis of theoretical calculations.[84] Formation of the *closo*-azadirhodadecaborane cluster [1-Et-6,7-(η^5-Cp^*)$_2$-*closo*-6,7,1-$Rh_2NB_7H_7$] was observed from the treatment of the azaborane [$EtH_2NB_8H_{11}$NHEt], sodium hydride, and the organometallic rhodium complex [Cp^*RhCl_2]$_2$.[85] The azairidaborane *nido*-[2,2,2-(PMe_3)$_3$-2,9-$IrNB_7H_9$] was formed in the reaction of the metallaborane *arachno*-[(PMe_3)$_2$(CO)$HIrB_8H_{12}$] and hydrazine.[86]



17 **18** **19**

Figure 8 Azadicarbaboranes.

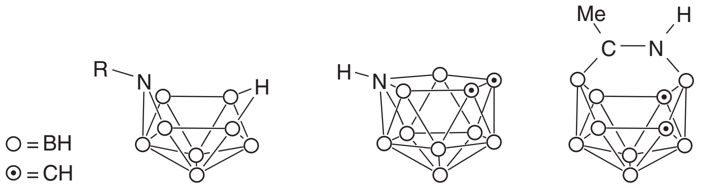
3.03.6.1.6 Eight boron atoms in the skeleton

Deboronation of the 10-vertex aza-*closo*-decaborane cluster in THF with *i*PrNH$_2$ or [NBu$_4$]F results in the formation of the anions [*nido*-RNB$_8$H$_9$]$^-$ **20** (see Figure 9). In less polar solvents like dichloromethane, [*arachno*-RNB$_8$H$_{10}$(NR′H$_2$)] (R = *p*-ClC$_6$H$_4$, R′ = *i*Pr; R = *p*-MeC$_6$H$_4$, R′ = Pr, Bu) was the product of the degradation.[87] Reactions between *arachno*-4-NB$_8$H$_{13}$ and Lewis bases L (L = pyridine, quinoline, isoquinoline, urotropine, MeCN) gave a series of unreported adducts [*exo*-6-L-*arachno*-4-NB$_8$H$_{11}$].[88] The structure in solid state of the pyridine adduct was determined by X-ray crystal structure analysis.[89] *arachno*- and *nido*-Metallaazaborane clusters [(PMe$_2$Ph)$_2$PtB$_8$H$_{10}$NH] and [(η^6-MeC$_6$H$_4$*i*Pr)-RuB$_8$H$_{10}$NH] have been synthesized and the structure of the platinum complex was discussed.[90]

The chemistry and formation of a variety of substitution patterns of the cluster (NHR)B$_8$H$_{11}$(NH$_2$R) was studied extensively in the last 10 years.[83,91–94] Furthermore, the electron count was discussed: *hypho*-nine-vertex cluster, *arachno*-eight-vertex versus *hypho*-eight-vertex cluster.[95,96] The formation mechanism of this azaborane and especially the position of the outgoing boron atom was investigated.[97,98] In the reaction of (NHR)B$_8$H$_{11}$(NH$_2$R) with phenylacetylene, RNH$_2$ was displaced and an azadicarbaborane cluster [6,9-μ-(NHR)-5-Ph-*arachno*-5,10-C$_2$B$_8$H$_{10}$] was formed and structurally characterized.[94] Three 11-vertex dicarbaazaundecaborane clusters [*nido*-10,7,8-NC$_2$B$_8$H$_{11}$ **21**, *arachno*-1,8,11-NC$_2$B$_8$H$_{13}$, and 5-Ph-*nido*-7,8,10-C$_2$NB$_8$H$_{10}$] were found in the acidified reaction mixture of the dicarbollide anion and NaNO$_2$. The proposed geometries based on NMR data were confirmed by quantum mechanical calculations.[99] Nitrile insertion into the cluster framework of [*nido*-5,6-C$_2$B$_8$H$_{11}$]$^-$ resulted to give in 65% yield the azatricarbaborane anion [*arachno*-7-CH$_3$-5,7,14,12-C$_3$NB$_8$H$_{11}$]$^-$ **22**. The observed basket structure can either be regarded as a 12-vertex or 10-vertex *arachno*-cluster.[100] On the basis of spectral and computational data, the CN unit in the heteroborane [*hypho*-8-R-8,13-CNB$_8$H$_{14}$] was discussed to be incorporated into the 10-vertex skeleton.[100]

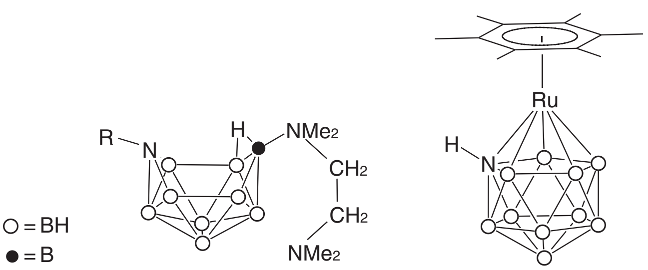
3.03.6.1.7 Nine boron atoms in the skeleton

The structure in the solid state and the chemistry of aza-*closo*-decaborane [RNB$_9$H$_9$] were investigated.[87,101–103] Electrophilic substitutions like halogenation and methylation were carried out. Nucleophilic degradation of the *closo*-cluster by the attack of either the amine *i*PrNH$_2$ or the fluoride [Bu$_4$N]F was studied.[87] Opening of the azaborane was found in the reaction with TMEDA or secondary amines to give RNB$_9$H$_9$(TMEDA) **23** or RNB$_9$H$_{10}$(NR^{1}R^2) (R = 4-ClC$_6$H$_4$, R^1/R^2 = H/*t*Bu, Et/Et, *i*Pr/*i*Pr) (see Figure 10).[103]



20 **21** **22**

Figure 9 Deboronation product of aza-*closo*-decaborane and azacarbaboranes.



23 **24**

Figure 10 Product of the opening of aza-*closo*-decaborane and a ruthenium azaborane.

Hydroboration of alkynes and alkenes with 6-aza-*nido*-decaborane (RNB_9H_{11}, R = H, Ph, $PhCH_2$, 4-C_6H_4Me, 4-C_6H_4Cl) was studied.[104,105] In the course of the investigations on the chemistry of the substitution derivatives of aza-*nido*-decaboranes [$RNB_9H_{10}X$] (R/X = H/H, Ph/H, *p*-MeC_6H_4/H, Bzl/H, H/N_3), the following clusters were isolated and characterized: $[RNB_9H_{11}X]^-$, $[S(RN)B_9H_{10}]^-$, $[Se(RN)B_9H_{10}]^-$, [$(MeS)(RN)B_9H_{10}$], [$(MeSe)(RN)B_9H_{10}$], and $[S(RN)B_9H_{10}F_2]^-$.[90,106] Substitution reactions with Lewis bases at *nido*-azaborane NB_9H_{12} resulted to give a series of derivatives of general type [*exo*-9-L-*arachno*-6-NB_9H_{12}].[107] Nitrogen vertex incorporation was found in the reaction of [4-($NHEt_2$)-*arachno*-B_9H_{13}] with the transition metal complex [$(Cp^*RhCl_2)_2$].[108] The azamonocarbaborane [*hypho*-12-R-12,13-CNB_9H_{15}] (R = Me, Bz) was isolated in low yield and the open-cage structure was characterized by NMR spectroscopy and X-ray crystal structure analysis.[100]

3.03.6.1.8 Ten boron atoms in the skeleton

A tri-*tert*-butylazaboriridine derivative of 7-aza-*nido*-undecaborane was synthesized and structurally characterized.[109,110] A variety of aza-metalla-*closo*-dodecaboranes were prepared and in the case of the ruthenium complex [$(HMB)RuNB_{10}H_{11}$] **24** the structure in the solid state was determined.[111] Reaction of nitriles with deprotonated decaborane $[B_{10}H_{13}]^-$ resulted to give in moderate yield an azacarbaborane $[\textit{arachno}\text{-}7\text{-}R\text{-}7,12\text{-}CNB_{10}H_{13}]^-$ exhibiting an open-cage structure.[100] Aza-*arachno*-undecaboranes ($HNB_{10}H_{12}X$, X = H, N_3) were formed in the reaction of deprotonated aza-*nido*-decaboranes with the electrophile BH_3.[106]

3.03.6.1.9 Eleven boron atoms in the skeleton

Aza-*closo*-dodecaborane [$RNB_{11}H_{11}$] derivatives were synthesized in yields around 41–47% starting with NB_9H_{12}.[105,112] Physical properties of the aza-*closo*-dodecaborane cluster were investigated and the electrophilic substitution was carried out resulting in the isolation of [$MeNB_{11}H_{10}Br$], [$MeNB_{11}H_9Br_2$], [$MeNB_{11}H_8Br_3$], [$MeNB_{11}H_{10}I$], [$HNB_{11}Cl_5I_6$], and [$MeNB_{11}H_5Me_6$].[102,113–115] The opening reaction mechanism of aza-*closo*-dodecaborane was studied and products from the attack with various nucleophiles were presented: $[\textit{nido}\text{-}RNB_{11}H_{11}X]^-$ (R/X = Me/H, Me/F, Ph/OH, H/OMe, Me/OMe, Me/O*t*Bu, Me/NEt_2, Me/Me, Me/Bu, Me/$CpFe(CO)_2$).[116–118]

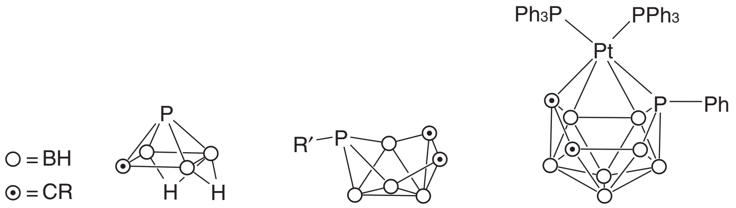
3.03.6.1.10 Macropolyhedral azaboranes

From the reaction of *n*-butyl nitrite with the macropolyhedral borane [*anti*-$B_{18}H_{22}$], an 18-vertex azaborane *anti*-[9-$NB_{17}H_{20}$] was isolated and characterized on the basis of NMR spectroscopy data.[119]

3.03.6.2 Phosphaboranes and Phosphacarbaboranes

3.03.6.2.1 Three boron atoms in the skeleton

Phosphacarba-*nido*-pentaborane [2-*t*Bu-1,2-PCB_3H_5] **25** was synthesized by gas-phase reaction of phosphaalkyne with tetraborane(10) (see Figure 11). In the ^{31}P NMR spectrum a signal at −501 ppm was detected for the apical phosphorus atom and confirmed by quantum mechanical calculations.[120]



25 **26** **27**

Figure 11 Phosphacarba-*nido*-pentaborane, phosphadicarba-*nido*-heptaborane, and a platinum complex with a phosphadicarbaborane ligand.

3.03.6.2.2 Four boron atoms in the skeleton

Halogenated phospha- and arsaboranes [1,2-$P_2B_4Cl_4$], [1,2-$P_2B_4Br_4$], and [1,2-$AsPB_4Cl_4$] were investigated by NMR spectroscopy. $^1J(^{31}P,\ ^{31}P)$, $^1J\ (^{31}P,\ ^{11}B)$, and $^1J(^{11}B,\ ^{11}B)$ coupling constants were determined for the respective heteroborane clusters.[121] High resolution vibrational spectra were measured and discussed for the tetrahalogenated *closo*-1,2-diphosphahexaboranes [$P_2B_4X_4$] (X = Cl, Br).[122] The dimeric phosphaborane [$(P_2B_4Cl_3)_2$] exhibiting a P–P bond was discussed to be formed in the reaction between 4 equiv. PCl_3 and 15 equiv. B_2Cl_4.[123] The arsaphospha-*closo*-hexaborane 1,2-$AsPB_4Cl_4$ was synthesized from a mixture of B_2Cl_4, PCl_3, and $AsCl_3$.[123]

The seven-vertex *nido*-phosphadicarbaborane [*nido*-6-R′-3,4-R_2-6,3,4-$PC_2B_4H_4$] (R = Et, Bz; R′ = Ph, *t*Bu, Me) **26** was prepared by salt eliminaton reaction between the dianion $[nido\text{-}2,3\text{-}R_2C_2B_4H_4]^{2-}$ and R′PCl_2. The proposed structure of the *nido*-phosphacarborane framework based upon NMR spectroscopical findings was confirmed by quantum mechanical calculations.[124]

3.03.6.2.3 Seven boron atoms in the skeleton

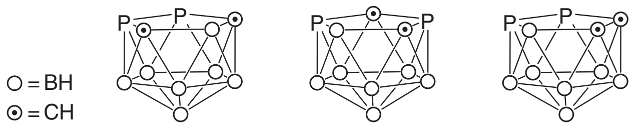
Ten-vertex phosphadicarbaboranes [6-R-*arachno*-6,8,9-$PC_2B_7H_{11}$] (R = Ph, Me) and [6-R-*arachno*-6,5,7-$PC_2B_7H_{11}$] were synthesized using dehydrohalogenation reactions of $RPCl_2$ with the respective dicarbaboranes [*arachno*-4,5-$C_2B_7H_{13}$] and [*arachno*-4,6-$C_2B_7H_{13}$].[125,126] The strong donor properties of the phosphadicarbaborane [6-Ph-*arachno*-6,5,7-$PC_2B_7H_{11}$] were proved in reactions with BH_3, elemental sulfur, hydrogen peroxide, $PtBr_2$, and $PdBr_2$. η^4-Coordination of the heteroborane [6-Ph-*arachno*-6,8,9-$PC_2B_7H_{11}$] was realized after deprotonation and reaction with [$(Ph_3P)_2PtCl_2$] **27** and $NiBr_2$ or by oxidative insertion with a CpCo fragment from [$CpCo(CO)_2$].[125] With the same dicarbaboranes [*arachno*-4,6-$C_2B_7H_{13}$] and [*arachno*-4,5-$C_2B_7H_{13}$] as the starting materials but in reaction with PCl_3, three isomeric 11-vertex *nido*-diphosphadicarbaboranes 7,8,9,11-, 7,9,8,10, and [7,8,9,10-*nido*-$P_2C_2B_7H_9$] **28, 29, 30** were isolated and structurally characterized in the case of the chloroderivatives [3-Cl-7,8,9,11-$P_2C_2B_7H_8$] and [11-Cl-7,8,9,10-$P_2C_2B_7H_8$] (see Figure 12).[127] Halogenation of [7,8,9,11-$P_2C_2B_7H_9$] under electrophilic conditions and with NBS/CH_2Cl_2 was investigated.[128]

From a mixture of the dicarbaborane *arachno*-4,5-$C_2B_7H_{13}$, excess NaH, 2 equiv. proton sponge, and 3 equiv. PCl_3 the triphosphacarbaborane 4-CH_3-*nido*-7,8,9,10-$P_3CB_7H_7$ was found and characterized by a combination of NMR spectroscopical investigations and quantum mechanical calculations.[129]

3.03.6.2.4 Eight boron atoms in the skeleton

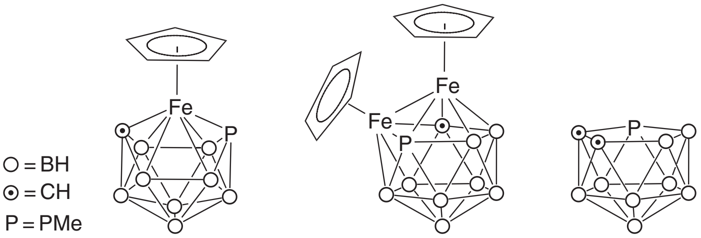
Two isomeric *closo*-phosphacarbaboranes [2,1-PCB_8H_9] and [6,1-PCB_8H_9] were synthesized from the reaction between PCl_3, proton sponge, and the carbaboranes [*arachno*-4-CB_8H_{14}] and [*nido*-1-CB_8H_{12}], respectively.[130] In the reaction with substituted phosphorus dihalide $RPCl_2$ (R = Ph, Me), the deprotonated *arachno*-carbaborane CB_8H_{14} was transferred in high yield into the phosphamonocarbaboranes [*exo*-6-R-*arachno*-6,7-PCB_8H_{12}] and $[6\text{-R-}nido\text{-}6,9\text{-}PCB_8H_9]^-$.[131] A variety of coordination modes of the polyborane ligand [*exo*-6-R-*arachno*-6,7-PCB_8H_{12}] were structurally characterized. The ligand exhibits *endo*-η^1-, *exo*-η^1-, η^4-, η^5-, η^6-coordination in complexes with the following fragments: $CpFe(CO)_2$, $Mn(CO)_5$, $(Ph_3P)_2PtCl$, $(Ph_3P)_2Pt$, CpFe **31, 32** (see Figure 13).[132]

A high yield synthesis for the 11-vertex *nido*-phosphadicarbaborane isomer [*nido*-7,10,11-$RPC_2B_8H_{10}$] (R = Me, Ph) **33** was presented with the reaction of [*nido*-5,6-$C_2B_8H_{12}$] in the presence of proton sponge with the respective alkylphosphorus dihalide ($RPCl_2$). The proposed structure based upon the experimental NMR data was confirmed by quantum mechanical calculations.[133] The analogous unsubstituted derivative [*nido*-7,8,9-$PC_2B_8H_{11}$] was synthesized from [*nido*-5,6-$C_2B_8H_{12}$] and PCl_3 and was structurally characterized as the 10-Cl-substituted isomer.[134] With [*nido*-7,8,11-$PC_2B_8H_{11}$], another isomer in the series of the 11-vertex *nido*-phosphadicarbaboranes was isolated from a mixture of Na_2[*nido*-6,9-$C_2B_8H_{10}$] and PCl_3. Furthermore, [7-Ph-7,8,10-$PC_2B_8H_{10}$] was produced in moderate yield from the reaction of Na_2[*nido*-6,9-$C_2B_8H_{10}$] and $PhPCl_2$.[135–137]



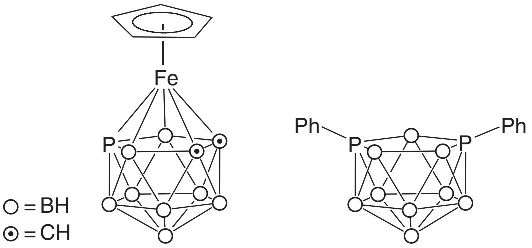
28 **29** **30**

Figure 12 Isomers of diphosphadicarba-*nido*-undecaborane.



31 **32** **33**

Figure 13 CpFe complexes with phosphacarba-*nido*-decaborane; phosphadicarba-*nido*-undecaborane.



34 **35**

Figure 14 Schematic drawing of [1-Cp-*closo*-1,2,4,5-$FePC_2B_8H_{10}$] and diphospha-*nido*-undecaborane.

Complexation with the cyclopentadienyl complex $[CpFe(CO)_2]_2$ was carried out with the [*nido*-7,8,9-$PC_2B_8H_{11}$] cluster and resulted, depending on the reaction temperature, in two η^1-bonded derivatives. Further heating at reflux temperature in xylene produced fully sandwiched complexes [1-Cp-*closo*-1,2,4,5-$FePC_2B_8H_{10}$] **34** and [1-Cp-*closo*-1,2,4,8-$FePC_2B_8H_{10}$] (see Figure 14). The structure of the 1,2,4,5-isomer was determined by X-ray crystal structure analysis.[138] Thermal isomerization of this ferraphosphadicarbaborane derivative was studied at temperatures between 180–350 °C.[139] Two isomeric ferrocene analogs *closo*-[$CpFeP_2CB_8H_9$] of the diphosphacarbaborane ligand [$P_2CB_8H_9$] were identified from the reaction of the *nido*-clusters $[7,8,9\text{-}P_2CB_8H_9]^-$ and $[7,8,10\text{-}P_2CB_8H_9]^-$ with the organometallic complex $[CpFe(CO)_2I]$.[140]

The *closo*-diphosphaborane cluster [1,10-$P_2B_8Cl_8$] was detected by NMR spectroscopy in a reaction mixture of B_2Cl_4 and PCl_3.[123]

3.03.6.2.5 Nine boron atoms in the skeleton

The 11-vertex *nido*-diphosphaborane [7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$] **35** was synthesized in 20% yield from $[B_9H_{12}]^-$ and $PhPCl_2$ and was characterized by NMR spectroscopy and X-ray crystal structure analysis.[141]

3.03.6.2.6 Ten boron atoms in the skeleton

A further synthesis for the 1,2-diphospha-*closo*-dodecaborane cluster was published together with the isolation of mono- and dichloro derivatives.[142] The halogenated polyhedral phosphaborane [*closo*-1,7-$P_2B_{10}Cl_{10}$] was isolated from a heated mixture of B_2Cl_4 and PCl_3.[121,123] Electrophilic iodination of 1-carba-7-phospha-*closo*-dodecaborane was studied to give 9,10-diiodo-1-carba-7-phospha-*closo*-dodecaborane.[143] Insertion of phosphorus into the framework of decaborane was further investigated with the high yield formation of [*nido*-7-$RPB_{10}H_{12}$] (R = Me, Ph), and with the reaction between phosphaalkyne $RP{\equiv}C$ and decaborane adducts [$B_{10}H_{12}L_2$] (R = *t*Bu, adamantyl; L = CH_3CN, SMe_2).[133,144–146]

3.03.6.3 Arsaboranes and Arsacarbaboranes

Co-pyrolysis of B_2Cl_4 and $AsCl_3$ was reported to give 3,4,5,6-tetrachloro-1,2-diarsa-*closo*-hexaborane, which was characterized by mass spectrometry, NMR spectroscopy, and X-ray crystal structure analysis.[121,123,147,148] Three isomers (7,8,9,11; 7,9,8,10; 7,8,9,10) of [*nido*-$As_2C_2B_7H_9$] were synthesized by the incorporation of an As vertex into [*arachno*-4,6-$C_2B_7H_{13}$] or [*arachno*-4,5-$C_2B_7H_{13}$].[149] Transition metal complexes showing η^5-coordination at the As_2B_9 cage as well as η^1-coordination at an As vertex of the As_2B_9 cluster were structurally characterized.[150–153]

3.03.6.4 Group 15 Heteroboranes Investigated by Theoretical Methods

Five-, six-, and seven-vertex *closo*-heteroboranes [XYB_nH_n ($n=3$–5, X, Y = N, CH, P, SiH)] with the heteroatom capping the *n*-membered borocyclic ring B_nH_n ($n=3$–5) were studied by *ab initio* MO calculations. Unsymmetrically capped *closo*-heteroboranes show ring substitutents which are bent toward the cap that provides the less diffuse orbitals.[69] *Ab initio* MO studies on a series of pyramidal structures [B_3H_6X (X = P, PH^+, PO, NH^+, N, NO)] indicate that in the case of phosphorus containing capping groups the terminal hydrogen atoms are directed away from the capping group and in the nitrogen case the hydrogen atoms are directed towards the heteroatom.[70] On the basis of theoretical investigations, the nature of the skeletal bonding was discussed from classical to delocalized in the five-membered *closo*-heteroborane clusters [1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH, Y = NH_2, CH_3, H)].[71–73] A prediction of the relative stabilities based on *ab initio* MO theory was presented for a series of heteroboranes [$(BH)_nX$ (X = NH, PH, $n=4$–6)].[154] The following azaborane clusters have been investigated by *ab initio* studies: 4-NB_8H_{13}, 6-NB_9H_{12}, and 6,9-$N_2B_8H_{12}$.[155] In an extensive computational study on *nido*-eight-vertex heteroboranes, the structures of azaboranes and deprotonated derivatives NB_7H_{10}, $[NB_7H_9]^-$, $[NB_7H_8]^{2-}$, and $N_2B_6H_8$ were predicted.[156] The molecular and electronic structures of *closo*-hexaboranes $[NB_5H_5]^-$, NB_5H_6, 1,6-$N_2B_4H_4$, and 1,2-$N_2B_4H_4$ were studied by *ab initio* and density functional methods.[157] The series of the homologous icosahedral heteroboranes $X_2B_{10}H_{10}$ (X = N, P, Sb) was studied by *ab initio* calculations and the relative stability of the ortho (1,2-), meta (1,7-), and para (1,12-) isomers was discussed.[74]

3.03.7 Derivatives Containing Group 16 Elements

3.03.7.1 Oxaboranes

The oxaplatinaborane cluster [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtOB_8H_{10}$] was synthesized and characterized by X-ray structure analysis.[158] An improved synthesis for oxa-*nido*-dodecaborate $[OB_{11}H_{12}]^-$ was presented, and the NMR spectroscopical data were discussed.[159–162] The macropolyhedral oxaborane $[OB_{18}H_{21}]^-$ was synthesized in moderate yield from [*anti*-$B_{18}H_{22}$] and the structure was crystallographically determined.[163]

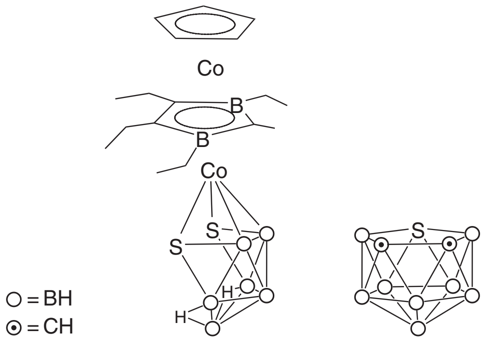
3.03.7.2 Thiaboranes and Thiacarbaboranes

3.03.7.2.1 Three boron atoms in the skeleton

Thiadicarba-*nido*-hexaborane was prepared by hydroboration of thiadiborolane and the structure in the solid state exhibits a five-membered C_2B_2S open face capped by a BH unit.[78,164]

3.03.7.2.2 Six boron atoms in the skeleton

The *hypho*-carbathiaboranes $[7,8\text{-}CSB_6H_{11}]^-$ and [8-Me-7,8-CSB_6H_{11}] were isolated and characterized by NMR spectroscopy.[165] The structure of the thiadicarbanonaborane [*i*$Pr_2C_2SB_6H_6$] was discussed on the basis of the NMR spectroscopical findings and quantum mechanical calculations.[164] The geometry of the nine-vertex *arachno*-thiadicarbaborane [4,6,8-$C_2SB_6H_{10}$] was determined by quantum mechanical calculations.[166] From the reaction of *n*-butyl nitrite with [*arachno*-4-SB_8H_{12}], azathiaborane [*hypho*-7,8-NSB_6H_{11}] was detected as one of the products.[167] Metalladithianonaborane clusters were presented in the following cases: $[Pd(PPh_3)S_2B_6H_8]_2$, $[Cp^*RhS_2B_6H_8]$, $[Pd(PMe_2Ph)_2S_2B_6H_8]$, $[CpCo\{\mu\text{-}(CEt)_2(BEt)_2CMe\}CoS_2B_6H_8]$ **36** (see Figure 15).[168–170]



36 **37**

Figure 15 A triple-decker complex with a dithiaborane, thiadicarba-*nido*-undecaborane.

3.03.7.2.3 Seven boron atoms in the skeleton

The carbathiaborane *arachno*-4,6-CSB_7H_{11} was found as one of the products of the thermolysis of [*arachno*-6,9-$CSB_8H_{11}]^-$.[165] From the reaction of the carbaborane cluster *nido*-5,6-$C_2B_8H_{12}$ with elemental sulfur and Et_3N, the 10-vertex cluster *arachno*-5,6,9-$C_2SB_7H_{11}$ was isolated in moderate yield.[171] Transition metal complexes of $\{S_2B_7\}$-based ligands were investigated and structurally characterized: [9,9-$(PR_3)_2$-9,6,8-$PtS_2B_7H_7$], $[(PPh_3)_2HRh(PPh_3)ClRhS_2B_7H_7]$.[172–174] A rhodium complex with a single Cl atom in bridging position was synthesized with [μ-6,9-Cl-8-(OMe)-6,9-$Cp^*{}_2$-*arachno*-6,9,5-$Rh_2SB_7H_7$].[175]

3.03.7.2.4 Eight boron atoms in the skeleton

Thianonaboranes of the type *exo*-6-L-*arachno*-4-SB_8H_{12} were prepared with variable donors L and in some cases structurally characterized.[176,177] The fluxional process of [*arachno*-4-$SB_8H_{11}]^-$ was studied by NMR spectroscopy and quantum mechanical calculations.[178] In the reaction of the *arachno*-iridaborane $[(PMe_3)_2(CO)HIrB_8H_{12}]$ with H_2S the formation of *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$], *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$], and *nido*-$[(PMe_3)_2HIrS_2B_8H_8]$ was reported.[86] Further complexes with the S_2B_8 ligand were characterized: [8-$\{I(CH_2)_5\}$-3-Cp^*-3,7,8-$RhS_2B_8H_9$], $[(PPh_3)_2HRhS_2B_8H_8]$.[179,180] A synthesis for the thiadicarbaborane [*nido*-7,10,11-$SC_2B_8H_{10}$] was presented and the molecular structure of the isomeric heteroborane [*nido*-7,8,10-$C_2SB_8H_{10}$] **37** was studied by electron diffraction.[133,181] The addition of elemental sulfur to the dicarbaborane [6,9-$C_2B_8H_{10}]^{2-}$ resulted to give an 11-vertex thiadicarbaborane [1,6,7-$C_2SB_8H_{11}]^-$.[182] From the reaction of the thiaborane [*arachno*-4-SB_8H_{12}] and [*nido*-6-SB_9H_{12}] with *n*-butyl nitrite, [*arachno*-6,9-NSB_8H_{11}] and [6-(OH)-*arachno*-6,9-NSB_8H_{10}] were identified.[167]

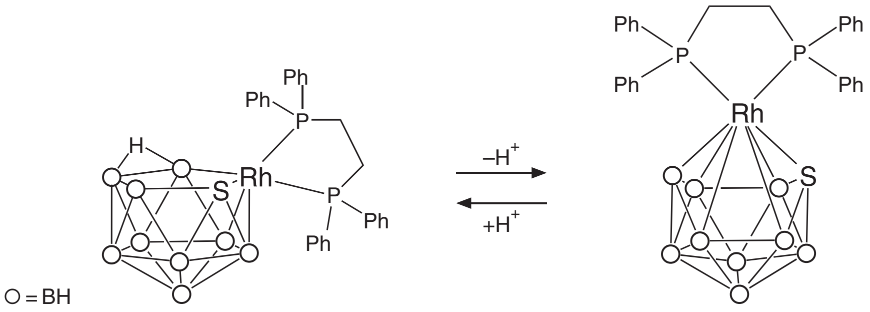
3.03.7.2.5 Nine boron atoms in the skeleton

The formation of adducts [*arachno*-9-L-6-SB_9H_{11}] was studied with several donors L.[107,183–185] The structure of the 1-thia-*closo*-decaborane $[SB_9H_9]$ cluster was determined by microwave spectroscopy.[186]

The structure of the 11-vertex metallathiaborane $[(dppe)RhSB_9H_{10}]$ **38** with a formal *closo* electron count and a *nido*-cluster geometry was investigated with respect to the known triphenylphosphine derivative $[(Ph_3P)_2RhSB_9H_{10}]$. Two Rh···H–C contacts were discussed to furnish the metal center and thus the found structure is consistent with theoretical predictions.[187–189] It was reported that on deprotonation of $[(dppe)RhSB_9H_{10}]$ the agostic bonding switches off and affords a *closo*-cluster geometry, and furthermore that this structural change is fully reversible on reprotonation (Scheme 1).[190,191]

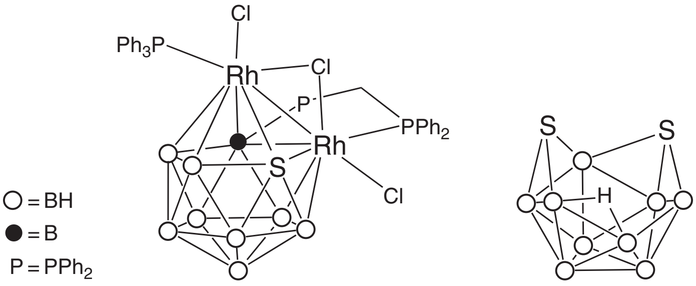
Dirhodathiaboranes $\{Rh_2SB_9\}$ exhibiting *closo*-12-vertex geometry **39** were isolated from the reaction of Cs[6-*arachno*-SB_9H_{12}] with $[RhCl(CO)(PPh_3)_2]$ and by metal insertion into the framework of the *isonido*-metallathiaborane $[(PPh_3)(dppm)RhSB_9H_8]$ (see Figure 16).[192,193] The organometallic chemistry of the rhodathiaborane derivatives [L_n-$RhSB_9H_{10}$] was studied intensively.[194–200]

Isolated from chromatography workup, the monothiaruthenaborane [8-(MeC_6H_4*i*Pr)$RuSB_9H_{11}$] was characterized by NMR spectroscopy.[201]



38

Scheme 1 Deprotonation and reprotonation.



39 **40**

Figure 16 A *closo*-dirhodathiaborane, dithia-*arachno*-undecaborane.

The 11-vertex dithiaborane cluster $[2,3\text{-}S_2B_9H_{10}]^-$ 40 with *arachno*-electron count was synthesized in 47% yield by sulfur insertion into $[nido\text{-}6\text{-}SB_9H_{10}]^-$.[202,203] Metalladithiaboranes $[(PPh_3)_3H_2IrS_2B_9H_{10}]$, $[CpCoS_2B_9H_9]$, and the triple-decker $[CpCo(C_2Et_2B_2Et_2CMe)CoS_2B_9H_9]$ were constructed by complexation of the respective dithiaborane, whereas $[Cp^*RhS_2B_9H_9]$ and $[(MeC_6H_4iPr)RuS_2B_9H_9]$ were formed via direct insertion of sulfur into metallaboranes.[170,180,201]

The *nido*-carbathiaborane $[7,9\text{-}CSB_9H_{11}]$ was one of the products of the thermolysis of $[arachno\text{-}6,9\text{-}CSB_8H_{12}]$.[165] Eleven-vertex azathiaboranes $[S(RN)B_9H_{10}]^-$ (R = Ph, *p*-MeC_6H_4), $[MeS(RN)B_9H_{10}]$ (R = *p*-MeC_6H_4), and $[S(RN)B_9H_{10}F_2]^-$ (R = *p*-MeC_6H_4) were characterized by NMR spectroscopy and single crystal structure analysis.[106]

With the reaction between $[arachno\text{-}6\text{-}SB_9H_{11}]$, $PhPCl_2$, and proton sponge a high yield synthesis for the phosphathiaborane $[nido\text{-}10\text{-}Ph\text{-}7,10\text{-}SPB_9H_9]$ was reported.[133]

3.03.7.2.6 Ten boron atoms in the skeleton

An almost quantitative synthesis of $[nido\text{-}7\text{-}SB_{10}H_{12}]$ was presented with the reaction of decaborane, S_2Cl_2, and proton sponge followed by protonation with concentrated H_2SO_4.[133] In $[2,2\text{-}(PMe_2Ph)_2\text{-}closo\text{-}2,1\text{-}PtSB_{10}H_{10}]$, the free energy of the barrier to the rotation of the $Pt(PMe_2Ph)_2$ fragment was determined.[151]

Trisulfane $(CH_3)_2S_3$ was found to react with decaborane at room temperature to give *arachno*-6,7-μ-$(CH_3S)B_{10}H_{13}$, which was characterized by NMR spectroscopy and quantum chemical calculations.[204]

3.03.7.2.7 Eleven boron atoms in the skeleton

The microwave and the HeI photoelectron (PE) spectra of $[closo\text{-}1\text{-}SB_{11}H_{11}]$ were recorded in order to determine the accurate substitution structure and electronic structure of the *closo*-thiaborate.[205,206] The perchlorinated derivative $[SB_{11}Cl_{11}]$ was identified in a reaction mixture of B_2Cl_4 and S_2Cl_2.[148]

3.03.7.2.8 Macropolyhedral thiaboranes

Reacting the two isomers of the macropolyhedral borane $B_{18}H_{22}$ {[*anti*-$B_{18}H_{22}$] or [*syn*-$B_{18}H_{22}$]} with elemental sulfur, two dithiaboranes were isolated in 48% yield each and structurally characterized: $[S_2B_{17}H_{18}]^-$ **41** from the *anti*-isomer, $[S_2B_{18}H_{19}]^-$ **42** from the *syn*-isomer (see Figure 17).[207,208]

Furthermore, the borane [*syn*-$B_{18}H_{22}$] was transferred into the monothiaborane $[SB_{17}H_{19}]^-$ in good yield by reacting the macropolyhedral borane in a mixture of THF and dilute HCl with $K_2S_2O_5$.[209] The dithiaborane $[S_2B_{17}H_{18}]^-$ was treated with H_2SO_4 to give $[S_2B_{17}H_{17}]$, which was characterized as the deprotonated anion $[S_2B_{17}H_{16}]^-$.[210]

Heating a cyclohexane solution of [*arachno*-4-SB_8H_{12}] for 2 h at 80 °C resulted to give a product of cluster fusion: $[S_2B_{16}H_{16}]$.[211] The triphenylphosphine adduct $[S_2B_{16}H_{14}(PPh_3)]$ was isolated in complexation studies with $[NiBr_2(PPh_3)_2]$.[212] Small amounts of $[S_2B_{17}H_{17}(SMe_2)]$ were found after heating the dimethylsulfide adduct $[SB_8H_{10}(SMe_2)]$ in toluene.[213]

The coordination chemistry of the 18-vertex dithiaborane [*anti*-9,9′-$S_2B_{16}H_{16}$] was studied in the reaction with three different transition metal complexes to give *syn*- and *anti*-$[Cp^*{}_2Rh_2S_2B_{15}H_{14}(OH)]$, $[(Ph_3P)NiS_2B_{16}H_{12}(PPh_3)]$, $[(PhMe_2P)_2PtS_2B_{15}H_{14}(NHCOMe)]$.[212,214,215] Insertion of sulfur into the macropolyhedral metallaborane [*syn*-$Cp^*IrB_{18}H_{20}$] resulted to give a 20-vertex cluster: $[Cp^*IrB_{18}H_{19}S]^-$.[216] The experimentally characterized thiaboranes $[S_2B_{17}H_{17}(SMe_2)]$ and $[S_2B_{18}H_{19}]^-$ were investigated by quantum mechanical calculations.[217]

3.03.7.2.9 Group 16 heteroboranes investigated by theoretical methods

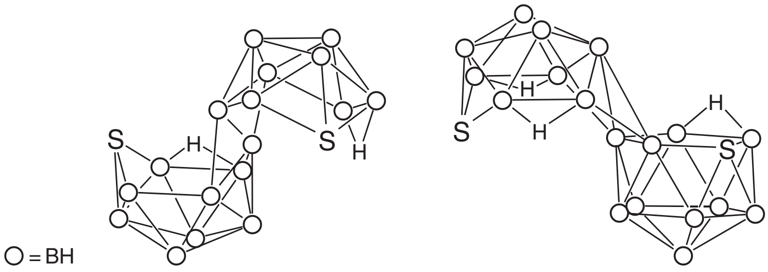
The oxaborane OB_5H_5 was investigated by quantum mechanical calculations.[157] The geometry of several oxa- and thiaboranes [SB_nH_n ($n=4$, 5, 6); $X_2B_6H_6$, XB_7H_9, $[XB_7H_8]^-$, $[XB_7H_7]^{2-}$ ($X=O$, S)] was determined by *ab initio* methods.[154,156] Structures of the 12-vertex oxa- and thia-*nido*-dodecaborates were investigated with the DFT/gauge-including atomic orbital (GIAO)/NMR method.[218]

3.03.7.3 Selenaboranes

The structure and bonding of [*nido*-7,9-$Se_2B_9H_9$] was discussed on the basis of the He(I) PE spectrum.[203] The synthesis and structure of selena-*arachno*-undecaborane $[MeSeB_{10}H_{13}]$ were reported.[203] Selenium was incorporated into the framework of azaboranes to give selenaaza-*arachno*-undecaborates $[Se(RN)B_9H_{10}]^-$ (R = Ph, *p*-MeC_6H_4) and $[(MeSe)(RN)B_9H_{10}]$ (R = *p*-MeC_6H_4).[106]

3.03.7.4 Telluraboranes

Coordination compounds with the TeB_{10} ligand were structurally characterized in the case of Mo, Pd, Rh, and Cu transition metal fragments.[219,220]



41 **42**

Figure 17 Macropolyhedral dithiaboranes.

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3.04
d- and *f*-Block Metallaboranes

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3.04.1 Introduction

This chapter deals with metallaborane chemistry and covers the period from 1994 to 2004. In many respects the format is the same as adopted by Barton and Srivastava in COMC (1995).[1]

Many reviews and book chapters have appeared over the period 1994–2004 on the subject of metallaborane chemistry or related topics (i.e., electronic structures of metallaboranes). Of particular note (in loose chronological order) are:

- The use of metalloorganic precursors for depositing inorganic electronic materials, encompassing the deposition of borides from metallaboranes or related complexes.[2]
- The structures and reactivity of transition metal borides.[3–5]
- Synthesis, structure, and reactions of hydride, borohydride, and aluminohydride compounds of the *f*-elements.[6]
- Chapters in the book *The Borane, Carborane, Carbocation Continuum* are of interest: “Patterns of structures in boranes and carboranes,” “The carboranecarbocation continuum,” “Untangling molecular structures,” and “New species of boranes and carboranes.”[7]

- A review article that deals mainly with monoboron transition metal complexes and also has some useful references for larger systems.[8]
- The hexahydro-*closo*-hexaborate dianion $[B_6H_6]^{2-}$ and its derivatives.[9]
- A *Dalton Transactions* feature article by N. N. Greenwood entitled "Main group chemistry at the millennium," in which the highlights of main group (including boron) chemistry over the last decade are reviewed.[10]
- A comprehensive summary of the theoretical contributions over the past 40 years towards the understanding of the relationship between two-dimensional aromaticity (hydrocarbons) and the electronic structure of three-dimensional deltahedral boranes. Note in particular that rearrangement processes and the "*isocloso* problem" in metallaboranes have also been discussed.[11]
- Main group hydrides which include borohydride species.[12]
- The concept of borane clusters acting as ligands through B–H–M bonds; although this review cites much of the pre-1995 literature, it is still useful.[13]
- The structural and electronic factors that influence metallaboranes of the earlier transition metals.[14]

3.04.2 Borohydride, Hydridoborate, and Related Complexes of the Transition Metals

This section reviews the developments in the chemistry of monoborane complexes of the transition metals especially borohydride and hydridoborate complexes. Although such complexes are not strictly metallaboranes in the sense that they are not cluster species, they are included here as they share many similarities with polyborane species of the transition metals such as three-center two-electron bonding. Additionally, as will be shown in Section 3.04.3.1 borohydride species can also be intermediates in the formation of larger M_xB_y clusters. In this chapter, three-coordinate monoborane species, which are best considered as σ-complexes between a transition metal and HBR_2 or metal–boryl (M–B) species, are not considered.

3.04.2.1 Complexes of $[BH_4]^-$

Some examples of metal complexes of $[BH_4]^-$ are given in Table 1.

3.04.2.1.1 Transition metal complexes

The binary borohydride species $Zr(BH_4)_4$ and $U(BH_4)_4$ have been investigated by quantum mechanical techniques and, for the zirconium case, also by gas-phase electron diffraction. All confirm that these simple molecules have a staggered conformation of borohydride ligands.[15] In a related study, the hafnium analog $Hf(BH_4)_4$ has also been analyzed and is essentially isostructural.[16] These studies show the molecules to possess tetrahedral symmetry with all of the BH_4 ligands triply (i.e., η^3) bridging. Photoelectron spectra [He(I)] of the half and bent metallocene complexes $Zr(\eta^5\text{-}C_5H_5)(BH_4)_4$, $M(\eta^5\text{-}C_5H_5)_2(BH_4)_2$ (M = Zr, Hf), and $Ta(\eta^5\text{-}C_5H_5)_2(BH_4)$ have been determined.[17]

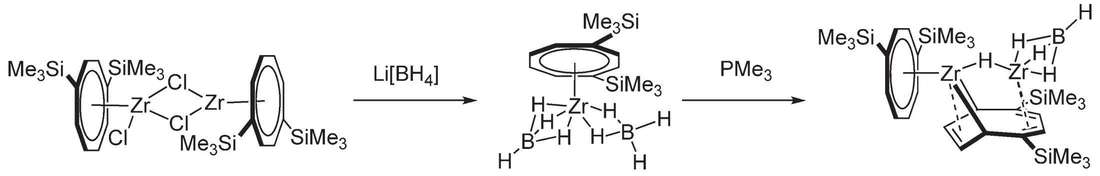
The reaction between $[Zr(COT'')Cl_2]_2$ (COT'' = 1,4-bis(trimethylsilyl)cyclooctatetrane) and excess $Li[BH_4]$ affords the complex $[Zr(\eta^8\text{-}C_8H_6(SiMe_3)_2)(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)]$ **1** in good yield. In the solid state, the two borohydride ligands are found in both η^3- and η^2-bridging modes. Addition of a Lewis base to **1** (e.g., PMe_3) results in the elimination of $H_3B{\cdot}PMe_3$ (a common reaction in metallaborane chemistry) and the isolation of bimetallic $(\eta^8\text{-}C_8H_6(SiMe_3)_2)Zr(\mu\text{-}\eta^6{:}\eta^4\text{-}C_8H_6(SiMe_3)_2)(\mu\text{-}H)Zr(\eta^3\text{-}BH_4)$ **2**.[18] Reaction of the Zr(III) species $Zr(\eta^5\text{-}C_5H_5)(BH_4)[N(SiMe_2CH_2PPr^i_2)_2]$ **3** with CO results in disproportionation to afford the Zr(IV) bisborohydride complex $Zr(\eta^5\text{-}C_5H_5)(BH_4)_2[N(SiMe_2CH_2PPr^i_2)_2]$ **4** and the Zr(II) biscarbonyl species $Zr(\eta^5\text{-}C_5H_5)(CO)_2[N(SiMe_2CH_2PPr^i_2)_2]$. Complex **4** undergoes a slow reaction with CO to form a formyl-ylide complex $Zr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}BH_4)(HCOPPr^i_2CH_2SiMe_2)N(SiMe_2CH_2PPr^i_2{\cdot}BH_3)$ **5**.[19] The hydride presumably arises from one of the $[BH_4]^-$ ligand, with the liberating BH_3 coordinated to one of the phosphine arms.

The zero-valent borohyride complex **6** $[Ti(CO)_3(\eta^3\text{-}BH_4)][K([15]crown\text{-}5)_2]$, which has an η^3-binding mode of the borohydride ligand, results from treatment of $[Ti(CO)_6][K([15]crown\text{-}5)_2]_2$ with $BH_3{\cdot}THF$.[20] Interestingly the structural metrics of the $\{Ti(CO)_3\}$ fragment are indistinguishable form those found in $[Ti(\eta^5\text{-}C_5H_5)(CO)_3]^-$, underlining the isolobal relationship between $[\eta^5\text{-}C_5H_5]^-$ and $[\eta^3\text{-}BH_4]^-$. Zirconium thiolate clusters $Zr_3S_3(Bu^tS)_2(BH_4)(THF)_2$ **7** and $Zr_6S_6(Bu^tS)_4(BH_4)_8(THF)_2$ **8** in which the $[BH_4]^-$ ligands bind either in an η^2- or η^3-coordination mode can be synthesized by the reaction (acidification) of $Zr(BH_4)_4$ with Bu^tSH.[21]

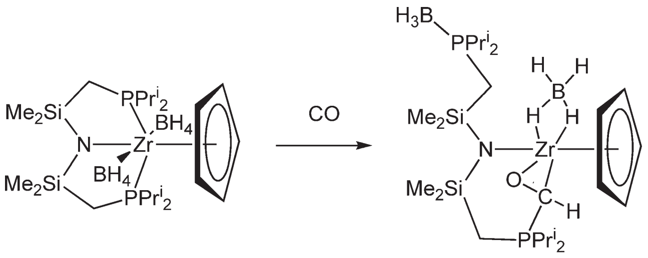
Table 1 Metal complexes of $[BH_4]^-$

No.	*Compound*	*Physical data*	*References*
1	$[Zr(\eta^8\text{-}C_8H_6(SiMe_3)_2)(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)]$	NMR, X-ray	18
2	$[(\eta^8\text{-}C_8H_6(SiMe_3)_2)Zr(\mu\text{-}\eta^6{:}\eta^4\text{-}C_8H_6(SiMe_3)_2)(\mu\text{-}H)Zr(\eta^3\text{-}BH_4)]$	NMR, X-ray	18
3	$Zr(\eta^5\text{-}C_5H_5)(BH_4)[N(SiMe_2CH_2PPr^i{}_2)_2]$	NMR	19
4	$Zr(\eta^5\text{-}C_5H_5)(BH_4)_2[N(SiMe_2CH_2PPr^i{}_2)_2]$	NMR, X-ray	19
5	$Zr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}BH_4)(HCOPPr^i{}_2CH_2SiMe_2)N(SiMe_2CH_2PPr^i{}_2\cdot BH_3)$	NMR, X-ray	19
6	$[Ti(CO)_3(\eta^3\text{-}BH_4)][K([15]crown\text{-}5)_2]$	NMR, X-ray	20
7	$Zr_3S_3(Bu^tS)_2(BH_4)(THF)_2$	NMR, X-ray	21
8	$Zr_6S_6(Bu^tS)_4(BH_4)_8(THF)_2$	NMR, X-ray	21
9	$Nb(\eta^5\text{-}C_5H_4)CEt_2(\eta^5\text{-}C_5H_4)(\eta^2\text{-}BH_4)$	NMR, X-ray	22
10	$Nb(\eta^5\text{-}C_5H_4)(C_5H_{10})(\eta^5\text{-}C_5H_4)(\eta^2\text{-}BH_4)$	NMR	22
11	$Nb(\eta^5\text{-}C_5H_4)C_2Me_2(\eta^5\text{-}C_5H_4)(\eta^2\text{-}BH_4)$	NMR, X-ray	22
12	$Nb(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)(\eta^2\text{-}BH_4)$	NMR, X-ray	22
13	$Nb(\eta^5\text{-}C_5H_3Bu^t)C_2Me_2(\eta^5\text{-}C_5H_3Bu^t)(\eta^2\text{-}BH_4)$	NMR, X-ray	22
14	$V(\eta^5\text{-}C_5H_4)(C_2Me_4)(\eta^5\text{-}C_5H_4)(\eta^2\text{-}BH_4)$	NMR, X-ray	22
15	$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}BH_4)$	NMR	23
16	$Nb(\eta^3\text{-}BH_4)\{N(CHMe_2)(3,5\text{-}C_6H_3Me_2)\}_2\{\eta^2\text{-}CMe_2N\text{-}3,5\text{-}C_6H_3Me_2)\}$	NMR, X-ray	24
17	$Ta_2(\eta\text{-}BH_3)(\mu\text{-}dmpm)_3(\eta^2\text{-}BH_4)_2$	NMR, X-ray	25
18	$Cr(py)_4(\eta^1\text{-}BH_4)_2$	X-ray	26
19	$Cr(tmeda)(\eta^2\text{-}BH_4)_2$	X-ray	26
20	$\{[(tmeda)(py)Cr(\eta^2\text{-}BH_4)]_2[(py)_2Cr(\eta^2\text{-}BH_4)_2]\}(\mu,\eta^1\text{-}BH_4)$	X-ray	26
21	$((\eta^5\text{-}C_5Me_5)Cr)_2(\mu^2\text{-}BH_4)_2$	NMR	27
22	$(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}SMe_2)_3(\mu\text{-}BH_4)$	NMR, X-ray	29
23	$[(Cl_4\text{-}catechol)(PPr_3)MoFe_3S_4(\eta^2\text{-}BH_4)_2]_2[Bu_4N]_4$	X-ray	30
24	$Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2$	NMR	31
25	$[Ru(\eta^1\text{-}BH_4)(CO)H(L)(PMe_2Ph)_2]$ (L = two-electron ligand)	NMR	31
26	$RuH(\eta^1\text{-}BH_4)(Me_8[16]aneS_4)$	NMR, X-ray	32
27	$RuH(\eta^1\text{-}BH_4)(Me_6[15]aneS_4)$	NMR	32
28	$RuH(\eta^1\text{-}BH_4)(binap)(1,2\text{-}diamine)$	NMR, X-ray	33
29	$OsH_3(\eta^2\text{-}BH_4)(PPr^i{}_3)_2$	NMR	35
30	$MeZn(\eta^2{:}\eta^2\text{-}BH_4)$	IR, NMR, X-ray	38

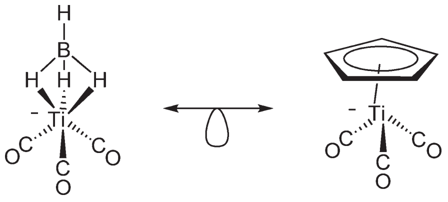
NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.
IR = Characterization by infrared spectroscopy.



1 **2**

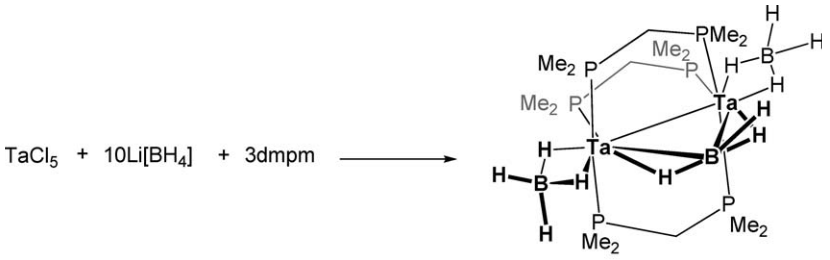


4 **5**



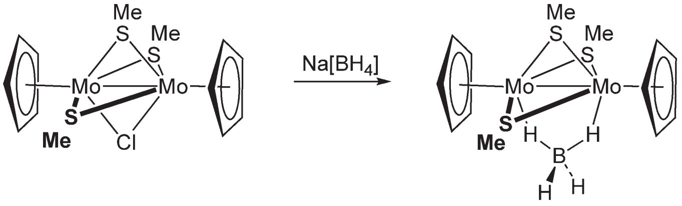
6

Of the group 5 borohydride complexes, a wide range of *ansa*-metallocenes of general formula Nb(η^5-C_5H_3R)-X(η^5-C_5H_3R)(η^2-BH_4) (R = H, X = CEt_2, C(C_5H_{10}), C_2Me_2, $SiMe_2$; R = Bu^t X = C_2Me_2) **9–13** and V(η^5-C_5H_4)-(C_2Me_4)(η^5-C_5H_4)(η^2-BH_4) **14** can be prepared by metathesis from the appropriate dihalide precursors and Li[BH_4]. All these compounds show a bidentate, η^2-, bonding mode for the borohydride in the solid state, while in solution an associative mechanism has been suggested to occur which makes the terminal and bridging hydrides equivalent.[22] The related niobium(III) complex Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-BH_4) **15** is prepared by the addition of BH_3.THF to Nb(η^5-$C_5H_4SiMe_3$)$_2H_3$.[23] The simple metathesis reaction of NbCl(OTf){N($CHMe_2$)(3,5-$C_6H_3Me_2$)}$_3$ and Li[BH_4] gives the η^3-borohydride metallaaziridine complex Nb(η^3-BH_4){N($CHMe_2$)(3,5-$C_6H_3Me_2$)}$_2$ {η^2-CMe_2N-3,5-$C_6H_3Me_2$)} **16**. Reaction with base (quinuclidine) eliminates BH_3·base and a putative hydride complex is formed that inserts ketones in the Nb–H bond.[24] Dinuclear (low-valent) tantalum complexes with borohydride ligands can result from reduction of $TaCl_5$ with $LiBH_4$ in the presence of dmpm (dmpm = bis (dimethylphosphino)methane). Ta_2(η^2-BH_3)(μ-dmpm)$_3$(η^2-BH_4)$_2$ **17** contains a {Ta_2} unit, each end of which has an η^2-BH_4 ligand, while the two metals are spanned by an unusual bridging BH_3 group. Overall the complex can be formulated as having an *arachno*-structure, similar to [B_3H_8]$^-$.[25]



17

Group 6 and 7 borohydride complexes extend to Cr(py)$_4$(BH_4)$_2$ **18**, Cr(tmeda)(BH_4)$_2$ **19**, and {[(tmeda)(py)Cr (η^2-BH_4)]$_2$[(py)$_2$Cr(η^2-BH_4)$_2$]}(μ,η^1-BH_4) **20**.[26] ((η^5-C_5Me_5)Cr)$_2$(BH_4)$_2$ **21** – formed from addition of Li[BH_4] to [(η^5-C_5Me_5)CrCl]$_2$ – and its CO adduct have been spectroscopically characterized.[27] *Ab initio* calculations on Mn(CO)$_4$(BH_4) demonstrate that an η^2-coordination mode for the borohydride ligand is favored and that bridging/terminal hydride exchange occurs through an associative mechanism.[28] Mo_2(η^5-C_5H_5)$_2$(μ-SMe_2)$_3$(μ-Cl) reacts with Na[BH_4] by direct metathesis to give the borohydride complex (η^5-C_5H_5)$_2Mo_2$(μ-SMe_2)$_3$(μ-BH_4) **22**.[29] Reaction of (Cl_4-catechol)$_2Mo_2Fe_6S_8$(PPr^i_3)$_6$ with 4 equiv. of [Bu_4N]BH_4 results in the formation of [(Cl_4-catechol) (PPr_3)$MoFe_3S_4$(η^2-BH_4)$_2$]$_2$[Bu_4N]$_4$ **23** (Cl_4-catechol = tetrachlorocatecholate) which has a double-fused cubane structure with the [BH_4]$^-$ ligands bound to four Fe atoms in a bidentate fashion.[30]



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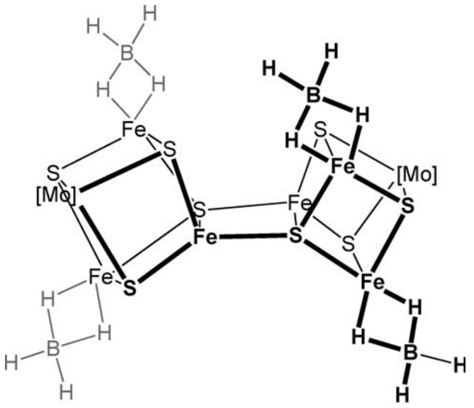
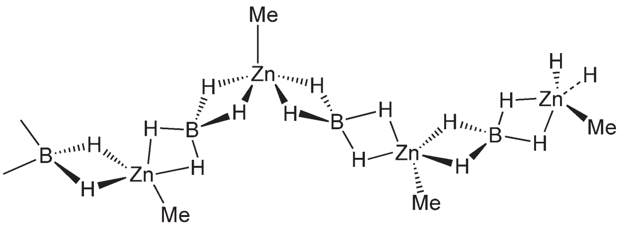


[Mo] = Mo(PPr_3)(Cl_4-catechol)

23

Group 8 complexes with borohydride ligands are represented by a number of complexes. Ru(η^2-BH_4)(CO)H(PMe_2Ph)$_2$ **24** adds two-electron ligands (e.g., L = CO, PR_3) at low temperature to form the η^1-borohydride adducts [Ru(η^1-BH_4)(CO)H(L)(PMe_2Ph)$_2$] **25** which on warming eliminate $H_3B\cdot L$ to give dihydride species.[31] The thioether adducts RuH(η^1-BH_4)(L) [L = Me_8[16]aneS_4 **26**, Me_6[15]aneS_4 **27**] are formed by reduction of dichloro precursors with Na[BH_4] in ethanol.[32] The complexes *trans*-RuH(η^1-BH_4)(binap)(1,2-diamine) **28** are effective catalysts for the asymmetric hydrogenation of simple ketones under base-free conditions.[33] The borohydride ligand is suggested to dissociate to form the adduct $H_3B\cdot HOPr^i$ and a catalytically active ruthenium-hydride species.[34] The exchange processes occurring in the borohydride complex $OsH_3(\eta^2$-$BH_4)(PPr^i{}_3)_2$ **29**[35] have been studied using MP2 calculations and dynamic NMR experiments and indicate that the exchange between terminal and bridging boron hydrides is a relatively high energy process.[36]

Studies on borohydride complexes of post-transition metals are as follows. Theoretical calculations on M(BH_4) (M = Cu, Ag, Au) at the *ab initio* level indicate that Cu(I) and Ag(I) congeners have tetrahydridoborate structures, while the gold(I) complex adopts a hydridoborane structure: HAu(BH_3).[37] MeZn(η^2:η^2-BH_4) **30** is prepared by addition of B_2H_6 to $ZnMe_2$ or MeZnCl and Li[BH_4]. The X-ray structure shows a polymeric helical arrangement of $\{ZnMe\}^+$ and $[BH_4]^-$ fragments—similar to Be(BH_4) or $H_2Ga(BH_4)$ **50**.[38]



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3.04.2.1.2 Lanthanide and actinide complexes

Some examples of borohydride complexes of lanthanide and actinide metals are given in Table 2.

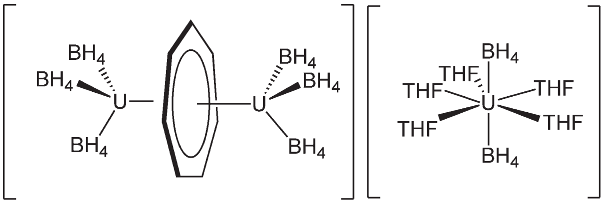
A number of lanthanide and actinide complexes of borohydrides have been synthesized. U(η^5-$C_5H_4PPh_2$)(BH_4)$_3$ **31** and U(η^5-$C_5H_4PPh_2$)$_2$(BH_4)$_2$ **32** have been spectroscopically characterized, along with the $\{C_5H_4Ph_2P\text{-}BH_3\}$ adducts.[39] $[U(BH_4)_2(THF)_5][(BH_4)_3U(\mu\text{-}\eta^7,\eta^7\text{-}C_7H_7)U(BH_4)_3]$ **33** which has a cycloheptatrienyl ligand sandwiched between two uranium centers is formed by the addition of U(BH_4)$_4$ to K[C_7H_9].[40] The simple borohydride complex U(η^3-BH_4)$_4$ has been investigated by DFT and gas-phase electron diffraction and these both show that it has a staggered T_d structure.[15] $[Y(THF)(BH_4)_2]^+$ has been studied at the DFT level and it was concluded that bonding is a combination of electrostatic and covalent interactions.[41] Salt methathesis from a dihalide precursor affords

Table 2 Borohydride complexes of lanthanide and actinide metals

No.	*Compound*	*Physical data*	*References*
31	$U(\eta^5\text{-}C_5H_4PPh_2)(BH_4)_3$	NMR	39
32	$U(\eta^5\text{-}C_5H_4PPh_2)_2(BH_4)_2$	NMR	39
33	$[U(BH_4)_2(THF)_5][(BH_4)_3U(\mu\text{-}\eta^7,\eta^7\text{-}C_7H_7)U(BH_4)_3]$	NMR, X-ray	40
34	$U\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2(BH_4)_2]$	NMR, X-ray	42
35	$(\eta^5\text{-}C_5HPr^i{}_4)Sm(\eta^3\text{-}BH_4)(THF)$	IR, NMR, X-ray	43
36	$(\eta^5\text{-}C_5HPr^i{}_4)_2Sm(\eta^3\text{-}BH_4)$	IR, NMR, X-ray	43
37	$(\eta^5\text{-}C_5HPr^i{}_4)Nd(\eta^3\text{-}BH_4)(THF)$	IR, NMR, X-ray	43
38	$(\eta^5\text{-}C_5HPr^i{}_4)_2Nd(\eta^3\text{-}BH_4)$	IR, NMR, X-ray	43
39	$(\eta^5\text{-}C_5HPr^i{}_4)U(\eta^3\text{-}BH_4)_3$	IR, NMR	43
40	$Sm(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}BH_4)(THF)$	NMR	44,55
41	$(\eta^5\text{-}C_5Me_4{}^nPr)Sm(BH_4)_2(THF)$	NMR	45
42	$[(\eta^5\text{-}C_5Me_4{}^nPr)Sm(BH_4)_2]_6$	NMR, X-ray	45

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.
IR = Characterization by infrared spectroscopy.

$U\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2(BH_4)_2$ **34**.[42] The half and full metallocences $(\eta^5\text{-}C_5HPr^i{}_4)M(\eta^3\text{-}BH_4)(THF)$ and $(\eta^5\text{-}C_5HPr^i{}_4)_2\text{-}M(\eta^3\text{-}BH_4)$ (M = Sm **35**, **36**, Nd **37**, **38**) can be prepared by the reaction of $Na[C_5HPr^i{}_4]$ with $Ln(BH_4)_3(THF)$. $(\eta^5\text{-}C_5HPr^i{}_4)U(\eta^3\text{-}BH_4)_3$ **39** is prepared by the same route.[43] The monoborohydride complex $Sm(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}BH_4)(THF)$ **40** has been successfully used for the controlled ring-opening polymerization of ε-caprolactone (ε-CL). The proposed mechanism is one that involves an $Sm(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}BH_4)(\varepsilon\text{-CL})]$ intermediate.[44] Finally, the samarium and neodymium borohydride complexes exemplified by $(\eta^5\text{-}C_5Me_4{}^nPr)Sm(BH_4)_2(THF)$ **41** are prepared by the reaction of $Sm(BH_4)_3(THF)_3$ and $K[C_5Me_4{}^nPr]$. Hexamers with bridging borohydride groups result from extended storage of **41**, as shown for $[(\eta^5\text{-}C_5Me_4{}^nPr)Sm(BH_4)_2]_6$ **42**.[45]



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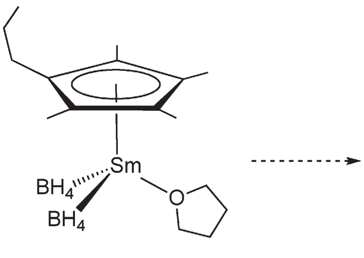

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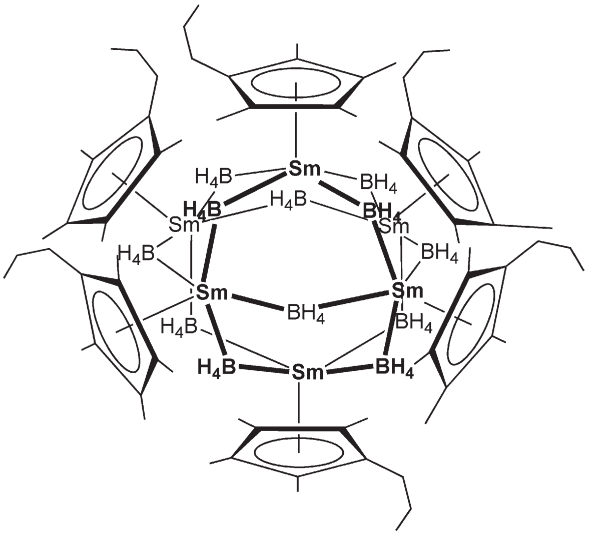

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3.04.2.1.3 Main group complexes

Some examples of borohydride complexes of main group elements are given in Table 3.

Main group borohydride complexes are represented by the following citations. The strontium and barium tetrahydridoborate complexes $M(\eta^3\text{-}BH_4)L$ ($L = O(CH_2CH_2OMe)_2$ or 18-crown-6 (M = Sr **43**, Ba **44**)) can be prepared by ligand displacement from $M(BH_4)_2{\cdot}THF_2$.[46] The structure of $Al(BH_4)_3$ has been probed by *ab initio* calculations, and these show the most stable structure to have D_3 symmetry and one in which the three borohydride ligands adopt an $\eta^2{:}\eta^2{:}\eta^2$ bonding mode.[41] The reactivity of $[HAl(BH_4)]_n$ **45** with a variety of Lewis basic reagents affords hydridoborohydride complexes of aluminum, for example, $Me_3N{\cdot}AlH(BH_4)_2$, compounds **46–49**.[47] Electron diffraction and *ab initio* calculations on $H_2Ga(\eta^2\text{-}BH_4)$ **50** show a structure entirely analogous to diborane in the gas phase, B_2H_6, while in the solid state (at 110 K) a polymeric, helical structure is revealed, with alternating $[GaH_4]^-$ and $[BH_4]^-$ units linked by hydride bridges.[48]

Germanium(IV) and tin(IV) compounds $M(BH_4)_4$ (M = Ge **51**, Sn **52**) have been synthesized by simple salt metathesis and characterized by IR spectroscopy.[49] The cyclic Lewis acid/base adducts between $(o\text{-}C_6F_4Hg)_3$ and $[BH_4]$-, for example, $[(o\text{-}C_6F_4Hg)_3(BH_4)_2]^{2-}$ **53** and $[\{(o\text{-}C_6F_4Hg)_3\}_2(BH_4)]^-$ **54**, have been characterized by IR and NMR spectroscopies.[50]

3.04.2.2 Complexes of $[H_3BR]^-$, $[H_2BR_2]^-$, and $[HBR_3]^-$

Some examples of metal complexes of $[BH_3R]^-$, $[BH_2R]^-$, and $[BHR_3]^-$ are given in Table 4.

3.04.2.2.1 Complexes of main group and lanthanide metals

Reaction of (Nacnac)ScCl(NHAr)(THF) [Nacnac = $ArNC(CH_3)CHC(CH_3)NAr$, Ar = 2,6-$^i\!Pr_2C_6H_3$] with $Na[HBEt_3]$ results in (Nacnac)$Sc(\eta^1\text{-}HBEt_3)$(NHAr)(THF) **55** in which there is one Sc–H–B interaction and two agostic Sc–H–C interactions.[51] **55** eliminates BEt_3 on addition of Et_2O or THF to form a putative scandium hydride that undergoes C–O bond cleavage reactions to form ethoxide or enolate complexes, respectively. Similar borane/agostic interactions are observed in $Ca(\eta^1\text{-}HBEt_3)(\eta^5\text{-}C_5(SiMe_3)_3H_2)(THF)_2$ **56** that is formed by addition of 2 equiv. of $Na[HBEt_3]$ to the $[Ca(\mu\text{-}I)(\eta^5\text{-}C_5(SiMe_3)_3H_2)(THF)]_2$ iodide precursor. In contrast to **55** the hydridoborate is not removed by addition of Lewis bases, with even PMe_3 not displacing borane.[52] Metathesis of the appropriate halide precursor with $Na[HBEt_3]$ results in $Nd(HBEt_3)(\eta^5\text{-}C_5H_4CH_2OCH_3)_2$ **57**[53] and $Sm(HBEt_3)(\eta^5\text{-}C_5H_4Bu^t)_2$ **58**.[54] $Nd(Tp^{Me2})_2(\eta^2\text{-}H_2BEt_2)$ **105** (Tp^{Me2} = Tris(dimethylpyrazolyl)borate) has been isolated serendipitously on reaction of $Nd(Tp^{Me2})_2Cl$ with "$K[BEt_3H]$" (superhydride) in toluene, the dihydridoborate ligand presumed to arise from the superhydride solution that is actually shown to be a mixture of $K[H_2BEt_2]$ and $K[BEt_4]$.[55]

Table 3 Borohydride complexes of main group elements

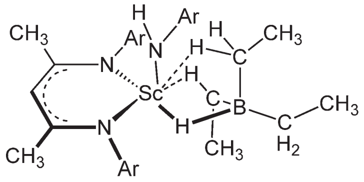
No.	*Compound*	*Physical data*	*References*
43	$Sr(\eta^3\text{-}BH_4)$(18-crown-6)	NMR, X-ray	46
44	$Ba(\eta^3\text{-}BH_4)$(18-crown-6)	NMR, X-ray	46
45	$[HAl(BH_4)_2]_n$	IR, NMR	47
46	$Me_3N{\cdot}AlH(BH_4)_2$	IR, NMR	47
47	$(Me_3N)_2{\cdot}AlH(BH_4)_2$	IR, NMR	47
48	$Et_2O{\cdot}AlH(BH_4)_2$	IR, NMR	47
50	$H_2Ga(\eta^2\text{-}BH_4)$	IR, NMR, X-ray, ED	48
51	$Ge(BH_4)_4$	IR	49
52	$Sn(BH_4)_4$	IR	49
53	$[(o\text{-}C_6F_4Hg)_3(BH_4)_2]^{2-}$	IR, NMR	50
54	$[\{(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$	IR, NMR	50

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.
IR = Characterization by infrared spectroscopy.
ED = Characterization by electron diffraction.

Table 4 Metal complexes of $[BH_3R]^-$, $[BH_2R]^-$, and $[BHR_3]^-$

No.	*Compound*	*Physical data*	*References*
55	$(Nacnac)Sc(\eta^1\text{-}HBEt_3)(NHAr)(THF)$	NMR, X-ray	51
56	$Ca(\eta^1\text{-}HBEt_3)(\eta^5\text{-}C_5(SiMe_3)_3H_2)(THF)_2$	NMR, X-ray	52
57	$Nd(HBEt_3)(\eta^5\text{-}C_5H_4CH_2OCH_3)_2$	NMR	53
58	$Sm(HBEt_3)(\eta^5\text{-}C_5H_4Bu^t)_2$	NMR, X-ray	54
59	$Zr(\eta^5\text{-}C_5H_5)_2Cl[(\mu\text{-}H)_2BC_4H_8]$	NMR, X-ray	56,57
60	$Hf(\eta^5\text{-}C_5H_5)_2Cl[(\mu\text{-}H)_2BC_4H_8]$	NMR, X-ray	56,57
61	$Zr(\eta^5\text{-}C_5H_5)_2H[(\mu\text{-}H)_2BC_4H_8\}$	NMR, X-ray	60
62	$Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR, X-ray	59
63	$Hf(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR	59
64	$Zr(\eta^5\text{-}C_5H_5)_2H\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR, X-ray	58
65	$Zr(\eta^5\text{-}C_5H_5)_2Me\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR, X-ray	58
66	$Zr(\eta^5\text{-}C_5H_5)_2(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$	NMR, X-ray	60
67	$Zr(\eta^5\text{-}C_5H_5)_2(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR, X-ray	60
68	$Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_5H_{10}\}_2$	NMR, X-ray	58
69	$Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)(CH_2Ph)BC_4H_8)(\mu\text{-}H)_2(BC_4H_8)\}$	NMR, X-ray	61
70	$Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)(CH_2Ph)BC_5H_{10})(\mu\text{-}H)_2(BC_5H_{10})\}$	NMR, X-ray	61
71	$Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_4H_8\}$	NMR, X-ray	63
72	$Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_5H_{10}\}$	NMR, X-ray	63
73	$Nb(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_4H_8\}$	NMR, X-ray	63
74	$Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_8H_{14}\}$	NMR, Neutron	63
75	$Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_8H_{14}\}$	NMR, X-ray	67
76	$Zr(\eta^5\text{-}C_5H_5)_2H\{(\mu\text{-}H)_2BC_8H_{14}\}$	NMR, X-ray	67
77	$[Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_4H_8)\}](\mu\text{-}H)][HB(C_6F_5)_3]$	NMR, X-ray	62
78	$Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2B(C_6F_5)_2\}$	X-ray	68
79	$[Nb(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\eta^5{:}\eta^1\text{-}C_5H_4)\text{-}Nb(\eta^5{:}\eta^1\text{-}C_5H_4)_2Nb\{(\mu\text{-}H)\ (\eta^5\text{-}C_5H_4B(C_6F_5)_2\}][HB(C_6F_5)_3]$	NMR, X-ray	64
80	$Nb(\eta^5\text{-}C_5H_5)(C_6F_5)\{(\mu\text{-}H)(\eta^5\text{-}C_5H_4B(C_6F_5)_2\}$	NMR, X-ray	64
81	$Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BHCH_3\}$	NMR, X-ray	69
82	$Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BHCH_3\}_2$	NMR, X-ray	69
83	$Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BHCH_3$	X-ray	69
84	$Zr(\eta^5\text{-}C_5H_5)\{(\mu\text{-}H)_2BC_5H_{10}\}_3$	NMR, X-ray	65
85	$Zr(\eta^5\text{-}C_5H_5)Cl\{(\mu\text{-}H)_2BC_8H_{14}\}_2$	NMR, X-ray	65
86	$Zr(\eta^5\text{-}C_5H_5)\{(\mu\text{-}H)_2BC_8H_{14}\}_3$	NMR, X-ray	65
87	$Zr(\eta^5\text{-}C_5Me_5)Cl\{(\mu\text{-}H)_2BC_8H_{14}\}_2$	NMR, X-ray	65
88	$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{(\mu\text{-}H)_2BO_2C_6H_4\}$	NMR	23
89	$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{(\mu\text{-}H)_2BC_8H_{14}\}$	NMR, X-ray	23
90	$(\eta^5\text{-}C_5H_5)_2Nb(H_2BR_2)$	NMR, X-ray	70
91	$(\eta^5\text{-}C_5H_5)_2Nb(H_2BR_2)$	NMR, X-ray	70
92	$RuH\{(\mu\text{-}H)_2BPin\}(\sigma\text{-}HBpin)(PCy_3)_2$	NMR, X-ray	71
93	$Ru\{(\mu\text{-}H)_2BC_8H_{14}\}_2(PCy_3)$	NMR, X-ray	72
94	$Rh(\eta^2\text{-}H_2BH\{C(CH_3)_2CH(CH_3)_2\})(DiPPE)$	NMR	73
95	$Rh(\eta^2\text{-}H_2C_8H_{14})DiPPE$	NMR	73
96	$Rh(\eta^2\text{-}H_2BC_8H_{14})(PPr^i{}_3)_2$	NMR	73
97	$(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}H_2BClH)(PMe_3)$	NMR, X-ray	79
98	$(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}H_2BCl_2)(PMe_3)$	NMR	79
99	$RuH(PMe_3)_2[\eta^1,\eta^1\text{-}PMe_2CH_2B(C_8H_{14})(\mu\text{-}H)]$	NMR, X-ray	75
100	$OsH(PMe_3)_2[\eta^1,\eta^1\text{-}PMe_2CH_2B(C_8H_{14})(\mu\text{-}H)]$	NMR	75
101	$RuH(PMe_3)_2[\eta^1,\eta^1\text{-}PMe_2CH_2B(thexyl)(\mu\text{-}H)]$	NMR	75
102	$OsH(PMe_3)_2[\eta^1,\eta^1\text{-}PMe_2CH_2B(thexyl)(\mu\text{-}H)]$	NMR	75
103	$Ru(PMe_3)_2[\eta^2,\eta^1\text{-}CH_2CHCMe_2BPh(\mu\text{-}H)_2]$	NMR, X-ray	75
104	$RuH(PMe_3)_2[\eta^2,\eta^1\text{-}CH_2{=}CHB(C_8H_{14})(\mu\text{-}H)]$	NMR, X-ray	75
105	$Nd(Tp^{Me2})_2(\eta^2\text{-}H_2BEt_2)$	X-ray	55

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.
Neutron = Characterization by neutron diffraction.



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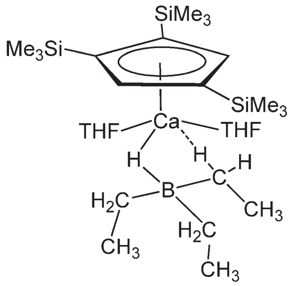

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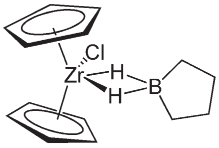
3.04.2.2.2 Complexes of groups 4 and 5

A significant body of work has been produced from the Shore laboratories regarding the coordination chemistry of dihydroborate $[H_2BR_2]^-$ with early transition metals.[56–67] Treatment of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ results in disproportionatation of the anion and the formation of $M(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_4H_8\}$ (M = Zr **59**, Hf **60**).[56,57,63] The related Zr–H hydride complexes $Zr(\eta^5\text{-}C_5H_5)_2H[(\mu\text{-}H)_2BC_4H_8]$ **61** are prepared by addition of $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ in a 2 : 1 ratio of borate to $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$. By employing the preformed salt of the cyclic six-membered organoborate, $K[H_2BC_5H_{10}]$, analogous complexes with this larger cyclic borate can also be accessed, $M(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_5H_{10})\}$ (M = Zr **62**, Hf **63**).[59] All of these complexes react with Lewis bases such as NH_3 to cleave the Zr–H_2B interaction. Reaction of **62** with LiH replaces the final chloride with a hydride to give $Zr(\eta^5\text{-}C_5H_5)_2H\{(\mu\text{-}H)_2BC_5H_{10}\}$ **64**, which undergoes rapid intramolecular hydrogen exchange between terminal hydride, bridging hydrides, and the (η^5-C_5H_5)-hydrogen atoms.[58] The methyl derivative $Zr(\eta^5\text{-}C_5H_5)_2Me\{(\mu\text{-}H)_2BC_5H_{10}\}$ **65** is accessed starting from $K[H_2BC_5H_{10}]$ and $Zr(\eta^5\text{-}C_5H_5)_2ClMe$. The benzyl derivatives $Zr(\eta^5\text{-}C_5H_5)_2(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$ **66** and $Zr(\eta^5\text{-}C_5H_5)_2(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$ **67** can be prepared similarly.[60] The bis-dihydridoborate complex $Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_5H_{10}\}_2$ **68** results from the addition of a further equivalent of $K[H_2BC_5H_{10}]$ to **62**.[58] Addition of $PhCH_2MgCl$ to $Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_4H_8\}$ or $Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_5H_{10}\}$ results in the complexes $Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)(CH_2Ph)BC_4H_8)(\mu\text{-}H)_2(BC_4H_8)\}$ **69** and $Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)(CH_2PhBC_5H_{10})(\mu\text{-}H)_2(BC_5H_{10})\}$ **70**, which have "unsupported" (i.e., not chelated) Zr–H–B bonds. Placing these complexes under extended vacuum liberates borane, for example, $B(C_4H_8)CH_2Ph$, and the hydrido complexes, for example, $ZrH(\eta^5\text{-}C_5H_5)_2)\{(\mu\text{-}H)_2BC_4H_8\}$ **61**, suggesting that the Zr–H bond acts as an electron pair donor to the trivalent boron in **69** and **70**.[61]



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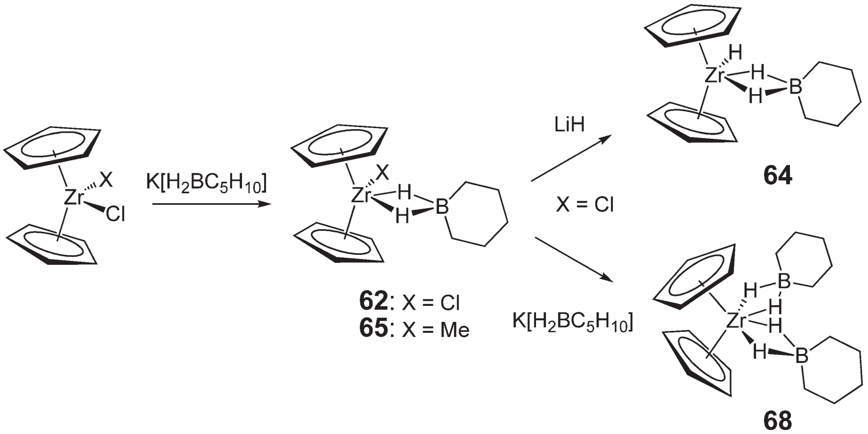


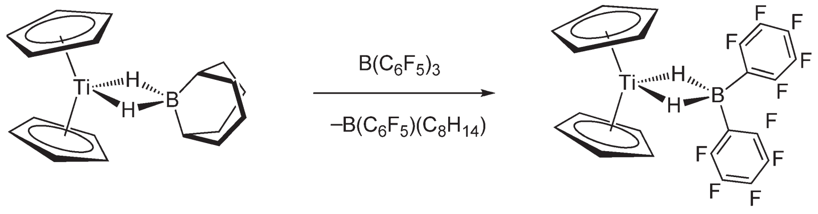
62: X = Cl
65: X = Me

64

68

Ti(III) and Nb(III) complexes of these cyclic borate ligands are prepared by reaction of the precursor cyclic neutral organoborates with tetravalent $M(\eta^5\text{-}C_5H_5)_2Cl_2$ in which one mole of the organoborate reduces M(IV) to M(III) and the second equivalent forms the complex.[63] The Ti(III) complexes are all paramagnetic: $M(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_4H_8\}$ (e.g., M = Ti **71**), $M(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_5H_{10}\}$ (M = Ti **72**, Nb **73**).

The bicyclic organohydridoborate $K[H_2BC_8H_{14}]$ can be used to prepare $Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_8H_{14}\}$ **74**[63] (for which a neutron diffraction study has also been performed[66]), $Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BC_8H_{14}\}$ **75**, $Zr(\eta^5\text{-}C_5H_5)_2H\text{-}\{(\mu\text{-}H)_2BC_8H_{14}\}$ **76**. This latter complex undergoes facile hydrogen scrambling between terminal hydride, bridging hydrides, and the $(\eta^5\text{-}C_5H_5)$ atoms,[67] as observed for complex **64**.

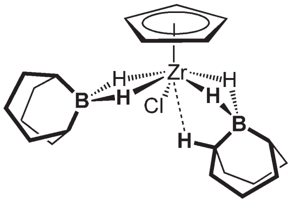


74 **78**

$Zr(\eta^5\text{-}C_5H_5)_2H\{(\mu\text{-}H)_2BC_4H_8\}$ reacts with the Lewis acid $B(C_6F_5)_3$ in benzene to form the unsupported hydride-bridged cation $[Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BC_4H_8\}(\mu\text{-}H)][HB(C_6F_5)_3]$ **77**.[62] Reaction between **67**, **69**, or **74** and $B(C_6F_5)_3$ results in the elimination of $B(C_6F_5)(BR_2)$ and the formation of the paramagnetic Ti(III) complex $Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2B(C_6F_5)_2\}$ **78**.[68] With the niobium complex **68** reaction with $B(C_6F_5)_3$ in toluene affords trimeric $[Nb(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\eta^5{:}\eta^1\text{-}C_5H_4)Nb(\eta^5{:}\eta^1\text{-}C_5H_4)_2Nb\{(\mu\text{-}H)(\eta^5\text{-}C_5H_4B(C_6F_5)_2\}][HB(C_6F_5)_3]$ **79**, while in diethyl ether monomeric $Nb(\eta^5\text{-}C_5H_5)(C_6F_5)\{(\mu\text{-}H)(\eta^5\text{-}C_5H_4B(C_6F_5)_2\}$ **80** forms.[64]

The acyclic dihydridoborate complexes $Zr(\eta^5\text{-}C_5H_5)_2Cl\{(\mu\text{-}H)_2BHCH_3\}$ **81**, $Zr(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BHCH_3\}_2$ **82**, and paramagnetic $Ti(\eta^5\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BHCH_3\}$ **83** are all formed by the addition of $Li[BH_3CH_3]$ to dihalide precursors, just as for the cyclic organoborates discussed previously in this section.[69]

Half metallocene complexes of cyclic organohydroborates can be produced by reaction of the precursor anions with $Zr(\eta^5\text{-}C_5H_5)Cl_3$, exemplified by the reaction of $Zr(\eta^5\text{-}C_5H_5)Cl_3$ with 3 equiv. of $K[H_2B(C_5H_{10})]$ to afford $Zr(\eta^5\text{-}C_5H_5)\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ **84**, or with 2 equiv. of $K[H_2B(C_8H_{14})]$ to afford $Zr(\eta^5\text{-}C_5H_5)Cl\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **85** which shows an agostic interaction between the metal center and a C–H group on the borate ligand. Related complexes with $\{(\mu\text{-}H)_2BC_8H_{14}\}$ **86** and Cp* ligands **87** have also been prepared.[65]



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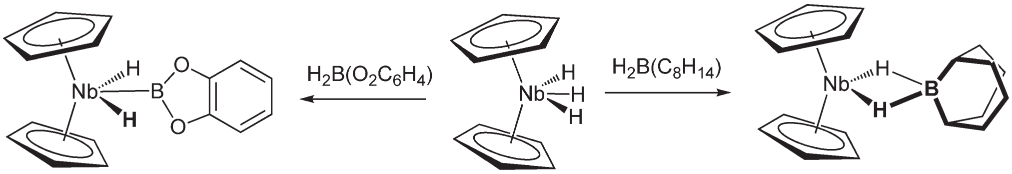
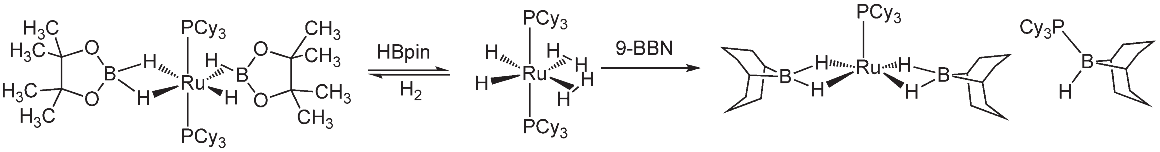
The niobium congener of **74**, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{(\mu\text{-}H)_2BR_2)\}$, can be prepared by the addition of HBR_2 to $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ ($R = O_2C_6H_4$ **88**, C_8H_{14} **89**).[23] Closely related complexes $(\eta^5\text{-}C_5H_5)_2Nb(H_2BR_2)$ ($R_2 =$ catechol, $O_2C_6H_4$ **90**, and C_8H_{14} **91**) can be synthesized by the addition of HBR_2 to the trihydride $(\eta^5\text{-}C_5H_5)_2NbH_3$. NMR and X-ray experiments demonstrate that **90** is best described as lying towards having a dihydridoboryl structure whilst **91** is best described as a dihydridoborate.[70]



90 **91**

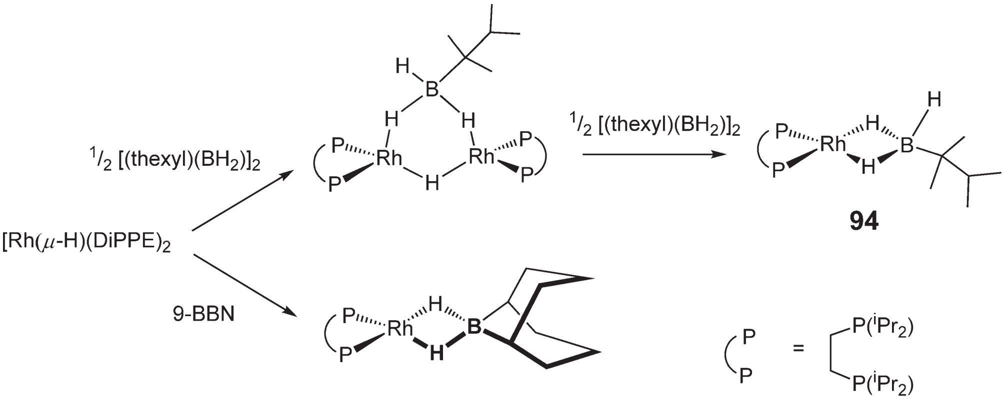
3.04.2.2.3 Complexes of groups 8 and 9

Dihydroborate complexes of ruthenium have been reported by a number of research groups. Addition of HBpin (pin = $O_2C_2H_4$) to $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ results in the formation of a complex that has both σ-borane and dihydroborate ligands in the same coordination sphere: $RuH\{(\mu\text{-}H)_2BPin\}(\sigma\text{-}HBpin)(PCy_3)_2$ **92**.[71] In contrast, reaction with 9-BBN (HBC_8H_{14}) results in a monophosphine/bisdihydroborate complex, $Ru\{(\mu\text{-}H)_2BC_8H_{14}\}_2(PCy_3)$ **93**, and the concomitant formation of $Cy_3P\cdot HBC_8H_{14}$.[72]



92 **93**

Addition of thexylborane or 9-H-BBN to dimeric bridged hydride $[Rh(\mu\text{-}H)DiPPE]_2$ [DiPPE = 1,2-bis(diisopropylphosphino)ethane] gives the corresponding mononuclear substituted borohydride complexes $Rh(\eta^2\text{-}H_2BRR')(DiPPE)$ **94** R = H, R′ = $C(CH_3)_2CH(CH_3)_2$ {thexyl}; **95** R,R′ = bicyclo-[3.3.1]-nonane {C_8H_{14}}). Complex **94** forms via the previously characterized bridging trihydridoborate complex $[Rh(DiPPE)]_2(\mu\text{-}H)\{\eta^2\text{-}H_2BH(thexyl)\}$. The monodentate dihydridoborate phosphine complex $Rh(\eta^2\text{-}H_2BC_8H_{14})(PPr^i_3)_2$ **96** was also isolated and structurally characterized.[73] $(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}H_2BClH)(PMe_3)$ **97** and $(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}H_2BCl_2)(PMe_3)$ **98** are isolated from a reaction of excess $BH_3\cdot PMe_3$ with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ or $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$, respectively,[74] transfer of chloride to borane occurring to afford the coordinated hydridochloroborate with concomitant transfer of the phosphine from borane to the metal. This is related to the chemistry observed on reaction of BH_3 with cyclopentadienyl metal halides (see Section 3.04.3.2.2.(ii)) in which the first step is replacement of a metal halide with hydride and formation of BH_2Cl. With metal fragments without a halide $BH_3\cdot PMe_3$ forms simple (albeit sometimes unstable) complexes in which the phosphine borane is a σ-ligand to the metal (as discussed in Section 3.04.2.3).



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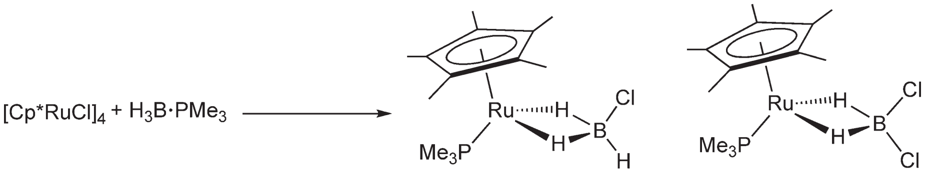
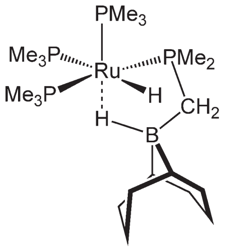


97 **98**

Chelated ruthenium hydridoborates $MH(PMe_3)_2[\eta^1,\eta^1\text{-}PMe_2CH_2BRR'(\mu\text{-}H)]$ (M = Ru, Os, RR′ = thexyl or C_8H_{14} **99**–**102**) result from addition of the appropriate organoborane BRR′H to $RuH(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$, via the insertion of B–H into an Ru–C bond (Figure 18). B–C bond formation also occurs in the reaction of $Ru(PMe_3)_4(\eta^2\text{-}C_6H_4)$ with thexylborane to give $Ru(PMe_3)_2[\eta^2,\eta^1\text{-}CH_2CHCMe_2BPh(\mu\text{-}H)_2]$ **103** and

$Me_3P{\cdot}BH_2$(thexyl). Reaction of $Ru(PMe_3)_4(\eta^2\text{-}C_2H_4)$ with 9-H-BBN gives a vinylborane complex $RuH(PMe_3)_2[\eta^2,\eta^1\text{-}CH_2{=}CHB(C_8H_{14})(\mu\text{-}H)]$ **104** and 1 equiv. of $Me_3P{\cdot}BH(C_8H_{14})$.[75]



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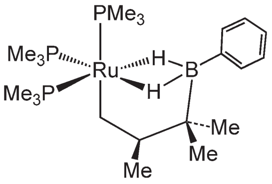

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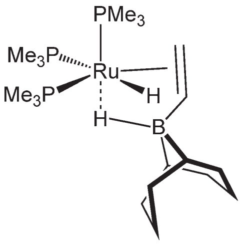


104

3.04.2.3 Complexes of $BH_3{\cdot}PR_3$

Some examples of complexes of $H_3B{\cdot}PR_3$ are given in Table 5.

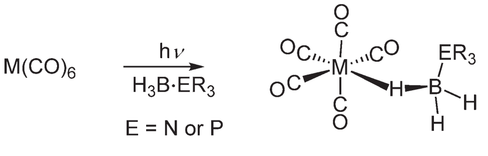
Photolysis of $M(CO)_6$ (M = Cr, W) in the presence of $BH_3{\cdot}L$ (L = NMe_3, PMe_3, PPh_3) gives the borane complexes $M(CO)_5(\eta^1\text{-}BH_3{\cdot}L)$ (M = Cr, L = PMe_3 **106**; PPh_3 **107**; NMe_3 **109**; M = W, L = PMe_3 **110**; PPh_3 **111**; NMe_3 **112**). The Mo analogs are unstable. In these products monoborane–Lewis base adduct coordinates to the metal center through a B–H–M three-center two-electron bond – analogous (and isolectronic with) transient alkane ligands.[76] The isolectronic manganese complexes $[Mn(CO)_4(PR_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)][BAr^F{}_4]$ (PR_3 = PMe_2Ph **113**; PEt_3 **114**) are formed by protonation of the σ-boryl complex $Mn(CO)_4(PMe_2Ph)(BH_2{\cdot}PMe_3)$ or displacement of weakly bound diethyl ether in $Mn(CO)_4(PMe_2Ph)(OEt_2)$ by $BH_3{\cdot}PR_3$.[77] The related, neutral complexes $Mn(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}BH_3{\cdot}L)$ (L = NMe_3, **115**; PMe_3 **116**) are prepared by photolysis of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ with $BH_3{\cdot}L$.[78] The complexes **106** to **116** are generally unstable, the phosphine borane being readily replaced by CO or other two-electron ligands. Putting the borane ligand in a chelate ring stabilizes this decomposition somewhat (see later). The fluxional behavior of chromium and tungsten complexes of the previously reported monodentate bis(trimethylphosphine)diborane(4), $M(CO)_5(\eta^1\text{-}B_2H_4{\cdot}2PMe_3)$ (M = Cr, W) shows that there are two fluxional processes in solution: a very rapid geminal exchange and a slower vicinal exchange. This behavior mimics that

Table 5 Complexes of $H_3B{\cdot}PR_3$

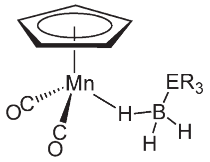
No.	*Compound*	*Physical data*	*References*
106	$M(CO)_5(\eta^1\text{-}BH_3{\cdot}PMe_3)$	NMR, X-ray	76
107	$Mo(CO)_5(\eta^1\text{-}BH_3{\cdot}PPh_3)$	NMR	76
109	$Mo(CO)_5(\eta^1\text{-}BH_3{\cdot}NMe_3)$	NMR	76
110	$W(CO)_5(\eta^1\text{-}BH_3{\cdot}PMe_3)$	NMR, X-ray	76
111	$W(CO)_5(\eta^1\text{-}BH_3{\cdot}PPh_3)$	NMR, X-ray	76
112	$W(CO)_5(\eta^1\text{-}BH_3{\cdot}NMe_3)$	NMR	76
113	$[Mn(CO)_4(PMe_2Ph)(\eta^1\text{-}BH_3{\cdot}PMe_3)][BAr^F{}_4]$	NMR	77
114	$[Mn(CO)_4(PEt_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)][BAr^F{}_4]$	NMR	77
115	$Mn(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}BH_3{\cdot}NMe_3)$	NMR, X-ray	78
116	$Mn(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}BH_3{\cdot}PMe_3)$	NMR, X-ray	78
117	$(\eta^2\text{-}dppm{\cdot}BH_3)RhSB_9H_{10}$	NMR, X-ray	81,82
118	$(\eta^2\text{-}dppm{\cdot}BH_3)RhC_2B_8H_{11}$	NMR, X-ray	82
119	$Cr(\eta^2\text{-}dppm{\cdot}BH_3)(CO)_4$	NMR, X-ray	84
120	$(\eta^5\text{-}C_5H_5)Ru(PMe_3)(\eta^2\text{-}dppm{\cdot}BH_3)$	NMR, X-ray	84
121	$(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}dppm{\cdot}BH_3)$	NMR, X-ray	84
122	$[Rh(cod)(\eta^2\text{-}dppm{\cdot}BH_3)][BF_4]$	NMR, X-ray	83
123	$[(pmdeta)Li\{Pr^n_2P(BH_3)\}(Me_3Si)CCH_2]_2$	NMR, X-ray	85

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

predicted for the isolobal ethane complex $W(CO)_5(\eta^1\text{-}C_2H_6)$.[79] $Re(\eta^1\text{-}BH_3{\cdot}PMe_3)(PPh_3)_2H_5$ is a putative intermediate in the H/D exchange reaction of $BH_3{\cdot}PMe_3$ to $BD_3{\cdot}PMe_3$ catalyzed by $Re(PPh_3)_2H_7$.[80]



106–112



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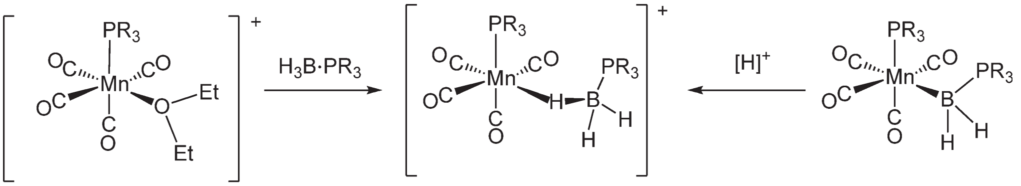
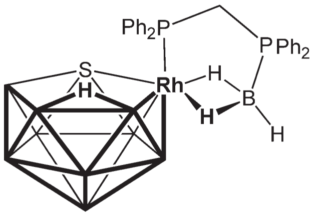
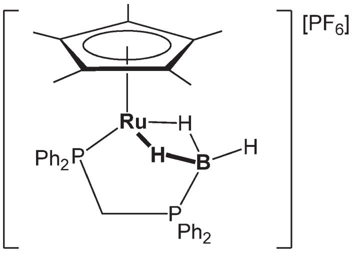
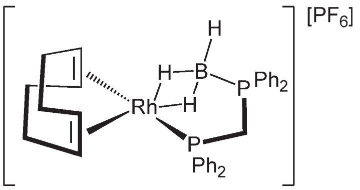


113, 114

Compounds with intramolecular, chelating $R_2P{\cdot}BH_3{\cdots}M$ interactions have been reported, and these have shown greater stability than the monodentate phosphine boranes – due to the chelate effect. Addition of excess $BH_3{\cdot}THF$ to $(\eta^2\text{-dppm})(\eta^1\text{-dppm})RhSB_9H_{10}$ or $(\eta^2\text{-dppm})(\eta^1\text{-dppm})RhC_2B_8H_{11}$, both if which contain a pendant dppm group, results in the loss of $dppm{\cdot}(BH_3)_2$ and clusters that have a bidentate $dppm{\cdot}BH_3$ group that coordinate via a PPh_2 and an $\eta^2\text{-}BH_3$ group, $(\eta^2\text{-dppm}{\cdot}BH_3)RhSB_9H_{10}$ **117** and $(\eta^2\text{-dppm}{\cdot}BH_3)RhC_2B_8H_{11}$ **118**.[81,82] An alternative approach to the synthesis of complexes with chelating $dppm{\cdot}BH_3$ ligands is to take preformed $dppm{\cdot}BH_3$ and react it with a suitable precursor metal fragment. Using this approach, chromium $Cr(\eta^2\text{-dppm}{\cdot}BH_3)(CO)_4$ **119**, ruthenium, for example, $(\eta^5\text{-}C_5H_5)Ru(PMe_3)(\eta^2\text{-dppm}{\cdot}BH_3)$ **120**, $(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-dppm}{\cdot}BH_3)$ **121**, and rhodium $[Rh(cod)(\eta^2\text{-dppm}{\cdot}BH_3)][BF_4]$ **122** complexes have been prepared.[83,84]

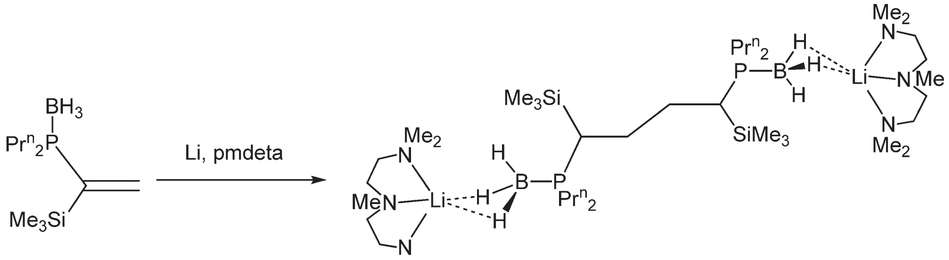






117 **121** **122**

The reaction (a Schlenk dimerization) between the phosphine–borane-substituted alkene $\{^nPr_2P(BH_3)\}(Me_3Si)C{=}CH_2$ and elemental lithium in THF yields the complex $[(pmdeta)Li\{Pr^n{}_2P(BH_3)\}(Me_3Si)CCH_2]_2$ **123** which in the solid state has a lithium bound to the BH_3 hydrogens of the ligand, and no Li–C(carbanion) contact (pmdeta = N,N,N′,N″,N″-pentamethyldiethylenetriamine).[85]



123

3.04.3 Metallaborane Complexes

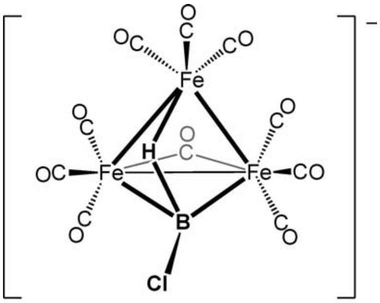
Metallaborane clusters constitute by far the largest subsection of this chapter and the last decade has seen much development of the synthesis and reaction chemistry of metallaborane systems. Three areas stand out in particular: (i) the chemistry of monoboron metallaboranes – especially the metal borides – which has been extensively investigated by Housecroft,[90–106] (ii) the rational and high yield routes to metallaboranes by sequential cluster buildup from addition of monoboron sources to cyclopentadienyl metal halides has been developed by Fehlner. Through this work metallaborane systems are now routinely available in good yield from commercially available starting materials (i.e., BH_3·THF and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$),[115,119–139,141–156,158,161–172,182] (iii) the development of macropolyhedral metallaborane chemistry – metallaborane chemistry past the icosahedron developed principally by Kennedy.[201–214]

In this section, monoboron clusters will be dealt with first, moving through the transition metals group by group with increasingly higher ratios of boron to metal. Many of these metallaborane species contain more than one type of metal and they are discussed in the order of the metal present in the starting material from which they are synthesized.

3.04.3.1 Monoboron Clusters

Some examples of monoboride metallaborane clusters are given in Table 6.

Monoboron cluster species of groups 8 and 9 show rich chemistry, much of which centers around deprotonation of bridging B–H–M hydrides in neutral clusters to leave an anionic cluster. For iron-based clusters deprotonation of $[Fe_3(CO)_9(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}BH)]^-$ affords the dianionic species $[Fe_3(CO)_9(\mu^3\text{-}BHCO)]^{2-}$ **124**. Reprotonatation leads to decomposition, while reaction with $FeCl_3$ affords the chlorometallaborane of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}BHCl)]^-$ **125**.[86] The anionic ferraboranes $[Fe_5H(CO)_{15}B]^-$ **126**, $[Fe_6H(CO)_{17}B]^-$ **127**, and $[Fe_7H(CO)_{19}B]^-$ **128** are sequentially formed on reaction of $[Fe_4(CO)_{12}HB]^{2-}$ with simple iron carbonyls.[87] The structure of **128** shows the boron atom to be residing inside a monocapped trigonal prism of iron atoms. Mixed metal metallaboranes $Fe_2Co(CO)_9(\mu\text{-}CO)BH_2$ **129**, $FeCo_2(CO)_9(\mu\text{-}CO)BH$ **130**, $FeCo_2(CO)_9(BH_2)$ **131**, and $HFe_3Co(CO)_{12}BH$ **132** can be prepared from reaction of $Co_2(CO)_8$ with a variety of ferramonoboranes.[88] The metallaborane analog of *nido*-$[B_4H_7]^-$, $\{Fe(CO)_2(PPh_3)\}\{Ir(CO)_2(PPh_3)\}B_2H_5$ **133**, is formed on reaction of $[\{\mu\text{-}Fe(CO)_4\}B_6H_9]^-$ with Vaska's complex.[89]



125

The mixed metal butterfly cluster $HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}BH$ is readily deprotonated, losing a bridging B–H–Ru hydride, to afford anionic $[HRu_3W((\eta^5\text{-}C_5H_5))(CO)_{11}B]^-$ **134**, which reacts with $ClAuPPh_3$ to give neutral $HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}B(AuPPh_3)$ **135**, in which the gold–phopsphine fragment takes the place of the bridging proton, as expected for these isolobal fragments.[90] Reactions with bidentate gold–phosphines have also been described affording, for example, $\{HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}BAu\}(\mu\text{-}dppf)$ **136** (dppf = 1,1′-bis(diphenylphosphino)ferrocene).[90] The butterfly cluster with mixed phopshine/carbonyl ligands $HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11-x}(PPh_3)_xBH$ ($x = 1$, $x = 2$ **137**) have been prepared by the reaction of PPh_3 with $HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}BH$ after Me_3NO/MeCN activation.[91]

Mixed metal ruthenium/group 9 clusters also show rich chemistry. Synthetically, such clusters are generally synthesized by the addition of a metal chloride to an anionic boridocluster in a cluster expansion reaction. For example, $[Ru_3(CO)_9BH_4]^-$ undergoes cluster expansion with $[Ru(\eta^6\text{-}arene)Cl_2]_2$ (arene = C_6H_6, C_6H_5Me, MeC_6H_4-4-^iPr) to afford $Ru_4H(\eta^6\text{-}C_6H_6Me)(CO)_9BH_2$ **138**.[92] Compared with the previously reported $Ru_4H(CO)_{12}BH_2$

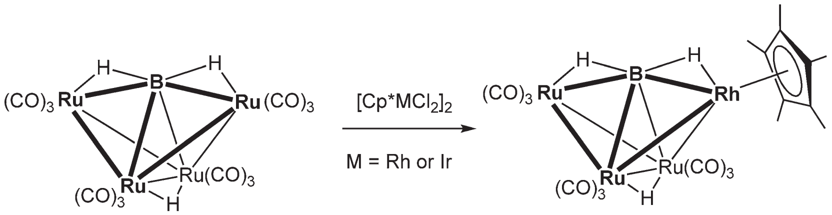
Table 6 Monoboride metallaborane clusters

No.	*Compound*	*Physical data*	*References*
124	$[Fe_3(CO)_9(\mu^3\text{-}BHCO)]^{2-}$	NMR	86
125	$[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}BHCl)]^-$	NMR, X-ray	86
126	$[Fe_5H(CO)_{15}B]^-$	NMR	87
127	$[Fe_6H(CO)_{17}B]^-$	NMR	87
128	$[Fe_7H(CO)_{19}B]^-$	NMR, X-ray	87
129	$Fe_2Co(CO)_9(\mu\text{-}CO)BH_2$	NMR	88
130	$FeCo_2(CO)_9(\mu\text{-}CO)BH$	NMR	88
131	$FeCo_2(CO)_9(BH_2)$	NMR	88
132	$HFe_3Co(CO)_{12}BH$	NMR	88
133	$\{Fe(CO)_2(PPh_3)\}\{Ir(CO)_2(PPh_3)\}B_2H_5$	NMR, X-ray	89
134	$[HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}B][PPN]$	NMR	90
135	$HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}B(AuPPh_3)$	NMR, X-ray	90
136	$\{HRu_3W(\eta^5\text{-}C_5H_5)(CO)_{11}BAu\}(\mu\text{-dppf})$	NMR	90
137	$HRu_3W(\eta^5\text{-}C_5H_5)(CO)_9(PPh_3)_2BH$	NMR	91
138	$Ru_4H(\eta^6\text{-}C_6H_6Me)(CO)_9BH_2$	NMR, X-ray	92
139	$RhRu_3(\eta^5\text{-}C_5Me_5)H(CO)_9BH_2$	NMR, X-ray	93
140	$IrRu_3(\eta^5\text{-}C_5Me_5)H(CO)_{10}BH_2$	NMR, X-ray	93
141	$RhRu_4H_2((\eta^5\text{-}C_5Me_5))(\mu\text{-}Cl)(CO)_{12}B$	NMR, X-ray	94
142	$RhRu_4H(nbd)(CO)_{12}B(AuPPh_3)$	NMR, X-ray	94
143	$RhRu_4H((\eta^5\text{-}C_5Me_5))(CO)_{13}BH_2$	X-ray	95
144	$[Rh_2Ru_4(CO)_{16}B]^-$	NMR, X-ray	96
145	$[Rh_3Ru_6(CO)_{23}B_2]^-$	NMR, X-ray	96
146	$Ru_4H(CO)_{12}BH(\mu\text{-}NCHMe)$	NMR, X-ray	97
147	$Rh_2Ru_4(CO)_{16}BAu(PCy_3)$	NMR, X-ray	98
148	$\{Rh_2Ru_4(CO)_{16}B\}_2\{\mu\text{-}Au(dppm)Au\}$	NMR	99
149	$\{Rh_2Ru_4(CO)_{16}B\}_2\{\mu\text{-}Au(dppp)Au\}$	NMR, X-ray	99
150	$RhRu_4(CO)_{14}B\{Au(dppm)Au\}$	NMR	99
151	$Ir_2Ru_4(CO)_{16}BAu(PCy_3)$	NMR, X-ray	98
152	$[Ir_2Ru_4(CO)_{16}B][PPN]$	NMR, X-ray	98
153	$\{Ru_6(CO)_{17}B\}_2(\mu\text{-}Au(dppp)Au)$	NMR	100
154	$Ru_6(CO)_{17}B\{Au(dppe)AuCl\}$	NMR	100
155	$\{Ru_6(CO)_{17}B\}_2(\mu\text{-}Au)$	NMR	100
156	$RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9B\{Au(PPh_3)\}_2AuCl$	NMR, X-ray	101
157	$RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9B\{Au_2(dppf)\}_2AuCl$	NMR, X-ray	101
158	$\{HRu_4(CO)_{12}B\}_2Cu_4(\mu\text{-}Cl)$	NMR, X-ray	102
159	$[(HRu_4(CO)_{12}BH)Ag]^-$	NMR, X-ray	102
160	$Ru_6(CO)_{16}B(PR_3)Au(PPh_3)$	NMR, X-ray	103
161	$Ru_4H(CO)_{11}(PPh_3)BH_2$	NMR, X-ray	104
162	$Ru_4H(CO)_{11}\{P(OMe)_3\}BH_2$	NMR, X-ray	104
163	$Ru_4H(CO)_{10}(dppe)BH_2$	NMR, X-ray	104
164	$Ru_4H(CO)_{10}(PHPh_2)_2BH_2$	NMR, X-ray	105
165	$Ru_4H_2(CO)_{10}(PHPh_2)(\mu\text{-}PPh_2)BH_2$	NMR	105
166	$RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(dppf)BH$	NMR	106
167	$RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(dppa)BH$	NMR	106
168	$[Ru_6(CO)_{16}B(PPh_3)][PPN]$	NMR	103
169	$[Ru_6(CO)_{16}B(P(OMe)_3)][PPN]$	NMR	103
179	$(\mu\text{-}H)_2Os_3(CO)_9(\mu\text{-}H)_2BH$	NMR, X-ray	108
180	$H_3Os_6(CO)_{16}B$	NMR, X-ray	109
181	$[\{Fe(PEt_3)_3\}_2(BH_6)][BPh_4]$	NMR, X-ray	110
182	$[\{Fe(HC(CH_2PPh_2))\}_2(BH_6)]^-$ [cation unknown]	NMR, X-ray	111

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

replacement of an isolobal $\{Ru(CO)_3\}$ vertex with $\{Ru(\eta^6\text{-arene})\}$ results in little change in the cluster core, perhaps as expected for these isolobal fragments. Treatment of $[Ru_3(CO)_9B_2H_5][N(PPh_3)_2]$ with $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ (M = Rh, Ir) gives different products dependent on the metal, the butterfly borido $RhRu_3(\eta^5\text{-}C_5Me_5)H(CO)_9BH_2$ **139** and the open-buttefly cluster $IrRu_3(\eta^5\text{-}C_5Me_5)H(CO)_{10}BH_2$ **140**, respectively.[93] The complexes $RhRu_4H_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)(CO)_{12}B$

141 and $RhRu_4H(nbd)(CO)_{12}B(AuPPh_3)$ **142** are formed from reaction of $[Ru_4H(CO)_{12}BH]^-$ with $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and $[Rh(nbd)Cl]_2/AuCl(PPh_3)$, respectively.[94] The pentametal cluster $RhRu_4H(\eta^5\text{-}C_5Me_5)(CO)_{13}BH_2$ **143**, formed in low yield in the synthesis of **139**, is best described as a spiked-butterfly.[95] Cluster expansion also occurs on reaction of $[Ru_3(CO)_9BH_4]^-$ with $[Rh(CO)_2Cl]_2$ yielding the mixed metal boride-centered cluster anions $[Rh_2Ru_4(CO)_{16}B]^-$ **144** and $[Rh_3Ru_6(CO)_{23}B_2]^-$ **145**.[96] The butterfly cluster $Ru_4H(CO)_{12}BH(\mu\text{-}NCHMe)$ **146**, which contains a semi-interstitial boron atom, results from photolysis of $Ru_3(CO)_9BH_5$ and $M(CO)_6$ ($M = Cr$, Mo, W) in acetonitrile solvent.[97]



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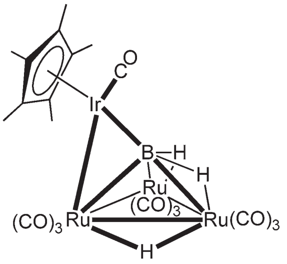

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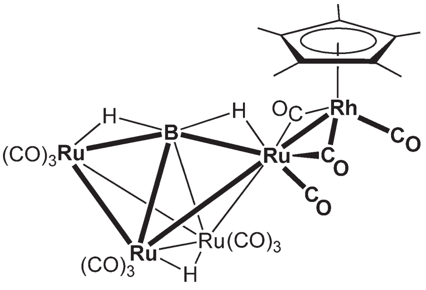

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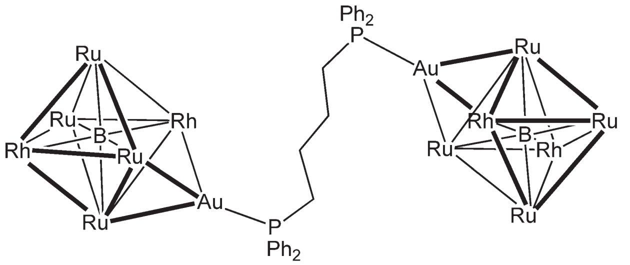
With coinage metal fragments similar cluster expansion chemistry occurs, most often to afford borido clusters with copper(I), silver(I) or gold(I) fragments decorating the surface of the starting borido-cluster. Reaction of Au(phosphine)Cl derivatives with anionic mixed metal $[Rh_2Ru_4(CO)_{16}B]^-$ results in a cluster with face-capping {Au(phosphine)} vertices, such as $Rh_2Ru_4(CO)_{16}BAu(PCy_3)$ **147**.[98] With bidentate gold(I) chloro phosphines (i.e., $dppm{\cdot}Au_2Cl_2$ or $dppb{\cdot}Au_2Cl_2$), linked clusters result: $\{Rh_2Ru_4(CO)_{16}B\}_2\{\mu\text{-}Au(L)Au\}$ [$L = dppm$ **148**, dppb **149**]. A side-product from use of dppm is the degradation product $RhRu_4(CO)_{14}B\{Au(dppm)Au\}$ **150**.[99] The iridium congener to **147** $Ir_2Ru_4(CO)_{16}BAu(PCy_3)$ **151** {synthesized from $[Ir_2Ru_4(CO)_{16}B]^-$ **152**} has the gold fragment bridging an Ir–Ir edge.[98] $[Ru_6(CO)_{17}B][PPN]$ also reacts with bidentate gold(I) complexes Cl–Au(L–L)AuCl (L–L = chelating phosphine) to result in phosphine-linked clusters, for example, $\{Ru_6(CO)_{17}B\}_2(\mu\text{-}Au(dppp)Au)$ **153**, clusters with pendant {AuCl} groups, $Ru_6(CO)_{17}B\{Au(dppe)AuCl\}$ **154**, and clusters fused around a central Au(I) fragment, $\{Ru_6(CO)_{17}B\}_2(\mu\text{-}Au)$ **155**.[100] The gold–boride clusters $RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9B\{Au(PPh_3)\}_2AuCl$ **156** and $RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9B\{Au_2(dppf)\}_2AuCl$ **157** are formed by the reaction of anionic $[RhRu_3H((\eta^5\text{-}C_5Me_5))(CO)_9BH]^-$ (generated by deprotonation of **139**) with Au(phosphine)Cl.[101] Cluster fusion of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ with $[Cu(NCMe)_4][BF_4]$ results in two butterfly clusters fused by a tetrahedral Cu_4 fragment,[102] **158**. With $Ag[BF_4]$, a single Ag(I) center spans the two butterfly clusters, $[(HRu_4(CO)_{12}BH)_2Ag]^-$ **159**.[102] Neutral gold(I) derivatives, such as $Ru_6(CO)_{16}B(P(OMe)_3)Au(PPh_3)$ **160**, result from addition of $AuCl(PPh_3)$ to $[Ru_6(CO)_{16}B(P(OMe)_3)]^-$ **169**. Protonation reactions have also been reported.[103]



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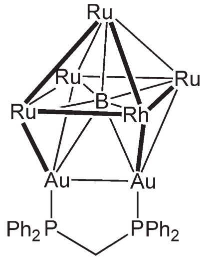
(carbonyl ligands not shown)



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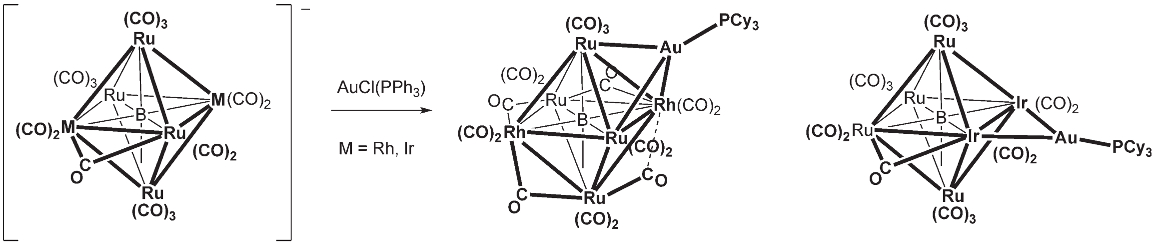

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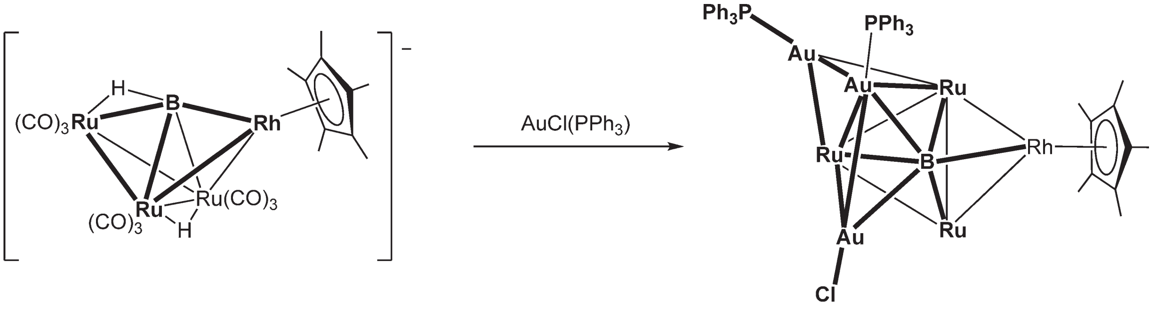

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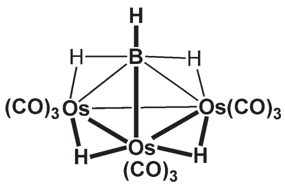
The butterfly cluster $Ru_4H(CO)_4BH_2$ reacts with a wide range of tertiary phosphines, diphosphines, and phosphites to give products that have up to four carbonyl ligands replaced. Crystallographically characterized examples include $Ru_4H(CO)_{11}(PPh_3)BH_2$ **170**, $Ru_4H(CO)_{11}\{P(OMe)_3\}BH_2$ **171**, $Ru_4H(CO)_{10}(dppe)BH_2$ **172**,[104] and $Ru_4H(CO)_{10}(PHPh_2)_2BH_2$ **173**. When heated to reflux this latter compound undergoes oxidative addition of one P–H bond to form $Ru_4H_2(CO)_{10}(PHPh_2)(\mu\text{-}PPh_2)BH_2$ **174**.[105] Carbonyl substitution reactions of $RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2$ with bidentate phosphines result in the phosphine replacing a wingtip carbonyl ligand and a redistribution of the cluster hydride ligands giving $RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(L\text{-}P)BH$ [dppf **175**, dppa **176**].[106] An improved synthesis of synthetically useful $Ru_6H(CO)_{17}B$, starting from $H_2Ru_6(CO)_{17}$ and $BH_3{\cdot}SMe_2$, has been reported.[107] The conjugate base of this borido cluster $[Ru_6(CO)_{17}B]^-$ undergoes substitution with PPh_3 and $P(OMe)_3$ to give $[Ru_6(CO)_{16}B(PR_3)]^-$ ($PR_3 = PPh_3$ **177**; $P(OMe)_3$ **178**). PPh_3 replaces only one carbonyl, while phosphite can induce further substitution to replace up to four carbonyl ligands.

The borylidyne cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu\text{-}H)_2BH$ **179**, a methylidyne cluster analog, is prepared in moderate yield from a reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ (which contains an Os–Os double bond) with $BH_3{\cdot}SMe_2$.[108] Thermolysis of $Os_3(CO)_9(BCO)$ affords the 86 valence electron hexaosmium boride cluster $H_3Os_6(CO)_{16}B$ **180** which does not conform to electron counting rules; that is, it does not have an octahedral or face-capped square pyramid structure. Instead, it has a structure derived from a pentagonal bipyramid with one equatorial vertex missing.[109]



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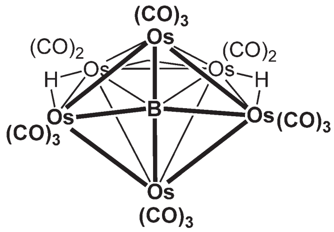

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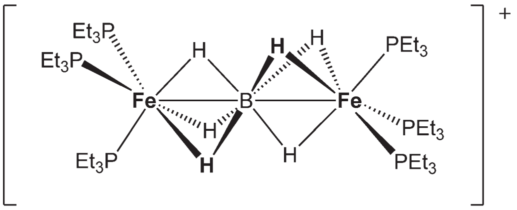
Finally for this section, $FeCl_2$ reacts with PEt_3 and $NaBH_4$ in ethanol to give $[\{Fe(PEt_3)_3\}_2(BH_6)]^+$ **181**, which has an unusual structure which is best described as consisting of two anionic $\{Fe(PEt_3)_2\}^-$ fragments centered by a $\{B\}^{3+}$ atom, that shows hypercoordination with six Fe–H interactions.[110] The triphos [triphos = $HC(CH_2PPh_2)_3$] analog **182** has also been independently reported and a similar analysis of the bonding holds.[111]



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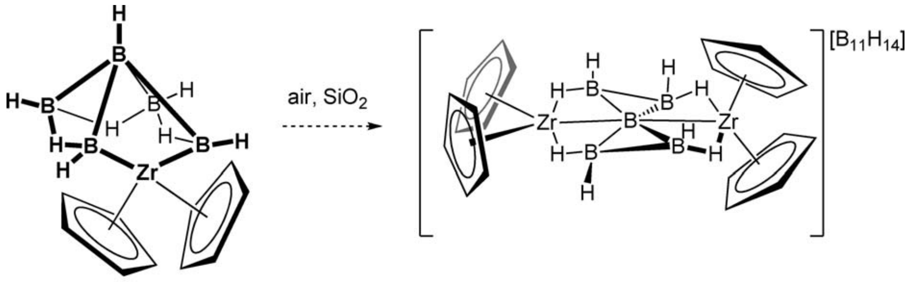
3.04.3.2 Metallaborane Cluster Complexes of Groups 4 to 7

Some examples of metallaboranes of groups 4 to 7 are given in Table 7.

3.04.3.2.1 Groups 4 and 5

Group 4 and 5 metallaboranes are relatively scarce and the number of examples reported is small. $[(\eta^5\text{-}C_5H_5)_2TiB_6H_9]_2$ **183**, a metallaborane derivative of hexaborane(10), can be prepared from the reaction of $K[B_6H_9]$ with the Ti(III) complex $Ti(\eta^5\text{-}C_5H_5)_2Cl$.[112] This paramagnetic complex is proposed to have a dimeric structure in which two $\{(\eta^5\text{-}C_5H_5)_2Ti\}^+$ fragments are sandwiched between two $\{B_6H_9\}^-$ cages. The novel metallaborane $[\{(\eta^5\text{-}C_5H_5)_2Zr\}_2B_5H_8][B_{11}H_{14}]$ **184**, which has an unusual spirocyclic-like borane structure, is isolated in moderate yield from the reaction between $Li[B_5H_8]$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, the reaction first forming $\mu\text{-}\{(\eta^5\text{-}C_5H_5)_2ZrCl\}B_5H_8$ **185** which on filtration through silica in air affords **184**.[113,114] The tantalum complex $((\eta^5\text{-}C_5Me_5)TaCl_2)B_4H_8$ **186** is prepared from $(\eta^5\text{-}C_5Me_5)TaCl_4$ and $BH_3.THF$.[115] Reactions of cyclopentadienyl metal halides with borane sources are discussed in more detail in Section 3.04.3.2.2.



185 **184**

Table 7 Metallaboranes of groups 4 to 7

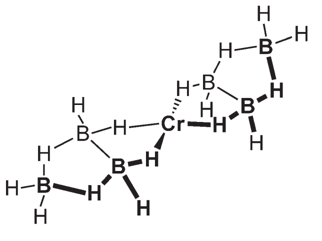
No.	*Compound*	*Physical Data*	*References*
183	$[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{B_6H_9}]_2$	NMR, EPR	112
184	$[\{(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}\}_2\mathrm{B_5H_8}][\mathrm{B_{11}H_{14}}]$	NMR, X-ray	113,114
185	$\mu\text{-}\{(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{ZrCl}\}\mathrm{B_5H_8}$	NMR	113,114
186	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{TaCl_2})\mathrm{B_4H_8}$	NMR, X-ray	115
187	$\mathrm{Cr(B_3H_8)_2}$	X-ray	116
188	$\mathrm{CrH(B_3H_8)_2}$	EPR	116
189	$\mathrm{Cr(B_3H_8)_2(OEt_2)_2}$	X-ray	116
190	$\mathrm{Cr(B_3H_8)_2(THF)_2}$	X-ray	116
191	$\mathrm{Cr(B_3H_8)_2(PMe_3)_2}$	X-ray	116
192	$\{(\mathrm{CO})_4\mathrm{Cr}\}_2(\eta^4\text{-}\mathrm{BH_2BH_2\cdot PMe_2CH_2PMe_2})$	NMR, X-ray	117
193	$[\mathrm{WBr(CO)_2}(\equiv\mathrm{C(2,6\text{-}C_6H_3Me_2)})(\mathrm{B_3H_8})][\mathrm{NBu_4}]$	NMR, X-ray	118
194	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr})_2\mathrm{B_4H_8}$	NMR, X-ray	27
195	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr})_2\mathrm{B_5H_9}$	NMR, X-ray	125
196	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr})_2(\mathrm{CH_2S_2B_4H_6})$	NMR, X-ray	126
197	$\{(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr(CO)}\}_2\mathrm{B_4H_8}$	NMR, X-ray	27
198	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr})_2\mathrm{B_4H_8Fe(CO)_3}$	NMR, X-ray	125
199	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cr})_2\mathrm{B_4H_7Co(CO)_3}$	NMR, X-ray	125
200	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Mo})_2\mathrm{B_5H_9}$	NMR, X-ray	130
201	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{W})_2\mathrm{B_5H_9}$	NMR, X-ray	131
202	$((\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cr})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}\mathrm{C_3H_6}\text{-}1,2\text{-}\mathrm{C_2B_4H_4}))$	NMR, X-ray	132
203	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Mo})_2\mathrm{Cl_2(B_2H_6)}$	NMR, X-ray	133
204	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Mo})_2\mathrm{(B_2H_6)_2}$	NMR	133
205	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Mo})_2\mathrm{Cl_2B_3H_7}$	NMR, X-ray	133
206	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{MoCl})_2\mathrm{B_4H_{10}}$	NMR, X-ray	130,133
207	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{WH_3})\mathrm{B_4H_8}$	NMR, X-ray	131
208	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{WCl})_2\mathrm{(B_2H_6)}$	NMR	131
209	$\{\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4Me})\}_2\mathrm{B_5H_9}$	NMR, X-ray	136
210	$\{\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{H_2}\}_2\mathrm{B_3H_7}$	NMR	136
211	$\{\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{H_3}\}\mathrm{B_4H_8}$	NMR	136
212	$\{\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_4Me})(\mathrm{PMe_3})\mathrm{H}\}\mathrm{B_3H_8}$	NMR	136
213	$\{\mathrm{W(PMe_3)_2H_4}\}\mathrm{B_4H_8}$	NMR	136
214	$\{\mathrm{W(PMe_3)H_3}\}\mathrm{B_3H_8}$	NMR	136
215	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{W})_2\mathrm{B_7H_9}$	NMR, X-ray	137,138
216	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{W})_3\mathrm{B_8H_9}$	NMR, X-ray	137,139
217	$(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Mo_2}(\mu\text{-}\mathrm{SMe})_2\mathrm{(B_2H_6)}$	NMR, X-ray	29
218	$[\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mu\text{-}\mathrm{CHBH_3})(\mathrm{CO})_2(\mu\text{-}\mathrm{dppm})][\mathrm{BF_4}]$	NMR, X-ray	140
219	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_4H_8}$	NMR, X-ray	147
220	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}\mathrm{B_4H_4Co_2(CO)_5})$	NMR, X-ray	148,150
221	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}\mathrm{B_6H_4Cl_2})$	NMR, X-ray	141,146
222	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_4H_6(CO)}$	NMR, X-ray	148,149
223	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_4H_8(CO)}$	NMR, X-ray	148,149
224	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})\mathrm{B_7H_7}$	NMR, X-ray	137,138
225	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_8H_8}$	NMR, X-ray	141,144
226	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_9H_9}$	NMR, X-ray	141,144
227	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_{10}H_{10}}$	NMR, X-ray	141,144
228	$((\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re})_2\mathrm{B_7H_{11}}$	NMR, X-ray	145

3.04.3.2.2 Group 6

Group 6 metallaboranes fall into two classes with regard to the synthetic routes that are used to prepare them. The first are those made by simple metathesis synthetic routes (i.e., replacement of a halide with an anionic borane fragment or simple substitution of a carbonyl ligand), while the second result from cluster buildup reactions using cyclopentadienyl metal fragments and monoborane sources. Because of the similarity of complexes that arise from the latter synthetic technique across the group 6 triad—both synthetically and structurally—they are treated together after complexes that are made by simple metathesis routes.

3.04.3.2.2.(i) Group 6 complexes formed by halide metathesis or related routes

The simple octahydridoborate complex of chromium, $Cr(B_3H_8)_2$ **187**, can be prepared by treating $CrCl_3$ with $Na[B_3H_8]$. The reaction proceeds though an intermediate species suggested to be paramagnetic $CrH(B_3H_8)_2$ **188**. Adducts of **187**, $Cr(B_3H_8)_2L_2$ (L = Et_2O **189**, THF **190**, PMe_3 **191**), have also been prepared. Complex **187** is an excellent precursor for the preparation of pure CrB_2 films.[116] The dichromatetraborane derivative $\{(CO)_4Cr\}_2$-(η^4-$BH_2BH_2{\cdot}PMe_2CH_2PMe_2$) **193** is formed in very low yield (1%) by photolysis of $Cr(CO)_6$ and $BH_3{\cdot}PMe_2CH_2PMe_2{\cdot}BH_3$. The overall transformation is one that involves intramolecular B–B bond formation via a dehydrogenative coupling of the phosphine borane. Structurally, complex **193** can be thought of as analogous to B_4H_{10} with two wingtip $\{BH_2\}^+$ groups replaced by isolobal $\{Cr(CO)_4\}$ and two terminal hydrides replaced with PMe_3.[117]



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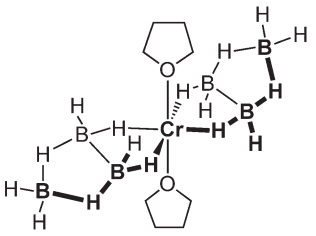

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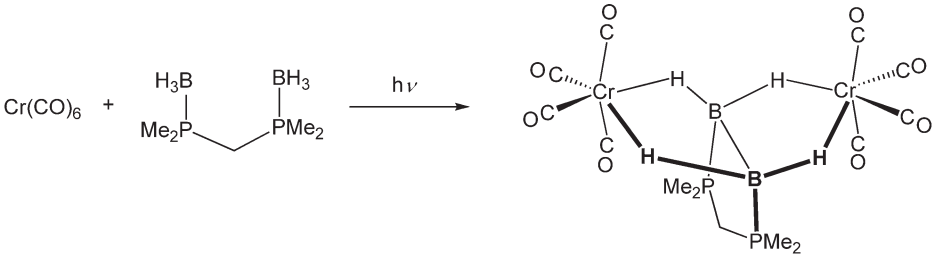
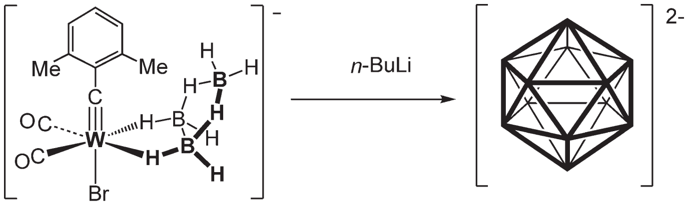


193

Treatment of the carbyne complex $WBr(CO)_4(\equiv C(2,6\text{-}C_6H_3Me_2))$ with $[Bu_4N][B_3H_8]$ results in the thermolabile $[WBr(CO)_2(\equiv C(2,6\text{-}C_6H_3Me_2))(B_3H_8)][NBu_4]$ **192**. Addition of *n*-BuLi to **192** results in the formation of $[B_{12}H_{12}]^{2-}$ by an unknown mechanism. The alkylidyene ligand is vital, however, as $Cs[W(B_3H_8)(CO)_4]$ does not decompose, and it is suggested that this ligand acts as a sink for successive hydride transfers during cluster buildup.[118] Carbyne **192** reacts with metal fragments such as $Fe_2(CO)_9$ or $Co_2(CO)_8$ to form dimetallic and trimetallic complexes with bridging alkylidyne groups—although these complexes are unstable and only characterized by infrared spectroscopy.



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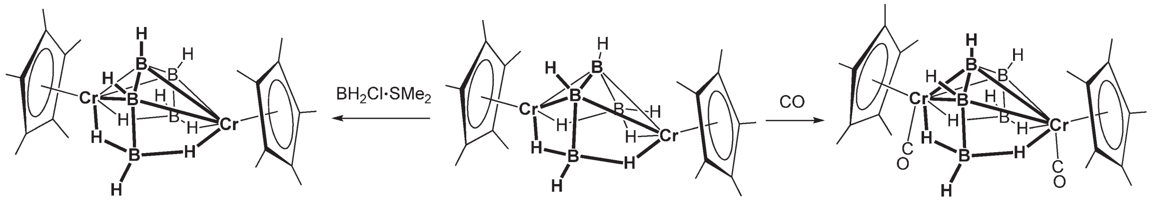
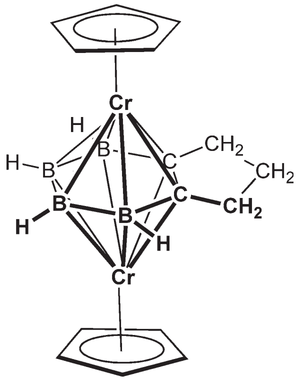
3.04.3.2.2.(ii) Group 6 metallaboranes formed by monoboron addition to CpMX$_n$

Much work has appeared from the laboratories of Fehlner on the use of monoboron reagents (such as $BH_3{\cdot}THF$ and $Li[BH_4]$) in cluster buildup reactions using simple $(\eta^5\text{-}C_5H_5)MCl_n$ starting material. The products of these reactions are dependent on both the starting oxidation state of the metal (i.e., the number of halides present) and the monoboron source used.[119] Many of these compounds, especially those of groups 6 and 7, are formally electron deficient with regard to the Wade/Mingos electron count/geometric structure rules. The response of the cluster to this unsaturation is to form metal–metal bonds and condensed, so-called hypoelectronic, structures.[14,120–122]

Reaction of $[(\eta^5\text{-}C_5Me_5)CrCl]_2$ with $BH_3{\cdot}THF$ results in the isolation of the electronically unsaturated cluster $((\eta^5\text{-}C_5Me_5)Cr)_2B_4H_8$ **194**.[27,123,124] This reacts further with $BHCl_2{\cdot}SMe_2$ to afford $((\eta^5\text{-}C_5Me_5)Cr)_2B_5H_9$ **195**,[125] with CS_2 to afford $((\eta^5\text{-}C_5Me_5)Cr)_2(CH_2S_2B_4H_6)$ **196**,[126] with CO to form the saturated complex $\{(\eta^5\text{-}C_5Me_5)Cr(CO)\}_2B_4H_8$ **197**,[27] and with $Fe_2(CO)_9$ or $Co_2(CO)_8$ to afford $((\eta^5\text{-}C_5Me_5)Cr)_2B_4H_8Fe(CO)_3$ **198**[127] and $((\eta^5\text{-}C_5Me_5)Cr)_2B_4H_7Co(CO)_3$ **199** (Figure 35).[125] The redox chemistry of **194** has also been described.[128] The Mo **200** and W **201** analogs[129] of **195** can be prepared similarly by addition of $BH_3{\cdot}THF$ to $[(\eta^5\text{-}C_5Me_5)MoCl]_2$[130] or $(\eta^5\text{-}C_5Me_5)WCl_4$.[131] Replacing $(\eta^5\text{-}C_5H_5)$ for $(\eta^5\text{-}C_5Me_5)$ in the chromium systems affords the triple-decker sandwich complex $((\eta^5\text{-}C_5H_5)Cr)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)$ **202**[132] in low yield, which presumably arises from the addition of C_5H_6 to the $(\eta^5\text{-}C_5H_5)$ analog of **194**.

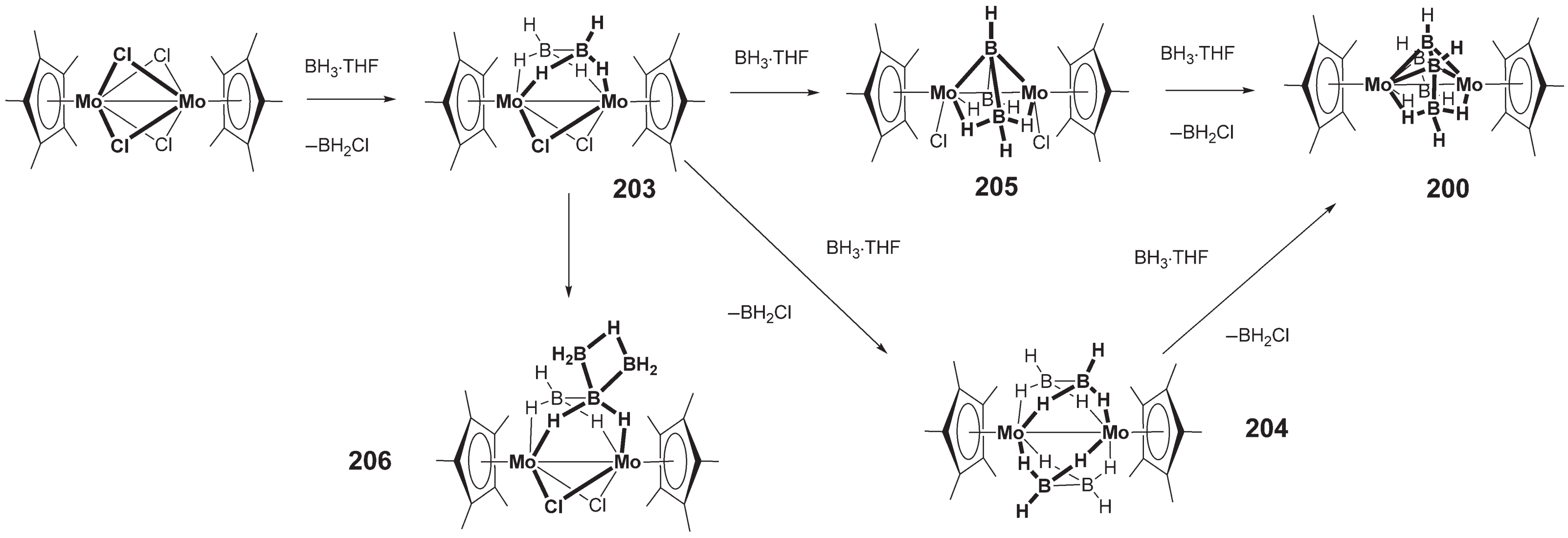


195 **194** **197**

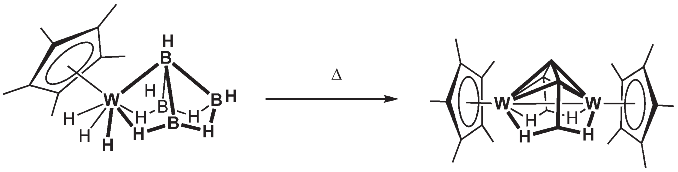


202

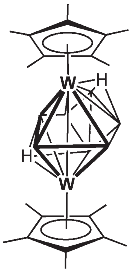
In an elegant piece of work, the sequential cluster buildup from $[(\eta^5\text{-}C_5Me_5)MoCl_2]_2$ by successive addition of $BH_3.THF$ has been shown to proceed through $((\eta^5\text{-}C_5Me_5)MoCl)_2(B_2H_6)$ **203**, $((\eta^5\text{-}C_5Me_5)Mo)_2(B_2H_6)_2$, **204**, $((\eta^5\text{-}C_5Me_5)Mo)_2Cl_2B_3H_7$ **205** (which can also be accessed directly from $(\eta^5\text{-}C_5Me_5)MoCl_4$ and $BH_3.THF$)[133], and finally $((\eta^5\text{-}C_5Me_5)Mo)_2B_5H_9$ **200**. The novel metallatetraborane $((\eta^5\text{-}C_5Me_5)MoCl)_2B_4H_{10}$ **206** is also isolated. Structurally, **206** can be thought of as an $\{(\eta^5\text{-}C_5Me_5)MoCl\}_2$ unit bridged by $\{B_4H_{10}\}^{2-}$ ligand.[130,134] In these reactions, the $BH_3.THF$ serves a dual role: to reduce the metal species, via elimination of BH_2Cl, and to provide boron units for the cluster buildup.


BH$_3$·THF
−BH$_2$Cl
203
BH$_3$·THF
205
BH$_3$·THF
−BH$_2$Cl
200
BH$_3$·THF
−BH$_2$Cl
206
BH$_3$·THF
−BH$_2$Cl
204

Replacing borohydride $Li[BH_4]$ for $BH_3{\cdot}THF$ related chemistry is observed, but now the chloride is removed as LiCl instead of BH_2Cl. For example, reaction with $(\eta^5\text{-}C_5Me_5)WCl_4$ ultimately results in $((\eta^5\text{-}C_5Me_5)WH_3)B_4H_8$ **207** (via $((\eta^5\text{-}C_5Me_5)WCl)_2(B_2H_6)$ **208**),[131] whereas with $BH_3{\cdot}THF$ **201** is the final product. Metallapentaborane **207** is closely related to $((\eta^5\text{-}C_5Me_5)TaCl_2)B_4H_8$ **186**, and although both of these clusters show *nido*-type square-based pyramidal structures similar to $((\eta^5\text{-}C_5H_5)Co)B_4H_7$ their electron counts differ by two electrons. The similarities and differences in the electronic descriptions of these three clusters has been discussed.[135] Green and co-workers have reported similar reactivity of cyclopentadienyl metal halides with $Li[BH_4]$[136] to afford bicapped-$\{Mo(\eta^5\text{-}C_5H_4Me)\}_2B_5H_9$ **209**, $\{W(\eta^5\text{-}C_5H_4Me)H_2\}_2B_3H_7$ **210**, $\{W(\eta^5\text{-}C_5H_4Me)H_3\}B_4H_8$ **211**, $\{Mo(\eta^5\text{-}C_5H_4Me)(PMe_3)H\}B_3H_8$ **212**, $\{W(PMe_3)_2H_4\}B_4H_8$ **213**, and $\{W(PMe_3)H_3\}B_3H_8$ **214**. Thermolysis of **207** results in H_2 loss and condensation to form the nine-vertex metallaborane $((\eta^5\text{-}C_5Me_5)W)B_7H_9$ **215**,[137,138] the 11-vertex species $((\eta^5\text{-}C_5Me_5)W)_3B_8H_9$ **216**[137,139] and **201**. Complexes **215** and **216** do not fit the Wade/Mingos/Williams paradigm connecting electron count to cluster geometry, being examples of $(n-2)$ and $(n-3)$ skeletal electron pair clusters (n = number of cluster vertices), respectively. Analysis of the structures, however, leads to the conclusion that **215** is best described as tricapped trigonal prism that has undergone a distortion to remove low-lying, empty, orbitals, while **216** has a condensed close-packed structure that is directly related to the cluster $[Ru_{11}H(CO)_{27}]^{3-}$. Both of these unusual cluster geometries arise as a consequence of the low electron count imposed by the early transition metal $\{(\eta^5\text{-}C_5Me_5)W\}$ fragment (formally "−1" electrons are donated to cluster bonding using the $v+x-12$ rule). An alternative view is to consider these condensed clusters as being hypoelectronic, using the analogy with Corbett's Zintl structures.



207 **201**



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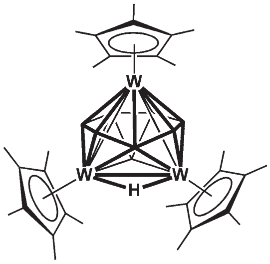

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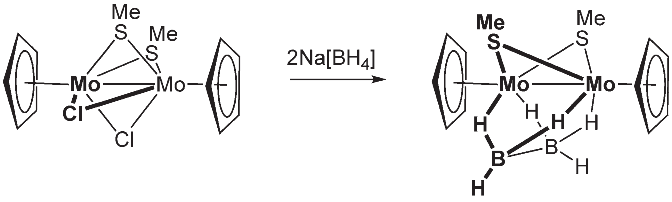
Completing this subsection on group 6 metallaboranes the reaction of the mono- or dichloro-dimolybdenum(III) complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)(\mu\text{-}Y)$ (Y = Cl, SMe) with $Na[BH_4]$ affords metallaborane complexes that are dependent on the number of chlorides in the starting material. This chemistry has clear parallels with that reported earlier in this section. Thus, monochloride $Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)$ gives the borohydride complex $(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}SMe)_3(\mu\text{-}BH_4)$ **22** while the dichloride affords the diborane complex $(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}SMe)_2(B_2H_6)$ **217**, presumably via a bisborohydride intermediate and subsequent elimination of H_2.[29] Structure **217** is closely related to $((\eta^5\text{-}C_5Me_5)MCl)_2(B_2H_6)$ **203** and **208** by replacement of bridging SMe_2 groups for bridging chlorides, and to $((\eta^5\text{-}C_5Me_5)Rh)_2B_2H_6$ **230** by replacement of Mo with Rh. Addition of $BH_3{\cdot}THF$ to the dimer $[W_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}COMe)(CO)_2(\mu\text{-}dppm)][BF_4]$ affords the four-vertex metallaborane $[W_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CHBH_3)(CO)_2(\mu\text{-}dppm)][BF_4]$ **218**.[140]



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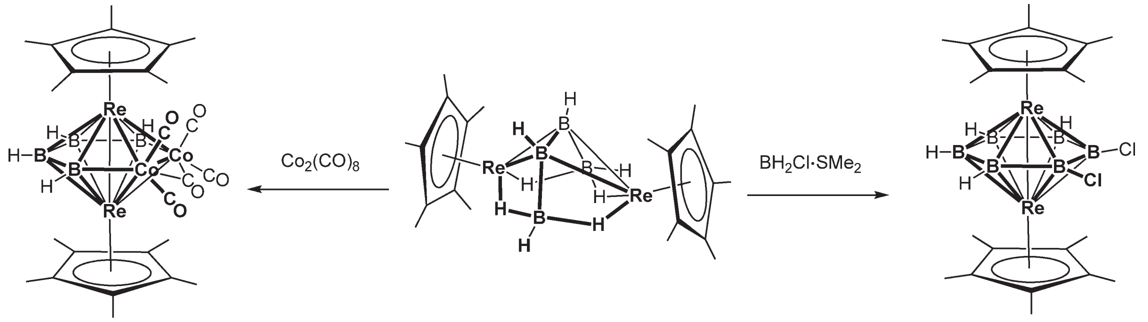
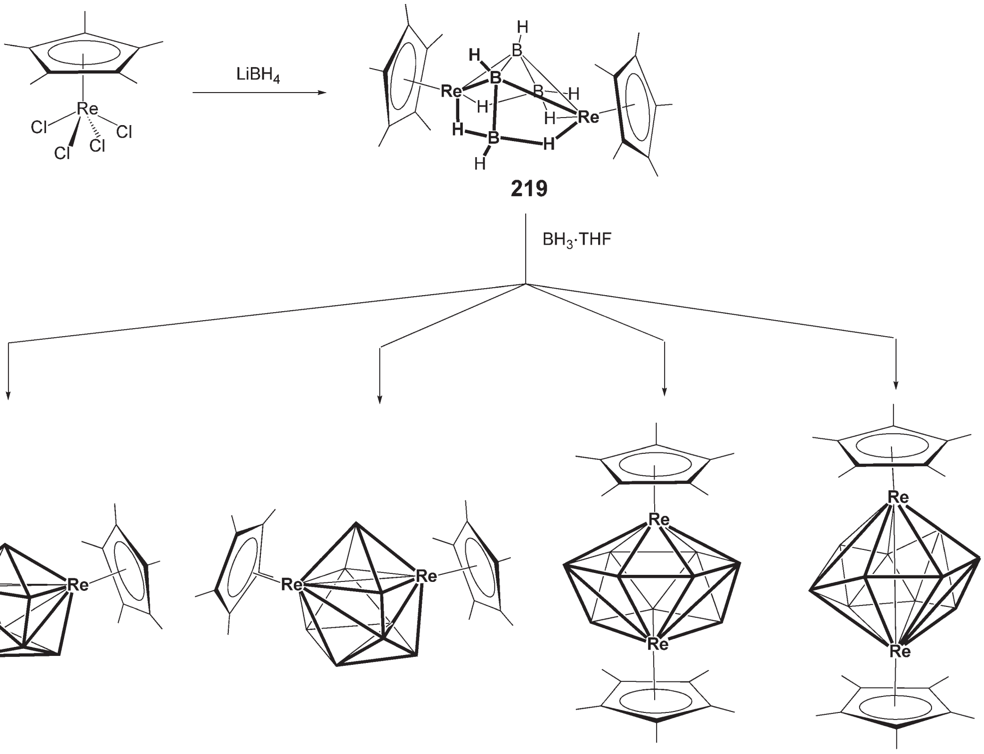
3.04.3.2.3 Group 7 metallaboranes formed by monoboron addition to $CpMX_n$

On moving to the group 7 $\{(\eta^5\text{-}C_5Me_5)Re\}$ fragment, which formally contributes zero electrons to cluster bonding, condensed structures also result as a consequence of having too few electrons donated by the metal. In a series of papers,[141–150] the synthesis and reactivity of metallaboranes containing the $\{(\eta^5\text{-}C_5Me_5)Re\}$ fragment have been reported. Reaction of (η^5-C_5Me_5)ReCl$_4$ with LiBH$_4$ affords the versatile rhenaborane starting cluster ((η^5-C_5Me_5)Re)$_2$B$_4$H$_8$ **219**, which has a similar structure to **194** even though the cluster electron count differs by two electrons. The electronic reasons for this have been discussed.[147] **219** reacts with Co$_2$(CO)$_8$ to afford ((η^5-C_5Me_5)Re)$_2$(μ-η^6:η^6-B$_4$H$_4$Co$_2$(CO)$_5$) **220**, described as having an inorganic benzene triple-decker sandwich structure,[148,150] while the analogous complex with a {B$_6$} central ring ((η^5-C_5Me_5)Re)$_2$(μ-η^6:η^6-B$_6$H$_4$Cl$_2$) **221** is prepared by addition of BH$_2$Cl·SMe$_2$ to **219**.[141,146] Cluster **219** also reacts with CO to afford ((η^5-C_5Me_5)Re)$_2$B$_4$H$_6$(CO) **222**, via the characterized intermediate complex ((η^5-C_5Me_5)Re)$_2$B$_4$H$_8$(CO) **223** which loses H$_2$ to form **222**.[148,149] Reaction of **219** with BH$_3$.THF results in sequential cluster buildup to afford ((η^5-C_5Me_5)Re)$_2$B$_n$H$_n$ ($n = 7$ **224**, 8 **225**, 9 **226** and 10 **227**), all of which have been structurally characterized.[137,138,141,144] As with some of the group 6 clusters discussed in the previous section, these compounds have *n*-2 skeletal electron pairs. The response to this unsaturation is the formation of (η^5-C_5Me_5)Re–Re(η^5-C_5Me_5) cross-cluster interactions that dominate the bonding and thus the observed cluster geometries. These clusters have been termed "hypoelectronic" to express the electronic and structural analogy between them and Corbett's hypoelectronic Zintl structures that have low skeletal electron pair counts. A minor product from these reactions is the *arachno*-cluster ((η^5-C_5Me_5)Re)$_2$B$_7$H$_{11}$ **228**.[145]



220 **219** **221**



224 **225** **226** **227**

3.04.3.3 Metallaborane Cluster Complexes of Groups 8 and 9

There is a significant body of work relating to the synthesis and reaction of the chemistry of metallaborane complexes of groups 8 and 9. As for groups 6 and 7, much of this is derived from the Fehlner laboratories, using cyclopentadienyl metal halides and monoboron reagents to sequentially build up cluster species. Because of their similarity both synthetically and structurally, groups 8 and 9 are considered together. That $\{(\eta^5\text{-}C_5R_5)M\}$ fragments (M = group 8, group 9 metal) contribute one and two electrons to the cluster bonding network means that metallaborane species of these groups are generally electron precise and follow the well-established patterns for cluster electron count/ geometry.

3.04.3.3.1 Metallaboranes of groups 8 and 9: M_xB_2

Some examples of complexes of metallaboranes of groups 8 and 9 (M_xB_2 species) are given in Table 8.

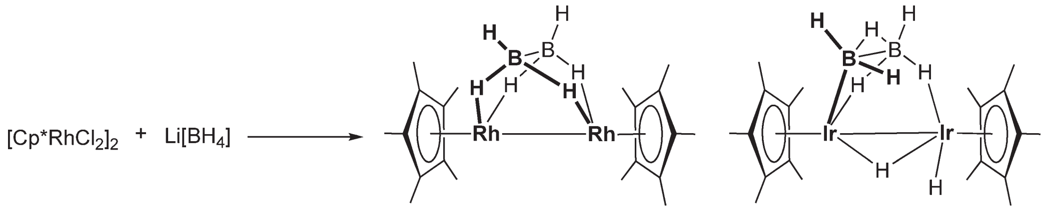
Metalladiboranes of groups 8 and 9 can be formed by the addition of lithium borohydride to cyclopentadienyl metal halides. This results in simple metathesis to give borohydride complexes. If two halides are replaced, to give a bis-$[BH_4]$ complex, elimination of H_2 can then occur to give complexes with direct B–B bonds. For example, $[(\eta^5\text{-}C_5Me_5)CoCl]_2$ reacts with $Li[BH_4]$ to give $\{(\eta^5\text{-}C_5Me_5)Co\}_3B_2H_4$ **249** as the major isolated product (20%), and $((\eta^5\text{-}C_5Me_5)Co)_4B_2H_4$ **229** which is formed in lower yield. The other products that result from this reaction have a higher B : M ratio.[151] $Li[BH_4]$ reacts with $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ by simple halide metathesis and H_2 elimination to produce the dimetallic metallaborane $((\eta^5\text{-}C_5Me_5)Rh)_2B_2H_6$ **230**.[152] Reaction of $[(\eta^5\text{-}C_5Me_5)IrHCl]_2$ with $Li[BH_4]$ leads exclusively to dimetallic $\{(\eta^5\text{-}C_5Me_5)IrH\}_2(\mu\text{-}H)B_2H_5$ **231** which is isolectronic with $(\eta^5\text{-}C_5Me_5)IrB_3H_9$ **270** (Section 3.04.3.3.2).[153,154] **230** has two more hydride ligands than **231** fully consistent with their *nido*- and *arachno*-structures, respectively. This difference is no doubt related to iridium forming stronger metal–hydride bonds than rhodium. Related group 6 metallaboranes to **230** and **231** arise from the treatment of $[(\eta^5\text{-}C_5Me_5)MoCl_2]_2$ with BH_3.THF, which first forms $((\eta^5\text{-}C_5Me_5)MoCl)_2(B_2H_6)$ **203**, which reacts further with $BH_3\cdot$THF to form larger clusters (Section 3.04.3.2.2). Reaction of $Co_2(CO)_8$ with $BH_3\cdot SMe_2$ affords, in low yield, $Co_2(CO)_6B_2H_4$ **232** which is related to **230** in terms of electron count. $Co_5(CO)_{14}B_2H$ **233** is also formed in this reaction – the structure of which is best described as a Co_4B_2 octahedron capped by a Co metal atom.[155] In this case, no halides are being removed by borane and the reaction is a simple addition of a $\{BH_3\}$

Table 8 Metallaboranes of groups 8 and 9: M_xB_2 species

No.	*Compound*	*Physical data*	*References*
229	*closo*-1,2,3,6-$\{(\eta^5\text{-}C_5Me_5)Co\}_4B_2H_4$	NMR, X-ray	151
230	$((\eta^5\text{-}C_5Me_5)Rh)_2B_2H_6$	NMR	152
231	$(\eta^5\text{-}C_5Me_5)_2Ir_2H_3B_2H_5$	NMR, X-ray	153
232	$Co_2(CO)_6B_2H_4$	NMR	155
233	$Co_5(CO)_{14}B_2H$	NMR, X-ray	155
234	$FeCo(CO)_6B_2H_5$	NMR	156
235	$((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)(B_2H_5)(PMe_3)$	NMR	157
236	$((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)(B_2H_5)(PMe_2Ph)$	NMR, X-ray	157
237	$((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}PMe_2)(B_2H_5)$	NMR, X-ray	157
238	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(PMe_2Ph)$	NMR	158
239	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(PMe_3)$	NMR, X-ray	158
240	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(PMePh_2)$	NMR, X-ray	158
241	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(PPh_3)$	NMR	158
242	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(py)$	NMR, X-ray	158
243	$(\eta^5\text{-}C_5Me_5)IrB_2H_6(NEt_3)$	NMR	158
249	$\{(\eta^5\text{-}C_5Me_5)Co\}_3B_2H_4$	NMR, X-ray	151
261	$\{((\eta^5\text{-}C_5Me_5)Ru(CO))\{Co(CO)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5Me_5)Ru\}B_2H_2(NC_4H_4C)$	NMR, X-ray	166
281	$(\eta^5\text{-}C_5Me_5)IrB_2H_4(PMe_3)$	NMR, X-ray	170

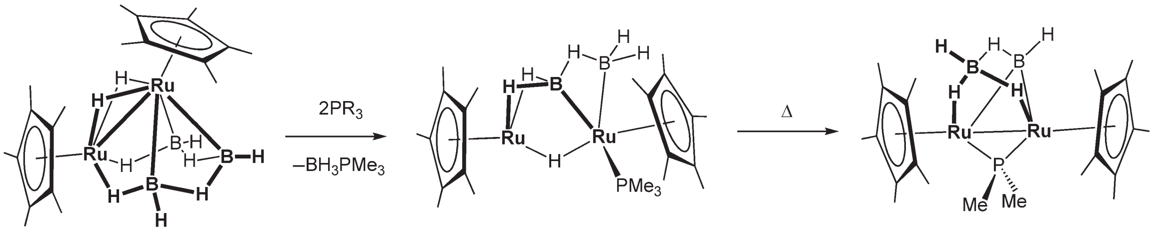
NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

fragment. Finally, the preformed ferradiborane $Fe_2Co(CO)_6B_2H_6$ reacts with $Co_2(CO)_8$ to afford $FeCo(CO)_6B_2H_5$ **234**.[156]



230 **231**

Metalladiborane species can also be accessed by the addition of Lewis base (usually a tertiary phopshine) to a triborane cluster and subsequent elimination of $H_3B{\cdot}PR_3$. For example, $((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)_2B_3H_7$ **252** (see Section 3.04.3.3.2) is degraded by tertiary phosphines to afford the diruthenatetraborane $((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)(B_2H_5)(PR_3)$ ($PR_3 = PMe_3$ **235**, PMe_2Ph **236**). In these compounds the $\{B_2H_5\}$ fragment interacts with the metals in an unusual manner, through a BBRu and a BH_2Ru interaction. Thermolysis of **235** gives the phosphido-bridged cluster $((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}PMe_2)(B_2H_5)$ **237**.[157] In a similar manner $(\eta^5\text{-}C_5Me_5)IrB_3H_9$ **270** (Section 3.04.3.3.2) is also degraded by a variety of Lewis bases to ultimately result in the substituted iridatriboranes $(\eta^5\text{-}C_5Me_5)IrB_2H_6L$ ($L = PMe_2Ph$ **238**, PMe_3 **239**, $PMePh_2$ **240** PPh_3 **241** py **242**, NEt_3 **243**) plus $BH_3{\cdot}L$ as a co-product in each case.[158]



252 **235** **237**

3.04.3.3.2 Metallaboranes of groups 8 and 9: M_xB_3 species

Some examples of complexes of metallaboranes of groups 8 and 9 (M_xB_3 species) are given in Table 9.

Just as for group 5, 6, and 7 $\{(\eta^5\text{-}C_5H_5)MCl_n\}$ species, Fehlner has shown that $BH_3{\cdot}THF$ or $Li[BH_4]$ react with group 8 and 9 cyclopentadienyl metal halides to result in metallaborane clusters, many of them having a metal : boron ratio of 1 : 3 and 1 : 4, and much of the synthetic chemistry and reactivity shows close connections with the earlier transition metals. The main difference between the early and later transition metallaboranes that result is that the latter are generally electron precise cluster species, while as has been shown, the former often adopt condensed structures. Indeed, as has been pointed out by King, many of the later transition metallaborane clusters that result from these syntheses have structures closely related to binary boranes and, in some cases, metal carbonyl clusters such as $H_2Os_6(CO)_{18}$.[159]

3.04.3.3.2.(i) Iron

Reaction of *nido*-$((\eta^5\text{-}C_5H_5)Fe)B_5H_{10}$ with group 6 hydridophosphines affords capped-*closo*-1-$((\eta^5\text{-}C_5H_5)Fe)$-2-$(M(PR_3)_3H)B_3H_7$ ($M = Mo$, $PR_3 = PMe_2Ph$ **244**; $M = W$, $PR_3 = PMe_3$ **245**).[160]

3.04.3.3.2.(ii) Cobalt

The dimetallic complex $[(\eta^5\text{-}C_5Me_5)CoCl]_2$ reacts with BH_3.THF to afford $((\eta^5\text{-}C_5Me_5)Co)\{(\eta^4\text{-}C_5Me_5H)Co\}B_3H_8$ **246** as the major product and *arachno*-$(\eta^5\text{-}C_5Me_5)CoB_4H_{10}$ **247** as the minor, via the metastable paramagnetic intermediate $[(\eta^5\text{-}C_5Me_5)Co(BH_3Cl)]_2$. Heating **246** leads to H_2 elimination and the formation of $((\eta^5\text{-}C_5Me_5)Co)_2B_3H_7$ **248**. In contrast, with $Li[BH_4]$, the cluster $\{(\eta^5\text{-}C_5Me_5)Co\}_3B_2H_4$ **249** is formed as the major isolated product (20%), with lesser amounts of $\{(\eta^5\text{-}C_5Me_5)Co\}_3B_3H_5$ **254** and $\{(\eta^5\text{-}C_5Me_5)Co\}_4B_2H_4$ **228**. The reaction proceeds via the sequential formation of the metastable intermediates: paramagnetic $\{(\eta^5\text{-}C_5Me_5)Co\}(BH_4)_n$ and then diamagnetic $\{(\eta^5\text{-}C_5Me_5)Co\}_2B_2H_6$, which have been identified spectroscopically.[151] Some of these clusters have been used as

Table 9 Metallaboranes of groups 8 and 9: M_xB_3 species

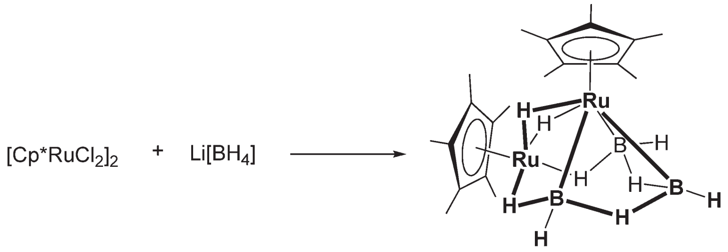
No.	*Compound*	*Physical data*	*References*
244	$\{(\eta^5\text{-}C_5H_5)Fe\}\{Mo(PMe_2Ph)H\}B_3H_7$	NMR	160
245	$\{(\eta^5\text{-}C_5H_5)Fe\}\{W(PMe_3)H\}B_3H_7$	NMR	160
246	$((\eta^5\text{-}C_5Me_5)Co)\{(\eta^4\text{-}C_5Me_5H)Co\}B_3H_8$	NMR, X-ray	151
248	$((\eta^5\text{-}C_5Me_5)Co)_2B_3H_7$	NMR, X-ray	151
250	$\{(\eta^5\text{-}C_5Me_5)Co\}((CO)_3Fe)B_3H_7$	NMR, X-ray	161
251	$(\eta^5\text{-}C_5Me_5)(CO)CoB_3H_7$	NMR, X-ray	161
252	$((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)_2B_3H_7$	NMR, X-ray	152,162
253	$((\eta^5\text{-}C_5Me_5)Ru)_3B_3H_8$	NMR, X-ray	163
254	$\{(\eta^5\text{-}C_5Me_5)Co\}_3B_3H_5$	NMR, X-ray	151
255	$\{(\eta^5\text{-}C_5Me_5)Ru\}\{(\eta^5\text{-}C_5Me_5)RuCO\}Co(CO)_2(\mu_3\text{-}CO)B_3H_6$	NMR, X-ray	152,164
256	$((\eta^5\text{-}C_5Me_5)Ru)(CO)(\mu\text{-}H)B_3H_7$	NMR, X-ray	152,164
257	$((\eta^5\text{-}C_5Me_5)Ru)_2(CO)_2B_3H_7$	NMR, X-ray	152,164
258	$Co(CO)_2((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}CO)(\mu_3\text{-}CO)B_3H_4$	NMR	152
259	$((\eta^5\text{-}C_5Me_5)Ru)_2\{Co(CO)PPh_3\}(\mu\text{-}CO)_2B_3H_4$	X-ray	166
260	$((\eta^5\text{-}C_5Me_5)Ru)_2\{Co(CO)PMe_2Ph\}(\mu\text{-}CO)_2B_3H_4$	NMR, X-ray	166
262	$((\eta^5\text{-}C_5Me_5)Ru)_2Co(CO)_4B_3H_4(NC_5H_5)$	NMR	166
263	$((\eta^5\text{-}C_5Me_5)Ru)_2\{Co(CO)_2\}(\mu\text{-}CO)_2B_2H_2B(NC_5H_5)$	NMR, X-ray	166
264	$Ru(PPh_3)(Tp)B_3H_8$	NMR, X-ray	167
265	$[RhH(DiPPE)]_2B_3H_7$	NMR, X-ray	73
266	$((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_7$	NMR, X-ray	152
267	$((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_6Cl$	NMR	152
268	$\{Co(CO)_2\}((\eta^5\text{-}C_5Me_5)Rh)_2(\mu_3\text{-}CO)B_3H_3Cl$	NMR, X-ray	152
269	$((\eta^5\text{-}C_5Me_5)Rh)_2Co_3(CO)_8B_3HCl$	NMR, X-ray	168
270	$(\eta^5\text{-}C_5Me_5)IrH_2B_3H_7$	NMR, X-ray	153
273	$\{(\eta^5\text{-}C_5Me_5)Ir(CO)\}B_3H_7$	NMR, X-ray	154
274	$\{(\eta^5\text{-}C_5Me_5)Ir\}Co_2(CO)_4(\mu\text{-}CO)B_3H_7$	NMR, X-ray	154
275	$\{(\eta^5\text{-}C_5Me_5)Ir\}Co_2(CO)_5B_3H_5$	NMR, X-ray	154
276	$(\eta^5\text{-}C_5Me_5)IrB_3H_7(PMe_3)$	NMR	158
277	$(\eta^5\text{-}C_5Me_5)IrB_3H_7(py)$	NMR	158
278	$(\eta^5\text{-}C_5Me_5)IrB_3H_7(NEt_3)$	NMR	158
279	$(\eta^5\text{-}C_5Me_5)IrB_3H_9$	NMR	154
280	$(\eta^5\text{-}C_5Me_5)IrB_3H_6(PMe_3)$	NMR	170

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

synthons to form bimetallic, mixed metal, clusters. For example, **248** reacts with $Fe_2(CO)_9$ and $Co_2(CO)_8$ to generate $\{(\eta^5\text{-}C_5Me_5)Co\}\{(CO)_3Fe\}B_3H_7$ **250** by metal fragment substitution and $\{(\eta^5\text{-}C_5Me_5)(CO)Co\}B_3H_7$ **251** by metal fragment degradation.[161]

3.04.3.3.2.(iii) Ruthenium

For ruthenium or reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ and $Li[BH_4]$, $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_2B_3H_7$ **252** is produced in high yield in a single synthetic step.[152,162] A minor product of this reaction is $((\eta^5\text{-}C_5Me_5)Ru)_3B_3H_8$ **253**.[163] This cluster has a *nido*-square pyramidal geometry capped with a {BH} vertex, with the four bridging hydrogens decorating the open face, and is in contrast with isoelectronic *closo*-1,2,3-$\{(\eta^5\text{-}C_5Me_5)Co\}_3B_3H_5$ **254** which has an octahedral cluster geometry (Figure 45). The steric and electronic demands of the three additional hydrogen atoms make a capped *nido*-structure more favored than a *closo*-one, presumably because it supplies more open faces to accommodate the bridging hydrogens.



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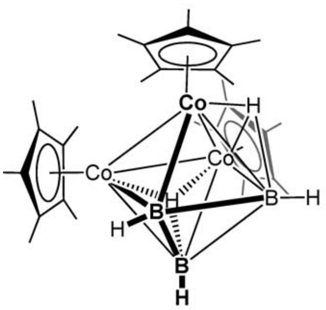

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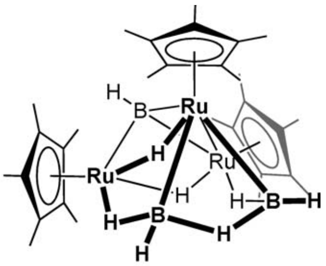
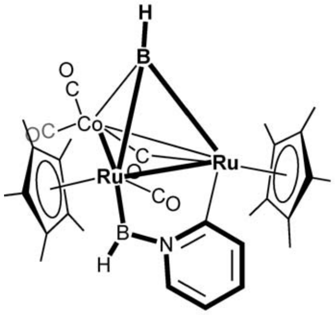


253

Reaction of **252** with $Co_2(CO)_8$ under conditions of high concentration of the di-cobalt carbonyl gives trimetallic $\{(\eta^5\text{-}C_5Me_5)Ru\}\{(\eta^5\text{-}C_5Me_5)RuCO\}Co(CO)_2(\mu_3\text{-}CO)B_3H_6$, **255**, whereas low concentrations allow competitive degradation to yield monometallic $\{(\eta^5\text{-}C_5Me_5)Ru\}(CO)(\mu\text{-}H)B_3H_7$ **256**.[153,164] This reaction also affords $((\eta^5\text{-}C_5Me_5)Ru)_2(CO)_2B_3H_7$ **257** in variable yield dependent on the solvent used, as well as the linear trimetallic cluster **314** (Section 3.04.3.3.5) in very low yield.[165]

Trimetallic$\{(\eta^5\text{-}C_5Me_5)Ru\}\{(\eta^5\text{-}C_5Me_5)RuCO\}Co(CO)_2(\mu_3\text{-}CO)B_3H_6$, **255**, serves as a starting point itself for further metallaborane chemistry. Mild thermolysis results in loss of hydrogen and the formation of $Co(CO)_2((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}CO)(\mu_3\text{-}CO)B_3H_4$ **258**.[152] Cluster **255** reacts with the Lewis bases PPh_3 or PMe_2Ph by substitution of a CO ligand on cobalt to give $((\eta^5\text{-}C_5Me_5)Ru)_2\{Co(CO)L\}(\mu\text{-}CO)_2B_3H_4$ ($L = PPh_3$ **259**, PMe_2Ph **260**). With pyridine three products are formed, characterized by borane loss and orthometallation of pyridine **261** $\{((\eta^5\text{-}C_5Me_5)Ru(CO)\}\{Co(CO)_2\}(\mu\text{-}CO)\{(\eta^5\text{-}C_5Me_5)Ru\}B_2H_2(NC_4H_4C)$, simple hydrogen substitution by pyridine **262** $((\eta^5\text{-}C_5Me_5)Ru)_2Co(CO)_4B_3H_4(NC_5H_5)$, or addition of pyridine and H_2 loss **263** $((\eta^5\text{-}C_5Me_5)Ru)_2\{Co(CO)_2\}(\mu\text{-}CO)_2B_2H_2B(NC_5H_5)$.[166]



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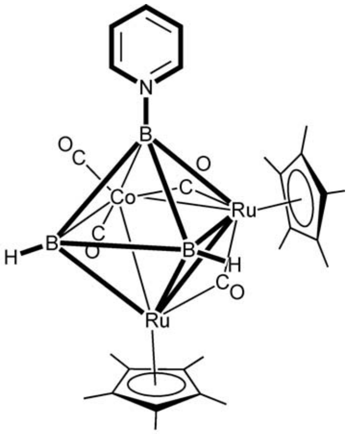


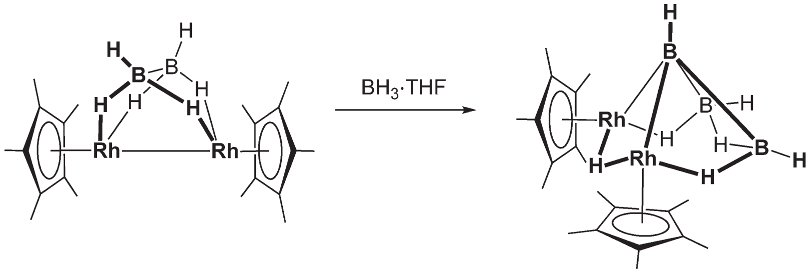
263

arachno-$[B_3H_8]^-$ reacts via halide metathesis with $Ru(Tp)(PPh_3)_2Cl$ (Tp = tris-pyrazol-1-yl borate) to afford *arachno*-$Ru(PPh_3)(Tp)B_3H_8$ **264** in which the ruthenium fragment occupies a wingtip position.[167]

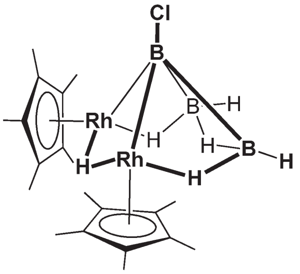
3.04.3.3.2.(iv) Rhodium

nido-$[RhH(DiPPE)]_2B_3H_7$ **265** results from the addition of $BH_3{\cdot}SMe_2$ to $[Rh(\mu\text{-}H)(DiPPE)]_2$ (DiPPE = 1,2-bis(di-isopropylphosphino)ethane). In two steps, the dirhodium analog of pentaborane(9) $((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_7$, **266**, is accessible by the reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ and $Li[BH_4]$ to first exclusively produce $((\eta^5\text{-}C_5Me_5)Rh)_2B_2H_6$, **230**, which adds $BH_3{\cdot}THF$ to give **266** as the major product (Figure 47).[152] Reaction of $BH_3{\cdot}THF$ directly with $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ results in the chloro derivative of **266**, $((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_6Cl$, **267** with high yield via an intermediate positional isomer. **267** reacts with $Co_2(CO)_8$ at room temperature to give $\{Co(CO)_2\}((\eta^5\text{-}C_5Me_5)Rh)_2(\mu_3\text{-}CO)B_3H_3Cl$ **268**.[152] The same reaction at +60 °C, rather than room temperature, gives pentametallic

$((\eta^5\text{-}C_5Me_5)Rh)_2Co_3(CO)_8B_3HCl$ **269**. The reaction is suggested to proceed via an initial σ-bond metathesis of B–H for B–$Co(CO)_4$.[168]



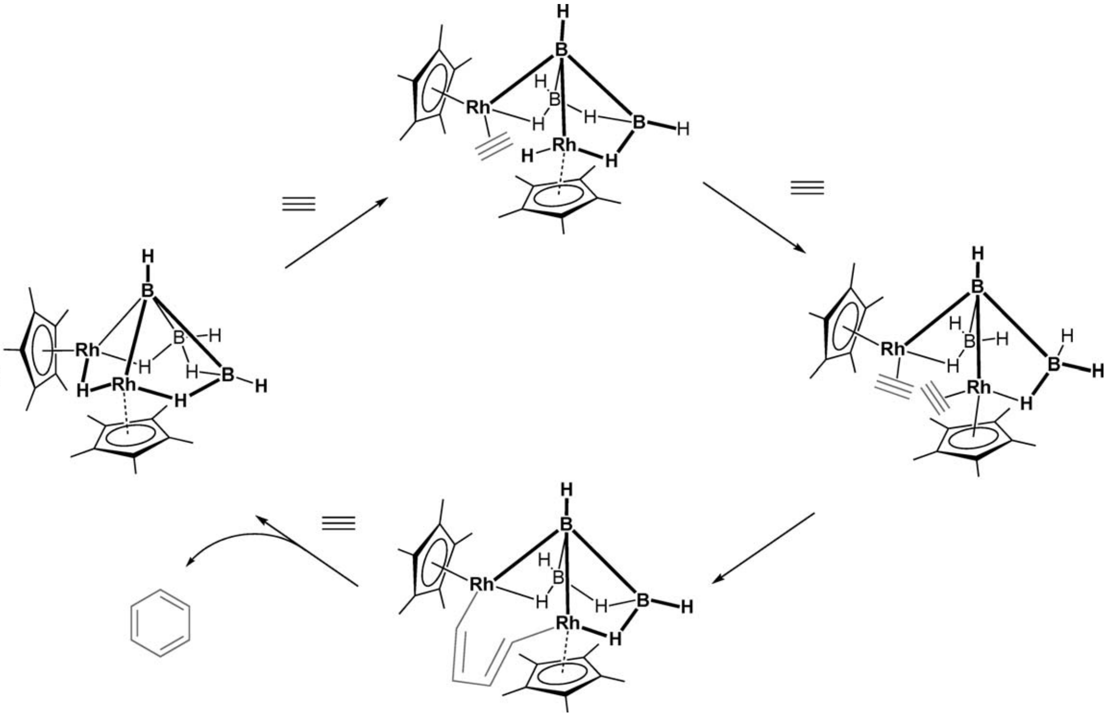
230 **266**



267

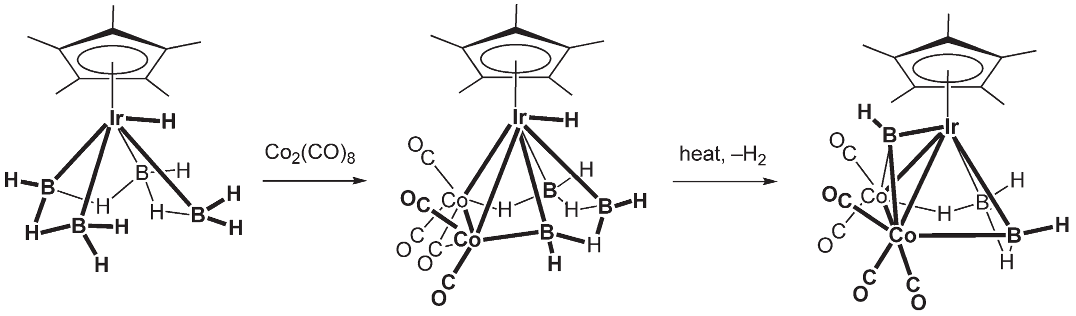
The various isomers of **266**, namely 1,2-$((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_7$, 1,2-$((\eta^5\text{-}C_5Me_5)Rh)_2(\mu\text{-}H)B_3H_6$, and 2,3-$((\eta^5\text{-}C_5Me_5)Rh)_2B_3H_7$ catalyze the cyclotrimerization of both terminal and internal alkynes. The suggested mechanism is one that initially involves metal edge opening on alkyne addition,[169] in which the borane cage is flexing (i.e., opening) to allow the reactivity of the metal centers with alkyne.

266



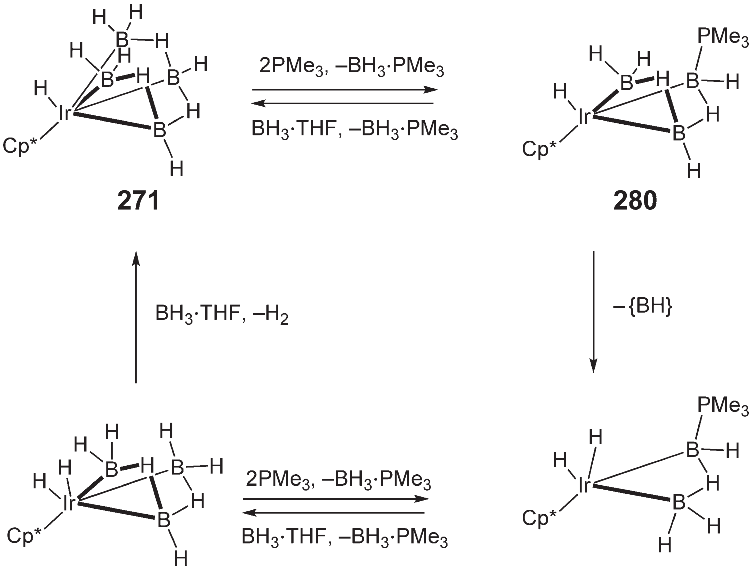
3.04.3.3.2.(v) Iridium

Reaction of either $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ or $(\eta^5\text{-}C_5Me_5)_2Ir_2HCl_3$ with $Li[BH_4]$ leads to the formation of $(\eta^5\text{-}C_5Me_5)IrB_3H_9$ **270** (which can be described either as a borallyl complex or as a cluster), in parallel with the formation $(\eta^5\text{-}C_5Me_5)IrH_4$, via the known borohydride complex $\{(\eta^5\text{-}C_5Me_5)IrH\}_2(\mu\text{-}H)(\mu\text{-}BH_4)$.[153,154] Addition of $BH_3{\cdot}THF$ to **270** results in cluster buildup and the isolation, in high yield, of $(\eta^5\text{-}C_5Me_5)IrB_4H_{10}$ **271**. Bimetallic $\{(\eta^5\text{-}C_5Me_5)IrH\}_2(\mu\text{-}H)B_2H_5$ **230** reacts with $BH_3{\cdot}THF$ to give $((\eta^5\text{-}C_5Me_5)Ir)_2(\mu\text{-}H)B_4H_7$ **272**. Reaction of **271** with $Co_2(CO)_8$ gives two bimetallic metallaboranes: $\{(\eta^5\text{-}C_5Me_5)Ir(CO)\}B_3H_7$ **273** and $\{(\eta^5\text{-}C_5Me_5)Ir\}Co_2(CO)_4(\mu\text{-}CO)B_3H_7$ **274**. Pyrolysis of **274** results in H_2 loss and the formation of $\{(\eta^5\text{-}C_5Me_5)Ir\}Co_2(CO)_5B_3H_5$ **275** which has a BH-capped square pyramidal structure.[154]



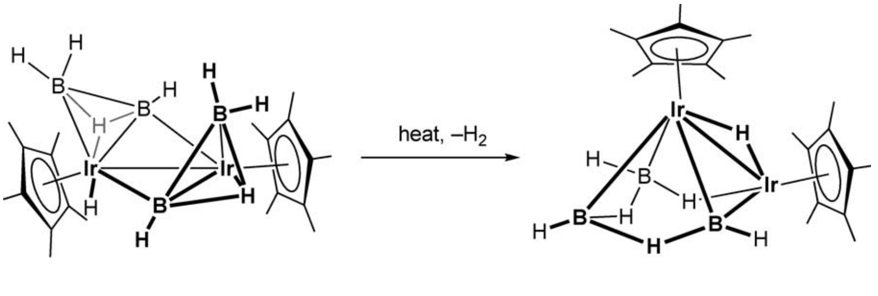
271 **274** **275**

(η^5-C$_5$Me$_5$)IrB$_4$H$_{10}$ **271**[154] reacts with a variety of Lewis bases to ultimately result in the substituted iridatriboranes (η^5-C$_5$Me$_5$)IrB$_3$H$_7$L (L = PMe$_3$ **276**, py **277**, NEt$_3$ **278**) plus BH$_3$·L as a co-product.[158] An interesting stoichiometric cycle in which the iridaboranes (η^5-C$_5$Me$_5$)IrB$_3$H$_{10}$ **279** and (η^5-C$_5$Me$_5$)IrB$_4$H$_{10}$ **271** are interconverted via novel phosphine-substituted derivatives has been reported. The chemistry is driven by Lewis acid/base chemistry of PMe$_3$ and BH$_3$. Thus, addition of PMe$_3$ to **271** gives (η^5-C$_5$Me$_5$)IrB$_3$H$_6$(PMe$_3$) **280**, and loss of BH$_3$·PMe$_3$, which then decomposes slowly by the loss of {BH} to afford (η^5-C$_5$Me$_5$)IrB$_2$H$_4$(PMe$_3$) **281**. The reaction of BH$_3$·THF with **281** proceeds by the addition of BH$_3$ to the cluster framework and concomitant liberation of BH$_3$·PMe$_3$ to afford *arachno*-iridaborane **279**. Addition of BH$_3$·THF to **279** results in the regeneration of **271** and the completion of the cycle.[170]



271 **280** **279** **281**

231 undergoes metal-assisted borane condensation on reaction with BH$_3$·THF to give {(η^5-C$_5$Me$_5$)IrH}B$_4$H$_4$ **282** which contains two separated {B$_2$H$_4$} fragments. Mild thermolysis of **282** results in the elimination of H$_2$ and a closing up of the cluster with the formation of ((η^5-C$_5$Me$_5$)Ir)$_2$(μ-H)B$_4$H$_7$ **283**.[171]



282 **283**

3.04.3.3.3 Metallaboranes of groups 8 and 9: M_xB_4

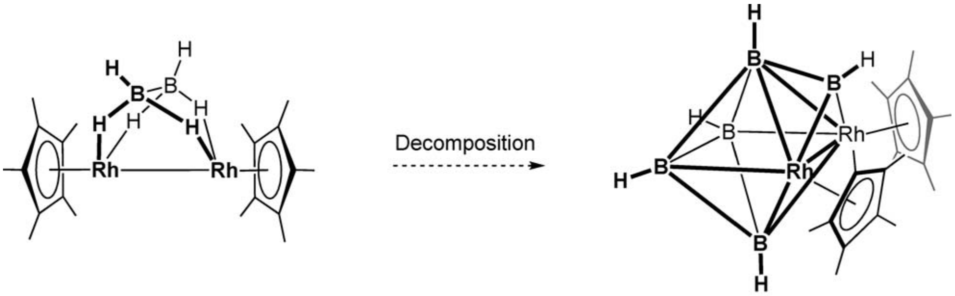
Some examples of complexes of metallaboranes of groups 8 and 9 (M_xB_4 species) are given in Table 10.

3.04.3.3.3.(i) Iron

The reaction of borane with hydride-starting material $[(\eta^5\text{-}C_5Me_5)FeH_2]_2$ has been explored, and results in the metastable $((\eta^5\text{-}C_5Me_5)Fe)B_4H_{11}$ **284**, which reacts further with $Co_2(CO)_8$ to give stable $((\eta^5\text{-}C_5Me_5)Fe)\{Co(CO)_3\}B_4H_8$ **285**.[172]

3.04.3.3.3.(ii) Ruthenium and rhodium

$\{(p\text{-cym})Ru\}\{(Ph_3P)_2(CO)Os\}B_4H_8$ **286** is prepared from $[(p\text{-cym})RuCl_2]_2$ and $Li[(PPh_3)_2(CO)OsB_5H_8]$.[173] Addition of $BH_3{\cdot}THF$ to **252** $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_2B_3H_7$ results in cluster buildup and conversion to $((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)B_4H_9$ **287** which on thermolysis eliminates dihydrogen and forms $((\eta^5\text{-}C_5Me_5)Ru)_2B_4H_8$, **288**, which has a BH-capped square pyramidal structure. This reacts further with $Fe_2(CO)_9$ to yield $Fe(CO)_3((\eta^5\text{-}C_5Me_5)Ru)_2(\mu_3\text{-}CO)B_4H_4$, **289**, which has a BH-capped octahedral cluster structure. The tetraboron cluster $((\eta^5\text{-}C_5Me_5)Rh)_3B_4H_4$ **290**, which has a capped octahedral structure, results from a slow decomposition of $((\eta^5\text{-}C_5Me_5)Rh)_2B_2H_6$ **230** at room temperature.[169]



230 **290**

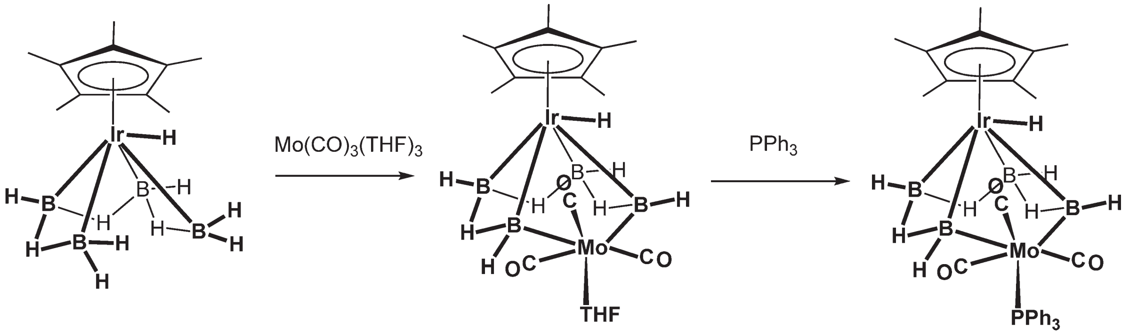
Table 10 Metallaboranes of groups 8 and 9: M_xB_4 species

No.	*Compound*	*Physical data*	*References*
247	$(\eta^5\text{-}C_5Me_5)CoB_4H_{10}$	NMR, X-ray	151
271	$(\eta^5\text{-}C_5Me_5)IrB_4H_{10}$	NMR, X-ray	154
272	$((\eta^5\text{-}C_5Me_5)Ir)_2(\mu\text{-}H)B_4H_7$	NMR, X-ray	154
282	$\{(\eta^5\text{-}C_5Me_5)IrH)B_4H_4$	NMR, X-ray	171
283	$((\eta^5\text{-}C_5Me_5)Ir)_2(\mu\text{-}H)B_4H_7$	NMR, X-ray	171
284	$((\eta^5\text{-}C_5Me_5)Fe)B_4H_{11}$	NMR	172
285	$((\eta^5\text{-}C_5Me_5)Fe)\{Co(CO)_3\}B_4H_8$	NMR, X-ray	172
286	$\{(p\text{-cym})Ru\}\{(Ph_3P)_2(CO)Os\}B_4H_8$	NMR	173
287	$((\eta^5\text{-}C_5Me_5)Ru)_2(\mu\text{-}H)B_4H_9$	NMR, X-ray	152
288	$((\eta^5\text{-}C_5Me_5)Ru)_2B_4H_8$	NMR, X-ray	152
289	$Fe(CO)_3((\eta^5\text{-}C_5Me_5)Ru)_2(\mu_3\text{-}CO)B_4H_4$	NMR	152
290	$((\eta^5\text{-}C_5Me_5)Rh)_3B_4H_4$	NMR, X-ray	169
291	$(\eta^5\text{-}C_5Me_5)Ir(CO)_3(THF)MoB_4H_8$	NMR	174
292	$(\eta^5\text{-}C_5Me_5)Ir(CO)_4MoB_4H_8$	NMR, X-ray	174
293	$(\eta^5\text{-}C_5Me_5)Ir(CO)_3(PPh_3)MoB_4H_8$	NMR	174
294	$(\eta^5\text{-}C_5Me_5)Ir(CO)_3(NCPh)MoB_4H_8$	NMR, X-ray	174
295	$(\eta^5\text{-}C_5Me_5)Ir(CO)_3(CNBu)MoB_4H_8$	NMR, X-ray	174
296	$(\eta^5\text{-}C_5Me_5)Ir(CO)_3(NH_3)MoB_4H_8$	NMR, X-ray	174
297	$(PPh_3)_2(CO)OsB_4H_7BH_2PPh_3$	NMR	176
298	$(PPh_3)_2(CO)OsB_4H_7BH_2PPh_2Me$	NMR, X-ray	176
299	$(PPh_3)_2(CO)OsB_4H_7BH_2PMe_3$	NMR	176
300	$(PPh_3)(CO)OsB_4H_7\text{-}\eta^2\text{-}(BH_2{\cdot}dppe)$	NMR	176
302	$(PPh_3)_2(CO)OsBH_7(BH_2{\cdot}dppe{\cdot}BH_3)$	NMR	176
303	$\{(PPh_3)_2(CO)Os\}B_4H_7BH_2PPh_2XPPh_2$	NMR	177
304	$[\{(PPh_3)_2(CO)Os\}B_4H_7BH_2PPh_2]_2X$	NMR	177
305	$\{(PPh_3)_2(CO)Os\}B_4H_7BH_2PPh_2XPPh_2{\cdot}BH_3$	NMR	177

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

3.04.3.3.3.(iii) Iridium

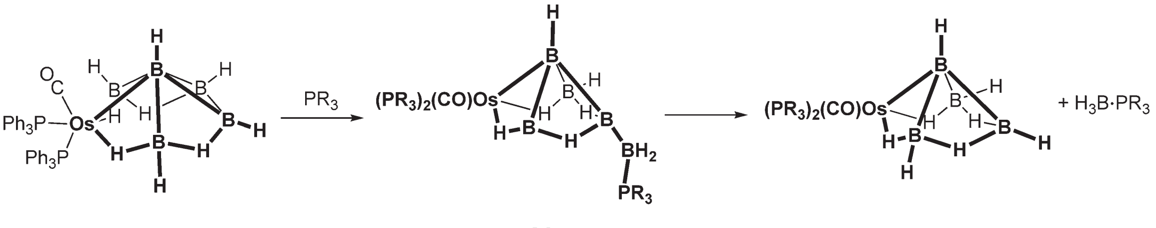
(η^5-C_5Me_5)IrB_4H_{10} **271** reacts with $Mo(CO)_3(THF)_3$ to give the mixed metallaborane (η^5-C_5Me_5)$Ir(CO)_3$-(THF)MoB_4H_8 **291**. The labile THF ligand in **291** can be replaced with CO to afford (η^5-C_5Me_5)$Ir(CO)_4MoB_4H_8$ **292**, and with various two-electron ligands to give (η^5-C_5Me_5)$Ir(CO)_3(PPh_3)MoB_4H_8$ **293**, (η^5-C_5Me_5)$Ir(CO)_3$(NCPh)MoB_4H_8 **294**, (η^5-C_5Me_5)$Ir(CO)_3$(CNBu)MoB_4H_8 **295**, and (η^5-C_5Me_5)$Ir(CO)_3(NH_3)MoB_4H_8$ **296**.[174]



271 **291** **293**

3.04.3.3.3.(iv) Osmium

Work from the laboratories of Barton on metallatetraboranes has produced some interesting and novel complexes which have pendant $BH_2{\cdot}PR_3$ groups. Addition of PPh_3 or PPh_2Me to *nido*-$Os(PPh_3)_2(CO)B_5H_9$ does not result in the opening up to an *arachno* cluster; instead, monoborane extrusion occurs and *nido* clusters with a pendant $BH_2{\cdot}PR_3$ group result: *nido*-{$Os(PPh_3)_2(CO)B_4H_7$}{$BH_2{\cdot}PR_2$} ($PR_3 = PPh_3$ **297**, PPh_2Me **298**, PMe_3 **299**). $BH_3{\cdot}PR_3$ is eventually eliminated, and thus complexes such as **297** are intermediates in cluster deboronation by phosphines. With the bidentate phosphine ligands, dppe or dppp, products with chelating $BH_2{\cdot}PR_2$ groups arise (e.g., $(PPh_3)(CO)OsB_4H_7$-η^2-(BH_2·dppe) **300**) or a pendant phosphine (e.g., $(PPh_3)_2(CO)OsB_4H_7$(BH_2·dppe) **301**). The borane adduct of this pendant phosphine complex **301** has also been prepared: $(PPh_3)_2(CO)OsB_4H_7$ (BH_2·dppe·BH_3) **302**.[175,176] With rigid phosphines, PPh_2XPPh_2 {X = 1,4-C_6H_4, 1,4-$CH_2C_6H_4CH_2$, $Fe(C_5H_4)_2$} boryl, linked metallaborane systems and pendant phosphines with coordinated BH_3 are observed, exemplified by {$(PPh_3)_2(CO)Os$}$B_4H_7BH_2PPh_2XPPh_2$ **303**, [{$(PPh_3)_2(CO)Os$}$B_4H_7BH_2PPh_2$]$_2$X **304**, and {$(PPh_3)_2(CO)Os$}B_4H_7 $BH_2PPh_2XPPh_2{\cdot}BH_3$ **305**.[177]



297 R = Ph

3.04.3.3.4 Metallaboranes of groups 8 and 9: M_xB_5

Some examples of complexes of metallaboranes of groups 8 and 9 (M_xB_5 species) are given in Table 11.

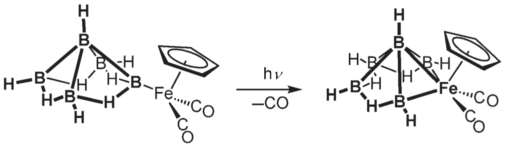
3.04.3.3.4.(i) Iron

Photochemical routes to metallapentaboranes have been explored by Spencer and co-workers. Irradiation of the σ-metallated pentaborane(9) complexes σ-{Fe(η^5-C_5H_5)$(CO)_2$}B_5H_8 **306** and σ-{Fe(η^5-C_5H_5)$(CO)_2$}$_2B_5H_7$ **307** results in loss of CO and insertion of the metal fragment into the cage to form the pentagonal pyramidal clusters {Fe(η^5-C_5H_5)$(CO)_2$}B_5H_8 **308** and {Fe(η^5-C_5H_5)$(CO)_2$}$_2B_5H_7$ **309**.[178] Deprotonation of **306** (or **308**) with NaH and subsequent reaction with Fe(η^5-C_5H_5)$(CO)_2$I also affords **307** (or **309**).

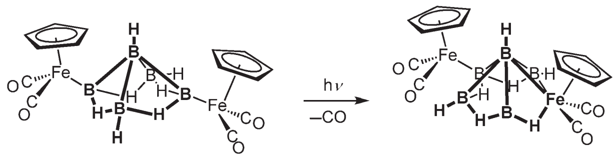
Table 11 Metallaboranes of groups 8 and 9: M_xB_5 species

No.	*Compound*	*Physical data*	*References*
306	σ-$\{Fe((\eta^5\text{-}C_5H_5))(CO)_2\}B_5H_8$	NMR	178
307	σ-$\{Fe((\eta^5\text{-}C_5H_5))(CO)_2\}_2B_5H_7$	NMR	178
308	$\{Fe((\eta^5\text{-}C_5H_5))(CO)_2\}B_5H_8$	NMR, X-ray	178
309	$\{Fe((\eta^5\text{-}C_5H_5))(CO)_2\}_2B_5H_7$	NMR	178
310	$\{Ir((\eta^5\text{-}C_5Me_5))\}_2B_5H_5$	NMR, X-ray	179
311	$\{Fe(CO)_3\{Ir(CO)_2(PPh_3)\}(B_5H_4)(PPh_3)$	NMR, X-ray	180
312	$\{Fe(CO)_3\}\{Ir(CO)_2(PPh_3)\}B_5H_4(PPh_3)$	NMR, X-ray	181
313	$\{Ir(CO)(PPh_3)_2\}\{PtCl(PMe_2Ph)\}B_5H_7$	NMR, X-ray	181

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.



306 **308**



307 **309**

3.04.3.3.4.(ii) Iridium

Addition of $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ to $Na_2[B_5H_9]$ results in $\{Ir((\eta^5\text{-}C_5Me_5))\}_2B_5H_5$ **310** which has an octahedral $\{Ir_2B_4\}$ core with a face-capping {BH} vertex.[179] $\{Fe(CO)_3\{Ir(CO)_2(PPh_3)\}(B_5H_4)(PPh_3)$ **311** results from the addition of $Fe_2(CO)_9$ to $Ir(CO)(PPh_3)_2B_5H_8$.[180] $\{Ir(PPh_3)_2(CO)\}B_5H_8$ reacts with $Fe_2(CO)_9$ to afford $\{Fe(CO)_3\}\{Ir(CO)_2(PPh_3)\}B_5H_4(PPh_3)$ **312**. The anion $Na[\{Ir(PPh_3)_2(CO)\}B_5H_7]$ (formed from deprotonation of $\{Ir(PPh_3)_2(CO)\}B_5H_8$ with NaH) reacts with $[Pt(PMe_2Ph)Cl_2]_2$ to give $\{Ir(CO)(PPh_3)_2\}\{PtCl(PMe_2Ph)\}B_5H_7$ **313**, which has a classical *nido* structure but possesses a cluster electron count that is two electrons short for the observed geometry.[181]

3.04.3.3.5 Metallaboranes of groups 8 and 9: M_xB_7, M_xB_9, M_xB_{10}

Some examples of complexes of metallaboranes of groups 8 and 9 (M_xB_7 to M_xB_{10} species) are given in Table 12.

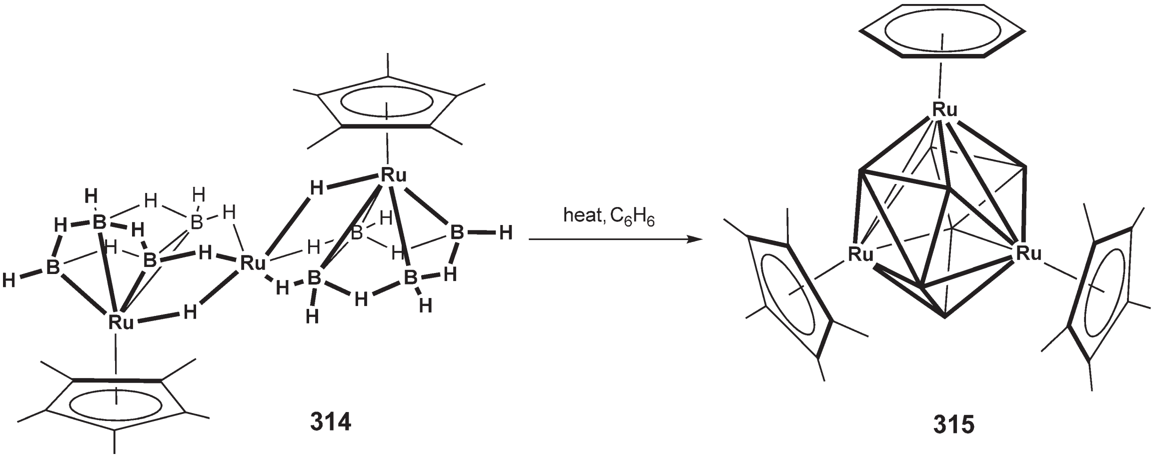
Table 12 Metallaboranes of groups 8 and 9: M_xB_7 to M_xB_{10} species

No.	*Compound*	*Physical data*	*References*
314	*commo*-$\{((\eta^5\text{-}C_5Me_5)Ru)(\mu\text{-}H)(B_4H_9)\}_2Ru$	NMR, X-ray	165
315	$\{(\eta^5\text{-}C_5Me_5)Ru\}_2\{(\eta^6\text{-}C_6H_6)Ru\}B_7H_7$	NMR, X-ray	182
316	$\{Ru(\eta^6\text{-}^iPrC_6H_4Me)\}_2B_8H_{12}$	NMR, X-ray	183
317	$\{Ru(\eta^6\text{-}^iPrC_6H_4Me)\}B_9H_{13}$	NMR, X-ray	183
318	*isocloso*-$(\eta^6\text{-}MeC_5H_4CMe_2H)RuB_9H_9$	NMR, X-ray	184
320	$[2\text{-}C_6Me_6$-*closo*-$2\text{-}RuB_9H_9]^{2-}$	NMR, X-ray	185
319	*isocloso*-$\{(\eta^6\text{-}MeC_5H_4CMe_2H)Ru\}_2B_8H_8$	NMR, X-ray	184
321	$(PPh_3)(C_6H_5COS)_2RuB_{10}H_8$	NMR, X-ray	186
322	$(PMe_3)_4(CO)_2Ir_2B_8H_8$	NMR, X-ray	187
323	$\{Ir(PPh_3)\}(\mu\text{-}S_2CH)_2$-*closo*-$B_9H_6(PPh_3)$	NMR, X-ray	188
324	$\{Ir(PPh_2(C_6H_4))\}(\mu\text{-}S_2CH)_2$-*closo*-$B_9H_5(PPh_3)$	NMR	188
325	$(\eta^6\text{-}C_6H_3Ph_3)HIrB_9H_6(PPh_3)$	NMR, X-ray	189
326	$(PPh_3)_2(PPh_2C_6H_4)IrB_9H_6(PPh_3)(\eta^5\text{-}C_5H_5)(CPh{=}CH)_2$	NMR, partial X-ray	189

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

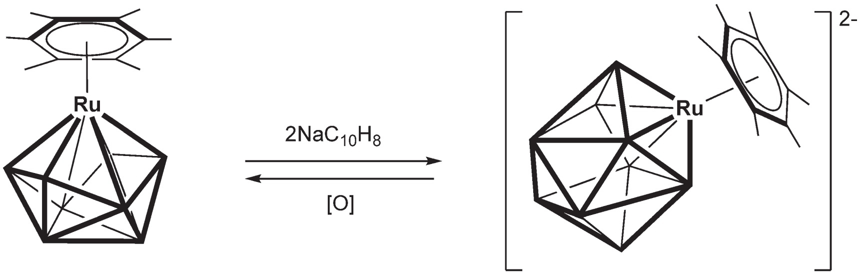
3.04.3.3.5.(i) Ruthenium

commo-$\{((\eta^5\text{-}C_5Me_5)Ru)(\mu\text{-}H)(B_4H_9)\}_2Ru$ **314**, which has a linear triruthenium fragment and is structurally related to $(B_5H_{10})M(B_5H_{10})$ (M = Be, Fe), is isolated in low yield from the addition of $Co_2(CO)_8$ to $((\eta^5\text{-}C_5Me_5)Ru)_2B_3H_9$ **252**, a reaction which also generates $((\eta^5\text{-}C_5Me_5)Ru)\{(\eta^5\text{-}C_5Me_5)Ru(CO)\}\{Co(CO)_3\}(\mu_3\text{-}CO)B_3H_6$ **255** and $((\eta^5\text{-}C_5Me_5)RuH)(CO)B_3H_7$ **256**.[165] Pyrolysis of the cluster **314** in benzene forms the "hypoelectronic" (*n*-1 s.e.p.) cluster species $\{(\eta^5\text{-}C_5Me_5)Ru\}_2\{(\eta^6\text{-}C_6H_6)Ru\}B_7H_7$ **315**, which is related to $((\eta^5\text{-}C_5Me_5)Re)_2B_8H_8$ **225**.[182] The coordinated benzene in the final product comes from the solvent. $\{Ru(\eta^6\text{-}{}^iPrC_6H_4Me)\}_2B_8H_{12}$ **316** and $\{Ru(\eta^6\text{-}{}^iPrC_6H_4Me)\}B_9H_{13}$ **317** are formed from the addition of $[Ru(\eta^6\text{-}{}^iPrC_6H_4Me)Cl_2]_2$ to $[NEt_4][B_9H_{14}]$.[183]



314 **315**

The geometric structures of *isocloso*-$(\eta^6\text{-}MeC_5H_4CMe_2H)RuB_9H_9$ **318** and *isocloso*-$\{(\eta^6\text{-}MeC_5H_4CMe_2H)Ru\}_2B_8H_8$ **319** are mono- and bimetallic examples of a parent 10-vertex "*iso–closo*" metallaborane complex.[184] The first example of a chemically reversible *hypercloso*→*closo*→*hypercloso* redox interconversion has been reported. In this, the known 10-vertex *hypercloso* compound 1-$(\eta^6\text{-}C_6Me_6)$-*hypercloso*-1-RuB_9H_9 undergoes a two-electron reduction to afford the 10-vertex *closo*-compound [2-$(\eta^6\text{-}C_6Me_6)$-*closo*-2-$RuB_9H_9]^{2-}$ **320** in high yield. This reaction is reversible as exposure to O_2 regenerating the *hypercloso* compound via an observable paramagnetic intermediate.[185]



320

$(PPh_3)(C_6H_5COS)_2RuB_{10}H_8$ **321** formed from the reaction of *closo*-$[B_{10}H_{10}]^{2-}$ and $(PPh_3)_2RuCl_2$ has two *exo*-polyhedral thiobenzoate sulfur atoms.[186]

3.04.3.3.5.(ii) Iridium

Reaction of $IrCl(CO)(PMe_3)_2$ with $[NEt_4]$[*nido*-B_9H_{12}] gives the 10-vertex, eight-boron cluster $(PMe_3)_4(CO)_2Ir_2B_8H_8$ **322**.[187] Reaction of carbon disulfide with *nido*-iridadecaboranes based on $\{IrB_9\}$ results in closed 10-vertex cluster compounds with boron-to-metal dithioformate bridges: $\{Ir(PPh_3)\}(\mu\text{-}S_2CH)_2$-*closo*-$B_9H_6(PPh_3)$ **323** and orthocycloboronated $\{Ir(PPh_2(C_6H_4))\}(\mu\text{-}S_2CH)_2$-*closo*-$B_9H_5(PPh_3)$ **324**.[188] The microwave-heated reaction between $(C_6H_5)C{\equiv}CH$ and $(PPh_3)_2HIrB_9H_{13}$ results in acetylene trimerization and the isolation of $(\eta^6\text{-}C_6H_3Ph_3)HIrB_9H_6(PPh_3)$ **325**.[189] From the same reaction and orthocycloboronated complex $(PPh_3)_2(PPh_2C_6H_4)IrB_9H_6(PPh_3)(CPh{=}CH)$ **326** is also isolated.

3.04.3.4 Metallaborane Cluster Complexes of Group 10

Some examples of complexes of metallaboranes of group 10 are given in Table 13.

The *closo*-seven-vertex anion $[Ni(\eta^5\text{-}C_5H_5)B_6H_6]^-$ **327** is prepared from $[NBu_4]_2[B_6H_6]$, 2 equiv. of $Ni(\eta^5\text{-}C_5H_5)_2$, and 1 equiv. of Na/Hg.[190] The *closo*-12-vertex dinickelaborane $\{Ni(PPh_3)(PPh_2C_6H_4)\}_2(\mu\text{-}Cl)B_{10}H_6$ has two cycloboronated triphenylphosphine ligands.[191] The *closo*-icosahedral cluster $[Ni(B_{11}H_{11})_2]^{4-}$ **328** has been synthesized from *nido*-$[B_{11}H_{14}]^-$ and $NiCl_2$.[192] Similarly, a $\{PdL_2\}$ fragment can be inserted into the open face of the *nido*-$[B_{11}H_{11}]^{3-}$ cage, by reaction of this trianion with $PdBr_2(PMe_2Ph)_2$ to form the paramagnetic icosahedral metallaborane 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$ **329**.[193]

arachno-$\{(dppe)Pt\}_2B_7H_{11}$ **330** is the final product from the reaction of B_5H_9 with $PtCl_2(dppe)$.[194] **330** appears not to conform to the polyhedral skeletal electron pair theory (PSEPT) counting rules as an *arachno*-nine-vertex cluster requires $n+3$ skeletal electron pairs, which for this cluster would be 12 electron pairs. Using the conventional electron-counting methods, **330** possesses 11 skeletal electron pairs. A number of other platinaborane species have electron counts anomalous with their geometric structures with regard to the electron-counting rules. For example, $(PMe_2Ph)_2PtB_9H_{11}Ru(\eta^6\text{-}MeC_5H_4CMe_2H)$ **331** has a *nido* geometry but a *closo*-electron count while $(PMe_2Ph)_2PtB_9H_9Ru(\eta^6\text{-}MeC_5H_4CMe_2H)$ **332** has a *closo* geometry but a sub-*closo* electron count.[195] Ten-vertex $(PMe_2Ph)_4Pd_2B_8H_{10}$ **333** isolated from the addition of $PdCl_2(PMe_2Ph)_2$ and 4-(NH_2Ph)-*arachno*-B_9H_{13}, has a *closo* electron count but an *arachno* structure. This anomaly is ascribed to the metal fragments being two orbital fragments with regard to cluster bonding, rather than three as usually encountered in cluster electron counting.[187] It is noted that such ambiguity has been observed for essentially all clusters containing three-connectivity group 10 metals.[194]

3.04.3.4.1 Metallaborane cluster complexes of the post-transition metals

Some examples of complexes of metallaboranes of post-transition metals are given in Table 14.

$[NBu_4]_2[Cd(B_6H_6)_2]$, **334**, prepared from $CdCl_2(PPh_3)_2$ and $[NBu_4]_2[B_6H_6]$, has a structure in which the central Cd^{2+} atoms are sandwiched between two borane cages, each using three B–H–Cd interactions.[196] Related compounds with Hg **335**,[197] Cu **336**, and Au **337**[198] have also been prepared. $\{(PPh_3)_2Cu\}_2B_6H_6$ **338**[199] and $\{(PPh_3)Cu\}_2B_6H_6$ **339**[198]

Table 13 Metallaboranes of group 10

No.	*Compound*	*Physical data*	*References*
327	$[Ni(\eta^5\text{-}C_5H_5)B_6H_6]^-$	NMR, X-ray	190
328	$[Ni(B_{11}H_{11})_2]^{4-}$	NMR	192
329	1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$	X-ray, EPR	193
330	*arachno*-$\{(dppe)Pt\}_2B_7H_{11}$	NMR, X-ray	194
331	$(PMe_2Ph)_2PtB_9H_{11}Ru(\eta^6\text{-}MeC_5H_4CMe_2H)$	NMR, X-ray	195
332	$(PMe_2Ph)_2PtB_9H_9Ru(\eta^6\text{-}MeC_5H_4CMe_2H)$	NMR, X-ray	195
333	$(PMe_2Ph)_4Pd_2B_8H_{10}$	NMR, X-ray	187

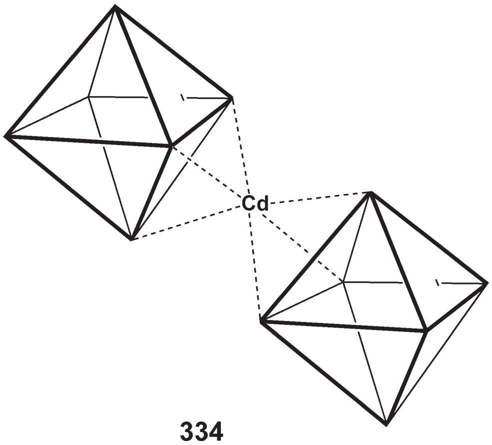
NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.
EPR = Characterization by electron paramagnetic resonance spectroscopy.

Table 14 Metallaboranes of the post-transition metals

No.	*Compound*	*Physical data*	*References*
334	$[NBu_4]_2\{Cd[B_6H_6]_2\}$	NMR, X-ray	196
335	$(Ph_4P)[Hg(B_6H_6)Ph]$	NMR, X-ray	197
336	$Cu_2(\mu\text{-}B_6H_6)_2(PPh_3)_2$	NMR, X-ray	198
337	$Au_2(\mu\text{-}B_6H_6)_2(PPh_3)_2$	NMR, X-ray	198
338	$\{(PPh_3)_2Cu\}_2B_6H_6$	NMR, X-ray	199
339	$\{(PPh_3)Cu\}_2B_6H_6$	NMR, X-ray	198
340	$[Cu(B_{11}H_{11})_2]^{3-}$	NMR, X-ray	192
341	$\{(MeZn)_2B_3H_7\}_2$	NMR, X-ray	200

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

have related structures, but this time the borane is complexed with two *exo*-copper phosphine fragments. $[Cu(B_{11}H_{11})_2]^{3-}$ **340** is formed from *nido*-$[B_{11}H_{14}]^-$ and CuO.[192] Gas-phase reaction of B_4H_{10} with $ZnMe_2$ affords the dimeric complex $\{(MeZn)_2B_3H_7\}_2$ **341** in which each of the two $\{B_3H_7ZnMe\}$ fragments function in a bis(bidentate) manner linking together two other {ZnMe} fragments through Zn–H–B bridges.[200]



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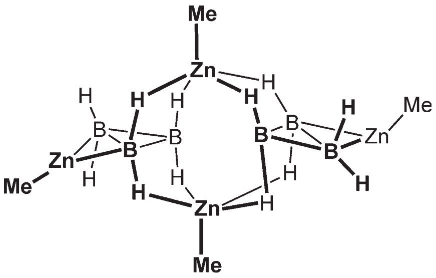

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3.04.3.5 Macropolyhedral Metallaboranes

Some examples of complexes of macropolyhedral metallaboranes are given in Table 15.

Macropolyheral boranes are boranes that consist of fused smaller borane clusters to afford clusters that have more than 12 vertices (i.e., greater than the icosahedron). They are of interest as they not only have extended borane chemistry beyond the icosahedron but also serve as a molecular link between discrete borane clusters and extended solid-state systems such as elemental boron. Macropolyhedral metallaboranes derive from the incorporation of one of more metal vertices into these large clusters. In the following section, complexes are dealt with in the order of increasing number of boron vertices. Of particular interest are the very large cluster species – or "megaloboranes" – which show boron only cores (i.e., no attendant hydrides) surrounded by borane hydride clusters. Synthetic routes to all of these large cluster species involve either the reaction of a preformed macropolyhedral borane with a metal fragment or thermolysis of a metallaborane, either on its own to result in a self-condensation or in molten borane such as $B_{10}H_{14}$ or $B_{18}H_{22}$.

nido-$B_{10}H_{12}$-(*nido*-B_5H_8)$_2$ **342** has a central *nido*-$\{B_{10}H_{12}\}$ core with two *nido*-$\{B_5H_8\}$ units, and models possible intermediates to globular megaloborane systems via the assembly of boron hydride units around a central cluster core.[201] Thermolysis of the nine-vertex *arachno*-monoiridaborane $(CO)(PMe_3)_2HIrB_8H_{12}$ affords 17-vertex $(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2$ **343** in low yield.[202] Similarly thermolysis of $(PPh_3)_2PdB_8H_{12}$ affords the 20-vertex macropolyhedral cluster $(PPh_3)_3ClPd_3B_{16}H_{17}Pd(PPh_3)$ **344**.[203]

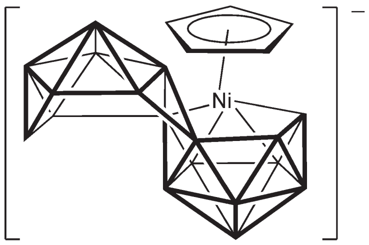
Eighteen-vertex $\{Ir(CO)(PMe_3)_2\}B_{17}H_{20}$ **345** is formed in low yield from the reaction of $(CO)(PMe_3)_2HIrB_8H_{12}$ with molten $B_{10}H_{14}$.[204] The reaction of *anti*-$B_{18}H_{22}$ with $(\eta^5\text{-}C_5H_5)_2Ni$ produces $[Ni(THF)_4(H_2O)_2][B_{18}H_{20}Ni$-

Table 15 Macropolyhedral metallaboranes

No.	*Compound*	*Physical data*	*References*
342	*nido*-$B_{10}H_{12}$-(*nido*-B_5H_8)$_2$	NMR, X-ray	201
343	$(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2$	NMR, X-ray	202
344	$(PPh_3)_3ClPd_3B_{16}H_{17}Pd(PPh_3)$	NMR, X-ray	203
345	$\{Ir(CO)(PMe_3)_2\}B_{17}H_{20}$	X-ray	204
346	$[Ni(THF)_4(H_2O)_2][B_{18}H_{20}Ni(\eta^5\text{-}C_5H_5)]_2$	NMR, X-ray	205
347	$B_{18}H_{20}Ni(\eta^5\text{-}C_5H_5)$	NMR	205
348	$[N(CH_3)_4][B_{18}H_{19}(2\text{-}THF)Ni(\eta^5\text{-}C_5H_5)]$	NMR, X-ray	205
349	$[Pt(B_{18}H_{20})_2]^{2-}$	NMR, X-ray	207
350	$(PPh_3)_2HIrB_{18}H_{18}(PPh_3)$	NMR, X-ray	206
351	*syn*-$(\eta^5\text{-}C_5Me_5)IrB_{18}H_{20}$	NMR, X-ray	208
352	$(\eta^5\text{-}C_5Me_5)HIrB_{18}H_{19}(PMe_2Ph)$	NMR, X-ray	208
353	$(\eta^5\text{-}C_5Me_5)HIrB_{18}H_{19}(C(NHMe_2))$	NMR, X-ray	208
354	$(\eta^5\text{-}C_5Me_5)HIrB_{18}H_{19}(PHPh_2)$	NMR, X-ray	209
355	$(\eta^5\text{-}C_5Me_5)IrB_{18}H_{18}(PHPh_2)$	NMR, X-ray	209
356	$(\eta^5\text{-}C_5Me_5)_3Ir_3B_{18}H_{15}(OH)$	NMR, X-ray	210
357	$(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)$	NMR, X-ray	211
358	$(PMe_2Ph)PtB_{22}H_{26}(PMe_2Ph)$	NMR, X-ray	212
359	$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$	NMR, X-ray	213,206
360	$(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)$	NMR, X-ray	214
361	$(PMe_2Ph)_2(PMe_2C_6H_4)_2Pt_2B_{28}H_{32}$	NMR, X-ray	206
362	$(PMe_2Ph)_2Pt_2B_{28}H_{32}$	NMR, X-ray	206

NMR = Characterization by NMR spectroscopy.
X-ray = Characterization by X-ray diffraction.

$(\eta^5\text{-}C_5H_5)]_2$ **346**, $B_{18}H_{20}Ni(\eta^5\text{-}C_5H_5)$ **347**, and $[N(CH_3)_4][B_{18}H_{19}(2\text{-}THF)Ni(\eta^5\text{-}C_5H_5)]$ **348**, in relatively high yields, the structures of which consist of 10-vertex *nido*-borane subunits edge-shared with 11-vertex *nido*-cluster subunits.[205] Reaction of $IrCl(PPh_3)_3$ with *anti*-$B_{18}H_{22}$ along with a hindered base results in the 19-vertex macropolyhedral cluster $(PPh_3)_2HIrB_{18}H_{18}(PPh_3)$ **350**;[206] $[Pt(B_{18}H_{20})_2]^{2-}$ **349** (as *syn*- and *anti*-isomers) is formed from the reaction of $[NEt_4][B_{18}H_{21}]$ with $Pt(cod)Cl_2$ and shows intimately packed anion layer structures in the solid states.[207]



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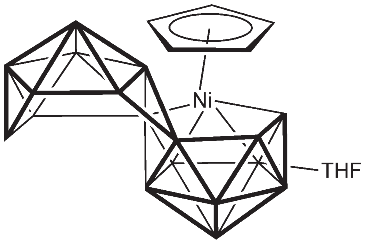

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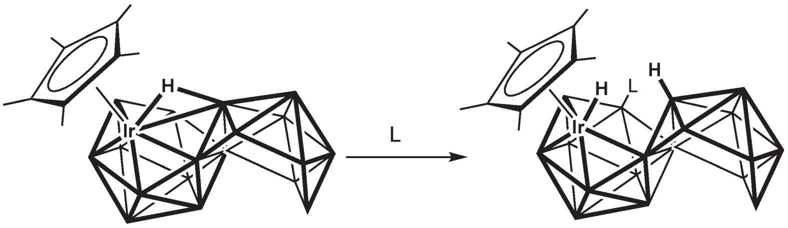
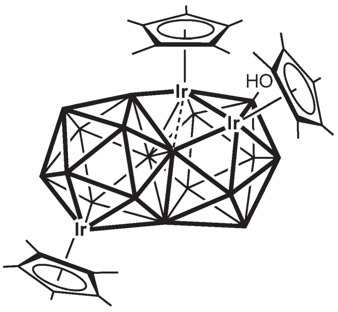
Addition of PMe_2Ph or MeNC to the fused cluster *syn*-$(\eta^5\text{-}C_5Me_5)IrB_{18}H_{20}$ **351** gives $(\eta^5\text{-}C_5Me_5)HIrB_{18}H_{19}(L)$ [L = PMe_2Ph **352** or $\{C(NHMe_2)\}$ **353**]. Interestingly, rather than a *nido→arachno* conversion that would commonly occur in smaller metallaboranes on addition of a two-electron ligand, macropolyhedral clusters **352** and **353** show a reduction in the intercluster fusion, from three-atoms-in-common to two-atoms-in-common.[208] Likewise, **351** also reacts with $PHPh_2$ to afford two-connected $(\eta^5\text{-}C_5Me_5)HIrB_{18}H_{19}(PHPh_2)$ **354**, whereas with the primary phosphine, PH_2Ph, the three-connected macropolyhedral cluster is retained: $(\eta^5\text{-}C_5Me_5)IrB_{18}H_{18}(PHPh_2)$ **355**.[209]



351 **352, 353**



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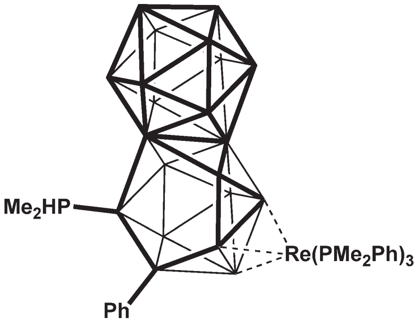
Reaction of *syn*-$B_{18}H_{20}$ with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ and base results in multiple metal center addition, coupled with oxidative cluster closure by multiple H_2 loss, giving the 21-vertex condensed globular cluster compound $(\eta^5\text{-}C_5Me_5)_3Ir_3B_{18}H_{15}(OH)$ **356** based on 12-vertex *closo*-$\{IrB_{11}\}$ and *isonido*-$\{IrB_{11}\}$ clusters fused with a common five-atom $\{IrB_4\}$ unit that contains a central tetrahedral $\{IrB_3\}$core.[210]

Reaction of $B_{20}H_{16}$ with $ReH_5(PMe_2Ph)_3$ yields the 21-vertex metallaborane $(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)$ **357** which consists of a *closo*-12-vertex {B12} unit and a *nido*-11-vertex {B11} unit fused with a common triangular face, with the $\{(PMe_2Ph)_3HRe\}$ moiety capping *exo*- to the *nido* {B} unit with three Re–H–B bonds. A phosphine ligand has also undergone reductive P–Ph cleavage to give a cluster-bound phenyl and $PHMe_2$ substituents.[211]



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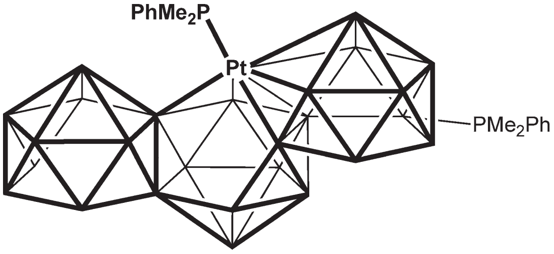
anti-$B_{18}H_{22}$ reacts with $(PMe_2Ph)_2PtB_8H_{12}$ to result in intimate cluster fusion to generate $(PMe_2Ph)\text{-}PtB_{22}H_{26}(PMe_2Ph)$ **358** which consists of a *nido*-11-vertex $\{PtB_{10}\}$ subcluster fused, to a second *nido*-11-vertex $\{PtB_{10}\}$ subcluster, which is fused, in turn, to a *nido*-10-vertex $\{B_{10}\}$ subcluster.[212] The 28-vertex "megaloborane" $(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$ **359** results from the same reaction.[213] The related plantina-metallaborane $(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)$ **360** arises from $(PMe_2Ph)_2PtB_8H_{12}$ and $B_{10}H_{14}$.[206,214] Although having the same number of vertices **359** and **360** display very different structures. The former has a five-boron core without any substituents, reminiscent of structural aspects of elemental (β-rhombohedral) boron while the latter is, essentially, a fusion of *nido*-11-vertex $\{PtB_{10}\}$, *nido*-eight-vertex $\{B_8\}$ and *nido*-shaped 10-vertex $\{PtB_9\}$ fragments. The same reaction conditions that afford **360** (molten $B_{10}H_{14}/(PMe_2Ph)_2PtB_8H_{12}$) also give orthometallated $(PMe_2Ph)_2(PMe_2C_6H_4)_2\text{-}Pt_2B_{28}H_{32}$ **361** and $(PMe_2Ph)_2Pt_2B_{28}H_{32}$ **362**.[206]



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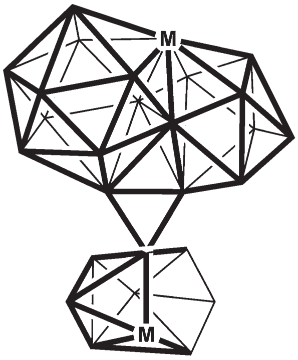

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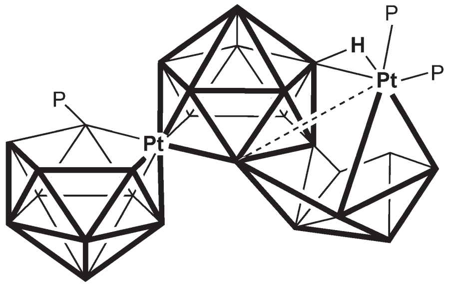

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3.05
Metallacarboranes of *d*- and *f*-Block Metals

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3.05.1 Introduction

Carboranes, or carbaboranes, are mixed hydride clusters of carbon and boron in which these elements occupy the vertices of "electron deficient" cages. Incorporating other atoms into the cage structures to give heterocarboranes can expand these clusters. When the heteroatom is a metal, the compounds are referred to as metallacarboranes. These compounds have been the subjects of a number of reviews and monographs, including the first two editions of this encyclopedia that adequately cover the general literature up to 1993, while later mini-reviews exemplify the rapid expansion of the area.[1–5d] This chapter will focus specifically on research that has been published since 1993 on the complexes in which *d*- and *f*-block metals are incorporated into carborane cages to form the respective metallacarboranes.

The structures of the heterocarboranes can be rationalized using a series of electron counting rules, collectively called "Wade's rules."[6,6a–6c] Two polyhedral structures will be commonly encountered in this review: one in which the cage atoms occupy all the vertices of a closed polyhedron to give a *closo*-structure, while in the other, one of the vertices is removed to give an open basket-like, *nido*-structure. More open geometries, such as *arachno*- and *hypho*-, can be obtained by successively removing other vertices from the *nido*-structure. The electron counting rules give a simple relationship between the geometry and the number of skeletal electron pairs. In a cluster having n skeletal atoms, a *closo*-structure is found when the number of skeletal electron pairs is equal to $n+1$, while a *nido*-structure is stabilized by $n+2$ electron pairs, an *arachno*-structure by $n+3$ pairs, and a *hypho*-structure by $n+4$ pairs.[6b] These rules, coupled with the isolobal analogies between BH vertices and the particular heteroatom group, offer a simple and elegant electron structure–geometry relationship. In this regard, it should be pointed out that the number of electrons, E, furnished by a transition metal group is conveniently given by the relationship, E = total number of valence electrons (metal group number + electrons supplied by the other ligands) − 12.[6c] Thus, the Co(Cp) group is a 14 (9 + 5) electron fragment that can furnish 2 (14 − 12) electrons for cluster bonding.

Metallacarboranes originated with the recognition that the *nido*-dicarbollide ion, $C_2B_9H_{11}{}^{2-}$, was similar to the cyclopentadienide ligand (Cp^-), in that both could bond to metals using a set of six electrons in delocalized π-type orbitals directed above the pentagonal face of the ligand.[7,8] This has led to the syntheses of metallacarboranes of two general structural types, half-sandwich complexes in which a metal moiety occupies the missing vertex of a *nido*-carborane to form a *closo*-metallacarborane, or full-sandwich compounds in which a metal occupies a common vertex of two carboranes to give *commo*-metallacarboranes. In general, the greater polarizability of boron compared to carbon and the higher ligand charge make the carboranes better ligands than the Cp derivatives, especially for the higher oxidation state metals.[10,11] Consequently, a wide variety of metal complexes of the carborane ligand systems has been synthesized and characterized.

Because this chapter is restricted to results published since 1993, when the chemistry of the *d*- and *f*-block metallacarboranes has experienced an upsurge, general research trends will be emphasized and no attempt will be made to cover the literature exhaustively. A sense of the scope of the research in this field can be obtained from perusing Table 1.

Table 1 Selected crystallographic parameters for heterocarboranes of elements in the *d*- and *f*-blocks

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
Heterocarboranes of Group 3 Elements			
(1) Scandium			
$[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$	Sc1–Cp*1 = 2.206 Sc2–Cp*2 = 2.182 Sc1–Cb1 = 2.802 Sc2–Cb2 = 2.081	Cb1–Sc1–Cp*1 = 136.3 Cb2–Sc2–Cp*2 = 136.5	239
(2) Yttrium			
$[\{\eta^7\text{-}[(CH_3OCH_2CH_2)_2C_2B_{10}H_{10}]Y\}\{Li(THF)_3\}]_2$	Y–C(2) = 2.344(8) Y–C(5) = 2.382(8) Y–B(av) = 2.723(9)		240
$\{\eta^7\text{-}[(CH_3OCH_2CH_2)_2C_2B_{10}H_{11}]Y(THF)\}^-$	Y–C(2) = 2.392(4) Y–C(5) = 2.378(4) Y–B(Av) = 2.723		240
$[Li^+(THF)_4]\{1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}4,4',5,5'\text{-}Li(C_4H_8O)\text{-}[1,1'\text{-}commo\text{-}Y(C_2B_4H_4)^2]\}^-$	Y–Cnt(1) = 2.362 Y–Cnt(2) = 2.389 Y–Cl = 2.582(4)	Cnt(1)–Y–Cl = 110.5 Cnt(2)–Y–Cl = 111.6 Cnt(1)–Y–Cnt(2) = 129.7	15a
$[\{[\eta^7\text{-}(3,5\text{-}(CH_3O)_2C_6H_3CH_{=2})_2C_2B_{10}H_{10}]\text{-}Y(THF)\}\{Na(THF)_3\}]_2$	Y–C(cage) = 2.367(10) Y–B(cage) = 2.644(12) Y–B = 2.828(12)		202c
$\{[\eta^7\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}]Y(THF)\}_2\{Na(THF)_3\}_2\cdot 2THF$	Y–av(C_2 atom) = 2.389 Y–av(B_5 atom) = 2.685		242
$\{[\eta^7\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}]Y(THF)\}_2\{Li(THF)_4\}_2$	Y–av(C_2 atom) = 2.377 Y–av(B_5 atom) = 2.685		242
(3) Lanthanum			
$[(\eta^5\text{-}C_2B_9H_{11})_2La(THF)_2]^-$	La(1)–Cnt(1) = 2.446 La(1)–Cnt(2) = 2.411 La(1)–O(1) = 2.537(3)	O(1)–La(1)–O(2) = 79.3(1) Cnt(1)–La(1)–O(2) = 104.9 Cnt(1)–La(1)–Cnt(2) = 132.7	243
Heterocarboranes of Group 4 Elements			
(1) Titanium			
$[commo\text{-}1\text{-}Cp\text{-}1\text{-}Ti\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$	Ti(1)–Cnt(11) = 1.964 Ti(2)–Cnt(12) = 1.976 Ti(1)–Cnt(13) = 2.039 Ti(2)–Cnt(14) = 2.029	Cnt(11)–Ti(1)–Cnt(13) = 142.8 Cnt(12)–Ti(2)–Cnt(14) = 142.5	26,26a
$commo\text{-}1\text{-}Cp\text{-}1\text{-}Cl\text{-}1\text{-}THF\text{-}1\text{-}Ti\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$	Ti–Cnt(71) = 1.991 Ti–Cnt(72) = 2.075	Cnt(1)–Ti–Cnt(2) = 131.6	26,26a
$(\eta^5C_2B_9H_{11})Cp^*TiMe$	Ti(1)–Cnt(Cp*) = 2.08 Ti(1)–Cnt(Cb) = 1.96 Ti(1)–Me = 2.160(2)	Cnt–Ti(1)–Cnt = 139.2	38
$(\eta^5C_2B_9H_{11})(\eta^5{:}\eta^1C_5Me_4CH_2)Ti$	Ti(1)–Cnt(C_5) = 1.94 Ti(1)–Cnt(Cb) = 1.83 Ti(1)–C(8) = 2.294(3)	Cnt–Ti(1)–Cnt = 150.5 Ti(1)–C(8)–C(3) = 64.5(2)	38
$(PMe_3)_2Cl_2Ti(Et_2C_2B_4H_4)$	Ti–Cl(av) = 2.326 Ti–av(C_2B_3 atoms) = 2.375 Ti–P(av) = 2.597	Cl1–Ti–Cl2 = 124.17(6) P1–Ti–P2 = 136.87(6) Cl1–Ti–P1 = 78.88(5)	28
$(dmpp)Cl_2Ti(Et_2C_2B_4H_4)$	Ti–Cl(av) = 2.332 Ti–P(av) = 2.598 Ti–av(C_2B_3 atoms) = 2.370	P2–Ti–Cl1 = 131.71(7) Cl2–Ti–P2 = 78.70(5) Cl–Ti–Cl = 91.57(6)	28

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
(dmpp)Me$_2$Ti(Et$_2$C$_2$B$_4$H$_4$)	Ti–Me(av) = 2.168 Ti–P(av) = 2.591 Ti–av(C$_2$B$_3$ atoms) = 2.376	Cl1–Ti–Cl2 = 89.7(2) P1–Ti–P2 = 77.81(4) Cl1–Ti–P1 = 78.9(1) P1–Ti–Cl2 = 132.6(1)	28
Cp*(η^5-C$_2$B$_9$H$_{11}$)Ti(N=CMe$_2$)(NCMe)	Ti–Cnt(Cb) = 2.02 Ti–Cnt(Cp*) = 2.09 Ti–N(*sp*^{2}) = 1.85(1) Ti–N(*sp*) = 2.19(1)	Cnt(Cb)–Ti–Cnt(Cp*) = 138.7 Cnt(Cb)–Ti–N(*sp*) = 105.0 Cnt(Cp*)–Ti–N(*sp*) = 103.2 N–Ti–N = 85.6(5)	37
Cp*(η^5-C$_2$B$_9$H$_{11}$)Ti(N=CMe$_2$)	Ti–Cnt(Cb) = 1.91 Ti–Cnt(Cp*) = 2.07 Ti–N = 1.89(2)	Cnt(Cb)–Ti–N = 111.0 Cnt(Cb)–Ti–Cnt(Cp*) = 114.6 Cnt(Cp*)–Ti–N = 104.4	37
{η^5:σ-(NMe$_2$CH$_2$)(C$_2$B$_9$H$_9$CH$_2$NMe$_2$)}Ti(NMe$_2$)$_2$	Ti–NMe$_2$(av) = 1.895 Ti–N(σ) = 2.240(3) Ti–av(C$_2$B$_3$ atom) = 2.432	NMe$_2$–Ti(1)–NMe$_2$ = 99.8(2) NMe$_2$(1)–Ti(1)–N(σ) = 107.6(2) NMe$_2$(2)–Ti(1)–N(σ) = 102.7(1)	32
[{η^5:σ-(NMe$_2$CH$_2$)(C$_2$B$_9$H$_9$CH$_2$NMe$_2$}-Ti(NMe$_2$)]$_2$-(μ^3-O)(μ^2-NMe)-Ti(NMe$_2$)	Ti–av(C$_2$B$_3$ atom) = 2.384 Ti(1)–O = 2.057 Ti(1)–Ti(av) = 2.922 Ti(1)–N(μ^2)av = 2.09	N(μ^2)–Ti(1)–N(μ^2) = 155.4(4) Ti–O–Ti = 170.8(4) Ti(1)–O–Ti = 94.3	32
[Li(TMEDA)]$_2$[1,1′-Ti-(2-Me-3-SiMe$_3$-2,3-C$_2$B$_4$H$_4$)$_2$]$_2$	Ti–Cnt(1) = 2.015 Ti–Cnt(2) = 2.008	Cnt(1)–Ti–Cnt(2) = 138.9	26a
Cp*(η^5:η^1-8-CHMeO-C$_2$B$_9$H$_{10}$)Ti	Ti–Cnt(Cb) = 1.830 Ti–Cnt(Cp*) = 2.041 Ti–O = 1.879(7) Ti(1)–B(4) = 2.28(1)	O–Ti(1)–Cnt(Cb) = 106.4 O–Ti(1)–Cnt(Cp*) = 106.9 Cnt(Cb)–Ti(1)–Cnt(Cp*) = 145.6	30
Cp*(η^5:η^1-4-CHMeO-C$_2$B$_9$H$_{10}$)Ti(CH$_3$CN)	Ti(1)–Cnt(Cb) = 1.961 Ti(1)–O(1) = 1.869(2) Ti(1)–Cnt(Cp*) = 2.113	Cnt(Cp*)–Ti(1)–Cnt(Cb) = 140.4 Cnt(Cp*)–Ti(1)–O(1) = 105.0 Cnt(Cp*)–Ti(1)–N(1) = 100.4	30
1-TMEDA-1-Cl-Ti(III)-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Ti–Cnt(6) = 1.948	Cnt(6)–Ti–Cl = 120.6	26a
Cp*(η^5:η^1-8-CHMeO-C$_2$B$_9$H$_{10}$)Ti	Ti(1)–Cnt(Cb) = 1.830 Ti(1)–Cnt(Cp*) = 2.041 Ti(1)–O(1) = 1.879(7)	O(1)–Ti(1)–Cnt(Cb) = 106.4 O(1)–Ti(1)–Cnt(Cp*) = 106.9 Cnt(Cb)–Ti(1)–Cnt(Cp*) = 145.6	30
Cp*(η^5:η^1-4-CHMeO-C$_2$B$_9$H$_{10}$)Ti(CH$_3$CN)	Ti(1)–Cnt(Cb) = 1.961 Ti(1)–O(1) = 1.869(2) Ti(1)–Cnt(Cp*) = 2.113	Cnt(Cp*)–Ti(1)–Cnt(Cb) = 140.4 Cnt(Cp*)–Ti(1)–O(1) = 105.0 Cnt(Dc)–Ti(1)–O(1) = 102.6	30
(3) Zirconium			
1-Cl-1-THF-2,2′,3,3′-(SiMe$_3$)$_4$-4,4′,5,5′-Li(THF)-1,1′-*commo*-Zr(2,3-C$_2$B$_4$H$_4$)$_2$	Zr–Cnt(1) = 2.176 Zr–Cnt(2) = 2.172	Cnt(1)–Zr–Cnt(2) = 130.4	19
[[{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}ZrCl(η^3-C$_2$B$_{10}$H$_{10}$)][Li(THF)$_4$]]	av Zr–C(C$_5$ring) = 2.515(5) Zr–Cl = 2.403(2)		29a
{[*o*-C$_6$H$_4$(CH$_2$)$_2$-C$_2$B$_{10}$H$_9$]$_2$ZrCl$_2$}{Na(THF)}$_2$	Zr–av(C$_2$B$_4$ring) = 2.70 Zr–Cl = 2.533(1)	C1–Zr–C1A = 85.00(6) Cnt–Zr–Cnt = 130.2	29
{[*o*-C$_6$H$_4$(CH$_2$)$_2$C$_2$B$_{10}$H$_{10}$]$_2$-Zr}{Na(THF)$_3$}$_2$	Zr–av(C$_2$B$_4$ring) = 2.50	Cnt–Zr–Cnt = 180.0	29
[η^4:η^2-{(C$_6$H$_5$CH$_2$)$_2$C$_2$B$_9$H$_9$}$_2$ZrCl(THF)]$^-$	Zr–av(η^4-CB$_3$) = 2.57 Zr–B23 = 2.643(6) Zr–B24 = 2.329(6) Zr–Cl = 2.395(2) Zr–O = 2.185(4)		29b
[η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]-Zr[N=C(Ph)NMe$_2$]$_2$	av Zr–C(C$_5$ring) = 2.544 av Zr–N = 1.972(2)	Cnt–Zr–C(cage) = 100.4 Zr–C(cage) = 2.359(2)	252

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
$[\eta^5{:}\sigma\text{-}(Me_2C(C_9H_6)(C_2B_{10}H_{10})]\text{-}Zr[\eta^2\text{-}SC(NMe_2Nbu^n]_2$	av Zr–C(C_5ring) = 2.559(10) av Zr–S = 2.578(3) av Zr–N = 2.268(8)	Cnt–Zr–C(cage) = 98.3 Zr–C(cage) = 2.398(9)	252
$1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,4',5'\text{-}Li(C_4H_8O)_2\text{-}[1,1'\text{-}\textit{commo}\text{-}Zr(C_2B_4H_4)_2]$	Zr–(C_2B_3Cnt1) = 2.175 Zr–(C_2B_3Cnt2) = 2.173 Zr–Cl = 2.461(1)	Cnt1–Zr–Cnt2 = 130.4 Cnt–Zr–O(25) = 105 Cnt–Zr–Cl = 109.1	19
$1\text{-}Cl\text{-}1\text{-}THF\text{-}2,2'\text{-}(SiMe_3)_2\text{-}3,3'\text{-}(Me)_2\text{-}4,4',5,5'\text{-}Li(THF)\text{-}1,1'\text{-}\textit{commo}\text{-}Zr(2,3\text{-}C_2B_4H_4)_2$	Zr–Cnt1 = 2.179 Zr–Cnt(2) = 2.169	Cnt(1)–Zr–Cnt(2) = 133.6	19a
$[Mg(THF)_6][1\text{-}Cl\text{-}1\text{-}(THF)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}1,1'\text{-}\textit{commo}\text{-}Zr(2,3\text{-}C_2B_4H_4)_2]_2{\cdot}4THF$	Zr–Cnt(1) = 2.173 Zr–Cnt(2) = 2.152	Cnt(1)–Zr–Cnt(2) = 130.5	19a
$1\text{-}Cl\text{-}1\text{-}(CH_2SiMe_3)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}4,4',5,5'\text{-}[(\mu\text{-}H)_4Li](\mu_3\text{-}Cl)[Mg(\mu_2\text{-}Cl)(THF)_3]_2\text{-}1,1'\text{-}\textit{commo}\text{-}Zr(C_2B_4H_4)_2$	Zr–Cnt(1) = 2.196 Zr–Cnt(2) = 2.222	Cnt(1)–Zr–Cnt(2) = 132.0	19a
$[\eta^5{:}\eta^6{:}\sigma\text{-}Me_2Si(C_9H_6)\text{-}(C_2B_{10}H_{10}CH_2NMe)]Zr(NC_5H_5)$	Zr1–av(C_2B_4ring) = 2.626 Zr1–C3 = 2.567(5)[2.579(6)] Average Zr–C_5 ring = 2.571(5) Zr1–NC_5H_5 = 2.354(5) Zr1–N(σ) = 2.054(4)	N1–Zr1–N(2) = 95.88(17) Cnt–Zr1–Cnt = 133.5	225
$(\eta^5C_2B_9H_{11})Zr(NEt_2)_2(HNEt_2)$	Zr–Cnt = 2.128(2) Zr–av(NEt_2) = 2.038	$NHEt_2$–Zr–Cnt = 112.6 NEt_2–Zr–Cnt = 123.5 NEt_2–Zr–$NHEt_2$ = 99.4(1)	35
$[\eta^5{:}\eta^1\text{-}C_2B_9H_{10}\text{-}CH_2NMe_2]_2Zr$	Zr(1)–N(av) = 2.474 Zr(1)–av(C_2B_9) = 2.2.526, 2.522	N(1)–Zr(1)–N(2) = 103.40(1)	31
$[\{(\mu\text{-}\eta^5){:}\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\text{-}\{Na_3(THF)_4\}]_n$	Zr–C(C_5ring) = 2.577 Zr1–avC_2 = 2.268 Zr1–avB_5 = 2.624		225
$[Li(THF)_3]\{[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2](\eta^5\text{-}Cp^*)ZrCl_2\}$	Zr–Cnt(Cb) = 2.151 Zr–Cp^* = 2.244	Cl(1)–Zr–Cl(2) = 94.6(1) Cp^*–Zr–Cnt(Cb) = 131.3	19
(4) Hafnium			
$4',5,5',6\text{-}Li(THF)\text{-}1,1'\text{-}\textit{commo}\text{-}Hf\ (THF)Cl[2\text{-}(SiMe_3)\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_4]_2$	Hf–Cnt(1) = 2.15 Hf–Cnt(2) = 2.16 Hf–C(1) = 2.503(14)	Cnt(1)–Hf–Cl = 106.4 Cnt(2)–Hf–Cl = 106.2 Cnt(1)–Hf–Cnt(2) = 134.1	21
$(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5{:}\eta^1\text{-}C_2B_9H_{10})Hf(Cp^*)$	Hf(1)–av(Cp^*) = 2.20 Hf(1)–Cnt = 1.96	Cnt–Hf(1)–Cnt = 137.6 Cnt–Hf(2)–Cnt = 132.8	36
Heterocarboranes of Group 5 Elements			
(1) Vanadium			
$1\text{-}Cp\text{-}1\text{-}Br\text{-}2\text{-}Ph\text{-}1,2,3,4\text{-}VC_3B_7H_9$	V(1)–Br = 2.4827(10) V–av(C_2) = 2.033 V–av(CB_3) = 2.392		43
(2) Niobium			
$[1\text{-}Cp\text{-}1,1'\text{-}\mu\text{-}Cl\text{-}2\text{-}Me\text{-}1,2,3,4\text{-}NbC_3B_7H_9]_2$	Nb(1)–C(1)(av) = 2.624 Nb–av(C_2) = 2.16 Nb(1)–(CB_4) = 2.496 Nb(1)–Nb(1)′ = 4.277(1)	C1–Nb–C1 = 71.7(2) Nb1–C1–Nb1′ = 108.33(5)	43
$\textit{commo}\text{-}Nb\text{-}1\text{-}Cl\text{-}(4\text{-}Me\text{-}1,2,3,4NbC_3B_7H_9)_2$	Nb–Cl = 2.388(4) Nb–av(C_2) = 2.222 Nb–a(CB_4) = 2.609		43

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
(3) Tantalum			
[2,2,2-(NMe$_2$)$_3$-*closo*-2,1,12-TaC$_2$B$_9$H$_{11}$]	Ta(2)–N(av) = 1.982 Ta(2)–Cb = 1.986(5) Ta(2)–N(3) = 1.990(2)	Cb–Ta(2)–N(1) = 122.6(2) Cb–Ta(2)–N(2) = 115.4(2) Cb–Ta(2)–N(3) = 116.7(2)	42a
[4,4,4-(NMe$_2$)$_3$-3-Me-4,1,2-*closo*-TaC$_2$B$_9$H$_{10}$]	Ta–N(av) = 1.986 Ta–Cb = 1.982	N(2)–Ta–N(3) = 96.63(16) N(2)–Ta–N(1) = 95.46(18) N(3)–Ta–N(1) = 105.35(16)	42b
{(μ-H)(C$_2$B$_9$H$_{10}$)$_2$}TaCl$_2$	Ta–Cl(av) = 2.355 Ta–Cnt(1) = 2.006 Ta–Cnt(2) = 2.010	Cl(1)–Ta–Cl(2) = 90.78(2) Cnt(1)–Ta–Cl(1) = 108.4 Cnt(1)–Ta–Cnt(2) = 124.2	41
[2,2,2-(NMe$_2$)$_3$-*closo*-2,1,7-TaC$_2$B$_9$H$_{11}$]	Ta–N(av) = 1.962 Ta–Cnt = 2.01 Ta(2)–N(3) = 1.994(15)	Cnt–Ta(2)–N(1) = 118.5(5) Cnt–Ta(2)–N(2) = 118.9(5) Cnt–Ta(2)–N(3) = 119.4(5)	42a
Cp[(Me$_3$Si)$_2$C$_2$B$_4$H$_4$]TaCl$_2$	Ta–Cnt(Cp) = 2.123(9) Ta–Cl(2) = 2.370(2)	Cl(1)–Ta–Cl(2) = 99.20(10) H(11)–Ta–H(31) = 79(3)	253
[*closo*-3,1,2-Ta{N═C(Me)NMe$_2$}$_3$(C$_2$B$_9$H$_{11}$)]	Ta–N(av) = 1.904(3) Ta(1)–Cnt = 2.097(5)	Cb–Ta(1)–N(10) = 106.4(2) Cb–Ta(1)–N(20) = 124.1(2) Cb–Ta(1)–N(30) = 118.4(2)	42d
[*closo*-3,1,2-Ta{N═C(C$_6$H$_4$F)NMe$_2$}$_3$(C$_2$B$_9$H$_{11}$)]	Ta–N(av) = 1.901(16) Ta–Cnt = 2.097(5)	Cnt–Ta(1)–N(1) = 124.3(2) Cnt–Ta(1)–N(3) = 113.1(2) Cnt–Ta(1)–N(5) = 113.5(2)	42d
[*closo*-3,1,2-Ta{N═C(C$_6$H$_4$F)NMe$_2$}$_2$Cl(C$_2$B$_9$H$_{11}$)]	Ta–N(av) = 1.864 Ta–Cnt = 2.018 Ta–Cl = 2.397(1)	Cnt–Ta(1)–N(1) = 116.7(3) Cnt–Ta(1)–N(3) = 123.5(2) Cnt–Ta(1)–Cl(1) = 112.2(1)	42d
[*closo*-3,1,2-Ta(OC$_6$H$_3$Me$_2$-2,6)$_3$(C$_2$B$_9$H$_{11}$)]	Ta–O(av) = 1.867 Ta–Cnt = 1.963(3)		42d
[*closo*-3-Ta(SPh)$_4$(9-NHMe$_2$-1,2-C$_2$B$_9$H$_{10}$)]	Ta–Cnt = 2.053(6) Ta–S(av) = 2.431	Cnt–Ta–S(1) = 123.3(3) Cnt–Ta–S(2) = 106.0(3) Cnt–Ta–S(3) = 119.1(3) Cnt–Ta–S(4) = 104.0(3) Cnt–Ta–S(1) = 123.3(3)	42d
Cp*Co(Et$_2$C$_2$B$_3$Br$_3$)Cl$_2$TaCp	Ta–Cl(av) = 2.359 Ta–av(C$_2$B$_3$) = 2.48 Co–av(C$_2$B$_3$) = 2.08	Cl(1)–Ta–Cl(2) = 95.1(2)	39
(Et$_2$C$_2$B$_4$H$_4$)CpTaCH$_3$(η^2-C,N-C{═N-t-Bu}CH$_3$)	Ta–N = 2.155(6) Ta–av(C$_2$B$_3$ atom) = 2.445 Ta–Me = 2.258(8) Ta–C(η^2) = 2.157(8) Ta–av(C$_5$ ring) = 2.454		40
(Et$_2$C$_2$B$_4$H$_4$)CpTaCH$_3$(η^2-C,N-C{═N-t-Bu}CH$_3$)	Ta–N(η^2) = 2.208(8) Ta–C(η^2) = 2.12(1) Ta–av(C$_2$B$_3$ atom) = 2.45 Ta–Me = 2.258(4) Ta–av(C$_5$ atom) = 2.43		40
(Et$_2$C$_2$B$_4$H$_4$)CpTaCH$_3$(η^2-C,N-C{═N(2,6-Me$_2$C$_6$H$_3$)}C$_6$H$_5$)	Ta–N(η^2) = 2.218(6) Ta–C(η^2) = 2.145(7) Ta–av(C$_5$ atom) = 2.438 Ta–av(C$_2$B$_3$ atom) = 2.449 Ta–Ph = 2.287	N((η^2)–Ta–C((η^2) = 33.5(2) N(η^2)–Ta–Ph = 83.4(2)	40
[(η^2-Et$_2$C$_2$B$_4$H$_3$(C$_6$H$_5$)(CHN(2,6-Me$_2$C$_6$H$_3$))]CpTa-(η^2-C,N-C{═N-(2,6-Me$_2$C$_6$H$_3$)}C$_6$H$_5$)	Ta–N(η^2) = 2.202(6) Ta–C(η^2) = 2.133(7) Ta–N($\eta^{2\prime}$) = 1.949(5) Ta–C($\eta^{2\prime}$) = 2.411(9) Ta–B(η^2) = 2.296(7) Ta–B(η^2) = 2.410(8) Ta–av(C$_5$ atom) = 2.437		40

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(C_6H_5)CC(CH_3))$	Ta–av(C_5 atom) = 2.42 Ta–Ph = 2.18(1) Ta–av(C_2B_3 atom) = 2.41		40b
$(Et_2C_2B_4H_3CH_2CH_2Ph)(Cp)Ta[C(Ph)(H)CH_2\text{-}C_6H_3(CH_2CH_2Ph)$	Ta–av(C_2B_3 atom) = 2.46 Ta–Ph = 2.176(7) Ta–av(C_5 atom) = 2.42		40b
Heterocarboranes of Group 6 Elements			
(1) Chromium			
$1,1'\text{-}\textit{commo}\text{-}Cr[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$	Cr–Cnt = 1.809	Cnt(1)–Cr–Cnt(2) = 180.0	47
$Li(THF)_4\{1,1'\text{-}\textit{commo}\text{-}Cr[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2\}$	Cr–Cnt = 1.809	Cnt(1)–Cr–Cnt(2) = 180.0	47
$(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}(\eta^6\text{-}C_6H_5)Cr(CO)_3$	Cr–av(C_6H_5 ring) = 2.225(13) Cr–av(CO) = 1.838(10) Fe–av(C_6H_6 atom) = 2.078(15) Fe–av(C_2B_3 atom) = 2.09		160a
$([(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-})]_2C_4H_2S_2$	Fe–av(C_6H_6 atom) = 2.067(5) Fe–av(C_2B_3 atom) = 2.10		160a
$([(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}]_2(C_6H_4)_3$	Fe–av(C_2B_3 atom) = 2.10		160a
$[(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}Ph)\text{-}Fe\text{-}(Et_2C_2B_4H_4\text{-}5\text{-}I)]$	Fe–av(C_2B_3 atom) = 2.10 Fe–av(C_6H_6 atom) = 2.085(6), 2.095(5)		160a
$Li(TMEDA)_2\{1,1'\text{-}\textit{commo}\text{-}Cr[2\text{-}(SiMe_3)\text{-}2,3\text{-}C_2B_4H_5]_2\}$	Cr–Cnt = 1.771	Cnt(1)–Cr–Cnt(2) = 175.3	47
$\{\eta^5\text{-}C_5H_5Cr\}_2\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$	Cr(1)–Cr(2) = 2.6626(11) Cr(1)–(av(C_2B_4 atom) = 2.097 Cr(2)–(av(C_2B_4 atom) = 2.099		50
$[ttf]^{\cdot+}[Cr(C_2B_9H_{11})_2]^-$	Cr(1)–(av(C_2B_3 atom) = 2.222		254
(2) Molybdenum			
$[Mo(CO)_4(\eta^5\text{-}7\text{-}CB_{10}H_{11}]^-$	Mo–av(CB_4 atom) = 2.379 Mo–av(CO) = 2.008		57
$[Mo(CO)_3PPh_3)\{(\eta^5\text{-}9\text{-}O(CH_2)_4\text{-}7\text{-}CB_{10}H_{10}\}]$	Mo–av(CB_4 atom) = 2.384 Mo–av(CO) = 2.008 Mo–P = 2.5542(7)		57
$[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}I\text{-}\textit{closo}\text{-}2,1]\text{-}MoCB_{10}H_{11}]$	Mo–I = 2.9241(9) Mo–av(CB_4 atom) = 2.397		58,58a–58c
$[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}7\text{-}\{O(CH_2)_4\}\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_{10}]$	Mo–av(CB_4 atom) = 2.369 Mo–I = 2.8839(8)		58,58a–58c
$[2,2,2\text{-}(CO)_3\text{-}2,3\text{-}\mu\text{-}I\text{-}n\text{-}\{cyclo\text{-}1,4,7\text{-}S_3(CH_2)_6\}\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_9]$ $(n = 7,11)$	Mo–av(CB_4 atom) = 2.367 Mo–I = 2.8375(9)		58,58a–58c
$[2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}3,\ 11\text{-}\{cyclo\text{-}1,4\text{-}S_2(CH_2)_4\}_2\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_9]$	Mo–av(CB_4 atom) = 2.387 Mo–I = 2.8693(8)		59
$[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7,8,12\text{-}(\mu\text{-}H)_3\text{-}7,8,12\text{-}\{Cu(PPh_3)\}\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_8]$	Mo–av(CB_4 atom) = 2.387		58a
$[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7,12\text{-}(\mu\text{-}H)_2\text{-}7,12\text{-}\{Ag(PPh_3)\}\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_9]$	Mo–av(CB_4 atom) = 2.384 Mo–CO(av) = 2.005		58a
$[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7,8,12\text{-}(\mu\text{-}H)_3\text{-}7,8,12\text{-}\{RuCl(PPh_3)_2\}\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_8]$	Mo–av(CB_4 atom) = 2.385 B(3)–Ru = 2.462(2) Mo–CO(av) = 2.011		58a
$2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7,8,12\text{-}(\mu\text{-}H)_3\text{-}7,8,12\text{-}[(Et_2C_2B_4H_5)Mo(CO)_2]_2(\mu\text{-}Br)_2$	Mo–av(CB_4 atom) = 2.385 Mo(1)–Mo(2) = 2.961(3)	Mo(1)–Br(1)–Mo(2) = 69.02(8)	58a

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Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
	Mo(1)–Br(av) = 2.622, 2.626 Mo(2)–av(C_2B_3 atom) = 2.35 Mo(1)–CO(av) = 1.99	Mo(1)–Br(2)–Mo(2) = 68.38(7)	
$[Cp^*Co(Et_2C_2B_3H_3)]_2Mo(CO)_2$	Mo–CO(av) = 1.961 Mo(2)–av(C_2B_3 atom) = 2.402 Co–av(C_2B_3 atom) = 2.074		52
$[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7\text{-}(CNC_6H_3Me_2\text{-}2,6)\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_{10}]$	Mo–av(CB_4 atom) = 2.386 Mo–P = 2.5575(9)		58b
$[1\text{-}Ph\text{-}3,3\text{-}(CO)_2\text{-}3\text{-}(\eta^3\text{-}C_3H_5)\text{-}3,1,2\text{-}\textit{closo}\text{-}MoC_2B_9H_{10}]^-$	Mo–CO(av) = 1.916 Mo–C(η^3) = 2.379(3) Mo–C(η^3) = 2.234(4) Mo–C(η^3) = 2.335(4)	CO–Mo–CO = 79.4(2)	255
$[1,2\text{-}Ph_2\text{-}5,5\text{-}(CO)_2\text{-}5\text{-}(\eta^3\text{-}C_3H_5)\text{-}5,1,2\text{-}MoC_2B_9H_9]^-$	Mo–CO(av) = 1.968 Mo(5)–C(η^3) = 2.338(9) Mo(5)–C(η^3) = 2.248(9) Mo(5)–C(η^3) = 2.395(9)	CO–Mo–CO = 79.4(3)	255
$[1,9\text{-}Ph_2\text{-}3,3\text{-}(CO)_2\text{-}3\text{-}(\eta^3\text{-}C_3H_5)\text{-}3,1,9\text{-}\textit{closo}\text{-}MoC_2B_9H_9]^-$	Mo(3)–CO(av) = 1.952 Mo(3)–C(η^3) = 2.36(2) Mo(3)–C(η^3) = 2.36(2) Mo(3)–C(η^3) = 2.252(14)	CO–Mo(3)–CO = 79.6(5)	255
$[4\text{-}(\eta^3\text{-}C_3H_5)\text{-}4,4\text{-}(CO)\text{-}4,1,6\text{-}\textit{closo}\text{-}MoC_2B_{10}H_{12}]^-$	Mo–av(C_2B_4 atom) = 2.413 Mo–CO(av) = 1.960 Mo–C(η^3) = 2.351(4) Mo–C(η^3) = 2.395(4) Mo–C(η^3) = 2.260(4)	CO–Mo–CO = 78.82(16)	59
$[1\text{-}NH^2Bu^t\text{-}2,2,2\text{-}(CO)_3\text{-}2\text{-}PEt_3\text{-}\textit{closo}\text{-}2,1\text{-}CB_{10}H_{10}]$	Mo–av(CB_4 atom) = 2.404 Mo–CO(av) = 1.997 Mo–P = 2.5625(6)	CO–Mo–CO = 106.35(8) CO–Mo–P = 77.52(6)	56
$[2,2'\text{-}\mu\text{-}Au\text{-}\{1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}\textit{closo}\text{-}2,1\text{-}MoCB_{10}H_{10}\}_2]^-$	Mo(1)–av(CB_4 atom) = 2.342 Mo(1)–N(1) = 2.319(4) Mo(1)–Au = 2.7377(9) Mo(2)–Au = 2.7422(8) Mo(1)–CO(av) = 2.046	Mo(1)–Au Mo(2) = 170.80(2) CO–Mo(1)–CO = 82.4(2) CO–Mo(1)–Au = 62.9(2)	56
$[\textit{closo}\text{-}(C_2B_9H_{11})Mo\ 3\cdot PPN(\mu\text{-}SPh)_2]_2\cdot PPN$	Mo–Mo = 2.7251(13) Mo–S(av) = 2.458 Mo–av(C_2B_3 atom) = 2.378 C(cage)–C(cage) = 1.663	C(cage)–Mo–C(cage) = 41.9(4) Mo–S1–Mo = 67.2	54
$[\textit{semicloso}\text{-}(C_2B_9H_{11})Mo\ 3\cdot PPN(\mu\text{-}SPh)_2]_2\cdot PPN$	Mo–Mo = 2.8153(12) Mo–S(av) = 2.515 Mo–av(C_2B_3 atom) = 2.100 C(cage)–C(cage) = 2.560	C(cage)–Mo–C(cage) = 72.34(17) Mo–S1–Mo = 68.1	54
$1,8\text{-}Ph_2\text{-}2\text{-}(\eta^3\text{-}C_3H_5)\text{-}2,2\text{-}(CO)_2\text{-}6\text{-}SMe_2\text{-}2,1,8\text{-}\textit{closo}\text{-}MoC_2B_9H_8$	Mo(2)–CO(av) = 1.941 Mo(2)–C(η^3) = 2.355(3) Mo(2)–C(η^3) = 2.360(3) Mo(2)–C(η^3) = 2.236(3)	CO–Mo–CO = 77.73(13)	256
$1,8\text{-}Ph_2\text{-}2\text{-}(\eta^3\text{-}C_3H_5)\text{-}2,2\text{-}(CO)_2\text{-}7\text{-}SMe_2\text{-}2,1,8\text{-}\textit{closo}\text{-}MoC_2B_9H_8$	Mo–CO(av) = 1.952 Mo–C(η^3) = 2.370(9) Mo–C(η^3) = 2.368(9) Mo–C(η^3) = 2.201(9)	CO–Mo–CO = 85.1(3)	256
(3) Tungsten			
$W(N^tBu)(NH^tBu)_2(C_2B_9H_{11})$	W–Cnt = 2.026(4)	Cnt–W–N(1) = 124.5(3) Cnt–W–N(2) = 113.0(3) Cnt–W–N(3) = 109.7(3)	53

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
{[W(N^{t}Bu)(NH^{t}Bu)-(C$_2$B$_9$H$_{11}$)]$_2$(μ-O)}	W–Cnt = 1.984(3)	Cnt–W–N(1) = 124.7(3) Cnt–W–N(2) = 112.9(3) Cnt–W–O = 108.5(3)	53
{[W(N^{t}Bu)$_2$[(N(H)C(Me)NH^{t}Bu](C$_2$B$_9$H$_{11}$)}	W(1)–Cnt = 2.065(4)	Cnt–W–N(1) = 114.5(4) Cnt–W–N(2) = 124.9(4) Cnt–W–N(3) = 109.3(4)	53
Cp*Co(Et$_2$C$_2$B$_3$H$_3$)W(CO)$_4$	W–av(C$_2$B$_3$ atom) = 2.356 W–CO(av) = 2.034		52
Cp*Co(2,3-C$_2$B$_3$H$_2$-5-CH$_2$Ph)W(CO)$_4$	W–CO(av) = 2.027 W–av(C$_2$B$_3$ atom) = 2.346		52
[(C$_2$B$_9$H$_{11}$)W(μ-SPh)$_2$·7PPN]$_2$·PPN	W–W = 2.7700(13) W–S(av) = 2.494 W–av(C$_2$B$_3$ atom) = 2.315		54
[2,2,2-(CO)$_3$-2-PPh$_3$-7-OEt$_2$-*closo*-2,1-WCB$_{10}$H$_{10}$]$^-$	W–av(CB$_4$ atom) = 2.378 W–P = 2.553(2)		58b
[2,2,2-(CO)$_3$-2-PPh$_3$-7-{O(Me)Bu^n}-*closo*-2,1-WCB$_{10}$H$_{10}$]	W–av(CB$_4$ atom) = 2.371 W–P = 2.546(2)		58b
[2,2,2-(CO)$_3$-2-PPh$_3$-7-{N(Me)═C(H)Me}-*closo*-2,1-WCB$_{10}$H$_{10}$]	W–av(CB$_4$ atom) = 2.385 W–P = 2.555(2)		58b
[N(PPh$_3$)$_2$][WBr(CO)$_3$(η^6-7,9-C$_2$B$_{10}$H$_{10}$Me$_2$)]	W(1)–av(C$_2$B$_4$ atom) = 2.401 W(1)–Br = 2.704(1) W(1)–CO(av) = 1.980		257
[1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-WCB$_{10}$H$_{10}$]$^-$	W–av(CB$_4$ atom) = 2.336 W–N(1) = 2.291(3) W–CO(av) = 1.996		56
Heterocarboranes of Group 7 Elements			
(1) Manganese			
[3,8-{Cu(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-3,1,2-*closo*-MnC$_2$B$_9$H$_{10}$]	Mn–AV(C$_2$B$_3$ atom) = 2.208 Mn–Cu = 2.5719(4) Mn–CO(av) = 1.818		245
[3,8-{Au(PPh$_3$)}-8-μ-H-3,3,3-(CO)$_3$-3,1,2-*closo*-MnC$_2$B$_9$H$_{10}$]	Mn–av(C$_2$B$_3$ atom) = 2.207 Mn–Au = 2.9284(4) Mn–CO(av) = 1.819		245
[8-{(*E*)-N(Me)═C(H)Me}-3,3,3-(CO)$_3$-*closo*-3,1,2,MnC$_2$B$_9$H$_{10}$]	Mn–av(C$_2$B$_3$ atom) = 2.262 Mn–CO(av) = 21.801		245
[8-(*p*-C$_6$H$_5$Me)-3,3,3-(CO)$_3$-1,2-(Me)$_2$-*closo*-3,1,2-MnC$_2$B$_9$H$_8$]$^-$	Mn–av(C$_2$B$_3$ atom) = 2.200 Mn–CO(av) = 1.785		245
[4-{(*Z*)-N(Me)═C(H)Me}-3,3,3-(CO)$_3$-1,2,8-(Me)$_3$-*closo*-3,1,2-MnC$_2$B$_9$H$_7$]	Mn–av(C$_2$B$_3$ atom) = 2.19 Mn–C(2) = 2.155(18)		245
(2) Rhenium			
[Re(CO)$_3$(η^5-2,3,10-(μ-H)$_3$-*exo*-{RuCl(PPh$_3$)$_2$}-7,8-C$_2$B$_9$H$_8$]	Re–CO(av) = 1.922 Re–av(C$_2$B$_3$ atom) = 2.338		69
[Re(CO)$_3$(η^5-10-(μ-H)-*exo*-{Ru(CO)$_2$Cp}-7,8-C$_2$B$_9$H$_8$]	Re–CO(av) = 1.89 Re–av(C$_2$B$_3$ atom) = 2.344 Re–Ru = 4.4147(11)		69
[ReCu(μ-10-H-7,8-C$_2$B$_9$H$_{10}$)(CO)$_3$(PPh$_3$)]	Re–CO(av) = 1.933 Re–av(C$_2$B$_3$ atom) = 2.338 Re–Cu = 2.6583(6)		69
[ReAg(μ-10-H-7,8-C$_2$B$_9$H$_{10}$)(CO)$_3$(PPh$_3$)]	Re–CO(av) = 1.898 Re–av(C$_2$B$_3$ atom) = 2.345 Re–Ag = 2.9344(12)		69

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
$[\mathrm{ReAg}(\mu\text{-10-H-7,8-C}_2\mathrm{B}_9\mathrm{H}_{10})(\mathrm{CO})_3\text{-}\{\mu\text{-Ph}_2\mathrm{P}(\mathrm{CH}_2)_2\mathrm{PPh}_2\}]$	Re–CO(av) = 1.926 Re–av(C_2B_3 atom) = 2.344 Re–Ag = 2.9457(6)		70
$[\mathrm{ReAg}(\mu\text{-10-H-7,8-C}_2\mathrm{B}_9\mathrm{H}_{10})(\mathrm{CO})_3\text{-}\{\kappa^2\text{-CH}_2\text{-}(\mathrm{C}_3\mathrm{H}_3\mathrm{N}_2\text{-1})_2\}]$	Re–C(4) = 1.906(5) Re–CO(av) = 1.918 Re–av(C_2B_3 atom) = 2.342 Re–Ag = 2.8825(7)		70
$[\mathrm{ReAg}(\mu\text{-10-H-7,8-C}_2\mathrm{B}_9\mathrm{H}_{10})(\mathrm{CO})_3\text{-}\{\kappa^3\text{-C}_5\mathrm{H}_3\mathrm{N}(\mathrm{C}_5\mathrm{H}_4\mathrm{N\text{-}2})_2\text{-2,6}\}]$	Re–CO(av) = 1.909 Re–av(C_2B_3 atom) = 2.340 Re–Ag = 3.0295(6)		70
$[\mathrm{ReAg}(\mu\text{-5,6,10-(H)}_3\text{-}\eta^5\text{-7,8-C}_2\mathrm{B}_9\mathrm{H}_8)\text{-}(\mathrm{CO})_3]_4$	Re–CO(av) = 1.933 Re–av(C_2B_3 atom) = 2.349 Re–Ag = 2.8702(6) Re–Re(a) = 6.7790(7)		70
$[\mathrm{ReRh}(\mathrm{CO})_3(\eta^5\text{-C}_5\mathrm{Me}_5)(\eta^5\text{-7-CB}_{10}\mathrm{H}_{11})]$ MOLECULE 1	Re(1)–CO(av) = 1.947 Re–av(C_2B_3 atom) = 2.325 Re(1)–Rh(1) = 2.8345(6)		258
$[\mathrm{ReRh}(\mathrm{CO})_3(\eta^5\text{-C}_5\mathrm{Me}_5)(\eta^5\text{-7-CB}_{10}\mathrm{H}_{11})]$ MOLECULE 3	Re(3)–CO(av) = 1.925 Re–av(CB_4 atom) = 2.319 Re(3)–Rh(3) = 2.8214(6)		258
$[\mathrm{Re}\{{=}\mathrm{C(OMe)C}_6\mathrm{H}_4\mathrm{Me\text{-}4}\}(\mathrm{NO})(\mathrm{CO})(\eta^5\text{-7,8-C}_2\mathrm{B}_9\mathrm{H}_{11})]$	Re–NO = 1.768(8) Re–CO = 1.963(10) Re–C(sp^2) = 2.052(9)		259
$[\mathrm{Re(NO)(CNBu^t)}\{\eta^5,\sigma\text{-7-C}{=}\mathrm{N(H)Bu^t\text{-}7,8\text{-}C_2B_9H_{10}}\}]$	Re–NO = 1.769(11) Re–(C=N(H)Bu^t) = 2.000(13) Re–(CNBu^t) = 2.02(2)		259
$[\mathrm{1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2\text{-}(CO)_2\text{-}3,2\text{-}\sigma{:}\eta^2\text{-}\{C({=}CHBu^t)\text{-}CH{=}CHBu^t\}}$-*closo*-$\mathrm{2,1\text{-}ReCB_{10}H_9}]$	Re–av(CB_4 atom) = 2.305 Re–N = 2.244(6) Re–CO(av) = 1.953		73
$[\mathrm{RePd(CO)_3\{Ph_2P(CH_2)_2PPh_2\}}(\eta^5\text{-7-CB}_{10}\mathrm{H}_{11})]$	Re–CO(av) = 1.948 Re–Pd = 2.7858(4) Re–av(CB_4 atom) = 2.319		260
$[\mathrm{RePt(CO)_3(PPh_3)_2}(\eta^5\text{-7-CB}_{10}\mathrm{H}_{11})]$	Re–av(CB_4 atom) = 2.310 Re(1)–CO(av) = 1.957 Pt(1)–Re(1) = 2.7931(4)		260
$[\mathrm{Re(CO)_3}(\eta^5\text{-2,3,10-}(\mu\text{-H})_3$-*exo*-$\{\mathrm{RuCl(PPh_3)_2}\}\text{-7,8-C}_2\mathrm{B}_9\mathrm{H}_8)]$	Re–av(C_2B_3 atom) = 2.338 Re–CO(av) = 1.922 Ru–P(av) = 2.298 Ru–Cl = 2.3819(7)		69
$[\mathrm{Re(CO)_3}(\eta^5\text{-10-}(\mu\text{-H})$-*exo*-$\{\mathrm{Ru(CO)_2\text{-}(Cp)}\}\text{-7,8-C}_2\mathrm{B}_9\mathrm{H}_{10})]$	Re–av(C_2B_3 atom) = 2.344 Re–Ru = 4.4147(11) Re–CO(av) = 1.893		69
$[\mathrm{(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)}]$	Re–P(av) = 2.359 Re(1)–av(B_3) = 2.403		261
$\mathrm{(Cp^*Re)_2B_7H_7}$	Re(1)–Re(2) = 2.7875(6) Re(1)–av(B_6 atom) = 2.157		262
$[\mathrm{Re(CO)_3}(\eta^5\text{-7-CB}_{10}\mathrm{H}_{11})]^{2-}$	Re–CO(av) = 1.90 Re–av(CB_4 atom) = 2.338		260
$[\mathrm{3,3,3\text{-}(CO)_3\text{-}3,8\text{-}(Pt\{PPh_2(CH_2)_2PPh_2\})\text{-}8\text{-}}(\mu\text{-H})$-*closo*-$\mathrm{3,1,2\text{-}ReC_2B_9H_{10}}]^+$	Re–CO = 1.56(3) Re–CO(av) = 1.94 Re–av(C_2B_3 atom) = 2.33 Pt–Re = 2.8126(10) Pt–B(4) = 2.34(2) Pt–P(av) = 2.26		71

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[3,3,3-(CO)$_3$-3,8-Pt{Ph$_2$P(CH$_2$)$_2$PPh$_2$}-8-(μ-H)-*closo*-3,1,2-ReC$_2$B$_9$H$_{10}$]$^+$	Re–CO(av) = 1.92 Re–av(C$_2$B$_3$ atom) = 2.33 Pt–Re = 2.7583(9) Pt–P(av) = 2.26 Pt–B(3) = 2.061		71
Heterocarboranes of Group 8 Elements			
(1) Iron			
[(C$_6$H$_6$)Fe(Et$_2$C$_2$B$_4$H$_3$-5-)]$_2$C$_4$H$_2$S	Fe(1)–av(C$_2$B$_3$ atom) = 2.103 Fe(1)–C(C$_6$H$_6$ring) = 2.067(5)		160a
[(C$_6$H$_6$)Fe(Et$_2$C$_2$B$_4$H$_3$-5-Ph)-(C$_6$H$_6$)Fe(Et$_2$C$_2$B$_4$H$_3$-5-I)]	Fe(1)–av(C$_2$B$_4$-5-Ph) = 2.120 Fe(2)–av(C$_2$B$_4$-5-I) = 2.103 Fe(1)–C(C$_6$H$_6$ring) = 2.085(6) Fe(2)–C(C$_6$H$_6$ring) = 2.095(5)		160a
(C$_6$H$_6$)Fe{Et$_2$C$_2$B$_4$H$_3$-5-[(C$_6$H$_6$)Cr(CO)$_3$]}	Fe(1)–av(C$_2$B$_4$ atom) = 2.093 Fe–C(C$_6$H$_6$ ring) = 2.078(15) Cr–C(C$_6$H$_5$ ring) = 2.225(13) Cr–CO(av) = 1.838(10)		160a
(MeNCH$_2$CH$_2$NMe)[(1-C$_5$H$_5$B)]$_2$Fe	Fe–B = 2.303(5) Fe–av(C$_5$ atom) = 2.116		244
[(3)-7-(CH$_3$)-1,7-PCB$_9$H$_{10}$]$_2$Fe	Fe–Cnt = 1.47	Cnt(1)–Fe–Cnt(2) = 178	264
[Fe(CO)$_3${η^5-9-O(CH$_2$)$_4$-7-CB$_{10}$H$_{10}$}]	Fe(1)–av(CB$_4$ atom) = 2.157 Fe(1)–CO(av) = 1.799		57
CpCo(μ-η^5-MeEt$_4$C$_3$B$_2$)-Fe(η^6-5-Me-2,3,5-C$_3$B$_7$H$_9$)	Fe–av(η^6–C$_2$ atom) = 1.970 Fe–av(η^6–CB$_3$ atom) = 2.288		107
1-Cp-2-Ph-1,2,3,4-FeC$_3$B$_7$H$_9$	Fe–av(η^6–C$_2$ atom) = 1.968 Fe–av(η^6–CB$_3$ atom) = 2.256 Fe–Cp(Cnt) = 1.695(3)		264
1-Cp-2-[(C$_6$H$_5$)Cr(CO)$_3$]-1-Fe-(η^6-2,3,4-C$_3$B$_7$H$_9$)	Fe–av(η^6–C$_2$ atom) = 1.966 Fe–av(η^6–CB$_3$ atom) = 2.252 Fe–Cp(Cnt) = 1.684(5)		264
8-Cp-8-(CNBu^t)-9-Ph-*nido*-8,7,9,10-FeC$_3$B$_7$H$_9$	Fe–av(C$_2$B$_2$ atom) = 2.150 Fe–(CNBu^t) = 3.020(8) Fe–Cp(Cnt) = 1.736(1)		264
[(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Fe(CO)$_2$]	Fe–av(C$_2$B$_3$ atom) = 2.11 Fe–N(1) = 2.05(1) Fe(1)–CO(av) = 1.756	CO(1)–Fe(1)–N(1) = 98.4(4) CO(2)–N(1)–Fe(1) = 116.8(6)	90
(η^6-C$_7$H$_8$)Fe(η^6-Me$_2$B$_2$C$_{12}$H$_8$)Fe	Fe(1)–av(C$_4$B$_2$ atom) = 2.212		110
[2-Cp-9-(Bu^{t}NH)-*closo*-2,1,7,9-FeC$_3$B$_8$H$_{10}$]	Fe–av(C$_2$B$_3$ atom) = 2.037 Fe–av(Cp atom) = 2.050(3)		100
[2-Cp-9-(Bu^{t}NH)-*closo*-2,1,7,9-FeC$_3$B$_8$H$_{10}$]	Fe–av(Cp atom) = 2.068 Fe–av(C$_2$B$_3$ atom) = 2.034		102
nido-8-(η^5-C$_5$H$_5$)Fe(CNBu^t)(η^4-[9-Ph-7,9,10-C$_3$B$_7$H$_9$])	Fe–av(C$_2$B$_2$ atom) = 2.148 Fe–CNBu^t = 1.854(8)		105
6,6,6,9,9,9-(CO)$_6$-6,9-Fe$_2$-5,7,8,10-C$_4$B$_4$Et$_4$	Fe(6)–Fe(9) = 2.685(1) Fe–av(C$_2$B atom) = 2.114		265

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[Fe(CO)$_2$(SMe$_2$)(η^5-9-SMe$_2$-7-CB$_{10}$-H$_{10}$)]	Fe–CO(av) = 1.768 Fe–S = 2.2842(9) Fe–av(CB$_4$ atom) = 2.148		75
[Fe(CO)$_3$(η^5-9-{(E)-N(Me)═C(H)Me}-7-CB$_{10}$H$_{10}$)]	Fe–CO(av) = 1.801 Fe–av(CB$_4$ atom) = 2.173		75
[Fe(CO)$_3$(η^5-9-{NH(Me)Et}-7-CB$_{10}$H$_{10}$)]	Fe–CO(av) = 1.781 Fe–av(CB$_4$ atom) = 2.161		75
[Fe(CO)$_2$(η^2:η^5-8-{(E)-C(H)═C(H)Bu^t}-10-{(E)-N(Me)═C(H)Me}-7-CB$_{10}$H$_9$)]	Fe–CO(av) = 1.772 Fe–av(CB$_4$ atom) = 2.161		75
[*cis*-FeRu(μ-CO)$_2$(CO)$_2$(Cp)(η^5-7,8-C$_2$B$_9$H$_{11}$)]$^-$	Ru(1)–Fe(1) = 2.6559(9) Ru–CO = 1.861(4) Fe(1)–μ–CO(av) = 1.946 Ru–μ–CO(av) = 2.032 Fe(1)–CO = 1.752(4) Ru–av(C$_2$B$_3$ atom) = 2.286 Fe(1)–av(Cp atom) = 2.125		266
[ttf]$^{\cdot +}$[Fe(C$_2$B$_9$H$_{11}$)$_2$]$^-$	Fe(3)–av(C$_2$B$_3$ atom) = 2.113		254
[9,9′-(Bu^{t}HN)$_2$-*commo*-2,2′-Fe-(1,7,9-(C$_3$B$_8$H$_{10}$)$_2$]	Fe–av(C$_2$B$_3$atom) = 2.056		267
nido-2-(Cp)Fe-8-(CH$_3$OC(O))-6,7,8,9-C$_4$B$_7$H$_{11}$	Fe–av(C$_4$B$_2$ atom) = 2.116 Fe–av(Cp atom) = 2.065		108
[Fe(C$_5$Me$_5$)$_2$][Fe(C$_2$B$_9$H$_{11}$)$_2$)]	Fe–av(C$_2$B$_3$ atom) = 2.117		268
nido-2-(Cp)Fe-7-CH$_3$-7,8,9,10,12-C$_5$B$_6$H$_{10}$	Fe–av(C$_3$B$_3$ atom) = 2.114		109
(2) Ruthenium			
[Ru$_3$(μ-σ:η^5-7,8-C$_2$B$_9$H$_8$)(CO)$_6$(PMe$_2$Ph)$_2$]	Ru(1)–av(C$_2$B$_3$ atom) = 2.25 Ru(1)–Ru(2) = 2.750(1) Ru(1)–Ru(3) = 2.812(1) Ru(2)–B(4) = 2.34 Ru(3)–B(5) = 2.15		269
1-Ph-3-(mes)-3,1,2-*closo*-RuC$_2$B$_9$H$_{10}$	Ru–av(C$_2$B$_3$ atom) = 2.191 Ru–av(C$_6$ atom) = 2.229		133
1-Ph-2-Me-3-(*p*-cym)-3,1,2-*closo*-RuC$_2$B$_9$H$_9$	Ru–av(C$_2$B$_3$ atom) = 2.192 Ru–av(C$_6$ atom) = 2.240		133
1,2-(CH$_2$OCH$_3$)$_2$-3-(*p*-cym)-3,1,2-*closo*-RuC$_2$B$_9$H$_9$	Ru–av(C$_6$ atom) = 2.242 Ru–av(C$_2$B$_3$ atom) = 2.194		246
closo-1-(η^5-C$_5$Me$_5$)-Ru(η^6-[2-Ph-2,3,4-C$_3$B$_7$H$_9$])	Ru–av(C$_2$) = 2.092 Ru–av(CB$_3$ atom) = 2.351		105
nido-8-(η^5-C$_5$H$_5$)Ru(CNBu)(n^4-[9-Ph-7,9,10-C$_3$B$_7$H$_9$])	Ru–av(C$_2$B$_2$ atom) = 2.235		105
[(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ru(CO)$_2$]	Ru–av(C$_2$B$_3$ atom) = 2.217 Ru(1)–N(1) = 2.185(7) Ru–CO = 1.889(6)	C(5)–Ru(1)–N(1) = 99.9(2) O(1)–C(5)–Ru(1) = 174.5(5)	90
[(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ru(CO)(NCMe)]	Ru–av(C$_2$B$_3$ atom) = 2.204 Ru–CO = 1.850(6) Ru–N(1) = 2.225(5) Ru–(NCMe) = 2.060(5)		90
[WRuO{μ-σ:η^5-9-CH(C$_6$H$_4$-Me-4)-7,8-C$_2$B$_9$H$_{10}$}(CO)$_2$Cp	Ru–av(C$_2$B$_3$ atom) = 2.285 Ru–W = 2.514(1) Ru–CO(av) = 1.880		95
[WRu(CO)$_4${η^5-9-CH(PMe$_3$)(C$_6$H$_4$Me-4)-7,8-C$_2$B$_9$H$_{10}$}Cp]	W–Ru = 2.921(1) Ru–av(C$_2$B$_3$ atom) = 2.253 Ru–CO(av) = 1.864 W–CO(av) = 1.954		95

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[WRuO{μ-σ:η^5-7,8-Me$_2$-10-CH(C$_6$H$_4$-Me-4)-7,8-C$_2$B$_9$H$_8$}(CO)$_2$Cp]	Ru–av(C$_2$B$_3$ atom) = 2.288 Ru–W = 2.522(1) Ru–CO(av) = 1.88		95
MoRu(μ-H){μ-η^5,$\eta^{5'}$-7,8-Me$_2$-9-C$_5$H$_4$-10-CH$_2$(C$_6$H$_4$Me-4)-7,8-C$_2$B$_9$H$_7$}(CO)$_5$]	Ru–H = 1.77 Ru–av(C$_2$B$_3$ atom) = 2.252 Ru–Mo = 3.294(1) Ru–CO(av) = 1.88 Mo–(CO(av) = 1.97 Mo–av(C$_5$ ring) = 2.317	H–Ru–CO(av) = 79.2 Ru–H–Mo = 131.2(1)	95
[WRu{μ-σ:η^5-2,7-Me$_2$-8-10-CH$_2$(C$_6$H$_4$Me-4)-9-C(H)O-2,7-C$_2$B$_9$H$_6$}(CO)$_4$Cp]	Ru–av(C$_2$B$_3$ atom) = 2.233 Ru–W = 2.823(1) Ru–CO(av) = 1.843	CO–Ru–CO = 87.3(3) Ru–W–B(4) = 48.7(2)	95
[Ru$_2$(μ-η^5-7,8-Me$_2$-10-CH$_2$NMe$_2$-7,8-C$_2$B$_9$H$_8$)(CO)$_5$]	Ru(1)–av(C$_2$B$_3$ atom) = 2.24 Ru(1)–Ru(2) = 2.727(1) Ru(1)–CO(av) = 1.872 Ru(2)–B(3) = 2.410(5) Ru(2)–H = 1.796		269
[NEt$_4$][Ru$_2$(μ-Tl)(CO)$_4$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)$_2$]	T1(1)–Ru(1) = 2.5994(4) Ru–av(C$_2$B$_3$ atom) = 2.274 Ru–CO(av) = 1.884	Ru(1)–T1(1)–Ru(1A) = 165.67(2)	92
[MoRu(CO)$_4${σ:η^5-9-CH(C$_6$H$_4$Me-4)-7,8-C$_2$B$_9$H$_{10}$}Cp	Ru–av(C$_2$B$_3$ atom) = 2.235 Ru–Mo = 2.976(1) Ru–CO(av) = 1.88		95
[Ru$_2$(CO)$_5$(NHMe$_2$)(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)]	Ru–av(C$_2$B$_3$ atom) = 2.235 Ru(1)–Ru(2) = 2.732(1) Ru(2)–N = 2.183(5) Ru(2)–B(4) = 2.419(7) Ru(2)–H(4) = 1.44		269
3-(Cp*)-4-SMe$_2$-3,1,2-*closo*-RuC$_2$B$_9$H$_{10}$	Ru–av(C$_2$B$_3$ atom) = 2.182 Ru–av(C$_5$ ring) = 2.20		135
1-Ph-3-(Cp*)-7-SMe$_2$-3,1,2-*closo*-RuC$_2$B$_9$H$_9$	Ru–av(C$_2$B$_3$ atom) = 2.19 Ru–av(C$_5$ ring) = 2.218		135
3-(Cp*)-4-SMe$_2$-11-Ph-3,1,2-*closo*-RuC$_2$B$_9$H$_9$	Ru–av(C$_2$B$_3$ atom) = 2.164 Ru–av(C$_5$ ring) = 2.233		135
1-Ph-3-(Cp*)-4-SMe$_2$-3,1,2-*closo*-RuC$_2$B$_9$H$_9$	Ru–av(C$_2$B$_3$ atom) = 2.169 Ru–av(C$_5$ ring) = 2.204		135
1,2-Ph$_2$-3-(Cp*)-4-SMe$_2$-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_8$	Ru–av(C$_2$B$_3$ atom) = 2.177 Ru–av(C$_5$ ring) = 2.240		135
1-H,1-Cl-1,1-(PPh$_3$)$_2$-*closo*-1,2,3-RuC$_2$B$_4$H$_6$	Ru–av(C$_2$B$_3$ atom) = 2.241 Ru(1)–p(av) = 2.371 Ru(1)–Cl(1) = 2.4311(5) Ru(1)–H(1M) = 1.41(3)	P(1)–Ru(1)–H(1M) = 79.0(12) P(2)–Ru(1)–Cl(1) = 90.36(2) Cl(1)–Ru(1)–H(1M) = 156.5(12) P(1)–Ru(1)–P(2) = 103.42(2)	81
[6-Cl-1-(η^6-C$_6$H$_5$Me)-1,2,4-RuC$_2$B$_8$H$_9$Ru]	Ru(1)–C(Ar) = 2.156(9)–2.269(9) Ru(1)–av(CB$_5$) = 2.218		81
2-Cl-2,5-(Ph$_3$P)$_2$-2-H-3,9-(MeO)$_2$-2,1-RuCB$_8$C$_6$	Ru(2)–Cl(1) = 2.4212(13) Ru(2)–P(1) = 2.3243(13) Ru(2)–H(2) = 1.63(4) Ru(2)–C(1) = 2.157(3) Ru(2)–avB(3,5) = 2.469 Ru(2)–avB(6,9) = 2.089 Ru(2)–B(10) = 2.346(4)		79
[Ru(CO)$_2$(MeC≡CPh)(η^5-7,8-C$_2$B$_9$H$_{11}$)]	Ru(1)–CO(av) = 1.898 Ru–av(C$_2$B$_3$ atom) = 2.263 Ru(1)–av(C≡C) = 2.305		271

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[Ru(CO)$_2${C(Me)=C(Ph)PEt$_3$}(η^5-7,8-C$_2$B$_9$H$_{11}$)]	Ru–CO(av) = 1.864 Ru–av(C$_2$B$_3$ atom) = 2.289 Ru–C(sp^2) = 2.141(2)		271
[Ru$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)$_2$]	Ru(1)–CO(av) = 1.883 Ru–av(C$_2$B$_3$ atom) = 2.266 Ru(1)–P(1) = 2.377(2) Ru(2)–P(2) = 2.364(2)		271
[NEt$_4$][Ru$_2$(μ-H)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)$_2$]	Ru(1)–Ru(2) = 3.189(6) Ru–av(C$_2$B$_3$ atom) = 2.2677 Ru(1)–CO(av) = 1.866 Ru(1)–H = 1.809 Ru(2)–B(24) = 2.296(5)		96
[9,9′-(Bu^{t}HN)$_2$-*commo*-2,2′-Ru-*closo*-1,7,9-(C$_3$B$_8$H$_{10}$)-1′,7′,9′-(C$_3$B$_8$H$_{10}$)]	Ru–av(C$_2$B$_3$atom) = 2.183		267
[RuCl(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$)]$^-$	Ru–av(C$_2$B$_3$atom) = 2.263 Ru–Cl = 2.452(1) Ru–CO(av) = 1.896		96
1-{PPh$_2$AuCl}-2-Ph-3-(*p*-cymene)-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$	Ru–av(C$_2$B$_3$ atom) = 2.183 Ru(3)–av(C$_6$ atom) = 2.290 C(1)–C(2) = 2.42		273
[Ru(CO)$_2$(η^2:η^5-9-C(H)=C(H)Bu^t-7,8-C$_2$B$_9$H$_{10}$)]	Ru–av(C$_2$B$_3$ atom) = 2.245 Ru–CO(av) = 1.893 Ru–C(sp^2) = 2.401(5) Ru–C(sp^2) = 2.249(6)		93
closo-2,2-(Ph$_3$P)$_2$-2-H-3,6,8-(MeO)$_3$-RuCB$_6$H$_4$	Ru(2)–P(av) = 2.362 Ru(2)–B(3-6) = 2.258(5)–2.336(5) Ru(2)–C(1) = 2.301(5) Ru(2)–B(8) = 1.961(5) Ru–H = 1.40	P(1)–Ru(2)–H(2) = 85.1(2) P(2)–Ru(2)–H(2) = 77.8(2)	80
1,2,3-Cp*Ru(H)(Et$_2$C$_2$B$_4$H$_4$)	Ru–av(C$_2$B$_3$ atom) = 2.258 Ru–H(1) = 1.55(8) Ru–av(C$_5$ ring) = 2.191		274
1,2-(SPh)$_2$-3-(p-cymene)-*pseudocloso*-3,1,2-RuC$_2$B$_9$H$_9$	C(1)–C(2) = 2.107(5) Ru(3)···B(6) = 3.198(3)		275
[η^5-Me$_2$C(C$_5$H$_3$)(C$_2$B$_{10}$H$_{10}$)]RuH(PPh$_3$)$_2$	Ru1–C$_5$(Cnt) = 1.910 Ru1–H1 = 1.54(1) Ru1–av(C$_5$ ring) = 2.263 Ru1–P(av) = 2.286		276
[η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]RuCl(PPh$_3$)$_2$	Ru1–C$_5$(Cnt) = 1.872	P1–Ru1–P2 = 99.0(1) Ru1–P(av) = 2.33	276
[5-Br-1-(η^6-C$_6$Me$_6$)-*closo*-1,2,4-RuC$_2$B$_8$H$_9$]	Ru–C(2 of C$_2$B$_4$) = 2.098(7) Ru–C(4 of C$_2$B$_4$) = 2.658(9) Ru–B(3 of C$_2$B$_4$) = 2.068(9) Ru–B(5–7 of C$_2$B$_4$) = 2.303 Ru–av(C$_5$ ring) = 2.256(5)		268
(η^4-COD)Rh(μ-H)Ru(PPh$_3$)$_2$(η^5-C$_2$B$_9$H$_{11}$)	Ru–P(av) = 2.352 Ru–av(C$_2$B$_3$ atom) = 2.281 Ru(1)–H(br) = 1.6(1) Ru(1)–Rh(1) = 2.889(1)		97
[*closo*-3,3-(PPh$_3$)$_2$-3-Cl-RuC$_2$B$_9$H$_{11}$]$^-$	Ru–P(av) = 2.345 Ru–av(C$_2$B$_3$ atom) = 2.230 Ru(3)–Cl(1) = 2.515(2)	P(1)–Ru(3)–P(2) = 100.3(1) Cl(1)–Ru(3)–P(2) = 90.5(1)	97
[*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RuC$_2$B$_9$H$_{11}$]$^-$	Ru–P(av) = 2.308 Ru–av(C$_2$B$_3$ atom) = 2.276 Ru(3)–H(Ru) = 1.67(9)	P(1)–Ru(3)–P(2) = 95.7(1) H(Ru)–Ru(3)–P(1) = 84(3) H(Ru)–Ru(3)–P(2) = 82(3)	97

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
$(CO)(PPh_3)Rh(\mu\text{-}Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$	Ru–P(av) = 2.348 Ru–av(C_2B_3 atom) = 2.248 Ru–Rh = 2.845(1) Ru–H(br) = 1.88(11)	P(1)–Ru–P(2) = 95.9(1) Ru–H(br)–Rh(1) = 110(6)	97
$[RuPt(\mu\text{-}H)(\mu\text{-}\sigma{:}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(PEt_3)_2]$	Ru–H = 1.817 Ru–av(C_2B_3 atom) = 2.255 Ru–Pt = 2.802(1) Ru–CO(av) = 1.859	H–Ru–Pt = 31.0(1)	96
[*cis*-$FeRu(\mu\text{-}CO)_2Cp(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$	Ru–av(C_2B_3 atom) = 2.285 Ru(1)–Fe(1) = 2.6559(9) Ru(1)–μ–CO(av) = 2.032 Ru(1)–CO(1) = 1.861(4)		266
$[3\text{-}H\text{-}3,3\text{-}(PPh_3)_2\text{-}8\text{-}SMe_2\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$	Ru–P(av) = 2.310 Ru–av(C_2B_3 atom) = 2.257 S–Ru = 3.435(3)	P–Ru–P = 96.1(1)	279
$[RuRh_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)(\eta^5\text{-}C_5Me_5)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$	Ru–av(C_2B_3 atom) = 2.276 Ru–Rh(2) = 2.7735(4) Ru–Rh(1) = 2.7600(5) Ru–μ–CO(av) = 2.009	Rh(1)–Ru–Rh(2) = 58.481(12) Rh(2)–Rh(1)–Ru = 61.009(12)	266
commo-Ru(2-Me-*closo*-1,2,3,4-$RuC_3B_7H_9)_2$	Ru–av(C_2 in C_3B_3) = 2.087 Ru–av(B_3 in C_3B_3) = 2.372 Ru–avC(in C_3B_3) = 2.49		264
1-Cp*-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$	Ru–av(C_2 in C_3B_3) = 2.092 Ru–av(B_3 in C_3B_3) = 2.350 Ru–C(in C_3B_3) = 2.355(4) Ru–Cp* = 1.829(2)		264
8-(Cp*)-8-(CNBu^t)-9-Me-*nido*-8,7,9,10-$RuC_3B_7H_9$	Ru–av(C_2B_2 atom) = 2.235 Ru–Cp* = 1.871(3) Ru–C(10) = 3.117(6) Ru–B(11) = 3.152(7)		264
closo-2-{7,11-*exo*-RuClPPh$_3$(μ-η^6-$C_6H_5PPh_2$)}-7,11-(μ-H)$_2$-2,1-$CB_{10}H_8$-6-MeO	Ru(1)–Ru(2) = 2.9774(7) Ru(1)–Cl(1) = 2.408(1) Ru(1)–P(av) = 2.229 Ru(2)–av(CB_4 atom) = 2.210 Ru(2)–av(C_6 ring) = 2.253 Ru(1)–H(7) = 1.57(5) Ru(1)–H(11) = 2.31(5)		280
[*closo*-2-(η^6-C_6H_6)10,11,12-{*exo*-RuCl(PPh$_3$)$_2$}-10,11,12-(μ-H)$_3$-2,1-$RuCB_{10}H_7$-6-/3-MeO)]	Ru(1)–Cl(1) = 2.400(1) Ru(1)–P(av) = 2.288 Ru(2)–av(CB_4 atom) = 2.191 Ru(2)–av(C_6 ring) = 2.222 Ru(1)–B(11) = 2.443(4) Ru(1)–B(12) = 2.270(5)	P(1)–Ru(1)–Cl(1) = 96.02(4) P(2)–Ru(1)–Cl(1) = 96.69(4) P(2)–Ru(1)–P(1) = 97.95(4)	280
$Ru(CO)_3\{\eta^6\text{-}C_4B_2Me_2(C_4H_4)_2\}$	Ru1–av(C_4B_2 atom) = 2.396 Ru1–avCO = 1.903		110
$[Ru(CO)_2(\sigma,\eta^5\text{-}10\text{-}C(H)(PMe_2Ph)CH_2\text{-}7,8\text{-}C_2B_9H_{10})]$	Ru1–av(C_2B_3 atom) = 2.29 Ru(1)–C(CH$_2$) = 2.142(9) Ru(1)–CO(av) = 1.82	 CO–Ru(1)–CO = 89.8(5)	93
$[Ru(CO)_2(PMe_3)\{\eta^5\text{-}9,10,11\text{-}[C(H){=}C(H)Bu^t]_3\text{-}7,8\text{-}C_2B_9H_8)]$	Ru1–av(C_2B_3 atom) = 2.283 Ru(1)–P(1) = 2.359(2) Ru(1)–CO(av) = 1.885	CO–Ru(1)–CO = 88.2(3) CO–Ru(1)–P(1) = 86.9	93
(3) Osmium			
closo-3,3-(PPh$_3$)$_2$-3-H-3-Cl-1,2-H$_2$-3,1,2-$OsC_2B_9H_9$	Os(3)–av(C_2B_3 atom) = 2.270 Os(3)–P(av) = 2.378	Cl(1)–Os(3)–H(3) = 131(2) P(2)–Os(3)–Cl(1) = 83.26(5)	281

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
	Os(3)–Cl = 2.432(2) Os(3)–H(3) = 1.39(4) Os(3)–C(2) = 2.217(3)	P(1)–Os(3)–Cl(1) = 82.87(5) P(2)–Os(3)–P(1) = 109.45(4)	
closo-3,3-$(PPh_3)_2$-3-H-3-H-1,2-Me_2-3,1,2-$OsC_2B_9H_9$	Os(3)–av(C_2B_3 atom) = 2.306 Os(3)–H(3A,B) = 1.53 Os(3)–P(av) = 2.350 Os(3)–C(1) = 2.375(3) Os(3)–C(2) = 2.338(3)	P(1)–Os(3)–H(3A) = 72(2) P(2)–Os(3)–H(3A) = 73(2) P(1)–Os(3)–H(3B) = 75.9(14) P(2)–Os(3)–H(3B) = 70.2(14) P(1)–Os(3)–P(2) = 100.46(5)	281
commo-Os-(4′-Me-1′,2′,3,′4′-$OsC_3B_7H_9$)(2-Me-1,2,3,4-$OsC_3B_7H_9$)	Os–av(C_3B_3 atom) = 2.307 Os–av($C'_3B'_3$ atom) = 2.265		264
Heterocarboranes of Group 9 Elements (1) Cobalt			
closo-1-(TMEDA)-1-Co-2,4-$(SiMe_3)_2$-2,3-$C_2B_4H_4$	Co–Cnt = 1.626 Co–N(av) = 2.027	Cnt–Co–N(21) = 135.2 Cnt–Co–N(22) = 138.8 N(21)–Co–N(22) = 86.0(2)	161
$Cp^*_2[Co(Et_2C_2B_3H_2Me)]_2$	Co(1)–av(C_2B_3 atom) = 2.094 Co(2)–av(C_2B_3 atom) = 2.096 Co(1)–av(C_5 ring) = 2.092 Co(2)–av(C_5 ring) = 2.099		282
$[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)]_2C_6H_4$	Co–av(C_5 ring) = 2.040 Co–av(C_2B_3 atom) = 2.072		119
$[Cp^*Co(Et_2C_2B_3H_3)CoCp^*]^-$	Co(1)–av(C_2B_3 atom) = 2.091 Co(1)–av(Cp^* ring) = 2.076		195
$[Cp^*Co(Et_2C_2B_3H_3)CoCp]$	Co(1)–av(C_2B_3 atom) = 2.082 Co(1)–av(Cp^* ring) = 2.050 Co(1)–av(Cp ring) = 2.042		195
[3,3′-Co-(8-C_4H_4N-$(CH_2)_2$-O-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$	Co(1)–av(C_2B_3 atom) = 2.080 Co(1)–av($C'_2B'_3$ atom) = 2.083		283
[1′,8-μ-SEt-3,3′-Co(1-Ph-2-SEt-1,2-$C_2B_9H_9$)-(9′-Ph-1′,9′-$C_2B_9H_8$)]	Co(1)–av(C_2B_3 atom) = 2.111 Co(1)–av($C'_2B'_3$ atom) = 2.101		284
$[Cp^*Co(Et_2C_2B_3H_3)]_2Mo(CO)_2$	Co(1)–av(C_2B_3 atom) = 2.075 Mo–av(C_2B_3 atom) = 2.402 Mo–CO(av) = 1.961		52
$(MePPh_3)$[3,3′-Co(8,9,12-$(CH_3)_3$-3,1,2-$CoC_2B_9H_8)_2$]	Co–av(C_2B_3 atom) = 2.106		285
$[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-})]_2MeCH$	Co–av(C_2B_3 atom) = 2.078		121
cis-$[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-})]_2C_2H_2$	Co–av(C_2B_3 atom) = 2.080		121
$[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-}C{\equiv}C)]_2$	Co–av(C_2B_3 atom) = 2.070 Co–av(Cp^* ring) = 2.036		286
$\{Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}5\text{-}C{\equiv}C)\}_3C_6H_3$	Co(1)–av(C_2B_3 atom) = 2.073		286
closo-[3-Co(η^5-$N(CH_3)_2C_4H_2$)-1,2-$C_2B_9H_{11}$]	Co–av(C_2B_3 atom) = 2.048 Co–av(C_4N ring) = 2.057		287
closo-[3-Co(η^5-$N(CH_3)_2C_4H_2$)-1-(C_6H_5-1,2-$C_2B_9H_{10}$]	Co–av(C_2B_3 atom) = 2.055 Co–av(C_4N ring) = 2.063		287
closo-[3-Co(η^5-NC_4H_4)-1-Me-1,2-$C_2B_9H_{10}$]	Co–av(C_2B_3 atom) = 2.030 Co–av(C_4N ring) = 2.045		287

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
3-(η^5-NC_4H_4)-1-(CH_3)-2-(C_4H_9)-3,1,2-$CoC_2B_9H_9$	Co–av(C_2B_3 atom) = 2.034 Co–av(NC_4 atom) = 2.047		263
3-(η^5-NC_4H_4)-1-(C_6H_5)-2-(C_3H_5)-3,1,2-$CoC_2B_9H_9$	Co–av(C_2B_3 atom) = 2.059 Co–av(NC_4 atom) = 2.057		263
Cp*Co($Et_2C_2B_3H_2Me$)CoH($Et_2C_2B_3H_5$)	Co(1)–av($C_2B_3H_5$ ring atom) = 2.069 Co(1)–av($C_2B_3H_2Me$ ring atom) = 2.161 Co(2)–av($C_2B_3H_2Me$ ring atom) = 2.068 Co(2)–av(Cp* ring atom) = 2.056	(C_2B_3 plane–C_2B_3 plane) = 12 (C_2B_3 plane–Cp* plane) = 4.9	303
[($Et_2C_2B_3H_5$)Co(Cp*)C_6H_4(Cp*)-Co(Et_2B_3H-4,5-Cl_2]$_2$Co	Co(1)–av(C_2B_3 atom) = 2.126 Co(2)–av(C_2B_3 atom) = 2.082 Co(2)–av(Cp* ring) = 2.082		196
[($Et_2C_2B_3H_2$-4,6-Br_2-5-Me-Co(C_5H_4)]$_2$	Co–av(C_2B_3 atom) = 2.042 Co–av(Cp ring) = 2.070		196
[Cp_2Co][Co($Et_2C_2B_4H_4$)$_2$]	Co(1)–av(C_2B_3 atom) = 2.087 Co–av(Cp ring) = 2.018		288
arachno-2-(Cp)Co-8-($CH_3OC(O)$)-7,8,9,10-$C_4B_7H_{11}$	Co2–C(8), av(C_2B_3) = 2.409(4), 2.131 Co2–av(C_5 ring) = 2.053		108
[4-{Co($C_2B_9H_{10}S$)$_2$}CH-$C_{10}H_5$-1,8-{(NMe_2)$_2$H}]	Co–av(C_2B_3 atom) = 2.085		289
meso-Co[(1-$C_2B_9H_{10}$)-CH_2]$_2$S	Co–av(C_2B_3 atom) = 2.090		290
[*commo*-3,3′-Co(8-F-3,1,2-$CoC_2B_9H_{10}$)$_2$]$^-$	Co–av(C_2B_3 atom) = 2.096		291
Co(Cp*)($C_2B_3H_2Me_5$)	Co–av(C_2B_3 atom) = 2.056 Co–av(Cp* ring) = 2.060		292
Cp*Co($Et_2C_2B_4H_3$-5-O(CH_2)$_4$)(η^4-C_5Me_5)-CoH($Et_2C_2B_4H_3$-5-I)	Co(1)–av(C_2B_3 atom) = 2.111 Co(2)–av(C_2B_3 atom) = 2.078 Co(1)–av(η^4-C_5 ring) = 2.029 Co(2)–C(Cp*) = 2.042(7)		293
[Cp*Co($Et_2C_2B_4H_3$-5-I)]$^-$	Co–av(C_2B_3 atom) = 2.179 Co–C(Cp*) = 2.103(7)		293
Cp*Co($Et_2C_2B_4H_3$-7-NMe_2)	Co(1)–av(C_2B_3 atom) = 2.074 Co(1)–C(C_5Me_5ring) = 2.045		293
(PC_4Me_4)Co($Et_2C_2B_3H_8$)Co(NC_4Me_4)	Co(1)–P = 2.318(3) Co(1)–av(C_4 of PC_4) = 2.081 Co(1)–av(C_2B_3 atom) = 2.080 Co(2)–av(C_2B_3 atom) = 2.069 Co(2)–av(NC_4 atom) = 2.065	Cnt(C_2B_3)–Co(2)–Cnt(NC_4) = 178.9(5) Cnt(PC_4)–Co(1)–Cnt(C_2B_3) = 178.0(5) Co(1)–Cnt(C_2B_3)–Co(2) = 173.7(8)	294
Cp*Co(2,3-$Et_2C_2B_3H_4$-5-C(=CH_2)OC(O)Me)	Co–av(C_2B_3 atom) = 2.052 Co–avC(Cp* ring)) = 2.064		117
1,4-[*nido*-($Et_2C_2B_3H_5$)Co(η^5-C_5Me_4-C≡C)]$_2$$C_6H_4$	Co–C_5 = 1.661 Co–C_2B_3 = 1.508		295
[Cp*Co(2,3-$Et_2C_2B_4H_3$-7-)]$_2$$C_2$	Co–av(C_2B_3 atom) = 2.079		121
Na[3,3′-Co(1-C_6H_5-1,2-$C_2B_9H_{10}$)$_2$]·0.4$C_6H_5CH_3$	Co–av(C_2B_3 atom) = 2.112		296

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[8,8′-μ-ClP(O)(O)$_2$<(1,2-C$_2$B$_9$H$_{10}$)$_2$-3,3′<Co]$^-$	Co–av(C$_2$B$_3$ atom) = 2.147		297
[8,8′-μ-(CH$_3$CH$_2$)$_2$NP-(O)(O)$_2$<(1,2-C$_2$B$_9$H$_{10}$)$_2$-3,3′-Co][K]	Co–av(C$_2$B$_3$ atom) = 2.081		297
CpCo(μ-η^5-(MeEt$_4$C$_4$B$_2$)-3-Co(2-Me-2,3,5-C$_3$B$_7$H$_9$)	Co–C(2) (of C$_3$B$_7$) = 2.047(6) Co–C(3) (of C$_3$B$_7$) = 1.960(6) Co–B(4),B(7) (of C$_3$B$_7$) = 2.201(7) Co–B(7) (of C$_3$B$_7$) = 2.201(7) Co–C(5) (of C$_3$B$_7$) = 2.673(8) Co–B(6) (of C$_3$B$_7$) = 2.586(9) Co(1)–av(C$_3$B$_2$ ring) = 2.114 Co(2)–av(C$_3$B$_2$ ring) = 2.063 Co(2)–av(Cp ring) = 2.051		107
1-(Cp)-Co-(2-Me-2,3,5-C$_3$B$_7$H$_9$)	Co–C(2),C(3) (of C$_3$B$_7$) = 1.950 Co–C(5) (of C$_3$B$_7$) = 2.549(6) Co–B(6) (of C$_3$B$_7$) = 2.456(7) Co–B(4),B(7)(of C$_3$B$_7$) = 2.250		107
[8-(1-(C$_5$H$_5$N)CH$_2$CH$_2$OCH$_2$CH$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]	Co(3)–av(C$_2$B$_3$ atom) = 2.076		299
Cp$^*{}_2$Co$_2$Et$_4$C$_4$B$_6$H$_4$Cl$_2$	Co(1)–av(C$_2$B$_4$ atom) = 2.185 Co(2)–av(C$_2$B$_4$ atom) = 2.160		241
[Cp*Co(Et$_2$C$_2$B$_3$H$_3$)]$_2$	Co–av(C$_2$B$_3$ ring) = 2.067 Co–avC(Cp*) = 2.065		241
closo-[(8-1-O-2-CH$_3$O-C$_6$H$_4$-(CH$_2$-CH$_2$O)$_2$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)-3,3′-Co]$^-$	Co–av(C$_2$B$_3$ ring) = 2.077 Co–C(1) = 2.034(3)		300
[Cp*Co(Et$_2$C$_2$B$_3$H$_2$-5-Cl)]$_2$Ni	Co–av(C$_2$B$_3$ ring) = 2.088 Ni–av(C$_2$B$_3$ ring) = 2.115	Co–Ni–Co = 171	248
[8,8′-(Me)$_2$-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$]$^-$	Co–av(C$_2$B$_3$ ring) = 2.076		146
[1,1′-μ-{S(CH$_2$CH$_2$O)$_3$CH$_2$CH$_2$S}-3,3′-Co(C$_2$B$_9$H$_{10}$)$_2$]$^-$	Co–av(C$_2$B$_3$ ring) = 2.109		146
[3,3′-Co(8-{O(CH$_2$CH$_2$O)$_2$CH$_2$CH$_3$}-(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]Na	Co–av(C$_2$B$_3$ ring) = 2.078 Co–av(C′$_2$B′$_3$ ring) = 2.078		146
[Cp*Co(2,3-Et$_2$C$_2$B$_3$H$_2$-5-Cl)]$_2$Ni	Co–av(C$_2$B$_3$ ring) = 2.073 Co–avC(Cp* ring) = 2.057 Ni–av(C$_2$B$_3$ ring) = 2.115		248
[Cp*Co(2,3-Et$_2$C$_2$B$_3$H$_2$-5-C(O)Me)]$_2$Ni	Co–av(C$_2$B$_3$ ring) = 2.094 Co–avC(Cp* ring) = 2.063 Ni–av(C$_2$B$_3$ ring) = 2.120		248
[Cp*Co]$_2$(2,3-Et$_2$C$_2$B$_3$H$_2$-5-Cl)-(2,3-Et$_2$C$_2$B$_3$H-4,5-Cl$_2$)Ru	Co–av(C$_2$B$_3$ ring) = 2.076 Co–avC(Cp* ring) = 2.081 Ru–av(C$_2$B$_3$ ring) = 2.226		248
[8,8′-μ-CH$_3$CH(O)$_2$ < (1,2-C$_2$B$_9$H$_{10}$)$_2$-3-Co]	Co–av(C$_2$B$_3$ ring) = 2.072	B8′–Co–B8 = 89.42(14)	298
CpCo{η^6-C$_4$B$_2$Me$_2$(C$_4$H$_4$)$_2$}	Co–av(C$_4$B$_2$ atom) = 2.177		110

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
11-Ph-7-Cp-(*nido*-11,7,9,10-CoPC$_2$B$_7$H$_9$)	Co–P = 2.1378(7) Co–C = 2.003(2) Co–B(5) = 2.059(3) Co–B(6) = 2.140(3)		165
[Cp*Co(Et$_2$C$_2$B$_3$H$_2$Me)Co(Et$_2$C$_2$B$_3$H$_3$)]$_2$H$_2$Co	Co(1)–avC(Cp* ring) = 2.05 Co(1)–av(C$_2$B$_3$ atom) = 2.04 Co(2)–av(C$_2$B$_3$ atom) = 2.11 Co(3)–av(C$_2$B$_3$ atom) = 2.09		301
closo-[1,2,3-Cp*Co(Et$_2$C$_2$B$_3$Br$_3$)]	Co–C$_2$B$_3$ = 1.605(2) Co–Cp* ring = 1.660(2)		302
Cp*Co(Et$_2$C$_2$B$_3$Br$_3$)Cl$_2$TaCp	Co–av(C$_2$B$_3$ atom) = 2.08 Ta–av(C$_2$B$_3$ atom) = 2.48 Ta–Cl(av) = 2.359		39
closo-[1,2,4-Cp*Co(Et$_2$C$_2$B$_4$-3,5,6-Br$_3$-7-Ph)]	Co–C$_2$B$_3$ ring = 1.581(1) Co–C$_5$ ring = 1.641(1)		302
closo-[3-Co(η^5-NC$_4$H$_4$)-1,2-(SMe)$_2$-1,2-C$_2$B$_9$H$_9$]	Co–av(C$_2$B$_3$ atom) = 2.056 C(cage)–C(cage) = 1.919(6) Co–av(C$_4$N atom) = 2.060		137
closo-[3-Co(η^5-NC$_4$H$_4$)-1,2-(SC$_6$H$_5$)$_2$-1,2-C$_2$B$_9$H$_9$]	Co–av(C$_2$B$_3$ atom) = 2.055 C(cage)–C(cage) = 1.864(6) Co–av(C$_4$N atom) = 2.058		137
closo-[3-Co(η^5-NC$_4$H$_4$)-1-C$_6$H$_5$-1,2-C$_2$B$_9$H$_9$]	Co–av(C$_2$B$_3$ atom) = 2.060 C(cage)–C(cage) = 1.682(9) Co–av(C$_4$N atom) = 2.050		137
(2) Rhodium			
[(Cp*)Ru{μ, η^5-(CMe)$_2$(BMe)$_2$(CMe)Rh-(2-Me-2,3,4-C$_3$B$_7$H$_9$)]	Ru–C(Cp*) = 2.156–2.173(4) Ru–av(C$_3$B$_2$ atom) = 2.236 Rh–av(C$_3$B$_2$ atom) = 2.208 Rh–av(C$_3$B$_3$ atom) = 2.313		278
[(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(dppe)Cl]$^+$	Rh–av(C$_3$B$_2$ atom) = 2.235 Rh(1)–P(av) = 2.308 Rh(1)–Cl = 2.4074(8)	P(1)–Rh–P(2) = 83.71(3) P(1)–Rh–Cl = 82.79(3) P(2)–Rh–Cl = 87.08(3)	141
[2-Me-1-(Cp*)-*closo*-1,2,3-RhC$_2$B$_8$H$_9$]	Rh–av(C$_2$ of C$_2$B$_4$) = 2.102 Rh–av(B$_4$ of C$_2$B$_4$) = 2.378		277
[Rh(COD){(SMe$_2$)$_2$C$_2$B$_9$H$_9$}][BF$_4$]	Rh–av(CB$_4$ ring) = 2.216		143
closo-2-(PPh$_3$)-1-N,2-[μ-η^2-CH$_2$CH═CH$_2$)]-1-N-(σ-CH$_2$CH═CH$_2$)-2,1-RhCB$_{10}$H$_{10}$	Rh(2)–av(CB$_4$ atom) = 2.193 Rh(2)–avC(η^2) = 2.31 Rh(2)–P(1) = 2.367(4)		304
1-CCPh-2-Ph-3-(Cp*)-*semipseudocloso*-3,1,2-RhC$_2$B$_9$H$_9$	Rh(3)–av(C$_2$B$_3$ atom) = 2.174 Rh(3)–C(Cp* ring) = 2.211 C(cage)–C(cage) = 2.052(5)	C(cage)–Rh(3)–C(cage) = 56.94(14)	134
1-CCPh-2-Ph-3-(Cp*)-*closo*-3,1,2-RhC$_2$B$_9$H$_9$	Rh(3)–av(C$_2$B$_3$ atom) = 2.178 Rh(3)–C(Cp* ring) = 2.208 C(cage)–C(cage) = 1.828(7)	C(cage)–Rh(3)–C(cage) = 49.80(18)	134
[3,3-(PPh$_3$)$_2$-8-SMe$_2$-*closo*-3,1,2-RhC$_2$B$_9$H$_{10}$]	Rh–P(av) = 2.259 Rh(3)–av(C$_2$B$_3$ atom) = 2.324	P(1)–Rh–P(2) = 97.13(4)	305
[3,3-COD-8-SMe$_2$-*closo*-RhC$_2$B$_9$H$_{10}$]	Rh–av(C$_2$B$_3$ atom) = 2.267 Rh–avC(COD) = 2.149		305
[3-(PPh$_3$)-3,3-Cl$_2$-8-SMe$_2$-*closo*-3,1,2-RhC$_2$B$_9$H$_{10}$]	Rh–av(C$_2$B$_3$ atom) = 2.196 Rh–Cl(av) = 2.410 Rh–P = 2.357(3)		305
[(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhCp*]$^+$	Rh(1)–av(C$_2$B$_3$ atom) = 2.195 Rh(1)–C(Cp* ring) = 2.195		141

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
9,9-η^2-{η^2-BH_3·dppm}-*nido*-9,7,8-$RhC_2B_8H_{11}$	Rh–av(CB_3 atom) = 2.162 Rh–P = 2.2857(15)		306
1-Ph-3,3-$(CO)_2$-7-SMe_2-3,1,2-*closo*-$RhC_2B_9H_9$	Rh(1)–av(C_2B_3 atom) = 2.267 Rh(3)–CO(av) = 1.872		307
[1-NH═CMe_2-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Rh(1)–av(CB_4 atom) = 2.168 Rh(1)–Cl(1) = 2.366(3) Rh(1)–P(1) = 2.336(3)		308
[1,2-μ-{NHC(CMe═CH_2)═O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Rh(1)–av(CB_4 atom) = 2.136 Rh(1)–O(1) = 2.133(3) Rh(1)–P(1) = 2.093(5)		308
[1-NH_2-2,2-$(CNBu')_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Rh–av(CB_4 atom) = 2.224 Rh–avC(*sp*) = 2.010 Rh–P = 2.340(2)		308
[Rh(η^6-$C_6H_3Me_3$-1,3,5)(η^5-7-$NHBu^t$-7-$CB_{10}H_{10}$)]	Rh–av(CB_4 atom) = 2.177 Rh–av(C_6 atom) = 2.320		309
(Cp^*)Rh(η^4-$C_2B_6H_{12}$)	Rh5–av(C_2B_2 atom) = 2.197		310
[2,5-$(Cp^*)_2$-10-Me-*nido*-2,5,1-$Rh_2CB_6H_9$]	Rh2–Rh5 = 2.8510(3) Rh2–Cl = 2.047(3), Rh5–Cl = 2.052(3) Rh2–B3 = 2.195(3), Rh5–B4 = 2.202(3) Rh2–B7 = 2.2323, Rh5–B9 = 2.215(3)		310
closo-2-(Ph_3P)-2-Cl-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$	Rh(2)–av(CB_4 atom) = 2.181 Rh(2)–P(1) = 2.357(2) Rh(2)–Cl = 2.370(2)	Cl(1)–Rh(2)–P(1) = 83.30(8)	311
closo-3,3-$(Ph_3P)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$	Rh–Cl = 2.422(2) Rh–P(av) = 2.381 Rh–av(C_2B_3 atom) = 2.254		311
[Rh(η^6-[2_2](1,4)-$C_{16}H_{16}$)-(η^5-7-$NHBu^t$-7-$CB_{10}H_{10}$)]	Rh–Av(CB_4 atom) = 2.176 Rh–av(C_6 atom) = 2.339		309
[$Rh_2(CO)_2$(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)$_2$]	Rh(1)–Rh(2) = 2.6993(4) Rh–av(CB_4 atom) = 2.210 Rh–CO(av) = 1.930		309
[Rh-HC$(pz)_3$-(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)][PF_2O_2]	Rh(1)–N(av) = 2.233 Rh(1)–av(CB_4 atom) = 2.163		309
(3) Iridium			
[7-{C$(CH_3)CH_2$}-9,9,9-(CO)$(PMe_3)_2$-*nido*-9,7,8-$IrC_2B_8H_{10}$]	Ir(9)–P(av) = 2.337 Ir(9)–av(CB_3 atom) = 2.226		310
[5,5,5-(CO)$(PMe_3)_2$-μ-6,7-{CHC-$(CH_3)CH_2$}-*nido*-5,6-$IrCB_8H_{11}$]	Ir(5)–P(av) = 2.358 Ir(5)–av(CB_3 atom) = 2.212		312
Cp^*Ir($Et_2C_2B_4H_4$)	Ir–av($C_{=2}B_3$ atom) = 2.20 Ir–av(Cp^* atom) = 2.20		124
Cp^*Ir(2,3-$Et_2C_2B_3H_2$-6-Cl)IrCp^*	Ir–av(C_2B_3 atom) = 2.17 Ir–av(Cp^* atom) = 2.16		124
nido-[9,9,9-$(PMe_3)_2$(CO)-9,8,7-$IrC_2B_8H_{11}$]	Ir–CO = 1.870(6) Ir–av(CB_3 atom)C(8) = 2.222 Ir(9)–P(av) = 2.336		313
closo-3,3-(σ:η^2-C_8H_{13})-1,2-μ-(*o*-xylene)3,1,2-$IrC_2B_9H_9$]	Ir–av(C_2B_3 atom) = 2.222 Ir–C(η^2) = 2.196 Ir–C(σ) = 2.098(4)		314

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[2,7-(Cp*)$_2$-*nido*-2,7,8,6-Ir$_2$CSB$_6$H$_8$]	Ir(2)–av(B$_3$ atom) = 2.16 Ir(2)–S(6) = 2.461(4) Ir(2)–Ir(7) = 2.8090(5) Ir(7)–S(6) = 2.402(4) Ir(7)–C(8) = 2.187(11)		315
[2,7-(Cp*)$_2$-*nido*-2,7,8,6-Ir$_2$CSB$_6$H$_7$-9-Cl]	Ir(2)–av(B$_3$ atom) = 2.212 Ir(2)–S(6) = 2.3477(15) Ir(2)–B(5) = 2.222(11) Ir(2)–Ir(7) = 2.8070(3) Ir(7)–C(8) = 2.187(11) Ir(7)–S(6) = 2.3200(16)		315
Heterocarboranes of Group 10 Elements			
(1) Nickel			
1,2-Ph$_2$-4,4-(PMe$_2$Ph)$_2$-4,1,2-*closo*-NiC$_2$B$_9$H$_9$	Ni(4)–av(CB$_4$ atom) = 2.145 Ni(4)–P(av) = 2.206	P(1)–Ni(4)–P(2) = 97.01(6)	316
1,2-Ph$_2$-4,4-(PEt$_3$)$_2$-4,1,2-*closo*-NiC$_2$B$_9$H$_9$	Ni(4)–av(CB$_4$ atom) = 2.172 Ni(4)–P(av) = 2.242	P(1)–Ni(4)–P(2) = 99.05(11)	316
1,2-Ph$_2$-4,4-(dppe)-4,1,2-*closo*-NiC$_2$B$_9$H$_9$	Ni(4)–av(CB$_4$ atom) = 2.120 Ni(4)–P(av) = 2.175	P(1)–Ni(4)–P(2) = 87.392(2)	316
[2-(η^3-C$_3$H$_4$Ph)-2,1,7-NiC$_2$B$_9$H$_{11}$]$^-$	Ni–av(C$_3$ atom) = 2.002 Ni–av(C$_2$B$_3$ atom) = 2.113 Ni–C(13) = 2.032(9)		162
[2-CO-2-PEt$_3$-*closo*-2,1,7-NiC$_2$B$_9$H$_{11}$]	Ni–av(C$_2$B$_3$ atom) = 2.128 Ni–P = 2.1843(11) Ni–CO = 1.777(4)	CO–Ni–P = 92.04(14)	162
[2-(η^2:η^2-C$_5$Me$_5$H)-*closo*-2,1,7-NiC$_2$B$_9$H$_{11}$]	Ni–av(C$_2$B$_3$ atom) = 2.084 Ni–C(η^2) = 2.090 Ni–C(η^2) = 2.004		162
[2,2′-μ-(1,2:5,6-η-3,4:7,8-η-cot)-(*closo*-2,1,7-NiC$_2$B$_9$H$_{11}$)$_2$]	Ni–av(C$_2$B$_3$ atom) = 2.153 Ni–av(cot atom) = 2.139		162
(*cis*-1,5-COD)-Ni(η^6-C$_4$B$_2$Me$_2$(C$_4$H$_4$)$_2$	Ni–av(C$_4$B$_2$ atom) = 2.281		110
commo-Ni-(7-Ni-8′-Ph-*nido*-8′,10′,11′-PC$_2$B$_7$H$_9$)-(7-Ni-8-Ph-*nido*-8,10,11-PC$_2$B$_7$H$_9$) = 116.16(16)	Ni–av(PCB$_2$ atom) = 2.130		165
[ttf]$^{\cdot+}$[Ni(C$_2$B$_9$H$_{11}$)$_2$]$^-$	Ni(3)–av(C$_2$B$_3$ atom) = 2.200		254
(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(PPh$_3$)	Ni–av(C$_2$B$_3$ atom) = 2.097 Ni(1)–N(1) = 2.061(6) Ni(1)–P(1) = 2.166(1)	N(1)–Ni(1)–P(1) = 105.0(1)	164
(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(bipy)	Ni(1)–N(1) = 1.979(5) Ni(1)–avN(bipy) = 2.039 Ni(1)–av(C$_2$B$_3$ atom) = 2.217		164
(η^5-C$_2$B$_9$H$_{10}$CH$_2$PPh$_3$)Ni(CNBu^t)(I)	Ni(1)–I(1) = 2.5574(1) Ni(1)–av(C$_2$B$_3$ atom) = 2.115		164
CpCo(μ-η^5-MeEt$_4$C$_3$B$_2$)-Ni(η^4-8-Me-7,8,10-C$_3$B$_7$H$_9$)	Ni–av(C$_2$ of C$_3$B$_7$) = 2.039 Ni–av(B$_2$ of C$_3$B$_7$) = 2.138		107
1-(η^3-C$_3$H$_5$)Ni(η^6-2-Me-2,3,5-C$_3$B$_7$H$_9$)	Ni–av(C$_2$ of C$_3$B$_3$ ring) = 1.971 Ni–av(B$_3$ of C$_3$B$_3$ ring) = 2.278 Ni–C(5)(of C$_3$B$_3$ ring) = 2.515(3)		107

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
1-(η^3-2-MeC_3H_4)Ni(η^6-2-Me-2,3,5-$C_3B_7H_9$)	Ni–av(C_2 of C_3B_3 ring) = 1.981 Ni–av(B_3 of C_3B_3 ring) = 2.278 Ni–C5(of C_3B_3 ring) = 2.588(2)		107
9-(Cp)Ni-(η^4-8-Me-7,8,10-$C_3B_7H_9$)	Ni–av(C_2B_2 atom) = 2.053		107
commo-Ni-(1-Ni-5-Me-2,3,5-$C_3B_7H_9$)(9′-Ni-7′-Me-11′-PMe_3-7′,8′,10′-$C_3B_7H_8$)	Ni–av(C_2B_2 atom) = 2.120		317
closo-(η^3-C_3H_5)Ni-(Me$C_3B_7H_9$)	Ni–av(C_2B_2 atom) = 2.074		317
(2) Palladium			
commo-Pd-(9-Pd-8-Me-7,8,10-$C_3B_7H_9$)(8′-Pd-9′-Me-7′,9′,10′-$C_3B_7H_9$)	Pd–av($C_{\equiv2}B_2$ atom) = 2.242		317
commo-Pd-(9-Pd-8-Me-7,8,10-$C_3B_7H_9$)(8′-Pd-10′-Me-7′,9′,10′-$C_3B_7H_9$)	Pd–av($C_{=2}B_2$ atom) = 2.240		317
[1-MeC_4H_2S-3,3-(PMe_2Ph)$_2$-3,1,2- Pd-$C_2B_9H_{10}$]	Pd(3)–av(C_2B_3 atom) = 2.391 Pd(3)–P(av) = 2.298		172
[1-C_4H_3S-8-PMe_2Ph-3,3-(PMe_2Ph)$_2$-3,1,2-Pd$C_2B_9H_9$]$^+$	Pd(3)–av(C_2B_3 atom) = 2.385 Pd(3)–P(av) = 2.298	P(27)–Pd(3)–P(36) = 98.2(3)	172
[1-MeC_4H_2S-3,3-(PMe_2Ph)$_2$-3,1,2-Pd$C_2B_9H_{10}$]	Pd(3)–av(C_2B_3 atom) = 2.289 Pd(3)–P(av) = 2.298	P(19)–Pd(3)–P(28) = 94.96(8)	172
(3) Platinum			
8-Ph-7-(PPh_3)$_2$-*nido*-7,8,10,11-Pt$C_2B_7H_9$	Pt(7)–av(PCB_2 atom)) = 2.270 Pt(7)–P(av) = 2.311		165
1,2-Ph_2-3,3-(PMe_2Ph)$_2$-6-Et-3,1,2-Pt$C_2B_9H_8$	Pt(3)–av(C_2 of C_2B_3) = 2.831 Pt(3)–av(B_3 of C_2B_3) = 2.269(11) Pt(3)–P(av) = 2.286		170
1,8-Ph_2-2,2-(PMe_2Ph)$_2$-4-Et-2,1,8-*closo*-Pt$C_2B_9H_8$	Pt(2)–C(1) = 2.628(4) Pt(2)–av(B_4 of CB_4) = 2.236 Pt(2)–P(av) = 2.298	P(1)–Pt(2)–P(2) = 96.16(4)	170
1,8-Ph_2-2,2-(PMe_2Ph)$_2$-4-F-2,1,8-*closo*-Pt$C_2B_9H_8$	Pt(2)–C(1) = 2.625(6) Pt(2)–av(B_4 of CB_4) = 2.23 Pt(2)–P(av) = 2.294		170
commo-Pt-(8-Pt-9-Me-7,9,10-$C_3B_7H_9$)$_2$	Pt–av(C_2B_2 atom) = 2.228		317
commo-Pt-(9-Pt-8-Me-7,8,10-$C_3B_7H_9$)-(8′-Pt-9′-Me-7′,9′,10′-$C_3B_7H_9$)	Pt″–av(C_2B_2 atom) = 2.240		317
1,1-(PMe_2Ph)$_2$-2,4-Ph_2-1,2,4-*closo*-Pt$C_2B_9H_9$	Pt(1)–P(av) = 2.280 Pt(1)–av(C_2B_3 atom) = 2.356		169
1-(CH_2OCH_3)-3,3-(Me_2PhP)$_2$-3,1,2-*closo*-Pt$C_2B_9H_{10}$	Pt(3)–av(CB_3 atom) = 2.193 Pt(3)–P(av) = 2.265		246
[PtH(PEt_3)$_2$(η^5-7-$CB_{10}H_{11}$)]	Pt(1)–H(1A) = 1.596 Pt(1)–av(CB_4 atom) = 2.261 Pt(1)–P(av) = 2.362	H(1A)–Pt(1)–P(1) = 85.1(1) P(1)–Pt(1)–P(2) = 98.6(1)	167
PtAu(PEt_3)$_2$(PPh_3)(η^5-7-$CB_{10}H_{11}$)	Pt–P = 2.3487(14) Au–Pt = 2.6112(7) Pt–av(CB_4 atom) = 2.28	P(2)–Au–Pt = 167.51(5) P(1)–Pt–P(1A) = 98.99(8)	167

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
PtCu(PEt$_3$)$_2$(PPh$_3$)(η^5-7-CB$_{10}$H$_{11}$)	Pt–av(CB$_4$ atom) = 2.304 Pt–P(av) = 2.318 Pt–Cu = 2.6058(5)		167
PtHgPh(PEt$_3$)$_2$(η^5-7-CB$_{10}$H$_{11}$)	Pt–av(CB$_4$ atom) = 2.285 Pt–P(av) = 2.357 Pt–Hg = 2.5850(5)		167
[Pt(CO)(PPh$_3$)(η^5-7-CB$_{10}$H$_{11}$)]$^-$	Pt–CO = 1.865(6) Pt–av(CB$_4$ atom) = 2.302 Pt–P(1) = 2.3093(10)		167
[Pt(SePh)(PEt$_3$)(η^5-8-SePh-7-CB$_{10}$H$_{10}$)]	Pt–av(CB$_4$ atom) = 2.222 Pt–P = 2.330(2) Pt–Se(1) = 2.4438(8)	P–Pt–Se(1) = 85.49(6)	318
Heterocarboranes of Group 12 Elements			
(1) Zinc			
[(*nido*-C$_2$B$_9$H$_{11}$)ZnNMe$_3$]$_2$	Zn(1)–B(10) = 2.315(3) Zn(1)–B(11) = 2.177(3) Zn(1)–B(30) = 2.340(3) Zn(1)–B(31) = 2.165(3) Zn(2)–B(9) = 2.160(3) Zn(2)–B(10) = 2.380(3) Zn(2)–B(29) = 2.163(3) Zn(2)–B(30) = 2.352 Zn–N(av) = 2.064		176
(2) Mercury			
7,8-(CH$_2$OCH$_3$)$_2$-10-*endo*-(Ph$_3$PHg)-7,8-*nido*-C$_2$B$_9$H$_9$	Hg(3)–B(4) = 2.502(7) Hg(3)–B(7) = 2.490(7) Hg(3)–B(8) = 2.231(7) Hg(3)–P(1) = 2.3922(15)		246
trans-5′,6′,10′-*exo*-*nido*-[Cl(Ph$_3$P)$_3$Ru]-5′,6′,10′-(μ-H)$_3$-10′-(1,2-C$_2$B$_{10}$H$_{11}$Hg-9)-7′,8′-C$_2$B$_9$H$_8$	Hg1–B9 = 2.00(4) Hg1–B10′ = 2.27(4) Hg1···B9′ = 2.63(5)		271
7,8-(CH$_2$OCH$_3$)$_2$-10-*endo*-(Ph$_3$PHg)-7,8-*nido*-C$_2$B$_9$H$_9$	Hg(3)–B(4) = 2.551(6) Hg(3)–B(7) = 2.511(7) Hg(3)–B(8) = 2.218(7) Hg(3)–P(1) = 2.4062(14)		246
Heterocarbons of f-*block Elements*			
(1) Cerium			
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$ Li(TMEDA)]-1,1′-*commo*-Ce(2,3-C$_2$B$_4$H$_4$)$_2$]	Ce–(C$_2$B$_3$ centroid 1,2) = 2.510, 2.484	(Cnt 1)–Ce–(Cnt 2) = 124.6	247
	Ce–Cl(1,2) = 2.759(3), 2.799(3)	Cl(1)–Ce–Cl(2) = 101.02(11)	
(2) Neodymium			
[2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Nd(η^5-2,4-C$_2$B$_4$H$_4$)$_2$]$^-$	Nd–Cnt(1) = 2.407 Nd–Cnt(2) = 2.435	Cnt(1)–Nd–Cnt(2) = 134.7	208
[2,2′,4,4′-(SiMe$_3$)$_4$-[5,6-(μ-H)$_2$-Na(THF)$_2$]-1,1′-*commo*-Nd(2,4-C$_2$B$_4$H$_4$)$_2$]	Nd–Cnt(1) = 2.407 Nd–Cnt(2) = 2.435	Cnt(1)–Er–Cnt(2) = 134.8	215
{[η^5-1-Nd-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$(μ_3-OBu^t)]-[μ_2-Li(C$_4$H$_8$O)]$_3$(μ_3-O)}	Nd–Cnt(av) = 2.460		203d
{2,2′,4,4′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$K(η^6-C$_6$H$_6$)$_2$]-1,1′-Nd(2,4-C$_2$B$_4$H$_4$)$_2$}$_2$	Nd–Cnt(1) = 2.392 Nd–Cnt(2) = 2.434	Cnt(1)–Nd–Cnt(2) = 135.1 Cnt(C$_6$H$_6$)–K–Cnt(C$_6$H$_6$) = 105/3	208a
	K–(C$_6$H$_6$ Cnt) = 2.320, 2.189		
{[*closo*-1-Nd(μ-H)$_6$-2,4-(SiMe$_3$)$_2$–]$^+$	Nd–Cnt(*closo*) = 2.430	Cnt(1)–Nd–Cnt(2) = 127.8	215
[1,1′-(THF)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-5,5′,6,6′-(μ-H)$_4$-1,1′-*commo*-Nd(2,4-C$_2$B$_4$H$_4$)$_2$]$^-$	Nd–Cnt(1) = 2.437 Nd–Cnt(2) = 2.447		

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
(3) Samarium			
{[η^5-1-Sm-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$(μ_3-OMe)][μ_2-Li(C$_4$H$_8$O)]$_3$(μ_3-O)}	Sm(1)···Sm(2) = 3.806(2) Sm(2)···Sm(3) = 3.827(2) Sm(1)···Sm(3) = 3.813(2) Sm(1)–Cnt(1) = 2.405 Sm(2)–Cnt(3) = 2.417 Sm(3)–Cnt(5) = 2.417	Sm(2)···Sm(1)···Sm(3) = 60.3 Sm(1)···Sm(3)···Sm(2) = 59.8 Sm(1)···Sm(2)···Sm(3) = 59.9	203c
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]1,1′-*commo*-Sm(2,3-C$_2$B$_4$H$_4$)$_2$]	Sm–Cnt(1) = 2.551 Sm–Cnt(2) = 2.544	Cnt(1)–Sm–Cnt(2) = 117.3	204
[η^5:η^6-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$	Sm–C(C$_5$ring) = 2.670(5) Sm–C(cage) = 2.764(3) Sm–B(cage) = 2.829(3) Sm–O = 2.415(3)	Cnt–Sm–Cnt = 132.6	223
[η^5-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]$_2$SmCl(THF)$_2$	Sm–C(C$_5$ ring) = 2.771(3) Sm–O = 2.556(2)	C(C$_5$ ring)–C–C(cage) = 109.1(3) Cnt–Sm–Cnt = 129.6	223
[{η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm][Li-(DME)$_3$]	Sm–C(C$_5$ ring) = 2.695(2) Sm–C(s) = 2.522(2)	C(C$_5$ ring)–C–C(cage) = 112.3 Cnt–Sm–Cnt = 129.0	223
[η^5-η^6-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$	Sm(1)–av(C$_5$ ring)(11) = 2.749 Sm(1)–av(C$_2$B$_4$ atom) = 2.823 Sm(1)–Cnt(5) = 2.468 Sm(1)–Cnt(6) = 2.298	O(1)–Sm(1)–O(2) = 82.68(7) O(1)–Sm(1)–Cnt(5) = 105.5 O(1)–Sm(1)–Cnt(6) = 107.1 Cnt(5)–Sm(1)–Cnt(6) = 126.0	221a
[η^5-η^6-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$	Sm(1)–O(av) = 2.463 Sm(1)–av(C$_2$B$_4$ atom) = 2.841 Sm(1)–av(C$_5$ ring) = 2.656 Sm(1)–Cnt = 2.390 Sm(1)–Bcent = 2.298	O(1)–Sm(1)–O(2) = 76.76(6) B(Cnt)-Sm(1)–O(1) = 123.1 Cnt–Sm(1)–B(Cnt) = 123.4 B(Cnt)–Sm(1)–O(2) = 114.3 Cnt–Sm(1)–O(1) = 99.9 Cnt–Sm(1)–O(2) = 109.7	222
[Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$]Sm(THF)$_2$]	av Sm(1)–C(C$_5$ring) = 2.664(2) av Sm(1)–(C$_2$B$_4$ cage) = 2.841(3)	O(1)–Sm(1)–O(2) = 76.76(6) Cnt(1)–Sm(1)–Cnt(2) = 123.4(1)	221
[{η^5:η^1:η^6-Me$_2$Si(C$_9$H$_5$-CH$_2$CH$_2$NMe$_2$)(C$_2$B$_{10}$H$_{10}$)Sm}$_2$(μ-Cl)]$^-$	Sm(1)–Cl1 = 2.688(3) Sm1–N1 = 2.709(8) Sm1–C$_5$ring = 2.731(8) Sm1–cage = 2.815(9) Sm1′–C$_5$ring = 2.732(8) Sm1′–cage = 2.803(9)	Sm1–Cl1–Sm1′ = 120.07(10)	228
[{η^5:η^6-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$	Sm–CC$_5$ ring = 2.670(5) Sm–Ccage = 2.764(3) Sm–B(cage) = 2.829(3) Sm–O = 2.415(3)	C(C$_5$ ring)–C–C(cage) = 98.5(3) Cnt–Sm–Cnt = 116.2	249
(4) Gadolinium			
[{η^5-1-Gd-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_3$-{μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_3$-(μ_3-OMe){μ_2-Li(C$_4$H$_8$O)}$_3$(μ_3-O)]	Gd(1)–Cnt(1) = 2.382 Gd(2)–Cnt(3) = 2.398 Gd(3)–Cnt(5) = 2.400 Gd(2)···Gd(3) = 3.787(2) Gd(1)···Gd(3) = 3.778(2) Gd(1)···Gd(2) = 3.772(2)	Gd(1)···Gd(3)···Gd(2) = 59.8(1) Gd(2)···Gd(1)···Gd(3) = 60.2(1) Gd(1)···Gd(2)···Gd(3) = 60.0(1)	203c

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]1,1′-*commo*-Gd(2,3-C$_2$B$_4$H$_4$)$_2$]	Gd–Cnt(4) = 2.397	Cnt(3)–Gd–Cnt(4) = 127.3	204
Gd–Cnt(3) = 2.435			
{1,1-Cl$_2$-[μ,μ′-Na(TMEDA)]-1-(THF)-2,4-(SiMe$_3$)$_2$-*closo*-1,2,4-GdC$_2$B$_4$H$_4$}$_2$	Gd–Cnt = 2.375 Gd–Cl(av) = 2.669	Cl–Gd–Cnt = 106.6	205
[2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Gd(η^5-2,4-C$_2$B$_4$H$_4$)$_2$]$^-$	Gd–Cnt(1) = 2.340 Gd–Cnt(2) = 2.360	Cnt(1)–Gd–Cnt(2) = 137.2	208
[η^6-{μ-1,2-[*o*-C$_6$H$_4$(CH$_2$)$_2$]-1,2-C$_2$B$_{10}$H$_{10}$]$_2$Gd}	C$_{cage}$–C$_{cage}$ = 1.535(9) Gd–avC$_{cage}$ = 2.587(6) Gd–avB$_{cage}$ = 2.738(6) Gd–avC$_2$B$_4$ = 2.688(6)		238
(5) Terbium			
{[η^5-1-Tb-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$-[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$-(μ_3-OMe)][μ_2-Li(C$_4$H$_8$O)]$_3$(μ_3-O)}	Tb(1)···Tb(2) = 3.7520(12)	Tb(1)···Tb(2)···Tb(3) = 59.92(2)	203c
	Tb(1)···Tb(3) = 3.7526(12)	Tb(1)···Tb(3)···Tb(2) = 59.91(2)	
	Tb(2)···Tb(3) = 3.7261(10)	Tb(2)···Tb(1)···Tb(3) = 60.17(2)	
	Tb(3)–Cnt(5) = 2.374 Tb(2)–Cnt(3) = 2.374 Tb(1)–Cnt(1) = 2.358		
[(η^5-2,4-(Me)$_2$C$_5$H$_5$)-(η^5-2,3-(SiMe$_3$)$_2$-C$_2$B$_4$H$_4$)Tb]$_2$	Tb–Cnt(C$_2$B$_3$) = 2.326 Tb–av(C$_5$) = 2.683		217
(6) Dysprosium			
{[η^5-1-Dy-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$-[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$-(μ_3-OMe)] [μ_2-Li(C$_4$H$_8$O)]$_3$(μ_3-O)}	Dy(1)···Dy(3) = 3.725(2)	Dy(1)···Dy(2)···Dy(3) = 59.8(1)	203c
	Dy(1)···Dy(2) = 3.726(2)	Dy(2)···Dy(1)···Dy(3) = 60.3(1)	
	Dy(2)···Dy(3) = 3.742(2)	Dy(1)···Dy(3)···Dy(2) = 59.9(1)	
	Dy(3)–Cnt(5) = 2.368 Dy(2)–Cnt(3) = 2.373 Dy(1)–Cnt(1) = 2.326		
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]1,1′-*commo*-Dy(2,3-C$_2$B$_4$H$_4$)$_2$]	Dy–Cnt(6) = 2.344 Dy–Cnt(5) = 2.380 Dy–Cl = 2.622(4)	Cnt(5)–Dy–Cnt(6) = 128.6	204
[1,1′-[5,6-(μ-H)$_2$-*nido*-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-[2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Dy(η^5-2,4-C$_2$B$_4$H$_4$)$_2$]$^-$	Dy–Cnt(1) = 2.336	Cnt(1)–Dy–Cnt(2) = 131.0	207
	Dy–Cnt(1) = 2.299 Dy–Cnt(2) = 2.322	Cnt(1)–Dy–Cnt(2) = 136.9	208
[1,1′-[5,6-(μ-H)$_2$-*nido*-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Dy(2,4-C$_2$B$_4$H$_4$)$_2$]$^{3+}$	Dy–Cnt(1) = 2.336 Dy–Cnt(2) = 2.342	Cnt(1)–Dy–Cnt(2) = 131.0	208
{[C$_6$H$_5$CH$_2$)$_2$C$_2$B$_{10}$H$_{10}$]Dy(THF)$_2$}$^{2+}$	Dy–av(C$_2$ of C$_2$B$_5$) = 2.388 Dy–av(B$_5$ of C$_2$B$_5$) = 2.688		242
[{η^5:η^7-[[Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Dy}$_2$]$^{4+}$	Dy–avC(C$_5$ring) = 2.755(6) Dy–avC(cage) = 2.426(5) Dy–avB(cage) = 2.737(7)		202c
(7) Holmium			
{[η^5-1-Ho-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$(μ_3-OMe)][μ_2-Li(C$_4$H$_8$O)]$_3$(μ_3-O)}	Ho(1)···Ho(2) = 3.713(1)	Ho(2)···Ho(1)···Ho(3) = 60.1(1)	203c
	Ho(1)···Ho(3) = 3.712(1)	Ho(1)···Ho(2)···Ho(3) = 59.9(1)	
	Ho(2)···Ho(3) = 3.718(1)	Ho(1)···Ho(3)···Ho(2) = 60.0(1)	
	Ho(1)–Cnt(1) = 3.327 Ho(2)–Cnt(3) = 2.350 Ho(3)–Cnt(5) = 2.350		

(*Continued*)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
[2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Ho (η^5-2,4-C$_2$B$_4$H$_4$)$_2$]$^-$	Ho–Cnt(1) = 2.289 Ho–Cnt(2) = 2.307	Cnt(1)–Ho–Cnt(2) = 137.1	208
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]1,1′-*commo*-Ho(2,3-C$_2$B$_4$H$_4$)$_2$]	Ho–Cnt(7) = 2.378 Ho–Cnt(8) = 2.350	Cnt(7)–Ho–Cnt(8) = 128.5	204
2,2′,4,4′-(SiMe$_3$)$_4$-5,5′,6,6′-[(μ-H)$_4$-Ho(TMEDA)-[(μ-Cl)$_2$Li(TMEDA)]-1,1′-Ho(2,4-C$_2$B$_4$H$_4$)$_2$	Ho–Cnt(1) = 2.340 Ho–Cnt(2) = 2.469 Ho–Cl(av) = 2.643	Cnt(1)–Ho–Cnt(2)	219
[1,1-Cl$_2$-2,2′,3,3′-(SiMe$_3$)$_4$-1,1′-Ho(2,4-C$_2$B$_4$H$_4$)$_2$]$^{3+}$	Ho–Cnt(1) = 2.378 Ho–Cnt(2) = 2.350 Ho–Cl(av) = 2.641	Cnt(1)–Ho–Cnt(2) = 128.5	320
{[η^5-1-Ho-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$)]$_4$-(μ-Cl)$_2$(μ_4-O)}	Ho–Cnt(av) = 2.328 Ho–O(av) = 2.283		214
(8) Erbium			
[Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]-1,1′-*commo*-Er(2,3-C$_2$B$_4$H$_4$)$_2$]	Er–Cnt(1) = 2.334 Er–Cnt(2) = 2.353 Er–Cl(1) = 2.583(5) Er–Cl(2) = 2.665(5)	Cnt(1)–Er–Cnt(2) = 129.8 Cl(1)–Er–Cl(2) = 97.0(2) Cnt(1)–Er–Cl(1) = 105.8 Cnt(1)–Er–Cl(2) = 103.0 Cnt(2)–Er–Cl(1) = 110.7 Cnt(2)–Er–Cl(2) = 105.5	204
[1,1′-[5,6-(μ-H)$_2$-*nido*-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,2′,4,4′-(SiMe$_3$)$_4$-*commo*-Er (2,4-C$_2$B$_4$H$_4$)$_2$]$^{3+}$	Er–Cnt(1) = 2.324 Er–Cnt(2) = 2.305	Cnt(1)–Er–Cnt(2) = 130.9	208
[2,2′,4,4′-(SiMe$_3$)$_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-C$_2$B$_4$H$_4$)$_2$]	Er–Cnt(1) = 2.274 Er–Cnt(2) = 2.302	Cnt(1)–Er–Cnt(2) = 137.4	207a
[{η^5:η^7-[[Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]-Er(THF)(μ-Cl)Na(THF)$_2$	Er–C(C$_5$ring) = 2.675(15) Er–B(cage) = 2.790(11) Er–C(cage) = 2.740(12)		202c
[(η^5-2,4-(Me)$_2$C$_5$H$_5$)-(η^5-2,3-(SiMe$_3$)$_2$-C$_2$B$_4$H$_4$)Er]$_2$	Er–Cnt(C$_2$B$_3$) = 2.270 Er–av(C$_5$) = 2.631		217
[{η^5:η^7-[Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Er}$_2$]$^{4+}$	Er–C(C$_5$ring) = 2.758(5) Er–C(cage) = 2.421(5) Er–B(cage) = 2.739(5)		202c
[{[η^7-(3,5-(CH$_3$O)$_2$C$_6$H$_3$CH$_2$)$_2$-(C$_2$B$_{10}$H$_{10}$]Er(THF)}$_2$}]$_2{}^{2+}$	Er–C(cage) = 2.367(10) Er–B(cage) = 2.666(11)		202c
[η^5:η^6-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Er(THF)$_2$	Er–C(C$_5$ring) = 2.602(5) Er–C(cage) = 2.770(4) Er–B(cage) = 2.680(3) Er–O = 2.301(3)	Cnt–Er–Cnt = 118.4	223
[{[η^5:η^7-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Er}$_2$]$^{4+}$	Er–C(C$_5$ring) = 2.671(8) Er–C(cage) = 2.410(6) Er–B(cage) = 2.671(7)	Cnt–Er–Cnt = 135.6	223
[{η^5:η^7-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)}Er$_2$(μ-Cl)(THF)$_3$]$_2$	Er–C(C$_5$ring) = 2.597(4) Er–C(cage) = 2.386(5) Er–B(cage) = 2.655(7) Er–O = 2.388(3)		223
{Li(TMEDA)$_2$}$_2$-{*commo*-1-[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]-1-Er-[2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]}$_2$	Er–(2,3-Cnt) = 2.280 Er–(2,4-Cnt) = 2.319		203b
[η^6-{μ-1,2-[*o*-C$_6$H$_4$(CH$_2$)$_2$]-1,2-C$_2$B$_{10}$H$_{10}$}]ErCl(THF)$_3$	C$_{cage}$–C$_{cage}$ = 1.45(2) Er–av(C$_{cage}$) = 2.85(2) Er–av(B$_{cage}$) = 2.72(2) xEr–vC$_2$B$_4$ = 2.77(2)		238
[η^6-{μ-1,2-[*o*-C$_6$H$_4$(CH$_2$)$_2$]-1,2-C$_2$B$_{10}$H$_{10}$}$_2$Er]{Li$_5$(THF)$_{10}$}	C$_{cage}$–C$_{cage}$ = 1.486(6) av Er–C$_{cage}$ = 2.471(4) av Er–B$_{cage}$ = 2.680(4) av Er–C$_2$B$_4$ = 2.610(4)		238

(Continued)

Table 1 (Continued)

Compound	*E–X* (length, Å)	*X–Y–Z* (angle, deg)	*References*
$[\{\eta^6\text{-}[\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}]_2Er\}\{Na_5(THF)_6\}]_4$	$C_{cage}–C_{cage} = 1.558(6)$ av $Er–C_{cage} = 2.559(4)$ av $Er–B_{cage} = 2.654(4)$ av $Er–C_2B_4 = 2.622(4)$		238
$[\{[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Er(THF)\}_2]^{2-}$	$Er–av(C_{cage}) = 2.366$ $Er–av(B_{cage}) = 2.665$		242
$[\{[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Er(DME)\}_2]^{2-}$	$Er–av(C_{cage}) = 2.402$ $Er–av(B_{cage}) = 2.678$		242
$[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$	$Er–C(C_5 \text{ ring}) = 2.602(5)$ $Er–B(cage) = 2.680(3)$ $Er–C(cage) = 2.770(4)$	Cnt–Er–Cnt = 118.4	249
$[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4\text{-}(THF)_9\}]_n$	$Er–C(C_5 \text{ ring}) = 2.671(8)$ $Er–av(C_{cage}) = 2.410(6)$ $Er–av(B_{cage}) = 2.671(7)$	Cnt–Er–Cnt = 135.6	249
$[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)\text{-}(THF)_3]_2$	$Er–avC(C_5 \text{ ring}) = 2.597(4)$ $Er–av(C_{cage}) = 2.386(5)$ $Er–av(B_{cage}) = 2.655(7)$		249
$[\eta^6\text{-}\{\mu\text{-}1,2\text{-}(o\text{-}C_6H_4(CH_2)_2)(C_2B_{10}H_{10})\}\text{-}ErCl(THF)_3$	av Er–C(cage) = 2.85(2) av Er–B(cage) = 2.72(2) av $Er–C_2B_4 = 2.77(2)$		251
(9) Ytterbium			
$[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}Yb(NC_5H_5)_3\{Na(NC_5H_5)_2\}_{0.5}]_2\text{-}(\mu\text{-}C1)$	$C_{cage}–C_{cage} = 1.439(3)$ Yb–av $C_{cage} = 2.917(2)$ Yb–av $B_{cage} = 2.883(4)$ Yb–av $C_2B_4 = 2.894(4)$		238
$\{\{[\eta^7\text{-}Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})]_2Yb^{III}\}_2Yb^{II}\}\text{-}\{Na_8(THF)_{20}\}$	$Yb2–av(C_2 \text{ of } C_2B_5) = 2.446$ $Yb2–av(B_5 \text{ of } C_2B_5) = 2.770$ Yb1···B6 = 2.905(4) Yb1···B7 = 2.882(4) Yb1···B16 = 2.888(5) Yb1···B17 = 2.872(4)		224
$[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}Yb(NC_5H_5)_3]\{NaNC_5H_5)_2\}_{0.5}(\mu\text{-}Cl)$	Yb–av C(cage) = 2.917(2) Yb–av B(cage) = 2.883(4) $Yb–C_2B_4 = 2.894(4)$		238
(10) Lutenium			
$2,2',4,4'\text{-}(SiMe_3)_4\text{-}3,5',6'\text{-}[(\mu\text{-}H)_3Na(THF)_2]\text{-}1,1'\text{-}$*commo*$\text{-}Lu(\eta^5\text{-}2,4\text{-}C_2B_4H_4)_2$	$Lu–(C_2B_3 \text{ Cnt } 1,2) = 2.261, 2.230$	(Cnt 1)–Lu–(Cnt 2) = 138.3	207b,208
Heterocarborane Actinide Elements			
(1) Uranium			
$[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^-$	$U–av(C_2B_3) = 2.699, 2.738$ U–Br = 2.8293(14), 2.8397(14)	Br–U–Br = 93.7(3)°	319
$[U(\eta^5\text{-}Me_2C_2B_9H_9)I_2(THF)_2]^-$	$U–av(C_2B_3) = 2.791$ U–I(av) = 3.143	O–U–O = 145.8(3)° I–U–I = 110.95(4)°	319
$[\{\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U][K_2(THF)_5]\}_2]$	$U–av(\eta^6\text{-}C_2B_4) = 2.87$ Å $U–avC(\eta^7) = 2.43$ Å $U–avB(\eta^7) = 2.78$ Å	$Cnt(\eta^6)–U–Cnt(\eta^7) = 136.3°$	250

3.05.2 Metallacarboranes of *d*-Block Elements

3.05.2.1 Introduction

Our discussion will be restricted to metallacarboranes in which the *d*-block metal is incorporated into the polyhedral framework of the carborane. No attempt will be made to cover those compounds where the transition metal atom is in a bridging group linking several carborane polyhedra together or is involved solely as a member of a substituent group. Since much of the insight into the chemistry of the metallacarboranes is obtained from structural and bonding studies, this section will place as much emphasis on these aspects as on their reaction chemistry. Most of the complexes described will be those in which the metal group bonds to a pentagonal, C_2B_3, or a hexagonal, C_2B_4, open face of a *nido*-carborane. There are two atom arrangements, the "carbons adjacent" isomers where the cage carbons occupy adjacent positions, and the "carbons apart" isomers where the carbons are separated by boron atoms. Since both isomers seem to bind metals equally, they will be discussed together. Because of chemical similarities and related interests, the discussion will be divided into three large sections, dealing with the early transition metals (groups 3–5), mid-transition metals (groups 6 and 7), and the late transition metals (groups 8–12). Sections will also be devoted to linked cage and multi-decker complexes, and alkene, alkyne aryl-linked polymetallacarborane clusters.

3.05.2.2 Metallacarboranes of Early Transition Elements

During the past few years there have been reports on the syntheses and structures of sandwich compounds of metals in groups 3–5. These groups have similar structures and potential uses and will be discussed together.

The first known examples of metallacarboranes of early transition metals were contained in the 1975 report by Salentine and Hawthorne on the syntheses of the π-complexes of Ti, Zr, and V with the dianion, $[1,2\text{-}C_2B_{10}H_{12}]^{2-}$, or its *C,C′*-dimethyl derivative.[12] Soon after this initial publication, these investigators reported the synthesis of the series, $[M^{II}(C_2B_{10}H_{10}R_2)_2]^{2-}$ (M = Ti, V, Cr, Mn, R = H; M = Ti, Zr, Hf, V, R = CH_3), as well as the mixed ligand titanacarboranes of the formula $[C_xH_xTiC_2B_nH_{n+2}]^{m-}$ ($x = 5$, $n = 10$, $m = 1$; $x = 8$, $n = 9$ or 10, $m = 0$ or 1).[13] The crystal structure of the $\{4,4'\text{-}Ti[1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10}]_2\}^{2-}$, as its tetraethyl ammonium salt, showed that the titanium metal, in a formal oxidation state of 2+, was sandwiched between two dinegative C_2B_{10}-carborane cages.[14] Similarities in the spectra of this titanium complex and those of the other $[M^{II}(C_2B_{10}H_{10}R_2)_2]^{2-}$ complexes indicated that all had similar structures. It was found that the *commo*-metallacarboranes were much more stable than their metallocene analogs; this has been found generally to be the case when comparing the carborane and the Cp ligand systems. In addition, unlike titanocene and pentamethyltitanocene, the metallacarboranes showed no tendency to expand their coordination spheres and go from 14-electron to 16-electron configurations.[13] Despite the rather interesting initial results, the area of early transition metal metallacarborane chemistry has remained somewhat dormant until the last few years.

The first carborane analogs of yttrocene, $[Li(THF)_4]\{1\text{-}Cl\text{-}1\text{-}(THF)\text{-}2,2'\text{-}(SiMe_3)_2\text{-}3,3'\text{-}(R)_2\text{-}4,4',5,5'\text{-}Li(THF)[1,1'\text{-}commo\text{-}Y(2,3\text{-}C_2B_4H_4)_2]\}$ (R = $SiMe_3$ (Figure 1) and Me) and $\{Na(THF)_3\}_2\text{-}\{[1\text{-}(THF)\text{-}1\text{-}(\mu\text{-}H)_2\text{-}2,2',4,4'\text{-}(SiMe_3)_4\text{-}1,1'\text{-}commo\text{-}Y(2,4\text{-}C_2B_4H_4)_2]_2\}$ (Figure 2) were synthesized in 74–83% yields by the reactions of YCl_3 with

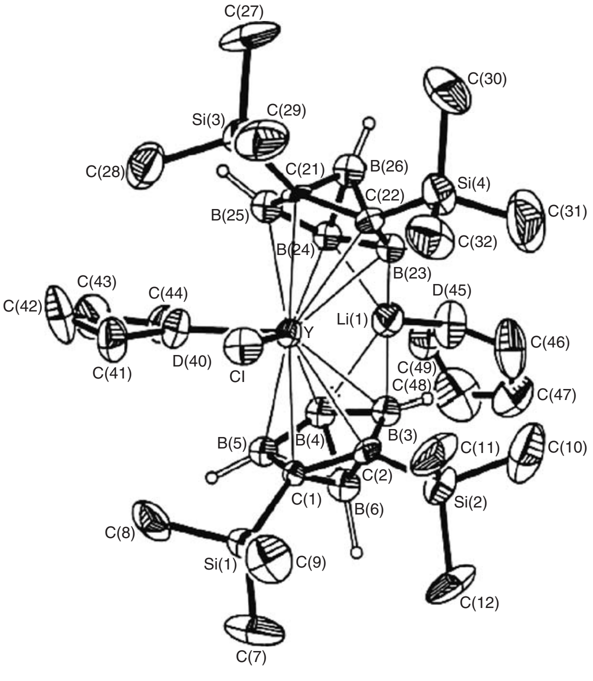


Figure 1 Crystal structure of a monomeric haloyttracarborane sandwich complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 3196.

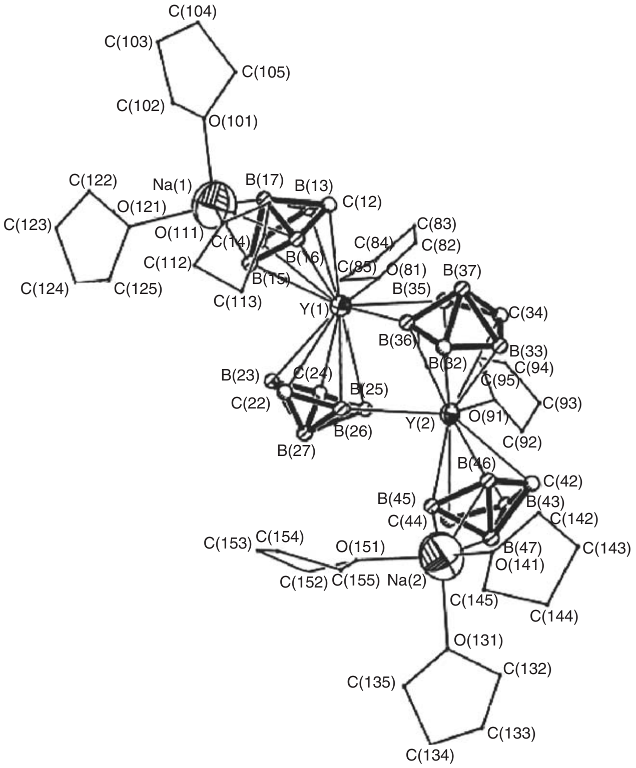
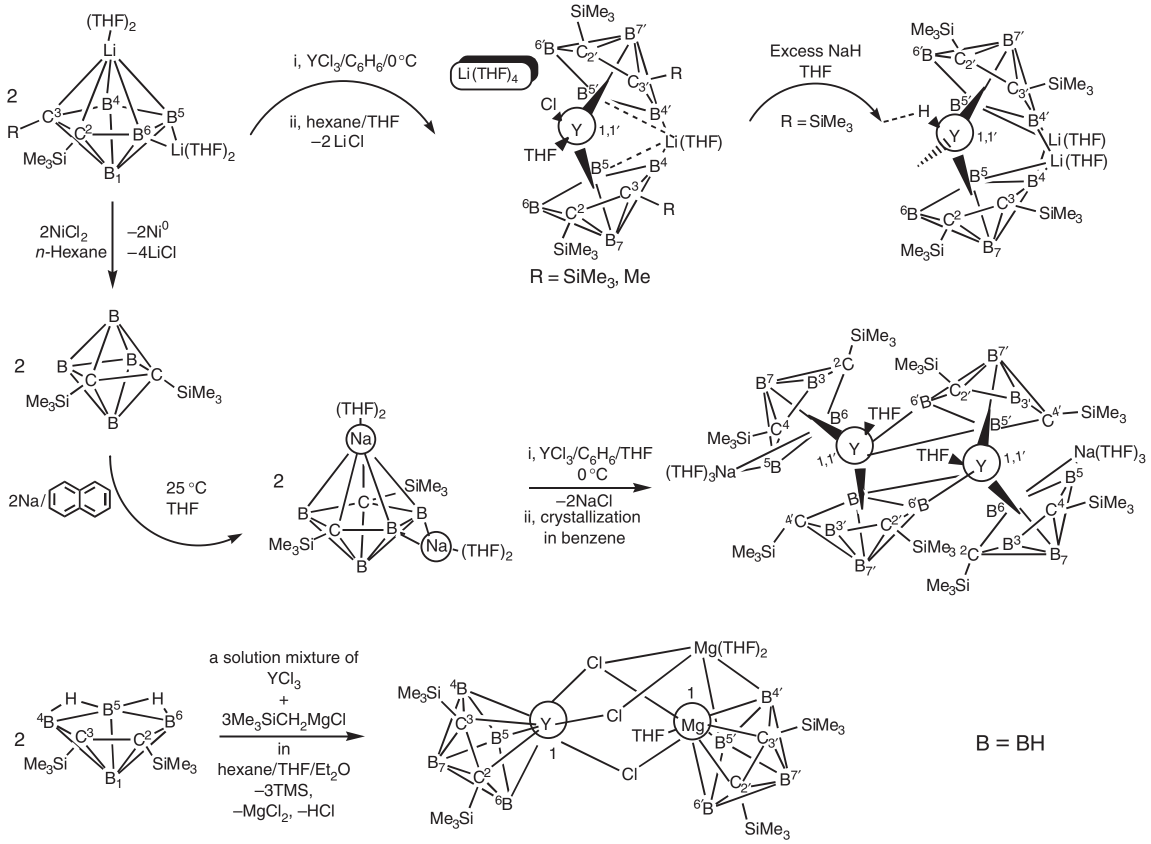


Figure 2 Crystal structure of a dimeric yttracarborane sandwich complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 3196.

the respective carborane dianions in 1 : 2 stoichiometries, as shown in Scheme 1.[15a] The yttracarboranes differ from their zirconium analogs in that, while the Cl and THF ligands in the latter complex were substitutionally inert, both could be removed from the former complex by reaction with NaH, to give the hydrido-complex, 1-H-2,2′,3,3′-$(\mathrm{SiMe_3})_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$\mathrm{C_2B_4H_4})_2$] (see Scheme 1). Although the structure of the hydride was not determined, it most likely exists as a dimer with two Y–H–Y bridge bonds and should better be formulated as {1-H-2,2′,3,3′-$(\mathrm{SiMe_3})_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$\mathrm{C_2B_4H_4})_2$]}$_2$. Dimer formation was also found in the “carbons apart” yttracarborane, {Na(THF)$_3$}$_2${[1-(THF)-1-(μ-H)$_2$-2,2′,4,4′-$(\mathrm{SiMe_3})_4$-1,1′-*commo*-Y(2,4-$\mathrm{C_2B_4H_4})_2$]$_2$} (Scheme 1). However, the direct synthesis of an alkyl-substituted yttracarborane proved unsuccessful. Scheme 1 shows the result of an attempted synthesis of such a complex by an initial reaction of $\mathrm{YCl_3}$ with the Grignard reagent, $\mathrm{Me_3SiCH_2MgCl}$, followed by reaction with the neutral carborane, *nido*-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_6}$, in a 1 : 2 molar ratio. The synthetic strategy was to first form the trialkyl compound, $\mathrm{Y(CH_2SiMe_3)_3}$, which would then form *closo*-1-Y($\mathrm{CH_2SiMe_3}$)-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_4}$ with the elimination of 2 equiv. of $\mathrm{Me_3SiCH_3}$ (TMS). Instead of the anticipated *closo*-yttracarborane, the mixed magnesa-/yttracarborane, *closo*-1-Y-{1,1′-(μ-Cl)$_2$-*exo*-[5,6-(μ-H)$_2$-Mg(THF)$_2$]-1,1′-(μ-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_4}$]}-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_4}$, was obtained (see Figure 3). The lower Y-Cnt distance (Cnt = ring centroid) in the mixed magnesa-/yttracarborane (2.308 Å, Figure 3), compared to that in the “carbons adjacent” (2.376 ± 0.013 Å, Figure 1) and the “carbons apart” (2.580 ± 0.036 Å, Figure 2) yttracarboranes, could be the result of steric factors. On the other hand, the Mg-Cnt distance of 2.032 Å found in the mixed complex is similar to the analogous Mg-Cnt distances in the half-sandwich complex, *closo*-1-(TMEDA)-1-Mg-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_4}$ (2.132 Å), and the full-sandwich complex, {*commo*-1,1′-Mg[2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_4}]_2\}^{2-}$ (2.018 Å).[16,16a]

The only other group 3 metallacarborane structural report was that of [Li(THF)$_3$]Li[Sc($\mathrm{C_2B_9H_{11}}$)(Cp*)(CH{Si(CH$_3$)$_3$}$_2$)]$_2$ (Cp* = [C$_5$(Me)$_5$]$^-$) in which the Sc was bonded to three centers, the Cp* centroid, the dicarbollide $\mathrm{C_2B_3}$ face centroid, and the C atom of the CH[Si(CH$_3$)$_3$]$_2$ group.[17,17a] The dimeric structure arose from the fact that two [Sc($\mathrm{C_2B_9H_{11}}$)(Cp*)(CH{Si(CH$_3$)$_3$)}$_2$]$^-$ units were loosely connected by one Li atom. It seems that the large coordinating ligands effectively prevented the Sc from increasing its coordination number to 4. One of the limitations



Scheme 1 Syntheses of the ''carbons adjacent'' and ''carbons apart'' yttracarboranes. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 3196.

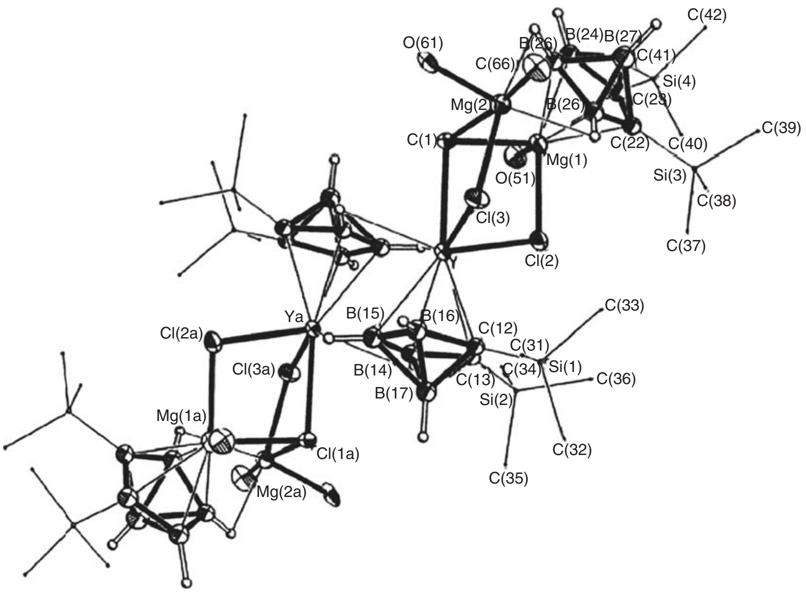
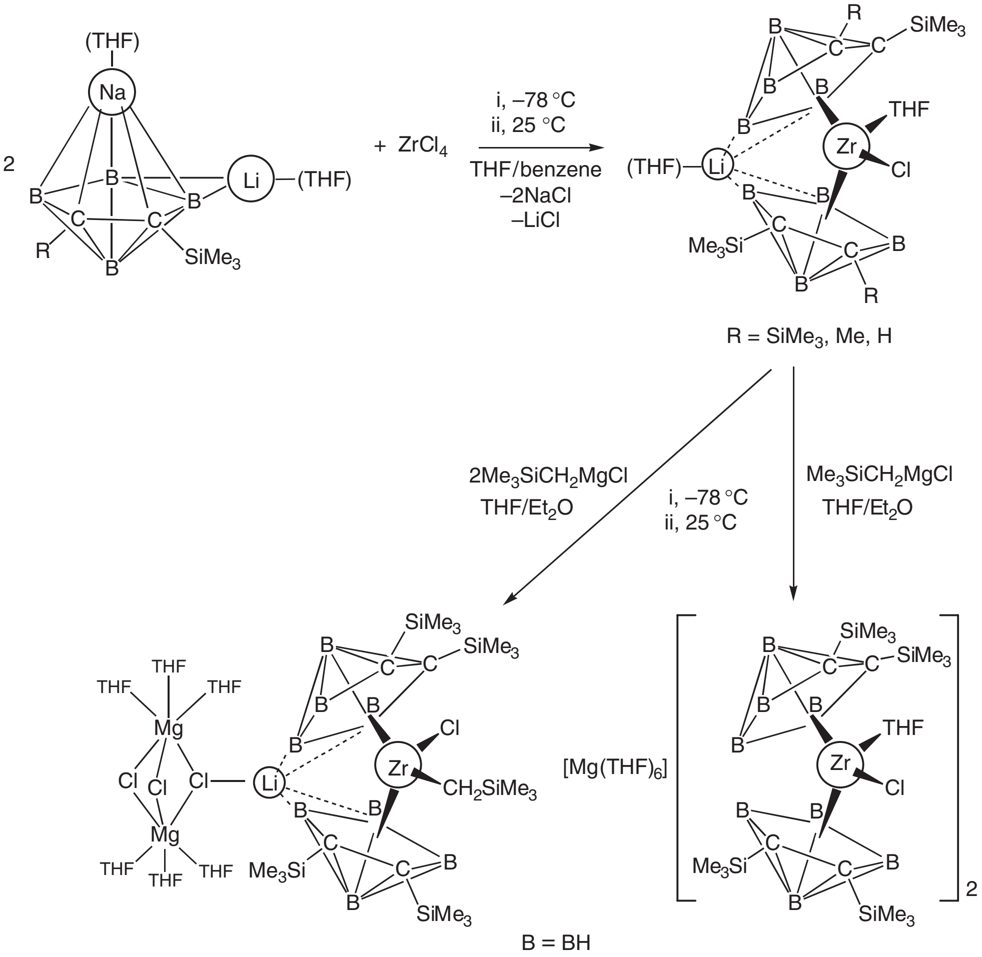


Figure 3 Crystal structure of a magnesium salt of mixed half-sandwich chloroyttra-/chloromagnesacarborane complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 3196.

of using carborane-ligand sandwich compounds of the group 3 metals as the bases for catalytic processes is that, with two dianionic ligands and a 3+ charge on the metal, the complexes are anionic, so that there is little possibility of adding reactive electron rich ligands, such as alkyls. Such an addition would be the first step in the potential use of these d^0 complexes as Ziegler–Natta type catalysts. The mixed carborane/Cp complexes offer a convenient solution to that problem. It would be anticipated that mixed complexes, such as the Sc species, or the purely carborane-based complexes, such as the yttrium bent-sandwich, should support α-olefin polymerization or oligomerization, as is found in many of the bent d^0 cyclopentadienyl complexes.[18,18a]

Because of their potential as homogeneous olefin polymerization catalysts, the group 4 metallacarboranes, where the transition metal is in a formal 4+ oxidation state, have been the subject of many studies. The first such complex was the zirconium(IV)–carborane sandwich, reported in the C_2B_4-cage system and synthesized as outlined in Scheme 2.[19a] One of the characteristics of these compounds was their ability, and tendency, to incorporate varying numbers of THF molecules of solvation, depending on the complex and conditions. The crystal structure of one of the zwitterionic zirconacarboranes (Figure 4) shows three THF molecules, two solvating the lithium and one coordinated to the zirconium. The most surprising and, from a practical standpoint, disappointing results were the products obtained by the reactions of chlorozirconacarborane with Me_3SiCH_2MgCl (see Scheme 2). A 1 : 1 molar ratio of the complex and the Grignard reagent resulted in the replacement of two Li^+'s by an Mg^{2+}, giving the ionic zirconacarborane. The only major alteration in the metallacarboranes is that a cation no longer occupies a bridging position on the zirconacarborane anions (see Figure 4). The same reaction with excess Me_3SiCH_2MgCl resulted in the formation of a complex double salt, in which a $Mg_2Cl_3(THF)_6$ moiety is associated with the bridging Li, with the



Scheme 2 Syntheses of zirconacarborane sandwich complexes. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 1365.

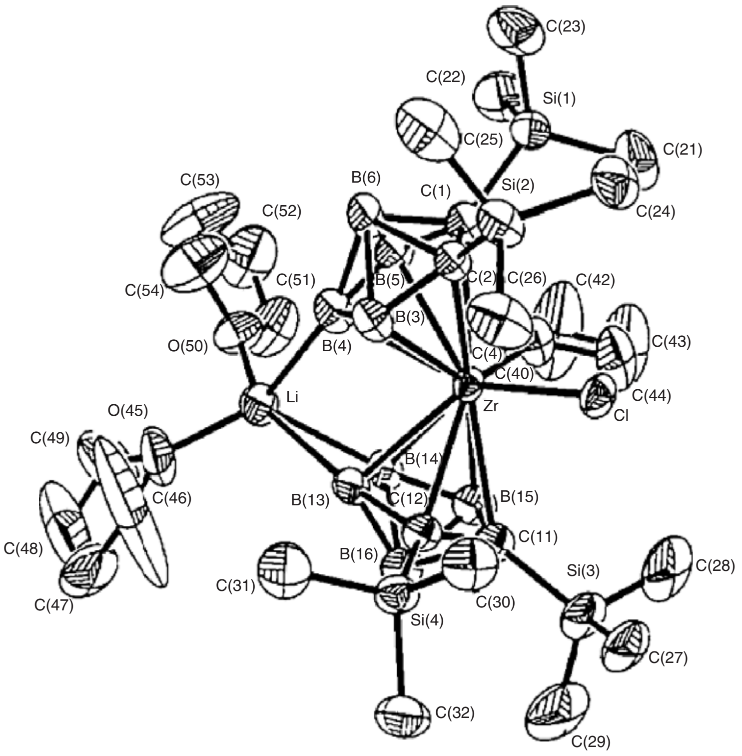
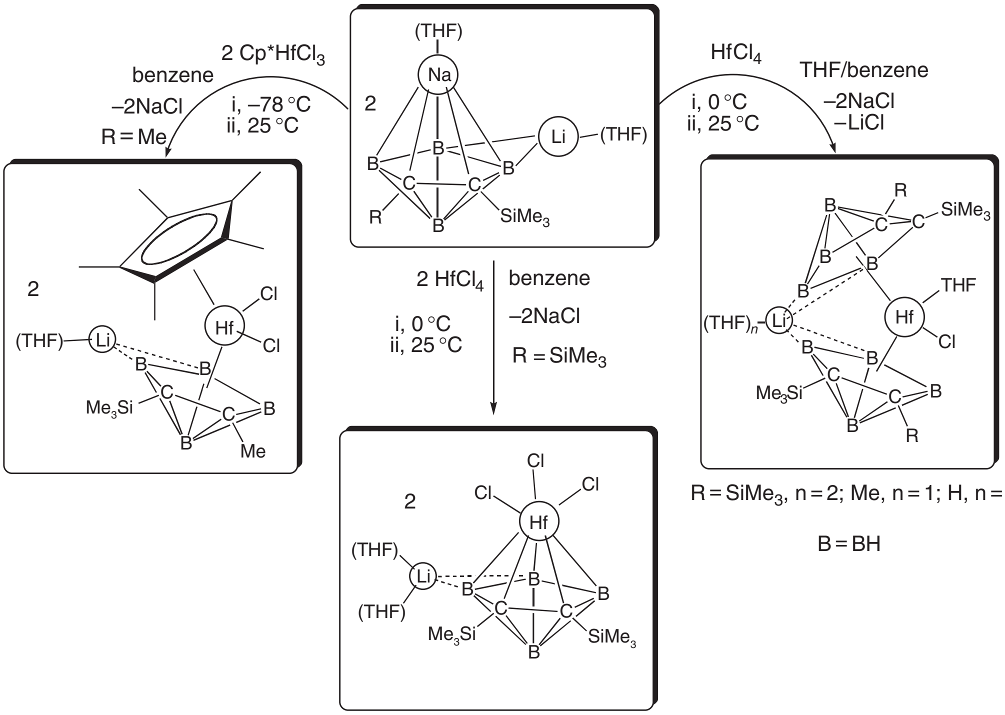


Figure 4 Crystal structure of a zwitterionic chlorozirconacarborane sandwich complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 1365.

zirconacarborane structure being little affected (see Scheme 2). The high (65%) yield of this compound indicates that it is a major product of the reaction of the chlorozirconacarborane with the Grignard reagent. The fact that an $[Me_3SiCH_2]^-$ replaced the THF in the primary coordination sphere of the zirconium demonstrates the inertness of the Zr–Cl bond; this is quite different from the behavior of corresponding chlorozirconocenes.[20,20a,20b] The corresponding *commo*-chlorohafnacarboranes, formed by the reaction of $HfCl_4$ and carborane in a 1 : 2 molar ratio, were found to have structures similar to that of the chlorozirconacarborane shown in Figure 4 (see Scheme 3).[21,21a] A 1 : 1 $HfCl_2$-to-carborane molar ratio produced the half-sandwich, $[Li(THF)_2][1,1,1\text{-}(Cl)_3\text{-}\textit{closo}\text{-}1\text{-}Hf\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]$. On the other hand, both 2 : 1 and 1 : 1 carborane-to-Cp^*HfCl_3 molar ratios produced exclusively the mixed-sandwich complex, $1,1'\text{-}(Cl)_2\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}4,5\text{-}Li(THF)\text{-}1,1'\text{-}\textit{commo}\text{-}Hf[(Cp^*)(\eta^5\text{-}2,3\text{-}C_2B_4H_4)]$ in 82% yield. While the formation of an alkali metal chloride is an important component of the driving force in these reactions, the stability (or inertness) of the resulting hafnacarboranes must also be considered. The formulas of all these compounds show that they contain the elements of LiCl, with the Cl's coordinated to the Hf metals and the Li's being present as *exo*-polyhedrally bound $Li(THF)_n{}^+$ cations. Despite that, they show little inclination to eliminate LiCl. It is an open question as to whether the three chlorides in the half-sandwich complex are equally coordinated to the hafnium to give a trichlorohafnium capping group, similar to those found in the MCl_3Cp^* (M = Zr or Hf) complexes,[22] or whether one Cl is more loosely bound to give an aggregate of a dichlorohafnacarborane and an LiCl. Since X-ray quality crystals of this could not be obtained and spectroscopic analysis could not resolve this question, there is no way at present to ascertain the exact nature of the capping group; the formulation as shown in Scheme 3 must be considered as tentative. In the same way, a number of other Zr(IV) and Hf(IV) sandwich complexes in the C_2B_9-carborane system has been synthesized.[23] It is of interest to note that these syntheses proceeded quite cleanly, while the reaction of $ZrCl_4$ with $Na_2C_2Me_2B_{10}H_{10}$ yielded only the $[Zr(C_2Me_2B_{10}H_{10})_2]^{2-}$ anionic complex in which the Zr was in a formal 2+ state. Moreover, cyclic voltametry of this Zr(II) complex showed no reversible oxidation or reduction waves.[12] Mixed $Cp^*/C_2B_9H_{11}$ bent-sandwich compounds of the form (Cp^*) $(C_2B_9H_{11})M(R)$ (M = Hf, Zr), where the metals are in 4+ states, have also been synthesized and characterized.[23]

The complex, $[Li(THF)_3]\{[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2](Cp^*)ZrCl_2\}$, was synthesized via reaction of $(Cp^*)ZrCl_3$ with the dianion, $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$.[24] This metallocene derivative can be described as an anionic, bent-sandwich



Scheme 3 Syntheses of hafnacarborane complexes. Reproduced by permission of the American Chemical Society from *Organometallics* **1999**, *18*, 516.

complex associated with an $[Li(THF)_3]^+$ cation via interaction with a B atom of the $[C_2B_4H_4(SiMe_3)_2]^{2-}$ cage as observed in its crystal structure analysis (Figure 5). The dianionic carborane and 5-pentamethylcyclopentadienide ligands are coordinated to the zirconium in an η^5 fashion; the coordination geometry about the Zr atom is that of a distorted tetrahedron defined by the two chlorides and the centroids of the pentamethylcyclopentadienyl and the

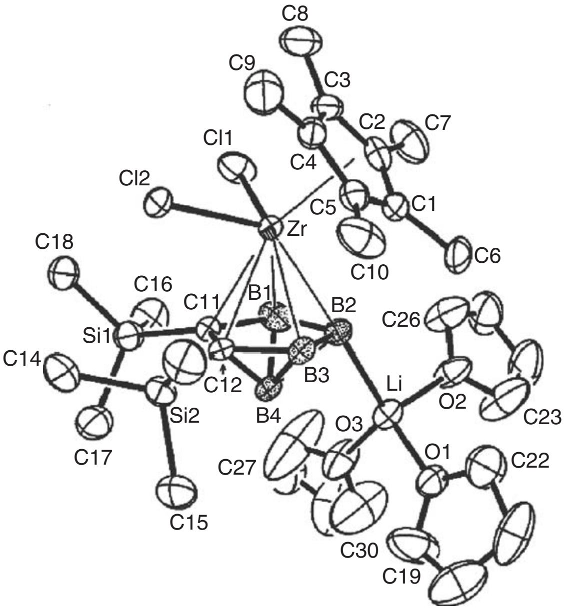


Figure 5 Crystal structure of a dichlorozirconacarborane derived from pentamethylcyclopentadiene and C_2B_4-carborane ligands. Reproduced by permission of Elsevier from *J. Organomet. Chem*. **1997**, *533*, 257.

carborane ligands. The Cl–Zr–Cl angle is 94.6(1)° and the (C_2B_3 centroid)–Zr–(C_5Me_5 centroid) angle is 131.3°. Attempts to synthesize zirconium silyl and alkyl complexes incorporating this carborane ligand did not prove successful.[24] Grimes and co-workers have synthesized bent-sandwich complexes of the mixed C_2B_4-carborane and Cp ligands, $Cp'MXY(R_2C_2B_4H_4)$ (M = Nb, Ta, R = $SiMe_3$, Me, Et, Cp′ = Cp or Cp^*, X, Y = Cl; M = Zr, R = Et, X = Cl, Y = THF, Cp′ = Cp or Cp^*).[25,25a] Crystal structures of several of the niobium and tantalum species showed bent-sandwich geometries, similar to that shown in Figure 5. Of particular interest are the reactions of $CpMCl_4$ with the cobaltacarborane anion, $Cp^*Co(Et_2C_2B_3H_4)^-$, which gave the bent triple-decker sandwich complexes, $Cp^*Co(Et_2C_2B_3H_3)M(Cl)_2Cp'$.[25,25a]

Somewhat different results were observed in the *C*-trimethylsilyl-substituted titanacarborane systems. The reaction of Cp_2TiCl_2 with the unsolvated "carbons adjacent" dilithium compounds, *closo-exo*-Li-1-Li-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H), produced the corresponding mixed ligand-sandwich titanacarboranes, [*commo*-1-Cp-1-Ti(III)-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$]$_2$ (R = $SiMe_3$ (Figure 6), Me, H).[26,26a,26b] Scheme 4 outlines the syntheses of the mixed ligand-sandwich Ti(III) complexes and their subsequent oxidation to the corresponding Ti(IV) complexes. The reactions represent an interesting series in that a 1 : 1 molar ratio reaction of the carborane dianion with Cp_2TiCl_2 produced the Ti(III) complex, [*commo*-1-Cp-1-Ti(III)-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$]$_2$, and dihydrofulvalene; the Ti(IV) could only be obtained by displacing the Ti(III) in the mixed-sandwich compounds with Ti(IV), to give [*commo*-1-Cp-1-Cl-1-(THF)-1-Ti(IV)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$], with a structure similar to that shown in Figure 4. The driving force for this last reaction was thought to be the formation of the stable $TiCl_3(THF)_3$. It is not known whether this reaction proceeds by an electron transfer or a substitution mechanism. Attempts to synthesize directly a Ti(IV) mixed ligand-sandwich complex by the reaction of the neutral *nido*-carboranes and Cp^*TiMe_3, following Jordan's successful synthesis of (Cp^*) (η^5-$C_2B_9H_{11}$)TiMe,[27] gave complex mixtures of products that could neither be separated nor characterized. Therefore, most of the synthetic efforts have involved the direct syntheses of Ti(III) complexes using $TiCl_3$ as the metallating agent.[26,26a,26b] Scheme 4 shows that the products of the reactions with $TiCl_3$ with the different dilithiacarborane compounds depended on steric factors arising from the nature of the cage-carbon substituents and the location of the cage carbons in the C_2B_3 bonding face of the carborane ligand. The structures of the different titanacarboranes have all been verified by single crystal X-ray diffraction studies.[26,26a,26b]

The only half-sandwich titanacarborane that could be formed was that of the "carbons apart" isomer, shown in Figure 7.[26a] At present, it is not known exactly why the "carbons apart" and "carbons adjacent" carboranes should give such different products when reacted with $TiCl_3$. It could be that, because of the intervening boron atom, the steric restrictions on additional coordination at the titanium imposed by the cage-carbon substituents would be somewhat tempered, allowing for the coordination of a chlorine atom and the large TMEDA molecule. Grimes and co-workers have recently reported the synthesis and reactivity of a series of 14-electron titanium complexes of the

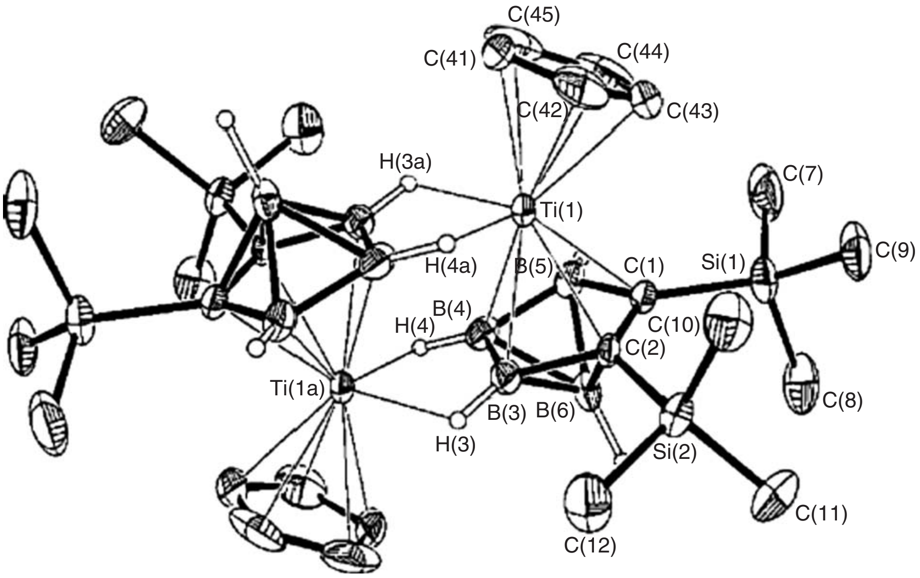
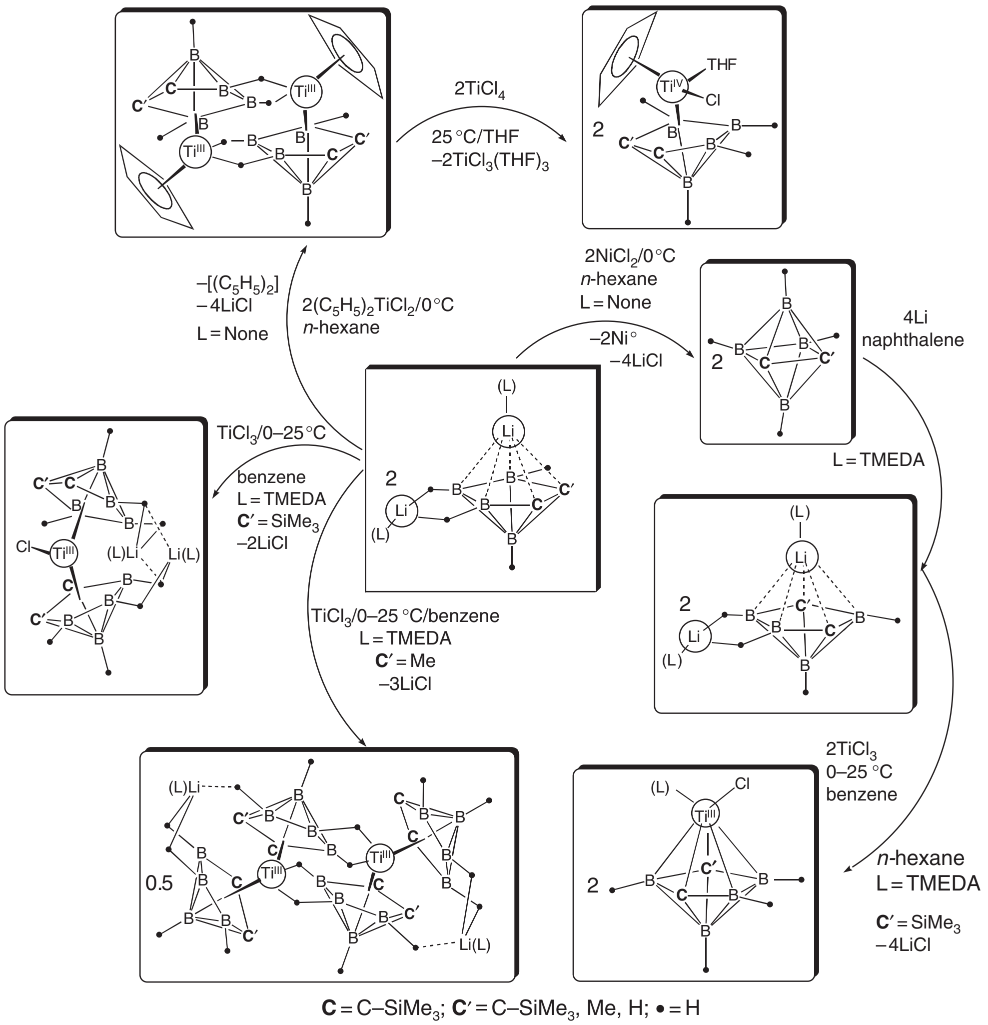


Figure 6 Crystal structure of the mixed ligand neutral metallacarboranes of titanium(III). Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 1365.



Scheme 4 Syntheses of the "carbons adjacent" and "carbons apart" titanacarboranes. Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 1365.

type $L_2Cl_2Ti(Et_2C_2B_4H_4)$ ($L_2 = 2PMe_3$, $Me_2P(CH_2)_xPMe_2$; $x = 2, 3$), $[Me_2P(CH_2)_3PMe_2]_2Me_2Ti(Et_2C_2B_4H_4)$, and a related zirconium complex, $L_2Cl_2Zr(Et_2C_2B_4H_4)$ ($L_2 = 2PMe_3$, $Me_2P(CH_2)_3PMe_2$).[28] These compounds were reported to be the catalyst precursors for the polymerization of ethylene at 1 atm pressure in the presence of methylaluminoxane (MAO). It was observed that the choice of phosphine ligand had a significant effect on catalytic activity.[28] Some of the titanium species, $L_2X_2Ti(Et_2C_2B_4H_4)$ ($L_2 = 2PMe_3$, X = Cl; dmpp, X = Cl, Me), have also been characterized by X-ray crystallography.[28] The general structural features are similar to that shown in Figure 7, except that the Ti has an extra Cl coordinated. Thus, these compounds, plus the bent Y, Zr, and Hf C_2B_4-carborane sandwich compounds discussed earlier, represent the initial phases of the syntheses of a class of 14-electron, d^0, bent-metallocene analogs, that could prove to be effective Ziegler–Natta type olefin polymerization catalysts.[20a]

An unusual Zr(IV) complex, $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_9]_2ZrCl_2\}\{Na(THF)_3\}_2{\cdot}THF$, and the corresponding Zr(II) species, $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_{10}]_2Zr\}\{Na(THF)_3\}_2$, were isolated from a single reaction in 8% and 49% yields, respectively.[29] The molecular geometries of these complexes are shown in Figures 8 and 9, respectively. The $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_{10}]_2Zr\}^{2-}$, shown in Figure 9, is the first structurally characterized example of a divalent zirconacarborane.[29] The reactivity patterns of these zirconacarboranes are expected to be significantly different from the *o*-carboranyl-appended zirconocene complex reported by the same investigators.[29a]

The carbonylation of $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})TiMe$ resulted in an unusual B–H activation, generating novel complexes containing linked carborane–alkoxide ligands.[30] However, dicarbollide analogs of the constrained-geometry complex,

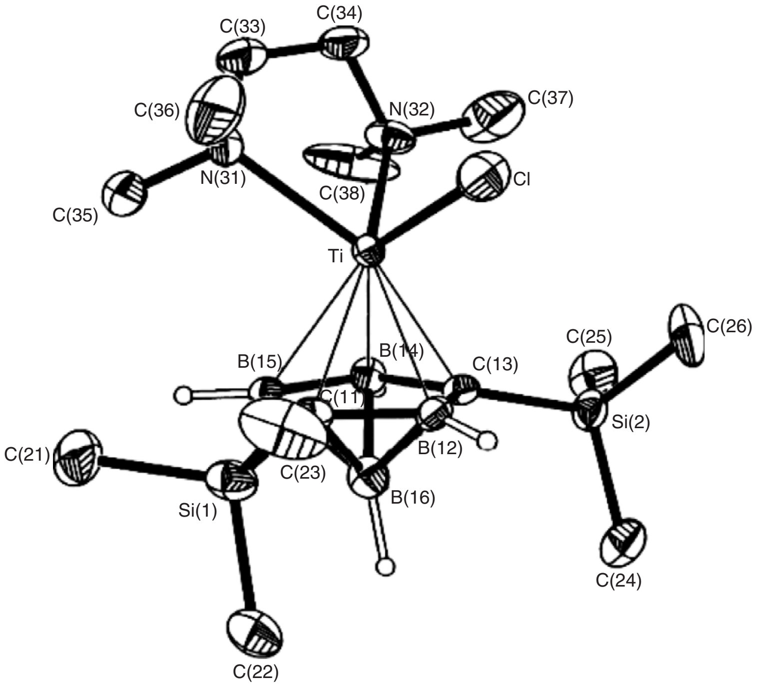


Figure 7 Crystal structure of a half-sandwich chlorotitanacarborane. Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 1365.

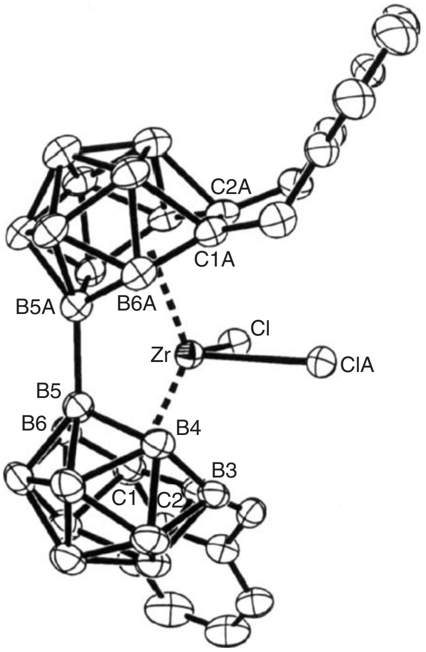


Figure 8 Crystal structure of the $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_9]_2ZrCl_2\}^{2-}$ complex. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 3098–3100.

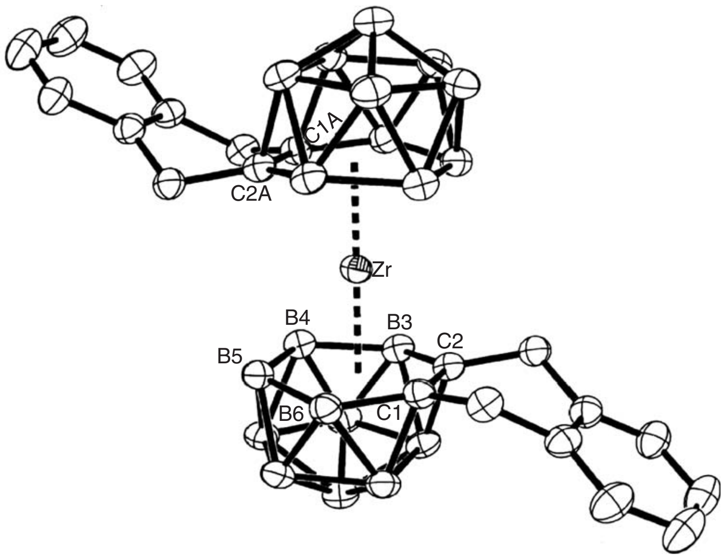


Figure 9 Crystal structure of the $\{[o\text{-}C_6H_4(CH_2)_2C_2B_{10}H_{10}]_2Zr\}^{2-}$ complex. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 3098–3100.

$[\eta^5:\eta^1\text{-}RC_2B_9H_9\text{-}CH_2NMe_2]TiCl_2$, in the presence of MAO, were found to exhibit moderate catalytic activities toward ethylene polymerization in yielding high molecular weight polymers.[31] The multidentate dicarbollide ligand, *nido*-7,8-$(NMe_2CH_2)_2$-7,8-$C_2B_9H_{11}$, was successfully employed in the formation of the corresponding constrained-geometry mono-titanacarboranes, $[\eta^5:\eta^1\text{-}(CH_2NMe_2)C_2B_9H_9\text{-}CH_2NMe_2]Ti(NMe_2)_2$; X-ray analysis showed that only one of the two tethered $–CH_2NMe_3$ groups was coordinated, the other was oriented away from the Ti atom.[32] Since the non-coordinated amine had the potential to react with another Ti, the titanacarborane was further allowed to react with $Ti(NMe_2)_4$ to produce the surprising oxygen-inserted trimetallic complex, $[\eta^5:\eta^1\text{-}(CH_2NMe_2)C_2B_9H_9CH_2NMe_2]Ti(NMe_2)_2\text{-}\mu_3\text{-}O\text{-}(Ti(NMe_2)_2)$ whose structure was determined by X-ray analyses (see Figure 10).[32] The source of oxygen atom in the complex was assumed to be trace

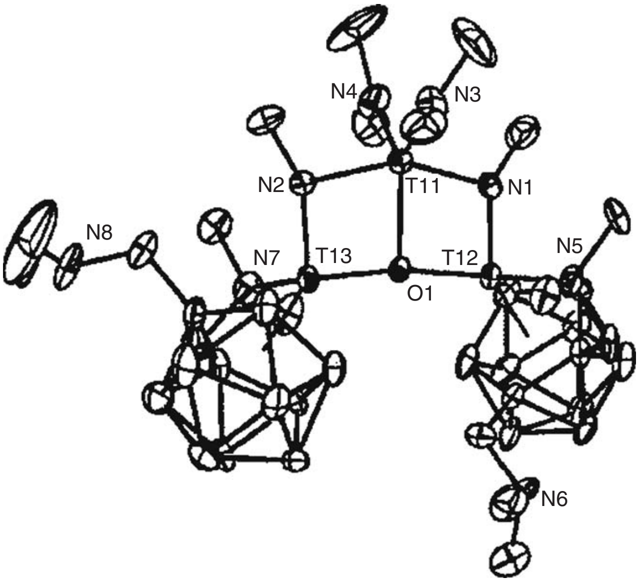


Figure 10 Crystal structure of $[\eta^5:\eta^1\text{-}(CH_2NMe_2)C_2B_9H_9CH_2NMe_2]Ti(NMe_2)_2\text{-}\mu_3\text{-}O\text{-}(Ti(NMe_2)_2$. Reproduced by permission of The Royal Society of Chemistry from Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun*. **2003**, 1364–1365.

quantities of water present in the solvent, toluene. This was verified by a controlled hydrolysis of a mixture of the mono-titanacarborane, $\text{Ti(NMe}_2)_4$, and H_2O.[32] Another series of constrained-geometry group 4 metal complexes of the dicarbollide ligands of the type, $[\eta^5\text{:}\sigma\text{-}{}^i\text{Pr}_2\text{NB(C}_9\text{H}_6)\ (\text{C}_2\text{B}_{10}\text{H}_{10})]\text{MX}_2$ (M = Ti, Zr, Hf; X = Cl, Me, NMe_2), derived from the ${}^i\text{Pr}_2\text{NB}$-bridged ansa-ligands.[33] The molecular structure of the compound where M = Zr and X = NMe_2, determined by X-ray analysis, showed that the Ti group was *exo*-polyhedrally bonded to carborane through a C(cage)–Ti bond.[33] While all of the complexes show catalytic activity for the polymerization of ethylene with MAO, the central metal ion and co-ligands were found to affect the catalytic performance in the order of $\text{Zr} \gg \text{Ti} > \text{Hf}$ and $\text{Cl} > \text{Me} \cong \text{NMe}_2$.[33]

The reaction of $(\text{Cp}^*)\text{HfMe}_3$ with $\text{C}_2\text{B}_9\text{H}_{13}$ gave the unusual dinuclear hafnium dicarbollide methyl complex, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^2\text{:}\eta^3\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{Cp}^*)\text{Me}_2$, in which a $(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf}$ unit was linked to a *nido*-$\text{C}_2\text{B}_9\text{H}_{11}$ unit through B–Hf–B bridge and two accompanying B–H–Hf links. The central *nido*-$\text{C}_2\text{B}_9\text{H}_{11}$ was in turn bonded to an *exo*-polyhedral $(\text{Cp}^*)\text{Hf(Me)}_2$ unit by three B–H–Hf bridges, as shown in Figure 11.[34] This complex reacts with terminal alkynes RC≡CH to produce, ultimately, a proposed $(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf(–C}{\equiv}\text{CR)}$ species that catalyzes the regioselective dimerization of RC≡CH (R = Me, ^{n}Pr, ^{t}Bu) to 2,4-disubstituted 1-buten-3-ynes $\text{CH}_2{=}\text{C(R)C}{\equiv}\text{CR}$ (see Scheme 5).[34a] The selectivity for dimer rather than trimer or higher oligomers results from a “self-correcting” mechanism in which the intermediate alkenyl complex (**5a** and **5b** in Scheme 5) that could potentially produce trimers or higher oligomers goes through an intramolecular cyclization reaction that ultimately produces the B-alkylated (**6a** and **6b** in Scheme 5) complex whose steric bulk prevents the formation of trimer in subsequent cycles.[34a]

The other group 4 metallacarboranes, derived from dicarbollide ligands, are those with a piano stool geometry $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{M(NR}_2)_2(\text{NHR}_2)$ (M = Zr, R = Et; M = Ti, R = Me, Et)[35] or an unusual sandwich complex, $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10})\text{Hf}(\text{Cp}^*)\ (\text{H})$,[36] in which the two $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}$ metal clusters are linked by a C–Hf bond from the $\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_2\text{B}_9\text{H}_{10}$ ligand and Hf–H–Hf and B–H–Hf bridges.[36] The latter compound, on reaction with RC≡CR and H_2, was found to form a complex that catalyzes the hydrogenation of additional RC≡CR alkynes to *cis*-alkenes.[36] It was proposed that the active species in this reaction is the mononuclear hydride, $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Hf(H)}$, that was formed by the initial RC≡CR/H_2 reaction.[36] Titanacarborane complexes of the general type, (Cp or $\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{TiMe}$,[37,38] were prepared by the methane elimination reaction of Cp or Cp^*TiMe_3 with *nido*-$\text{C}_2\text{B}_9\text{H}_{13}$ and the methodology was extended to synthesize the corresponding zircona- and hafnacarboranes.

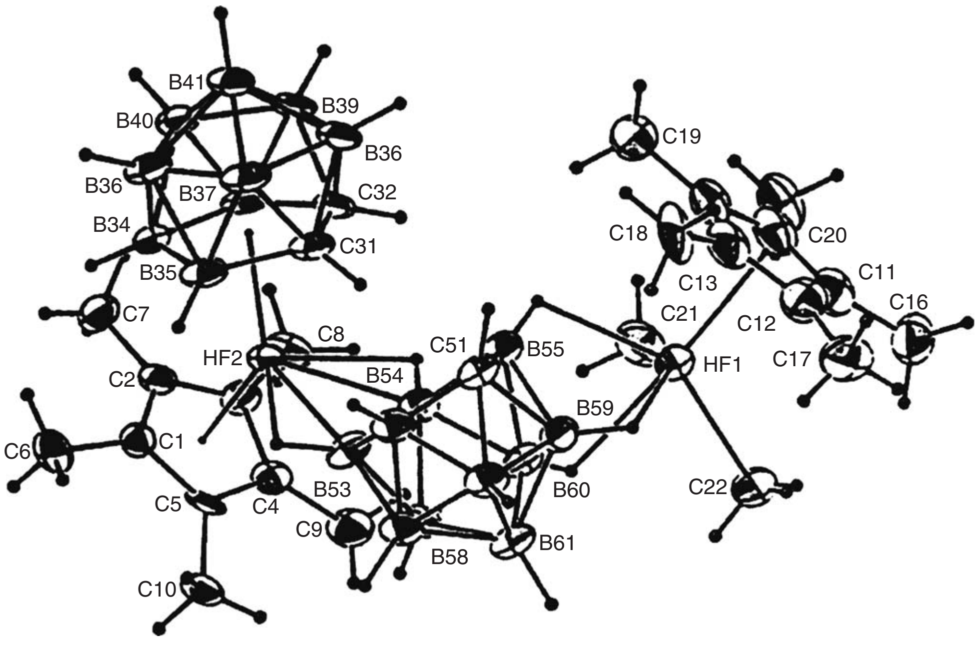
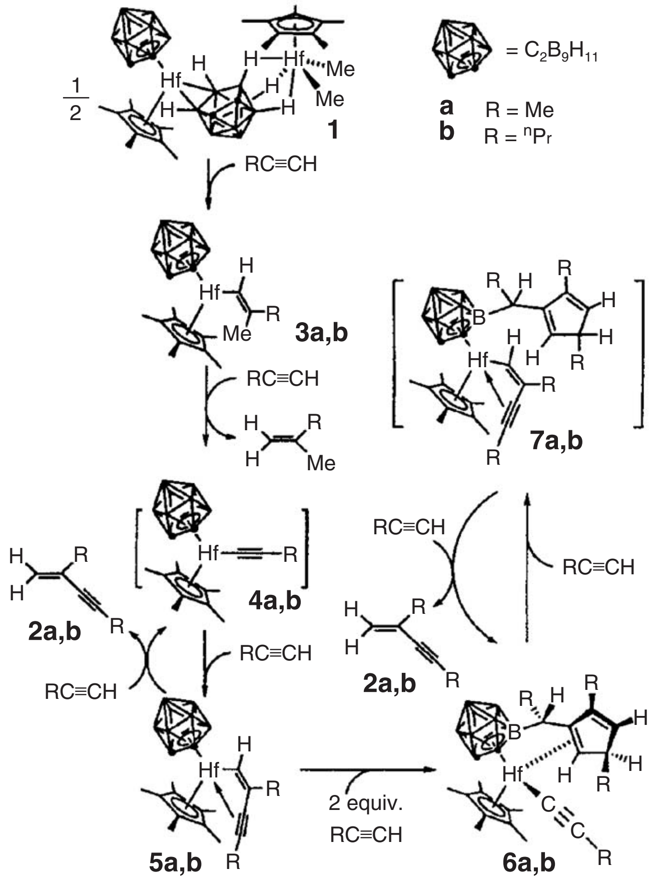


Figure 11 Crystal structure of $(\text{Cp}^*)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\mu\text{-}\eta^2\text{:}\eta^3\text{-C}_2\text{B}_9\text{H}_{11})\text{Hf}(\text{Cp}^*)\text{Me}_2$. Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc*. **1995**, *117*, 10403.



Scheme 5 Proposed mechanism for the catalysis of the dimerization of terminal alkynes by the mixed hafnacarborane complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 4508.

Grimes and co-workers have extended their initial study on the group 5 metallacarboranes[25,25a] by derivatizing the sandwich complexes of tantalum and niobium, $CpCl_2M(2,3\text{-}Et_2C_2B_4H_4)$ ($M = Ta$, Nb).[39] This was accomplished by the treatment of the parent species with elemental halogens or *N*-halosuccinimides to produce $B_{(unique)}$- or $B_{(basal)}$-substituted halo derivatives, and in some cases, all of the ring boron atoms were halogenated. These compounds in turn reacted with Grignard reagents to yield the corresponding B-alkyl and B-aryl-substituted complexes.[39] Similarly, the heterodinuclear bent triple-decker sandwich complex, $Cp^*Co(Et_2C_2B_3H_3)Cl_2Ta(Et_2C_2B_4H_4)$, discussed above, could be converted to the corresponding B-tribromo derivative.[39] While the alkyl- and aryl-substituted tantalacarboranes, $(Et_2C_2B_4H_4)CpTaR_2$ ($R = Me_3$, Ph), underwent insertion reactions with nitriles and isonitriles, the dimethyltantalacarborane undergoes clean photochemical insertion of alkynes to give vinyltantalum species, unlike their metallocene analogs that produce methylidyne intermediates.[40,40a,40b] The analogous diphenyltantalacarborane is thermally reactive, eliminating benzene and undergoing trapping reactions of the derived benzyne intermediate with alkynes. The structures of the resulting tantalaindene species have been confirmed by X-ray crystallography, protonolysis, and spectroscopy.[40b] The authors have hypothesized that a Ta–C fragment can undergo intramolecular insertion into a carborane B–H bond, a step unknown for cyclopentadienyl C–H bonds and one that is potentially relevant to the use of metallacarborane complexes as catalysts for olefin polymerization and related processes.[40b] On the other hand, the dichlorotantalacarborane, $(Et_2C_2B_4H_4)CpTaCl_2$, was converted to the corresponding hydridotantalacarborane dimer, $[(Et_2C_2B_4H_4)CpTa(H)]_2(\mu\text{-}Cl)_2$, by treatment with $LiAlH_4$ in THF which, in turn, underwent alkyne insertion with *p*-tolylacetylene to generate exclusively *trans*-$CpCl(p\text{-}MeC_6H_4\text{-}CH{=}CH)Ta(Et_2C_2B_4H_4)$. This product underwent reaction with anhydrous HCl to produce *p*-tolylstyrene while generating the original dichlorotantalacarborane catalyst.[40a]

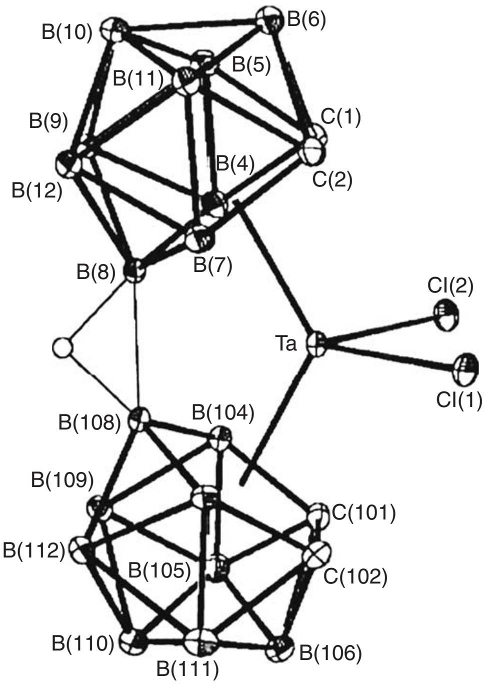


Figure 12 Crystal structure of $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$. Reproduced by permission of the American Chemical Society from *Organometallics* **2000**, *19*, 4858.

Group 5 metal bent metallacarboranes are isolobal and isoelectronic with (Cp or Cp*)$_2$ZrR$^+$ cations that are known to be active catalysts in olefin polymerization.[20a] In a continuation of their investigation in this area, Jordan *et al.* have synthesized the unusual linked tantalacarborane sandwich, $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$, from the reaction of $TaCl_5$ with 2 equiv. of $Li_2[C_2B_9H_{11}]$ in refluxing toluene through formal oxidative coupling of two dicarbollide ligands.[41] The structure of this tantalacarborane was determined by X-ray diffraction analysis (see Figure 12). Alkylation of this complex with $ZnMe_2$ produced $\{(\mu\text{-H})\ (C_2B_9H_{10})_2\}TaMeCl$ that still retained the B–H–B linkage between the two cages.[41]

A number of icosahedral metallacarboranes of Nb and Ta have been reported in recent years.[42,42a–42d] The general synthetic methodology involved group 5 M(NMe$_2$)$_5$ reagents (M = Nb, Ta) reacting with *nido*-$C_2B_9H_{13}$ to yield the corresponding 3,3,3-(NMe$_2$)$_3$-*closo*-3,1,2-$MC_2B_9H_{11}$ compounds. The resulting complexes react further by insertion of the metal–amide bonds with polar multiple bonds in CO_2 and CS_2, and with nitriles. Nitrile insertion gave rise to rare examples of the extensively delocalized strong π-donor N,N-dimethyl amidinate ligand; protic reagents can cleave the amide bonds. The isomeric 2,1,12- and 2,1,7-metallacarboranes were obtained from *nido*-2,9-$C_2B_9H_{13}$ and (Me$_3$NH) (*nido*-7,9-$C_2B_9H_{12}$). The cage-alkylated carborane, *nido*-11-Me-2,7-$C_2B_9H_{12}$, was metallated by Ta(NMe$_2$)$_5$ to give 4,4,4-(NMe$_2$)$_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$. The isomeric metallacarboranes, 3,3,3-(NMe$_2$)$_3$-4-Me-3,1,2-*closo*-$TaC_2B_9H_{10}$ and 2,2,2-(NMe$_2$)$_3$-3-Me-2,1,7-*closo*-$TaC_2B_9H_{10}$, were obtained from reaction of (Me$_3$NH) (*nido*-9-Me-7,8-$C_2B_9H_{11}$) and (Me$_3$NH) (*nido*-8-Me-7,9-$C_2B_9H_{11}$).[42,42a–42d] The chemistry of the imide- and amide-supported group 5 and 6 metallacarboranes has been summarized by Hughes.[42c]

The syntheses and structural characterizations of the vanadium and niobium monohalide tricarbadecaboranyl complexes, 1-(η^5-C_5H_5)-1-Br-2-Ph-1,2,3,4-$VC_3B_7H_9$, [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Ph-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$, [1-(η^5-C_5H_5)-1,1′-μ-Cl-2-Me-*closo*-1,2,3,4-$NbC_3B_7H_9$]$_2$, and *commo*-Nb-1-Cl-(4-Me-1,2,3,4-$NbC_3B_7H_9$)$_2$ have been reported.[43] The crystal structure confirmed that they are monohalo-complexes in which the V^{3+} and Nb^{3+} ions are sandwiched between Cp and/or tricarbadecaboranyl monoanions (see Figure 13 when M = Nb).[43] Unlike their metallocene counterparts, these complexes are air and water stable, further illustrating the unique ability of the tricarbadecaboranyl ligand to stabilize complexes with the metals in lower oxidation states. Because of their abilities to directly bind to biomolecules, many early transition metal metallocene dihalide complexes, such as (η^5-C_5H_5)$_2MX_2$ (M = Ti, V, Nb, Mo, W), have potent anti-tumor properties.[44,44a–44f] Although the vanadocene and niobocene complexes have proved to be active *in vivo* against Ehrlich ascites carcinoma growth in mice and against breast

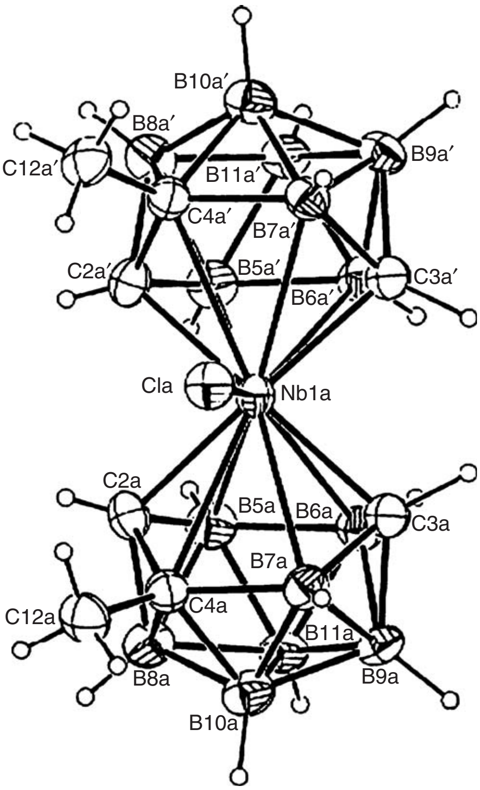


Figure 13 Crystal structure of the *commo*-Nb-1-Cl-(4-Me-1,2,3,4-NbC$_3$B$_7$H$_9$)$_2$ complex. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 2989.

cancer, their monohalo derivatives are extremely reactive toward both air and moisture and, consequently, they are unsuitable for bioapplications.[44,44a–44f] The remarkable air and water stability of the vanada- and nioba-tricarbadecaboranyl monohalide complexes gives hope that they will prove to have useful bioactivity properties that could be exploited. Whether or not that proves to be the case, the results do indicate that the stabilizing effect of the tricarbadecaboranyl ligand might generate a wide variety of early transition metal monohalide complexes with properties compatible with bioapplications.

3.05.2.3 Metallacarboranes of Mid-transition Metal Elements

In group 6, the first anionic chromium sandwich complex, [3,3′-Cr{1,2-(Me)$_2$-1,2-C$_2$B$_9$H$_9$}$_2$]$^-$, along with the corresponding mixed Cp/carborane analog, (η^5-Cp)Cr(C$_2$B$_9$H$_{11}$), were synthesized nearly 35 years ago by Ruhle and Hawthorne.[45] The crystal structure of the sandwich complex consisted of two icosahedral cages joined at the formal Cr(III) metal ion center.[46] Unlike the chromocenium analog and the mixed ligand complex, both of which were extremely moisture sensitive, the *commo*-chromacarborane was found to be so stable to hydrolysis that it was not affected even by hot, concentrated sulfuric acid.[45] Moreover, the complex showed no tendency to undergo either oxidation or reduction without cluster demolition.[45] On the other hand, it was reported that the Cr(III) sandwich complex of a C$_2$B$_4$-carborane system could easily be oxidized to the corresponding neutral Cr(IV) complex.[10,47] The anionic Cr(III) sandwich complexes of the type [1,1′-*commo*-Cr{2-(SiMe$_3$)-3-(R)-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ (R = SiMe$_3$, Me, H), having either Li(THF)$_4^+$ or Li(TMEDA)$_2^+$ counter ions, could be synthesized by the reactions of CrCl$_3$ and the corresponding THF-solvated lithium/sodium carborane double salts.[47] Chemical oxidation of the anionic Cr(III) sandwich species with PbCl$_2$ produced a diamagnetic, neutral Cr(IV) sandwich complex as a dark-red, air-sensitive, crystalline solid in 63% yield. Structures of the Cr(III) and Cr(IV) metallacarboranes, where R = SiMe$_3$, were essentially the same, indicating that the complexes are isostructural (see Figure 14). The Cr–C(cage) bond distances are shorter than those found in the corresponding icosahedral analog,[46] and about the same as those in the mixed ligand complex, 1-Cr(η^7-C$_7$H$_7$)-2,3-(Et)$_2$-2,3-C$_2$B$_4$H$_4$,[48] and in chromocene.[49]

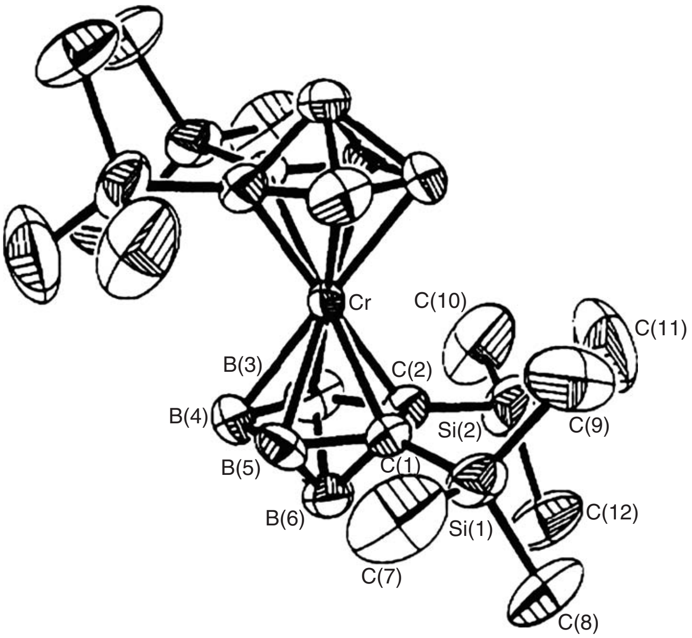


Figure 14 Crystal structure of the [1,1′-*commo*-Cr{2-(SiMe$_3$)-3-(R)-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ complex. Reproduced by permission of the American Chemical Society from *Organometallics* **1992**, *11*, 4202.

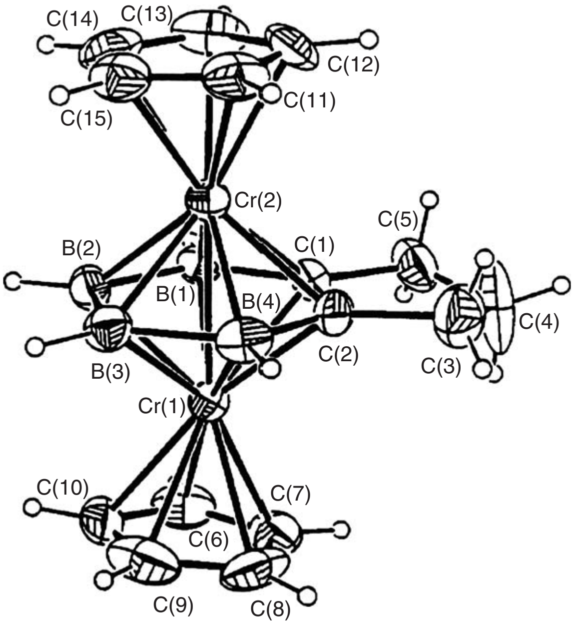


Figure 15 Crystal structure of the triple-decker complex, {(CpCr)$_2$(1,2-C$_3$H$_6$-1,2-C$_2$B$_4$H$_4$)}. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **1998**, *37*, 608.

An unusual 24-electron triple-decker chromium sandwich complex, {(CpCr)$_2$(1,2-C$_3$H$_6$-1,2-C$_2$B$_4$H$_4$)} (see Figure 15), was isolated by Fehlner *et al.*[50] in an attempt to synthesize Cp$^*_2$Cr$_2$B$_4$H$_8$. The hexagonal bipyramidal geometry of the complex is unique in metallacarborane chemistry and is not one of the polyhedra normally associated with eight-vertex closed clusters.[51] The available cluster bonding electrons are insufficient to meet the requirements of a single eight-vertex *closo*-cage.

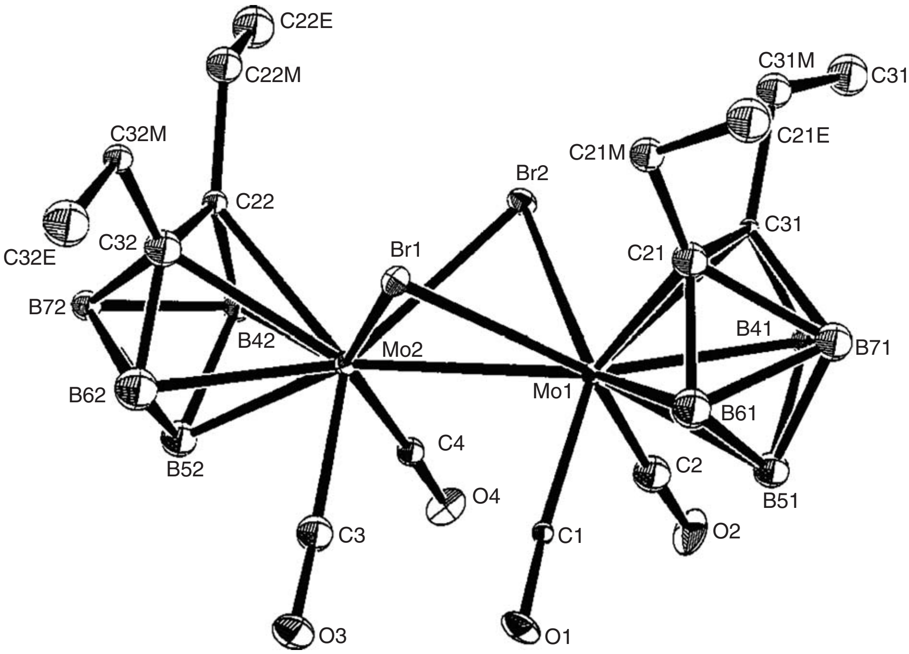


Figure 16 Crystal structure of the dimeric complex, $[(Et_2C_2B_4H_4)Mo(CO)_2]_2(\mu\text{-}Br)_2$. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **1998**, *37*, 102.

The dianionic molybda- and tungstacarboranes of the C_2B_4-cage systems have been reported by Grimes and co-workers, who have shown that the carborane dianion undergoes reactions with $(RCN)_3M(CO)_3$ (M = Mo, W; R = Me, Et) to produce the lithium salts of the corresponding metallacarboranes, $[(Et_2C_2B_4H_4)M(CO)_3]^{2-}$.[52] When treated with Ph_4PX in the presence of triflic acid, the molybdenum species subsequently forms the dimeric complex, $[(Et_2C_2B_4H_4)Mo(CO)_2]_2(\mu\text{-}X)_2$ (X = Cl, Br, I). The dimeric nature of the product was confirmed by X-ray crystallography that shows the two MC_2B_4 pentagonal pyramidal clusters that are linked via an intercluster metal–metal bond, as well as two halide bridges (see Figure 16).[52] Both the molybdenum and tungsten carbonyl species have also been incorporated into cobalt metal complexes to form the mixed metal multi-decker sandwich species (see Figure 17).[52]

The amine elimination reaction of *nido*-$C_2B_9H_{13}$ with $W(N^tBu)_2(NH^tBu)_2$ yields 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$; one of the remaining amide ligands can be substituted by 2,6-dimethylphenol, H_2O, or Me_3SiCl. MeCN inserts into the W–amide bond to give the *N,N*-dimethyl acetamidine adduct of $W(N^tBu)_2(C_2B_9H_{11})$, containing a hydrogen bond between the amidine and a bent imide. Structural studies reveal that the imide is the dominant π-donor in these complexes.[42,42a–42d,53]

A series of molybdenum and tungsten complexes $\{[(C_2B_9H_{11})M(\mu\text{-}SPh)_2]_2\}^n$ (M = Mo, W; $n = 2-$, $1-$, 0), were reported by Do and co-workers. These undergo novel redox cycles in which the cage C–C bonds are reversibly broken and reformed (see Scheme 6).[54] They are the first examples in the non-substituted 12-vertex systems of cage deformation leading to *semicloso*-structures; the C(cage)–C(cage) bond distances are 2.560 Å and 2.600 Å for the Mo and W complexes, respectively. Cage distortion versus the electron content feature of the dicarbollide ligand is clearly seen in this series. The *semicloso*- → *closo*-cage conversion occurs during the one-electron oxidation process; the reverse during a one electron reduction process (see Scheme 6). In the Mo complex the one-electron oxidation leads to a full closure of the C–C bond (1.663 Å), while with W only a partial closure is observed (C–C = 2.170 Å).[54]

A number of studies by Stone and co-workers have focused on the molybda- and tungstacarboranes. The earlier studies were on the reactivity of the bis(alkyne)carborane complexes of molybdenum and tungsten toward *tert*-butyl isocyanide in producing the corresponding molybda- and tungstacarboranes containing vinylcarbene ligand.[55] Their later work focused on the syntheses and reactivity of the monocarbon molybdacarborane anions, such as $[1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$ and $[2,2,2,2\text{-}(CO)_4\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]^-$.[56–58c] It was found that $Li[7\text{-}NHBu^t\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]$ reacted with $[Mo(CO)_6]$ in MeCN at reflux temperatures, followed by addition of $[N(PPh_3)_2]Cl$, to give $[N(PPh_3)_2][1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$.[56] The tungsten and chromium analogs were similarly obtained, but the latter was unstable and was isolated in low yield. An X-ray diffraction study of

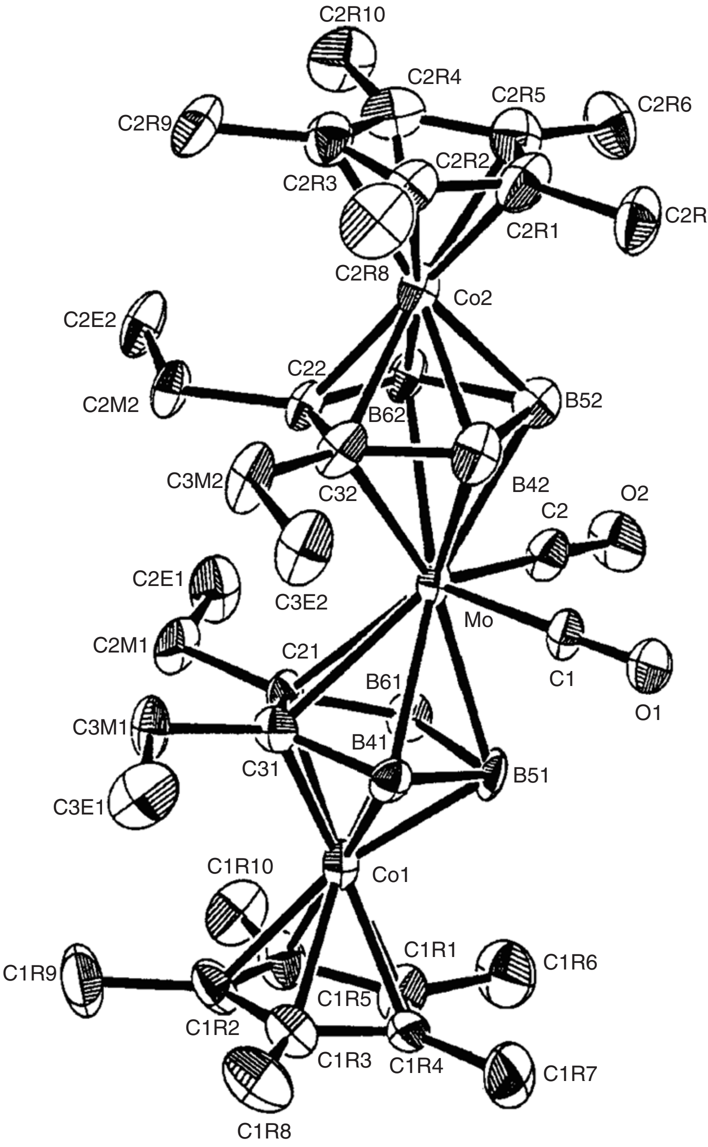
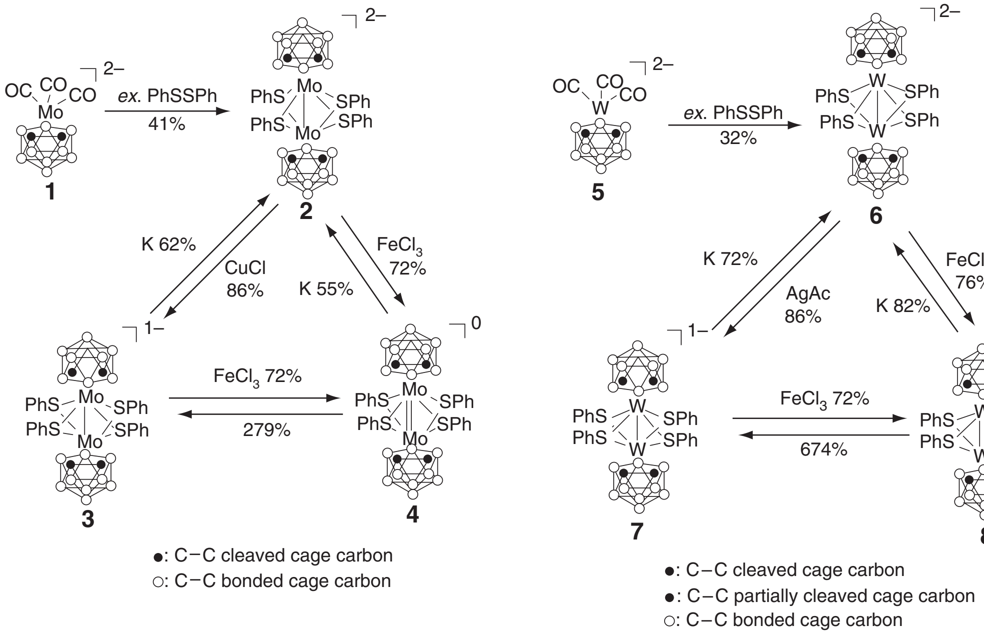


Figure 17 Crystal structure of the tetradecker [Cp*Co(Et$_2$C$_2$B$_3$H$_3$)]$_2$Mo(CO)$_2$. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **1998**, *37*, 102.

the tungstacarborane confirmed that the *exo*-polyhedral NHBu^t group formed a bridge between the cage-carbon atom and the tungsten. For the molybdacarborane, this intramolecular donor bond is lifted on protonation in the presence of donor molecules L (CO, PPh$_3$, PMe$_3$, PEt$_3$, PMe$_2$Ph) to give the zwitterionic complexes [1-NH$_2$Bu^t-2,2,2-(CO)$_3$-2-L-*closo*-2,1-MoCB$_{10}$H$_{10}$]. In contrast, protonation with HCl gives a salt [N(PPh$_3$)$_2$][1-NH$_2$Bu^t-2,2,2-(CO)$_3$-2-Cl-*closo*-2,1-MoCB$_{10}$H$_{10}$]. The molybdacarborane, [1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^-$, can be converted to the bimetallic compounds [*exo*-{Cu(PPh$_3$)}-1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$], [1,2-μ-NHBu^t-2-{Au(PPh$_3$)}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$], and [Au(PPh$_3$)$_2$][2,2′-μ-Au-{1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$}$_2$]; the structure of the latter compound shows that the two MoCB$_{10}$H$_{10}$ cages are joined through an almost linear, 170.8°, Mo–Au–Mo bond.[56] The CO ligands in the tetracarbonyl complex, [2,2,2,2-(CO)$_4$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^-$, could be substituted for CNBu^t and oxidized by iodine, to give the Mo(IV), 2-I-2,2,2-(CNBu^t)$_3$-2-L-2,1-MoCB$_{10}$H$_{11}$ (L = CNBu^t or CO, depending on the CNBu^t:complex reaction ratio).[57,58,58a–58c] Reaction with just I$_2$ in THF gave the zwitterionic complex, [2,2,2-(CO)$_3$-2-I-7-{O(CH$_2$)$_4$}-2,1-*closo*-MoCB$_{10}$H$_{10}$]$^-$, oxidation by I$_2$ in the presence of thioethers gave similar thioether-substituted isomers.[57,58,58a–58c] The metal oxidation versus cage



Scheme 6 Redox cycles of 3,3,3-$(CO)_3$-3,1,2-$MC_2B_9H_{12}$ (M = Mo, W). Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc*. **2001**, *123*, 9054.

substitution was further explored in molybda- and tungstacarboranes in a series of experiments to conclude that these metallacarboranes do not react readily with $CNBu^t$, ethers, or thioethers at ambient temperatures, but only in the presence of iodine.[57,58,58a–58c] The nature of the products isolated thereafter depends greatly on whether the donor molecules present are those of $CNBu'$ or are those of a dialkyl sulfide or THF. With the isocyanide present, the metal is oxidized and the cage adopts its classical spectator role in the complexes. On the other hand, if sulfides or THF are present, the metal retains its formal M(II) oxidation state with the carborane cage becoming mono- or disubstituted.[58,58a–58c]

A 13-vertex molybdacarborane, $[4\text{-}(\eta\text{-}C_3H_5)\text{-}4\text{-}(CO)_2\text{-}4,1,6\text{-}closo\text{-}MoC_2B_{10}H_{12}]^-$, was prepared and structurally characterized by Welch and co-workers.[59] The polarization of the frontier orbitals of the carborane away from the cage carbons, giving rise the an increase in the *trans*-effect of the BBB side if the C_2B_4 carborane face compared to the CBC side, was used to rationalize the orientation of the allyl ligand in the $\{Mo(C_3H_5)\ (CO)_2\}$ over the CBC part of the face. This molybdacarborane displays fluxionality in solution at room temperature, with an activation energy for the presumed double diamond-square-diamond fluxional process calculated to be *ca.* 40 kJ mol^{-1} by analysis of its ^{1}H NMR spectrum.[59]

The manganese or rhenium (group 7) complexes of a number of carborane ligand systems have been known since the original report on $Cs[(C_2B_9H_{11})M(CO)_3]$ (M = Mn(I) or Re(I)) by Hawthorne and Andrews in 1965.[60] However, most of the reported manganacarborane complexes were the half-sandwiched *closo*-species with an $Mn(R_3P)_x(CO)_{3-x}$ (R = alkyl or aryl group; $x = 0$, 1, or 2) unit occupying a vertex of either an icosahedron or one of its lower homologs.[61,61a] Until recently, the only known *commo*-manganacarboranes have been the anionic complexes of the types $[4,4'\text{-}Mn^{II}(1,6\text{-}C_2B_{10}H_{12})_2]^{2-}$ and $[Mn^{IV}(CB_{10}H_{11})_2]^{2-}$, whose geometries could not be confirmed by X-ray crystallography.[13,62] The synthesis and crystal structure of a zwitterionic and paramagnetic manganese sandwich complex, $\{[Li(THF)]\ [Li(TMEDA)]_2\}\{commo\text{-}Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}$, has since been reported.[63] The synthetic pathway to this compound is given in Equation (1) and its structure is shown in Figure 18.

$$9Na(THF)Li[2,3\text{-}(SiMe_3)_2C_2B_4H_4] + 6MnCl_2 \xrightarrow[\text{ii, Hexane/THF/TMEDA}]{\text{i, THF 0 °C, 1 h and 25 °C, 24 h}} 3LiCl + 9NaCl$$
$$+\ 2\{[Li(THF)][Li(TMEDA)]_2\}\ \{commo\text{-}Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}$$
$$+\ closo\text{-}1,2\text{-}(SiMe_3)_2\text{-}1,2\text{-}C_2B_4H_4 \qquad (1)$$

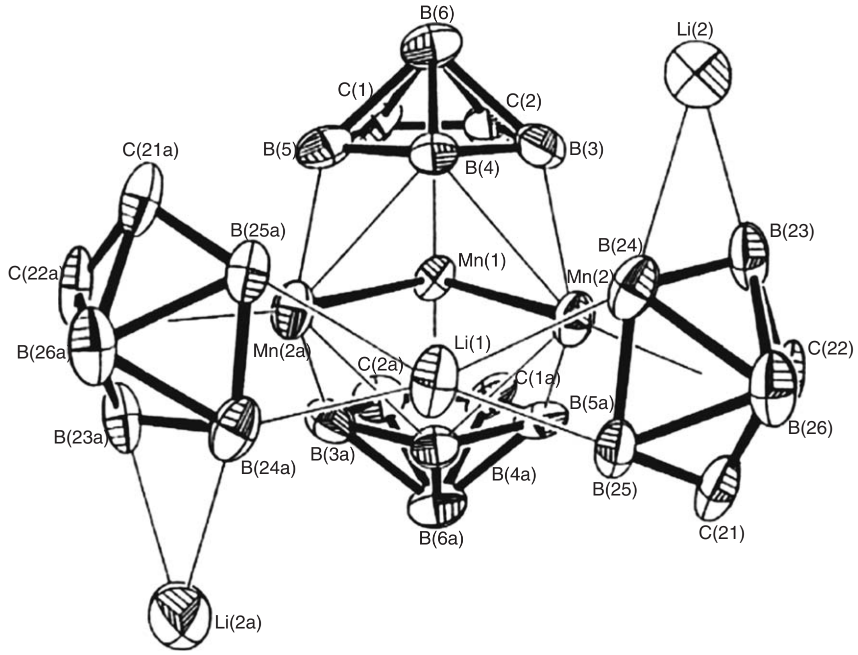


Figure 18 Crystal structure of the trimetallic, $\{$*commo*-$Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}^{2-}$. Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc*. **1991**, *113*, 8531.

Figure 18 shows that the complex has a "butterfly" structure in which the three Mn atoms are coordinated by the carborane ligands and form a central trigonal plane. There seems to be no direct interaction between the two terminal Mn atoms, and all metal–metal interactions take place through the central Mn atom. The central Mn atom is essentially η^5-bonded to two parallel C_2B_3 carborane faces, with metal to cage-atom distances ranging from 2.155 to 2.249 Å. These are significantly shorter than the Mn–C bond distances of 2.42 Å found in the corresponding high-spin Cp analog.[64] The "butterfly" geometry of the complex is presumably stabilized by direct Mn–Mn bonding and by the additional interaction of the terminal Mn atoms with the unique and basal borons on the central manganese sandwich. In a formal sense, the Mn complex is a trimetallic cluster composed of both a sandwich (*commo*) and two half-sandwich (*closo-*) geometries.

An entirely different result was obtained by the reaction of the trinuclear half-sandwich gadolinacarborane cluster, $\{$*closo*-$Gd_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3$-($\mu$-*closo*-$Li_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3$)-[$\mu$-Li(THF)]$_3$-($\mu_3$-OMe)($\mu_3$-O)$\}$,[65,66] with $MnCl_2$. The product of this reaction was a simpler manganacarborane, 3,3′,4,4′-Mn(TMEDA)-*commo*-Mn[2,3-$(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ (see Figure 19).[66] The crystal structure of the cluster clearly shows that an Mn atom, formally in 2+ oxidation state, is coordinated to two somewhat parallel carborane cages. For charge balance, an additional *exo*-polyhedral Mn^{II}(TMEDA) unit is present within the coordination sphere and interacts strongly with two borons of each cage as well as with the central Mn atom (Mn–Mn = 2.665 Å). The incorporation of a second metal atom into the structure of a sandwich complex as a counter ion has been observed previously in the carborane complexes of Sc, Y, Zr, and Hf.[5,5a,5b]

A high-yield method for the synthesis of $[M(CO)_3(\eta^5\text{-}2,3\text{-}C_2B_9H_{11})]^-$ and *rac*-$[M(CO)_3(\eta^5\text{-}2\text{-}(CH_2CH_2CO_2H)\text{-}2,3\text{-}C_2B_9H_{10})]^-$ from $[M(CO)_3Br_3]^{2-}$ (M = Re, ^{99}Tc) has been developed by Valliant *et al.*[67] The general approach involved the addition of *nido*-$[(C_2B_9H_{12})^-]$, or the acid-substituted analog, to $[M(CO)_3Br_3]^{2-}$ (M = Re, ^{99}Tc) in the presence of TlOEt in THF. The TlOEt deprotonated the carborane, producing a insoluble salt, and addition of a THF solution of $[NEt_4]_2[M(CO)_3Br_3]$ led to solubilization, followed by rapid precipitation of TlBr. After refluxing overnight, the complexes were isolated in 80% (Tc) and 93% (Re) yields. The *rac*-$[M(CO)_3(\eta^5\text{-}2\text{-}(CH_2CH_2CO_2H)\text{-}2,3\text{-}C_2B_9H_{10})]^-$ was synthesized in a similar way starting with $[7\text{-}(CH_2CH_2CO_2H)\text{-}7,8\text{-}C_2B_9H_{11}]^-$. The resulting rhena- and technacarboranes were characterized spectroscopically and their structures were determined by X-ray crystallography.[67] The crystal structure of ^{99m}Tc(I)-complexed metallacarborane, $[Tc(CO)_3(\eta^5\text{-}2,3\text{-}C_2B_9H_{11})]^-$, is shown in Figure 20. The metal to C_2B_3-centroid distance is 2.32 Å, which is nearly identical to the corresponding distance reported for the Re complex.[68] The carborane cage itself appears to be a slightly irregular icosahedron with the average B–B, B–C, and C–C bond distances being 1.76, 1.71, and 1.60 Å, respectively. This is the first

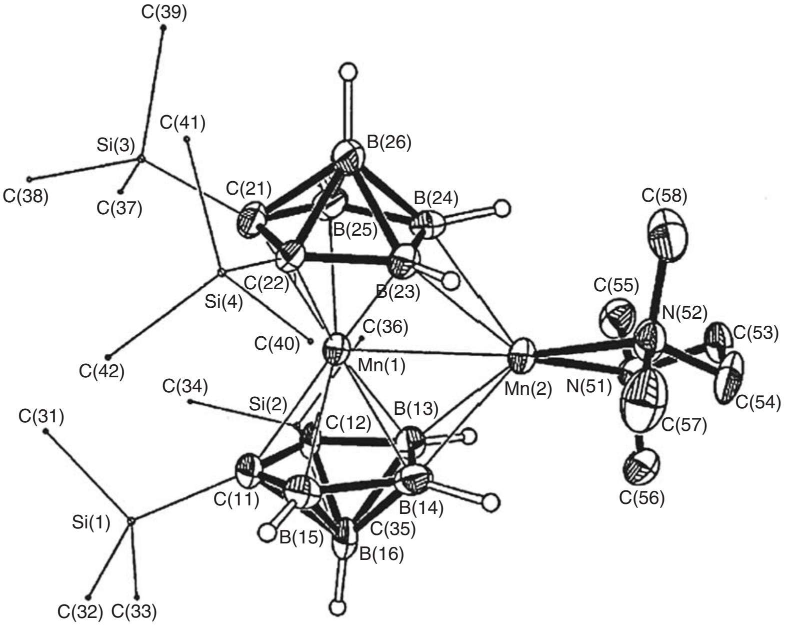


Figure 19 Crystal structure of the wedged manganese complex, 3,3′,4,4′-Mn(TMEDA)-*commo*-Mn[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$. Reproduced by permission of the American Chemical Society from *Organometallics* **1996**, *15*, 626.

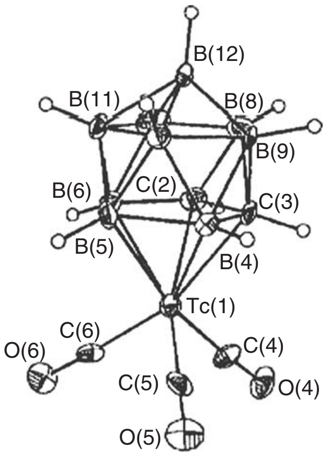


Figure 20 Crystal structure of $[Tc(CO)_3(\eta^5\text{-}2,3\text{-}C_2B_9H_{11})]^-$. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **2002**, *41*, 628.

Tc-carborane complex reported to date. A new method for the preparation of Re- and ^{99m}Tc-metallacarboranes in water under mild reaction conditions was later developed by the same investigators.[67a]

The rhenacarborane salt $Cs[Re(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$[69] has been used to synthesize the tetranuclear metal complex $[\{ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3\}_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$, where two $[ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3]$ fragments are bridged by a single 1,2-bis(diphenylphosphino)ethane ligand.[70] Reaction of this precursor rhenacarborane salt with $Ag[BF_4]$ in the presence of the ligands bis- or tris(pyrazol-1-yl)methane yields the complexes $[ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3\{\kappa^2\text{-}CH_2(C_3H_3N_2\text{-}1)_2\}]$ or $[\{ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3\}_2\{\mu\text{-}\kappa^1,\kappa^2\text{-}CH(C_3H_3N_2\text{-}1)_3\}]$, respectively. From X-ray diffraction analyses, the former complex comprises a $(CO)_3ReC_2B_9H_{10}$ fragment, bonded to an Ag by an Re–Ag bond and a B–H–Ag bridge; the Ag center is attached to a bis(pyrazol-1-yl)methane coordinating in an asymmetric κ^2 mode. The latter complex was found to contain a tris(pyrazol-1-yl)methane bridging two

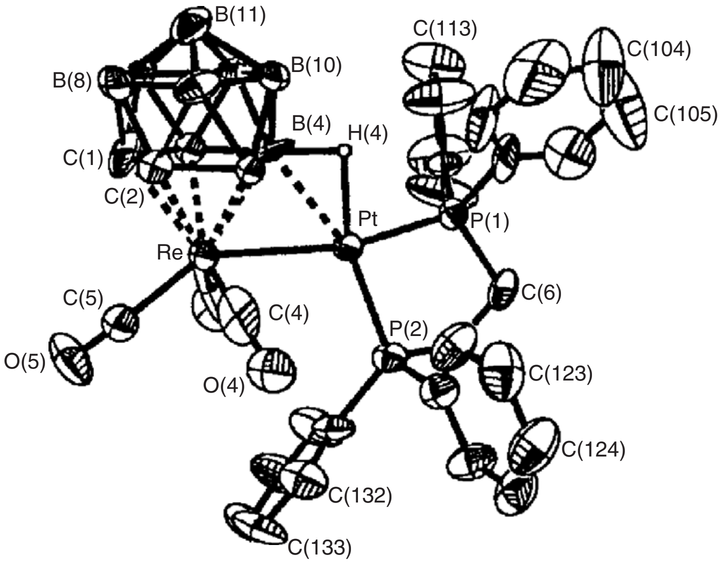


Figure 21 Crystal structure of [3,3,3-$(CO)_3$-3,8-(Pt{$Ph_2P(CH_2)_2PPh_2$})-8-(μ-H)-*closo*-3,1,2-$ReC_2B_9H_{10}$]$^+$. Reproduced by permission of The Royal Society of Chemistry from Ellis, D. D.; Jellis, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans*. **2000**, 2113–2122.

[ReAg(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3$] fragments in a κ^1,κ^2 manner. On the other hand, the reactivity of the Cs salt precursor with Ag[BF_4] in the presence of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine yields [ReAg(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3${κ^2-(bipy)$_2$} and [ReAg(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3${(κ^3-terpy)$_2$-2,6}].[70] The X-ray structure of the latter complex revealed an [ReAg(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3$] fragment having an unusual pentacoordinated silver(I) center, asymmetrically ligated by a terpyridine molecule. The same synthetic procedure using *N*,*N*,*N*′,*N*′-tetramethylethylenediamine gave the corresponding tetranuclear metallacarborane that was bridged between the silver atoms by two of the diamine molecules. In the absence of any added ligand, the reaction of Cs[Re$(CO)_3$(η^5-7,8-$C_2B_9H_{11}$)] gave the tetrameric cluster in which four [ReAg(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3$] units are held together by long interunit B-H···Ag bonds.[70]

The reactivity studies on the rhenacarborane salt Cs[Re$(CO)_3$(η^5-7,8-$C_2B_9H_{11}$)] was extended to the synthesis of Re–Pt containing cationic metallacarborane salts, [3,3,3-$(CO)_3$-3,8-(Pt{$Ph_2P(CH_2)_2PPh_2$})-8-(μ-H)-*closo*-3,1,2-$ReC_2B_9H_{10}$]$^+$.[71] The X-ray crystal structure, given in Figure 21, shows that the Re occupies a capping position over the C_2B_3 face of the carborane, with an *exo*-polyhedral Pt{$(Ph_2PCH_2)_2$} fragment attached through an Re–Pt bond and a B(4)–H–Pt bridge. Deprotonation of the complex with strong base gave an isomeric mixture of 3,3,3-$(CO)_3$-3,*n*-(Pt{$Ph_2P(CH_2)_2PPh_2$})-*closo*-3,1,2-$ReC_2B_9H_{10}$ ($n=4$, $n=8$). Reaction of the rhenacarborane with [PtH(THF)$(PEt_3)_2$][BF_4] led to similar complexes with B–Pt sigma bonds.[71] Subsequent reports from this laboratory,[72] and elsewhere,[73] involved the alkyne coupling reactions of the rhenacarboranes and the photochemistry of their nitrosyl derivatives, yielding the corresponding diene-linked species[72] and η^2-NO linkage isomers,[73] respectively.

3.05.2.4 Metallacarboranes of Late Transition Elements

A variety of late (groups 8–12) transition metal–carborane complexes, encompassing both large and small carborane ligands, have been described. The ferracarboranes, [$Fe^{II}(C_2B_9H_{11})_2$]$^{2-}$ and [$Fe^{III}(C_2B_9H_{11})_2$]$^-$, were among the first metallacarboranes to be synthesized.[7] Since then, the late transition metal carborane complexes have been a lively area of research. There have been a number of review articles, monographs, and chapters in books, including the first two editions of this encyclopedia, that adequately cover most of the earlier published work.[1–5d,74,74a–74c] Therefore, our discussions in this part of the review will attempt to summarize recent work on the sandwiched and half-sandwiched complexes of the group 8–12 metals. No attempt will be made to discuss those compounds in which the metal is solely a member of an *exo*-polyhedral group. This is especially restrictive in the case of the group 11 and

12 compounds where, more times than not, the metal lies well outside of the cage boundaries. Insofar as possible, we will attempt to follow a group order; however, many reports cover metals spanning several groups.

Iron in either a formal II+ or III+ state has been found to form complexes with mono-, di-, tri-, tetra-, and penta-carbaboranes. Stone and co-workers have reported the reactions of $\mathrm{Fe_3(CO)_{12}}$ with $[\mathrm{NHMe_3}][\textit{nido}\text{-}7\text{-}\mathrm{CB_{10}H_{13}}]$ to form the anionic $[\mathrm{Fe(CO)_3}(\eta^5\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]^-$.[57] The complex could react with nucleophiles to produce a series of $[\mathrm{Fe(CO)_2(L)}(\eta^5\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]^-$ ($\mathrm{L = PPh_3}$ and $\mathrm{NCBu^t}$), or with donor molecules such as THF, $\mathrm{Et_2O}$, and $\mathrm{SMe_2}$, in the presence of hydride abstracting agents, to give the charge compensated $[\mathrm{Fe(CO)_3}(\eta^5\text{-}9\text{-}(\mathrm{L})\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$ ($\mathrm{L = O(CH_2)_4}$, $\mathrm{Et_2O}$, $\mathrm{SMe_2}$) complexes, in which L was always on the boron once removed from the carbon on the $\mathrm{CB_4}$ bonding face (the β boron), as shown in Figure 22.[57] This study was extended to include the syntheses of $[\mathrm{Fe(CO)_2(L)}$ $(\eta^5\text{-}9\text{-}\{(\mathrm{E})\text{-}\mathrm{N(Me){=}C(H)Me}\}\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$, from the reaction of $[\mathrm{N(PPh_3)_2}][\mathrm{Fe(CO)_2(L)}(\eta^5\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$, NCMe, and $\mathrm{CF_3SO_3Me}$.[75] In a similar fashion, the reaction of $[\mathrm{N(PPh_3)_2}][\mathrm{Fe(CO)_3}(\eta^5\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$ with $\mathrm{Bu^tC{\equiv}CH}$ gives $[\mathrm{N(PPh_3)_2}][\mathrm{Fe(CO)_3}(\eta^2{:}\eta^5\text{-}8\text{-}\{(\mathrm{E})\text{-}\mathrm{CH{=}CHBu'}\}\text{-}7\text{-}\mathrm{CB_{10}H_{10}})]$, which, when reacted with NCMe and $\mathrm{CF_3SO_3CH_3}$, gave the structurally characterized $[\mathrm{Fe(CO)_2}(\eta^2{:}\eta^5\text{-}8\text{-}\{(\mathrm{E})\text{-}\mathrm{CH{=}CHBu^t}\}\text{-}9\text{-}\{(\mathrm{E})\text{-}\mathrm{N(Me){=}C(H)Me}\}\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$ (see Figure 23).[75] An extension to the reaction of the *nido*-$\mathrm{CB_{10}}$ carboranes having *exo*-polyhedral $\mathrm{NR_3}$ and $\mathrm{NR_2}$ groups with $\mathrm{M_3(CO)_{12}}$ (M = Ru, Os) gave quite different results. The reaction of 7-$\mathrm{NMe_3}$-*nido*-$\mathrm{CB_{10}H_{12}}$ with $\mathrm{M_3(CO)_{12}}$ (M = Ru[76], Os[77]) produced the corresponding $\mathrm{M_3(CO)_8}(\eta^5\text{-}7\text{-}\mathrm{NMe_3}\text{-}7\text{-}\mathrm{CB_{10}H_{10}})$ consisting of a triangular core with one metal, having two CO molecules, being η^5-bonded to the carborane giving a *closo*-$\mathrm{MCB_{10}}$ cage. The two boron atoms in the β-positions of the $\mathrm{CB_4}$ bonding face interact with the other two metals via B–H–M bridge bonds. The triosmium compound is shown in Figure 24;[77] the triruthenium compound has a similar structure. McGrath and Stone have recently reviewed the chemistry of these 7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{10}}$ complexes.[78]

Chizhevsky and co-workers have reported several cage contraction products resulting from the reaction of $\mathrm{Cs^+}[\textit{nido}\text{-}\mathrm{CB_{10}H_{13}}]^-$ and $\mathrm{RuCl_2(PPh_3)_3}$ in hot methanol. Among the products were the 10-vertex 2-Cl-2,5-$(\mathrm{PPh_3})_2$-2-H-3,9-$(\mathrm{MeO})_2$-2,1-$\mathrm{RuCB_8H_6}$, whose structure is shown in Figure 25,[79] and the eight-vertex *closo*-2,2-$(\mathrm{PPh_3})_2$-2-H-3,6,8-$(\mathrm{MeO})_3$-2,1-$\mathrm{RuCB_6H_4}$ (see Figure 26).[80] On the basis of electron counting rules, these were considered to be *hypercloso*-type ruthenacarboranes. When equimolar amounts of $\mathrm{RuCl_2(PPh_3)_3}$ and *nido*-5,6-$\mathrm{C_2B_8H_{12}}$ were heated in toluene, cage reduction again occurred, yielding the seven-vertex *closo*-1-Cl-1-H-1,1-$(\mathrm{PPh_3})_2$-1,2,3-$\mathrm{RuC_2B_4H_6}$, in

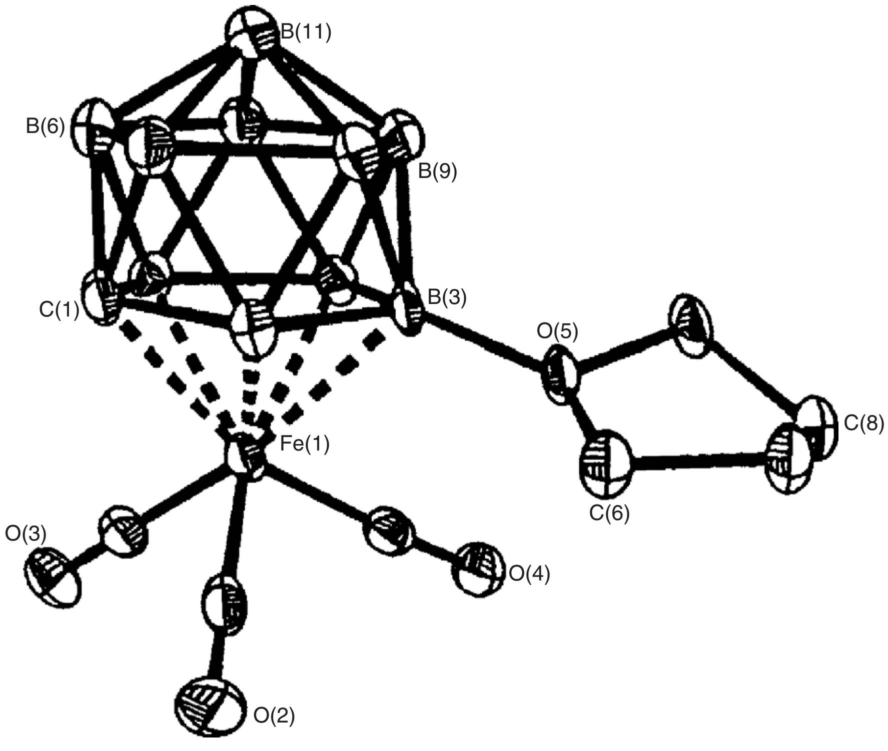


Figure 22 Crystal structure of $[\mathrm{Fe(CO)_3}(\eta^5\text{-}9\text{-}\mathrm{O(CH_2)_4}\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]$. Reproduced by permission of the American Chemical Society from *Organometallics* **2000**, *19*, 1993.

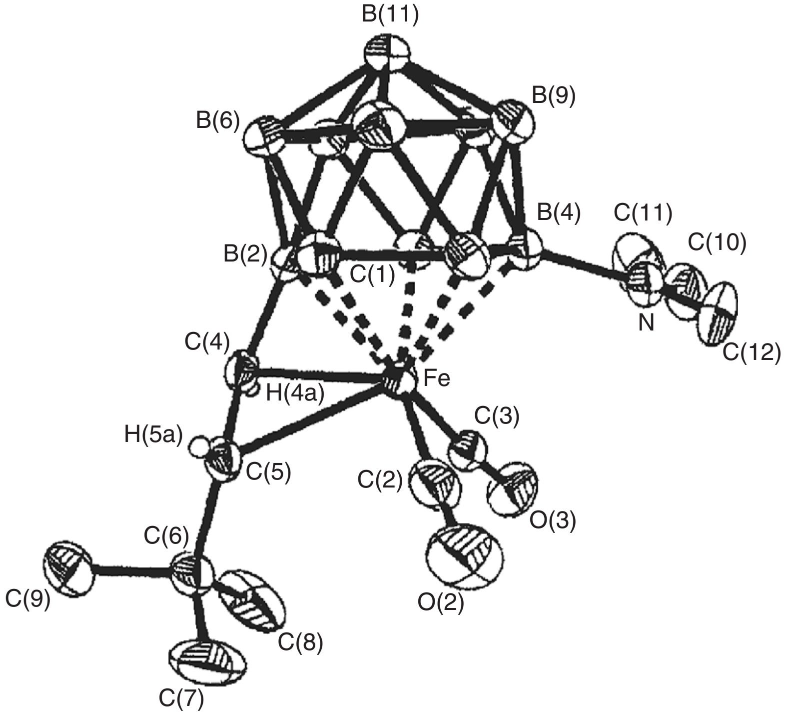


Figure 23 Crystal structure of [Fe(CO)$_2$(η^2:η^5-8-{(E)-CH═CHBu^t}-9-{(E)-N(Me)═C(H)Me}-7-CB$_{10}$H$_{11}$)]. Reproduced by permission of the American Chemical Society from *Organometallics* **2001**, *20*, 1597.

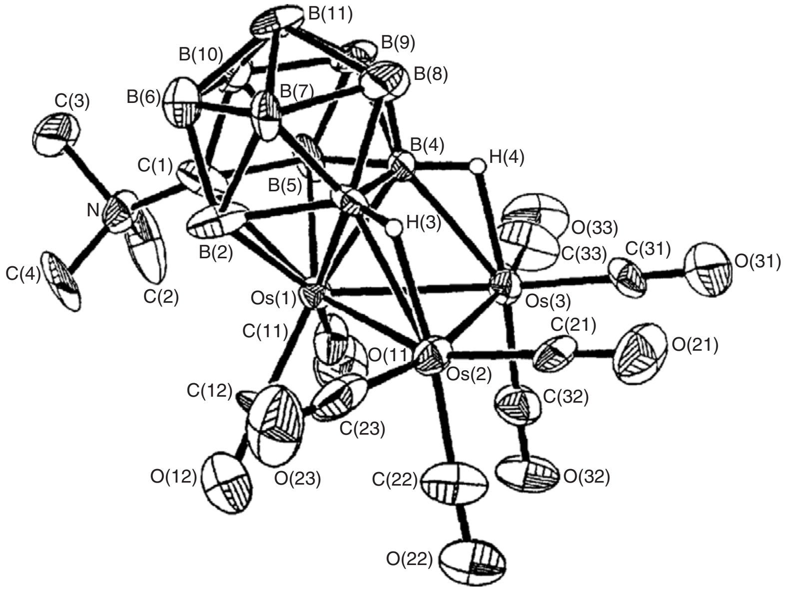


Figure 24 Crystal structure of Os$_3$(CO)$_8$(η^5-7-NMe$_3$-7-CB$_{10}$H$_{10}$). Reproduced by permission of Elsevier from *J. Organomet. Chem*. **1997**, *536–537*, 537.

which the RuClH(PPh$_3$)$_2$ group, functioning as a two-electron cage donor $(8+6-12)$ occupies the apical position above the C$_2$B$_3$ face of the carborane.[81] In the same way, OsCl$_2$(PPh$_3$)$_3$ reacted with either [6-Ph-*nido*-6-CB$_9$H$_{11}$]$^-$ or [*arachno*-6-CB$_9$H$_{14}$]$^-$ in MeOH with the elimination of a boron-containing group to give a series of 10-vertex *isocloso*-OsCB$_8$ clusters, [1-H-1,1-(PPh$_3$)$_2$-2-Ph-3-MeO-1,2-OsCB$_8$H$_7$], [1-H-1,1-(PPh$_3$)$_2$-3-MeO-1,2-OsCB$_8$H$_8$], and

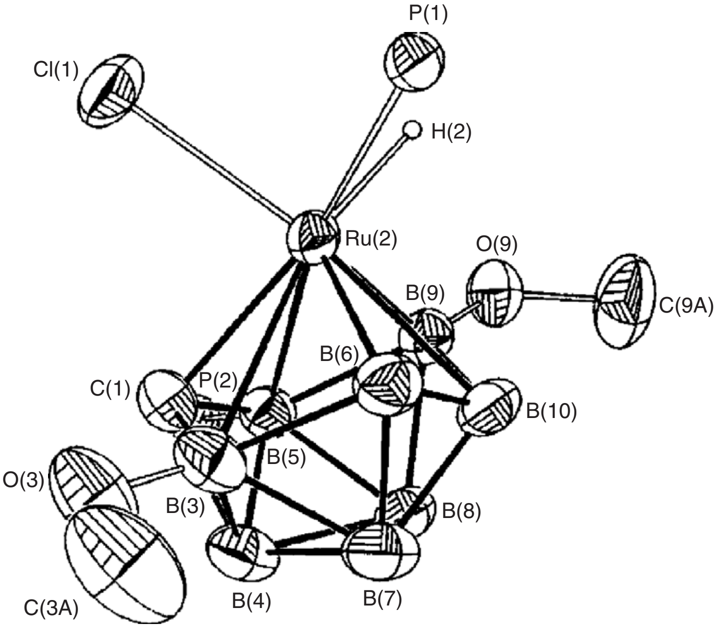


Figure 25 Crystal structure of the 10-vertex, 2-Cl-2,5-$(PPh_3)_2$-2-H-3,9-$(MeO)_2$-2,1-$RuCB_8H_6$. Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 5598.

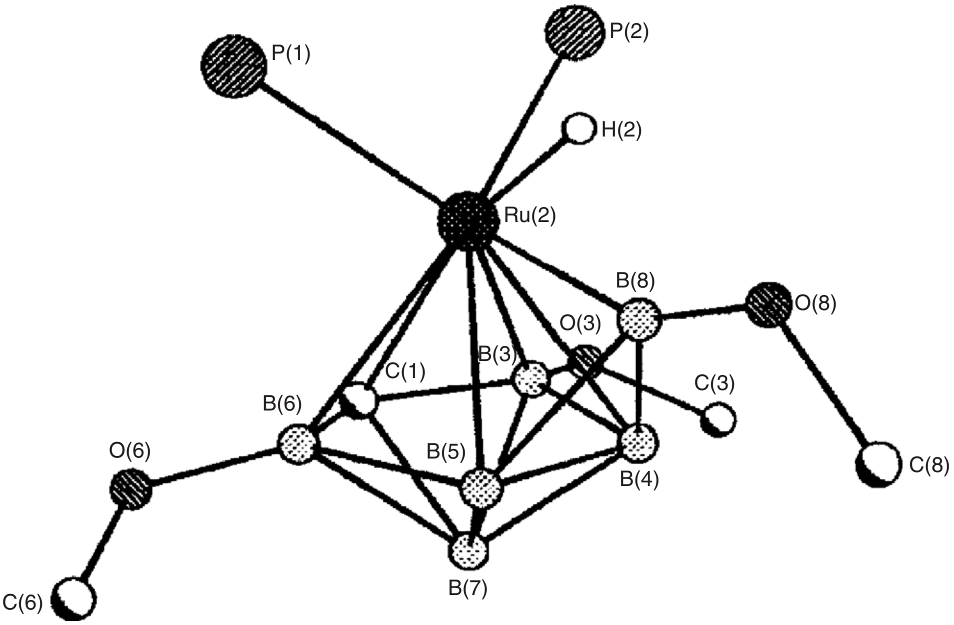
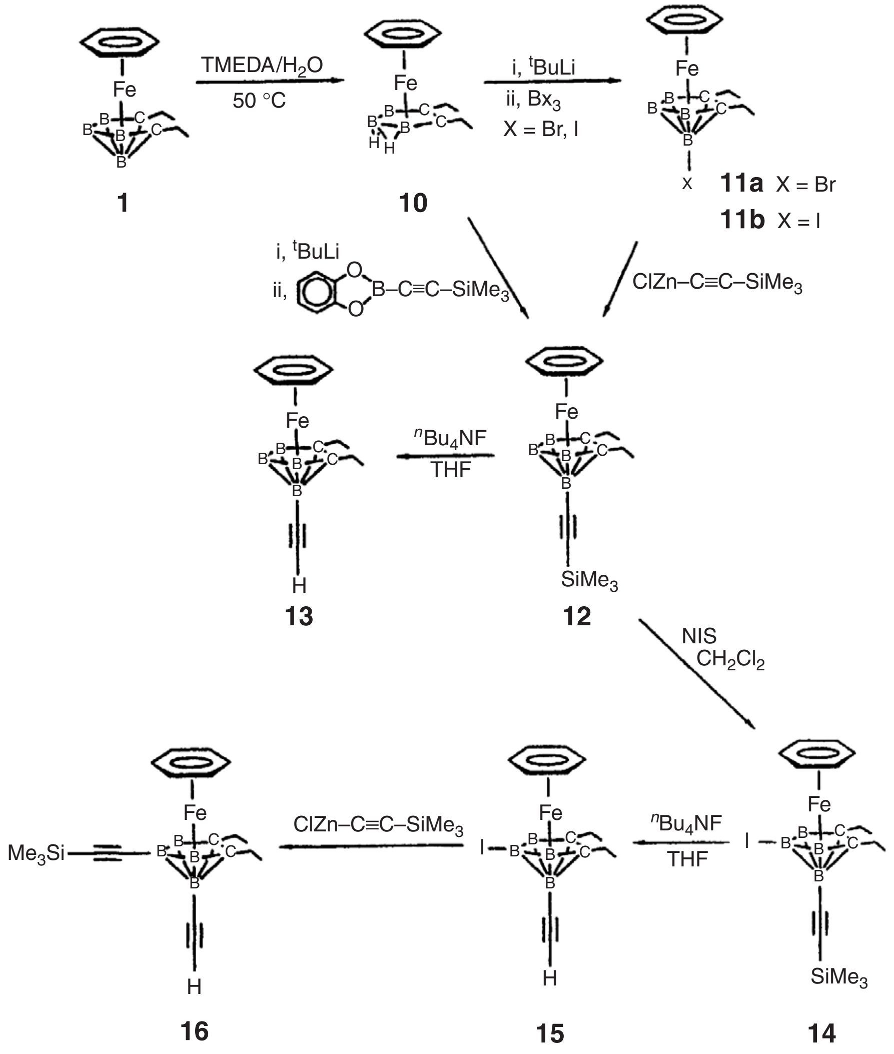


Figure 26 Crystal Structure of the eight-vertex *closo*-2,2-$(PPh_3)_2$-2-H-3,6,8-$(MeO)_3$-2,1-$RuCB_6H_4$. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **2001**, *40*, 5318.

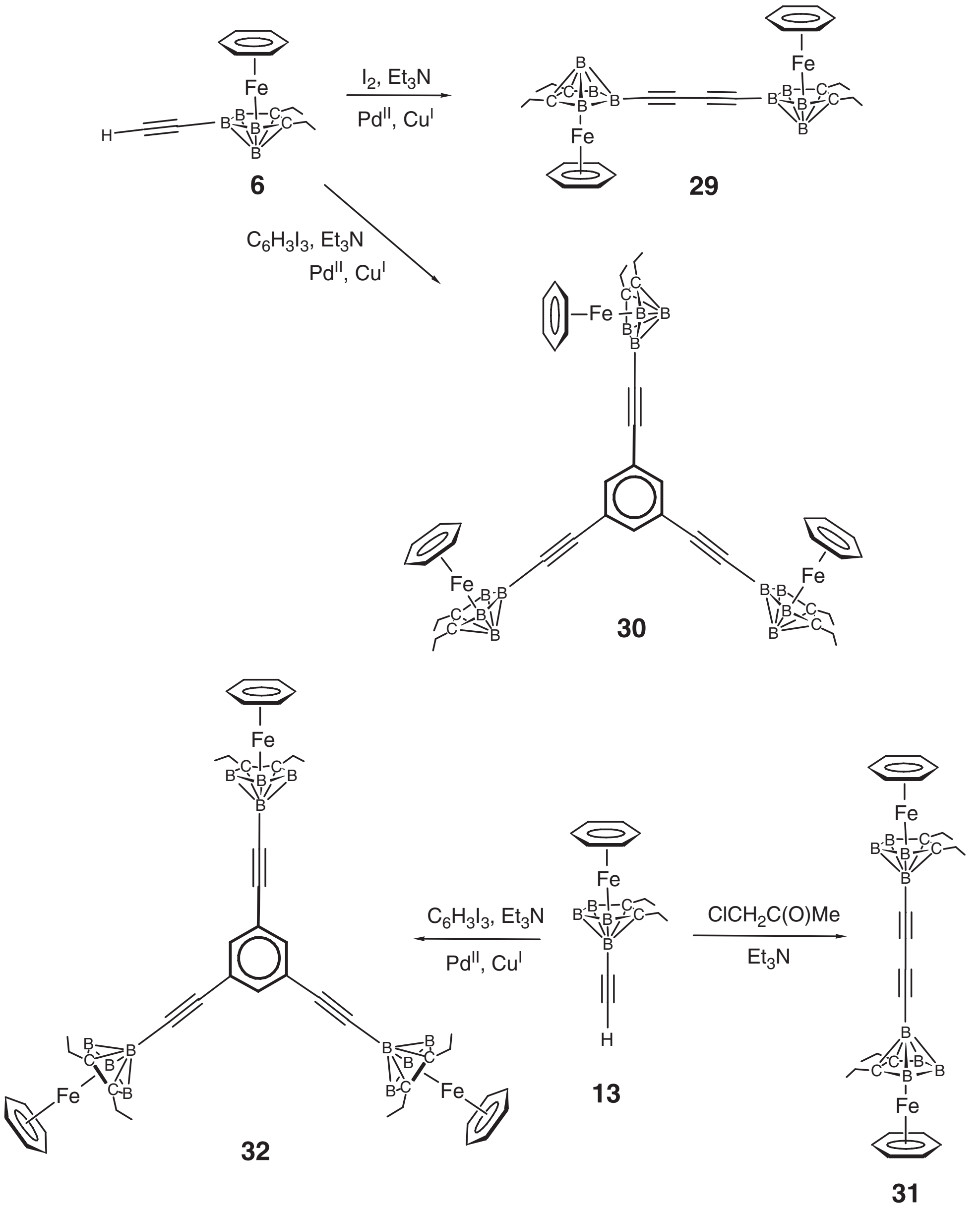
[1-H-1,1-$(PPh_3)_2$-1,2-$OsCB_8H_9$]; the X-ray crystal structure of the 2-Ph-3-MeO-substituted osmacarborane showed that the $OsCB_8$ cage was the same as that shown in Figure 25.[82]

In a series of earlier papers on the metal-promoted face-to-face fusion of carborane cages, Grimes and co-workers have reported the results of investigations of the formation of single polyhedral C_4B_8-clusters from the iron sandwich precursor, $(R_2C_2B_4H_4)_2FeH_2$, or its cobalt analog, $(R_2C_2B_4H_4)_2CoH$ (R = Me, Et, or *n*-propyl).[83–86] The X-ray crystal structure of the iron complex, [2,3-$(CH_3)_2$-2,3-$C_2B_4H_4$]$_2FeH_2$, showed that iron occupied the apical position between two carborane ligands; the metal-bound hydrogens could not be located and their presence was inferred by the observation of a high-field resonance at $\delta - 10.44$ in the proton NMR and a sterically unfavorable orientation of the cage-bound Me groups.[83a] However, more recently Wrackmeyer and co-workers reported the structure of the per-ethylated ferracarborane, $[Et_6\text{-}2,4\text{-}C_2B_4]_2FeH_2$, in which the two hydrogens were found bonded to the iron, with weaker interactions with the adjacent borons on the C_2B_3 open faces.[87]

The $(\eta^6\text{-}C_6H_6)$Fe group is isolobal with a BH as well as a two-cage-electron donor and hence, mixed-sandwich arene-ferracarboranes are quite stable and have been used as centers for the construction of more extended clusters. Grimes and co-workers have carried out a number of controlled substitutions at the boron atoms by applying Negishi cross-coupling reactions of 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-5-X-1,2,3-$FeC_2B_4H_3$ (X = I, Br) with vinly-, butyl-, (trimethylsilyl)ethynyl-, and phenyl-organozinc reagents to give the five-substituted products.[88] The apical boron of 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-1,2,3-$FeC_2B_4H_4$ could be removed using moist TMEDA (a decapitation reaction) to give the corresponding 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-1,2,3-$FeC_2B_3H_5$, which in turn could be "recapitated" by reaction with ^{t}BuLi and BX_3 (X = I, Br), to give the corresponding 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-7-X-1,2,3-$FeC_2B_4H_3$. The seven-halogenated product was found to react with ClZnC≡CSiMe$_3$ to give the 7-C≡CSiMe$_3$ ferracarborane, which, in turn, could be reacted with ^{n}BuNF to give 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-7-(–C≡CH)-1,2,3-$FeC_2B_4H_3$ or with N-iodosuccinimide (NIS) to give 1-$(\eta^6\text{-}C_6H_6)$-2,3-$(Et)_2$-5-I-7-(–C≡CSiMe$_3$)-1,2,3-$FeC_2B_4H_2$.[88] Application of similar procedures has resulted in a number of linked multi-metal clusters, as shown in Schemes 7 and 8.[88] The electronic interactions of some of these



Scheme 7 Apical boron coupling reactions of 1-(C_6H_6)-2,3-$(Et)_2$-1,2,3-$FeC_2B_4H_4$ and alkynes. Reproduced by permission of the American Chemical Society from *Organometallics* **2002**, *21*, 4113.



Scheme 8 Basal boron coupling reactions of 1-(C_6H_6)-2,3-(Et)$_2$-1,2,3-Fe$C_2B_4H_4$ and alkynes. Reproduced by permission of the American Chemical Society from *Organometallics* **2002**, *21*, 4113.

multiple-linked clusters were probed by cyclic voltametry; with the exception of the thiophene cation, 2,5-[(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$-5-)]$_2$S$C_4H_2^+$, none evidenced metal–metal communication.[89]

The two-cage-electron donating ability of the group 8 ML_3 (L_3 = a six electron donor or collections of donors) moieties was exploited in the syntheses of a number of *closo*-metallacarboranes, for example, constrained-geometry complexes of the form [(η^1:η^5-1-CH_2NMe-3,2,1-$MC_2B_9H_{10}$)] (M = FeL_2, L = CO, CNBu^t, PMe$_3$, and COD; M = Ru(CO)$_2$).[90] These are of interest in that the amino carborane resembles the methylaminocyclopentadienyl (CpA) ligand, which has been used in a number of catalytic systems.[91]

A number of mixed metal complexes involving ruthenacarboranes in the MC_2B_9 cage system have been described. Stone and co-workers reported the synthesis and structure of the thallium-bridged complex, [Ru_2(μ-Tl)(CO)$_4$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)$_2$]$^-$, which was one of a pair of products obtained from the reaction of [RuBr(CO)$_3$(η^3-C_3H_5)] with Tl[1,2-Me_2-*closo*-3,1,2-Tl$C_2B_9H_9$] in THF, the other product being [Ru(CO)$_3$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)].[92] The structure is that of two *closo*-[$Ru(CO)_2(\eta^5$-7,8-Me_2-7,8-$C_2B_9H_9$)] fragments attached by a Ru–Tl–Ru bridge. Both products could be converted to [NEt_4][$RuI(CO)_2(\eta^5$-7,8-Me_2-7,8-$C_2B_9H_9$)] by reaction with [NEt_4]I. Reaction of the iodide with $AgBF_4$ produced $Ru(CO)_2$(THF) (η^5-7,8-Me_2-7,8-$C_2B_9H_9$), which itself proved to be a versatile starting material. The THF could easily be replaced by two-electron donors to give [Ru(L)$(CO)_2(\eta^5$-7,8-Me_2-7,8-$C_2B_9H_9$)] (L = PPh_3, $CNBu^t$, NC_5H_5,NCMe). The additions of alkenes and alkynes were not so straightforward.[92] On the other hand, [Ru(THF)$(CO)_2(\eta^5$-7,8-$C_2B_9H_{11}$)] was found to react readily with alkenes and disubstituted alkynes (RC≡CR) to give [Ru(L)(CO)(η^5-7,8-$C_2B_9H_{11}$)] (L = alkene, alkyne).[93] Terminal alkynes, RC≡CH (R = Ph, Bu^t, $SiMe_3$) gave more complex products.[94] When R = Ph, the product was found by X-ray diffraction to be [Ru(CO)(PPh_3)(η^2:η^5-9-(E)-C(H)=C(H)Ph-7,8-$C_2B_9H_{11}$)], where the η^2-bonding, E-C(H)=C(H)Ph group is on a boron adjacent to a carbon in the C_2B_3 bonding face.[94] The [Ru(THF)$(CO)_2(\eta^5$-7,8-$C_2B_9H_{11}$)] has also proved to be a convenient precursor for the syntheses of poly-metallic complexes. The complex reacts with alkylidyne reagents, [M(≡CC_6H_4Me-4)$(CO)_2(\eta^5$-C_5H_5)] (M = Mo, W), to give the bimetallic [MRu(μ-CC_6H_4Me-4)$(CO)_4(\eta^5$-7,8-$C_2B_9H_{11}$)(η^5-C_5H_5)], which consists of a *closo*-$Ru(CO)_2C_2B_9H_{11}$ and an $M(CO)_2(\eta^5$-C_5H_5) moiety bridged by a (≡CC_6H_4Me-4) group.[95] This complex readily isomerizes to give [MRu$(CO)_4${σ,η^5-9-CH(C_6H_4Me-4)-7,8-$C_2B_9H_{10}$}(η^5-C_5H_5)]; the structure of the complex where M = Mo is shown in Figure 27.[95] As can be seen, the $Mo(CO)_2(\eta^5$-C_5H_5) group is attached to the RuC_2B_9 cluster by an Ru–Mo and a B–H–Mo bridge, involving a boron adjacent to a cage carbon, while the opposite boron has the CH(C_6H_4Me-4) group that bridges to the Ru center. Reaction of [Ru(THF)(CO)(η^5-7,8-$C_2B_9H_{11}$)] with molecular hydrogen produced the diruthenacarborane, [Ru_2(μ-H)$(CO)_4(\eta^5$-7,8-$C_2B_9H_{11})_2$]$^-$, whose structure is shown in Figure 28.[96] The two *closo*-$Ru(CO)_2(\eta^5$-7,8-$C_2B_9H_{11}$) fragments are connected by an Ru–Ru and an Ru–H–Ru bond. The anion could be deprotonated by NaH to give [$Ru_2(\mu$-$CO)_2(CO)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$]$^{2-}$. The structure is similar to that shown in Figure 28, except the hydrido group is replaced by two bridging CO molecules, leaving each Ru with one terminal CO.[96] Reaction of the monomeric anion [Ru(H)$(CO)_2(\eta^5$-7,8-$C_2B_9H_{11}$)]$^-$ with [PtH(Cl)$(PEt_3)_2$] in THF in the presence of $TlPF_6$ produced the mixed metal complex, [RuPt(μ-H)-(μ-σ:η^5-7,8-$C_2B_9H_{11}$)$(CO)_2(PEt_3)_2$], whose structure is shown in Figure 29.[96] Effectively, the $Pt(PEt_3)_2$ inserts between B(5) and its terminal hydrogen, giving an Ru–H–Pt bridge as well as an Ru–Pt and a Pt–B(5) bond. An alternate approach to bimetallic compounds of this type involves the reaction of *exo-nido*-5,6,10-[Cl$(PPh_3)_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$, in which the RuCl$(PPh_3)_2$ complex is attached to a *nido*-$C_2B_9H_{11}$ cage by three B–H–Ru bonds with [(η^4-diene)$RhCl_2$]$_2$ (diene = C_8H_{12}(COD), C_7H_8(NBD)) to give the (η^4-diene)Rh(μ-H)Ru$(PPh_3)_2(\eta^5$-$C_2B_9H_{11}$); when [$(CO)_2RhCl$]$_2$ was used, (CO)(PPh_3)Rh(μ-H)Ru$(PPh_3)_2$

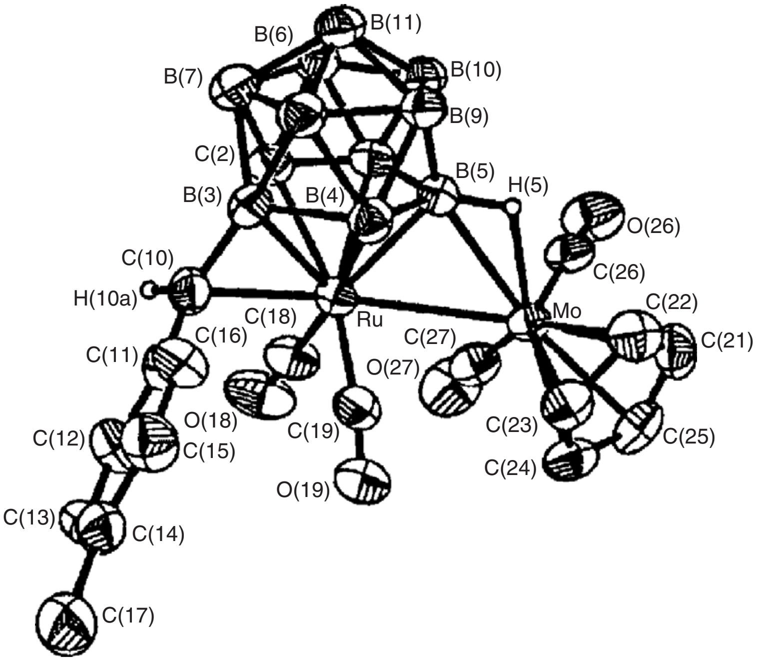


Figure 27 Crystal structure of [MoRu$(CO)_4${σ,η^5-9-CH(C_6H_4Me-4)-7,8-$C_2B_9H_{10}$}(η^5-C_5H_5)]. Reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 958.

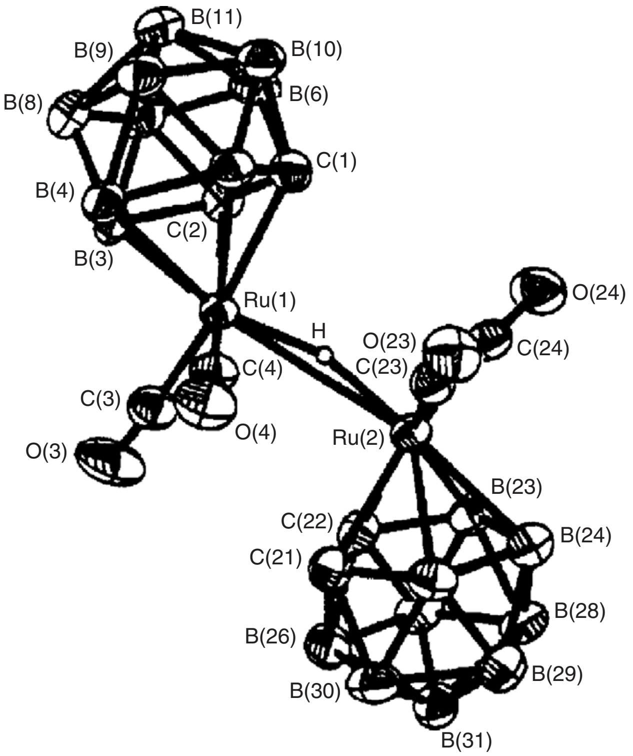


Figure 28 Crystal structure of the diruthenacarborane, $[Ru_2(\mu\text{-}H)(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 3516.

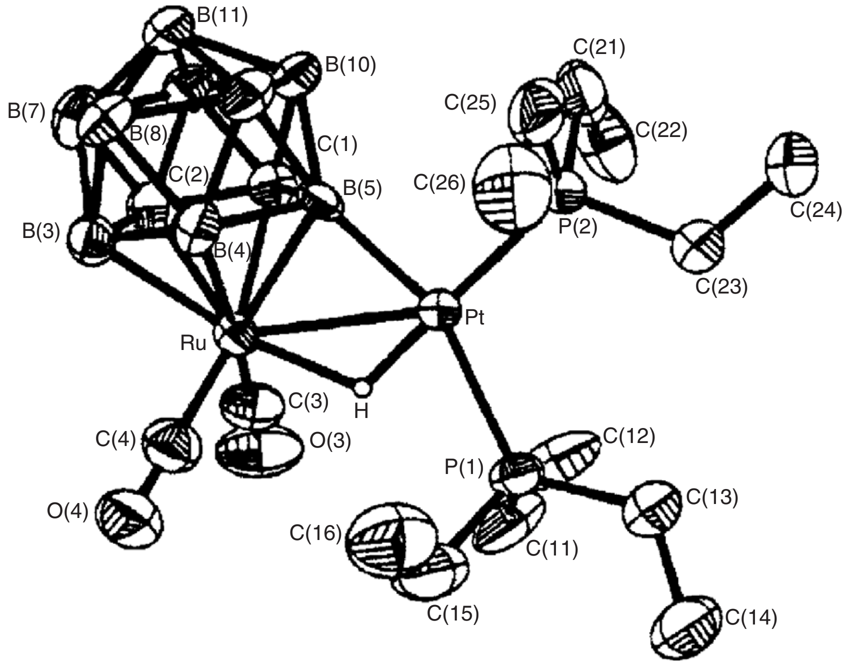


Figure 29 Crystal structure of the mixed metal complex, $[RuPt(\mu\text{-}H)\text{-}(\mu\text{-}\sigma\text{:}\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(CO)_2(PEt_3)_2]$. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 3516.

(η^5-$C_2B_9H_{11}$) was obtained.[97] Both complexes were composed of a *closo*-Ru(PPh_3)$_2$(H)($C_2B_9H_{11}$) fragment that was bonded to an Rh atom by an Ru–H–Rh and a B–H–Rh bridge as well as an Ru–Rh bond. The Rh was also coordinated by either the diene or CO and PPh_3 ligands. The *exo-nido*-carboranes of rhodium, ruthenium, and osmium are not only versatile starting materials,[98] but have also been studied as catalyst precursors.[99] In all these bimetallic compounds, the ruthenium group acts as a two-cage-electron donor, leading to a *closo*-RuC_2B_9 cage, with the other metal being bonded *exo*-polyhedrally, usually through a combination of metal–metal bonds and B–H–M bridges. In this regard, they are not polymetallacarboranes in the same sense as those described below.

Just as advantage was taken of the fact that (C_6H_6)Fe is a two-cage-electron donor, the one electron donor, CpFe, has been used in the metallation of the 25-electron tricarbaboranes, *nido*-7,8,9-$C_3B_8H_{12}$. The zwitterionic 7-XH-*nido*-7,8,9-$C_3B_8H_{10}$ (X = NH_2, Me_2N, ^tBuHN, $^tBu(Me)N$) was found to react with [CpFe(CO)$_2$]$_2$ in refluxing xylene to give corresponding [2-Cp-9-X-*closo*-2,1,7,9-$FeC_3B_8H_{10}$].[100] In all cases, metallation was accompanied by an isomerization so that the C–X vertex was in the apical position, opposite to the metal group (see Figure 30). The isomerization was very clean and no other isomers were found in the reaction mixtures; the reaction of [CpFe(CO)$_2$I] with the unsubstituted Tl^+[*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ in refluxing toluene gave the same results.[101] However, heating the complexes to 300 °C for about 10 min caused isomerization to [2-Cp-10-X-*closo*-2,1,7,10-$FeC_3B_8H_{10}$]; for the case where X = Bu^tHN, see Figure 31.[102] The 9 → 10 rearrangement was thought to be due

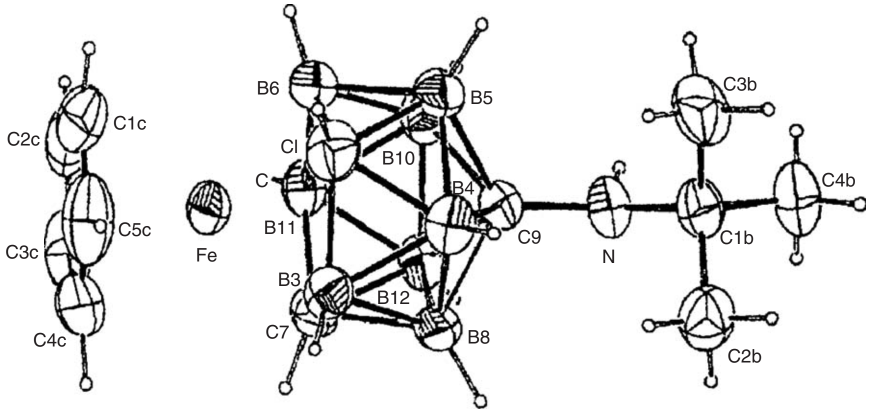


Figure 30 Crystal structure of [2-Cp-9-Bu^tNH-*closo*-2,1,7,9-$FeC_3B_8H_{10}$]. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **1999**, *38*, 2775.

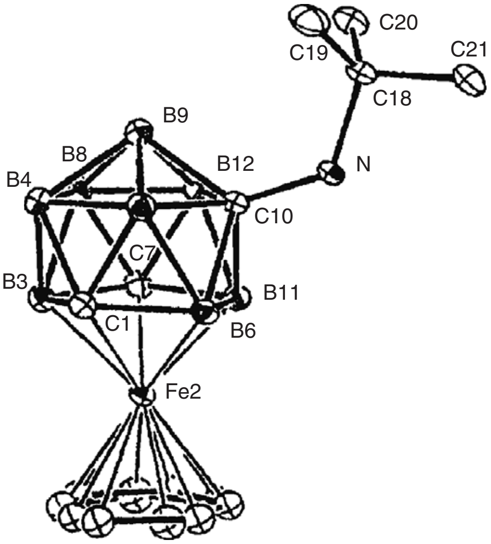


Figure 31 Crystal structure of [2-Cp-10-Bu^tNH-*closo*-2,1,7,10-$FeC_3B_8H_{10}$]. Reproduced by permission of the American Chemical Society from *Inorg. Chem*. **2000**, *39*, 2577.

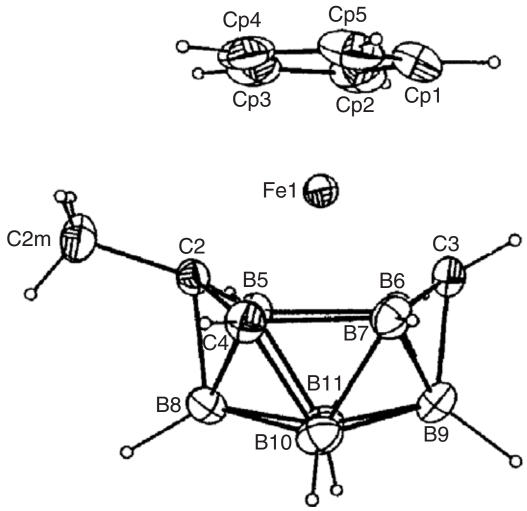


Figure 32 Crystal structure of 1-(Cp)Fe-2-CH_3-2,3,4-$C_3B_7H_9$. Reproduced by permission of the American Chemical Society from *Organometallics* **1992**, *11*, 1665.

to the greater thermodynamic stability of the 10-isomer in that the unsubstituted compound was found to exist as [2-(Cp)-*closo*-2,1,7,10-$FeC_3B_8H_{11}$].[101] The tricarbaborane, *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$ has a nonplanar, six-membered C_3B_3 face that can bond to metal groups. The monoanion of this carborane was found to react with $CpFe(CO)_2I$ to give a series of products, with 1-(Cp)Fe-*n*-CH_3-2,3,4-$C_3B_7H_9$ ($n = 2$ or 4) being the main products.[103] They have a distorted *closo*-octadecahedral structure, as shown in Figure 32. The 4-isomer is the same except that the CH_3 group has migrated to C(4). The 2-isomer could be quantitatively converted to the 4-isomer by heating at 240 °C. Both $(CO)_5MnBr$ and $[CpNiCO]_2$ were found to react in a similar manner to give carborane metallation. Based on electron counting rules, 1-$Mn(CO)_3$-2-CH_3-2,3,4-$C_3B_7H_9$ was assigned a *closo*-structure, while the three-skeletal-electron donating CpNi fragment produced *nido*-9-(Cp)Ni-8-CH_8-7,8,10-$C_3B_7H_9$.[103] The 2 : 1 molar ratio of Na^+[*nido*-6-CH_3-5,6,9-$C_3B_7H_9$]$^-$ with $FeCl_2$ produced a number of isomeric iron bis(tricarbaborane) complexes of the type, *commo*-Fe-(1-Fe-*n*-CH_3-2,3,5-$C_3B_7H_9$)$_2$ ($n = 2, 5$) and *commo*-Fe-(1-Fe-5-CH_3-2,3,5-$C_3B_7H_9$)(1-Fe-4-CH_3-2,3,4-$C_3B_7H_9$).[104] All reverted to *commo*-Fe-(1-Fe-10-CH_3-2,3,10-$C_3B_7H_9$)$_2$ on heating; Figure 33 shows the structure of the latter compound along with the atom numbering system.[104] Cobalt(II) chloride was found to react similarly to give *commo*-cobaltacarborane isomers, as did Na_2OsCl_6.[104,105] Both the iron and cobalt sandwich showed metal slip distortion. The slip distortion in the group 8 tricarbaboranes was further investigated by studying the geometric changes accompanying the metal coordination of the undistorted *closo*-1-Cp′-M(η^6-[2-Ph-2,3,4-$C_3B_7H_9$]) (M = Ru, Cp′ = C_5Me_5; M = Fe, Cp′ = C_5H_5) with $CNBu^t$.[105] In both cases, the carborane changed from η^6-coordinated to η^4-coordinated giving *nido*-8-Cp′-M($CNBu^t$)-(η^4-[9-R-7,9,10-$C_3B_7H_9$]). Figure 34 shows the structure of the *nido*-8-Cp′-Fe($CNBu^t$)-(η^4-[9-Ph-7,9,10-$C_3B_7H_9$]).[105,106] The progress in slip distortion was also seen in the structures of the triple-decker complexes, CpCo-(μ-η^5-$MeEt_4C_3B_2$)-M($MeC_3B_7H_9$) (M = Fe, Co, Ni).[107] The structure of CpCo-(μ-η^5-$MeEt_4C_3B_2$)-Fe(5-Me-2,3,5-$C_3B_7H_9$) shows no metal distortion, CpCo-(μ-η^5-$MeEt_4C_3B_2$)-Co(2-Me-2,3,5-$C_3B_7H_9$) shows a slight distortion, while CpCo-(μ-η^5-$MeEt_4C_3B_2$)-Ni(η^4-8-Me-7,8,10-$C_3B_7H_9$) is highly distorted. These structures are consistent with the 11-vertex MC_3B_7 having 24 (Fe, $2n + 2$), 25 (Co), and 26 (Ni, $2n + 4$) skeletal electron counts.[107]

There have been only a few studies of the metal complexes of the tetracarba- and pentacarbaboranes, these done by Sneddon and co-workers.[108] The reaction of the [*arachno*-8-($CH_3OC(O)$)-7,8,9,10-$C_4B_8H_{13}$]$^-$ monoanion with $CpFe(CO)_2I$ produced the ferratetracarbaborane, *nido*-2-CpFe-12-((CH_3)C(O))-6,7,8,9-$C_4B_7H_{11}$, along with several ferratricarbaborane co-products. The structure, given in Figure 35, shows that the CpFe moiety is bonded to an open C_4B_2 face, in which the carbons are all adjacent. One carbon, C(8) in Figure 35, is directed out of the plane of the other five atoms, toward the iron group. The starting carborane has four adjacent carbon atoms on an irregular C_4B_2 face, suggesting that *nido*-2-CpFe-12-(CH_3)C(O)-6,7,8,9-$C_4B_7H_{11}$ is a kinetic product formed by the insertion of the CpFe group in the open face of the carborane. Another argument in favor of a kinetic rather than a thermodynamic product is that one carbon (C(6)) occupies a high-energy five-coordinate position. The authors report that the ferracarborane isomerizes at 190 °C to give a compound whose ^{11}B NMR spectrum is consistent with *nido*-2-CpFe-8-(CH_3)C(O)-7,8,9,12-$C_4B_7H_{11}$ in which all four carbons are on the open face.[108] [*arachno*-8-($CH_3OC(O)$)-7,8,9,

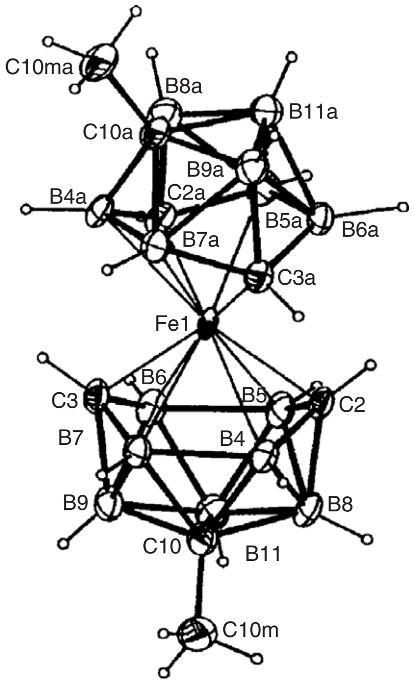


Figure 33 Crystal structure of *commo*-Fe-(1-Fe-5-CH$_3$-2,3,5-C$_3$B$_7$H$_9$)(1-Fe-4-CH$_3$-2,3,4-C$_3$B$_7$H$_9$). Reproduced by permission of the American Chemical Society from *Organometallics* **1992**, *11*, 1672.

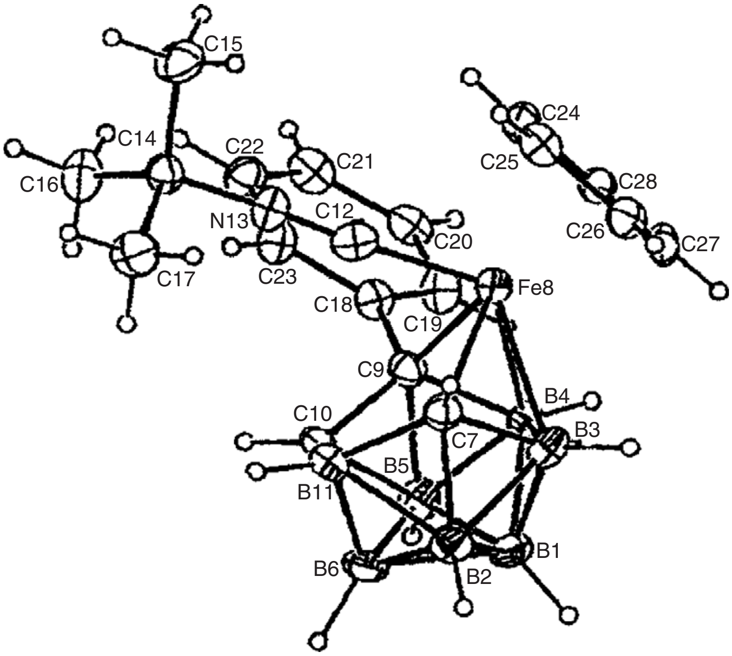


Figure 34 Crystal structure of *nido*-8-Cp′-Fe(CNBu^t)-(η^4-[9-Ph-7,9,10-C$_3$B$_7$H$_9$]). Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **2000**, *122*, 11033.

10-C$_4$B$_8$H$_{13}$]$^-$ reacts with CoCl$_2$ and NaCp to give *arachno*-2-CpCo-8-(CH$_3$OC(O))-7,8,9,10-C$_4$B$_7$H$_{12}$, which has a structure similar to that in Figure 35, except that a boron atom and a carbon atom are switched between positions 10 and 6.[108] The reaction of K$^+$[*arachno*-6-(CH$_3$C(O)CH$_2$)-5,6,7-C$_3$B$_7$H$_{11}$]$^-$ with CpFe(CO)$_2$I gives the ferrapentacarbaborane, *nido*-2-CpFe-7-CH$_3$-7,8,9,10,12-C$_5$B$_6$H$_{10}$ (see Figure 36), in 13% isolated yield.[109] Scheme 9 outlines a

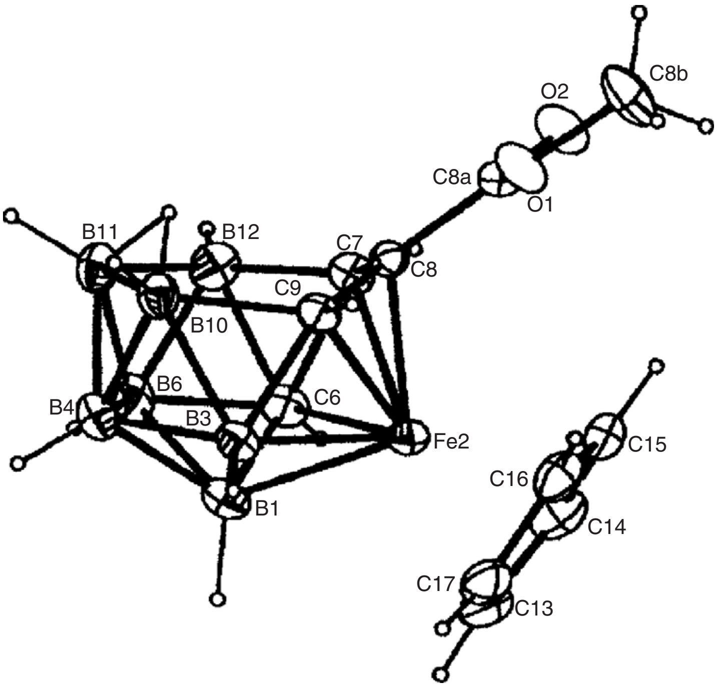


Figure 35 Crystal structure of *nido*-2-CpFe-12-((CH$_3$)C(O))-6,7,8,9-C$_4$B$_7$H$_{11}$. Reproduced by permission of Elsevier from *J. Organomet. Chem*. **1998**, *550*, 77.

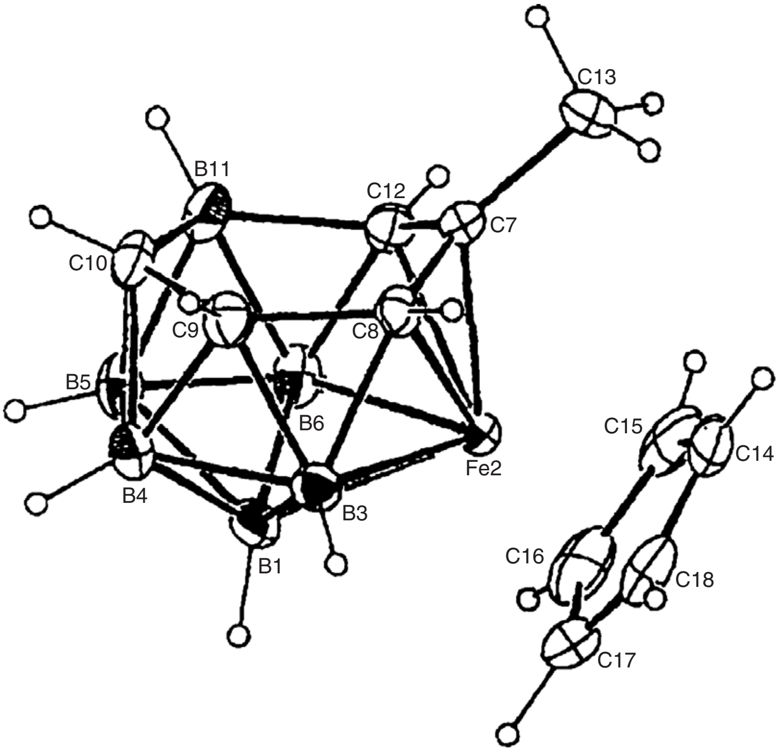
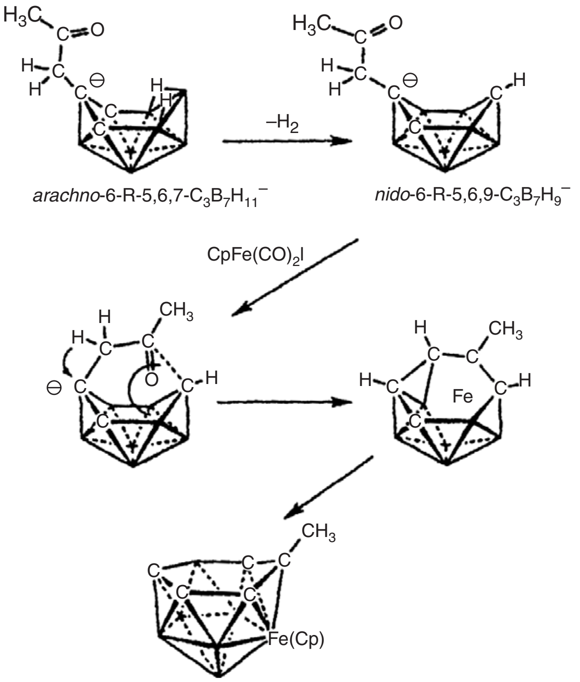


Figure 36 Crystal structure of the pentacarbaborane complex of iron. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 4463.



Scheme 9 Proposed cage expansion reactions leading to a ferrapentacarbaborane. Reproduced by permission of the American Chemical Society from *Organometallics* **1995**, *14*, 4463.

possible sequence for this reaction. Controlled reactions carried out in the absence of $CpFe(CO)_2I$ gave no hint of pentacarbaborane formation, indicating that the CpFe group plays an integral part in the reaction.[109]

Late transition metal complexes of a very different tetracarbon boranyl ligand, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene, have been described by Siebert and co-workers.[110] This ligand consists of two phenyl groups bridged by two MeB groups. The molecule is planar and presents a metal group with two different coordination sites, either the end phenyls, which are six-electron donors, or the central $Me_2B_2C_4$ region, which functions as a four-electron donor. Thus, of the 14-valence electron fragments, FeC_7H_8, $Ru(CO)_3$, $Co(C_5H_5)$, and Ni(COD) gave complexes where the metal group resided above the B_2C_4 ring (see Figure 37 for the structure of the iron structure), while the 12-valence electron $Cr(CO)_3$ moiety preferred to coordinate to one of the end arene groups. The reaction of the Co(Cp) bound complex with $(CO)_3Cr(CH_3CN)_3$ gave the novel triple-decker bimetallic complex where the Co(Cp) group was bonded to the B_2C_4 ring and the $Cr(CO)_3$ was bonded to a phenyl ring.[110] A similar B_2C_4-Co(Cp) complex was obtained from the reaction of 2,3-diethyl-1,4,5,6-tetramethyl-1,4-dibora-2-cyclohexene with $(C_2H_4)_2Co(Cp)$.[111] The product was the mixed-sandwich complex, $(Cp)Co(\eta^6\text{-}B_2C_4(Me)_4(Et)_2)$, in which the B_2C_4 is aromatic; the double-decker,

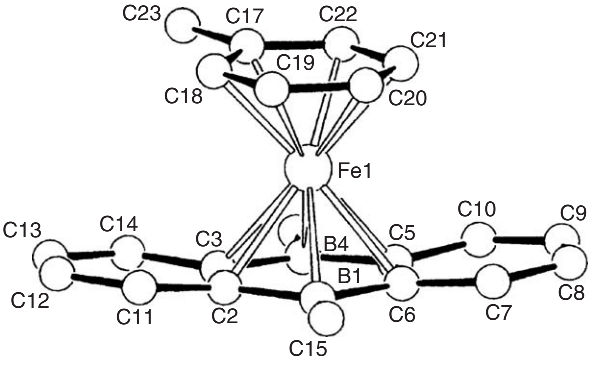


Figure 37 Crystal structure of the diboroanthracene complex of iron. Reproduced by permission of Elsevier from *J. Organomet. Chem*. **1995**, *487*, 235.

$(Cp)Co(\eta^6\text{-}B_2C_4(Me)_4(Et)_2)Co(Cp)$ where the $B_2C_4(Me)_4(Et)_2$ sandwiched between two (Cp)Co groups was a co-product. Similar complexes using other substituents on the B_2C_4 ring have also been reported.[112]

One of the most frequently encountered organometallic fragments found in the metallacarboranes is the $Co(\eta^5\text{-}C_5R_5)$ ($R = Me(Cp^*)$, H(Cp)). It is a two-cage-electron donor that is isolobal with BH and forms stable complexes, especially with the dicarbaboranes derived from the C_2B_9 and C_2B_4, although other cage systems have been studied.[4] Rather than try to exhaustively review examples of these metallacarboranes, only selective topics will be addressed. The reader is also directed to Table 1.

The reaction of $[C_2B_{10}H_{12}]^{2-}$ with $Cp^*Co(CO)I_2$ to give the 13-vertex, $4\text{-}Cp^*\text{-}4,1,6\text{-}CoC_2B_{10}H_{14}$, has been reported, but in low yields.[113] This compound was a kinetic product and was isomerized to give successive thermodynamic products, $4\text{-}Cp^*\text{-}4,1,8\text{-}CoC_2B_{10}H_{14}$ and $4\text{-}Cp^*\text{-}4,1,12\text{-}CoC_2B_{10}H_{14}$; all compounds were structurally characterized. Figure 38 shows the structure of the initial 4,1,6-isomer and the atom numbering system. One of the most vexing problems in the crystallographic structural determinations of the heterocarboranes is to differentiate between a C–H and a B–H vertex. They differ by only one electron and many times cannot be distinguished by the criteria of U_{eq}. The authors described a rather interesting process for locating the cage carbons in the CoC_2B_{10} cages that involved identifying a particular site as either a C or a B and then allowing the H atom bound to that site to freely refine; an incorrect choice yields an unrealistic vertex-H bond distance. This selection process worked quite well in this study.[113] A minor amount of the icosahedral, $3\text{-}(Cp^*)\text{-}3,1,2\text{-}$*closo*$\text{-}CoC_2B_9H_{11}$, was also produced in the synthesis, which arose from the elimination of the B(3)–H vertex that is between the cage carbons. This "carbons adjacent" *closo*-structure is of interest since reductive cage opening of *closo*-$C_2B_{10}H_{12}$ yields a *nido*-cage in which the carbons are separated by a boron atom. Research on the supraicosahedral metallacarboranes is continuing,[114,114a] the results of which will be covered in a later edition of this encyclopedia.

Reports have been made of many studies on the systematic substitution of the terminal hydrogens on the boron atoms of the cobaltacarboranes with other substituents that can give rise to precursors for the syntheses of more extended clusters. For example, the reaction of the mercurated cobaltacarborane, $3\text{-}(Cp)\text{-}9\text{-}ClHg\text{-}3,1,2\text{-}CoC_2B_9H_{10}$, with either [*nido*-$C_2B_9H_{12}]^-$ or *exo-nido*-$5,6,10\text{-}[Cl(PPh_3)_2Ru]\text{-}5,6,10\text{-}(\mu\text{-}H)_3\text{-}10\text{-}H\text{-}7,8\text{-}C_2B_9H_8$ gave the mercury-linked dicarboranes,

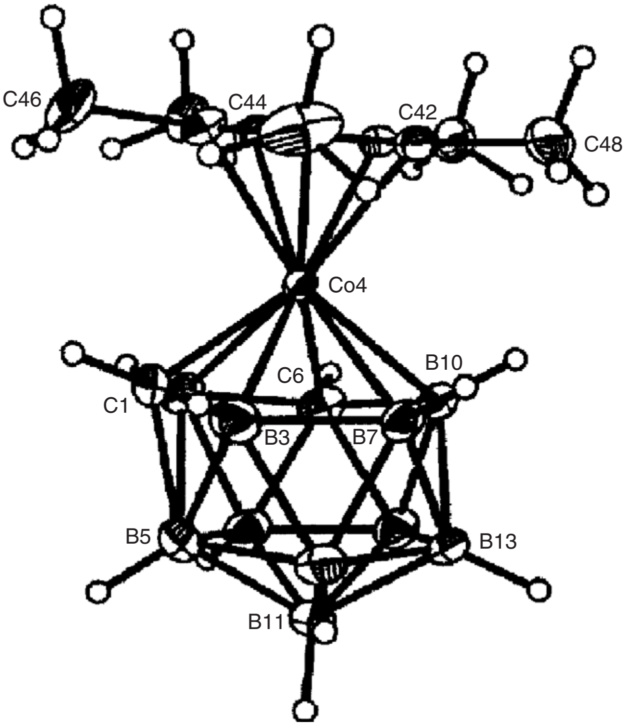
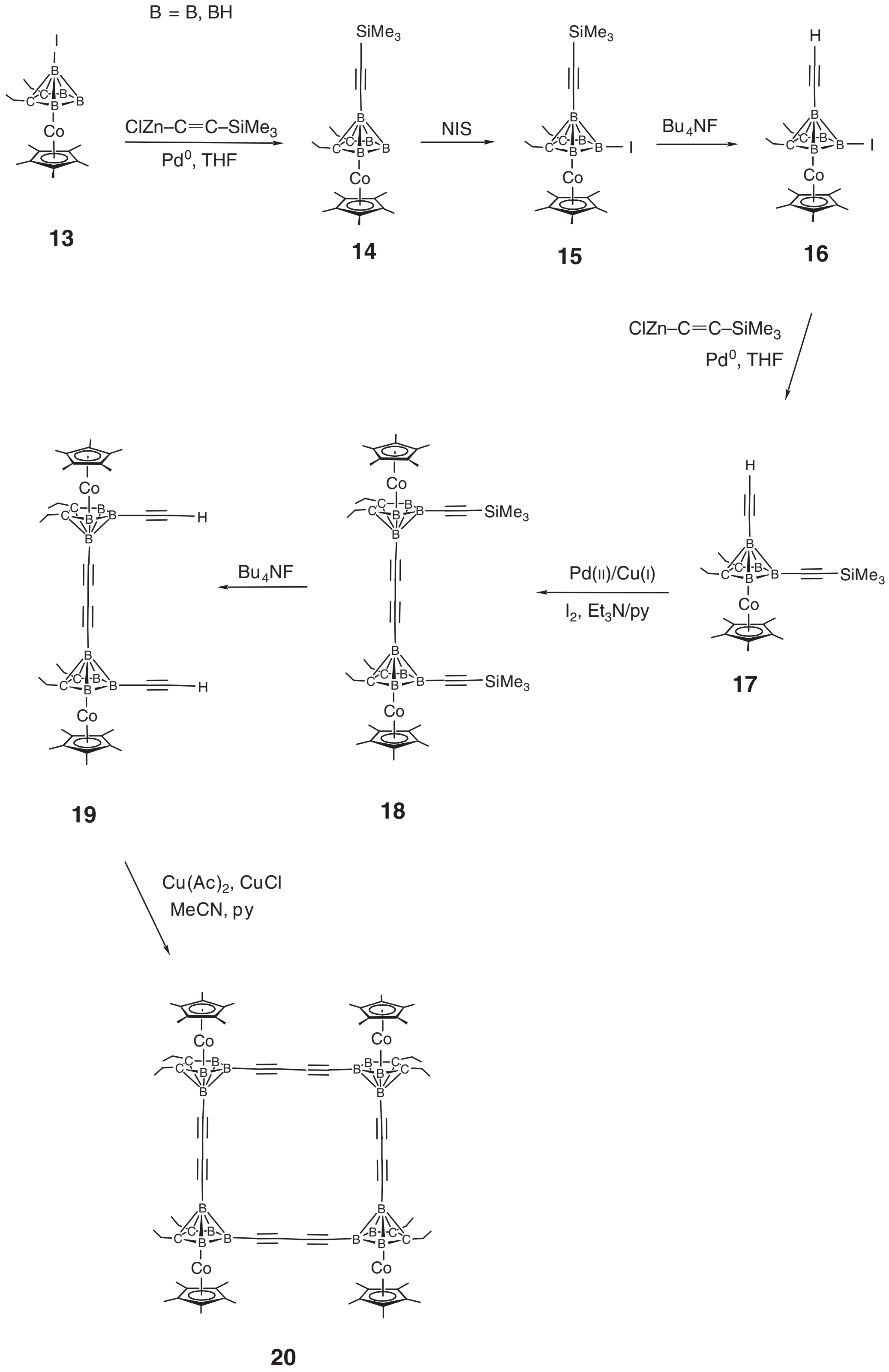


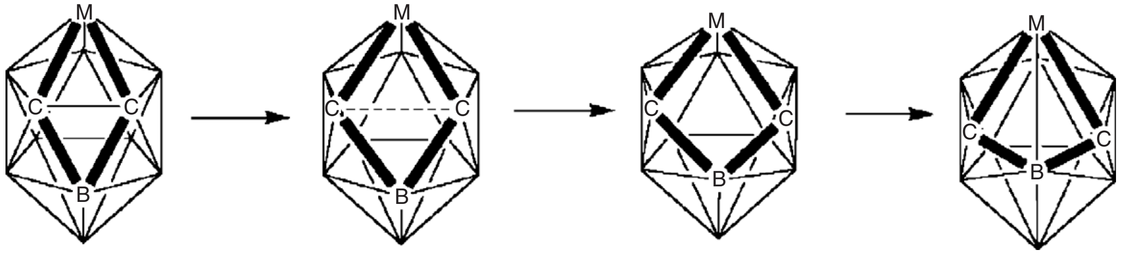
Figure 38 Crystal structure of $4\text{-}Cp^*\text{-}4,1,6\text{-}CoC_2B_{10}H_{14}$. This figure is reproduced from Burke, A.; McIntosh, R.; Ellis, D.; Rosair, G. M.; Welch, A. J. *Collect. Czech. Chem. Commun*. **2002**, *67*, 991 with permission of the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic.

[10-{3′-(Cp)-3′,1′,2′-CoC$_2$B$_9$H$_{10}$-9′-Hg}-7,8-C$_2$B$_9$H$_{11}$]$^-$ and 5,6,10-*exo*-*nido*-[Cl(PPh$_3$)$_2$Ru]-5,6,10-(μ-H)$_3$-10-{3′-(Cp)-3′,1′,2′CoC$_2$B$_9$H$_{10}$-9′-Hg}-7,8-C$_2$B$_9$H$_8$, respectively.[115] In the small cage systems, the chemical reactivity of (Cp*)Co(Et$_2$C$_2$B$_3$H$_5$) toward electrophilic reagents has been exploited successfully by Grimes and co-workers to prepare a number of such functionalized cobaltacarborane derivatives.[116–118] These studies parallel somewhat those described above for the (C$_6$H$_6$)Fe carboranes. The reaction of the mono-anion [(Cp*)Co(Et$_2$C$_2$B$_3$H$_4$)]$^-$ with alkyl reagents gave a series of B(5)-substituted (B(5) = unique boron) compounds of the form (Cp*)Co(Et$_2$C$_2$B$_3$H$_4$-5-CH$_2$-R′), in which R′ was an aryl, cyano, alkoxy, acyl, alkenyl, alkynyl, ester, fluoroalkyl, or fluoroaryl group; some of these functional groups could be further reacted to give other substituents. In all cases, the integrity of the cobaltacarborane unit was maintained. In a like manner, the reactions of [(Cp*)Co(Et$_2$C$_2$B$_3$H$_4$)]$^-$ with MeSO$_2$Cl, BrCH$_2$CN, and CF$_3$I gave [(Cp*)Co(Et$_2$C$_2$B$_3$H$_4$-5-X)] (X = Cl, Br, I).[117] On the other hand, reaction with CF$_3$C(O)Cl produced exclusively a B(nonunique)-C(O)CF$_3$ derivative, while monohalo B(nonunique)-X derivatives were obtained by the reaction of (Cp*)Co(Et$_2$C$_2$B$_3$H$_5$) with N-halosuccinimides.[117] The reaction of [(Cp*)Co(Et$_2$C$_2$B$_3$H$_4$)]$^-$ with acetyl chloride gave a boron(unique)-substituted 2-vinyl acetate derivative instead of the expected acetyl one. The base-catalyzed cleavage of this complex produced a B(unique)-substituted acetyl complex.[116] The (Cp*)Co(Et$_2$C$_2$B$_3$H$_5$) starting material in these studies was derived from the parent (Cp*)Co(Et$_2$C$_2$B$_4$H$_4$) by reaction with moist TMEDA (a decapitation reaction). As in the (C$_6$H$_6$)Fe system, the process can be reversed by the reaction of (Cp*)Co(Et$_2$C$_2$B$_3$H$_5$) with BX$_3$ or other boron halide compounds, to give substituents on the apical boron, B(7).[119] Using this and the basal hydrogen substitution reactions discussed above, all the terminal borons of this parent cobaltacarborane could be systematically replaced to give peralkylated and perhalogenated products.[120] Depending on the choice of the reboronation reagent, a wide range of complexes are accessible. When the dianion [(Cp*)Co(Et$_2$C$_2$B$_3$H$_5$)]$^{2-}$ reacts with 1,4-(Br$_2$B)$_2$C$_6$H$_4$, [(Cp*)Co(Et$_2$C$_2$B$_4$H$_3$-7)$_2$]C$_6$H$_4$ was obtained.[119] In this way a number of [(Cp*)Co(Et$_2$C$_2$B$_4$H$_3$-7)$_2$]X (X = MeCH, HC = CH, C≡C) as well as 7,7′-[(Cp*)Co(Et$_2$C$_2$B$_4$H$_3$)]$_2$ have been prepared and characterized.[121] Scheme 10 shows a series of reactions starting with (Cp*)Co(Et$_2$C$_2$B$_4$H$_3$-7-I) that leads to a number of di- and tetracobaltacaboranes connected by –C≡C–C≡C– links. Other macrocyclic cobaltacarboranes with different linking groups are also reported.[120,122,123] In the same way as Co, (Cp*)Ir(Et$_2$C$_2$B$_4$H$_3$-5-X) (X = H, Cl) can be prepared and the apical boron was removed in a so-called decapitation reaction.[124] The resulting (Cp*)Ir(Et$_2$C$_2$B$_3$H$_4$-5-Cl) was deprotonated and then mixed with [(Cp*)IrCl$_2$]$_2$ (X = H) or Rh(MeCN)$_3$Cl$_3$ (X = Cl) to give the multi-decker complexes, Cp*Ir(Et$_2$C$_2$B$_3$H$_2$-6-Cl)IrCp* and [Cp*Ir(Et$_2$C$_2$B$_3$H$_2$-5-Cl)]$_2$RhH, respectively.[124] Polynuclear cobaltacarborane dendrimers have been obtained from the reaction of *nido*-[η^5-C$_5$H$_4$C(O)Cl]Co(2,3-Et$_2$C$_2$B$_3$H$_5$) with diaminobutane-dend-(NH$_2$)$_n$ (n = 16 (DAB-16), 32 (DAB-32)) to give the 16- and 32-cobalt metalladendrimers, DAB-*dend*-[NHC(O)-C$_5$H$_4$Co(2,3-Et$_2$C$_2$B$_3$H$_5$)]$_n$ (n = 16 or 32, respectively).[125]

The effects of steric crowding on the structures of the MC$_2$B$_9$ cages have been studied extensively by Welch and co-workers.[126] Structural studies of a series of metallacarboranes with the general formula, 1-(Ph)-2(R)-3-(η^5-L)-3,2,1-MC$_2$B$_9$H$_9$, showed an increase in the distortion of these complexes from their idealized *closo*-MC$_2$B$_9$ structure that were functions of the steric requirements of R and L. The distortion could range from minor ones, such as an increased slippage of the metal away to the cage carbons, to a complete deformation of the cage, in which the C(cage)–C(cage) bond has ruptured. An example of the former is seen in the increased value of the slip distortion parameter, Δ,[127] for 1,2-(R)$_2$-3-COD-3,1,2-PdC$_2$B$_9$H$_9$ when going from R = H (0.24 Å)[128] to R = Ph (0.52 Å).[129] On the other hand, in the complexes 1,2-(Ph)$_2$-3-(η^5-L)-3,2,1-MC$_2$B$_9$H$_9$ (M = Rh, L = Cp*;[130] M = Ir, L = Cp*;[131] M = Ru, L = C$_6$H$_6$, MeC$_6$H$_4$-Pr^i (cym), C6Me6131), the distortion is such that the C(cage)–C(cage) bond is essentially broken ($r_{C-C} \sim 2.5$ Å) to give a *pseudocloso*-structure (see Figure 39 for cage definitions and atom arrangements). A comparison of the ^{11}B NMR spectra of the *pseudocloso*-metallacarboranes with their respective *closo*-analogs shows that the weighted average of the ^{11}B chemical shifts, $<\delta(^{11}\mathrm{B})>$, of the former are shifted to higher frequencies by ca. 15 ppm.[131] An inverse correlation was also noted between the M–B(6) and the C(1)–C(2) distances (B(6) is the boron in the second tier that is bonded to the two cage carbons), suggesting a continuum from *pseudocloso*- to *hypercloso*-structures.[132] The structures of the less sterically crowded metallacarboranes [1-(Ph)-2-Me-3-(cym)-3,1,2-RuC$_2$B$_9$H$_9$][133] and [1-Ph-2-(PhC≡C)-3-(cym)-3,1,2-RuC$_2$B$_9$H$_9$][132] show C$_{\text{cage}}$–C$_{\text{cage}}$ distances of 1.754(11) and 2.1844 Å, respectively, which are intermediate between what is expected in a *closo*- and a *pseudocloso*-structure; the authors referred to these as having *semipseudocloso*-structures. The $<\delta(^{11}\mathrm{B})>$ of the ^{11}B NMR spectra of these compounds is not as much shifted to higher frequencies as those found in the *pseudocloso*-structures, consistent with an intermediate structure. The reaction of Tl$_2$[7-(PhC≡C)-8-Ph-7,8-*nido*-C$_2$B$_9$H$_9$] and [Cp*RhCl$_2$]$_2$ in CH$_2$Cl$_2$ gave [1-Ph-2-(PhC≡C)-3-(Cp*)-3,1,2-RhC$_2$B$_9$H$_9$] that crystallized in an essentially equimolar mixture of two solid forms, both of which were structurally characterized.[134] One form, "a," was found to have a *closo*-structure, with a C(cage)–C(cage) distance of 1.828(7) Å, while the other "b" had C(cage)–C(Cage) distance of 2.052(5) Å for a *semipseudocloso*-rhodacarborane; these compare to the value 2.51 Å for the *pseudocloso*-[1,2-(Ph)$_2$-3-(Cp*)-3,1,2-RhC$_2$B$_9$H$_9$].[132,134] The effect of steric crowding has been extended to the charge-compensated metallacarboranes. The reaction of



Scheme 10 Sequence of reactions leading to alkyne-coupled polyferracarborane clusters. Reproduced by permission from *J. Organomet. Chem*. **2003**, *680*, 51.



closo *semipseudocloso* *pseudocloso* *hypercloso*

Figure 39 Structure of $MC_2B_9H_{11}$ showing the progression from *closo*- to *hypercloso*-.

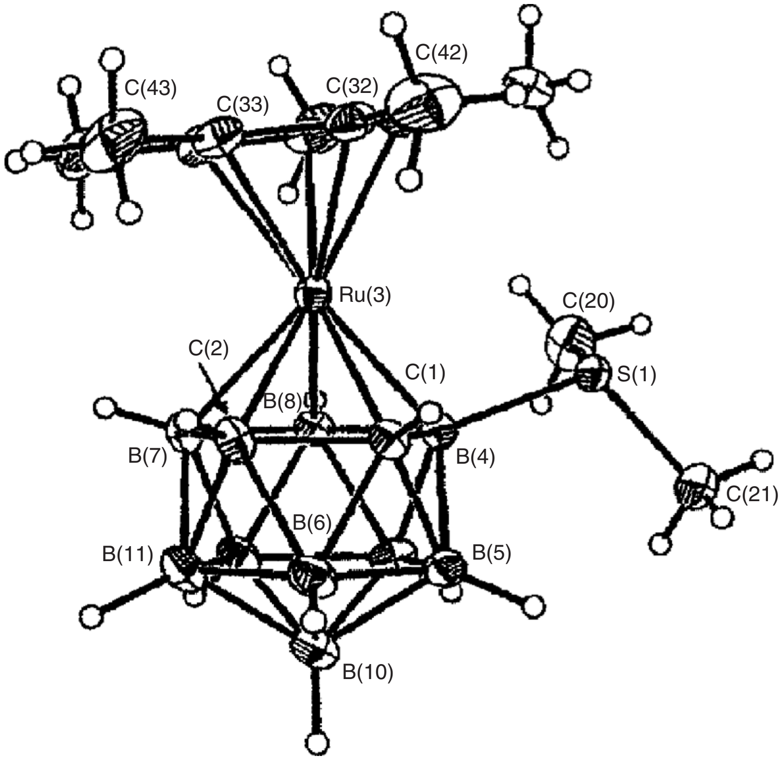


Figure 40 Crystal structure of 3-(Cp*)-4-SMe_2-3,1,2-$RuC_2B_9H_{10}$. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 3227.

$[Ru(Cp^*)Cl]_4$ with the monoanion, $[7\text{-}R_1\text{-}8\text{-}R_2\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_8]^-$, gave different isomers, depending on the identities of R^1 and R^2.[135] When $R^1 = R^2 = H$, the expected 3-(Cp^*)-4-SMe_2-3,1,2-$RuC_2B_9H_{10}$ was obtained; the structure and the atom numbering system is given in Figure 40. When $R^1 = Ph$ and $R^2 = H$, 1-Ph-3-(Cp^*)-7-SMe_2-3,1,2-$RuC_2B_9H_9$ was obtained, but rapidly isomerized when warmed to 3-(Cp^*)-4-SMe_2-11-Ph-3,1,11-$RuC_2B_9H_9$, in which the C–Ph group was on the second-tier pentagonal ring of the cage. Surprisingly, the 1-Ph-3-(Cp^*)-4-SMe_2-3,1,2-$RuC_2B_9H_9$, in which the SMe_2 and Ph groups were adjacent, showed no signs of isomerization, even when heated. On the other hand, when $R^1 = R^2 = Ph$, 1,2-$(Ph)_2$-3-(Cp^*)-4-SMe_2-3,1,2-*pseudocloso*-$RuC_2B_9H_8$ was the only product. Factors other than just steric crowding could also be at work. This was demonstrated in the structural investigation of some C(cage)-substituted pyrolyl cobaltacarboranes of the type, 3-(η^5-NC_4H_4)-1,2-$(X)_2$-$CoC_2B_9H_9$.[136] The C(cage)–C(cage) distances were found to increase from 1.640(7) Å for X = H, to 1.919 Å for $X = SCH_3$ and 1.864 Å for X = SPh. It was argued that the available lone pairs could feed electron density into antibonding orbitals localized on the cage carbons, thereby increasing the bond distance. On the other hand, purely alkyl substituents (Ph/H, Bu/Me, Pr/Ph) had little effect on the C(cage)–C(cage) bond distance. Such interactions were also found to affect the redox potentials of several cobaltacarboranes.[137] The structural changes accompanying the redox cycles of $\{[(C_2B_9H_{11})M(\mu\text{-}SPh)_2]_2\}^{n}$

(M = Mo, W; *n* = 2−, 1−, 0),[54] that were discussed earlier, are consistent with these observations. Thus, several possible interactions can lead to the continuum: *closo*- → slipped *closo*- → *semipseudocloso*- → *pseudocloso*- → *hypercloso*-structures. Hopefully, all future metallacarboranes will fall within this spectrum lest we run out of descriptive prefixes.

Much of the early, and present, interest in the [*nido*-$C_2B_9H_{11}$]$^{2-}$ anion is that its primary metal binding orbitals are a set of π-type orbitals delocalized above the open C_2B_3 pentagonal face that bear a striking resemblance to those on [C_5H_5]$^-$; however, the difference in the charge on the two ligands makes any direct comparison difficult. For this reason, there has been considerable interest in the charge-compensated carboranes, such as [*nido*-9-(Me_2S)-7,8-$C_2B_9H_{10}$]$^-$, which should be more analogous to the Cp ligand. A number of reactions of this carborane monoanion with various metallating reagents have been described that give rise to complexes of the type, [4-(Me_2S)-3,2,1-$MC_2B_9H_{10}$] (M = Ru(C_6H_6),[138] Ru(1,3,5-$Me_3C_6H_3$),[138] Fe(Cp*),[139] Rh(CO)$_2$,[140] Rh(COD),[140] Pd(η^2,σ-5-OMe-C_8H_{12}),[140] Rh(CO)I$_2$, and Rh(PPh$_3$)Cl$_2$[141], Ir(COD)[141a]). Stable 1 : 1 charge transfer salts, such as [3-(Cp*)-4-(Me_2S)-3,2,1-$FeC_2B_9H_{10}$]$^+$ddq$^{\cdot-}$ (ddq = 2,3-dichloro-5,6-dicyano-benzoquinone), could be prepared in 75% yield by mixing a solution of the ferracarborane, dissolved in CH_2Cl_2, with an equivalent amount of ddq in the same solvent.[139] The ferracarborane reacts in a similar manner with 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane (tcntfq). The crystal structure of [3-(Cp*)-4-(Me_2S)-3,2,1-$FeC_2B_9H_{10}$]$^+$ddq$^{\cdot-}$ shows that the ddq$^{\cdot-}$ anions form isolated stacked dimers.[139] The dimers are arranged in rows that fit into channels, which are lined with rows of the cations. Conductivity measurements on single crystals of the salt gave extremely low conductivities of less than 10^{-7} S cm^{-1}. The lack of conductivity was consistent with the structure of noninteracting [ddq$_2$]$^{2-}$ dimers. The charge-compensated full-sandwich complex, *commo*-[3,3′-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$] was synthesized by the reaction of [*nido*-9-(Me_2S)-7,8-$C_2B_9H_{10}$]$^-$ with a suspension of FeCl$_2$ in THF.[142] The *meso* and DD/LL isomers could be separated by fractional crystallization from acetone. The charge transfer salt, [3,3′-Fe{4-(Me_2S)-1,2-$C_2B_9H_{10}$}$_2$]$^+$[ddq]$^{\cdot-}$, was synthesized by reacting the DD/LL racemate with ddq. The X-ray structure of the salt showed that the cations and anions formed alternating layers in the crystal. The single crystal electrical conductivity of the salt showed it to have an insulating nature (conductivity less than 10^{-8} S cm^{-1}).[142] The neutral, charge-compensated, arene-like carborane, 7,10-(Me_2S)$_2$-7,8-$C_2B_9H_9$, was found to react with [Rh(COD)]$^+$ to give the cationic complex, [3-(COD)-8,11-(SMe_2)$_2$-2,1,8-$RhC_2B_9H_9$]$^+$, that was isolated as its [BF$_4$]$^-$ salt.[143] The X-ray crystal structure of this compound, given in Figure 41, shows that metallation was accompanied by a shift of the C–SMe$_2$ from the bonding face to a position in the lower belt of the carborane.[143]

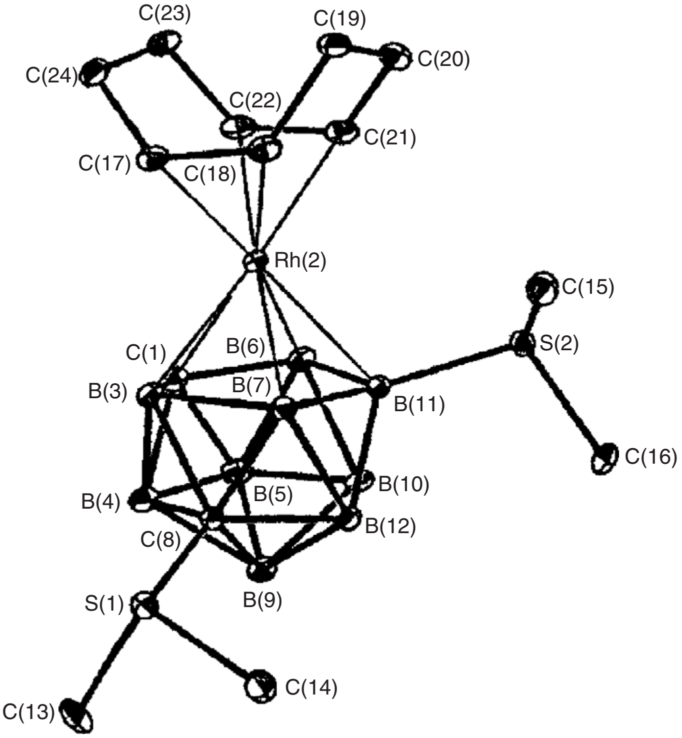
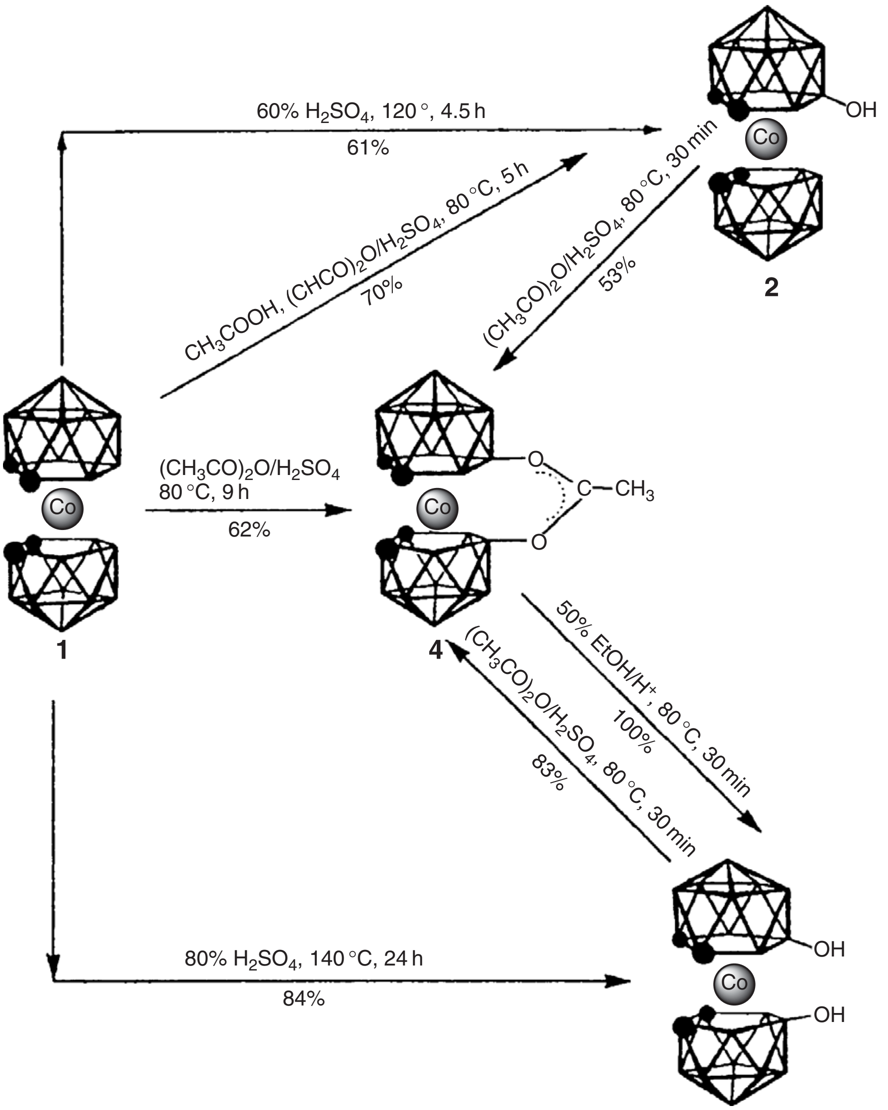


Figure 41 Crystal structure of the cationic complex, [3-(COD)-8,11-(SMe_2)$_2$-2,1,8-$RhC_2B_9H_9$]$^+$. Reproduced by permission of The Royal Society of Chemistry from Tutusaus, O.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Teixidor, F. *Chem. Commun*. **2003**, 2458.

The full sandwich, $[Co(C_2B_9H_{11})]^-$, has also been the subject of a number of derivatization studies.[144] The syntheses of the dihalo-cobaltacarboranes, $[3,3'-Co(8,8'-X-1,2-C_2B_9H_{10}]^-$, were studied using several preparative methods, including reaction with HOCl (X = Cl), N-halosuccinimide, and direct reaction with the halogen elements.[145] In the case of Cl_2, the extent of chlorination could be controlled by the presence of iron powder. This was not required for Br_2, while with I_2, no iodination was found after 24 h reflux in THF. The diiodo compound could be prepared by the reaction of $[Co(C_2B_9H_{11})_2]^-$ with ICl in refluxing EtOH.[146] The dihalogenated products are useful as starting materials, for example, $[3,3'-Co(8,8'-I-1,2-C_2B_9H_{10})_2]^-$ when treated with MgMeBr, followed by $[Pd(PPh_3)_2Cl_2]$/CuI, produced a mixture of $[3,3'-Co(8,8'-(Me)_2-1,2-C_2B_9H_{10})_2]^-$ (60% yield) and $[3,3'-Co(8-OH-8'-Me-1,2-C_2B_9H_{10})_2]^-$ (33% yield).[146] The corresponding 8,8′-$(Et)_2$ and 8-(OH)-8′-Et substituted compounds could be prepared when MgEtBr was used in place of MgMeBr. The $[3,3'-Co(8-OH-8'-Me-1,2-C_2B_9H_{10})_2]^-$ further reacted with I_2 in EtOH to give the bridged compound, $[8,8'-(\mu-O)-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$, in a 47% yield.[146] The dichloro- and dibromo-cobaltacarborane sandwich compounds are of interest in themselves. The cobalt(bis)dicarbollides are capable of selectively removing cesium ions from solution,[147] and dihalogenation has been shown to impart increased stability toward degradation by radiation.[148] Therefore, the dihalogenated cobalt dicarbollides are excellent candidates as scavengers for the removal of ^{137}Cs from radioactive wastes. The monoiodinated cobalt(bis)dicarbollide, $[3,3'-Co(8-I-1,2-C_2B_9H_{10})\ (1',2'-C_2B_9H_{11})]^-$, was found to react with trimethylsilylacetylene ($Me_3SiC{\equiv}CH$) in the presence of $[Pd(PPh_3)_2Cl_2$/CuI and $^iPr_2NH$ in refluxing THF to give the alkene-linked compound $[8,8'-(\mu-C_2H_2)-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$.[149] The cobalt(bis)dihydroxo-carbollide, $[3,3'-Co(8,8'-(OH)_2-1,2-C_2B_9H_{10}]^-$, has also been shown to be a versatile starting material. The compound can be made by heating $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ in 80% aqueous sulfuric acid to 140 °C for 24 h.[150] It reacts with acetic anhydride $(Me_2C(O))_2O$ in H_2SO_4 to give $[8,8'-(\mu-MeCO_2)-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$. It is of interest that this compound can be made directly from $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ by the reaction of $(Me_2C(O))_2O/H_2SO_4$ in acetic acid, which can then, in turn, be hydrolyzed to give $[3,3'-Co(8,8'-(OH)_2-1,2-C_2B_9H_{10})]^-$; Scheme 11 shows the conditions under which the different compounds, including $[3,3'-Co(8-(OH)-1,2-C_2B_9H_{10})(1',2,-C_2B_9H_{11})]^-$, can be interconverted.[150] Repeated additions of $POCl_3$ and Et_3N to a solution of $[3,3'-Co(8,8'-(OH)_2-1,2-C_2B_9H_{10})]^-$ in chloroform produced the bridged phosphochloride compound, $[8,8'-(\mu-P(O)ClO_2)-3,3'-Co(1,2-C_2B_9H_{10})]^-$, which could be converted to a phosphoric bridge compound, $[8,8'-(\mu-(OH)\ (O)-PO_2)-3,3'-Co(1,2-C_2B_9H_{10})]^-$, by treatment with aqueous EtOH/KOH.[151] Reaction of the monohydroxo compound $[3,3'-Co(8-(OH)-1,2-C_2B_9H_{10})\ (1',2,-C_2B_9H_{11})]^-$ with $Cl_2(R)P(O)$ (R = Cl and Ph), followed by hydrolysis, produced the respective 8-phosphorylated species.[151] The crown ether appended compound $[3,3'-Co(8-(21-crown-7-CH_2O)1,2-C_2B_9H_{10})\ (8'-OH-1'2'-C_2B_9H_{10})]^-$ could be obtained by the reaction of the zwitterionic $[3,3'-Co(8-(C_4H_8O_2)-1,2-C_2B_9H_{10})\ (1',2'-C_2B_9H_{11})]$ with $CRWCH_2ONa$ (CRW = 15-crown-5, 18-crown-6, and 21-crown-7).[152] The crown ether complexes were studied as Cs^+ and Sr^{2+} complex agents in liquid–liquid extraction.[152] A different route to the synthesis of the bridging crown ether derivative of the cobalt(bis)dicarbollide, $[1,1'-\mu-\{S(CH_2CH_2O)_3CH_2CH_2S\}-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$, involved an initial linking of two 1-(SH)-*closo*-$1,2-C_2B_{10}H_{11}$ molecules by reaction with bis[2-(2-chloroethoxy)ethyl] ether, $(ClC_2H_4OC_2H_4)_2O$, followed by decapitation and reaction with $CoCl_2$ and ^tBuOK.[153] A similar approach, involving the reaction of ethyl-3,4-dipropagyloxylbenzoate with $B_{10}H_{12}(SEt)_2$, then followed by decapitation with either pyrrolidine or piperidine and reaction with $CoCl_2$, gave ultimately $3,3'-Co(1-C_4H_8N-1,2-C_2B_9H_{10})(1'-C_4H_8NH-1,2-C_2B_9H_{10})$ or $3,3'-Co(1-C_5H_{10}N-1,2-C_2B_9H_{10})(1'-C_5H_{10}NH-1,2-C_2B_9H_{10})$, respectively, as seen in Scheme 12.[154]

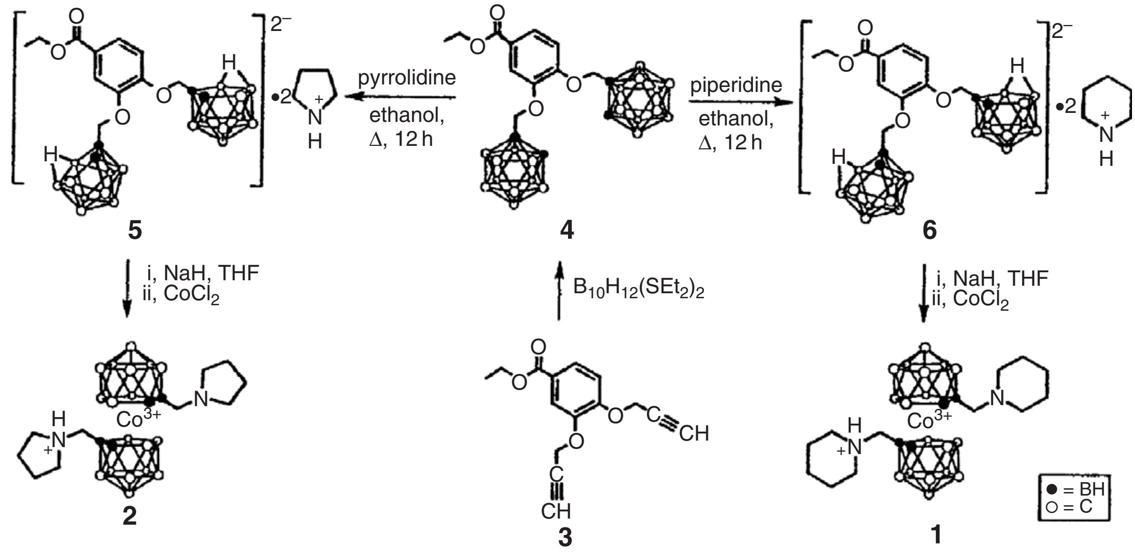
In the small cage system, the behavior of the late transition metal carborane complexes depends on the thermodynamic stabilities of the two isomeric *nido*-C_2B_4 carboranes.[95] In general, both the "carbons adjacent" and the "carbons apart" isomers seem to bind metals equally well, but the latter isomer is thermodynamically the more stable one. This was demonstrated by the reactions of anhydrous $NiCl_2$ with the two isomeric *nido*-C_2B_4 carboranes. The reaction with the dilithium-complexed "carbons adjacent" *nido*-carborane dianions $[2-(SiMe_3)-3-(R)-2,3-C_2B_4H_4]^{2-}$ (R = $SiMe_3$, Me) in *n*-hexane, THF, or TMEDA gave the oxidative cage closure product, 1-$(SiMe_3)$-2-(R)-1,2-*closo*-$C_2B_4H_4$ derivatives in 40–59% yields, along with small quantities of C_4B_8-carborane derivatives, with no evidence of a persisting nickelacarborane.[9h] Platinum salts were found to give the same oxidative cage closure reactions. A face-to-face fused C_4B_8 cage product was earlier reported by Grimes and co-workers that also proceeded from the less thermodynamically stable "carbons adjacent" metallacarboranes.[155–158] On the other hand, as shown in Scheme 13, the reaction of $NiCl_2$ with the "carbons apart", THF-solvated dilithium compound of $[2,4-(SiMe_3)_2$-*nido*-$2,4-C_2B_4H_4]^{2-}$ produced an Ni(IV) complex, *commo*-1,1′-$Ni[2,4-(SiMe_3)_2-2,4-C_2B_4H_4]_2$ and Ni(0), with no evidence of the cage oxidation product.[159] In the presence of TMEDA, the Ni(II) half-sandwich 1-(TMEDA)-*closo*-$Ni[2,3-(SiMe_3)_2-2,4-C_2B_4H_4]$ could be obtained.[159] Reaction of the Ni(IV) complex with moist TMEDA produced 1-(TMEDA)-*closo*-$Ni[2,3-(SiMe_3)_2-2,4-C_2B_4H_4]$ and 1,2-$(SiMe_3)_2$-1,2-*closo*-$C_2B_4H_4$. This is one of the few instances when the more stable "carbons apart" undergoes oxidative cage closure. Thus, in the presence of good coordinating



Scheme 11 Synthetic cycles of the hydroxocobaltacarboranes. Reproduced by permission from *J. Organomet. Chem*. **2002**, *649*, 181.

solvents, the half-sandwich *closo*-metallacarboranes can be stabilized.[159–161] Another example is seen in the fact that a full sandwich Co(III) complex, $\{1,1'\text{-}commo\text{-Co}[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2\}^-$, was formed by the reaction of $CoCl_2$ with the THF-solvated trinuclear *closo*-samaracarborane precursor,[66] while the TMEDA-solvated dilithiacarborane was found to react with $CoCl_2$ to give the half-sandwich 1-Co(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$.[161] The nickelacarboranes illustrate a factor that is prevalent in metallacarborane chemistry, that is the relationship between the metal's oxidation state and cluster structure. When different oxidation states are available to the metal, the higher states are found in the full-sandwich (*commo*-) compounds, while the half-sandwich (*closo*-) compounds support lower states. This is true for both transition metals and main group metals. The nickelacarboranes nicely illustrate this oxidation state/structure correlation. The metallacarboranes of Ni(II), Ni(III) and Ni(IV) have been reported in both the small, C_2B_4, and the larger, C_2B_9,[162,163] cage systems, with the Ni(II) involved in *closo*-metallacarboranes and the two higher oxidation states in sandwiched *commo*-complexes.

In the larger cage systems, the nickel group metals form stable half-sandwich complexes, as outlined in COMC (1982) and COMC (1995).[4,4a] More recently, the constrained-geometry nickelacarborane, $[(\eta^1\!:\!\eta^5\text{-}C_2B_9H_{10}\text{-}CH_2NMe_2)Ni(PPh_3)]$, was synthesized by the reaction of the carborane dianion with $(PPh_3)_2NiCl_2$; the structure showed that the Ni(II) resides above the C_2B_3 open face of the carborane and is also coordinated by the tethered

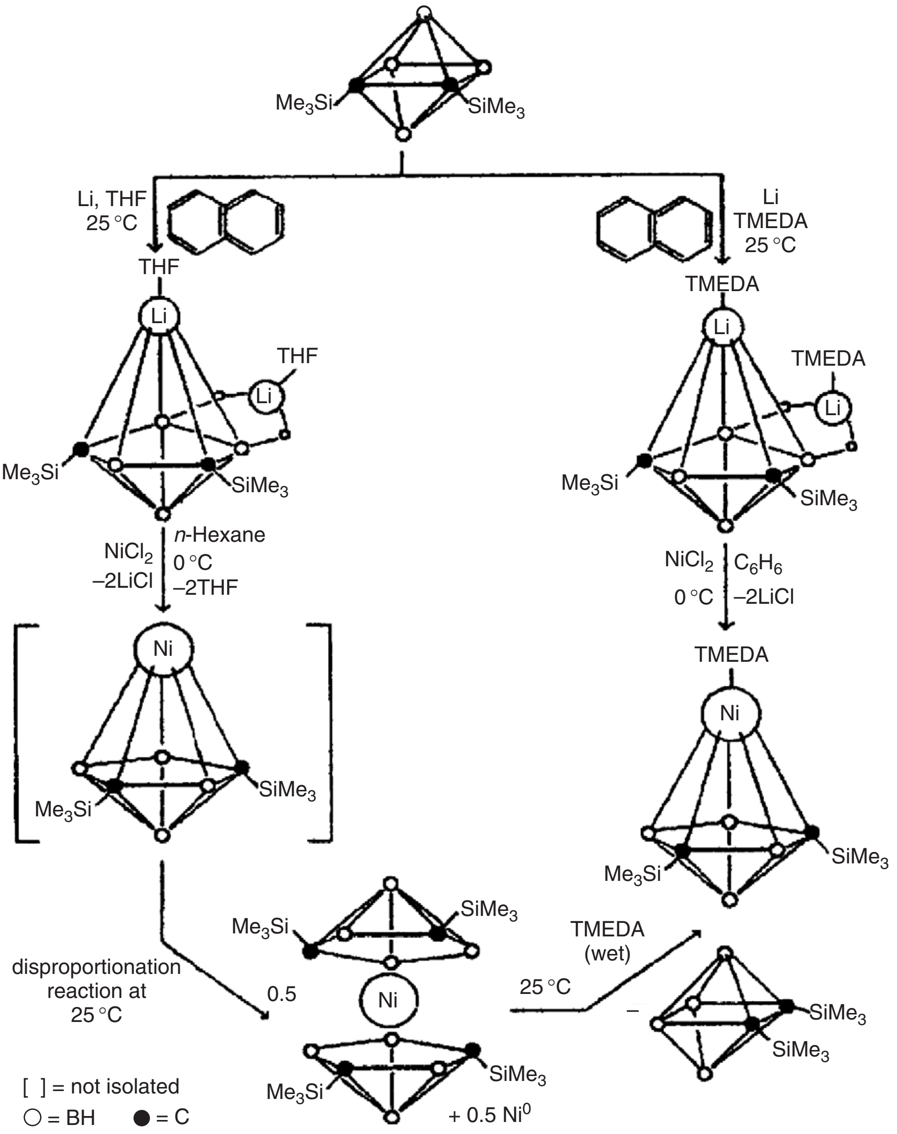


Scheme 12 Syntheses of the piperdinium and pyrrolidinium cobaltacarboranes. Reproduced by permission from *J. Mol. Struct*. **2003**, *656*, 239.

amino group and a triphenylphosphine ligand.[164] Reactivity studies showed that the amine group can be displaced by the monodentate ligands, PMe$_3$ and CNBu^t, but the bidentate ligands, PPh$_2$(CH$_2$)$_2$PPh$_2$ (dpe) and bipy, resulted in replacement off the PPh$_3$ group. The authors attributed this to the lability of the Ni–N bond due to a presumed mismatch between the "soft" late transition metal and the "hard" nitrogen base; the PPh$_3$ replacement was attributed to the enhanced stability of a chelating ligand compared to a monodentate one.[164] The reactivity of several phosphacarboranes, 6-Ph-*arachno*-6,8,9-PC$_2$B$_7$H$_{11}$ and 6-Ph-*arachno*-6,5,7-PC$_2$B$_7$H$_{11}$, and their anions, toward Co, Ni, Pt, and Pd metal groups has been reported (see Figure 42 for the cage structure and numbering system).[165] The neutral 6-Ph-6,8,9-*arachno*-6,8,9-PC$_2$B$_7$H$_{11}$ did not react with (PPh$_3$)$_2$MBr$_2$ (M = Pd, Pt). However, its dianion reacted readily with either (PPh$_3$)$_2$PtCl$_2$ or CpCo(CO)$_2$ to give the corresponding half-sandwich complexes, 8-Ph-7(PPh$_3$)2-*nido*-7,8,10,11-PtPC$_2$B$_7$H$_9$ and 7-Ph-11-Cp-*nido*-11,7,9,10-CoPC$_2$B$_7$H$_9$. The structure of the former compound is shown in Figure 42, while the structure of the Co compound is similar, despite the different numbering system. As can be seen, the Pt is bonded to the C(11)–B(6)–B(2)–P side of the open carborane face. The carborane is η^4-bonded to the Co in a like manner. The reaction of the carborane mono-anion with NiBr$_2$ in a 2 : 1 molar ratio produced the full-sandwich *commo*-7,7′-Ni(8-Ph-*nido*-8,10,11-PC$_2$B$_7$H$_9$)$_2$. In this compound, the two phosphacarboranes are η^4-bonded to the central Ni. Since both phosphacarboranes have lost an additional proton and are now di-anionic, the nickel is now in a formal +IV state. This is another instance of the full-sandwich metallacarborane complexes supporting a high metal oxidation state. It is of interest that the isomeric phosphacarborane, 6-Ph-*arachno*-6,5,7-PC$_2$B$_7$H$_{11}$, where the two cage carbons are adjacent to the phosphorus, was η^1-bonded through the P in complexes with Pd and Pt.[165]

The 13-vertex nickelacarborane, 4-dppe-4,1,6-*closo*-NiC$_2$B$_{10}$H$_{12}$, was recently reported by Welch and co-workers.[59] The structure of the CH$_2$Cl$_2$ solvate of the complex was determined by X-ray crystallography and is shown in Figure 43. The structure shows that the Ni occupies the capping position above the C$_2$B$_4$ face of the carborane, as with the other supraicosahedral metallacarboranes (see above), the bonding face is not planar, causing the Ni-ring-atom distances to range from 2.051 Å for Ni–C(1) to 2.381 Å for Ni–C(6) Å, the two Ni–P distances also differ by 0.05 Å. The difference in the Ni–P bonds was explained in terms of the greater *trans* effect of the boron side of the bonding face. Although the compound is asymmetric, there are only single P and CH resonances in the ^{31}P NMR and ^{1}H NMR spectra, indicating fluxionality. The fluxional behavior of the MC$_2$B$_{10}$ complexes is well known and is thought to proceed by a double diamond–square–diamond mechanism.[166] An activation energy for the fluxional process was calculated to be ca. 47 kJ mol^{-1} by ^{31}P and ^{1}H NMR spectral analysis.[59]

A number of the heavier group 10 metallacarboranes have been synthesized and many structurally characterized. As part of their investigations of the metal complexes of the monocarbaboranes, Stone and co-workers studied the reactions of the hydrido complexes [PtH(PEt$_3$)$_2$(η^5-7-CB$_{10}$H$_{11}$)] with [AuCl(PPh$_3$)], [HgClPh], and [CuCl(PPh$_3$)]$_4$ to



Scheme 13 Syntheses of the full- and half-sandwich nickelacarboranes in the "carbons apart" system. Reproduced by permission of the American Chemical Society from *Organometallics* **1993**, *12*, 3933.

yield the bimetallic compounds, [PtM(PPh$_3$)(PEt$_3$)$_2$(η^5-7-CB$_{10}$H$_{11}$)] (M = Au, Cu) and [PtHg(Ph)(PEt$_3$)$_2$(η^5-7-CB$_{10}$H$_{11}$)]. The structures of the compounds are similar in that the metal group had replaced the H in the hydrido complex and was σ-bonded to the Pt; the Cu(PPh$_3$) moiety was attached by two B–H–Cu bonds in addition to the Pt–Cu bond.[167] A number of platinum and palladium complexes of the type MC$_2$B$_9$, in which the cage carbons have bulky substituents, have been characterized by Welch and co-workers in an attempt to elucidate the mechanism of the thermal rearrangements of icosahedral heterocarboranes. The reaction of *cis*-Pt(PMe$_2$Ph)$_2$Cl$_2$ with Tl$_2$[7-Ph-7,8-C$_2$B9H$_{10}$] gave 1-Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-PtC$_2$B$_9$H$_{10}$, which rearranged on mild thermolysis (55 °C) to give 1-Ph-3,3-(PMe$_2$Ph)$_2$-3,1,11-PtC$_2$B$_9$H$_{10}$ and 11-Ph-3,3-(PMe$_2$Ph)$_2$-3,1,11-PtC$_2$B$_9$H$_{10}$, in which either the C–Ph or the C–H vertex moved down to the second tier pentagonal ring.[168] On the other hand, the reaction of *cis*-Pt(PMe$_2$Ph)$_2$Cl$_2$ with Tl$_2$[7,8-(Ph)$_2$-7,8-C$_2$B$_9$H$_9$] at room temperature yields only 1,11-(Ph)$_2$-3,3-(PMe$_2$Ph)$_2$-3,1,11-PtC$_2$B$_9$H$_9$.[168] However, the "carbons apart" platinacarborane, 1,1-(Me$_2$Ph)-2,4-(Ph)$_2$-1,2,4-PtC$_2$B$_9$H$_9$, was stable in refluxing toluene and showed no sign of isomerization.[169] The stability of this compound, which would be an intermediate in a diamond–square–diamond isomerization of the 3,1,2-PtC$_2$B$_9$ to the 3,1,11-PtC$_2$B$_9$ isomer, precludes that mechanism as operable in these isomerizations. The reaction of the boron-labeled, [3-X-7,8-*nido*-C$_2$B$_9$H$_8$]$^{2-}$ (X = Et, F), with

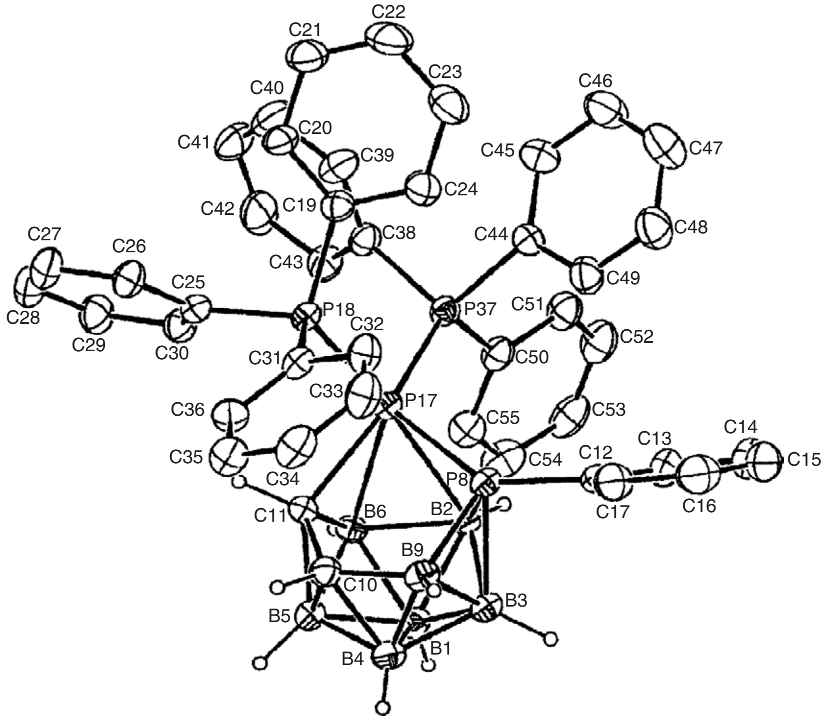


Figure 42 Crystal structure of 8-Ph-7(PPh$_3$)2-*nido*-7,8,10,11-PtPC$_2$B$_7$H$_9$. Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc*. **2003**, *125*, 16058.

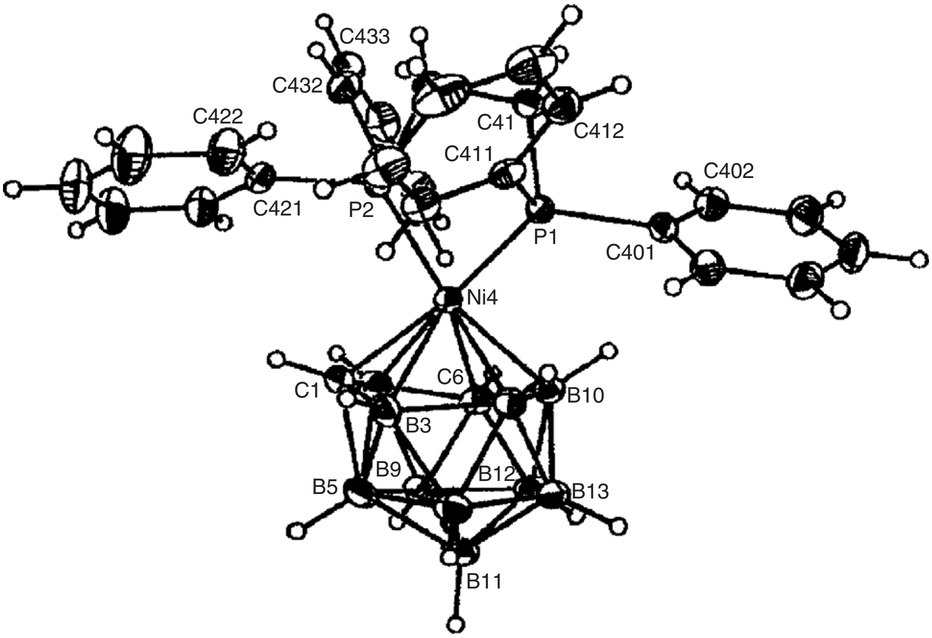


Figure 43 Crystal structure of 13-vertex nickelacarborane, 4-dppe-4,1,6-*closo*-NiC$_2$B$_{10}$H$_{12}$. Reproduced by permission of Elsevier from *Inorg. Chim. Acta* **2003**, *347*, 161.

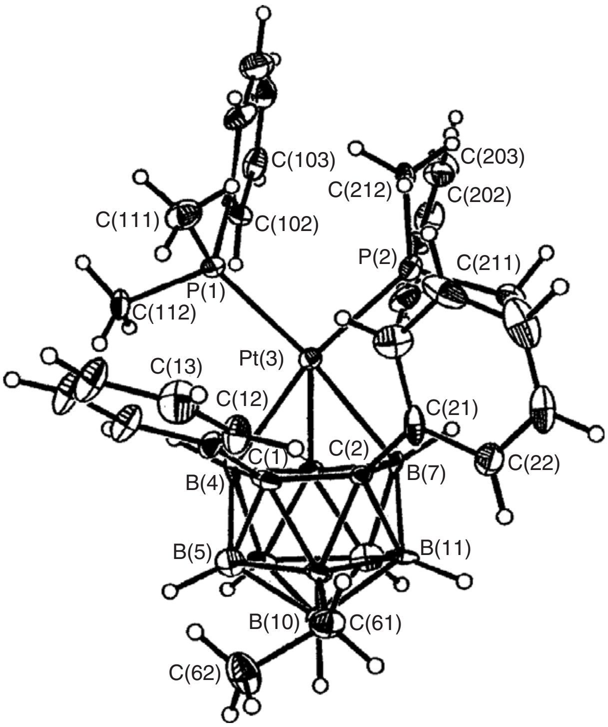


Figure 44 Crystal structure of 1,2-$(Ph)_2$-3,3-$(PMe_2Ph)_2$-6-Et-3,1,2-$PtC_2B_9H_8$. Reproduced by permission of Elsevier from *J. Organomet. Chem*. **2003**, *680*, 286.

cis-$(PMe_2Ph)_2PtCl_2$ produced either the 1,2-$(Ph)_2$-3,3-$(PMe_2Ph)_2$-6-Et-3,1,2-$PtC_2B_9H_8$ (see Figure 44 for the structure and the atom numbering system) or the isomerized product 1,8-$(Ph)_2$-2,2-$(PMe_2Ph)_2$-4-F-2,1,8-$PtC_2B_9H_8$. The 3,1,2-PtC_2B_9 was a very slip-distorted ($\Delta = 0.72$ Å) intermediate that isomerized to 1,8-$(Ph)_2$-2,2-$(PMe_2Ph)_2$-4-Et-2,1,8-PtC_2B_9H, slowly at room temperature but more rapidly on warming.[170] The simplest mechanism for isomerization is a rotation of the C(2)B(7)B(11) trigonal face. The nature of the capping metal is also important in determining the ease of isomerization. This was demonstrated by the fact that the palladium complex 1,2-$(Ph)_2$-3-(COD)-3,1,2-$PdC_2B_9H_9$ was formed by the reaction of $Pd(COD)Cl_2$ with $Tl_2[7,8\text{-}(Ph)_2\text{-}7,8\text{-}C_2B_9H_9]$, while, under similar conditions, $Pt(COD)Cl_2$ reacted with the carborane to give the isomerized product 1,11-$(Ph)_2$-3-(COD)-3,1,11-$PtC_2B_9H_9$.[171] The palladium complex relieves steric crowding through slip distortion, $\Delta = 0.56$ Å, and an elongation of the C–B distances in the C_2B_3 face; the initially formed 3,1,2-PtC_2B_9 can alleviate crowding by isomerizing. The monophenyl carborane, $[7\text{-Ph-}7,8\text{-}C_2B_9H_{10}]^{2-}$, reacted with $M(COD)Cl_2$ (M = Pd, Pt) to give exclusively the un-rearranged products, 1-(Ph)-3-(COD)-3,1,2-$MC_2B_9H_{10}$ (M = Pd, Pt).[171] In the same way, $Tl_2[7\text{-}(C_4H_2RS)\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = H, Me) was found to react with $Pd(PMe_2Ph)_2Cl_2$ to give 1-(C_4H_2RS)-3,3-$(PMe_2Ph)_2$-3,1,2-$PdC_2B_9H_{10}$ as the major product.[172]

There are very few clear-cut examples where group 11 or 12 metals have been incorporated into carborane cages. In most cases the metals occupy *exo*-polyhedral positions or replace terminal hydrogens on the carborane cage. Although some of these compounds are of interest and are of potential use,[173] they lie outside the scope of this chapter. Early studies by Hawthorne and co-workers showed that in $[3\text{-}(PPh_3)\text{-}3,1,2\text{-}CuC_2B_9H_{11}]^-$, the Cu(I) occupied the apical position above the C_2B_3 bonding face, but was slightly slipped toward the boron side of the face.[174] The apical Cu was found to bond another Cu to form the dimetallic [*closo*-*exo*-4,8-$\{(\mu\text{-}H)_2Cu(PPh_3)\}$-3-$(PPh_3)$-3,1,2-$CuC_2B_9H_9$] in which the *exo*-polyhedral $Cu(PPh_3)$ group is bonded to the CuB_2 face through a Cu–Cu bond and two B–H–Cu bridges; the presence of the extra Cu exerts little influence of the Cu(apical)–cage bond distances.[174] The situation is quite different in the more sterically crowded bimetallic complexes, $(R_3PCu)_2(CPh)_2B_9H_9$ (R = PPh_3, PCy_3, P(*o*-tol)$_3$).[175] In these complexes, an *exo*-polyhedral (R_3PCu) group was bound to the B_3 triangular face opposite to the cage carbons and the capping Cu is quite slip-distorted, the distortion being greater when R = *o*-tol than when R = Ph.[175] This is another demonstration of the importance of steric interactions in determining the geometries of metallacarboranes.

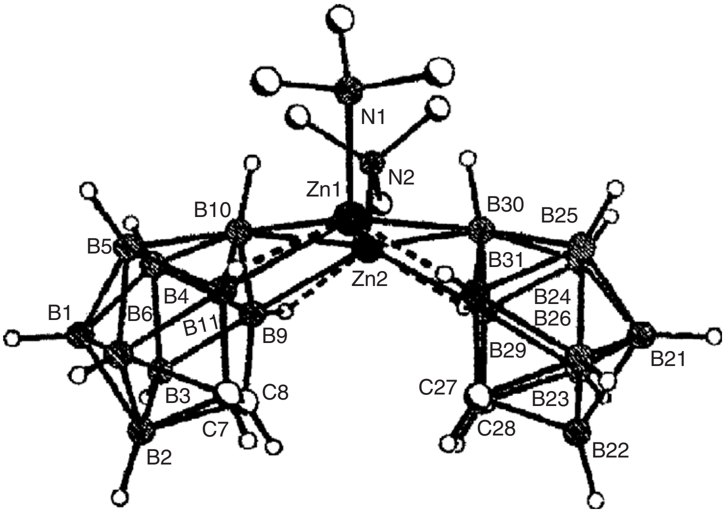


Figure 45 Crystal structure of zinc carborane dimer, $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$. Reproduced by permission of The Royal Society of Chemistry from Goeta, A. E.; Howard, A. K.; Hughes, A. K.; Johnson, A. L.; Wade, K. *Chem. Commun.* **1998**, 1713.

An interesting zinc carborane dimer, $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$, has been synthesized, in which two C_2B_9 cages are oriented such that their C_2B_3 faces are opposite and parallel to one another; the two carboranes are held in place by a set of two Me_3NZn groups that are bridged between two boron atoms on each carborane, resulting in an unusual Zn_2B_2 ring. Figure 45 shows the structure of this compound.[176]

Mercuracarboranes have been synthesized in both the small (C_2B_4) and large (C_2B_9) cage systems. In the small cage mercuracarboranes, the Hg occupies bridge positions between the unique and basal borons, replacing a bridged hydrogen. Since an R-Hg group is isolobal with H, such a replacement is not surprising. In some cases the Hg bridges two C_2B_4 cages.[177,177a,177b] In the larger C_2B_9 cage system, the Hg occupies an *endo*- or slipped apical position above an open face of the carborane, giving an η^3- or η^1-carborane–metal interaction. This slip distortion is commonly found in the later *d*-block metallacarboranes.[113] Whether the metal is described as η^3- or η^1- depends on the other groups on the carborane cage and the predisposition of the investigator. A mercury complex, described as 7,8-$(Ph)_2$-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$, was synthesized and structurally characterized.[178] The structure was rationalized as one arising from the replacement of the *endo*-H in $[7,8\text{-}(CPh)_2B_9H_{10}]^-$ with an isolobal $[PPh_3Hg]^{2+}$. The Hg was extremely slip-distorted ($\Delta = 1.10$ Å) with the Hg being much closer to the unique boron (2.178(8) Å) than to the two adjacent borons (2.616(7) and 2.536(8) Å) with the P–Hg–B (unique) angle being 169°. The slip distortion parameter was ~0.2 Å greater than that found in the 10-*endo*-PPh_3Hg-7,8-$C_2B_9H_9$ ($\Delta = 0.92$ Å, Hg–$B_{(unique)} = 2.20$ Å, Hg–B (basal) = 2.50 and 2.52 Å).[179] The increase in the slippage was attributed to the greater steric crowding in the former complex. Essentially, the same Hg–cage-atom distances were found in 10-*endo*-PPh_3Hg-7,8-$\mu(SCH_2S)$-7,8-$C_2B_9H_9$.[180] Pendent groups on the cage carbons that can interact with the metal can exert an opposite effect. In a structural study of a number of d^6 (ML_3), d^8 (ML_2), and d^{10} (ML) metal complexes with the diether carborane, $[7,8\text{-}(CH_2OCH_3)_2\text{-}7,8\text{-}C_2B_9H_9]^{2-}$, Welch and co-workers found that in the mercuracarborane, [10-*endo*-PPh_3Hg-7,8-$(CH_2OCH_3)_2$-7,8-$C_2B_9H_9$], Hg···O interactions actually pulled the $(PPh_3)Hg$ group, causing a decrease in slip distortions ($\Delta = 0.83$ Å, Hg–B (unique) = 2.218(7) Å, Hg-B (basal) = 2.406 and 2.551 Å).[181]

It is apparent from the above discussions that recent synthetic, structural, bonding, and reactivity studies have established transition metal containing metallacarborane complexes as an important area of study in organometallic chemistry.

3.05.2.5 Metallacarboranes of Linked Cage and Multi-decker Complexes

The synthesis of new materials having novel electronic or optical properties is of great current interest. One approach to the synthesis of such materials is to systematically link small sandwich units together to form an extended multi-decker sandwich system. Immediately following the discovery of the triple-decker structure of the $Cp_3Ni_2^+$ complex in early 1970s,[181] Grimes and co-workers synthesized the first neutral triple-decker metallacarborane sandwich compound.[182,182a] Most of the subsequent research in this field, some of which has been described above, has been dominated by Grimes, Siebert, and co-workers, who have repeatedly demonstrated how small metallacarboranes can be stacked and then linked systematically to give extended arrays. A number of reviews by both Grimes[4,4a,74a–74c,183–185] and Siebert[186–188] have adequately described the latest developments in this area of research. Therefore, our discussions in this section will cover only the highlights of the results in this area.

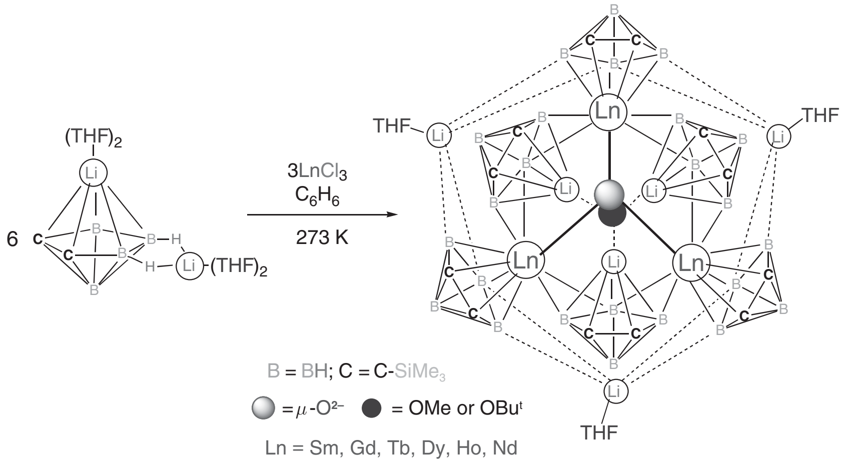
The key breakthrough reaction leading to the production of multi-decker metallacarboranes involves the removal of an apical BH unit in metallacarboranes by treatment of a particular metallacarborane with TMEDA and H_2O or methanol at elevated temperatures, in a so-called "decapitation" reaction.[189,189a–189c] Examples have been cited earlier in this review. Removal of the bridge H's with appropriate reagents afforded the key anionic intermediate that was used to construct a number of desired multi-decker species.[183,183a,183b,184,184a,189,189a–189c,190,190a] In this way, the syntheses of large families of isolable, electrically neutral multi-decker sandwich complexes having 3, 4, 5, or 6 decks, and incorporating C_2B_3 or C_3B_2 planar rings, have been prepared and structurally characterized. This gives rise to an area of carborane chemistry that has no parallel in the larger, C_2B_9-, C_2B_{10}-, and C_3B_8-carborane system.[191–193a] Since the retirements of Professors Grimes and Siebert from the active laboratory research, an enormous burden has been transmitted to the younger scientists, who have been trained in their laboratories, to extend and develop these species into electronic materials.

3.05.2.6 Polymetallacarboranes of Alkene, Alkyne, and Aryl Linkages

During the last decade, there has been an upsurge in reports dealing with the syntheses and characterizations of the polymetalla species of the C_2B_4-carborane ligands that are linked to aliphatic and aromatic unsaturated hydrocarbons (see Schemes 8 and 10). These substances have the potential of being the precursors for conducting or semiconducting nanoscale electronic materials. The electron-delocalized "super-aromatic" bonding environment of these cluster systems, along with their thermal and oxidative stability, as well as their synthetic viability make the smaller C_2B_4-carboranes attractive ligands for further investigation. Some of the details were discussed in an earlier part of this review; readers are advised to consult these and the recently published articles and reviews of Grimes and Siebert that adequately described these developments.[192–197a]

3.05.3 Metallacarboranes of *f*-Block Elements

During the last decade or so, the chemistry of the lanthanide elements has increased in scope such that it is no longer limited to the formation of purely ionic compounds. New classes of lanthanide complexes with unusual structures and novel reactivities have emerged.[198,198a–198c] Although a variety of ligands has been reported in different organolanthanide systems, the cyclopentadienide anion and its *C*-substituted derivatives are most often utilized.[199] The first report of the synthesis and structural characterization of an *f*-block metallacarborane was that of the uranacarborane, $[U(C_2B_9H_{11})_2Cl_2]^{2-}$, in 1977,[200] followed, in 1988, by those of the compounds, *closo*-3-Yb(DMF)$_4$-1,2-$C_2B_9H_{11}$ and [3,3′-(THF)$_2$-*commo*-3,3′-Sm($C_2B_9H_{11}$)$_2$]$^-$.[201] Since these initial reports, a number of lanthanide complexes, mainly in the C_2B_{10} and C_2B_9 cage systems, have been described. (For recent reviews of the lanthanacarboranes in the C_2B_{10} and C_2B_9 cage, see Refs: 202 and 202a–202c.) The lanthanide complexes of the C_2B_4 cage systems exhibit reaction characteristics that are not found in the larger cages. For example, the reaction of the THF-solvated dilithium salt of the [2,3-(SiMe$_3$)$_2$$C_2B_4H_4$]$^{2-}$ dianion with anhydrous LnCl$_3$ in a molar ratio of 2 : 1 in dry benzene and THF produced the trinuclear Ln(III)-carboranes of the form, {[η^5-1-Ln-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$]$_3$[(μ-1-Li-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$)$_3$(μ_3-OMe)][μ-Li(THF)]$_3$(μ_3-O)} (Ln = Sm, Gd, Tb, Dy, Ho, and Nd), instead of the expected full-sandwich lanthacarboranes (see Scheme 14).[203,203a–203d] These clusters, shown in Figure 46, are composed of three half-sandwich lanthanacarboranes and three lithiacarboranes arranged around an oxide ion and a methoxide ion, respectively.[203c] These unexpected products were believed to arise from the initial formation of a half-sandwich lanthanacarborane, which reacts further with the THF solvent, or its decomposition product, to form the final trinuclear cluster. On the other hand, in the absence of THF, the reaction of the TMEDA-solvated dilithium salt of the [2,3-(SiMe$_3$)$_2$$C_2B_4H_4$]$^{2-}$ dianion with anhydrous LnCl$_3$ under equivalent 2 : 1 molar ratios produced the full-sandwich 1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5,5′-[(μ-H$_3$)Li(TMEDA)-*commo*-Ln(2,3-$C_2B_4H_4$)$_2$]$^-$ (Ln = Sm, Gd, Dy, Ho, and Er; see Figure 47 for example).[203b,204] In addition, several half-sandwich complexes have been reported.[205,205a,205b] Most of the small cage lanthanacarboranes have involved the use of the "carbons adjacent" (2,3-C_2B_4) isomer, but the "carbons apart" isomers have also been studied.[205a,206,206a,207,207a,207b] The reactions of *closo*-*exo*-5,6-Na(THF)$_2$-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ with anhydrous LnCl$_3$ (Ln = Nd, Gd, Dy, Ho, Er, Tb, and Lu), in molar ratios of 2 : 1 in dry benzene (C_6H_6) produced



Scheme 14 Synthesis of trinuclear oxolanthanacarborane clusters. Reproduced by permission of the American Chemical Society from *Organometallics* **2005**, *24*, 1356–1389.

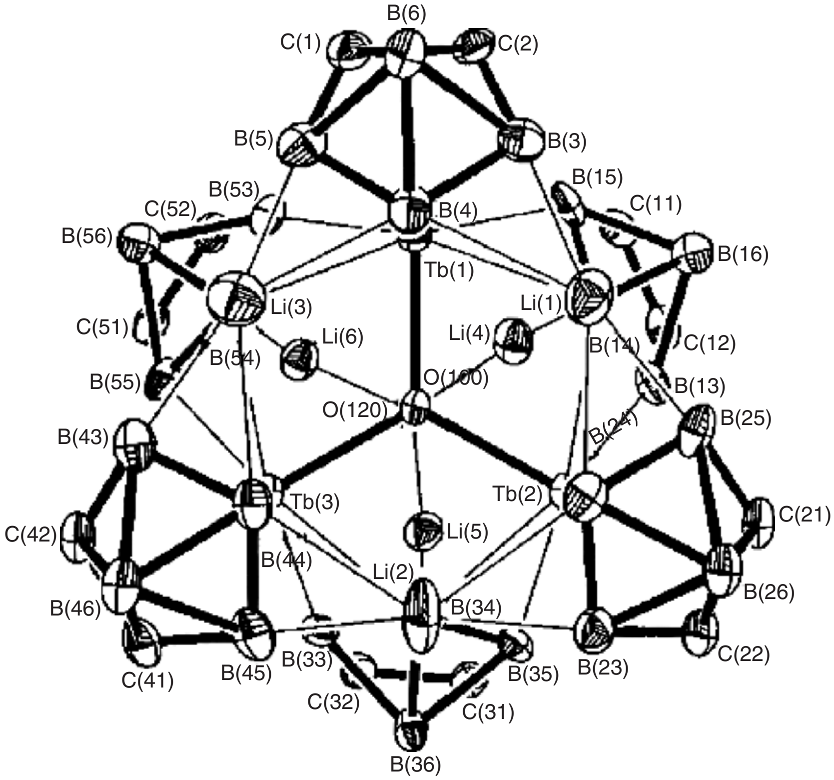


Figure 46 Crystal structure of the trinuclear cluster {[η^5-1-Tb-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$[(μ-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$(μ_3-OMe)][μ-Li(THF)]$_3$(μ_3-O)}. Reproduced by permission of the American Chemical Society from *Organometallics* **2005**, *24*, 1356–1389.

the full-sandwiched lanthanacarborane complexes, 2,2′,4,4′-(SiMe$_3$)$_4$-3,5′,6′-[(μ-H)$_3$Na(X)$_n$(Y)$_m$]-1,1′-*commo*-Ln(η^5-2,4-C$_2$B$_4$H$_4$)$_2$ (Ln = Nd, X = THF, n = 2, Y = none; Gd, X = THF, n = 3, Y = none; Dy, X = THF, n = 1; Y = TMEDA, m = 1; Ho, X = DME, n = 1, Y = none; Er, X = THF, n = 1, Y = none; Tb, X, Y = none; and Lu, X = THF, n = 2, Y = none) in 70–93% yields.[208,208a] A general synthetic procedure is outlined in Scheme 15. While the solid-state structures of the dimeric Nd, Gd, Dy, Ho, and Lu sandwich metallacarboranes were determined by X-ray crystallography, only one of them (when Ln = Gd) is shown in Figure 48.[208,208a] These results differ markedly from those obtained in the "carbons adjacent" system where a very similar procedure gave exclusively

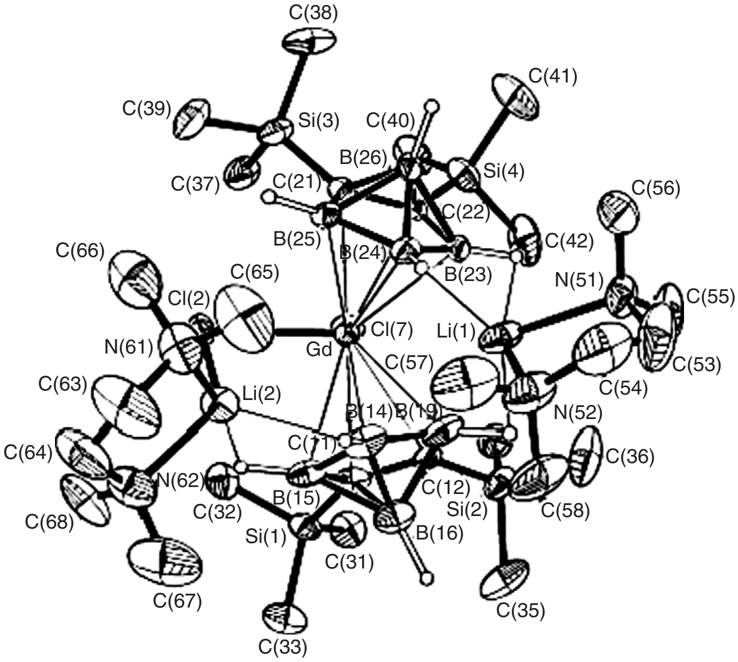
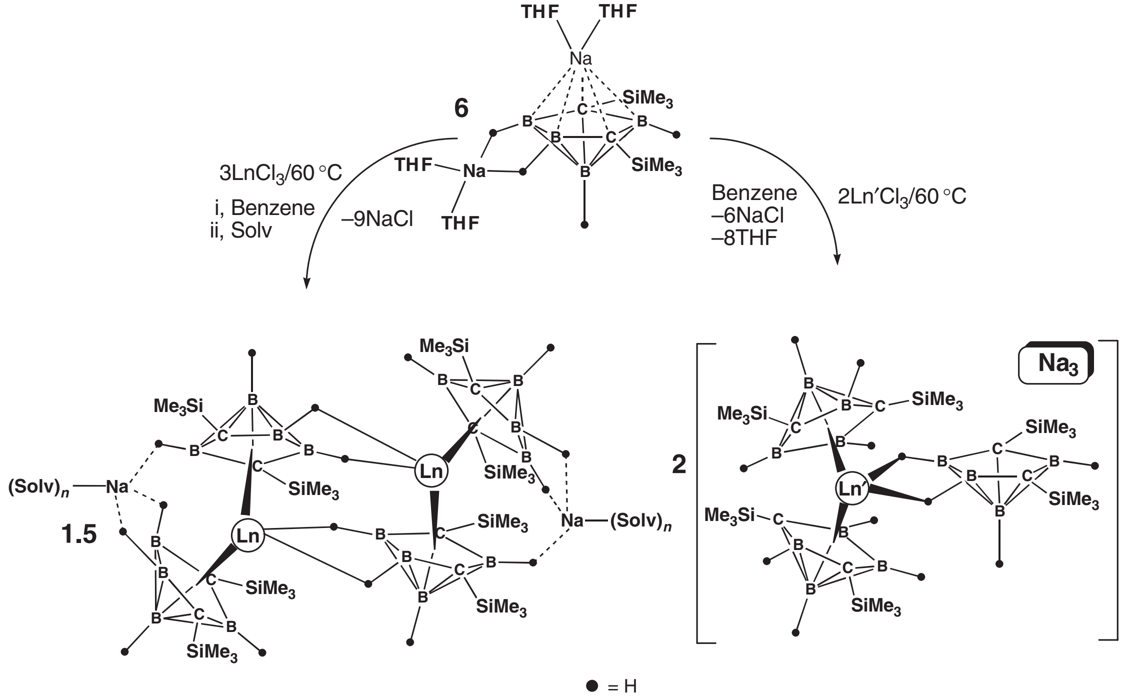


Figure 47 Crystal structure of [1-Cl-1-(μ-Cl)-2,2′,3,3′-$(SiMe_3)_4$-5,6-[$(\mu\text{-H})_2$Li(TMEDA)]-4,4′,5,5′-[$(\mu\text{-H}_3)$Li(TMEDA)]-*commo*-Gd$(2,3\text{-}C_2B_4H_4)_2]^-$. Reproduced by permission of the American Chemical Society from *Organometallics* **1996**, *15*, 1006.



Ln = Nd, Gd, Tb, Dy, Ho, Er, Lu; Ln′ = Dy, Er; Solv = THF and/or TMEDA; *n* = 1–3

Scheme 15 Syntheses of ''carbons apart'' lanthanacarborane complexes. Reproduced by permission of the American Chemical Society from *Organometallics* **2003**, *22*, 4334.

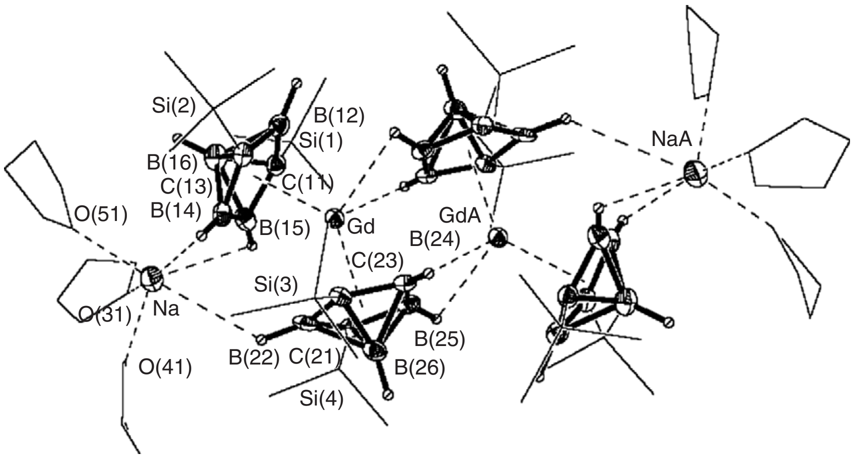
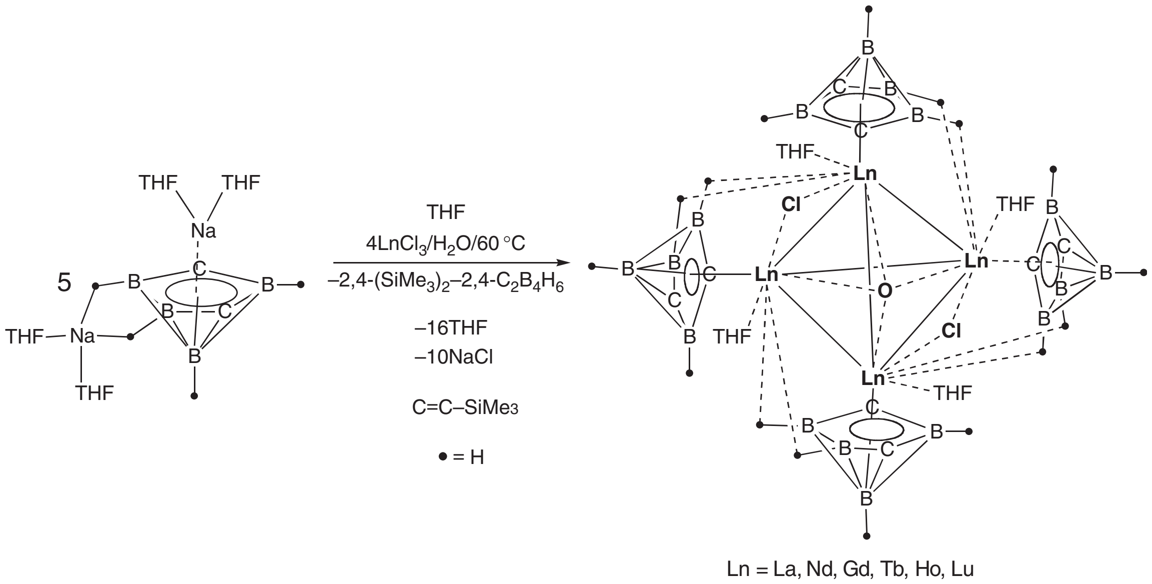


Figure 48 Crystal structure of 2,2′,4,4′-$(SiMe_3)_4$-3,5′,6′-[$(\mu\text{-H})_3$Na$(THF)_3$]-1,1′-*commo*-Gd(η^5-2,4-$C_2B_4H_4$)$_2$. Reproduced by permission of the American Chemical Society from *Organometallics* **2003**, *22*, 4334.

the trinuclear clusters of the half-sandwiched lanthanacarboranes and lithiacarboranes at room temperature. The "carbons adjacent" carborane requires the use of *t*-BuLi as a deprotonating agent. Since both *t*-BuLi and lanthanide compounds are known to degrade THF, and other oxygen-containing compounds,[209,209a,209b,210] it could well be that such degradation reactions produce the methoxide and oxide products that effectively prevented the formation of the expected full-sandwich compounds.[203c] The results described in Scheme 15 are obtained in the absence of the *t*-BuLi, which further supports this contention. This is consistent with the fact that when the TMEDA-solvated dilithiacarborane *closo*-*exo*-5,6-[$(\mu\text{-H})_2$Li(TMEDA)-1-Li(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$] was reacted with $LnCl_3$, only the full-sandwich complexes were formed.[204] The reactions of the larger, *nido*-C_2B_9-carborane, anion with $LnCl_3$ in a 2 : 1 molar ratio produced only the expected full-sandwiched lanthanacarboranes.[200,201,211]

The effect of the reaction stoichiometry on the nature of the products was probed by studying the reactions of *closo*-*exo*-5,6-Na$(THF)_2$-1-Na$(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ with anhydrous $LnCl_3$ (Ln = Dy, Er) in molar ratios of 3 : 1, under the same experimental conditions as that used in the preparation of "carbons apart" lanthanacarborane sandwich complexes. In the Cp system, such a molar ratio gave complexes of the form Ln$(Cp)_3$ in which the three Cp^- ligands were η^5-bonded to a lanthanide metal.[212,213,213a] However, in the carborane system the products were the mixed complexes [Na_3][1,1′-{5,6-$(\mu\text{-H})_2$-*nido*-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$}-2,2′,4,4′-$(SiMe_3)_4$-1,1′-*commo*-Ln-(2,4-$C_2B_4H_4)_2$] (Ln = Dy, Er), in which two of the three carboranes were in η^5-bonding modes to give a bent sandwich complex such as shown in Figures 47 and 48, while the third was η^2-bonded through a set of two Ln–H–B bridges. [207,208,208a] Although these are stoichiometric analogs of tris(cyclopentadienyl) lanthanide complexes, their structures and bonding modes are quite different. Thus, the reactions of the "carbons-apart" C_2B_4-carborane ligands with a number of $LnCl_3$ salts in molar ratios of either 2 : 1 or 3 : 1 produced the same general type of structure, a full-sandwiched lanthanacarborane in which each Ln(III) occupied the apical positions above the open faces of two carborane dianions and is bonded to a third by two Ln–H–B bridges. If excess carborane is not available, this bonding pattern is satisfied by dimerization as shown in Figure 48.

Several other oxide-centered lanthanacarboranes in the small cage system have also been reported. These were synthesized by introducing stoichiometric amounts of an oxide donor, such as H_2O, into a synthetic scheme. It was found that when anhydrous $LnCl_3$ (Ln = La, Nd, Gd, Tb, Ho, and Lu) was treated with stoichiometric quantities of freshly distilled H_2O under reflux conditions in THF and the resulting mixtures mixed with *closo*-*exo*-5,6-Na$(THF)_2$-1-Na$(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ in an overall carborane: $LnCl_3$: H_2O molar ratio of 5 : 4 : 1, a series of oxide-encapsulated complexes, {[η^5-1-Ln$(THF)_n$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_4$$(\mu\text{-Cl})_2$$(\mu_4\text{-O})$}·$(THF)_y$ (Ln = La, $n = 0$, $y = 1$; Nd, $n = 1$, $y = 0$; Gd, $n = 0$, $y = 1$; Tb, $n = 1$, $y = 0$; Ho, $n = 0$, $y = 1$; and Lu, $n = 1$, $y = 0$), were produced in 73–86% yields.[214,214a] A general synthetic procedure is outlined in Scheme 16 and an example of the general molecular geometry of the complexes, when Ln = Tb, is shown in Figure 49.[214] The reactions are very sensitive to both stoichiometry and procedure: the $LnCl_3$/H_2O/THF mixture must be refluxed until a homogeneous solution is obtained and the reactions must be carried out initially at −78 °C and then completed at reflux temperatures, otherwise decomposition or incomplete reaction occurred. The ionic nature of the bonding is also seen in the DFT results on the model compound La_4OCl_2(2,4-$C_2B_4H_6$)$_4$$(OH_2)_4$.[214a]



Scheme 16 Synthesis of an oxide ion encapsulating tetralanthanide tetrahedron, surrounded by ‘‘carbons apart’’ carborane cages. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 4621.

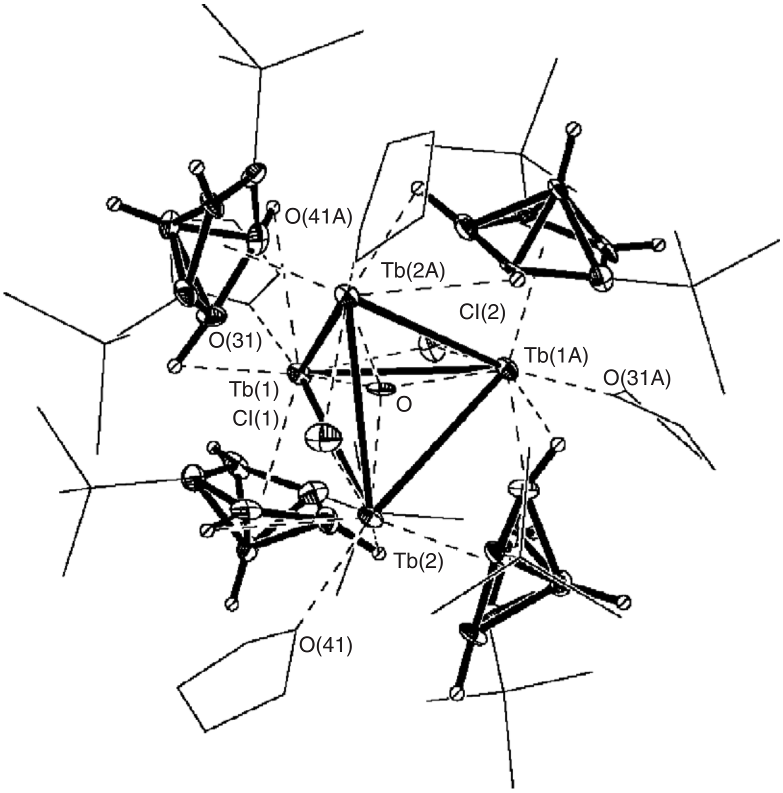


Figure 49 Crystal structure of the oxide encapsulated $\{[\eta^5\text{-1-Tb(THF)-2,4-(SiMe}_3)_2\text{-2,4-C}_2B_4H_4]_4(\mu\text{-Cl})_2(\mu_4\text{-O})\}$. Reproduced by permission of the American Chemical Society *Organometallics* **2004**, *23*, 4621.

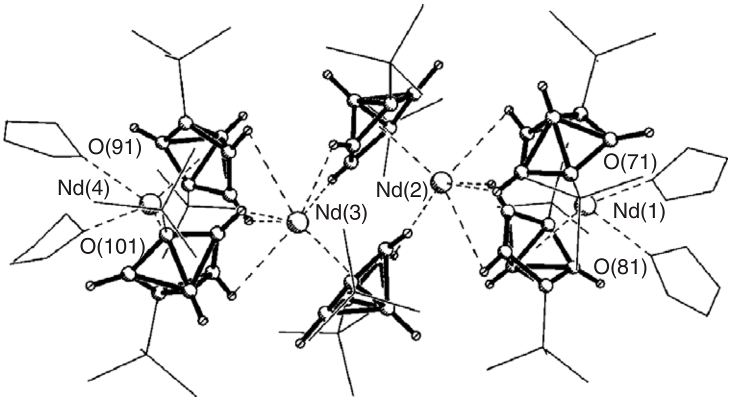


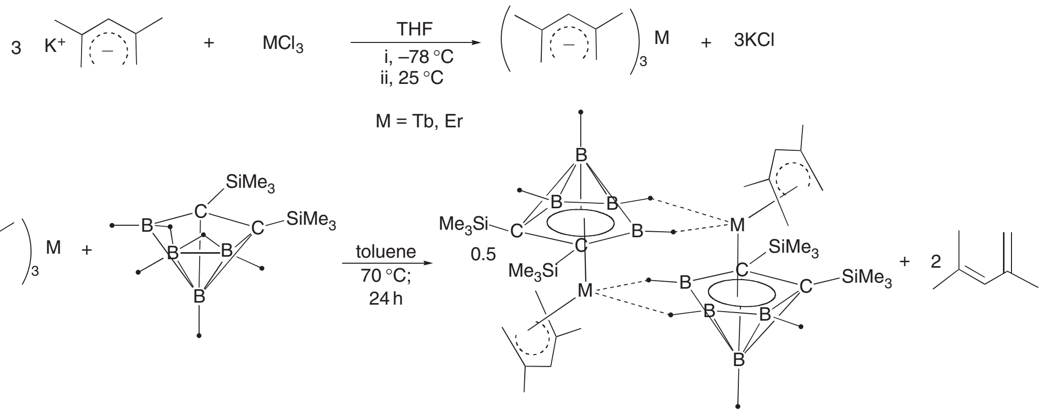
Figure 50 Crystal structure of the dimeric ion-pair, {[*closo*-1-Nd(μ-H)$_6$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]$^+$[1,1′-(THF)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-5,5′,6,6′-(μ-H)$_4$-1,1′-*commo*-Nd(η^5-2,4-C$_2$B$_4$H$_4$)]$^{-}$·(C$_4$H$_8$O)(C$_6$H$_6$)$_2$}$_2$. Reproduced by permission from *Inorg. Chem. Commun*. **2003**, *6*, 549.

In the "carbons apart" 2,4-C$_2$B$_4$-cage system, only the full-sandwich lanthanacarboranes of Nd, Gd, Dy, Ho, Er, Tb, and Lu were obtained, and the preparation of the corresponding half-sandwich complexes has proved to be very difficult, irrespective of the reaction stoichiometry.[208,208a] The half-sandwich complexes were obtained only by reacting the monosodium compound *nido*-1-Na(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$ with anhydrous LnX$_3$ in a molar ratio of 2 : 1 in dry THF.[205b] This reaction produced the dimeric half-sandwich species, [1-(X)-1,1-(THF)$_2$-2,3-(SiMe$_3$)$_2$-1-Ln(η^5-2,3-C$_2$B$_4$H$_4$)]$_2$ (2, Ln = Ce, X = Br; 3, Ln = Gd, X = Cl; 4, Ln = Lu, X = Cl), in high yields, along with 1 equiv. of the neutral *nido*-carborane precursor, 2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_6$. The method covered the syntheses involving metals at the beginning, in the middle, and at the end of the lanthanide series, so it should be generally applicable to all lanthanide metals, and most likely the actinides as well. A mixed half- and full-sandwich lanthanacarborane complex was obtained by a two-step process involving the initial formation of the full-sandwiched neodymacarborane, 2,2′,4,4′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Na(THF)$_2$]-1,1′-*commo*-Nd(η^5-2,4-C$_2$B$_4$H$_4$)$_2$, followed by further reaction of with NdCl$_3$. The final product was the dimeric ion pair, {[*closo*-1-Nd(μ-H)$_6$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]$^+$[1,1′-(THF)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-5,5′,6,6′-(μ-H)$_4$-1,1′-*commo*-Nd(η^5-2,4-C$_2$B$_4$H$_4$)]$^{-}$·(C$_4$H$_8$O)(C$_6$H$_6$)$_2$}$_2$.[215] The compound, shown in Figure 50, consists of an Nd$_4$(C$_2$B$_4$)$_6$ network where the two inner half-sandwich cationic neodymacarboranes are flanked by two full sandwich ones. Each of the Nd atoms of the half-sandwich complexes is also η^2-coordinated by three carborane units.[215]

A combined reductive cage opening-metallation process has been described that consisted of the reaction of anhydrous ErCl$_3$ with 4 equiv. of potassium metal, under refluxing conditions in THF, followed by the direct addition of the *closo*-carborane, 1,2-(SiMe$_3$)$_2$-1,2-C$_2$B$_4$H$_4$.[207a] The product was the "carbons apart" erbacarborane sandwich, 2,2′,4,4′-(SiMe$_3$)$_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-C$_2$B$_4$H$_4$)$_2$. The net reaction, given in Equation (2), is the same as that for the normal multi-step sequence of naphthalene-catalyzed reduction of the *closo*-carborane, followed by isolation and purification of the K salt of the corresponding dianion, and then its reaction with ErCl$_3$.[207] Therefore, the same driving forces are at work in both methods, except that Er acts as the electron transfer agent. Since there is nothing particularly unique about Er, it will be interesting to see if the method proves to be a general route to the formation of a number of diverse metallacarboranes in the sub-icosahedral cage systems. However, this as yet remains to be demonstrated.

$$\mathrm{ErCl_3} + 4\mathrm{K} + 2\,closo\text{-}(\mathrm{CSiMe_3})_2\mathrm{B_4H_4} \xrightarrow{\mathrm{THF}} [\mathrm{K(THF)_2}]\mathrm{Er}((\mathrm{CSiMe_3})_2\mathrm{B_4H_4})_2 + 3\mathrm{KCl} \qquad (2)$$

In addition to the mixed Cp/carborane complexes, there has been one report on the lanthanacarboranes with the open pentadienyl ligand, R$_7$C$_5$ (R = H or an alkyl derivative). This is an alternate 6-π electron donor that has led to the syntheses of number of so-called "open metallocenes" where the pentadienyl group replaces one or more Cp ligands.[216,216–216d] This lanthanacarborane report covered the syntheses and structural determinations of two open sandwich complexes, [(η^5-2,4-(Me)$_2$C$_5$H$_5$)(η^5-2,3-(Me$_3$Si)$_2$-2,3-C$_2$B$_4$H$_4$)Ln]$_2$ (Ln = Tb, Er). The compounds were synthesized in a two-step process as outlined in Scheme 17.[217] The tris(pentadienyl)lanthanide complex was first synthesized by the 3 : 1 molar ratio reaction of K[2,4-(Me)$_2$C$_5$H$_5$] and LnCl$_3$ (Ln = Tb, Er) in THF; the



Scheme 17 Syntheses of lanthanacarboranes of mixed open-pentadienyl and carborane ligands. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 3091–3093.

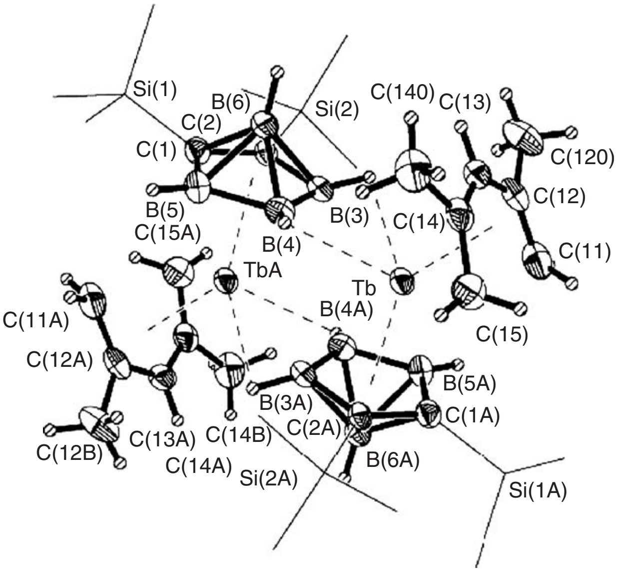
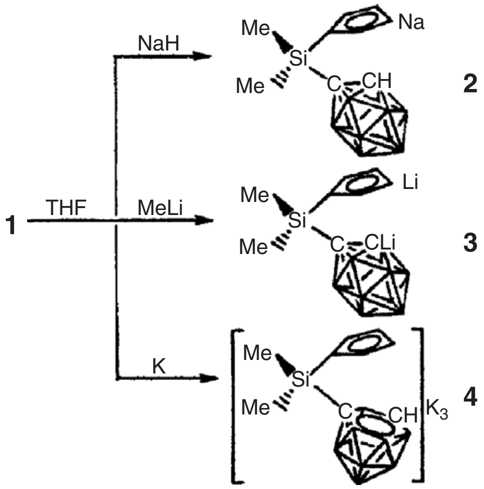


Figure 51 Crystal structure of the open sandwich lanthanacarborane, $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Tb]_2$. Reproduced by permission of the American Chemical Society from *Organometallics* **2004**, *23*, 3091.

$Ln(2,4\text{-}(Me)_2C_5H_5)_3$ compounds were then treated immediately with $2,3\text{-}(SiMe_3)_2$-*nido*-$2,3\text{-}C_2B_4H_6$ in a 1 : 1 molar ratio in toluene to give the $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb, Er) dimers. The crystal structures were determined and showed that each compound crystallizes as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$, a dimer in which a planar pentadienyl and carborane ligands are η^5-bonded to a metal atom. In addition, each carborane is η^2-bonded to the neighboring metal in the dimer (see Figure 51 for Ln = Tb).[217] Since the synthesis outlined in Scheme 17 is based on the higher acidity of the bridged hydrogens in *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ compared to the methylene hydrogens on the neutral pentadiene, $2,4\text{-}(Me)_2C_5H_6$, and the metal plays somewhat of a passive role, it should be possible to expand the scope of these reactions to other metal-pentadienyl systems and *nido*-carboranes.

The chemistry of the larger cage lanthanacarboranes, predominantly the C_2B_9 and C_2B_{10} systems, has also been extensively studied; full-, half-, and mixed-sandwich have been described. Xie has summarized much of this work in several recent reviews.[202,202a–202c] The straightforward syntheses of the lanthanacarboranes are complicated in many cases by ligand exchange interactions. For example, attempts to prepare the mixed-sandwich lanthanacarborane, $[(C_5Me_5)(C_2B_{10}H_{12})Eu(THF)_2]^-$, using standard methods have failed, giving only mixtures of $(C_5Me_5)_2Eu(THF)_2$

and $[(C_2B_{10}H_{12})_2Eu(THF)_2]^{2-}$.[218] This is not just restricted to the large cage mixed-sandwich complexes; in the small cage system a 1 : 1 molar ratio reaction of $HoCl_3$ and the TMEDA-solvated dilithium salt of $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ did not give the expected half-sandwich complex but rather the full-sandwich complex associated with an *exo*-polyhedral holmium group.[219] The first mixed-sandwich lanthanacarborane was that reported by Xie and co-workers using the bifunctional ligand derived from $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$.[220] This precursor can be converted into mono-, di-, and trianionic ligands as shown in Scheme 18; complexes have been reported for all three.[221–223] The reaction of 2 equiv. of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$ with $SmI_2(THF)_x$ produced the constrained-geometry complex, $[Me_2Si(\eta^6\text{-}C_2B_{10}H_{11})(\eta^5\text{-}C_5H_4)]Sm(THF)_2$.[221,221a] The structure, shown in Figure 52, is that of a bent mixed-sandwich complex in which an Sm(III) was bonded to the two π-ligands and two THF molecules.[221,221a] The reaction also produced the tris-ligated, $[\eta^5\text{-}Me_2Si(C_5H_4)(\textit{closo}\text{-}C_2B_{10}H_{11})]_3Sm$. This suggested the mechanism, outlined in Scheme 19, consisting of an initial formation of an $[(\eta^5\text{-}Me_2Si(C_5H_4)(\textit{closo}\text{-}C_2B_{10}H_{11})]_2Sm(THF)_2$ intermediate which could undergo an intramolecular electron transfer and an intermolecular electron transfer from another molecule of the intermediate, resulting in a $[(\eta^5\text{-}Me_2Si(C_5H_4)(\textit{closo}\text{-}C_2B_{10}H_{11})]_2Sm(THF)_2]\}^+$ and a $\{[(\eta^5\text{-}Me_2Si(C_5H_4))(\textit{nido}\text{-}C_2B_{10}H_{11})](\eta^5\text{-}Me_2Si(C_5H_4))(\textit{closo}\text{-}C_2B_{10}H_{11})]Sm(THF)_2\}^-$, which, after ligand



Scheme 18 Conversion of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ into mono-, di-, and trianionic ligands. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 489.

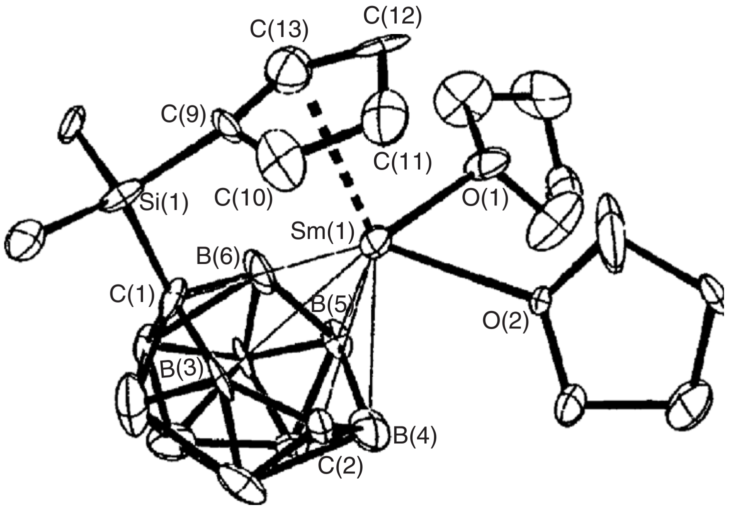
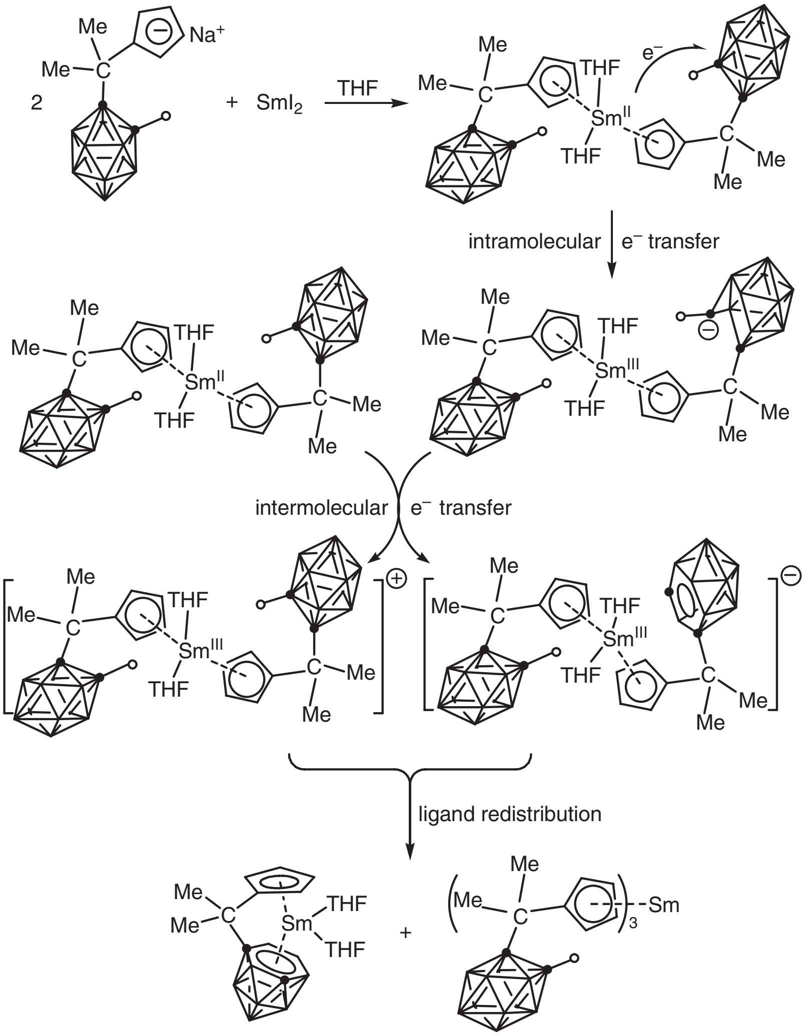


Figure 52 Crystal structure of the constrained geometry complex, $[Me_2Si(\eta^6\text{-}C_2B_{10}H_{11})(\eta^5\text{-}C_5H_4)]Sm(THF)_2$. Reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 1907.



Scheme 19 Proposed mechanism for the reaction of SmI$_2$ with [Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]$^-$. Reproduced by permission of the American Chemical Society from *Organometallics* **2000**, *19*, 1391.

redistribution, gave [Me$_2$Si(η^6-C$_2$B$_{10}$H$_{11}$)(η^5-C$_5$H$_4$)]Sm(THF)$_2$ and the tris-product.[223] The net result is that the two Sm(II) ions will reductively open the *closo*-C$_2$B$_{10}$ cage; this is not possible for most other lanthanides. The interaction between SmI$_2$(THF)$_x$ and dianionic salts of the hybrid ligand offered different products. The disodium ligand, Na$_2$[Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)], reacted with SmI$_2$(THF)$_x$, yielding an Sm(III) complex, [{η^5:σ-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm][Na(THF)$_6$], via an intermolecular electron-transfer reaction. This complex was also prepared in a much higher yield from the reaction of Na$_2$[Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)] with SmI$_2$(THF)$_x$, followed by treatment with [Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Na, through an intramolecular electron-transfer reaction.[221a]

There are two general methods to prepare the [Me$_2$Si(η^6-C$_2$B$_{10}$H$_{11}$)(η^5-C$_5$H$_4$)]ML$_x$ complexes: salt metathesis between the trianion [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]$^{3-}$ and LnCl$_3$, and reduction of [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]LnCl$_2$(THF)$_3$ with 2 equiv. of group 1 metals. The structures of the products are dependent on the metal.[222,223] In the case of Er, either method gave the expected product.[223] When LnCl$_3$ (L = Sm, Yb) was mixed with [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]$^{3-}$, the organolanthanide(II) compounds, [Me$_2$Si(η^6-C$_2$B$_{10}$H$_{11}$)(η^5-C$_5$H$_4$)Ln(THF)$_2$]$^-$, were the products.[222] On the other hand, the interaction between YbCl$_3$, [Me$_2$Si(C$_{13}$H$_8$)(C$_2$B$_{10}$H$_{11}$)]Li(OEt$_2$)$_2$, and excess finely cut Na metal in THF, followed by treatment with 1 equiv. of dry Me$_3$NHCl, gave a novel full-sandwich, mixed-valent metallacarborane complex, {{[η^7-Me$_2$Si(C$_{13}$H$_9$)(C$_2$B$_{10}$H$_{11}$)]$_2$Yb$^{\mathrm{III}}$}$_2$Yb$^{\mathrm{II}}$}{Na$_8$(THF)$_{20}$}.[224] A similar η^7-bonding complex was obtained from the reaction of [Me$_2$Si(η^6-C$_2$B$_{10}$H$_{11}$)(η^5-C$_5$H$_4$)]Er(THF)$_2$ with excess Na, [{[η^5-Me$_2$C(C$_5$H$_4$)(η^7-C$_2$B$_{10}$H$_{11}$)]Er}$_2${Na$_4$(THF)$_9$}]$_n$,

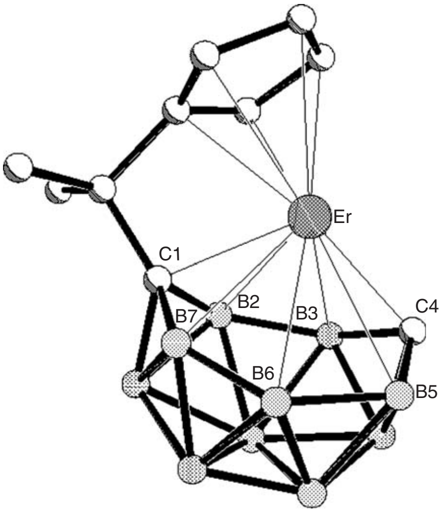
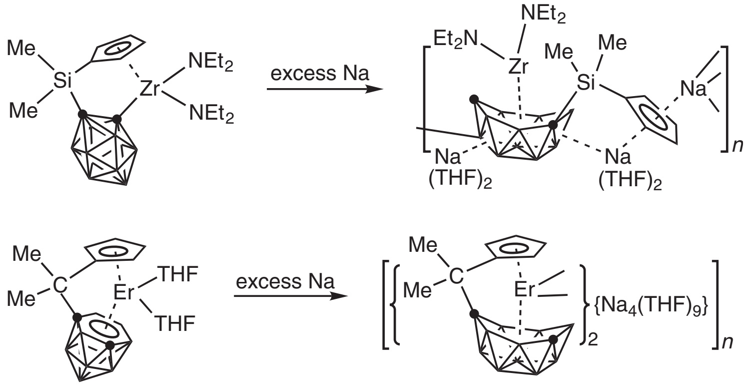


Figure 53 Crystal structure of the η^7-bonding in an $[\{\eta^5{:}\eta^7\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Er}]^{2+}$ complex. Reproduced by permission of the American Chemical Society from *Acc. Chem. Res*. **2003**, *36*, 1.



Scheme 20 Syntheses of *arachno*-carborane tetranionic complexes of Zr and Er. Reproduced by permission of the American Chemical Society from *Organometallics* **2002**, *21*, 3311.

the structure of one of the Er units is shown in Figure 53.[223] The corresponding Dy analog was made in a similar fashion.[223] The further reduction of the $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]$M cage is not restricted to the lanthanides, the direct reaction of $[\eta^5{:}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NEt}_2)_2$ with excess Na metal afforded a half-sandwich complex, $[\{(\mu\text{-}\eta^5){:}\eta^7\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Zr}(\text{NEt}_2)_2\{\text{Na}_3(\text{THF})_4\}]_n$ (see Scheme 20).[225]

The most important structural feature in these complexes is the *arachno*-carborane tetraanion, which is η^7-bound to the metal ion (Figure 53). This η^7-carboranyl ligand is responsible for stabilizing the high oxidation state of the metals, as illustrated in $\{\{[\eta^7\text{-Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}^{\text{III}}\}_2\text{Yb}^{\text{II}}\}\{\text{Na}_8(\text{THF})_{20}\}$, which has Yb(III) in capping positions and Yb(II) is *exo*-polyhedral. The dibenzyl-substituted 1,2-$(\text{C}_6\text{H}_5\text{CH}_2)$-1,2-$\text{C}_2\text{B}_{10}\text{H}_{10}$ could be reductively opened by a group 1 metal, which could then react with MCl_3 (M = Y, Er, Dy) and excess Na or Li to give $\{[\eta^7\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{M}(\text{THF})\}^-$ dimeric units.[226] Molecular orbital calculations show that the [*arachno*-$\text{C}_2\text{B}_{10}\text{H}_{12}]^{4-}$ ion is a 10-electron donor which will bond to transition metals giving five-bonding and five-antibonding molecular orbitals, hence bonding readily with d^0 metals such as Zr(IV), Yb(III).[226] Since the lanthanide ions' interactions are mainly electrostatic, they should interact strongly with the tetra-negative ligand.[225,226] It has been reported that high-oxidation-state metal ions such as Ln^{3+} (Ln = Eu,[219] Sm,[222] Yb[222]) and M^{4+} (M = Ti, Zr, Hf)[227] can oxidize *nido*-$\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}{}^{2-}$ dianionic species back to the *o*-$\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ neutral carboranes. Under certain reaction conditions, however, metallacarboranes bearing both oxidative and reductive components can be achieved via redox reactions using η^7-carboranyl ligand systems.

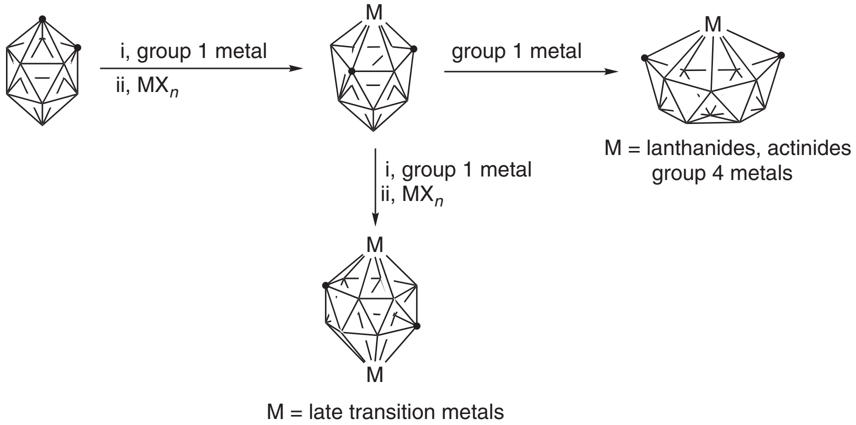
While $[Me_2Si(\eta^6\text{-}C_2B_{10}H_{11})(\eta^5\text{-}C_9H_6)]^{2-}$ behaved in much the same way as its C_5H_4- analog,[221a] substituents on the aromatic ring have a profound influence on the formation of the product. For example, reaction of $[Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})]Li_2(OEt_2)2{\cdot}LiCl$ with $SmI_2(THF)_x$ gave novel samaracarboranes $[\{\eta^5{:}\eta^1{:}\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})Sm\}_2\text{-}(\mu\text{-}Cl)][Li(THF)_4]$ ($G = NMe_2$, OMe), in which the reduction and coupling of the carborane cage occurred in a tandem manner.[228]

Recently developed constrained-geometry ligands containing both monocyclopentadienyl and σ-heteroatom (N, O, and P) components have attracted considerable attention.[229] Both salt metathesis and amine elimination methods are useful in the preparation of constrained-geometry metal complexes. Reaction of $LnCl_3$ with 0.5 equiv. of $[\{[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]$ gave organolanthanide complexes of the general formula $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnCl(\mu\text{-}Cl)]_2[Li(THF)_4]_2$ (Ln = Sm, Y, Yb).[230] Reaction of the Y product with $NaN(SiMe_3)_2$ led to substitution of the chloro groups by a bulky amido moiety, yielding an unsolvated complex $[\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]YN(SiMe_3)_2$.[230] Amine elimination reaction of the complex, ${}^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$, where indenyl and carboranyl units are bridged through a boron, with $Ln[N(SiHMe_2)_2]_3(THF)_2$ generated directly the metal amides $[\eta^5{:}\sigma\text{-}{}^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]LnN(SiHMe_2)_2(THF)_2$ (Ln = Nd, Er, Y).[231] The Nd compound was found to initiate the polymerization of methyl methacrylate (MMA), leading to *syn*-rich poly(MMA)'s. However, the activity was found to be very low.[231] On the other hand, the analogous d^0 metal complexes exhibited moderate to high ethylene polymerization activity upon activation with MAO,[232] as did $\{[\eta^5{:}\sigma\text{-}AMe_2(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2-$ (A = Si, C).[233,233a]

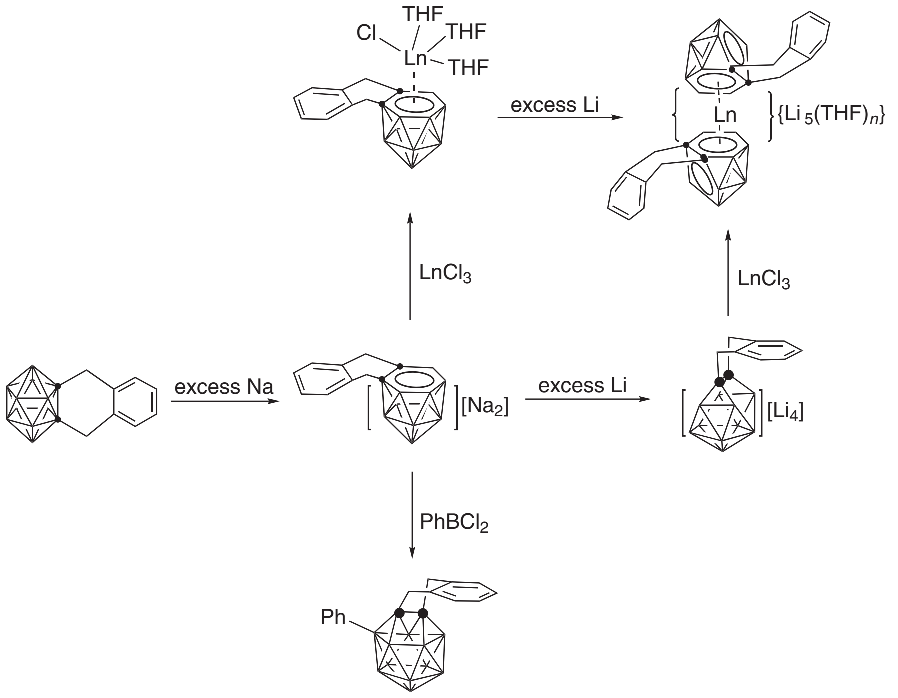
From the above discussions, it is apparent that Xie and co-workers have developed a versatile set of ligands incorporating both cyclic π-ligands and carboranyl cages. They possess not only the common features of both moieties but also unique properties of their own. These ligands can be readily converted into the mono-, di-, tri-, and pentaanionic species under suitable reaction conditions, leading to the generation of a new class of organometallic compounds in which the carboranyl moiety serves as a σ-, η^5-, η^6-, or η^7- π-ligand or as just a bulky substituent.

Polyhedral expansion has been widely used to prepare a series of 13- and 14-vertex metallacarboranes through the insertion of one or two metal fragments into the *nido*-12-vertex cage. The cage is usually the product of a two-electron reduction of the corresponding *closo*-1,2-$C_2B_{10}H_{12}$ carborane. Such a reduction leads to the "carbon apart" isomer in which the cage carbons on the bonding face are separated by a boron atom. This isomer can be metallated or further reduced and metallated, as outlined in Scheme 21; in all subsequent products, the "carbons apart" configuration is maintained.

The controlled synthesis of "carbons adjacent" *nido*- and *arachno*-carborane anions can be achieved by the reduction of C (cage)–C (cage)-linked *o*-carboranes with group 1 metals.[234–237] Typical examples are illustrated in Scheme 22. These have been found to undergo metallation reactions similar to their "carbons apart" analogs, forming full- and half-sandwich complexes of lanthanide metals.[238]



Scheme 21 Reduction/metallation sequences for *closo*-1,2-$C_2B_{10}H_{12}$.



Scheme 22 Reduction/metallation sequences for 1,2-[μ-1,2-*o*-$C_6H_4(CH_2)_2$)]-1,2-*closo*-$C_2B_{10}H_{10}$.

3.05.4 Current and Future Directions

Our discussion summarizes some of the main avenues of research published during the past 10 years on the *d*- and *f*-block metallacarboranes. Although each individual report has its own particular focus, one overriding concern has been to systematize the chemistry of these compounds in order to promote their use as possible electronic, ceramic, catalytic materials. In addition, they provide information on which we can test, and expand, our knowledge about the fundamental interactions that are at work in determining the structures and properties of these fascinating clusters. Many times they test our sense of humor as well as our wit. The results of these studies are establishing a unique and useful area of organometallic chemistry that will continue to grow and bear fruit in the twenty-first century.

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3.06
Aluminum Organometallics

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3.06.1 Introduction

Aluminum is the third most abundant element in the Earth's crust and so applications involving this element are expected to be economical. Moreover, aluminum has unique properties such as its strong bonding to oxygen, three oxidation states (I, II and III), the ability to form cationic and anionic compounds, and the Lewis acidity of its organocompounds. For these and other reasons, organoaluminum compounds have broad utility in areas such as synthesis, catalysis, and materials science. Synthetic methods for new compounds and new areas of application are continually being discovered. COMC(1982) and COMC(1995) extensively covered the work on organoaluminum compounds prior to 1993.[1,2] The more recent edition, written by Eisch, covers in great detail the various reactions, particularly the organic reactions, that employ organoaluminum reagents. Since then, the interest in this field has expanded rapidly and excellent book chapters and reviews have been devoted to this area. A listing of the various areas covered by these reviews is included in the following table:

Areas of study	*References*
Low-valent (Al(I)) aluminum complexes	3,4
Organoaluminum halides	5–8
Alanes	9
Organoaluminum cluster compounds and compounds with low-valent aluminum	3,4,10
Hydrolysis of organoaluminum compounds	11
Coordination chemistry of aluminum at transition metals	12
Multiple bonds involving aluminum	13,14
Group 13 donor–acceptor bonds involving aluminum	15
Catalysis with organoaluminum compounds	16–21
Aluminum compounds with Schiff bases and β-diketiminates	22,23

Alumoxanes[24] and hydroalumination reactions[25–27] continue to enjoy extensive research attention, whereas group 13/15 compounds in MOCVD[28] as well as organometallic chalcogen compounds of aluminum[29] are now mature fields. Reviews specifically directed to structural[30] and thermodynamic[31] data on organoaluminum compounds have been published. A new area of great concern in aluminum chemistry is the potential biological activity of the element. An excellent coverage of this emerging subject with respect to Alzheimer's disease is given.[32] There are many reviews and book chapters that cover the organometallic chemistry of aluminum in general.[33–37]

Given the enormous body of literature focused on compounds containing an Al–C bond, this chapter will focus on new compounds that can now be viewed as separate classes of Al–C bonded compounds, and the new important results that have been achieved for the pre-existing compound classes. For example, 1993 marked the beginning of an understanding of how alkylaluminum compounds combine with oxygen and water (with particular relevance to the use of MAO in olefin polymerization). Charged compounds, both low coordinate and chelated, were discovered and fully developed in the past decade. This time period also saw the first multiply bonded group 13 compounds. As always, aluminum research created stunning new compounds that are difficult to classify. These will be briefly mentioned, but could be regarded as the vanguard for totally new classes of compounds.

3.06.2 Alkylaluminum Reactions

3.06.2.1 With Oxygen

Aluminum compounds such as $AlMe_3$ are well known to be highly air and moisture sensitive due to the strength of the Al–O bond ($\sim 350\,kJ\,mol^{-1}$) versus the Al–C bond ($\sim 255\,kJ\,mol^{-1}$). Complete oxidation of 1 ml of $AlMe_3$ in ambient air can produce a fireball 3 ft in diameter. Recent studies under controlled conditions have produced a better understanding of the reactivity of aluminum alkyls.

In a matrix-isolation reaction of $AlMe_3$ with pure O_2, it was demonstrated that the first reaction product is the insertion of oxygen into one of the Al–C bonds to produce [Me_2AlOMe], which, in turn, becomes either dimeric or trimeric. The reaction is thought to proceed by interaction of O_2 with the $[AlMe_3]_2$ dimer to give this product (Figure 1(a)). This would help rationalize the breaking of a strong O–O bond. There was no evidence for the presence of peroxo compounds.[38] However, depending on the conditions, there may be multiple possibilities for the insertion

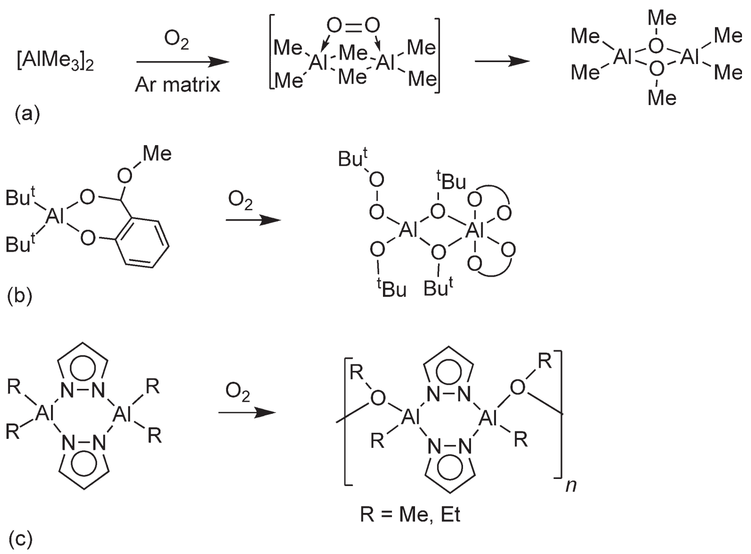


Figure 1 Insertion of oxygen into Al–C bonds.

of O_2 into group 13–carbon bonds. For example, in the combination of $GaMe_3$ with O_2, a peroxide is produced, $Me_2Ga(OOMe)$.[39] Indeed, there is a great deal of evidence for the presence of peroxide group 13 compounds. The combination of $M(^tBu)_3$ (M = Ga,[40] In[41]) with O_2 resulted in the formation of the oxygen-bridged dimers, $[(^tBu)_2M(OO^tBu)]_2$. In contrast, the same reaction with the aluminum derivative led to the formation of a dimeric alkoxide.[42]

Thus, peroxide compounds of aluminum could not be obtained with traditional organometallic reagents and those possessing bulky groups (for which insertion chemistry should be favored). The first structural characterization of an Al–OOR bond occurred when exploring the oxygen insertion into monomeric $(^tBu)_2Al$(methylsalicylate). When conducted at low temperature, this reaction produced a compound with the typical alkoxide linkages, but also with a peroxo group (Figure 1(b)).[43] At higher temperatures the reaction led to a mixture of products that was difficult to characterize. The peroxo O–O distance of 1.38(2) Å is slightly shorter than other main group or transition metal peroxide compounds. The Al–O distance for this group is 1.725(7) Å. Over several hours under ambient conditions, the compound slowly decomposes to the full alkoxide derivative, indicating the unstable nature of the peroxo species.

Subsequent work has shown that the steric effects of the group 13 substituents may dictate the outcome of the reaction. In studying the O_2-insertion chemistry of $[R_2Al(\text{pyrazole})]_2$ (R = Me, Et, ^tBu), it was found that the bulky ^tBu derivative did not insert oxygen under any conditions.[44] The crystal structure of this compound revealed that the Al_2N_4 six-membered ring was essentially planar. The C–Al–C angles were distorted from ideal Td geometry at 122° as were the N–Al–N angles at 100°. Similar bonding parameters would be expected for the Me and Et derivatives, which insert a single oxygen atom to give a compound having the putative structure shown in Figure 1(c). A key difference between the ^tBu starting material and the Me and Et derivatives is that the latter are known to invert their configurations in solutions, potentially opening the aluminum to insertion by oxygen. Based on the matrix-isolation work described above, it would be useful to consider here the possibility of a bridging O_2 group spanning the two Al–C bonds. Noting that the O_2 bond length will be shorter than the N–N distance in the pyrazole ligand, it appears that there might be enough space for this type of interaction to take place in these compounds. However, the sequence of events culminating in a bis-alkoxide is clearly much more complicated.

3.06.2.2 Insertion of CO and Allenes into Al–C Bonds

Matrix-isolation methods were used to identify the first CO adduct of a trialkyl aluminum. The matrix conditions allowed for the stabilization of a monomeric $AlMe_3$ unit, which formed the Lewis acid–base adduct, $Me_3Al–CO$.[45] The dimer, $[AlMe_3]_2$, did not form the CO adduct. Subsequent work utilized $^tBu_3Al$, which is known to be monomeric at room temperature. Moreover, $^tBu_3Al$ was known to insert ethylene, thus giving rise to the expectation that CO would also form an insertion product. This was easily achieved by bubbling CO into a flask containing $^tBu_3Al$ dissolved in

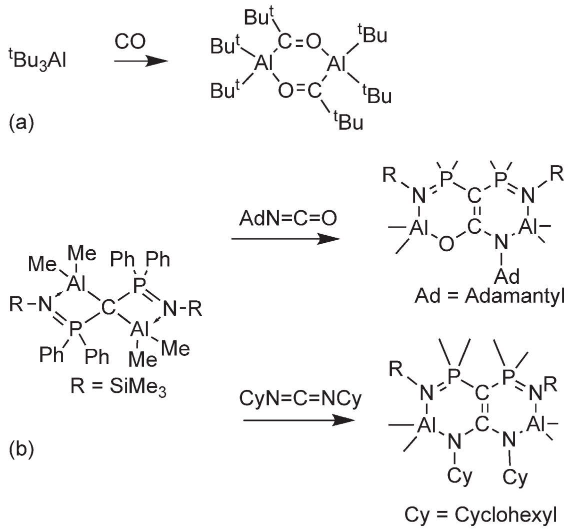


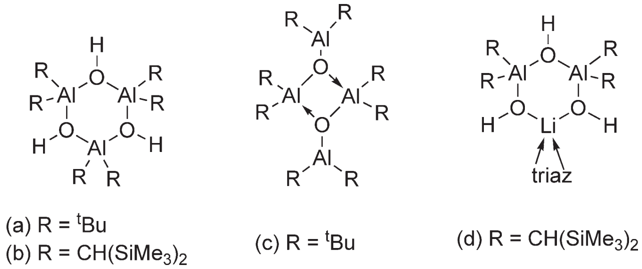
Figure 2 Insertion of CO and allenes into Al–C bonds.

hexane.[46] The original colorless solution became bright yellow once the gas was introduced, and X-ray quality crystals were subsequently obtained in high yield (62%). The spectroscopic data and structure of the compound (Figure 2(a)) confirmed the insertion of a CO molecule into one of the Al–^{t}Bu bonds forming a dimeric acyl compound. In the structure, the aluminum atoms are in a distorted tetrahedral geometry with an Al–O distance of 1.866(2) Å and C–O distance of 1.252(3) Å. These distances are similar to those found in ketones coordinated to four-coordinate aluminum. The compound is the first structurally characterized example of a CO insertion into an Al–C bond.

In two separate reactions, a new carbon–carbon double bond was created by the insertion of a heteroallene into the Al–C–Al bonds of a spirocyclic dimethylaluminum bis(iminophosphorano)methandiide compound (Figure 2(b)).[47] In both compounds, the C–C bond is shorter than a single bond but longer than a typical double bond, indicating delocalization within the interesting bicyclic ring systems.

3.06.2.3 With Water

The controlled hydrolysis of aluminum alkyls yields industrially important oligomeric compounds of the formula $(RAlO)_n$. These oligomers belong to a general class of compounds called alumoxanes, species which contain at least one bridging oxo group between two aluminum centers. The first structural characterization of alkylalumoxanes $[(R_2Al)_2O]_n$ and $(RAlO)_n$ was obtained after hydrolysis of tri-*tert*-butylaluminum.[48] The low temperature (−78 °C) hydrolysis of $Al(^tBu)_3$ in pentane resulted in the formation of the trimeric hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_3$ (Figure 3(a)) as the major product (20–55% yield) with the liberation of isobutene. A single ^{1}H NMR resonance at $\delta = 2.02$ ppm and a sharp O–H stretch at 3,584 cm^{-1} in the infrared spectrum substantiated the presence of hydroxyl groups. The ^{17}O NMR spectrum showed a singlet at $\delta = 1$ ppm, which was downfield from that observed for the gallium analog ($\delta = -17$ ppm). The ^{27}Al NMR exhibited a broad resonance at $\delta = 139$ ppm for the four-coordinate aluminum. The crystal structure of



(a) R = ^{t}Bu
(b) R = $CH(SiMe_3)_2$
(c) R = ^{t}Bu
(d) R = $CH(SiMe_3)_2$

Figure 3 Examples of compounds formed from the reaction of aluminum alkyls with water.

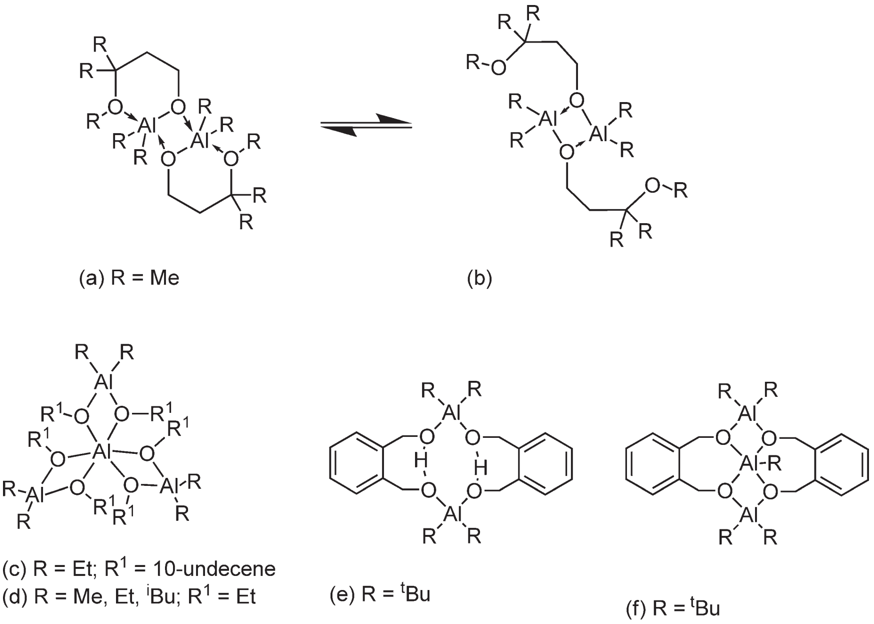
the compound revealed a planar hexagonal Al_3O_3 ring. The ring was distorted, with the average intraring angle at oxygen (142°) being significantly larger than at aluminum (98°). The angle at oxygen was significantly larger than 125.8° as found in the gas-phase electron-diffraction determination of $[Me_2Al(\mu\text{-OMe})]_3$ or 127.8° as calculated for the model compound $[H_2Al(\mu\text{-OH})]_3$. This was explained by the presence of significant intramolecular inter-*tert*-butyl repulsion that caused an increase in the intraring Al···Al distance compared to the other two compounds. Since the Al–O distance as well as O···O distance remained invariant, the Al–O–Al angle must increase to accommodate the interligand steric interaction. The low-temperature hydrated salt hydrolysis of $Al(^tBu)_3$ with $Al_2(SO_4)_3{\cdot}18H_2O$, followed by thermolysis, yielded the tetrameric alumoxane $[(^tBu)_2Al\{(\mu\text{-OAl})(^tBu)_2\}]_2$ (Figure 3(c)) as the major product and the octameric alumoxane $[(^tBu)Al(\mu_3\text{-O})]_8$ as the minor product. The absence of hydroxyl groups in $[(^tBu)_2Al\{(\mu\text{-OAl})(^tBu)_2\}]_2$ was confirmed by ^1H NMR and IR. A four-coordinate aluminum was indicated by a broad resonance at $\delta = 142$ ppm. However, a resonance for a three-coordinate aluminum center was not observed in the ^{27}Al NMR at room temperature, but it was clearly visible after warming the sample to 80 °C.

The hydrated salt hydrolysis of $Al(^tBu)_3$ in toluene using $Al_2(SO_4)_3{\cdot}14H_2O$ resulted in the formation of the dimeric hydroxide $[(^tBu)_2Al(\mu\text{-OH})]_2$ as the major product.[49] This compound could also be prepared by the addition of water to a refluxing toluene solution of $Al(^tBu)_3$. The ^1H NMR showed a singlet at $\delta = 1.12$ ppm and IR showed a stretch at $3697\ cm^{-1}$, thus confirming the presence of the hydroxyl group. The ^{27}Al NMR had a broad resonance at 132 ppm for the four-coordinate aluminum.

An earlier attempt to insert an oxygen atom into the bonds of the dialane, $R_2Al–AlR_2$ ($R = CH(SiMe_3)_2$), led to the formation, instead, of a 10–20% yield of the oligomeric hydroxide derivative, $[R_2Al(OH)]_n$, due to the presence of adventitious water.[50] In a subsequent study, the reaction was carried out in DMSO with 1 equiv. of water.[51] This produced $[R_2Al(OH)]_3$ in 91% yield (Figure 3(b)). The IR showed a sharp absorption at $3{,}700\ cm^{-1}$ for the OH group and the methane protons and carbon atoms exhibited significant high-field shifts in the ^1H and ^{13}C NMR spectra at $\delta = -0.88$ and 1.4 ppm, respectively. The hydroxy proton is shifted to low field at $\delta = 2.71$ ppm by comparison to the trimeric compound $[(^tBu)_2Al(\mu\text{-OH})]_3$ and the dimeric compound $[(^tBu)_2Al(\mu\text{-OH})]_2$ discussed previously. In an attempt to explore the reactivity of the hydroxy group, an equimolar amount of isobutyllithium was added with N,N′,N″-trimethyl triazinane, leading to an 84% yield of the lithium-bridged compound with elimination of one AlR_3 group (Figure 3(d)). Thus, the expected deprotonation reaction did not occur. Surprisingly, the acidity of the OH group is apparently reduced by bonding to aluminum. The Al–O bonds to the bridging OH group are ~1.89 Å, in the range found for other aluminum compounds with bridging hydroxide. In contrast, the Al–O bonds to the O–Li group are significantly shortened to ~1.76 Å. The Al_2LiO_3 heterocycle has a distorted boat conformation. The endocyclic angles of the heterocycle are larger at the oxygen atoms (135.9(3)–143.7(2)°) than those at the metal centers (97.1(1)–108.8(4)°).

3.06.2.4 With Alcohols

A series of dimethyl- and dichloroaluminum compounds have been prepared in combination with alkoxylalcohols.[52] The compounds can be generally represented by the formula, $[X_2Al(\mu\text{-OCHR}^1(CH_2)_n(CR^2R^3)OR^4)]_2$, with X = Me or Cl and R^1–R^4 being various combinations of H, Me, Et, Pr, and ^tBu. Six compounds were characterized by X-ray crystallography, and all of the compounds were dimeric in the solid state with coordination environments around the aluminum atoms approximating trigonal bipyramidal (tbp). One representative compound (shown in Figure 4(a)) contained a four-membered ring with Al–O distances of 1.805(2) and 1.905(3) Å. The Al–ether oxygen bond distance was 2.388 Å, signifying weaker secondary bonding. This weaker bonding resulted in a solution-state equilibrium between four- and five-coordinate species (Figure 4(a) and 4(b)). However, this equilibrium was not observed in the Cl_2Al analogues, due to the increased Lewis acidity of the aluminum atom. The combination of an unsaturated long-chain alcohol, such as 10-undecen-1-ol ($CH_2{=}CH(CH_2)_8CH_2OH$), with $AlEt_3$ and MAO produced the compounds, $[R_2AlOR^1]_2$ and $[RAl(OR^1)_2]_2$ (where R = Me, Et and R^1 = 10-undecen).[53] In the presence of excess alcohol, the tetrametallic “Mitsubishi”™ compounds $Al_4R_6(OR^1)_6$ (Figure 4(c)) form. The compounds consist of a central aluminum atom (with a ^{27}Al NMR resonance at either $\delta = 8.21$ or 7.3 ppm) bonded to six oxygen atoms. The Mitsubishi™ compounds could also be prepared from the reaction of an aluminum trialkyl with aluminum trialkoxide. The compounds $[Al\{(\mu\text{-OEt})_2AlR_2\}_3]$ (R = Me, Et, ^iBu) (Figure 4(d)) were characterized structurally and spectroscopically.[54] The compounds are approximately D_3-symmetric with a planar Al_2O_2 ring. The Al–O distances are longer around the central six-coordinate aluminum (av. 1.9 Å) than for the terminal four-coordinate aluminums (av. 1.8 Å). The ^{27}Al NMR had peaks around $\delta = 10$ ppm for the central six-coordinate aluminum and around $\delta = 150$ ppm for the terminal four-coordinate aluminum. These compounds are precursors for the preparation of Al_2O_3 nanoparticles.[55]In addition, they could be further derivatized by alkane-elimination reaction.



(a) R = Me (b)

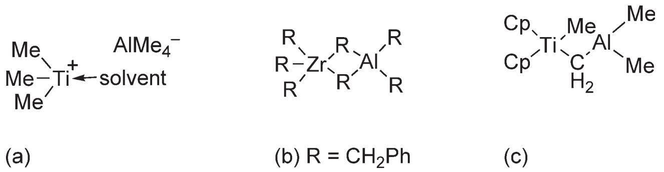
(c) R = Et; R^1 = 10-undecene
(d) R = Me, Et, ^{i}Bu; R^1 = Et
(e) R = ^{t}Bu
(f) R = ^{t}Bu

Figure 4 Examples of alkoxy compounds formed from the reaction between aluminum alkyls and alcohols.

The combination of $^tBu_3Al$ with 1,2-di(hydroxymethyl)benzene produces the binuclear complex $[^tBu_4Al_2(OCH_2C_6H_4CH_2OH)_2]$ (Figure 4(e)) in quantitative yield.[56] The OH protons in the compounds are involved in intramolecular hydrogen bonding. Their chemical shifts in the ^1H NMR appeared at $\delta = 16.35$ ppm. The methylene units are equivalent and appear as singlets at 4.61 ppm. This compound reacts with excess of $^tBu_3Al$ to give the trimetallic compound $[^tBu_5Al_3(OCH_2C_6H_4CH_2O)_2]$ (Figure 4(f)). The methylene protons now become a doublet of doublet AB system, with chemical shifts at $\delta = 4.73$ and 4.58 ppm due to the hindered rotation introduced by the presence of the third aluminum.

3.06.2.5 With Transition Metals for Polymerization

Transition metal compounds formed with alkylaluminum reagents, or activated by these reagents, are important in olefin oligomerization and polymerization. The exact nature of the compounds formed in these combinations is still uncertain, although there is a growing consensus that a range of compounds may be forming in an equilibrium mixture. Evidence for two general types of compounds has been obtained. The first are ionic compounds such as $[Me_3Ti(solvent)]^+[AlMe_4]^-$ (Figure 5(a)), which was spectroscopically characterized in the mixture of Me_4Ti and $AlMe_3$.[57] The second type of compound is a neutral alkyl-bridged compound, formed, for example, in the combination of ZrR_4 with AlR_3 (with $R = CH_2Ph$) (Figure 5(b)).[58] Another compound in this second group is the methylene-bridged compound $Cp_2Ti(\mu\text{-}CH_3)(\mu\text{-}CH_2)AlMe_2$, formed from the reaction of Cp_2TiMe_2 with $AlMe_3$ (Figure 5(c)).[59] This compound is a derivative of the Tebbe reagent, a similar derivative with a bridging chloride in the place of the methyl group, which acts as a carbene in subsequent reactions.[60] Despite the evidence for these two categories, it is still likely that the alkyl-bridged species separate to form a cationic catalytic transition metal species and an aluminate anion. The ease of formation of this cation, and its stability, will affect the resulting oligomerization and polymerization



(a) (b) R = CH_2Ph (c)

Figure 5 Examples of some transition metal–aluminum compounds used in polymerization.

reactions. It should be noted that the cationic nature of the boron analogs, for example, $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$, are well established. The following subsections will provide examples of the combination of metal and alkyl groups that appear to form in these two types of compounds. Details of the activities of these systems and the nature of the oligomers and polymers formed will not be given here, as they are covered in great detail in the various articles as well as the many reviews that have appeared on this subject (for details, see References).

3.06.2.5.1 Ionic compounds

Ni(sacsac)P(^{n}Bu$_3$)Cl (sacsac = pentane-2,4-dithionate) was activated by $AlEt_2Cl$ to form a catalytically active species for the oligomerization of ethene and propene.[61] This study is noteworthy in that it uses *in situ* UV–VIS spectroscopy to monitor the course of the polymerization. In this reaction, the aluminum reagent serves both to activate the transition metal and to scavenge any moisture present.

A comprehensive study of 15 zirconecene monomethyl monochloro compounds and their exchange of chloride for methyl with $AlMe_3$ indicates that the exchange process is a function of the electron deficiency at the metal.[62] With low electron densities, the zirconium is more likely to exchange chloride for methyl. The study revealed low electron densities at the metal for the indenyl compounds by comparison to the cyclopentadienyl compounds. The study also revealed that steric effects are minor compared to the electronic effects of the ligands on the zirconium.

A recent new discovery is the fact that the hydrolysis of branched β-alkyl-substituted aluminoxanes are, in some cases, as effective as co-catalysts in olefin polymerization as MAO.[63,64] For example, when combined with the the metallocenes, $Cp^*{}_2ZrCl_2$, the hydrolysis products ($Al/H_2O = 2$) of R_3Al (R = ^{i}Bu and ^{i}Oct) produced akylated ion pairs with high polymerization activities.[65] The same combinations with Cp_2ZrCl_2 did not produce active catalysts, a result interpreted as due to the inhibition of β-hydride elimination in the substituted metallocene derivatives.

A catalyst system formed from the reaction of $Cp^*{}_2Zr(NMe_2)_2$ and $AlMe_3$ showed no olefin-polymerization activity due to the formation of the stable but inactive heterodinuclear cation, $[Cp^*{}_2Zr(\mu\text{-}Me)_2AlMe_2]^+$. In contrast, bulky AlR_3 (R = Et, ^{i}Bu) co-catalyzed systems were highly active.[66] In particular, the $Cp^*{}_2Zr(NMe_2)_2$ combination with Al(^{i}Bu)$_3$ showed higher catalytic activity and higher molecular weight polymers than when using MAO as the aluminum co-catalyst.

3.06.2.5.2 Neutral alkyl-bridged compounds

The combination of $TiMe_4$, Cp_2ZrMe_2, $Hf(CH_2SiMe_3)_4$ with $AlMe_3$ was investigated using conductivity measurements and ^{1}H NMR spectroscopy.[67] The conductivity of the CH_2Cl_2 solutions of the mixtures containing Hf and Zr did not differ substantially from the conductivity of the reactants, so it is likely that alkyl-bridged species may be formed. This was confirmed spectroscopically in the Hf–Al couple.

3.06.2.5.3 Chain-transfer reactions

Chain transfer was observed to occur for Al(^{i}Bu)$_3$ in olefin-polymerization systems with $CpTiCl_3$[68] and $LZrCl_2$ (L = *rac*-dimethylsilylenebis(indenyl)).[69] There was no effect of increase in Al(^{i}Bu)$_3$ concentration on the molecular weight of the polymer produced for the Zr system, but for the Ti system, there was a sharp decrease in molecular weight. The use of $AlMe_3$ instead of Al(^{i}Bu)$_3$ led to decrease in both catalytic activity and polymer molecular weight with increasing concentration.

3.06.2.5.4 Generalizations for cation- versus alkyl-bridged compound formation

The use of chlorinated aluminum alkyls, such as $AlEt_2Cl$, favors the formation of cation–anion pairs through the increased Lewis acidity created on the aluminum atom due to the presence of the chloride. The use of non-halogenated aluminum alkyls leads to bridged structures that are more difficult to separate into ions. Moreover, trialkylaluminum and MAO systems undergo rapid alkyl exchange.[70] Adding further complexity to these systems, there is evidence that the chloroaluminum compounds form dimeric chloride-bridged aluminum compounds, which are much more stable than the analogous alkyl-bridged aluminum dimers.[62]

The use of bulky trialkylaluminum reagents, such as Al(^{i}Bu)$_3$, with various group 4 metallocenes led to olefin-polymerization catalysts that rivaled those formed with MAO as the co-catalyst.

3.06.3 Low-Coordinate Cations

One of the more important recent developments in organometallic aluminum chemistry has been the formation and isolation of low-coordinate compounds, and, in particular, cations. These were first prepared in reactions of various aluminum reagents with crown ethers to form the inclusion compounds known as "liquid clathrates."[71,72] Most of the evidence supports the presence of ion pairs as the basis of the solvent inclusion effect. Indeed, the compound $[AlMe_2\text{-}18\text{-crown-}6]^+[AlMe_2Cl_2]^-$ was isolated from one such system (the cation is shown in Figure 6(a)).[73] This was the first time the Me_2Al^+ unit had been structurally characterized.

Subsequently, the base-free cation Cp_2Al^+ (see Figure 6(b)) was characterized, and, importantly, used in the polymerization of isobutylene.[74] The compound was made by combining Cp_2AlMe with $B(C_6F_5)_3$ in dichloromethane. The ^{27}Al NMR of the compound had a single sharp peak at $\delta = -126.4$ ppm, which was in agreement with the calculated value.[75]

The discovery that cationic organometallic aluminum compounds could polymerize olefins led to the search for other ligand–$AlMe^+$ systems that might be as catalytically active as metallocene cations. Compounds incorporating amidinate ligands were among the first to be found,[76] but were generally base stabilized (Figure 6(c)). The fact that base-free systems were not isolated with these ligands was attributed to steric unsaturation. For example, the N–Al–N bond angles were 69°.[77] The troponiminate ligands offered more steric protection, but their use still led to the isolation of alkyl-bridged and base-stabilized compounds, when 0.5 equiv. of the alkyl-abstraction reagent, $[Ph_3C][B(C_6F_5)_4]$, was employed.[78] However, with an equimolar amount of the reagent, the base-free cations could be obtained as liquid clathrates in high yields (Figure 6(d)). The compounds were found to be active in the polymerization of ethylene and methylmethacrylate.[79]

Another structure of a base-free three-coordinate aluminum alkyl cation was obtained when using β-diketiminate ligands (Figure 6(e)).[80] In the structure, the N_2AlC plane is nearly planar. The Al–C bond length is 1.905(2) Å. The N–Al–N angle is 102° and the N–Al–C angles are ~126°. There were long secondary $Al^+\cdots F$ contacts in the structure.

Schiff base ligands were used to prepare cations of the form $[LAlMe]^+$ after combining the chloride-containing starting material with 1 equiv. of either $AlCl_3$ or $NaBPh_4$ (Figure 6(f)).[81] Exposure of the cation to dry O_2 at 0 °C produced cationic alkoxy cations. These latter compounds were efficient catalysts for the polymerization of ε-caprolactone. After 1 h, the conversion was 95%, and the resulting polymers had a PDI of 1.24–1.30.

3.06.4 Five-Coordinate Aluminum Alkyls

3.06.4.1 General Considerations

Most five-coordinate aluminum alkyls are prepared by alkane elimination. The first structurally characterized five-coordinate simple aluminum alkyl chelate compound was reported in 1993.[82] The compound $AlMe[MeO_2CC_6H_4\text{-}o\text{-}O]_2$ was formed by the reaction of Me_3Al with 2 equiv. of $MeO_2CC_6H_4$-o-OH. The commonly

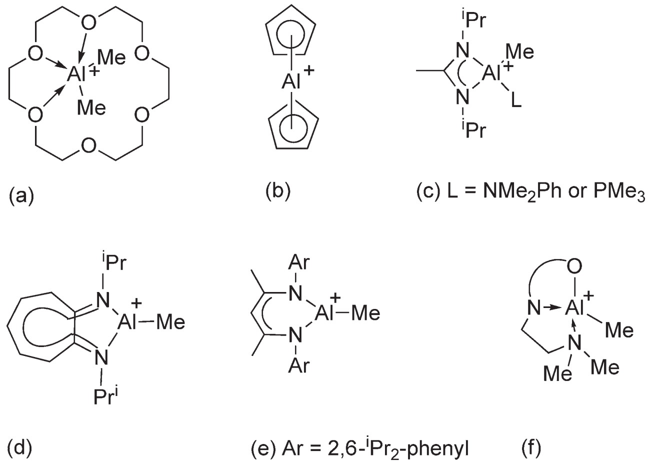


Figure 6 Examples of low-coordinate cationic aluminum compounds.

used ligands to support five-coordinate aluminum alkyls are Schiff bases,[22] substituted pyrroles,[83] multidentate phenolates,[84,85] amidophosphines,[86] acac,[87] and ketiminates.[88] Some representative examples of five-coordinate aluminum alkyls with different types of ligands are shown in Figures 7(a)–7(g). Each of these compounds was structurally characterized by X-ray crystallography. The aluminum atoms in these compounds are in geometries that are not completely tbp or square planar (sqp). A quantitative measure has been proposed to describe the distortion from perfectly sqp or tbp geometry in five-coordinate compounds. The amount of this distortion is expressed by a value "τ."[89] A perfectly sqp geometry has a τ value equal to zero, whereas a perfectly tbp geometry has a τ value equal to 1. This value may be important in determining the accessibility of a sixth coordination site.[90]

Five-coordinate aluminum alkyls have been part of a previous review with emphasis on crystallographic data.[30] Examples of chelated five-coordinate aluminum alkyls include mononuclear, dinuclear,[91] and trinuclear[56] compounds. Some are mixed metal compounds with another group 13 metal, for example, gallium.[92] Trimetallic compounds shown in Figure 7(g) were prepared by the reaction of 3 equiv. of R_3Al (R = Me, Et, ^{i}Bu) with 2 equiv. of 2,2′-di(hydroxymethyl)biphenyl. The X-ray crystal structures were determined for R = Me and R = ^{i}Bu. The structure consists of two four-membered and two nine-membered rings. The central aluminum is in a tbp geometry. These compounds are the first alkylaluminum diolates with a tbp geometry at the central atom.

A unique example of a compound with five Al–C bonds is (η^5-Cp*)Al(I). The gas-phase electron-diffraction study of (η^5-Cp*)Al(I) shows the compound to be monomeric with a C_{5v}-symmetry and Al–C bond distances of 2.39 Å.[93]

The effect of *trans*-influences on the stability of monomeric five-coordinate aluminum alkyls have been discussed.[94] Studies have also focused on the equilibrium between four-coordinate and five-coordinate isomers in compounds of the type $[R_2Al\{\mu\text{-}O(CH_2)_nER^1_x\}]_2$ ($n = 2$, 3; $ER^1_x = OR^1$, SR^1, NR^1_2) (shown in Figure 7(h) for $n = 2$). Factors that control this equilibrium and hence the coordination around the aluminum include the steric bulk of the substitutent at the aluminum (R), and the Lewis base donor R^1, the basicity of the neutral donor group ER^1_x, and the chelate ring size (as determined by n).[95]

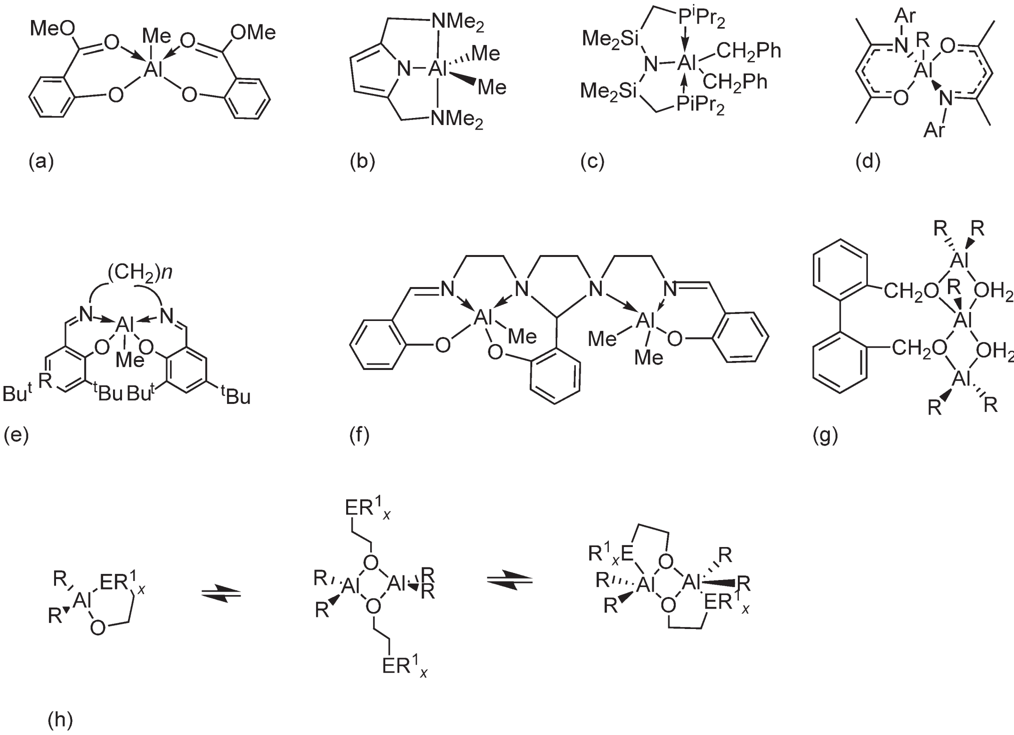


Figure 7 Examples of five-coordinate aluminum alkyls with different ligands.

3.06.4.2 Five-coordinate Salen Aluminum Alkyls

Considerable interest has focused on five-coordinate Salen aluminum compounds. The Salen class of compounds are Schiff base ligands with two nitrogen and two oxygen atoms as the coordinating sites, and their complexes with aluminum have been surveyed extensively in a recent review.[22] In monomeric chelated Al alkyls of this type, the ^{1}H NMR shows a single peak for the Al–Me protons. The chemical shift is not much different from that of four-coordinate aluminum compounds. For example, in Salen(^{t}Bu)Me, this peak appears at $\delta = -1.11$ ppm.[96] The ^{27}Al NMR has been used as a convenient tool for determining the solution-state coordination environment of the aluminum in these compounds. The chemical shifts for five-coordinate Salen aluminum appear at $\delta = 50$–100 ppm. These compounds have either a distorted tbp or a distorted sqp geometry. The geometry is partially determined by the nature of the ligand. For example, in Salen aluminum compounds, a Salen ligand with a rigid methylene or arylene backbone gives rise to distorted sqp geometry, whereas the more flexible propylene backbone shows distorted tbp structures. In the sqp compounds, the Al atom is generally perched above the plane formed by the four equatorial atoms. The bimetallic compound LAlMe(AlMe$_2$) (Figure 7(f)) was formed by the reaction between a heptadentate Schiff base ligand with 2 equiv. of trimethylaluminum. The ^{27}Al NMR shows a peak at 65.40 ppm for five-coordinate aluminum, whereas in the ^{1}H NMR, there are two Al–Me shifts in a 1 : 2 ratio. Surprisingly, in reactions with 3 equiv. of the aluminum reagent, one of the N=C bonds undergoes an unusual alkylalumination reaction to form a trimetallic derivative with two five-coordinate aluminum and one four-coordinate aluminum atoms.

3.06.4.3 Five-coordinate Aluminum Compounds with Salen Ligands

The reduced form of the Salen ligands, the Salen class of ligands, have also been successfully used to prepare mono-, di-, and tetranuclear five-coordinate aluminum alkyls (Figure 8), and have been discussed in a recent review.[97] The bimetallic compound (salan)HAlR(AlR$_2$) (Figure 8(b)) was characterized spectroscopically, although no crystal structures were determined. The ^{27}Al NMR showed peaks corresponding to both five-coordinate and four-coordinate aluminum. The ^{1}H NMR showed extensive coupling, which was further studied by COSY and HECTOR NMR. The tetrametallic compound shown in Figure 8(c) was obtained by refluxing the bimetallic compound (Figure 8(b)) in toluene for a day or more at a concentration of 0.075 to 0.25 g ml^{-1}.

3.06.4.4 Derivatization of Five-coordinate Aluminum Compounds

The polarity of the Al–C bond allows easy derivatization of the five-coordinate aluminum alkyls by alkane elimination (Figure 9). For example, Salen aluminum alkyls LAlMe could be converted to dimeric or polymeric Salen aluminum phosphinates [LAl{O$_2$P(H)Ph}]$_n$ [98] ($n = 2$ or ∞, depending on the Salen ligand backbone)[98,99] by reaction with phenyl phosphinic acid, Salen aluminum siloxides LAlOSiPh$_3$ by reaction with triphenyl silanol,[96] or Salen aluminum alkoxides LAlOR by reaction with an alcohol.[100]

3.06.4.5 Five-coordinate Cationic Aluminum Alkyls

In addition to neutral five-coordinate aluminum alkyls, rare examples of five-coordinate cationic compounds have also been reported.[101] The cationic compound [(PMDETA)AlMe$_2$][Me$_2$AlCl$_2$] (PMDETA = pentamethyldiethylene triamine) (Figure 10(a)) was prepared by the reaction of Me$_2$AlCl with PMDETA in toluene. The ^{1}H NMR showed

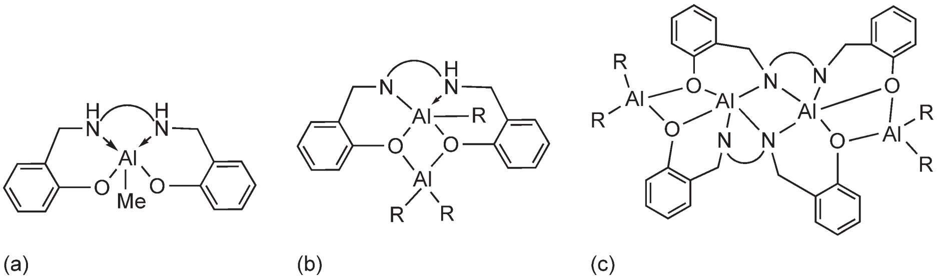


Figure 8 Five-coordinate aluminum compounds with Salen ligands.

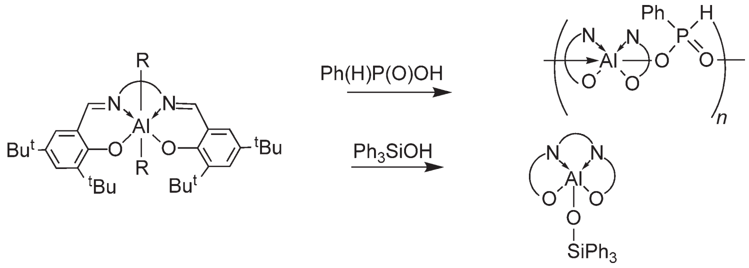
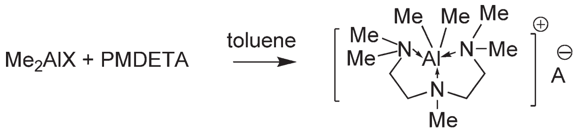


Figure 9 Derivatization of five coordinate aluminum compounds.



(a) X = Cl; A = Me_2AlCl_2
(b) X = A = Br
PMDETA = N,N′,N″,N‴-pentamethyldiethylene triamine

Figure 10 Five-coordinate cationic aluminum alkyls.

two sets of AlMe resonances. The ^{27}Al NMR showed two aluminum peaks at $\delta = 132$ and 154 ppm for the aluminum cation and the anion, respectively. The X-ray structure confirmed the presence of the five-coordinate aluminum atom in the cation in a distorted tbp geometry. The Al–N bond lengths range from 2.067(3) Å for the equatorial nitrogen to 2.286(4) Å for the axial nitrogen. These are longer than previously characterized four-coordinate cations. The use of Me_2AlBr instead of Me_2AlCl gave a different product (Figure 10(b)), with bromide present as the anion, which is confirmed by only one ^{27}Al peak at $\delta = 134$ ppm.

3.06.4.6 Catalysis

Five-coordinate aluminum alkyls are useful as oxirane-polymerization catalysts. Controlled polymerization of lactones[102] and lactides[103] has been achieved with Schiff base aluminum alkyl complexes. Ketiminate-based five-coordinate aluminum alkyl (OCMeCHCMeNAr)$AlEt_2$ were found to be active catalyst for the ring-opening polymerization of ε-caprolactone.[88] Salen aluminum alkyls have also been found to be active catalysts for the preparation of ethylene carbonate from sc CO_2 and ethylene oxide.[104] Their catalytic activity is markedly enhanced in the presence of a Lewis base or a quaternary salt.

3.06.5 Hydroalumination Reaction

Hydroalumination (addition of an Al–H bond) and carbalumination (addition of an Al–C bond) have been discussed in COMC(1982) and COMC(1995).[1,2] In addition, a number of contemporary reviews[25–27,105] discuss these reactions in detail. The generality and feasibility of these reactions for both unconjugated alkenes and alkynes, and also for a wide variety of carbonyl and related compounds, were uncovered by Zeigler and co-workers.[106,107] The beginning was the hydroalumination of an ordinary C=C bond in ethene with $LiAlH_4$ or AlH_3 (Figure 11(a)). In addition, the carbalumination of the C=C was achieved with the insertion of further ethene units by the generated triethylaluminum to yield higher aluminum alkyls (Figure 11(b)). The carbalumination and hydroalumination for alkynes was established in later research efforts.[108–111] Such additions occur in a kinetically controlled *syn*-fashion. The stereochemistry and regiochemistry of the additions depend upon the steric and polar nature of the substituents. The detailed mechanistic pathway has been previously discussed in COMC(1982).[1] It involves the electrophilic attack of R_3Al or R_2AlH monomers on the unshared electron pair or π-electron cloud of the substrates and formation of a π-complex intermediate (Figure 11(c)).

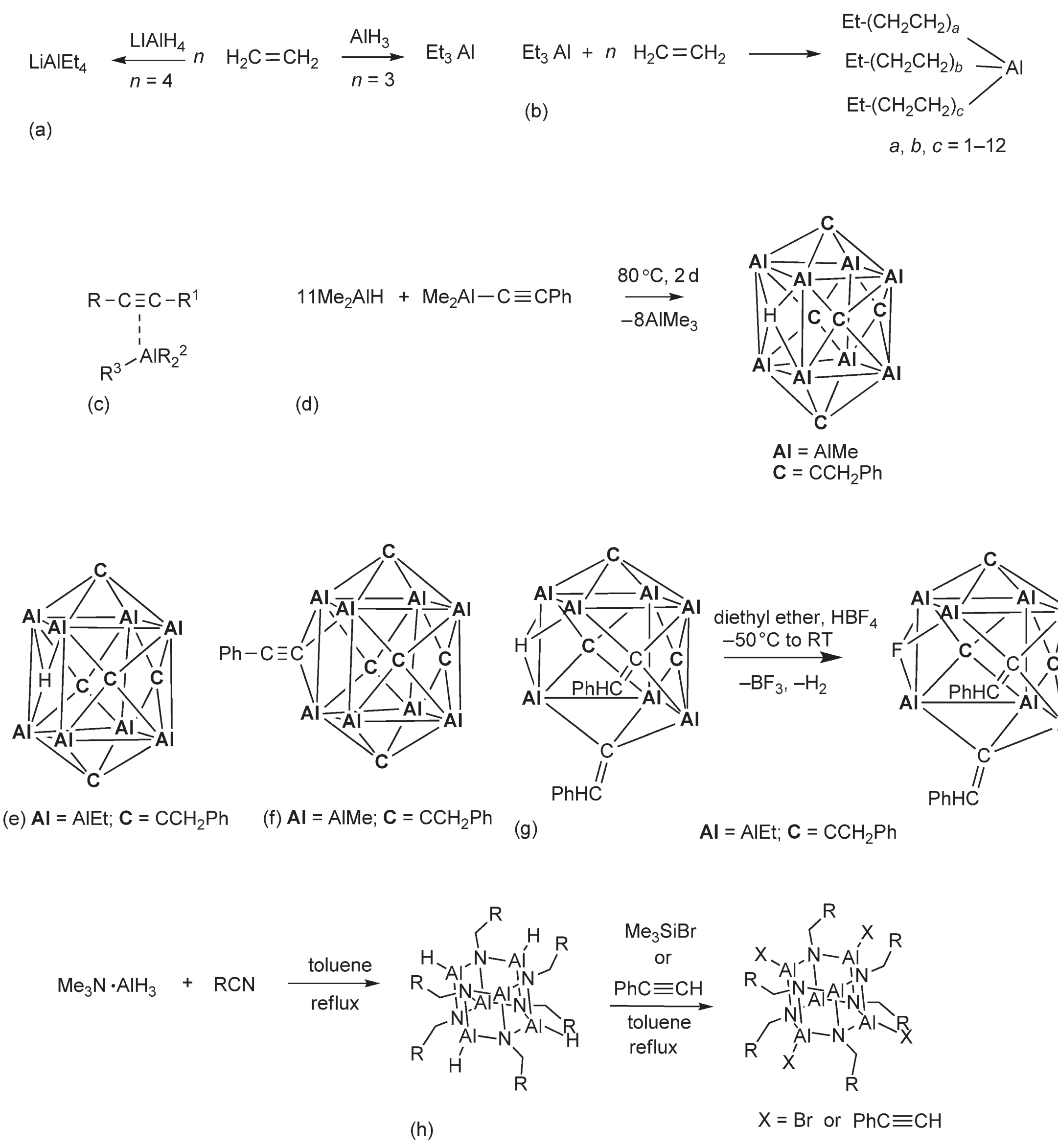


Figure 11 Hydroalumination and carbalumination reactions and some recent cluster derivatives.

Attempts are currently being made to study the intermediates and the new compounds formed. Hydroalumination was used to prepare new carbaalane cluster compounds.[112,113] The first structurally characterized polyhedral carbalane $(AlMe)_8(CCH_2Ph)_5H$ was prepared in 1999 by carrying out the hydroalumination reaction between excess dimethylaluminum hydride and dimethylaluminum phenyl acetylide at 80 °C for 2 days (60% yield) (Figure 11(d)).[114] The skeleton consists of eight aluminum and five carbon atoms. The eight aluminum atoms form a slightly distorted cube, five faces of which are occupied by the carbon atoms. The remaining face is bridged by a hydrogen atom. A total of 16 cluster electron pairs result, which is in accordance with an *arachno*-configuration. Long Al–Al distances (av. 2.80 Å) were observed for the hydrogen-bridged face of the Al_8 cube, but the remaining eight edges are shortened to 2.60 Å.

The Al_7C_5 cluster $(AlEt)_7(C{=}CHC_6H_5)_2(CCH_2C_6H_5)_3H$ and Al_7C_4 cluster $(AlEt)_7(CCH_2C_6H_5)_4(C{\equiv}CC_6H_5)H$ were formed if the methyl groups of the starting compounds were replaced by ethyl groups.[115] The open carbaalane cluster $(AlEt)_7(C{=}CHC_6H_5)_2(CCH_2C_6H_5)_3H$ reacted with excess diethylaluminum hydride to form $(AlEt)_8(CCH_2C_6H_5)_5H$ (Figure 11(e)).[112] The carbaalane $(AlMe)_8(CCH_2C_6H_5)_5(C{\equiv}C_6H_5)$ was obtained by hydroalumination of $Me_2AlCC{\equiv}C_6H_5$ by Me_2AlH (Figure 11(f)). The first carbaalane possessing only aliphatic substituents, $(AlMe)_7(CCH_2CH_3)_4H_2$, was obtained by the reaction of $Me_2AlC{\equiv}CH_3$ with Me_2AlH. Its structure contains an AlC_4 cluster, which is quite similar to that of the *closo*-borate$[B_{11}H_{11}]^{2-}$. Carbaalanes have also been prepared by treating monosubstituted acetylenes with $AlH_3{\cdot}NMe_3$. Reaction of acetylenes such as $PhC{\equiv}CH$, $Me_3SiCH_2C{\equiv}CH$, and $FcC{\equiv}CH$ (Fc = ferrocenyl) with an excess of $AlH_3{\cdot}NMe_3$ in boiling toluene leads to the formation of carbaalanes $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$,[116] $(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6$,[116] and $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$.[117]

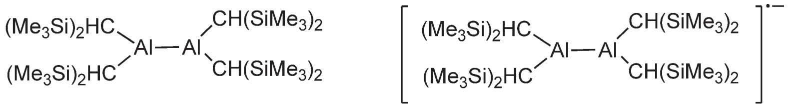
The carbaalanes could be further functionalized, for example, with halides. The carbaalane $(AlEt)_7(C{=}CHPh)_2$-$(CCH_2Ph)_3H$ was functionalized to $(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3(\mu_3\text{-}F)$ with a bridging fluorine atom by treating with $HBF_4{\cdot}OEt_2$ (Figure 11(g)). However, the treatment of the carbaalane $(AlMe)_8(CCH_2Ph)_5H$ with HCl gave $(AlMe)_7(AlCl)(CCH_2C_6H_5)_5(\mu\text{-}H)$ with a terminal Cl.[118]

Hydroalumination of nitriles was used to prepare imidoalanes, for example, hexameric imidoalane $(RCH_2NAlH)_6$ (R = Ph,[119] *p*-MeC_6H_4,[119] *p*-$CF_3C_6H_4$,[119] and C_4H_3S)[120] and heptameric imidoalane $(RCH_2NAlH)_7$ (R = 1-adamantyl)[121] by treatment of PhCN, *p*-MeC_6H_4CN, *p*-$CF_3C_6H_4CN$, 2-cyanothiophene, and 1-adamantylnitrile, respectively, with slight excess of $AlH_3{\cdot}NMe_3$ (Figure 11(h)). Imidoalanes can also be further derivatized with Me_3SiBr or phenyl acetylide (Figure 11(h)).

3.06.6 Multiple Bonding

Double and triple bonds are very common for carbon but are unusual for heavier main group elements. The so-called "double-bond rule," which stated that elements outside the first row of the periodic table do not form multiple bonds either with themselves or with other elements, collapsed with the discovery of stable chemical compounds containing silicon–carbon and silicon–silicon double bonds in the beginning of the 1980s.[122,123] The key to the discovery of these compounds was the protection of the double bonds by bulky subsituent groups, which provided both kinetic and thermodynamic stability. This breakthrough paved the way for a broader research on the multiple bonding involving heavier elements. However, the synthesis of multiple-bonded compounds of group 13 was complicated by the lower M–M bond energies for this group compared to group 14 or 15 elements, as pointed out by computational and spectroscopic data. The reason for the low bond strength lies in the fact that these elements are relatively large and electropositive. Additionally, they have a limited number of valence electrons available for bond formation. The attempt to prepare compounds with gallium–gallium multiple bond yielded $Na_2[RGa_2R]$ (R = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$), which has been referred to as "digallyne," indicating it to be the first compound containing a Ga–Ga triple bond (Ga–Ga distance = 2.319(3) Å).[124]

The first example of a compound containing an Al–Al bond was tetrakis[bis(trimethylsilyl)methyl]dialane, $[(SiMe_3)_2CH]_2Al\text{–}Al[CH(SiMe_3)_2]_2$ (Figure 12(a)), which was prepared by the potassium reduction of bis[bis(trimethylsilyl)methyl]aluminum chloride.[50] The Al–Al bond distance is 2.660(1) Å. The aluminum atoms were found in trigonal-planar environments about a nearly planar $C_2Al\text{–}AlC_2$ core. Like single bonds, the stabilization of multiple bonds between group 13 elements also requires the use of bulky substituents. However, due to the insufficient number of electrons available for the formation of multiple bonds between these elements, multiple bonds are usually observed only when electrons are added to the group 13–group 13 bonded system, for example, by alkali metal reduction. So far, all the compounds reported had a "one-electron π-bond" between the Al atoms. The radical anion $[(SiMe_3)_2CH]_2Al\text{–}Al[CH(SiMe_3)_2]_2^{\cdot -}$ (Figure 12(b)) was prepared by sodium or potassium reduction of $[(SiMe_3)_2CH]_2Al\text{–}Al[CH(SiMe_3)_2]_2$ in dimethoxyethane (DME)[125] in the form of dark blue crystals or by lithium reduction in the presence of TMEDA (TMEDA = tetramethylethylenediamine) in ether in the form of fine black crystals (47% yield).[126]. The Al–Al bond in this radical anion (2.53(1) Å) is considerably shorter than that observed in the neutral dialane (2.660(1) Å), which is consistent with the multiple-bonding character. The radical anion $[Pr^i{}_3C_6H_2]_2Al\text{–}Al[C_6H_2Pr^i{}_3]_2^{\cdot -}$ was prepared by the lithium reduction of the neutral dialane.[127] The Al–Al bond



(a) (b)

Figure 12 Examples of compounds containing Al–Al and "Al–Al one electron π-bonds."

distance decreased from 2.647(3) Å in the neutral dialane, $[Pr^i_3C_6H_2]_2Al–Al[C_6H_2Pr^i_3]_2$, to 2.470(2) Å in the radical anion, $[Pr^i_3C_6H_2]_2Al\text{-}Al[C_6H_2Pr^i_3]_2^{\cdot -}$, which shows multiple-bond character. The EPR spectroscopy of these radical anions showed that the unpaired electron occupied an orbital that is shared equally between the metals, which is consistent with the generation of a π-bond between the metals. The attempted addition of a second electron to afford the dianion $[R_2AlAlR_2]^{2-}$ has not been successful so far.

3.06.7 Fluoride Compounds

The interest in organoaluminum fluorides arises from the potential use of these compounds as models of certain catalytic reactions. The strong Al–F interaction can be used in the cleavage and formation of C–F bonds. The cluster $(Cp^*Ti)_2F_8(AlMe_2)_4$ is formed by the reaction of Cp^*TiF_3 with $AlMe_3$ (Figure 13(a)).[128] The ^{19}F NMR of the compound is silent. The X-ray structure shows that the core structure of the compound consists of an Al_4Ti_2 octahedron with two Ti atoms occupying *trans*-positions. The edges of the octahedron are μ-bridged by the eight fluorine atoms. The Al atoms are four coordinate with an average Al–F bond length of 1.76 Å.

The reaction of Cp^*ZrF_3 and $AlMe_3$ in 1 : 1 mol ratio yields the tricyclic compound $[Cp^*(Me)Zr(\mu\text{-}F)AlMe_2(\mu\text{-}F)_2]$ with selective exchange of fluorine atoms for methyl groups (Figure 13(b)).[129,130] The ^{19}F NMR showed that the fluorine atoms bridging the Zr atoms were chemically different due to the *trans*-effect of either the Cp^* or the methyl groups. The X-ray structure showed that the Zr atoms were in distorted octahedral and the Al atoms in distorted tetrahedral environments. The Zr–F distances were 2.11–2.18 Å and mean Zr–C bond length in Zr–Me units were 2.28 Å. The reaction of Cp^*HfF_3 with $AlMe_3$ in equimolar ratio gave $\{[Cp^*HfMe(\mu_2\text{-}F)][(\mu_2\text{-}F)_2AlMe_2]\}_2$ in quantitative yield (Figure 13(c)).[129] The reaction stereospecifcally gave the *cis*-isomer. The ^{19}F NMR showed three magnetic non-equivalent types of fluorine atoms with chemical shifts of $\delta = -87.3$, -56.7, and -109.8 ppm. The X-ray structure showed the Hf–C bond distances to be 2.24 Å and the F–F bond distances to be 2.10–2.17 Å. With 3 equiv. of $AlMe_3$, however, the reaction gave Cp^*HfMe_3 as the main product (85% yield) and the $Hf_3Al_6C_7$ cluster $(Cp^*Hf)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)$ as the byproduct (5% yield). In this cluster, all the metal atoms are tetragonally coordinated. The X-ray crystal structure showed that the Hf–μ-C bond lengths varied widely (2.13–2.27 Å).

3.06.8 Lewis Acid Catalysis

3.06.8.1 Oxidation of Alcohols

The Oppenauer oxidation of alcohols is a very useful method, and is widely used for the synthesis of steroids and terpenoids. The aluminum alkoxides used in this reaction have the problem of low reactivity, use of a large excess of a hydride acceptor under relatively drastic conditions, and undergo undesirable side-reactions. One useful improvement in this method was obtained by using an organoaluminum compound as the catalyst (Figure 14(a)) with ^tBu–CHO as the hydride acceptor.[131] Very high yields (up to 98%) were obtained for a variety of alcohols under mild conditions (21 °C, 0.5 h) with only 1–2 mol% of the catalyst and 1.2–3 equiv. of ^tBu–CHO. The catalyst was, however, not found to be very useful for simple primary alcohols. The catalyst system was further improved as a practical general oxidation method by using acetone (1.2–3 equiv.) as a more general and convenient hydride acceptor with

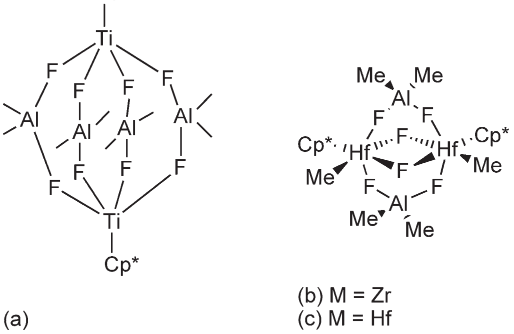


Figure 13 Examples of some organoaluminum fluoride compounds.

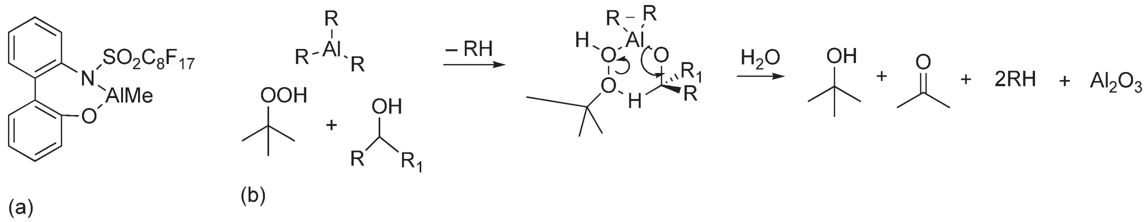


Figure 14 (a) Example of an organoaluminum catalyst for the oxidation of alcohols, and (b) a postulated mechanism using R_3Al.

5 mol% of the aluminum compound, and very good yields (up to 97%) were obtained for oxidation of carveol, α-ionone, and allocholesterol.

In another example, oxidation of various saturated and unsaturated alcohols, such as geraniol, hexenols, and nonenols, was obtained under mild condition by using alkylaluminum R_3Al (R = Me, Et, ^{i}Bu, and 2-methylbutane)/*t*-butyl hydroperoxide system.[132] Two conclusions could be made. First, the conversion increased substantially with increasing steric bulk on the aluminum atom. Second, stoichiometric reactions were needed to have the least sterically encumbered reagents, such as $AlMe_3$, produce any product at all. The postulated mechanism is shown in Figure 14(b). The reaction pathway was suggested to proceed through a tetracoordinate aluminum complex. The electrophilic character of the peroxidic oxygen is increased by the polarization of the O–O bond by the metal center.

3.06.8.2 Olefin Polymerization

The bulky aluminum alkyl compound $MeAl(OAr)_2$ (Ar = 2,6-di-*tert*-butyl-4-methylphenyl) was used as a noninteracting scavenger.[133] The compound is used with a transition metal catalyst precursor and an activator. The scavenger is used to avoid adventitious catalyst deactivation. Addition of 1 equiv. of H_2O to a THF-d_8 solution of the compound at −40 °C gave the first structurally characterized aquo complex of an aluminum alkyl, $MeAl(OAr)_2OH_2(THF)_2$. There is strong hydrogen bonding between the coordinated H_2O and the two THF molecules. This compound is unstable in THF-d_8 above 0 °C and decomposes to form ArOH as the major product. The hindered phenol ArOH slowly reacts with $[Cp_2ZrMe][Me(BC_6F_5)_3]$ in bromobenzene-d_5 solution to produce the $[Cp_2ZrOAr][Me(BC_6F_5)_3]$; however, the rate is too slow to affect the ethylene-polymerization kinetics.

3.06.8.3 Aluminum-mediated 1,2-Alkyl Migration

Hydrocyanation of an α-epoxy ketone with Et_2AlCN gave regioselective ring opening of the epoxide and subsequent 1,2-cyanomethyl migration to yield the α-hydroxy ketone (Figure 15). The reaction was postulated to proceed through a chelated intermediate (Figure 15). The migration is assisted by the relief of steric congestion resulting from the adjacent vicinal quaternary center in the intermediate.

3.06.8.4 Reduction of Alcohols with $LiAlH_4$

Low-temperature reduction of 4-aryl-substituted 3-butyn-1-ols with lithium aluminum hydride in THF solvent gave *cis*-olefin resulting from the hydride addition at the δ-carbon of the triple bond.[134] This was in contrast to the propargyl alchohol that gives the *trans*-product resulting from the γ-addition.

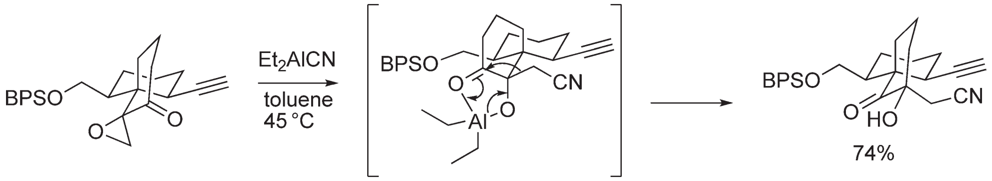


Figure 15 Postulated mechanism for the hydrocyanation of an α-epoxy ketone by Et_2AlCN.

3.06.8.5 Acrylate Polylmerization Catalysts

The mechanism and kinetics of the anionic polymerization of acrylates initiated by metal salts in the presence of aluminum alkyls was studied in detail. The kinetic studies of polymerization of *n*-butyl acrylate inititated by α-lithioisobutyrate at $-78\,^\circ C$ revealed that the presence of trialkylaluminum increases the percent conversion and narrows the molecular weight distribution.[135] The ^6Li and ^{13}C NMR studies and DFT calculations of ethyl α-lithioisobutyrate (EiBLi) and methyl α-lithioisobutyrate (MiBLi) as the model compounds for the acrylate elucidated the structure of the active center for the anionic polymerization of methacrylates in the presence of triethylaluminum.[136] The studies reveal that ester enolate/aluminum alkyl complexes with different degrees of association, $(MiBLi\cdot AlEt_3)_n$ ($n = 1, 2, 4$), and different stoichiometries, $MiBLi\cdot xAlEt_3$ ($x = 1, 2$), are formed. When methyl pivalate is added to the system containing EiBLi and Et_3Al, there is an equilibrium of monomeric and dimeric compounds $(EiBLi\cdot MPiv\cdot AlEt_3)_n (n = 1, 2)$. While the existence of aluminum alkyl compounds in dimeric or polymeric forms is somewhat responsible for their diminished polymerization activities, sterically hindered aluminum alkyl complexes (Figures 16(a) and 16(b)) were found to be active catalysts for the polymerization of acrylates and styrene to give high molecular weight polymers. The compounds could be easily synthesized from the reaction of trialkylaluminum with corresponding phenols. The dinuclear aluminum complex $\{(\pm)$-*trans*-$Cy(NSiMe_3)_2\}Al_2Me_4$ (Figure 16(c)) was prepared in 88% yield from the reaction of racemic $(\pm)$-*trans*-1,2-$(NHSiMe_3)_2$-cyclohexane with 2 equiv. of $AlMe_3$.[137] The ^1H NMR of this compound contains two peaks at $\delta = 0.14$ and -0.38 ppm for two diastereotopic Al–CH_3 groups at each aluminum center. The X-ray crystal structure shows that the cyclohexane ring adopts a chair conformation with the $(NSiMe_3)Al_2$ group placed in an equatorial position, while two five-membered Al–N–C–C–N rings adopt envelope conformations. This compound, upon activation with $Al(C_6F_5)_3$, was found to be highly active for the polymerization of methyl methacrylate. The polymer produced was mainly syndiotactic ($[rr] = 72.9\%$). A bimetallic chain propagation involving enoaluminates was proposed.

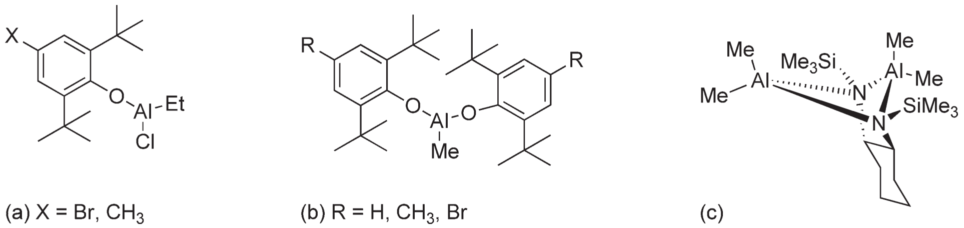
3.06.9 New Developments

3.06.9.1 Intermetallic Compounds

New organoaluminum compounds with transition metals have been prepared as potential precursors for MOCVD mixed metal thin films for microelectronics. Ferrocene and nickelocene complexes with N-donor functionalized ligands were combined with alanes or alkylaluminum compounds to form bimetallic M/Al donor–acceptor compounds with various stoichiometries. These include the iron alane compound $\{[(C_5H_5C_5H_4CH_2NMe_2)]Fe\}_2AlH_3$ (Figure 17(a) $[(C_5H_4CH_2CH_2NMe_2)_2Fe](AlMe_3)_2$ (Figure 17(b)), and nickel aluminum compounds $[(C_5H_4CH_2CH_2NMe_2)_2Ni](AlR_3)_2$ (R = Me, Et) (Figure 17(c)).[138] The X-ray crystal structure of $\{[(C_5H_5C_5H_4CH_2NMe_2)]Fe\}_2AlH_3$ shows that the aluminum is in a tbp geometry connected to three equatorial hydride ligands and two apical amine ligands. The Al–N bond lengths are about 2.18 Å. The ^{27}Al NMR showed a peak at $\delta = 109$ ppm for the five-coordinate aluminum and the IR spectra showed a broad band at $1717\ cm^{-1}$ corresponding to the terminal Al–H vibration.

3.06.9.2 μ_3-O-bridged Compounds

A unique tetranuclear organoaluminum complex $(Me_3Al)(C_{22}H_{28}N_2O_3)(AlMe_2)_2(AlMe_3)(\mu_3\text{-}O)$ was formed in a nearly quantitative yield from the reaction of $AlMe_3$ with the macrobicyclic ligand 1,15-diaza-3,4 : 12,13-dibenzo-5,8,11-trioxabicyclo[13,3,1]nonadecane ($C_{22}H_{28}N_2O_3$) (Figure 18) in a 4 : 1 ratio in the presence of trace water.[139]



(a) X = Br, CH_3 (b) R = H, CH_3, Br (c)

Figure 16 Examples of aluminum alkyls used for acrylate polymerization.

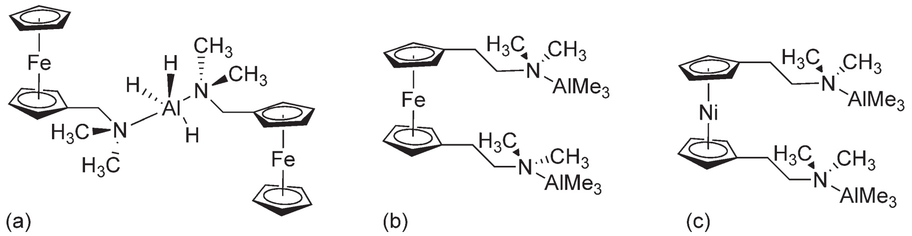


Figure 17 Bimetallic ferrocene and nickelocene complexes of aluminum.

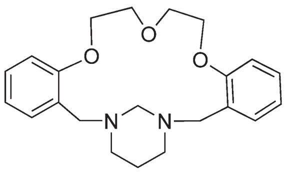


Figure 18 Macrobicyclic ligand 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxybicyclo[13,3,1]nonadecane ($C_{22}H_{28}N_2O_3$).

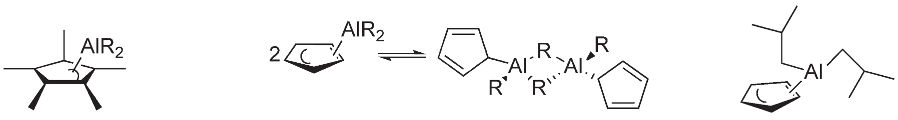
The ^1H NMR showed singlets at $\delta = -0.57$ and -0.33 ppm for the $AlMe_3$ and $AlMe_2$ methyl groups, respectively. The X-ray diffraction study reveals a μ_3-oxygen atom bridging three different alkylaluminum centers in a trigonal planar geometry, and the fourth aluminum center is bonded to the ether oxygen of the macrobicycle with a dative bond. The N_2O_3 donor set in the complex has a completely non-planar arrangement with the mean deviation from the best square planes of 0.43 Å, and the structure is asymmetric. This is in contrast to the free ligand where the N_3O_3 donor plane is almost planar and the macrobicycle shows a mirror symmetry.

3.06.9.3 Cyclopentadienyl Compounds

Novel monomeric organoaluminum compounds $(C_5Me)AlR_2$ (R = Me, Et, ^tBu) (Figure 19(a)) were prepared by the reaction of $(C_5Me_5)K$ with dialkylaluminum chlorides.[140] The compounds were characterized by ^1H, ^{13}C, ^{27}Al, NMR, and MS. There is only one singlet for the Me group due to the fluxional behavior of the molecule. The C_5Me_5 ligands are coordinated to the aluminum in a η^3-mode. The ^{27}Al NMR showed chemical shifts between $\delta = 71.6$ and 72.7 ppm, which is consistent with the shifts of five-coordinate aluminum. The unsubstituted or monosubstituted Cp systems $Cp'AlR_2$ (Cp′ = Cp, MeCp; R = Me, Et) show an equilibrium between monomeric and dimeric species in solution (example shown in Figure 19(b)). The Cp′ rings in monomeric species are bound in an η^2-symmetry, whereas the dimeric, alkyl-bridged molecules show σ-coordinated Cp′ systems. The compound $(^tBuCp)Al(^iBu)_2$ (Figure 19(c)) showed an η^2-coordinated ring system with ^{27}Al shift of 147.1 ppm corresponding to a four-coordinate aluminum atom. The disubstituted dimeric compounds $(Cp'RAlCl)_2$ were prepared by the salt elimination reaction of $(Cp'AlCl)_2$ (Cp′ = Me_4EtC_5) and $(Cp^*AlCl_2)_2$ ($Cp^* = Me_4C_5$) with alkyl- and arylalkali metal compounds.[141]

3.06.9.4 Methylaluminum Cyanide

The reaction of Me_3Al with excess trimethylsilylcyanide under reflux produced methylaluminum dicyanide $CH_3Al(CN)_2$ as an off-white powder.[142] No X-ray crystal structure was reported; however, the IR showed the presence of both bridging and terminal cyanide groups in the compound.



(a) R = Me, Et, ^{i}Bu (b) R = Me, Et (c)

Figure 19 Examples of some cyclopentadienyl compounds of aluminum.

3.06.9.5 Lithium Aluminum Amides

The bimetallic mixed metal complex $[Me_2Al\{(PhCH_2)_2N\}_2Li\cdot pyr]$ (Figure 20) was formed by the reaction of the amides $[(PhCH_2)_2NLi]$ and $[Me_2AlN(CH_2Ph)_2]$ in the presence of pyridine.[143] The X-ray crystal structure revealed that the compound contained a four-membered LiNAlN ring with bridging amido groups linking the lithium and aluminum centers. The four-membered core is non-planar with mean deviation from the plane at 0.159 Å. *Ab initio* calculations showed that a major contributing factor in the stabilization of the compound was a reduction in steric crowding in the mixed metal compound compared to the dialkylaluminum starting material. The compound showed significant benzyl to lithium interactions, which was unusual in the presence of a donor solvent.

The monomeric aluminum amides $(^tBu)_2AlNR_2$ (R = Mes, $SiPh_3$) and $(^tBu)_2AlN(R^1)SiPh_3$ ($R^1 = 2,6\text{-}^iPr_2C_6H_3$-(Dipp) and 1-adamantyl (1-Ad)) were prepared by LiCl elimination.[144] The aluminum in these compounds has a trigonal-planar coordination. The Al–N bond lengths range from 1.82 to 1.89 Å. The variations in Al–N bond lengths were attributed to the different sizes and electronic properties of the Al substituents. There was some evidence for Al–N *p*–*p* π-bonding for some of these compounds.

3.06.9.6 Aluminum Complexes of Phenyl Hydrazones and Amidines

The dinuclear aluminum compounds of the general formula $[(Me_2Al)\{NC_5H_4C(R)NNC_6H_5\}(AlMe_3)]$ ($R = CH_3$, H) (Figure 21(a)) were prepared by mixing of 2-pyridinecarboxaldehyde phenyl hydrazone ligands with trimethylaluminum.[144] The X-ray crystal structure of the compound for $R = CH_3$ was determined, and it showed the pyridyl Al–N distance (2.00(2) Å) to be slightly longer than the amido Al–N distance (1.97(5) Å). The ^{27}Al NMR had two peaks at 152 and 138 ppm. Both of these shifts correspond to four-coordinate aluminum. The compound $[(Me_2Al)(SC_4H_3CHNNC_6H_5)]_2$ (Figure 21(b)) was synthesized by the methane-elimination reaction of thiophenecarboxaldehyde phenyl hydrazone with trimethylaluminum.[144] All of these compounds contain four-coordinate tetrahedral aluminum. The ^{1}H NMR showed two peaks for the methyl region at both room temperature and at −60 °C.

Two new amidine compounds $(C_6H_2Ph_3)C(N^iPr)_2Al(CH_3)_2$ and $(C_6H_2Ph_3)C(NCy)_2Al(CH_3)_2$ (Figure 21(c)) were prepared from the reaction of *m*-terphenyl-substituted amidines *N*,*N*′-diisopropyl(or dicyclohexyl) benzamidine with trimethylaluminum.[146] The ^{27}Al NMR showed broad peaks between $\delta = 184$ and 170 ppm. The coordination environment around the aluminum atoms is distorted tetrahedral. The acute N–Al–N (~69°) angle indicated considerable strain around the aluminum.

3.06.9.7 Tris(pyrazolyl)borate Compounds

A dimethylaluminum complex $[HB(3,5\text{-}(CF_3)_2Pz)_3]AlMe_2$ (Figure 22) of the highly fluorinated tris(pyrazolyl)borate ligand $[HB(3,5\text{-}(CF_3)_2Pz_3]^-$ was obtained from the reaction between the silver adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$

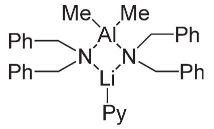
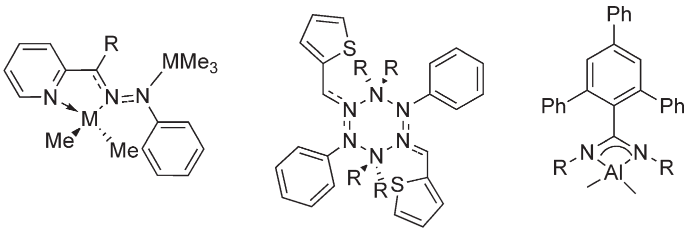


Figure 20 Bimetallic mixed metal compound, $[Me_2Al\{(PhCH_2)_2N\}_2$ Li.pyr.



(a) R = CH_3, H
M = Al

(b)

(c) R = ^{i}Pr, Cy

Figure 21 Examples of aluminum complexes of phenyl hydrazones and amidines.

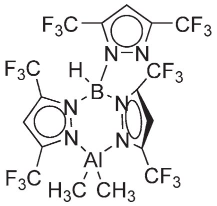


Figure 22 Example of an alkyl aluminum complex of tris(pyrazolyl)borate.

and Me_3Al.[147] The X-ray crystal structure reveals that the tris(pyrazolyl)borate coordinates to the aluminum center in a k^2-fashion. The aluminum atom adopts a distorted tetrahedral geometry with a large C–Al–C angle (128.4(2)°). Two of the fluorine atoms are pointed toward the aluminum at distances of 2.845 and 2.886 Å, which are smaller than the sum of the van der Waals radii of Al and F (3.40 Å). This suggests weak Al···F–C interactions.

3.06.10 Future Directions

Even after half a century of active research in organoaluminum chemistry, this field is still growing at a rapid rate. The ready availability of aluminum allows access to inexpensive reagents for the preparation of new compounds. The use of bulky ligands to overcome the air and moisture instability of the organoaluminum reagents is opening new applications in organic synthesis. The cationic aluminum compounds are probably going to be major candidates in this area during the subsequent years. The search for new compounds containing multiple bonds involving aluminum is likely to continue, as are the studies involving MAO. In addition, the use of organoaluminum reagents as precursors to nanoparticular materials is likely to expand.

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3.07
Gallium, Indium, and Thallium, Excluding Transition Metal Derivatives

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3.07.1 Introduction and Scope

Since the publication of COMCII (1995), the chemistry of group 13 elements Ga, In, and Tl has seen substantial progresses in several fields. Detailed investigations on the synthesis of metal organic compounds, their structures and bonding properties in the solid state, in solution, and in the gas phase as well as their general reactivity patterns has led to a dramatic increase of our knowledge about this fascinating class of compounds within the last decade. Adduct formation reactions between Lewis-acidic group 13 compounds and Lewis bases such as group 15 and group 16 complexes, which are already known for almost two centuries, have been continuously investigated in detail. In addition, new types of compounds such as multiple-bonded group 13/15 compounds containing sterically demanding organic substituents (e.g., terphenyl groups) as well as cage-like group 13/15 and group 13/16 complexes have been synthesized for the first time and their unusual and fascinating structures have stimulated the work of both preparative and theoretical chemists. However, probably the most fascinating field of research that was investigated in the last decade deals with the chemistry of low-valent group 13 compounds. The number of metal–metal bonded species of the types $[MR]_x$ and $R_2M–MR_2$, formally exhibiting the metal centers in the oxidation state I and II, respectively, has systematically increased. Moreover, neutral clusters as well as anionic "metalloid" cluster compounds containing "naked" metal atoms that are only bonded to other metal centers became available only within the last decade by reactions of metastabile GaX (X = Cl, Br, I) solutions as was demonstrated by Schnöckel *et al.* and others. The number of metal atoms in these fascinating compounds reaches up to 84 as was observed in two $[Ga_{84}(NTMS_2)_{20}]^{x-}$ ($x = 3$, 4) clusters. Both clusters, whose structures are precedenceless even in transition metal chemistry, contain 64 ligand-free ("naked") Ga atoms. They represent the largest metalloid clusters structurally characterized, to date.

Fundamental research activities may form the basis of forthcoming technological applications in the future. Group 13 compounds have a long-standing history in several industrially important research fields such as catalysis and material sciences. Fifty years after the epoch-making studies of Ziegler *et al.* on the synthesis and use of organoaluminum compounds, the potential capability of cationic organoalanes and -gallanes to serve as catalysts in olefin polymerization reactions was demonstrated. In addition, the interest in binary, ternary, and multinary III–V and III–VI materials has continued to be the driving force for the synthesis of novel compounds containing these specific element combinations within a single molecule. They were shown to be valuable starting reagents for the synthesis of the desired class of materials by different ways such as wet chemistry routes, often referred to as "soft chemistry methods," as well as gas-phase based techniques. In particular, the search for new "single source precursor" for the deposition of thin films by use of the MOCVD process has played a major role for the synthesis of new group 13/15 and group 13/16 compounds.

This chapter will give an overview on the synthesis, structure, and reactivity of organometallic compounds of the group 13 elements Ga, In, and Tl, which have been synthesized since 1993. Only those, which contain at least one metal–carbon or metal–hydrogen bond, are considered. (Consequently, compounds containing only metal–halide (F, Cl, Br, . . .), metal–hexele (O, S, . . .), or metal–pentele bonds (N, P, . . .) are not considered.) It will particularly emphasize on low-valent complexes, which were almost unknown 10 years ago, and on heteroatomic compounds of groups 15 and 16. However, it is quite clear that the entire range of the chemistry of Ga, In, and Tl cannot be expressed in its whole detail within this single chapter. Therefore, wherever possible the reader is referred to review articles which deal with the particular subject in more detail. Potential applications of the compounds are only roughly presented and compounds containing group 13 metals bonded to transition metal are the subject to another chapter in this volume.

3.07.2 Organometallic Alkyls, Aryls, Hydrides, and (Pseudo)Halides

This specific class of compounds has a long-known history in main group element chemistry. Many compounds have been prepared in the past and their structures and reactivities have been studied in detail as was shown in COMCI (1982) and COMCII (1995). However, novel class of substituents such as sterically demanding terphenyl groups have been developed in the last decade, yielding novel group 13 organometallic compounds. These are valuable starting reagents for so far unknown complexes as is demonstrated in the following.

3.07.2.1 Syntheses and Structures of R_3M (R = Alkyl, Aryl, Alkynyl) and Lewis Base Adducts

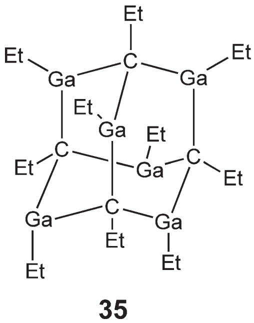
The trimethyls MMe_3 (Me = methyl) and trimesityls $MMes_3$ (M = B **1**,[1,2] Al **2**,[3] Ga **3**,[4] In **4**,[5,5a] Tl **5**[5a]) are the only group 13 organometallics, which have been completely structurally characterized. In contrast to the trimesityls, the solid-state structures of the trimethyls differ significantly. BMe_3 **6** is monomeric and adopts the expected D_{3h} symmetric geometry;[6] however, the molecules pack in layers through weak van der Waals or electrostatic interactions to a closed packed array. $AlMe_3$ **7**[7] forms a well-known dimer with bridging Me groups (also in the gas phase), whereas $GaMe_3$ **8**,[8] $InMe_3$ **9**,[9] and $TlMe_3$ **10**[6] form two-dimensional networks built by tetrameric units of MMe_3. The latter are formed through weak intermolecular metal···Me interactions with long metal···C bond distances (**8** 313.4(2), **9** 308.3(12), **10** 324.3(8) pm). The tetramers are connected to each other by even longer metal···Me bridges yielding two-dimensional networks. Interestingly, among the tetragonal phase a second polymorph of $GaMe_3$ **8**, a monoclinic phase, in which the tetramers are replaced by a polymeric chain, was decribed.[6] The solid-state structures of $GaEt_3$ **11**[8] and $GaBu^t_3$ **12**[10] (Bu^t = *tert*-Butyl) were also determined. Structure **11** consists of layers of wavelike networks built by four independent molecules in the unit cell. The Ga atoms interact to neighboring methylene and methyl carbon atoms. The intermolecular Ga···C distances range from 308.7 to 359.3 pm. The wide Ga–C–C bond angle (113.3(2)–118.8(2)°), which is comparable to that observed in solid BEt_3 **13** (118.7–119.3°), was explained by hyperconjugation of the gallium *p*-orbital into C–H orbitals. Structure **12** crystallizes with six independent molecules in the asymmetric unit. The slight deviation from exact trigonal planar environment (357.5–359.5°) again results from intermolecular interactions (Ga–C 320–360 pm) between Bu^t_3Ga molecules. Compared to the gas-phase structure of $\mathrm{Bu^t{}_3Ga}$ (Ga–C 203.4(2) pm; C–Ga–C 120°),[11] the average Ga–C bond length observed in the solid state is slightly shorter.

Donor-free group 13 trialkyls and triaryls $\mathrm{MR_3}$, which are easily obtained by standard Grignard reactions or salt elimination reactions (transmetallation reaction) using Li organyls, typically contain sterically bulky substituents, which kinetically stabilize the monomeric moiety. Examples are $\mathrm{Ga(C_6Me_5)_3}$ **14**,[12] $\mathrm{GaCp^*{}_3}$ **15** ($\mathrm{C_p{}^*}$ = pentamethylcyclo pentadienyl),[13] $\mathrm{GaTripp_3}$ **16** (Tripp = 2,4,6-tri(*iso*)propylphenyl),[14] $\mathrm{GaR^f{}_3}$ **17** ($\mathrm{R^f}$ = 2,4,6-tris(trifluoromethyl)phenyl),[15] $\mathrm{InBu^t{}_3}$ **18**,[16] $\mathrm{InMes_3}$ **4** (Mes = mesityl, 2,4,6-trimethylphenyl),[5a] $\mathrm{InR^f{}_3}$ **19**,[17] and $\mathrm{TlMes_3}$ **5**.[5a] $\mathrm{GaMes_3}$ **3**,[18] which was firstly prepared by Beachley *et al.* in 1986 and whose Lewis acidity was found to be too low to undergo adduct formation with $\mathrm{Et_2O}$ or THF, reacts with the stronger Lewis base acetonitrile to give $\mathrm{MeCN–GaMes_3}$ **20**.[19] In addition, several mixed alkyl/aryl compounds such as $\mathrm{MeGa(C_6F_5)_2}$ **21**[20] and $\mathrm{MeIn(CTMS_3)_2}$ **22**[21] have been structurally characterized. Structure **21** shows intermolecular aryl-F· · ·Ga interactions (Ga· · ·F about 272 pm) from the *meta*-F atoms on each $\mathrm{C_6F_5}$ group leading to a linear, chain-like structure. Consequently, the Ga atoms show pseudo-trigonal bipyramidal coordination geometries. Finally, metal alkynyl complexes have gained some interest because the aluminum analog[22] were found to be valuable starting reagents for novel carbaalanes. (For review articles on this specific class of compounds, see Ref: 23 and 23a.) Dimeric compounds $\mathrm{[R_2GaC{\equiv}CPh]_2}$ (R = Me **23**, $\mathrm{Bu^t}$ **24**) are accessible either by reaction of the corresponding dialkylgallanes $\mathrm{R_2GaH}$ and $\mathrm{HC{\equiv}CPh}$ or by reaction of $\mathrm{R_2GaCl}$ and $\mathrm{LiC{\equiv}CPh}$, respectively.[24] In addition, several dialkynylchlorogallanes and -indanes $\mathrm{((thf)_xClMC{\equiv}CBu^t}$ (M = Ga **25**, $x = 1$; In **26**, $x = 2$),[25] donor-stabilized trialkynyl derivatives ($\mathrm{dioxane–Ga(C{\equiv}CBu^t)_3}$ **27**,[25] $\mathrm{Me_3N–Ga(C{\equiv}CPh)_3}$ **28**,[25] $\mathrm{Et_3N–In(C{\equiv}CBu^t)_3}$ **29**,[25] $\mathrm{(thf)_2In(C{\equiv}CCF_3)_3}$ **30**[26]), as well as anionic compounds such as $\mathrm{[Li_2(thf)_6(dioxane)][(TMSC{\equiv}C)_3MN(TMS)Dipp]}$ (TMS = trimethylsilyl; Dipp = 2,6-di(*iso*)propylphenyl; M = Ga **31**, In **32**)[25] and $\mathrm{[Li(thf)_4][In(C{\equiv}CPh)_4]}$ **33**[27] have been synthesized. However, dialkylgalliumalkynides did not yield carbagallane clusters upon hydrogallation with dialkylgallium hydrides, but gave complexes with adamantane-like structures $\mathrm{[(RGa)_6(CR')_4]}$ (R = Me, R′ = Et **34**; R = Et, R′ = Et **35**, $\mathrm{Bu^t}$ **36**), consisting of six coordinatively unsaturated gallium atoms in the bridging positions and a localized bonding system (Figure 1).[28]

$\mathrm{MR_3}$ compounds described so far contain organic substituents, which have been typically used in main group element chemistry in the last century. However, the last decade also showed the introduction of a new class of substituents, which are typically referred to as terphenyl substituents. These extremely bulky phenyl substituents contain at least two bulky aryl groups (Mes, Tripp, supermesityl ($\mathrm{Mes^*}$, 2,4,6-tri(*tert*)butylphenyl)) in both *ortho*-positions. They were found to perfectly stabilize unusual low-valent compounds as will be shown later. Consequently, several mixed triorganyls $\mathrm{MR_3}$ containing this novel class of substituents such as $\mathrm{(2,6\text{-}Mes_2C_6H_3)_2GaR}$ (R = Me **37**, $\mathrm{Bu^t}$ **38**)[29] and $\mathrm{(2,6\text{-}Mes_2C_6H_3)GaMes_2}$ **39**[30] were synthesized and structurally characterized (Figure 2). According to their extreme steric demand, not more than two terphenyl ligands can bind to the metal center.

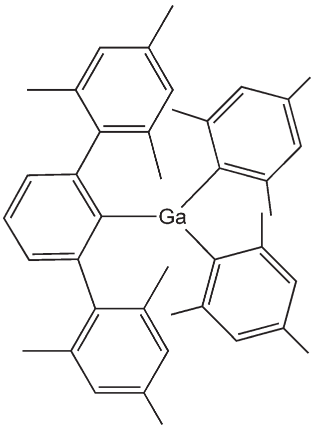
The reaction of $\mathrm{Cp_2Zr(C_4Me_4)}$ and $\mathrm{Mes^*MCl_2}$ yielded remarkable metallacyclopentadienides $\mathrm{Mes^*M(C_4Me_4)}$ (M = Ga **40**, In **41**).[31] Structure **40** is monomeric, the sum of the C–Ga–C bond angles is 360°, and the planar five-membered $\mathrm{GaC_4}$ ring shows localized C=C double bonds. It reacts with $\mathrm{CpCo(C_2H_4)}$ with elimination of $\mathrm{C_2H_4}$ and subsequent formation of the corresponding CpCo complex. In addition, metallafluorenes (M = Ga **42**, In **43**) and gallacyclohexadiene **44** have been obtained from salt elimination reactions between $\mathrm{Mes^*MCl_2}$ (M = Ga, In) and 2,2′-dilithiobiphenyl[32] and 1,5-dilithio-1,4-pentadienide,[33] respectively. Structure **44** reacts with Lewis bases with deprotonation to yield the anionic gallatabenzene **45**, which reacts with $\mathrm{[(CH_3CN)_3(CO)_3Mn]PF_6}$ with formation of the tricarbonyl manganese complex.

Among donor-free trialkyls $\mathrm{MR_3}$, several intramolecularly stabilized metal organics such as $\mathrm{[(\mathit{o}\text{-}Ph_2PCH_2)C_6H_4]_3M}$ (M = Ga 46, In 47, Tl 48),[34] $\mathrm{[(\mathit{o}\text{-}Me_2NCH_2)C_6H_4]_3M}$ (M = Ga **49**[26,35a] In **50**),[35] $\mathrm{Me_2Ga(2\text{-}Me_2NCH_2CH_2)C_5H_4}$ **51**,[36]



35

Figure 1 Structure of the adamantane-like organogallane 35.

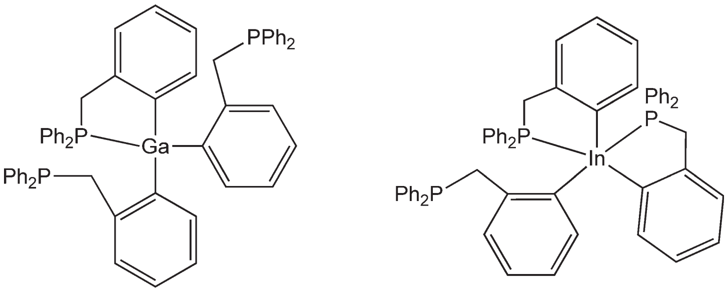


39

Figure 2 Structure of the monomeric triorganylgallane **39**.

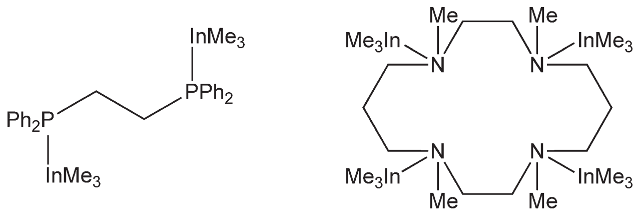
$Me_2Ga(2\text{-}Bu^t{}_2PCH_2CH_2)C_5H_4$ **52**,[37] $Ga(CH_2CH_2CH_2NMe_2)_3$ **53**,[26] $[(o\text{-}N(TMS){=}PPh_2)C_6H_4]_3M$ (M = Ga **54**, In **55**)[38,38a] and $(C_6F_5)_2InCH_2CH_2CH_2NMe_2$ **56**[39] have been prepared. The metal centers are either four- or five-coordinate. In particular, indanes tend to increase their coordination number (c.n.) due to the larger size of the central metal atom. This can clearly be seen when comparing identically substituted organometallics $[(o\text{-}Ph_2PCH_2)C_6H_4]_3M$ (M = Ga **46**, In **47**). The Ga center in **46** adopts a tetrahedral coordination sphere (c.n. 4), whereas the metal center in **47** is five-coordinate (Figure 3).

The need for extremely pure group 13 trialkyls, which are typically used for the production of semiconducting III–V materials by MOCVD processes, as well as the still ongoing academic interest in the bonding situation of Lewis acid–base adducts $R_3M{-}ER'_3$ has forced continuous experimental and theoretical investigations on this specific class of compounds. In particular, amine and phosphine adducts (E = N, P) have been studied in detail. (For instance, the bonding properties of $H_3B{-}NH_3$ are still in the focus of theoretical chemists.[40,40a]) These adducts have been found to be valuable starting compounds for the production of electronic grade group 13 trialkyls by adduct purification processes[41,41a–41d] and can also be used as "single source precursor" for MOCVD processes. They show some advantages compared to pure group 13 trialkyls and group 15 trihydrides since they are less toxic, easier to handle, and typically allow film growth at lower temperatures.[42,42a,42b] Simple amine and phosphine adducts of the types $R_3M{-}ER'_3$ (E = N, P; R, R′ = alkyl) such as $Me_3Ga{-}PMe_3$ **57**,[43] $Bu^t{}_2(Bu^i)Ga{-}PPr^i{}_3$ **58**,[10] $Cp_3In{-}PPh_3$ **59**[44] and $(Bu^tC{\equiv}C)_3M{-}NMe_3$ (M = Ga **60**, In **61**)[45]) and $R_3M{-}N_{aryl}$ (bis(5,6-benzoquinoline)-trimethylindane **62**,[46] (5,6-ben-zoquinoline)-trimethylindane **63**[47]) have been structurally characterized. The use of the strong Lewis base dmap (dmap = 4-dimethylamino-pyridine) allowed the synthesis and structural comparison of a whole series of Me_3M–dmap adducts (M = Ga **64**, In **65**, Tl **66**),[48] including the first Me_3Tl adduct **66**, and of different substituted alane adducts X_3Al–dmap (X = Cl **67**, H **68**, Me **69**, Bu^t **70**).[48] Among those, several adducts containing bidentate group 15 ligands such as μ_2-bis(N,N)dimethylaniline-4-yl-methane-N,N′-bis($InMe_3$) **71**,[41b] μ_2-bis(diphenylphosphino)ethane-bis($InMe_3$)



46 **47**

Figure 3 Structures of analogously substituted, intramolecularly stabilized triorganylmetallanes **46** and **47**, illustrating the different coordination modes of gallanes and indanes.



72 **76**

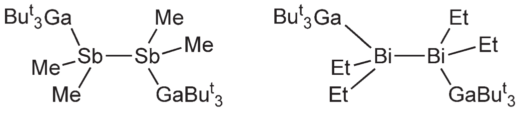
Figure 4 Structures of Lewis acid-base adducts of a bidentate **72** and a macrocyclic Lewis base **76**.

72,[49] μ_2-N,N-dimethylethylendiamine-bis(GaMe$_3$) **73**[50] and 2,2′-dimethyl-1,3-propanediamine(GaBu$^t_3$)$_x$ ($x = 1$ **74**, 2 **75**),[51] and macrocyclic amines (μ_4-1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)-tetrakis(MR$_3$) (MR$_3$ = InMe$_3$ **76**,[41b] GaEt$_3$ **77**,[41a] GaPr$^i_3$ **78**[41a]), μ_6-1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexa-azacyclooctadecane)-hexakis(MR$_3$) MR$_3$ = InMe$_3$ **79**,[41b] GaEt$_3$ **80**,[41a] GaPr$^i_3$ **81**[41a]), N,N′,N″,N‴-hexamethylenetetramine-tetrakis (trimethylgallane) **82**[52]) have been prepared by standard reactions (Figure 4).

Even though numerous amine and phosphine adducts R$_3$M–ER$_3$ have been prepared since the synthesis of F$_3$B–NH$_3$, the prototype of this important class of compounds, by Gay-Lussac almost 200 years ago,[53,53a] Lewis acid–base adducts containing the heavier elements of group 15, As, Sb and Bi, remained almost unknown. This rather surprising finding most likely results from the steadily decreasing Lewis basicity of ER$_3$ and the decreasing Lewis acidity of MR$_3$ with increasing atomic numbers. As a consequence, the acid–base interaction of a given group 13 Lewis acid MR$_3$ (M = Ga, In, Tl) with a group 15 Lewis base ER′$_3$ becomes weaker with increasing atomic number. This has been already observed by Coates 50 years ago,[54] who examined the thermodynamic stability of adducts obtained from the reactions of GaMe$_3$ with EMe$_3$ (E = N, P, As, Sb, Bi). Adducts were formed except for the reaction with BiMe$_3$. The first completely alkyl-substituted adducts R$_3$M–ER$_3$ of the heavier elements (M = Ga, In, Tl; E = As, Sb, Bi; R, R′ = alkyl, aryl) were structurally characterized only within the last decade. Bu$^t_3$Ga–SbR$_3$ (R = Me **83**,[55] Et **84**[56]), Bu$^t_3$Ga–EPr$^i_3$ (E = As **85**,[10] Sb **86**,[55] Bi **87**[57]) and Bu$^t_3$Ga–BiEt$_3$ **88**[58] are stabilized by sterically demanding organic substituents. The bismuthine adducts are very temperature labile. According to NMR spectroscopic studies, they dissociate in solution, indicating only weak acid–base interaction. The Lewis basicity of group 15 triorganyls generally increases by the introduction of (electropositive) TMS substituents at the central atom. Consequently, several ETMS$_3$ adducts (E = P, As, Sb, Bi) of the types R$_3$M–PTMS$_3$ (R = CH$_2$TMS, M = Ga **89**,[59] In **90**,[59] Tl **91**;[60] M = Ga, R = Ph **92**,[61] Et **93**;[10] R = *neo*-pent, M = In **94**[62]), R$_3$M–AsTMS$_3$ (M = Ga, R = Et **95**,[10] Ph **96**;[63] M = In, R = *neo*-pent **97**,[62] CH$_2$TMS **98**[63]), R$_3$M–SbTMS$_3$ (M = Ga, R = Et **99**,[64,10] Bu^t **100**;[65] M = In, R = CH$_2$TMS **101**[64]), Et$_3$Ga–As(SiPh$_3$)TMS$_2$ **102**,[66] and Et$_3$Ga–BiTMS$_3$ **103**[57] have been structurally characterized.

Among simple adducts as mentioned above, the synthesis and X-ray structures of the first distibine and dibismuthine adducts of group 13 triorganyls MR$_3$ of the types [Bu$^t_3$Ga]$_2$[Sb$_2$R$_4$] (R = Me **104**, Et **105**)[67] and [Bu$^t_3$Ga]$_2$[Bi$_2$Et$_4$] **106**[68] have been reported (Figure 5). Distibine adducts tend to undergo E–E bond cleavage reactions with subsequent formation of GaSb heterocycles (see Section 3.07.5.2), whereas the dibismuthine adducts disproportionate with formation of elemental bismuth and BiEt$_3$.[58]

Lewis acid–base adducts typically show the central group 13/15 atoms in distorted tetrahedral environments. The central M–E bond distance is significantly longer than the sum of the atomic radii. In particular, the bismuthine adducts show very long M–Bi bond distances, which range from 296.6(1) (Et$_3$Ga–BiTMS$_3$ **103**,[57] Bu$^t_3$Ga–BiEt$_3$ **88**[58]) to 313.5(1) pm (Bu$^t_3$Ga–BiPr$^i_3$ **87**[57]). The Ga–Bi bond lengths as observed in **106** (309.9(2), 311.4(2) pm) are in between. Interestingly, the Bi–Bi bond distance in the dibismuthine bisadduct **106** (298.4(1) pm) is comparable to those observed in uncomplexed dibismuthines such as Bi$_2$Ph$_4$ (299.0 pm) and Bi$_2$TMS$_4$ (303.5 pm).[69] The strength of the acid–base interaction can be estimated using a simple model as described by Haaland.[70] Adduct formation results in a lengthening



104 **106**

Figure 5 Structures of GaBu$^t_3$ adducts of a distibine **104** and a dibismuthine **106**.

of the M–C bond and a decrease of the C–M–C bond angles from 120° (trigonal planar) toward 109.5° (tetrahedral). The stronger the acid–base interaction, the longer the M–C bond and the smaller the C–M–C bond angle. This can clearly be seen when comparing the Me_3M–dmap adducts (M = Al **69**, Ga **64**, In **65**, Tl **66**). The sum of the C–M–C bond angles steadily increases with increasing atomic number of the group 13 element (**69** 344.1; **64** 347.0; **65** 351.8; **66** 357.7°).[48] Unfortunately, this simple model can only give a qualitative trend of the adduct stability.

3.07.2.2 Syntheses and Structures of Organohydrides R_xMH_{3-x}

Only a very few examples of binary group 13 element hydrides MH_3 of the heavier elements (M = Al, Ga, In, Tl) are known. AlH_3 forms an almost insoluble polymeric solid, which is isostructural to AlF_3. In contrast, the solid-state structures of GaH_3, which most likely forms a discrete oligomer such as $[GaH_3]_4$[71], and InH_3, that has been isolated only in solid argon matrix,[72] and TlH_3 are unknown, to date. According to theoretical calculations, InH_3 and TlH_3 are thermodynamically unstable in the solid state and the gas phase. Electron diffraction studies demonstrated that GaH_3, which is accessible from the reaction of H_2GaCl and $LiGaH_4$ at −30 °C,[73] forms the dimer Ga_2H_6 **107** with two bridging and four terminal H atoms as was found in diborane B_2H_6. Very recently, Wang and Andrews synthesized and characterized the corresponding dialane Al_2H_6 **108** by reaction of laser-ablated Al atoms with H_2 in a matrix of solid hydrogen.[74]

Base-stabilized compounds of the type base–MH_3, which are thermodynamically much more stable than base-free trihydrides, have been investigated in more detail.[75,75a–75c] Gallane adducts of the type R_3E–GaH_3 such as Me_3N–GaH_3 **109**,[76,76a] 3,5-dimethylpyridine–GaH_3 **110**,[77] $Bz(Me)_2N$–GaH_3 **111** (Bz = benzyl),[76] Me_3P–GaH_3 **112**,[78] $Bu^t{}_3P$–GaH_3 **113**,[79] Cy_3P–GaH_3 **114**,(Cy = cyclohexyl)[80] and $Bu^t(NHBu^t)_2P$–GaH_3 **115**[81] have been synthesized and their solid-state and gas-phase structures were determined by single crystal X-ray and electron diffraction, respectively. They are of particular interest in organic and organometallic syntheses as well as in material sciences. Theoretical calculations on the dissociation energies of H_3E–GaH_3 and Me_3E–GaH_3 (E = N, P) clearly proved that the amines are more strongly bonded to GaH_3 than the phosphines (NH_3 by about 39 kJ mol^{-1}; NMe_3 by about 19 kJ mol^{-1}). However, these differences are significantly smaller compared to those observed for the corresponding alane adducts H_3E–AlH_3 and Me_3E–AlH_3 (NH_3 by about 59 kJ mol^{-1}; NMe_3 by about 36 kJ mol^{-1}).[78] The most remarkable difference between alane and gallane is the more electropositive nature of Al compared to Ga. Consequently, AlH_3 is a stronger Lewis acid than GaH_3 and it tends to increase its coordination number from 4, which is typical for Ga, to 5 and even 6. In sharp contrast, only a very few examples of five-coordinate gallanes (Me_3N–GaH_3–NMe_3 **116**,[73] μ_2-1,3-bis(dimethylamino)propane–GaH_3 **117**[82]), have been characterized by single crystal X-ray diffraction, to date.

Only a very few amine-stabilized indanes (Me_3N–InH_3 **118**, quinuclidine–InH_3 **119**)[83] have been prepared, whereas adducts of TlH_3 are completely unknown, to date. The stability of the indane adducts in solution was found to be rather low and they generally have to be handled at low temperatures (e.g., **118** below −30 °C). In addition, several phosphine adducts of the types R_3P–InH_3 with four-coordinate In atoms (R = Cy **120**, Ph **121**, cy-pent **122** (cy-pent = cyclopentyl)) and R_3P–InH_3–PR_3, which exhibit five-coordinate In centers (R = Cy **123**, cy-pent **124**), were prepared by reaction of *in situ* prepared Me_3N–InH_3 and Cy_3P.[84,84a] Bisadducts **123** and **124** are almost unprecedented in group 13 trihydride/phosphine chemistry since neither AlH_3 (only the polymeric compound $[H_3Al(R_2PCH_2CH_2PR_2)$ **125**] is known[85]) nor GaH_3 forms bisphosphine adducts. Their synthesis is even more remarkable since phosphines bind weaker to InH_3 than amines according to theoretical calculations.[86] However, **120** is stable in its pure form up to 50 °C, whereas in benzene solution decomposition occurs at ambient temperature within an hour. The solid-state structures of **120**[84] and **123**[84a] were determined by single crystal X-ray analyses. The In–P bond distances in **123** (298.7(1) pm) are about 34 pm elongated compared to that in **120** (264.7(1) pm) (Figure 6).

A further remarkable InH_3 adduct was obtained by the reaction of Me_3N–InH_3 with an imidazol-2-ylidene carbene, which is typically referred to as Arduengo carbene.[87] In fact, H_3In–$\{CN(Pr^i)C_2Me_2N(Pr^i)\}$ **126** was the first InH_3 complex that could be structurally characterized (Figure 7). Adduct **126** decomposes in solution at temperatures above −20 °C with subsequent formation of In metal and H_2. Reaction of Me_3N–InH_3 with 2 equiv. of the imidazol-2-ylidene carbene did not yield the bisadduct as was observed for the reactions with indium trihalides InX_3.[88] Obviously, InH_3 is less Lewis acidic than InX_3 and the carbene is less Lewis basic than Cy_3P. Since the first report on this specific class of compounds, additional H_3In–carbene adducts such as H_3In–$\{CN(Mes)C_2H_2N(Mes)\}$ **127**,[89] which shows a remarkable thermal stability (dec. 115 °C), and μ_2-1,1′-ethylene-3,3′-di-t-butyl-bis(imidazole-2,2′-diylidene)-bis(trihydridoindane) **128**[90] have been structurally characterized.

Arduengo-type carbenes have also been successfully employed for complexation of group 13 trialkyls (Me_3Ga–$\{CN(Pr^i)C_2Me_2N(Pr^i)\}$ **130**[91]) and mixed hydrido/alkyls ($Cp^*{}_2(H)Ga$–$\{CN(Me)C_2Me_2N(Me)\}$ **131**[92]). Adduct **131**

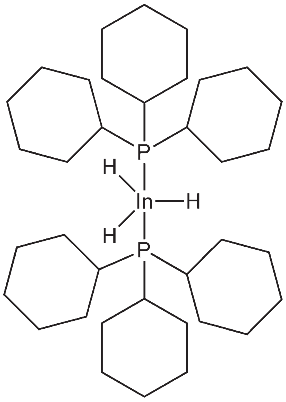


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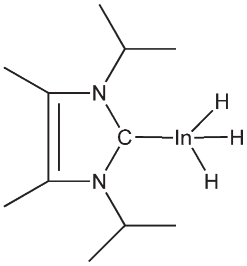
Figure 6 Structure of a InH_3 adduct containing a five-coordinated In atom.



126

Figure 7 InH_3 adduct of an Arduengo-type carbene.

was obtained by reaction of $Cp^*{}_3Ga$, which was described not to form complexes with weak Lewis bases Et_2O and THF, and the free carbene, indicating that the carbene is a stronger Lewis base. In addition, mixed hydrido/halides ($H_2(Cl)In$–{CN(Mes)C_2H_2N(Mes)} **132**,[89] $H_2(I)Ga$–{CN(Mes)C_2H_2N(Mes)} **133**[93]) and trihalides (Cl_3In–{CN(Mes)C_2H_2N(Mes)} **134**,[89] Br_3In–{CN(Pr^i)C_2Me_2N(Pr^i)} **135**,[88] Br_3In–{CN(Mes)C_2H_2N(Mes)} **136**,[94] Br_3In–{CN(Dipp)C_2H_2N(Dipp)} **137**,[94] Cl_3Tl–{CN(Mes)C_2H_2N(Mes)} **138**[95]) were structurally characterized. The influence of the increasing Lewis acidity on the metal–C bond distances of the resulting adduct can be estimated when comparing the indane adducts of the mesityl-substituted carbene {CN(Mes)C_2H_2N(Mes)} (**127, 132–134**, and **136**). As expected, the In–C bond length increases from 220.0(7) pm **134** to 225.3(5) pm **127** according to the decreasing Lewis acidity of the indane ($InH_3 < InH_2Cl < InCl_3$).[89] The more Lewis-acidic character of InX_3 compared to InH_3 also accounts for the formation of biscarbene complexes {N(Pr^i)C_2Me_2N(Pr^i)C}–X_3In–{CN(Pr^i)C_2Me_2N(Pr^i)} (X = Cl **139**, Br 140) (Figure 8).[88] Interestingly, the In–C bond distances observed in 140 (223.0(1), 223.1(1) pm) are only slightly elongated compared to the corresponding mono-adduct **135** (219.9(5) pm). The In atoms in the biscarbene adducts adopt distorted trigonal bipyramidal coordination spheres with two halides surprisingly in the apical positions and the third halide and the carbon atoms in the equatorial sites. The synthesis of Cl_3Tl–{CN(Mes)C_2H_2N(Mes)} **138** is remarkable since adducts of Tl-trihalides are very rare. For instance, no tertiary phosphine or dialkylsulfide adducts of TlX_3 have been prepared, to date, due to the strong oxidizing character of Tl(III).[96]

Among group 13 trihydrides, several monomeric, base-free monohydridogallanes ((2,6-$Mes_2C_6H_3$)$_2$GaH **141**,[29] $Mes^*{}_2GaH$ **142**,[97] $Mes^*Ga(H)CH_2C(Me_2)C_6H_3(2,4\text{-}Bu^t{}_2)$ **142**[108], $Tripp_2GaH$ **143**[97]) containing sterically demanding substituents, which have a kinetically stabilizing effect, have been prepared. Reduction of the steric demand of the organic substituents results in oligomerization of the gallane. This can clearly be seen when comparing the solid-state structures of R_2GaH (R = Me **144**, Et **145**, Pr^i **146**, Bu^i **147**, Bu^t **148**, neopentyl **149**),[98,98a] which were synthesized in high yields either by reaction of R_2GaCl and LiH or from H_3Ga–NMe_2Et and GaR_3.[98a] Dialkylgallanes R_2GaH containing small substituents typically adopt H-bridged dimeric or trimeric structures in the solid state. However, a

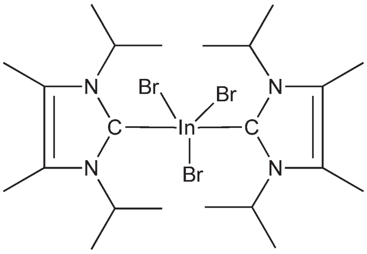


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Figure 8 $InBr_3$ bisadduct of an Arduengo-type carbene.

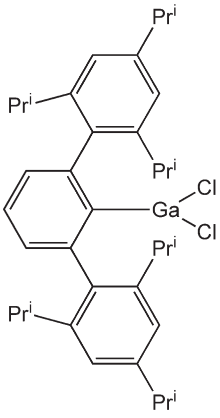
monomeric compound was realized in 1-hydrido-5-methyl-1-galla-5-aza-cyclooctane **153**.[99] In **153**, the Ga center is stabilized by introducing it into a rigid ring system. Dialkylgallanes R_2GaH are valuable starting reagents in organic and organometallic syntheses, for example, reactions with alkynes $RC{\equiv}CH$ occurred with initial H_2 elimination followed by addition of R_2GaH to the carbon–carbon triple bond (hydrogallation reaction) and subsequent formation of adamantane-like cages.[28] In addition, reactions with 2,3-diazabutadienes yielded gallium hydrazonides (see Section 3.07.5.2). Another very promising starting compound for the synthesis of dialkylgallanes is $HGaCl_2$ **150**. Compound **150** has been firstly prepared almost 40 years ago,[100] but its solid-state structure, which consists of a dimer with bridging Cl atoms, was only recently reported.[101] Its Lewis acid–base bisadduct (3,5-dimethylpyridine)$_2$Ga(H)Cl$_2$ **151** undergoes Ga–Ga bond formation reactions when heated to 110 °C with subsequent formation of base-stabilized digallane $(L)_2Ga_2Cl_4$ (L = 3,5-dimethylpyridine) **152**.[102]

Neutral hydrides of In and Tl are almost unknown, to date. Only base-stabilized bis-(2-dimethylamino-methyl)-phenyl-indane **154** has been prepared by reaction of $LiGaH_4$ and the corresponding dichloroindane $RInCl_2$.[103] The intermediately formed dihydride RMH_2 is only stable up to −20 °C in solution. At higher temperature, it rearranges to the monohydride R_2MH. In addition, monoanionic indanates $[Me_3In\text{-}\mu\text{-}H\text{-}InMe_3]^-$ **155**[104] and [(*neo*-pentyl)$_3$InH]$^-$ **156**[105] as well as dimethylindiumtetrahydridoborate **158**[106] have been structurally characterized. The analogous galliumhydridoborate **159** was obtained from the reaction of $LiBH_4$ and Me_2GaCl.[107]

Reports on the synthesis of group 13 dihydrides RMH_2 are very rare. Mes^*GaH_2 **160**[108] represents the only structurally characterized base-free dihydridogallane, in which the Ga center is three-coordinate. In addition, a very few base-stabilized gallanes $(2\text{-}(M_2NCH_2)C_5H_4)GaH_2$ **161**,[109,109a] $2\text{-}(M_2NCH_2)C_6H_3GaH_2$ **162**,[103] $2,6\text{-}(M_2NCH_2)_2C_6H_3GaH_2$ **163**[110]), which contain four- or five-coordinate Ga atoms, have been synthesized. Uhl *et al.* reported on the synthesis of the sesquihydride $[Bu^t{}_2GaH]_2[GaH_2Bu^t]_2$ **164**,[28] that forms an eight-membered Ga_4H_4 ring.

3.07.2.3 Syntheses and Structures of Organometallic (Pseudo)Halides R_xMX_{3-x} (X = Halogen, N_3)

Organohalides of group 13 elements R_2MX and RMX_2 (X = F, Cl, Br, I) are valuable starting reagents in organometallic chemistry. In accordance with the increasing interest in low-valent cluster compounds of group 13 elements in the last decade (see Section 3.07.4), there is substantial interest in the synthesis of compounds containing sterically demanding organic groups such as terphenyl ligands ($2,6\text{-}R_2C_6H_3$ or $2,4,6\text{-}R_3C_6H_2$; R = Ph, Mes, Dipp, Tripp, Mes*). Therefore, monomeric diorganohalides of the type R_2MX ($[2,6\text{-}Ph_2C_6H_3]_2GaI$ **165**,[111] $[2,6\text{-}Mes_2C_6H_3]_2GaX$ (X = Cl **166**,[112] Br **167**[113]), $Tripp_2GaX$ (X = Cl **168**, Br **169**),[114] $Mes^*{}_2GaCl$ **170**,[115] $Mes^*(Cl)GaCH_2C(Me_2)\text{-}3,5\text{-}Bu^t{}_2C_6H_3$ **171**,[115] $Mes^*{}_2InX$ (X = Cl **172**,[116] Br **173**[117]), $[2,6\text{-}Mes_2C_6H_3]_2InBr$ **174**,[118] $Mes^*(Br)InCH_2C(Me_2)\text{-}3,5\text{-}Bu^t{}_2C_6H_3$ **175**[119]) as well as organodihalides of the type RMX_2 ($2,6\text{-}Tripp_2C_6H_3GaCl_2$ **176**,[120] Mes^*GaX_2 (X = Cl **177**, Br **178**),[114,121] Mes^*InX_2 (X = Cl **179**, Br **180**, I **181**)[114,121,122]) have been prepared. Each monomer exhibits three-coordinate metal centers. The influence of the ring substituents of the terphenyl ligands on the structure of the group 13 organometallics becomes obvious when comparing **176**[120] and $[2,6\text{-}Mes_2C_6H_3GaCl_2]_2$ **182**.[113] Even though the steric shielding of Mes-substituted terphenyl ligand is only marginally less pronounced than that of the Tripp-substituted one, **176** is monomeric whereas **182** is dimeric in the solid state. Interestingly, $[2,6\text{-}Tripp_2C_6H_3InCl_2]_2$ **183**[120] is dimeric in the solid state, which has to be due to steric (increased atomic radius of In compared to Ga) than to electronic factors (Lewis acidity) since organoindanes are less Lewis acidic than organogallanes (Figure 9).



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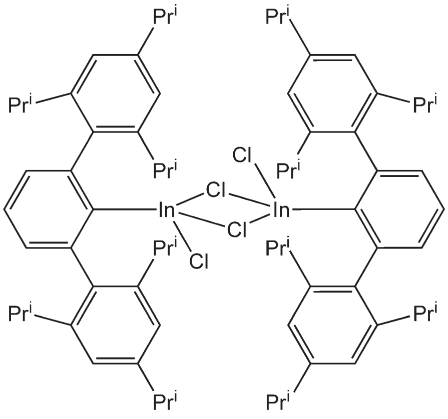

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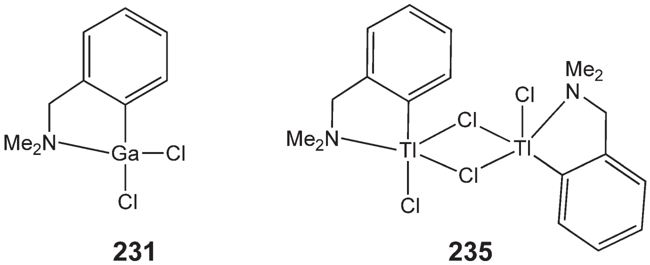
Figure 9 Monomeric and dimeric terphenyldichlorogallane and -indane.

Among so-called monomeric compounds, several dimeric derivatives of the types $[R_2MX]_2$ and $[RMX_2]_2$ such as $[Me_2GaCl]_2$ **184**,[123] $[Bu^t{}_2GaI]_2$ **185**,[124] $[(Et_3C)_2GaCl]_2$ **186**,[125] $[(TMS_3C)_2Ga(Me)I]_2$ **187**,[126] $[(PhCH_2)_2GaX]_2$ **188** (X = Cl **189**,[127] Br **190**[128]), $[Me_2(PhCCH_2)_2GaCl]_2$ **191**,[129] $[Mes_2GaX]_2$ (X = F **192**,[130] Cl **193**[114]), $[(TMS_2CH)_2GaF]_2$ **194**,[131] $[TMS_3CGaI_2]_2$ **195**,[132] $[(3{,}5\text{-}Me_2C_6H_3CH_2)_2GaBrI]_2$ **196**,[133] $[(TMS_2CH)_2InCl]_2$ **197**,[134] $[(TMSCH_2)_2InCl]_2$ **198**,[135] ($[MeGaCl_2]_2$ **199**,[123] $[MesGaCl_2]_2$ **200**,[136] and $[Cp^*GaI_2]_2$ **201**[137] have been structurally characterized within the last decade. Dimerization and formation of four-membered, halide-bridged heterocycles typically occurs when sterically less bulky organic substituents are present. As a consequence of the formation of such head-to-tail-like adducts, the metal centers adopt tetrahedral coordination spheres. Among dimerization, the Lewis-acidic metal center can compensate its electron deficiency by coordination of suitable electron donors. Consequently, both intramolecular-stabilized $(Me_2NSi(Me_2)C(TMS_2)GaCl_2$ **202**,[138] $(2\text{-}Me_2NCH_2CH_2)C_5H_4GaX_2$ (X = Cl **203**, Br **204**, I **205**),[36] $(2\text{-}{}^iPr_2NCH_2CH_2)C_5H_4GaCl_2$ **206**,[109a] $(2\text{-}Me_2NCH_2CH_2)C_5Me_4InCl_2$ **207**,[139] $(2\text{-}Bu^t{}_2PCH_2CH_2)C_5H_4InCl_2$ **208**[37]) and intermolecular-stabilized (Bu^tNH_2–$Ga(Cl)(CH_2C(Me_2)Ph)_2$ **209**,[129] Bu^tNH_2–$Ga(F)(CH_2Ph)_2$ **210**,[140] $PrNH_2$–$Ga(Cl)(Bu^t)_2$ **211**,[141] Bu^tNH_2–$Ga(F)Mes_2$ **212**,[142] R_2NH_2–$Ga(Cl)Me_2$ (R = Ph **213**, Pr^i **214**),[143] TMS_3P–$Ga(Cl)(CH_2Bu^t)_2$ **215**,[144] $Bu^tN(H)NH_2$–$Ga(Me)Cl_2$ **216**,[145] $Bu^tN(H)NH_2$–$In(Cl)Bu^t{}_2$ **217**[151]) monomeric derivatives have been prepared. In accordance with the larger atomic radius of In compared to Ga, indanes show a stronger tendency to increase their c.n. from 4 to 5. This may occur either by dimerization as was observed for $[(o\text{-}Me_2NCH_2)C_6H_4In(R)I]_2$ (R = I **218**, Pr^i **219**),[146] $[Me_2NCH_2CH_2CH_2InBr_2]_2$ **220**,[147] and $[8\text{-}Me_2N\text{-}1\text{-naphthyl-}InCl_2]_2$ **221**[148] or by addition of a second electron donor ($[Me_2N(CH_2)_3]_2InI$ **222**,[26] $[(2{,}6\text{-}(Me_2NCH_2)_2]C_6H_3InI_2$ **223**,[146] $4\text{-}Bu^t\text{-}2{,}6\text{-}(Me_2NCH_2)_2\text{-}C_6H_2InI_2$ **224**,[149] ($[2{,}6\text{-}(Me_2NCH_2)_2C_6H_3]_2InX$ (X = Br **225**, I **226**),[149] and $(tmeda)In(Cl)Me_2$ **227**[150] (tmeda = N,N,N′,N′-tetramethylethylenediamine)). Five-coordinate gallanes are very rare. They were only observed for $[(o\text{-}Me_2NCH_2)C_6H_4]_2GaCl$ **228**,[26,35a] $(Me_2NCH_2CH_2CH_2)_2GaCl$ **229**[35a] and $\{[(o\text{-}Me_2NCH_2)C_6H_4]_2GaCl\}_2$ **230**.[26] The influence of the group 13 metal on the degree of oligomerization can clearly be seen when comparing dimeric indanes **218**[146] and **221**[148] with the corresponding monomeric gallanes $(o\text{-}Me_2NCH_2)C_6H_4GaCl_2$ **231**[103] and $8\text{-}Me_2N\text{-}1\text{-naphthyl-}GaCl_2$ **232**.[148]

The reaction of Me_2InCl with phenylhydrazine yielded $[PhN(H)NH_2]_2[Me_2InCl]_4$ **233**.[151] Compound **233** shows both types of electronic stabilization (dimerization and adduct formation) since it consists of a chain of four Cl-bridged Me_2InCl units, in which the terminal ones each coordinate to one hydrazine donor. The In atoms each adopt a trigonal–bipyramidal environment.

Thallanes also tend to adopt a (distorted) trigonal–bipyramidal coordination sphere with five-coordinate Tl centers as was observed for $[(2\text{-}Me_2NCH_2)fc]_2TlCl$ **234**,[152] $[(o\text{-}Me_2NCH_2)C_6H_4TlCl_2]_2$ **235**,[153] and $[(Ph_3P{=}O)Tl(C_6F_5)_2Cl]_2$ **236**.[154] Interestingly, the central Tl atom in $[(2\text{-}Me_2NCH_2)fc]_3Tl$ **237**[152] (fc = ferrocenyl) is only four coordinate, most likely due to the reduced Lewis acidity of the Tl atom in **237** compared to **234** (Figure 10).

Mono- and diazidogallanes and -indanes of the general types R_2MN_3 and $RM(N_3)_2$ (M = Ga, In, Tl) have received an increasing interest in the last decade due to their potential application to serve as precursors for the corresponding binary nitrides MN.[155] They have been prepared by standard organometallic reactions such as salt metathesis, σ-bond metathesis or substitution reactions.[155] Typically, azido-bridged dimers ($[TMS_2N(Cp^*)GaN_3]_2$ **238**,[156]



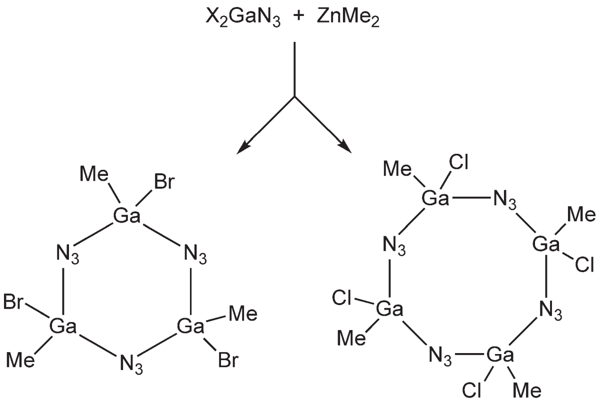
231 **235**

Figure 10 Structure of monomeric and dimeric *o*-(dimethylaminomethyl)phenyldichlorogallane and -thallane.

[Mes$_2$GaN$_3$]$_2$ **239**,[157] [Me$_2$InN$_3$]$_2$ **240**[158]), and trimers ([(TMSCH$_2$)$_2$GaN$_3$]$_3$ **241**[159]) or higher oligomers ([R$_2$InN$_3$]$_x$ (R = Pr^i **242**, Bu^t **243**),[160] [N$_3$Ga(NMe$_2$)$_2$]$_x$ **244**[161]) are formed in the solid state. Oligomerization typically occurs via the α-N atom of the azido group.[162] Interestingly, [N$_3$Ga(NMe$_2$)$_2$]$_x$ **245** forms an Me$_2$N-bridged dimer, that aggregates to a polymeric chain by dative interactions of the γ-N atom of the terminal azido group. An increase of the Lewis acidity of the metal center may result in higher coordination numbers as was found for [Me$_2$InN$_3$]$_2$ **246** and [Cl$_2$InN$_3$(thf)$_2$]$_2$ **247**,[163] which is additionally coordinated by two thf molecules. Even though oligomeric structures are typically observed in the solid state, disaggregation occurs in solution yielding monomeric or mixtures of monomeric and dimeric compounds as was found for **241**.[159]

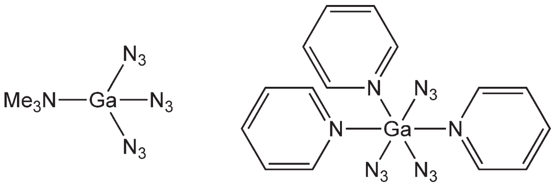
Of particular interest for further CVD experiments are group 13 metal azides, which contain less bulky organic substituents. Kouvetakis *et al.* reported on the synthesis of [N$_3$GaX$_2$]$_4$ (X = Cl **248**,[164] Br **249**[165]), which have been found to be valuable reagents for the synthesis of [N$_3$Ga(H)Br]$_x$ **250**,[165] [N$_3$Ga(Me)X]$_x$ (X = Cl **251**, Br **252**),[166] and [N$_3$Ga(Me)H]$_x$ **253**. (Figure 11)[166] Interestingly, **252** forms a six-membered ring ($x = 3$), whereas **251** adopts a cyclooctane-like structure ($x = 4$), which is rather non-typical in group 13/15 chemistry. [N$_3$Ga(H)Cl]$_4$ **254**,[167] which was obtained from the reaction of HGaCl$_2$ and LiN$_3$, also forms an eight-membered ring. By far the most promising candidate for CVD studies is [N$_3$GaH$_2$]$_3$ **255**.[165,167] Compound **255** adopts a cyclohexane-like structure in the gas phase according to IR studies and theoretical calculations[165] and was found to produce crystalline GaN films in UHV–CVD experiments at temperatures as low as 150 °C.[168]

Intra- and intermolecular coordination of a Lewis base is a suitable strategy for the stabilization of monomeric monoazides R$_2$MN$_3$ and diazides RM(N$_3$)$_2$ as was already found for the corresponding monomeric organohalides. The resulting compounds exhibit four-coordinate (Me$_2$NCH$_2$CH$_2$CH$_2$Ga(N$_3$)$_2$ **256**,[169,169a] quin–Ga(N$_3$)H$_2$ **257**[170] (quin = quinuclidine)), five-coordinate ([2,6-(Me$_2$NCH$_2$)$_2$]C$_6$H$_3$Ga(N$_3$)$_2$ **258**,[171] (Me$_2$NCH$_2$CH$_2$CH$_2$)$_2$GaN$_3$ **259**,[169a] (Et$_2$NCH$_2$CH$_2$)$_2$NGa(N$_3$)$_2$ **260**[172]), six-coordinate ((Me$_2$NCH$_2$CH$_2$CH$_2$)$_2$InN$_3$ **261**[173]), and even seven-coordinate metal centers (4-hydroxybutanato-2,2′,6,2″-terpyridine-bis(azido)indane **262**[174]). In contrast, organoazides with trigonal coordination environments are unknown, to date. As was observed for the organohalides, indanes tend to adopt higher coordination numbers than comparable gallanes. This can clearly be seen when comparing analogously



252 **251**

Figure 11 Synthesis of heterocyclic organogalliumazides containing six-membered or eight-membered Ga$_4$(N$_3$)$_4$ rings.



264 **265**

Figure 12 Structures of Lewis base-stabilized trisazidogallanes.

substituted gallium azide **259**[169a] and indium azide **261**[173]. Structure **259** exhibits a five-coordinate metal center, whereas the In atom in **261** adopts a distorted octahedral coordination environment due to additional dative interactions between the terminal azido group and neighboring In atoms. Base-stabilized organoazides can be used in MOCVD reactions as was shown in detail by the Fischer group using $Me_2NCH_2CH_2CH_2Ga(N_3)_2$ **256**.[175,175a]

Triazides $M(N_3)_3$, which are explosive in their pure form, have been stabilized by coordination of one ($Et_3N–Ga(N_3)_3$ **263**,[176,169a] $Me_3N–Ga(N_3)_3$ **264**[169a]) or three Lewis bases ($py_3Ga(N_3)_3$ **265**,[177,177a] $py_3In(N_3)_3$ **266**[173] (py = pyridine)). The metal centers adopt either distorted tetrahedral or octahedral environments. Base-stabilized triazides are suitable precursors for the synthesis of GaN[176] and InN[160] nanoparticles (Figure 12).

3.07.3 Cationic and Anionic Organometallic Derivatives Excluding Metal–Metal Bonded Species

In the following subsections, only cationic and anionic species containing at least one M–H or M–C bond are considered. Consequently, compounds containing exclusively M–X bonds (X = N, O, halide) are not discussed. (Interested readers are referred to Refs: 178 and 179.)

3.07.3.1 Cationic Derivatives

There has been a growing interest in cationic group 13 organometallics R_2M^+ (R = H, alkyl, aryl) due to their potential application as alternate, transition metal-free olefin polymerization catalysts. (Halide-substituted compounds of the type X_2M^+ (X = F, Cl, Br, I) are not considered as "organometallic" species and are consequently not discussed in this chapter.) Even though the major work has focused on the synthesis of highly reactive cationic organoaluminum compounds AlR_2^+, the corresponding gallium derivatives GaR_2^+ are of particular interest due to the relative stability of the Ga–R bond toward hydrolysis and electrophilic cleavage compared to the Al–R group (less polar; several $GaMe_2^+$ complexes are stable in water!).

Monomeric, two-coordinate organometallic group 13 cations R_2M^+ are expected to be even more Lewis acidic than group 13 triorganyls R_3M. Consequently, stabilization by use of sterically demanding organic substituents and weak (non-coordinating) anions is neccessary as was shown for $[(2,6\text{-}Mes_2C_6H_3)_2Ga][Li\{Al(OCH(CF_3)_2)_4\}_2]$ **267**,[180] and $[Mes_2In][BF_4]$ **268**.[181] Compound **267** has been prepared by chloride abstraction from $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ **166** with $Li[Al(OCH(CF_3)_2)_4]$,[180] as well as from reactions between $(2,6\text{-}Mes_2C_6H_3)_2GaR$ (R = H **141**, Me **37**) and $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$,[29] respectively. The GaC_2 moiety in the cation of **267** is almost linear (C–Ga–C bond angle 175.7(1)°) and the Ga–C bond distances are rather short (av. 191.4 pm) (Figure 13).

If sterically less bulky organic substituents are used, the cations tend to compensate their electron deficiency by coordination of a Lewis base. Consequently, Lewis base-stabilized compounds, which typically show the c.n. 4, are formed as was shown for $[Me_2Ga(NH_2Bu^t)_2][Br]$ **269**,[182] $[Me_2Ga(tmeda)][Cl_2GaMe_2]$ **270**,[150] $[2\text{-}(Me_2N–C_6H_4)_2Ga][GaCl_4]$ **271**,[183] $[2,6\text{-}(Me_2NCH_2)_2C_6H_3GaH(trifl)][trifl]$ **272**,[110] $[Me_2Ga(tmeda)][MeB(C_6F_5)_3]$ **273**,[184] $[Me_2In(NH_2Bu^t)_2][Me_2InCl_2]$ **274**,[16] and $[^iPr_2In(thf)_2][BF_4]$ **275**.[185] Interestingly, even though Me_2Ga^+ has been described as early as 1933, it took about 60 years until its solid-state structure (as $NH_2{}^tBu$ adduct **269**) was determined by X-ray crystallography.[182] The solid-state structure of the unsolvated cation $GaMe_2^+$ is unknown, to date, whereas those of the heavier congeners Me_2In^+ and Me_2Tl^+ are long known (structurally characterized almost 30 years ago).[186,186a] In recent years, several attempts to stabilize the cationic gallium center by introducing it into a rigid ring system have been applied and N,N′ chelating substituents such as 1,2-bisiminocycloheptadiene,[187]

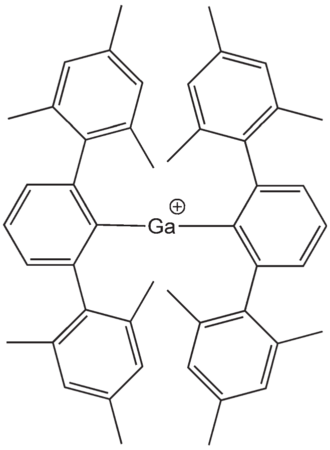


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Figure 13 Structure of a two-coordinate, cationic diorganylgallane R_2Ga^-.

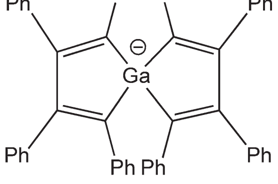
salomphen,[188] β-diketiminato,[189] aminotroponiminate,[187,190] and amidinate[191] have been studied in detail. Again, the metal centers in the resulting cations typically adopt distorted tetrahedral coordination geometries.

3.07.3.2 Anionic Derivatives

Anionic group 13 metallates $[MR_4]^-$ are very well known in a group 13 organometallic chemistry. They have been prepared in a large number by reactions of MR_3 and metal hydrides, alkyls, aryls, and tetraalkyl ammonium halides. Numerous alkyl- and aryl-substituted derivatives as well as mixed organo/halide-substituted metallates have been structurally characterized in the past. However, they are not the object to this chapter since they have been discussed extensively in several reviews, as by Tuck in COMC (1982). Only the synthesis of tetrakis(pentafluorophenyl)gallanate **276** and -indanate $[M(C_6F_5)_4]^-$ **277**,[192,193,193a–193c] which are frequently used as weakly, non-coordinating anions for the stabilization of unusual cationic species, as well as indenyl-substituted derivatives $[M(Ind)_4]^-$ **278** should be noted.[194,194a,194b]

Dialkyldifluorometallates became accessible by reaction of MMe_3 and $[Bu^n{}_4N][HF_2]$, which proceed with elimination of methane and subsequent formation of $[Me_2MF_2][N(Bu^n)_4]$ ($M = Ga$ **279**, In **280**).[195] In addition, α,ω-alkanediylbis(tribromoindanate) dianions have been synthesized by a particular THF displacement reaction between α,ω-$(CH_2)_n(InBr_2(thf)_2)$ ($n = 4, 5, 6$) and Ph_4PBr.[196] Following an analogous reaction scheme, α,α'-*m*-xylene-bridged bis(trichloroindanates) have been prepared.[197]

The first spirogallanate $[Li(thf)12\text{-crown-4}][(PhC{=}CPhPhC{=}CPh)_2Ga]$ **281** was isolated from the reaction of 1,4-dilithiotetraphenylbutadiene and $GaCl_3$.[198] The gallium center adopts a severely distorted tetrahedral coordination sphere with bond angles ranging from 87.4(2)° to 131.8(2)° (Figure 14).



281

Figure 14 Structure of the anionic spirogallanate **281**.

3.07.4 Low Oxidation State Complexes and Clusters

Low-valent group 13 organometallics became an intensely investigated research area within the last decade. Even though several research groups investigated the synthesis, structures, and reactivity of these interesting compounds, the tremendous progress that has been made in the last decade is inextricably associated with the fascinating work of Philip P. Power, Werner Uhl, and Hansgeorg Schnöckel. The Schnöckel group has developed a new synthetic pathway for low-valent organoaluminum and -gallium compounds starting with metastable solutions of aluminum and gallium subhalides MX. For instance, reactions of AlCl which is a high-temperature species that can be prepared by reaction of Al and HCl at 1200 K,[199] have led not only to first neutral tetrahedral Al cluster $[Cp^*Al]_4$ **282**,[200] but also yielded several low-valent Al cluster compounds with formal oxidation numbers between 0 and I, including a novel Al_{77} cluster $[(Et_2O)_5Li_2I]_2[Al_{77}(NTMS_2)_{20}]$ **283**.[201] Structure **283** represents an outstanding example for the class of “metalloid” clusters, which contain “naked” metal atoms that are only bound to other metal atoms. These studies have been extended on the synthesis of novel Ga clusters by reactions of a metastabile GaCl solution, yielding among other interesting cluster-type compounds two remarkable Ga_{84} clusters[202,202a] as will be shown later.

3.07.4.1 Oxidation State II

Neutral group 13 organometallic compounds of the type $M_2(CHTMS_2)_4$ (M = Al **285**,[203] Ga **286**,[204] and In **287**[205]) have been initially prepared by Uhl *et al.* only 15 years ago either by Wurtz-coupling (M = Al) or metathesis reactions between bis(trimethylsilyl)methyllithium and $Ga_2Br_4(dioxane)_2$ or $In_2Br_4(tmeda)_2$, respectively. Since then, new dialanes Al_2R_4 (R = Tripp **288**,[206] $Bu^t{}_3Si$ **289**[207]), digallanes Ga_2R_4 (R = $SiTMS_3$ **290**,[208] Tripp **291**,[209] 1,4-$Bu^t{}_2$-1,4-diazabutadiene **292**,[210] 2,2,6,6-tetramethylpiperidine **293**,[211] 1,2-diamino-bis-(N,N′-Dipp)-ethene **294**,[212] 1,2-diaminopropane **295**,[213] and bisamidophosphines **296**[214]), diindanes In_2R_4 (R = Tripp **297**,[215] $SiTMS_3$ **298**,[216] $SiBu^t{}_3$ **299**,[217] $Si(Ph)Bu^t{}_2$ **300**,[218] and R^f **301**[219]) as well as dithallanes Tl_2R_4 (R = $SiTMS_3$ **302**,[220] $SiBu^t{}_3$ **303**,[217,221] $Si(Ph)Bu^t{}_2$ **304**,[218] and bisamidophosphines **305**[214]) have been structurally characterized. They were typically obtained from metathesis reactions between organolithium derivatives and donor-stabilized tetrahalides $M_2X_4(donor)_2$ (M = Ga, In; X = Cl, Br). Donor-stabilized digallanes $Ga_2X_4(donor)_2$, structurally characterized for the first time almost 25 years ago ($[Ga_2Cl_4(1,4\text{-dioxane})_2]$ **306**[222,222a]), have been prepared in large number in the last decade by use of several electron donors (X = Cl, donor = $(Me_2N)_3P{=}O$ **307**,[223] PEt_3 **308**,[224] 4-Me-pyridine **309**,[225] NMe_3 **310**;[226] X = Br, donor = PEt_3 **311**[224]; X = I, donor = $CyNH_2$ **312**,[227] Cy_2NH **313**,[227] Bu^tNH_2 **314**,[227] Cy_2PH **315**,[227] $Bu^t{}_2Ph$ **316**,[227] NEt_3 **317**,[228] PEt_3 **318**,[229] PPh_3 **319**,[229] and $AsEt_3$ **320**[230]). They are valuable starting reagents for the syntheis of low-valent organometallics Ga_2R_4. The same holds for donor-stabilized diindanes $In_2X_4(donor)_2$ (X = Cl, donor = thf **321**;[231] X = Br, donor = 2,5-Mes_2-imidazol-1yl **322**;[232] and X = I, donor = PPr^n_3 **323**[233]). In addition, diindanes and dithallanes M_2R_4 have been prepared by reaction of In(I) and Tl(I) halides. This particular reaction type requires a disproportionation reaction of the initially formed M(I) species (MR) into the M(II) compound (M_2R_4) and elemental In and Tl, respectively. Finally, silyl-substituted compounds of the desired type $M_2(SiR_3)_4$ (M = Al **324**, Ga **325**, In **326**, Tl **327**) have been synthesized by electron transfer reactions between corresponding trihalides MX_3 and sterically demanding silanides $NaSiR_3$ (Figure 15).[234]

Among completely organosubstituted compounds M_2R_4, quite a few mixed organo/halide-substituted derivatives $M_2R_2X_2$ containing alkyl ($[Ga_2(CTMS_3)_2(I)_2]$ **328**[235]), aryl ($[Ga_2(2,6\text{-}Dipp_2C_6H_3)_2(I)_2]$ **329**[236,236a]; $[Ga_2(2,6\text{-}Trip_2C_6H_3)_2(I)_2]$ **330**;[236a] $[Ga_2(Mes^*)_2(Cl)_2]$ **331**[237]), and silyl substituents ($[Ga_2(SiTMS_3)_2(X)_2]_2$ (X = Cl **332**,[208] Br **333**[238])) have been structurally characterized. Digallanes **328**, **332**, and **333** have been prepared by reaction of the tetrahedral Ga(I) cluster $[GaCTMS_3]_4$ with C_2Cl_6, $AlBr_3$, or ICl, respectively. In addition, chelating organic ligands such as $Bu^tNC_2H_4N(H)Bu^t$ (M = Ga **334**[239]), 1-aza-allyl (M = Ga **335**, In **336**[240]), diazabutadiene (M = Ga **337**, In **338**[241]), β-diketonate (M = Ga **339**[242]), β-diketiminate (M = In **340**[243]), and 2,6-bisaminomethylphenyl (M = In **341**[244]) have been shown to be valuable systems for the stabilization of low-valent species of the desired type. The Lewis acidity of the halide substituent significantly influences the solid-state structure of the digallanes as was shown for monomeric **328** and dimeric **332** and **333**. Comparable dimeric units were observed for diindanes $[In_2(CTMS_3)_2(X)_2]_2$ (X = Cl **342**, Br **343**) (Figure 16).[245]

The rather unexpected paramagnetic M(II) compounds $[Bu^t{}_2N_2(CH)_2GaI]$ **337**[241] and $[Dipp_2N_2(CH)_2InCl]$ **344**[246] have been prepared by reactions of “GaI” and InCl, respectively, and $Li_2[Bu^t{}_2N_2(CH)_2]$ via one-electron reduction of the organic ligand. The NMR spectra of both compounds are of limited value due to their paramagnetic nature, but X-band EPR spectra were recorded and satisfactorily simulated. In the solid state, the metal centers in **337** and **344** adopt distorted tetrahedral environments with typical M–M bond distances of 242.3(1) pm **337** and 272.8(1) pm **344** (Figure 17). Mixed organohalides are of potential interest for further metathesis reactions or Wurtz coupling reactions

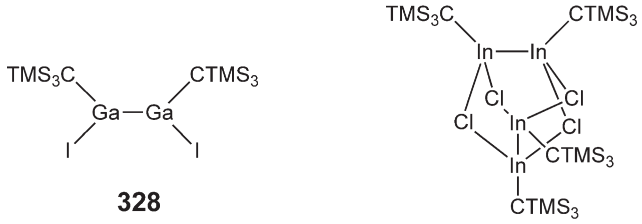
$$2\ R_2MX\ +\ 2\ M' \xrightarrow[-2\ M'X]{} R_2M{-}MR_2 \quad M = Ga, In;\ X = Cl, Br, I;\ M' = Na, K$$

$$M_2X_4(L)_2\ +\ 4\ RLi \xrightarrow[-4\ LiX]{} R_2M{-}MR_2 \quad M = Ga, In;\ X = Cl, Br, I;\ L = dioxane, tmeda$$

$$2\ MX_3\ +\ 6\ M'SiR_3 \xrightarrow[-6\ M'X,\ -(R_3Si)_2]{} (R_3Si)_2M{-}M(SiR_3)_2 \quad M = In, Tl;\ X = Cl, Br, I;\ M' = Li, Na$$

$$4\ MBr\ +\ 4\ M'SiR_3 \xrightarrow[-4\ M'Br,\ -2\ M]{} (R_3Si)_2M{-}M(SiR_3)_2 \quad M = In, Tl;\ M' = Li, Na$$

Figure 15 General reaction pathways for the synthesis of tetraorganyldimetallanes.



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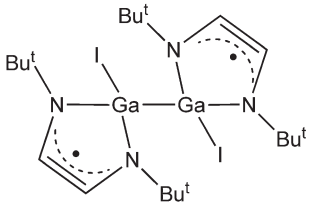
342

Figure 16 Structural comparison of analogously substituted digallane and diindane.

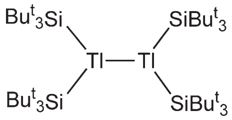


337

Figure 17 Structure of the paramagnetic digallane 337.

as was only recently demonstrated by Wiberg *et al.* The reduction reaction of $Bu^t_3SiGaCl_2(thf)_2$ with sodium or potassium proceeds with initial formation of the mixed silylhalide $[(Bu^t_3Si)_2Ga_2Cl_2]_2$ **345**, which consequently reacts with formation of the tetragallane $[Bu^t_3SiGa]_4$ **346** and the tetragallanide $Na_2(thf)_2[Bu^t_3SiGa]_4$ **347**.[247]

The coordinatively unsaturated, three-coordinate metal centers within dimetallanes M_2R_4 each show planar coordination environments with torsion angles across the M–M bond ranging from 0° (ideal planar) to 90° (staggered conformation). These findings indicate rather small rotational barriers as was proven for several digallanes Ga_2R_4 ($R = H$, Me, SiH_3, NH_2) by quantum chemical calculations.[212] In addition, the planar conformation (D_{2h} symmetry) was identified as transition state and the staggered conformation (D_{2d} symmetry) as energy minima for each digallane that was investigated. Interestingly, digallanes show significantly shorter metal–metal bonds than the corresponding dialanes, most likely due the relatively smaller covalent radius of Ga compared to Al and to reduced electrostatic interactions. The M–M bond distances of analogously substituted derivatives typically increase from digallanes to



303

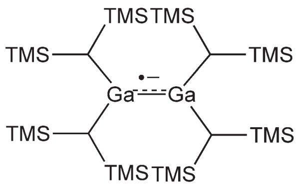
Figure 18 Structure of tetrakis[tri(tert)butylsilyl]dithallane **303**.

dithallanes with one exception: $Tl_2[Si(Ph)Bu^t{}_2]_4$ was found to exhibit a shorter Tl–Tl bond (288.1(2) pm) than the corresponding diindane (In–In 293.8(1) pm).[218] In this context, it should be noted that the mixed-valent Tl(I)/Tl(II) amide $[MeC(CH_2NTMS)_3Tl_2]$ **348**[248] exhibits a significantly shorter Tl–Tl bond distance (273.4(2) pm) than as-described dithallanes Tl_2R_4. Metal–metal bond distances depend not only on steric interactions between the organic substituent but also on their electronic nature. Electron-withdrawing substituents yield shorter M–M bond distances, whereas electron-donating substituents lead to an elongation of the metal–metal bond. Consequently, aryl-substituted compounds, in particular R^f-substituted derivatives, exhibit shorter M–M bond distances than alkyl- and silyl-substituted ones. One of the shortest Ga–Ga bond distance reported for Ga–Ga single bonds was observed in 2,4-dicarba-nido-hexaborate substituted derivative **349** (234.0(2) pm),[249] most likely due to less steric repulsion. However, electronic effects such as the hybridization of the Ga atoms (high *s*-character in the Ga–Ga bond) and reduced electrostatic interactions may also account for the short metal–metal bond (Figure 18).

Since the first synthesis of dimetallanes M_2R_4 almost 15 years ago, detailed investigations concerning their chemical reactivity have been performed. By far the best investigated compounds are Uhl's $CHTMS_2$-substituted derivatives $M_2(CHTMS_2)_4$,[250,250a,250b] for which several general reaction types have been explored. Of particular interest are electron transfer reactions, Lewis base addition reactions, and ligand exchange reactions, which proceed under retention of the central M–M bond. In addition, insertion reactions into the M–M bond have been investigated, in detail.

Electron transfer reactions. Ga_2Tripp_4 **291** reacts with elemental Li with formation of the radical anion $[Tripp_2Ga–GaTripp_2]^{\cdot-}$ **350**, which has a formal bond order (BO) of 1.5.[209] The corresponding $CHTMS_2$-substituted anion $[Ga_2(CHTMS_2)_4]^{\cdot-}$ **351** was obtained from the reaction of $Ga_2(CHTMS_2)_4$ **286** with EtLi.[251] In contrast, the analogous dialane $Al_2(CHTMS_2)_4$ **285** reacts with EtLi[252] as well as with Bu^tLi[253] with addition of one carbanion R^- to the metal center followed by elimination of C_2H_4 by β-H elimination process and subsequent formation of the anionic hydride $[(TMS_2HC)_2Al(H)–Al(CHTMS_2)_4]^-$ **352**. The Ga–Ga bond distances as observed in the radical anions $[Ga_2R_4]^{\cdot-}$ (234.3(2) pm **350**; 240.1(1) pm **351**), which can be described as one electron π-bond gallenides, are significantly shortened compared to the neutral digallanes Ga_2R_4 (251.3(3) pm **291**; 254.1(1) pm **285**). In addition, the torsion angles of the gallenides (15.5° **350**; 0° **351**) are significantly smaller compared to those of the neutral derivatives (43.8° **291**; 8° **285**). These findings clearly indicate the formation of a single-electron Ga–Ga π–bond, which was also confirmed by EPR spectroscopy. The Ga–C bond distances within the radical anions are elongated, most likely due to increased steric interactions between the organic substituents due to the shortened Ga–Ga bond. Any attempts of further reduction of the radical monoanion $[Ga_2R_4]^{\cdot-}$ to a dianion $[Ga_2R_4]^{2-}$, which have a formal BO of 2.0, failed. However, reduction of **350** with sodium yielded $Na_2[Ga(GaTripp_2)_3]$ **353**. Structure **353** (BO = 1.33) shows a trigonal-planar arrangement of four Ga atoms with Ga–Ga bond distances of 238.9(2) pm.[254] Oxidation with 1 equiv. of O_2 gave the corresponding neutral derivative $Ga(GaTripp_2)_3$ **354**. According to a decrease of the formal BO from 1.33 to 1, the Ga–Ga bond lengths of **354** are elongated by almost 8 pm (247.6(7) pm).[254] The comparable indane $In(InTripp_2)_3$ was obtained by reduction reaction of In_2Tripp_4 (Figure 19).[215]

Lewis base addition reactions. Dimetallanes of the type M_2R_4 generally tend to react with Lewis bases due to the presence of an unoccupied *p*-orbital at each metal center. $M_2(CHTMS_2)_4$ (M = Ga **285**, In **286**) react with LiCCPh with formation of the monoadducts of the general type $[LiL_x]^+[M_2(CHTMS_2)_4CCPh]^-$ (M = Ga **355**, In **356**)[255] The central M–M bond distances are only slightly elongated by 1.7 **355** and 2.5 pm **356**, respectively. The comparable pentasilyldigallanate was obtained from the reaction of "GaI" and $LiSiPh_3$.[256] In sharp contrast, bisadducts are extremely rare. In particular, those of the type $[M_2R_6]^{2-}$ containing two anionic ligands (carbanions) are strongly disfavored due to repulsive electrostatic interactions. To date, $[In_2(CHTMS_2)_4(CNR)_2]$ (R = Bu^t **357**, Ph **358**) are the only structurally characterized neutral bisadducts of the desired type.[257] They adopt ethane-like staggered conformations as was expected from theoretical calculations ($[Ga_2H_6]^{2-}$ [258a]) with the isonitrile ligands arranged in a *transoid* **357** or *cisoid* orientation to each other **358**. Again, the In–In bond distances are only slightly elongated, whereas the In–C distances to the isonitrile ligands are very long (>240 pm). These findings give strong evidence that the acid–base interactions are only weak. Comparable bisadducts have also been observed in mixed organohalides



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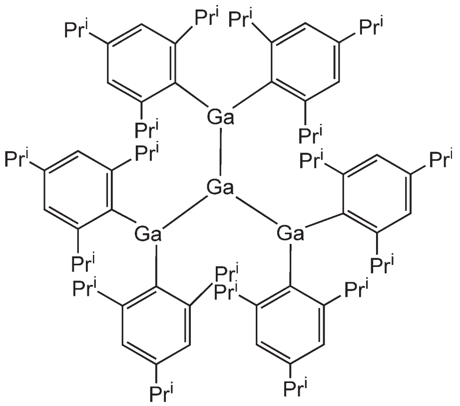

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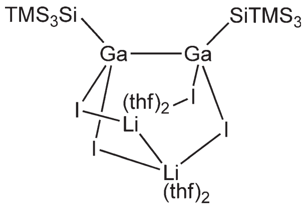
Figure 19 Structures of the radical anion 351 and the unusual neutral tetragallane 354.

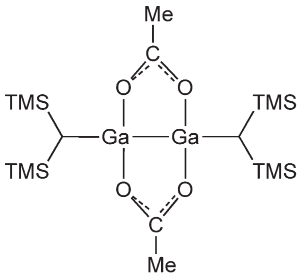


360

Figure 20 Structure of the mixed organogalliumhalide 360.

[Li(thf)$_2$]$_2$[Ga$_2$(SiTMS$_3$)$_2$(X)$_4$] (X = Br **359**, I 360), which were obtained from reaction of Li(thf)$_3$SiTMS$_3$ with Ga$_2$Br$_4$(dioxane)$_2$ and "GaI," respectively (Figure 20).[259]

Ligand exchange reactions. Digallane **285** reacts with relatively strong chelating protonic acids such as carboxylic acids RCOOH[260,260a,260b] and dicarboxylic acids R(COOH)$_2$[260a,261] as well as with diphenyltriazene Ph$_2$N$_3$H,[262] dibenzoylmethane H$_2$C(COPh)$_2$,[131] and imidotetraphenyldiphosphinato HN(P(O)Ph$_2$)$_2$[263] with preservation of the metal–metal bond. These findings are in remarkable contrast to those observed for analogous reactions of the corresponding dialane and diindane [M$_2$(CHTMS$_2$)$_4$] (M = Al **284**, In **286**). The chelating substituents either adopt terminal or bridging positions. In addition, di(μ-acetato)digallane [Ga$_2$(O$_2$CMe)$_2$(CHTMS$_2$)$_2$] **361** has been proved to be a suitable starting reagent for ligands exchange reactions with lithium diphenyltriazenido,[260b] diphenylbenzamidinate,[260b] benzimidazolate,[264] and others (Figure 21).[250,250a,250b]



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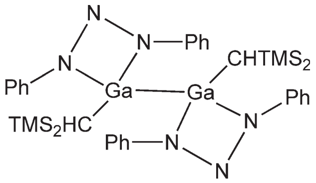


Figure 21 Structures of digallane adducts illustrating the different coordination modes of carboxylic and triazenato ligands.

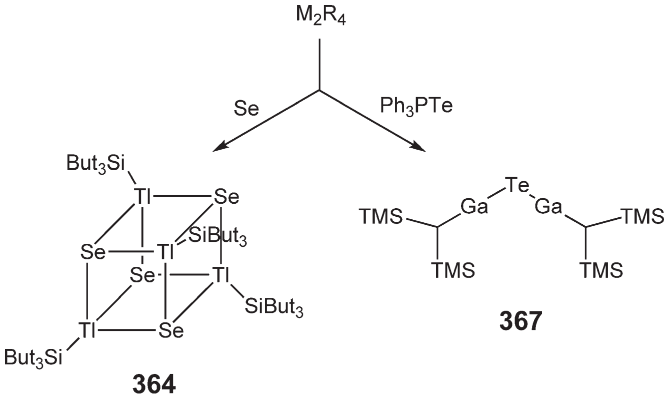


Figure 22 Synthesis of group 13/16 compounds by reaction of dimetallanes M_2R_4 with elemental Se and Ph_3PTe.

Insertion reactions. $[Al_2(CHTMS_2)_4]$ **284** easily undergoes insertion reactions into the Al–Al bond with isocyanides, isocyanates, carbenes, and trimethylsilylazide. In sharp contrast, the digallane **285** only reacts with isocyanides. Two molecules are inserted with subsequent formation of $[(TMS_2CH)_2GaC(NR)C(NR)Ga(CHTMS_2)_2]$ **362** containing a C–C single bond.[265] In addition, chalcogen atoms can easily be inserted into the M–M bond by reaction with elemental chalcogens as was observed for reactions of $[M_2(SiBu^t_3)_4]$ with selenium, leading to the formation of heterocubanes $[Bu^t_3SiMSe]_4$ (M = In **363**, Tl **364**).[218] In contrast, reactions of **285** and **286** with chalcogen atom donors such as triethylphosphoniumchalcogenides Et_3PE (E = S, Se, Te) or propylene sulfide yielded chalcogen-bridged compounds of the general type $[(TMS_2CH)_2M\text{-}E\text{-}M(CHTMS_2)_2]$ (Ga: E = S **365**, Se **366**, Te **367**; In: S **368**, Se **369**, Te **370**),[266,266a,266b] which are monomeric both in the solid-state and in solution (Figure 22). The reaction of $[Ga_2(CHTMS_2)_4]$ with DMSO yielded the hydroxo-bridged dimer $[(TMS_2CH)_2GaOH]_2$ **371**, whose formation probably occurs by the reaction of radical intermediates with solvent molecules.[267]

3.07.4.2 Oxidation State I

Neutral organometallic In(I) and Tl(I) complexes of the general type $[R_nM_n]_x$ ($x \geq 1$) with the metal center in the oxidation state I have a long-standing history in metalorganic chemistry (Figure 23). (In this chapter, only organometallic Tl(I) compounds containing a Tl–C bond are described. The chemistry of Tl(I) containing other types of ligands has been reviewed several times within the last decade.[268,268a,268b]) In particular, the cyclopentadienyl substituent (including its substituted derivatives) has been demonstrated to stabilize this class of compound (see Refs: 269, 269a, and 269b, and the references cited therein). For instance, CpIn **372**[270] and CpTl **373**[271,271a] have been known for almost 50

$$RMX_2 + 2\,M' \xrightarrow[-\,2\,M'X]{} 1/x\,[MR]_x$$

M = Ga, In; X = Cl, Br, I
M′ = Na, K

$$MX + M'R \xrightarrow[-M'X]{} 1/x\,[MR]_x$$

M = Ga, In, Tl; X = Cl, Br, I

$$2\,GaCl_3 + 6\,NaSiR_3 \xrightarrow[\substack{-\,6\,NaCl\\ -\,(R_3Si)_2}]{} [Ga_2(SiR_3)_3]^{\bullet} \xrightarrow[-\,R_3Si^{\bullet}]{\Delta T} 1/2\,[GaSiR_3]_4$$

$$CpTl + LiCTMS_3 \xrightarrow[-CpLi]{} 1/4\,[TlCTMS_3]_4$$

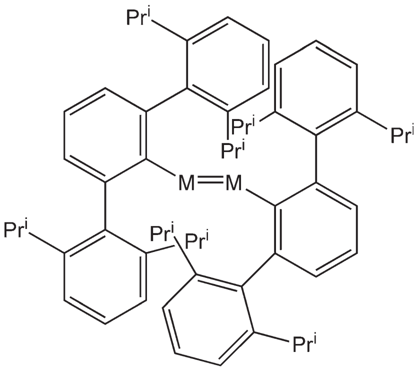
Figure 23 General reaction pathways for the synthesis of neutral M(I)-clusters.

years. In sharp contrast, low-valent organometallic compounds of the lighter elements of group 13, Al and Ga, have been studied, to a far lesser extent, due to their strong tendency toward disproportionation reactions with subsequent formation of elemental metal M and MR_3. Isolable Ga(I) compounds became available for the first time almost 20 years ago by the pioneering work of Schmidbaur *et al.* Reactions of Ga[$GaCl_4$] with aromatic solvents yielded arene complexes, which exhibit the metal center in the oxidation state I.[272] A breakthrough in low-valent organoaluminum and -gallium chemistry has been the synthesis of metastabile solutions of AlX (X = Cl **374**, Br **375**) and GaX (X = Cl **376**, Br **377**) by Schnöckel *et al.* almost 15 years ago.[273] In the following years, these subhalides have been proved powerful starting reagents for the synthesis of novel metal and metalloid cluster compounds by standard salt elimination reactions. [Cp^*Al]$_4$ **282**, the first structurally characterized, neutral Al(I) compound of the desired type, has been synthesized by reaction of AlCl and $MgCp^*_2$ in 1991.[200] Since then, several neutral compounds of the desired type containing alkyl, aryl, organosilyl, cyclopentadienyl, and other types of ligands have been prepared, most of them by reaction of element subhalides of the general type MX (those of M = In, Tl are stable at ambient temperature) with organolithium or Grignard reagents. Reduction reactions of organohalides RMX_2 with alkali metals (Na, K) or Mg as well as thermal decomposition of silylsubstituted digallanes $Ga_2(SiR_3)_4$ were also shown to give the desired compounds. (For most recent review articles on low-valent gallium cluster compounds, see Refs: 274 and 275.) In addition, the first alkyl-substituted Tl(I) cluster was obtained by reaction of CpTl and $LiCTMS_3$.[276]

Structures. Cp-substituted In(I) and Tl(I) compounds are long known to form oligomeric zigzag chains with bridging Cp ligands between two metal centers with no direct M–M bonds. (However, some of them show weak metal–metal interactions between the individual chains.) In sharp contrast, only a very few examples of metal–metal bonded species such as the only loosely bonded dimeric [Bz_5C_5M]$_2$ (M = In **378**,[277] Tl **379**[278]) and hexameric compounds [Cp^*In]$_6$ **380**[279] have been prepared, most likely resulting from the only weak metal–metal interactions. This situation has dramatically changed in the last decade. The introduction of novel classes of organic substituents such as β-diketiminato or terphenyl ligands with tunable sterical and electronical properties as well as the development of suitable starting reagents such as gallium subhalides GaX gave access to compounds, which exhibit novel structural features. The metal center was found to play a key role on the resulting structure as can clearly be seen when comparing solid-state structures of analogously substituted compounds such as the Cp^*-substituted M(I) derivatives. [Cp^*Al]$_4$ **282**[200] is tetrameric in the solid state with short Al–Al bonds (277 pm), whereas [Cp^*Ga]$_6$ **381**[280] and [Cp^*In]$_6$ **380**[279] are hexameric. Structures **380** and **381** exhibit very long M–M distances (av.; M = Ga 412 pm; In 395 pm), indicating only weak M–M bonding character. [Cp^*Tl]$_x$ **382**, however, forms an oligomeric zigzag chain in which the Cp^* ring bridges two Tl centers (Tl···Tl distance 640 pm). A comparable trend was observed for the tetrahedral clusters [$MCTMS_3$]$_4$ (M = Ga **383**, In **384**, Tl **385**). The Tl–Tl distances (332.2(1)–363.8(1) pm)[276] are significantly longer compared to the In–In (298.9(1)–301.2(1) pm)[281,281a] and Ga–Ga distances (267.8(4)–270.2(3) pm)[282] than was expected due to the increase of the atomic radius. Obviously, the tendency of Tl(I) compounds to form cluster compounds [MR]$_x$ containing metal–metal bonds is significantly less pronounced.

Neutral monomeric, dimeric, and trimeric compounds. The use of extremely bulky organic substituents[283] allowed the synthesis of kinetically stabilized monomers of the type [RM] (M = Ga, R = $(N(Dipp)CMe)_2CH$ **386**,[284] {HC(CMe–DippN)$_2$} **387**,[285] $Tp^{Bu^t_2}$ **388**[286] (Tp = hydridotris(pyrazol-1-yl)borate); M = In, R = 2,6-$Tripp_2$–C_6H_3 **389**[287]; M = Tl, R = 2,6-$Tripp_2$–C_6H_3 **390**,[288] N(TMS)Dipp **391**[289]).[290] These isolable compounds are valuable starting reagents for the synthesis of novel metalorganic compounds (see Section 3.07.5). However, even sterically less bulky substituted low-valent derivates can be synthesized as is illustrated with the synthesis of MeGa **391**, the simplest metalorganic Ga(I) derivative.[291] Compound **391**, obtained by photolysis of a CH_4-doped Ar matrix with broadband UV–Vis light, has been characterized by IR spectroscopy.[292]

Neutral dimeric compounds [2,6-$Dipp_2$–C_6H_3M]$_2$ (M = Ga **392**,[293] In **393**,[294] and Tl **394**[295]), formally featuring an M=M double bond, have been synthesized and structurally characterized for the first time. These remarkable compounds each show a *trans*-bent C–M–M–C array (M–M–C bond angle: 123.2(1)° **392**; 121.1(1)° **393**; 119.7(2)° **394**). The M–M bond distances (262.7(1) pm **392**; 297.9(1) pm **393**; 309.4(1) pm **394**) are significantly shorter than those in the weakly bonded dimers [Bz_5C_5M]$_2$ (M = In 363.1(2) pm; Tl 363.2(1) pm), but longer than typical M–M bonds in compounds of the type M_2R_4, which range from 233 to 254 pm (M = Ga) and 270 to 294 pm (M = In), respectively. These findings indicate that the metal–metal bonds in [2,6-$Dipp_2$–C_6H_3M]$_2$ are rather weak. Interestingly, the presence of a Pr^i-group in *para*-position of the flanking *ortho*-bonded substituents determines whether the compounds are monomeric (Tripp) or dimeric (Dipp) in the solid state. The influence of the steric bulk of the *ortho*-substituents on the degree of oligomerization can also be seen in case of the dimeric and trimeric Tl derivatives [2,6-$Dipp_2$–C_6H_3Tl]$_2$ **394** and [2,6-Dmp_2–C_6H_3Tl]$_3$ **395** (Dmp = 2,6-dimethylphenyl). The bonding properties of the neutral digallenes, diindenes, and dithallenes RMMR have also been subject to several computational calculations,[296] which clearly demonstrated the weak bonding character of the metal–metal interactions.



M = Ga **392**, In **393**, Tl **394**

Figure 24 Structure of dimeric metallenes 392–394 illustrating the trans-bent arrangement of the organic substituents.

The *trans*-bent structure was unexceptional and found to be energetically favored compared to the linear arrangement, but even more stable forms such as vinylidene, mono-bridged or double-bridged isomers exist. Compounds 392–395 are unexceptional monomeric in solution, as is typical for M(I) cluster compounds.[297]

Among the dimeric derivatives 392–394, the only multiply bonded group 13 metal species, which has been structurally characterized, to date, has been synthesized by Wiberg *et al.* in about 10% yield by reaction of $\mathrm{GaCl_3}$ and $\mathrm{Na(SiBu^t{}_3)}$.[299] (For review articles dealing with multiply bonded group 13 metal species, see Refs: 280, 298, and 298a.) The formation of the black-blue digallanyl $\mathrm{[Ga_2(SiBu^t{}_3)_3]^{\cdot}}$ 396 most likely proceeds through formation of the digallane $\mathrm{[Ga_2(SiBu^t{}_3)_4]}$ **397** as non-isolable intermediate. A comparable reaction mechanism has been reported for the synthesis of the corresponding dialanyl radical $\mathrm{[Al_2(SiBu^t{}_3)_3]^{\cdot}}$, which was obtained by thermolysis of $\mathrm{[Al_2(SiBu^t{}_3)_4]}$ at 80 °C.[207,300] $\mathrm{[Ga_2(SiBu^t{}_3)_3]^{\cdot}}$ 396 represents one of the very few examples of multiply bonded group 13 metal species. It features a relatively short Ga–Ga bond length (242.3(1) pm) and a wide C–Ga–Ga bond angle (170.3(1)°) at the two-coordinate Ga center. Structure 396 can formally be described as a mixed Ga(I)/Ga(II) species that is σ-bonded by the overlap of an *sp* and sp^2 hybrid orbital. The remaining single electron occupies a π-MO orbital, which is formed by the overlap of two p_z-orbitals of the metal centers. The radical character of 396 was proved by EPR spectroscopy.[299] Radical 396 shows some very interesting chemical properties. For instance, it reacts with elemental sodium or with $\mathrm{Na(SiBu^t_3)}$ in THF with formation of the deep-red salt $\mathrm{Na(thf)_3[Ga_2(SiBu^t{}_3)_3]}$ 398.[302] The radical anion of this salt, $\mathrm{[Ga_2(SiBu^t_3)_3]^{\cdot-}}$, shows a relatively short Ga–Ga bond distance of 238.0(1) pm), which is slightly shorter than that of 396 (242.3(1) pm).[302] Structure 398 further reacts with 18-crown-6, with subsequent formation of the deep-blue trigallanide $\mathrm{[Na(18\text{-}crown\text{-}6)(thf)_2][Ga_3(SiBu^t{}_3)_4]}$ 399, which can be oxidized by $\mathrm{Bu^t{}_3SiBr}$ or tetracyanoethylene to give the tricyclic radical $\mathrm{[Ga_3(SiBu^t{}_3)_4]^{\cdot}}$ 400.[302] In additon, thermal decomposition of 396 in heptane at 100 °C yielded the dark-violet tetragallane $\mathrm{[Bu^t{}_3SiGa]_4}$ 401, which exhibits significantly longer Ga–Ga bond distances of about 260 pm (Figure 25).[303]

Neutral tetrameric and hexameric clusters. Alkyl and silyl substituents such as $\mathrm{CTMS_3}$[304] or $\mathrm{SiTMS_3}$ typically yielded tetrahedral clusters $\mathrm{[RM]_4}$ (M = **Ga**: R = $\mathrm{CTMS_3}$ **383**,[282] $\mathrm{C(SiMe_2Et)_3}$ **402**,[305] $\mathrm{SiBu^t{}_3}$ **401**,[303] $\mathrm{SiTMS_3}$ **403**,[306] $\mathrm{GeTMS_3}$ **404**[307]; **In**: R = $\mathrm{CTMS_3}$ **384**,[281] $\mathrm{C(SiMe_2Et)_3}$ **405**,[308] $\mathrm{C(SiMe_2Pr^i)_3}$ **406**[308]; **Tl**: R = $\mathrm{CTMS_3}$ **385**,[276] $\mathrm{Tp^{Cpr}}$ **407**[290]). These clusters tend to dissociate both in solution and in the gas phase with the formation of monomeric species. The nature of the metal–metal bonds within the cluster compounds has received considerable attention over the last decade and has been investigated in detail by computational calculations (see the Refs: 309, 309a, 309b, and 309c). Among these tetrameric species, the octahedral hexagallane $\mathrm{[TMS_2(Me)SiGa]_6}$ 408 has been obtained from the reaction of "GaI"[310] and $\mathrm{Li(thf)_3SiMeTMS_2}$.[311] The formation of 408 most likely results from the reduced steric bulk of the organic substituents $\mathrm{SiMeTMS_2}$ compared to $\mathrm{SiTMS_3}$. The central $\mathrm{Ga_6}$ metal core of 408 significantly deviates from the idealized octahedral geometry. It exhibits six short Ga–Ga bond distances (av. 250.7 pm), which are in the range of typical Ga–Ga single bonds, and six long Ga–Ga distances (av. 296.1 pm) (Table 1). However, even the long Ga–Ga bond distances are significantly shorter compared to those observed in $\mathrm{[Cp^*Ga]_6}$ **381** (about 400 pm, weak van der Waals interactions). The

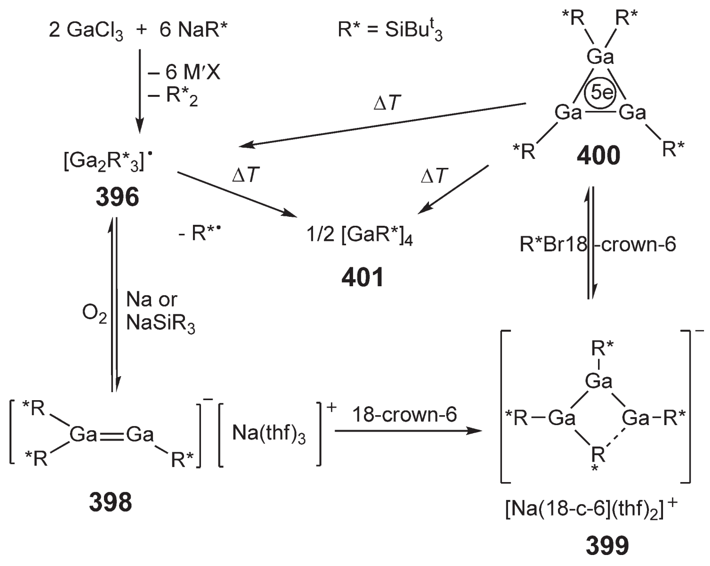


Figure 25 Synthesis and structures of supersilyl-substituted gallanyls **396** and **400**, gallanide **398** and tetrahedrane **401**.

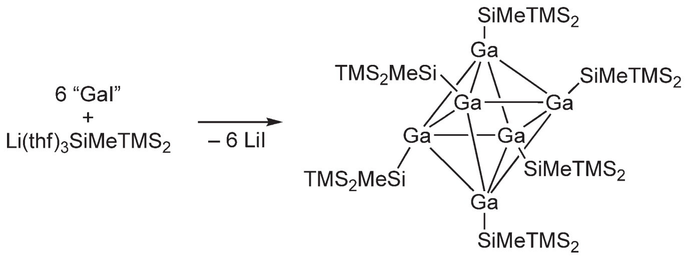
Table 1 Neutral clusters of the general type $[MR]_x$ (M = Ga, In, Tl; $x \geq 2$)

M	*R*	*x*	*(av.) M–M* (pm)
Ga	2,6-Dipp$_2$–C$_6$H$_3$	2	262.7(1)
Ga	SiBu$^t_3$	4	257.3
Ga	CTMS$_3$	4	268.8
Ga	C(SiMe$_2$Et)$_3$	4	271.1
Ga	SiTMS$_3$	4	258.2
Ga	GeTMS$_3$	4	258.7
Ga	SiMeTMS$_2$	6	249.6(2)–296.1(1)
Ga	Cp*	6	412.3
Ga	Bu^t	9	256.9(1)–300.7(1)
In	2,6-Dipp$_2$–C$_6$H$_3$	2	297.9(1)
In	CTMS$_3$	4	300.2
In	C(SiMe$_2$Et)$_3$	4	300.4
In	C(SiMe$_2$Pr^i)$_3$	4	315.5
Tl	2,6-Dipp$_2$–C$_6$H$_3$	2	309.4(1)
Tl	2,6-Dmp$_2$–C$_6$H$_3$	3	331.7
Tl	CTMS$_3$	4	332.2(1)–363.8(1)
Tl	Tp^{Cpr}	4	364.7(1)

structure of **408**, which can be derived from an octahedron by a Jahn–Teller distortion, does not match the Wade–Mingos rules (Figure 26).

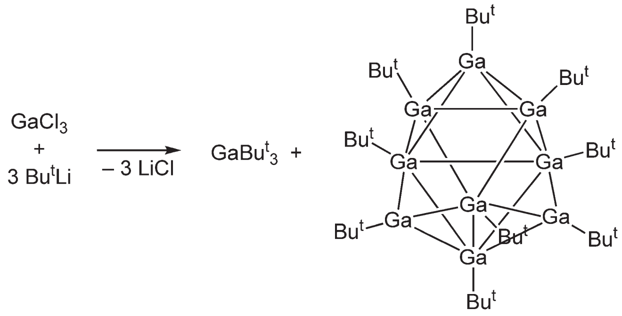
Larger neutral clusters. Only a very few larger neutral oligomers such as $[Bu^tGa]_9$ **409**[312] and $[Me_2(Ph)CCH_2Ga]_x$ **410**,[313,314] have been synthesized. Unfortunately, the solid-state structure of **410** could not be determined, to date. Structure **409** was obtained in low yield from the reaction of GaCl$_3$ and Bu^{t}Li. The central Ga$_9$ core consists of a tricapped trigonal prism with Ga–Ga bond distances ranging from 256.9(1) pm for the capping Ga atoms to 300.7(1) pm at the edge of the prism perpendicular to the prisms. The clusters are thermally remarkable stable up to 228 °C (Figure 27).

Low-valent clusters $[RM]_x$ are valuable starting reagents for various oxidation reactions as will be shown in the following for the tetrahedral cluster $[TMS_3CM]_4$ (M = Ga **383**, In **384**). (Reactions with metal carbonyl complexes,



408

Figure 26 Synthesis and structure of the octahedral hexagallane **408**.



409

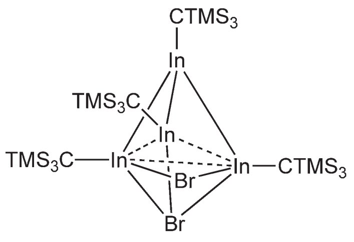
Figure 27 Synthesis and structure of the nonagallane **409**.

which yielded intermetallic complexes with the monomeric fragment RM (M = Ga, In) serving as two electron donors comparable to carbon monoxide are not discussed in this chapter.)

Insertion reactions. $[TMS_3CM]_4$ (M = Ga, In) react with halogen donors such as C_2Cl_6 and $C_2H_4Br_2$ as well as with X_2/AlX_3 mixtures (X = Br, I) with partial oxidation and subsequent formation of organometal subhalides. The resulting compounds show a remarkable structural variety. Partially oxidized clusters such as $In_4Br_2(CTMS_3)_4$ **411**,[315] in which the central In_4 core is still preserved (average oxidation state of In = 1.5), were formed as well as $M_3I_2(CTMS_3)_3$ clusters (M = Ga **412**,[316] In **413**[317]) containing M_3 chains. Among these types of complexes, realgar-type cages $[(TMS_3C)_2In_2X_2]_2$ (X = Cl **414**, Br **415**),[315] which exhibit the In atoms in the oxidation state II, were obtained. Interestingly, $[(TMS_3C)_2Ga_2X_2]$ (X = Br **416**, I **417**) are monomeric even in the solid state.[316] The organosubhalides **411**–**417** are powerful reagents for further salt elimination reactions.[275] A structurally slightly different tetragallane, $[(TMS_3Si)_4Ga_4I_3]^-$ **418**, was obtained from the reaction of "GaI" with $Li(thf)_3SiTMS_3$.[318] It shows a heterocubane-type arrangement of four Ga and three iodine atoms (Figure 28).

Reactions of $[TMS_3CM]_4$ with elemental chalcogens and chalcogen donors typically occur with complete oxidation of the M_4 cluster (M = Ga, In) and subsequent formation of heterocubane-type cages $[RME]_4$ (E = O, S, Se, Te) as will be shown in Section 3.07.5.3. However, partial oxidation was observed for the reaction of $[TMS_3CIn]_4$ with propylene sulfide, leading to the formation of the mixed-valent cluster $[(TMS_3C)_4In_4S]$ **419**, in which only one face of the tetrahedral cluster is bridged by a sulfur atom.[319] Another remarkable compound, $[(TMS_3CGa)_3P_4]$ **420**, was obtained from the reaction of $[TMS_3CGa]_4$ with P_4. Its formation proceeds through insertion reactions of three $GaCTMS_3$ monomers into three P–P bonds of the P_4 tetrahedron. In contrast, the reaction of $[Cp^*Al]_4$ **282** and P_4 yielded $[Cp^*{}_6Al_6P_4]$ **421**.[320]

Mixed-valence compounds. The ground state of monomeric species RM (M = B, Al, Ga, In), which have an electron lone pair at the metal center, is singlet and the singlet–triplet energy gap increases with increasing atomic number. Consequently, these compounds are able to act as Lewis bases. Reactions with Lewis-acidic



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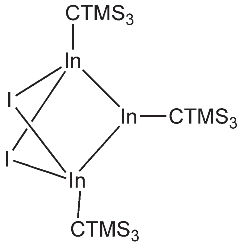

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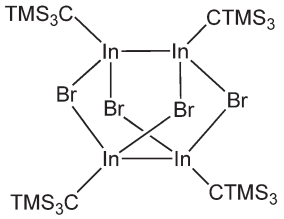

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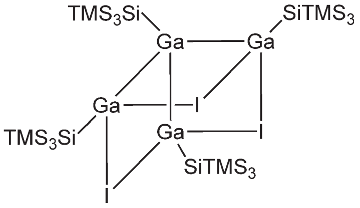

418

Figure 28 Structures of organometal subhalides as obtained from insertion reactions of tetrahedral M(I) clusters with halogen donors.

$M'R'_3$ compounds of group 13 elements yielded mixed-valence compounds of the general type $RM–M'R'_3$,[321] which are valence isomers of M_2R_4 (Section 3.07.4.1). To date, several homonuclear and heteronuclear species have been synthesized and structurally characterized and their stability was investigated by computational calculations (Table 2).[322,322a,323]

The M–M bond distances within the homonuclear compounds ($Cp^*Ga–Ga(Cl)_2Cp^*$ **422**,[323] $Cp^*Ga–Ga(I)_2Cp^*$ **423**,[324] $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga–GaI_3}$ **424**,[286] $[\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_2\}\text{(5-Bu}^t\text{pz(}\eta^1\text{-5-Bu}^t\text{pzH))]In–InI}_3$ **425**[325]) are comparable to those observed in M(II) compounds M_2R_4. Interestingly, **424**[286] and **425**[325] were obtained from reactions of "GaI" with $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Na}$ and $InCl_3$ with $\mathrm{KHB(3\text{-}Bu^tpz)_3}$, respectively. Heteronuclear compounds are almost limited to those containing $B(C_6F_5)_3$ as strong Lewis acid. $Cp^*Ga–B(C_6F_5)_3$ **426**,[326,324] $(2,6\text{-Tripp–}C_6H_3)Ga–B(C_6F_5)_3$ **427**,[327] $(2,6\text{-Dipp–}C_6H_3)Ga–B(C_6F_5)_3$ **428**,[326] $(2,6\text{-Bu}^t\text{Dipp–}C_6H_3)Ga–B(C_6F_5)_3$ **429**,[327] $HC(C(Me)N(Dipp))_2Ga–B(C_6F_5)_3$ **430**,[326] $(2,6\text{-Tripp–}C_6H_3)In–B(C_6F_5)_3$ **431**,[294] and $(2,6\text{-Dipp–}C_6H_3)In–B(C_6F_5)_3$ **432**[294] were obtained from the reaction of RM and $B(C_6F_5)_3$ (Figure 29). In addition, the synthesis of the heteronuclear adduct

Table 2 Mixed-valence compounds of the type $RM–M'R'_3$ (M = Ga, In, Tl; M′ = B–Ga)

RM-M′X₃	*Σ∠X–M′–X* (°)	*M–M′* (pm)
$[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga–GaI_3}$	315.1	250.6(3)
$Cp^*Ga–Ga(Cl)_2Cp^*$	335.6	242.5(1)
$Cp^*Ga(Ga(I)_2Cp^*$	335.7	243.7(2)
$Cp^*Ga–B(C_6F_5)_3$	342.4(2)/33.5(2)	216.0(2)/214.9(3)
$(2,6\text{-Dipp–}C_6H_3)Ga–B(C_6F_5)_3$	337.5	212.4(6)
$(2,6\text{-Tripp–}C_6H_3)Ga–B(C_6F_5)_3$	337.1	211.0(3)
$(2,6\text{-Bu}^t\text{Dipp–}C_6H_3)Ga–B(C_6F_5)_3$	340.0	210.8(2)
$(2,6\text{-Dipp–}C_6H_3)In–B(C_6F_5)_3$	339.3	229.2(2)
$(2,6\text{-Tripp–}C_6H_3)In–B(C_6F_5)_3$	337.8	232.2(2)
$[\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_2\}\text{(5-Bu}^t\text{pz(}\eta^1\text{-5-Bu}^t\text{pzH)]In–InI}_3$	319.1	274.8(4)
$(2,6\text{-Dipp–}C_6H_3)Tl–B(C_6F_5)_3$	341.0	231.1(2)

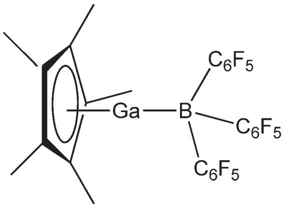

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Figure 29 Structure of a Lewis acid-base adduct containing Lewis basic Cp*Ga.

Cp*Ga–Al(C_6F_5)$_3$ **433** was reported.[321] The relative basicity of the group 13 diyl donors was estimated by comparing the sum of the C–B–C bond angles of the B(C_6F_5)$_3$ adducts.[321]

3.07.4.3 Neutral and Anionic Compounds $[M_nR_m]^{x-}$ ($m \geq n$) with an Oxidation State between I and II

Among neutral low-valent organoelement compounds of the types [M_2R_4] and [M_nR_n], a few anionic compounds of the general type $[M_nR_m]^{x-}$ ($m = n$) with equal metal/substituent ratios have been prepared. (Anions of the type $[M_2R_{4+n}]^{n-}$ ($n = 1$, 2) have been described in Section 3.07.4.1.). These range from very small molecules containing one or two metal centers to larger clusters with up to nine metal atoms. In addition, several anionic compounds of the general type $[Ga_nR_m]^{x-}$ ($m > n$) with the number of substituents being larger than the number of metal atoms have been structurally characterized.

The smallest anionic compound of the desired type, the monoanionic carbene analog $[\{HCN(Bu^t)\}_2Ga]^-$ **434**, has been prepared by Schmidbaur *et al.* by reaction of $Li_2[Bu^t{}_2N_2(CH)_2]$ with $GaCl_3$ followed by reduction with potassium in the presence of 18-crown-6.[328] The initially formed $[\{HCN(Bu^t)\}_2GaCl]_2$ **435** adopts a rather unexpected dimeric structure with inequivalent Ga centers. In contrast, the reactions of $Li_2[Bu^t{}_2N_2(CH)_2]$ with $HGaCl_2$ and $Li_2[Cy_2N_2(CH)_2]$ with $GaCl_3$ yielded $[\{HCN(Bu^t)\}_2GaH]_2$ **436** and $[\{HCN(Cy)\}_2GaCl]_2$ **437**. Compounds **436** and **437** adopt "normal" dimeric structures in the solid state with the substituents (H, Cl) in *trans*-positions,[329] as was previously observed for $[\{HCN(Bu^t)\}_2GaBu^t]$ **438**.[330] The anionic galla-heterocycle **434** is almost planar and shows no sub-van der Waals contacts with the cation. However, if 18-crown-6 was replaced by tmeda, the potassium cation becomes η^5-bonded to the five-membered galla-heterocycle. These monomeric units further aggregate to dimeric species $\{[\{HCN(Bu^t)\}_2Ga]^-[K(tmeda)]\}_2$ **439** through (intermolecular) Ga···K contacts (343.8(1) pm), which are even slightly shorter than the intramolecular interactions (346.8(1) pm).[331] The strong influence of the nature of the solvated cation was also observed for $[KL_x][\{HCN(Dipp)\}_2Ga]$ ($[KL_x] = [KOEt_2]$ **440**, [K(tmeda)] **441**, [K_2(18-crown-6)$_3$] **442**), which were obtained by reduction of the paramagnetic gallane $[\{HCN(Dipp)\}_2GaI_2]$ with potassium.[241] As observed for the Bu^t-substituted carbene analog, a monomeric compound was formed with 18-crown-6, whereas dimeric species were obtained with Et_2O and tmeda in the solid state (Figure 30).

Carbene analogs 434 and 440–442 are valuable ligands in transition metal chemistry and several complexes such as $[\{HCN(Dipp)\}_2Ga]_2Ni[CN_2(Dipp)_2(CMe)_2]_2$ **443**[332] have been synthesized. In addition, Jones *et al.* demonstrated that they might become also very powerful reagents in main group metal chemistry in the future. They synthesized the novel trimetallic group 13 hydride complexes $K(tmeda)_2[\{(HCNDipp)_2Ga\}_2MH_2]$ (M = Ga **444**, In **445**) by reaction of $[K(tmeda)][\{HCN(Dipp)\}_2Ga]$ with Me_3N–MH_3.[333] The reaction mechanism is still unclear, but probably occurs through the formation of the neutral intermediate $[\{(HCNDipp)_2Ga\}MH_2]$ followed by addition of $[K(tmeda)][\{HCN(Dipp)\}_2Ga]$. The compounds are remarkable since they represent the first covalently bonded metal complexes derived from an anionic gallium carbene analog. $K(tmeda)_2[\{(HCNDipp)_2Ga\}_2InH_2]$ **445** is also the first compound with a covalent Ga–In bond. The central metal atoms reside in distorted tetrahedral environments with Ga–M–Ga angles of 107.2(1)° **444** and 103.2(1)° **445**, respectively. The heterocyclic carbene fragments are essentially planar. The Ga–Ga bond distances (240.7(1) pm) are quite typical for normal covalent Ga–Ga single bonds. The Ga–In distances are significantly longer (av. 259.5 pm) due to the increased atomic radius of In compared to Ga (Figure 31).

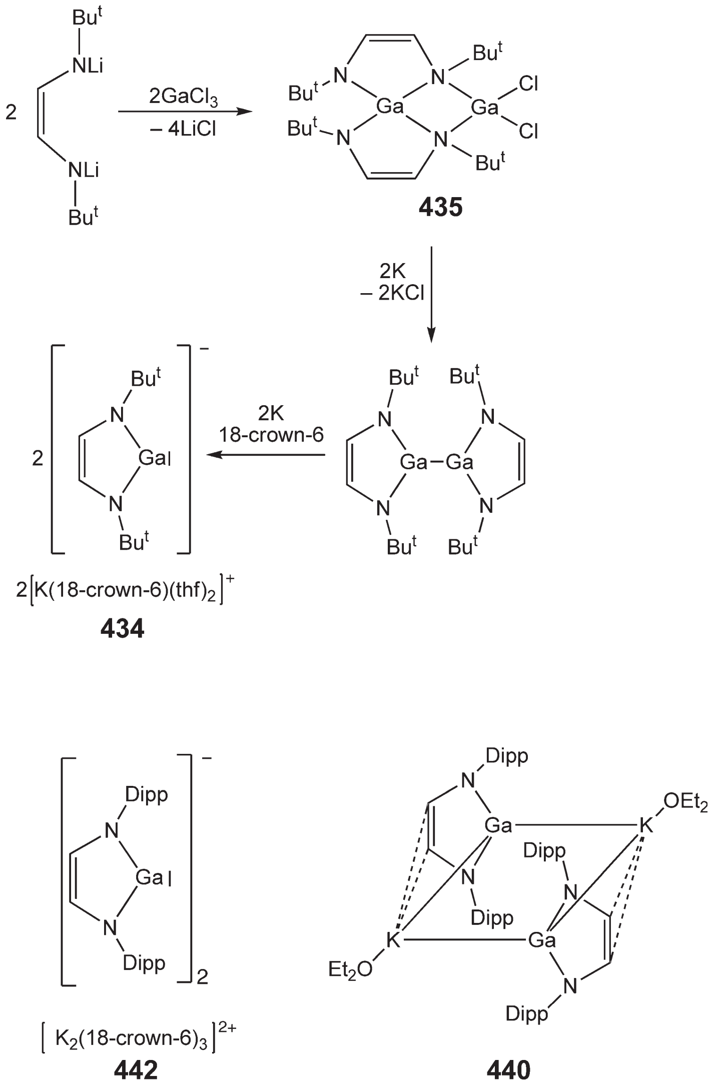

Figure 30 Synthesis of carbene analog **434** and influence of the coordinating solvent on its aggregation mode.

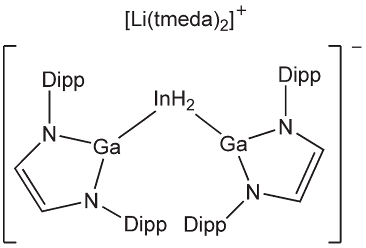

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Figure 31 Structure of the trimetallic complex **445**.

The dianionic, dinuclear compound $Na_2[(2,6\text{-}Dipp_2\text{–}C_6H_3)Ga]_2$ 446 has probably been the most controversial discussed main group organometallic compound of the last decade. Compound 446 was synthesized by Robinson *et al.* by reduction of $(2,6\text{-}Tripp_2\text{–}C_6H_3)GaCl_2$ with elemental sodium.[334] The dianion $[Ga_2R_2]^{2-}$ shows a *trans*-bent C–Ga–Ga–C backbone with C–Ga–Ga bond angles of 128.5(4)° and 133.5(4)°, respectively, and the Ga–Ga bond distance is the shortest ever observed (231.9(3) pm). In addition, there are also close interactions between the sodium cations and the aryl ligands (305.6(6)–310.6(6) pm).[335] The description of the anionic $[Ga_2R_2]^{2-}$ fragment as a "gallyne," expressing the formation of a $Ga{\equiv}Ga$ triple bond (acetylene analog), has been lively debated in the literature. According to several computational calculations, the bonding situation can be described in different ways:

(i) One π-bond and two (weak) donor–acceptor interactions between the electron lone pairs and an empty *p*-orbital of each metal center resulting in a triple bond.[336,336a]

(ii) One σ-bond, one π-bond, and a weak "slipped" π-bond yielding a triple bond with a BO less than 3 due to the weak π-bond.[337,337a]

(iii) One σ-bond and one π-bond as well as a rather non-bonding or anti-bonding π-orbital (this corresponds to the slipped π-bond as described in (ii)), the BO being 2 or even less.[338,338a]

(iv) Recent calculations show a strong influence of the alkaline metal on the Ga–Ga bond distance.[339] Consequently, the whole Na_2Ga_2 cluster has to be discussed rather than the isolated Ga–Ga bond (for additional calculations, see Refs: 340, 340a, and 340b, and references cited therein). The crucial role of the alkali metal was also experimentally shown by Power *et al.*, investigating the reaction of $(2,6\text{-}Tripp_2\text{–}C_6H_3)GaCl_2$ **176** with different alkali metals (Li, Na, K, Cs). The reaction with K did not yield the expected potassium analog $K_2[(2,6\text{-}Dipp_2\text{–}C_6H_3)Ga]_2$ **447** but the novel square-planar Ga_4 cluster $K_2[(2,6\text{-}Dipp_2\text{–}C_6H_3)_2Ga_4]$ **448**, in which only two of the four Ga atoms show an organic substituent.[335] The Ga–Ga bond distances (246.2(1) pm, 246.9(1) pm) are elongated compared to those in $Na_2[(2,6\text{-}Dipp_2\text{–}C_6H_3)Ga]_2$ **446**, and the endocyclic Ga–Ga–Ga bond angles are 87.2(1)° and 92.8(1)°. The K^+ counterions adopt non-centered positions on both sides of the four-membered ring.

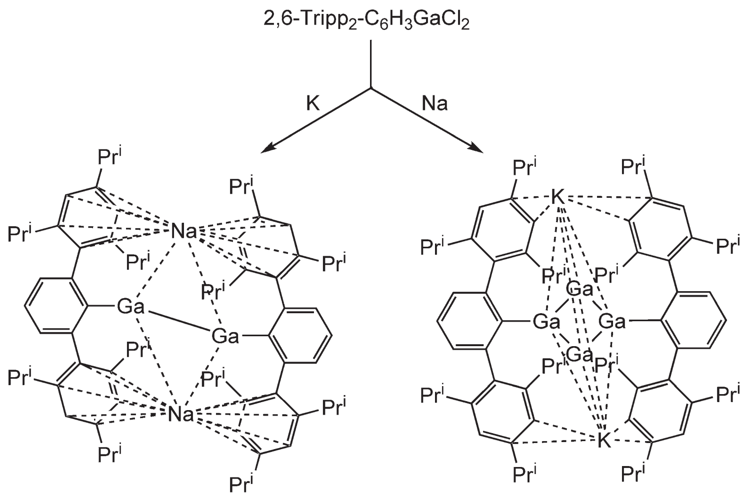
Tricyclic anionic compounds of the general type $M_2[(2,6\text{-}Mes_2\text{–}C_6H_3)Ga]_3$ (M = Na **449**,[341] K **450**[342]) have been prepared by alkali metal reduction of $(2,6\text{-}Mes_2\text{–}C_6H_3)_2GaCl$ **166**. Both compounds, which were described as metalloaromatic cyclogallenes, contain a central three-membered Ga_3 ring with the two metal atoms (Na or K) perfectly centered up and below the centroid of the ring. The Ga–Ga bonds have a formal BO of 1.33. They are longer (244.1(1) pm **449**; 242.4 pm **450** (av.)) than those observed in the radical anions $[Ga_2R_4]^{\cdot-}$ (R = Tripp 234.3(2) pm; $CHTMS_2$ 240.1(1) pm; BO 1.5), but significantly shorter than those of neutral digallanes Ga_2R_4 (BO 1.0). The endocyclic Ga–Ga–Ga bond angles are 60°. The bonding situation within the twofold negatively charged three-membered Ga_3 heterocycles, whose NICSs values (nucleus-independent chemical shifts) indicate the formation of 2π aromatic systems, was investigated in detail by computational calculations.[343,343a]

Larger cluster compounds of the type $[M_nR_n]^{x-}$ containing four (tetragallanide $Na_2(thf)_2[Bu^t_3SiGa]_4$ **451** with a butterfly-shaped framework, Section 3.07.4.1[247]), six, eight, or nine Ga atoms have also been structurally characterized. The reaction of "GaI" and $Na(thf)_3SiBu^t_3$ in toluene yielded the *closo*-hexagallanate $[(Bu^t_3Si)_4(PhCH_2)_2Ga_6]^{2-}$ **452**, whose formation obviously occurs by deprotonation through the strong basic silanide.[311] The central Ga_6 core deviates only slightly from the ideal octahedral geometry and the Ga–Ga bond distances are significantly shortened (252.9(1)–265.3(1) pm) compared to the neutral hexagallane $[TMS_2MeSiGa]_6$ **408**. The average value of 258.7 pm agrees very well to the value that was calculated for $[H_6Ga_6]^{2-}$ (258.2 pm).

The dianionic Ga_8 cluster $[Ga_8(flu)_8]^{2-}$ **453** (flu = fluorenyl) has been synthesized by salt metathesis reaction between a metastable Ga^IBr solution and fluorenyllithium.[344] The eight Ga atoms form a square antiprismatic core. This is rather unexpected because **453**, which is a *closo*-cluster according to the Wade–Mingos rules, was expected to adopt the dodecahedral structure as was observed for the corresponding boron clusters. However, computational calculations demonstrated that in the case of eight Ga atoms, the formation of a square antiprismatic structure is energetically favored (Figure 33).

Electrochemical reduction of neutral $[Bu^tGa]_9$ **409** by one electron yielded the persistent radical monoanion $[Bu^tGa]_9^{\cdot-}$ **454**.[312] The reduction was also observed when **409** was reacted with Cp_2Co.[345] The X-ray structure analysis of **454** shows significant changes within the central Ga_9 cluster core compared to **409**. Even though the central structural motif, a tricapped trigonal prism, is still unchanged, the Ga–Ga distances along the triangular faces of the prism are elongated by almost 8 pm. In contrast, the Ga–Ga distances between the triangular faces of the prisms are significantly shortened from an average value of 298.8 pm in the neutral cluster **409** to 281.9 pm in $[Bu^tGa]_9^{\cdot-}$ **454**.

Metal-poor neutral and anionic compounds of the general type $[M_nR_m]^{x-}$ ($m > n$) containing two ($[Ga_2(SiBu^t_3)_3]^{\cdot}$ **396**,[302] $[Ga_2(SiBu^t_3)_3]^{\cdot-}$ **398**[302]), three ($[Ga_3(SiBu^t_3)_4]^{\cdot}$ **400**[302], $[Ga_3(SiBu^t_3)_4]^-$ **399**,[302] $[In_3C(TMS_3)_3I_2]$ **413**[245]) and



446 **448**

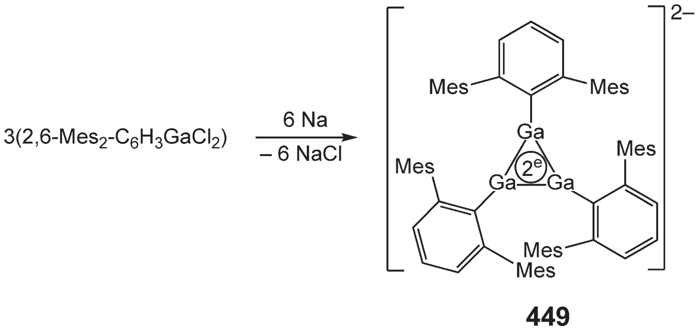


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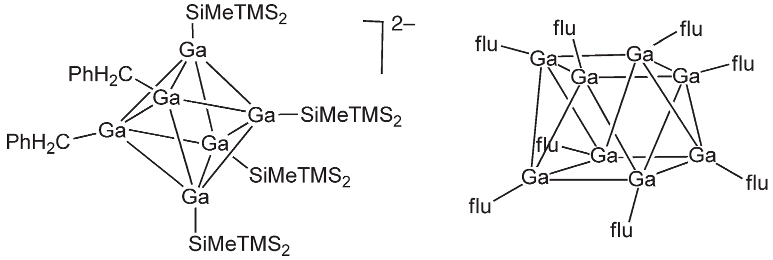
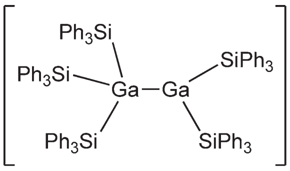
Figure 32 Syntheses and structures of dianionic di-, tri- and tetranuclear gallium compounds **446, 448**, and **449**.



452 **453**

Figure 33 Structures of the gallium cluster compounds **452** and **453**.

four metal centers ($[Ga_4(TMS_3Si)_3I_3]^-$ **418**,[318] $[Ga_4(SiTMS_3)_3I_2]$,[318] $M(MTripp_2)_3$ (M = Ga **354**,[254] In **455**[215]) have been mentioned before. Among those, several compounds have been prepared, which adopt different metal frames. The reaction of InBr and $LiCTMS_3$ yielded $[InCTMS_3]_4$ and small amounts of $[In_3C(TMS_3)_3Br_3]^-$ **456**.[346] Its structure slightly differs from that of $[In_3C(TMS_3)_3I_2]$ **413**[245] since the central In atom of the In_3 chain is attached to an additional Br atom.



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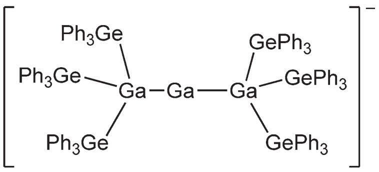

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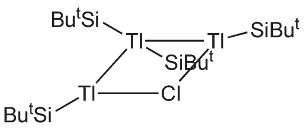
Figure 34 Synthesis and structure of anionic di- and trigallanates.

$[Ga_3(GePh_3)_6]^-$ **457**,[256] that has been prepared by reaction of “GaI” with $LiGePh_3$, consists of a three-membered, almost linear Ga_3 chain (Ga–Ga–Ga bond angle 178.8°) with both terminal Ga atoms carrying three $GePh_3$ ligands. Interestingly, the analogous reaction of “GaI” and $LiSiPh_3$ yielded the pentasilyldigallanate $[Li(thf)_4]^+[Ga_2(SiPh_3)_5]^-$ **458** (Figure 34).[256]

Probably, the most remarkable clusters of the desired type have been obtained from the reaction of $TlCl_3$ with two molar equivalents of $NaSiBu^t_3$ at low temperatures. The resulting trithallane $[Tl_3(SiBu^t_3)_4Cl]$[347] **459** and hexathallane $[Tl_6(SiBu^t_3)_6Cl_2]$ **460**[347] represent the first Tl cluster with more than two covalently linked Tl atoms. (The tetrameric $[TlCTMS_3]_4$ cluster **385** as described in Section 3.07.4.2 shows only weak Tl–Tl interactions with bond distances ranging from 332.2 to 363.8 pm.). Their formations impressively illustrate the distinguished potential of the supersilyl substituent to stabilize unusual low-valent group 13 organometallics. Even though the reaction mechanism is still not completely understood, the formation of the novel clusters most likely involves the formation of the intermediates $Bu^t_3SiTlCl_2$ and $(Bu^t_3Si)_2TlCl$. Structures **459** and **460** contain four-membered Tl_3Cl heterocycles with Tl–Tl bond distances far below 300 pm ($[Tl_3Si(TMS_3)_4Cl]$: av. 292 pm; $[Tl_6Si(TMS_3)_6Cl_2]$: av. 293 pm) (Figure 35). In **460**, two non-planar four-membered heterocycles are linked through the central Tl atom. This Tl–Tl bond distance (285.4(2) pm) is even shorter than those observed in the dithallanes Tl_2R_4 (R = $SiTMS_3$ **302**,[220] $SiBu^t_3$ **303**,[217,221] and $SiBu^t_2Ph$ **304**[218]) as described in Section 3.07.4.1, which range from 288 to 296 pm.

The anionic Ga_6 cluster $[Li(thf)_4]_2[Ga_6(SiMePh_2)_8]^{2-}$ **461** was synthesized by reaction of GaBr and $LiSiMePh_2$ in THF/toluene.[348] Surprisingly, the six Ga atoms do not adopt the expected octahedral geometry but a planar frame (C_{2h} symmetry). Four Ga atoms carry two $SiMePh_2$ substituents, whereas the remaining two Ga centers are “naked.” DFT calculations verified that this rather unexpected planar arrangement, which is precedenceless in boron chemistry, is energetically more favored, whereas the corresponding B and Al species tend to form octahedral clusters. Obviously, the Wade–Mingos rules are too general and cannot predict the correct structure for each group 13 element cluster.

The novel disiladigalletane $[TMS_3SiGaSiTMS_2]_2$ **462** and silatrigalletane $[Li(thf)_4][(TMS_3SiGa)_2(TMS_3Si(TMS)Ga)(SiTMS_2)]$ **463** have been obtained from the reactions of $Ga_2X_4(dioxane)_2$ (X = Cl, Br) with 4 equiv. of $TMS_3SiLi(thf)_3$.[349] In addition, the silatetragallane $[(TMS_3SiGa)_3(TMSGa)(TMSSi)]$ **464** was formed when “Ga_2I_3” was reacted with $TMS_3SiLi(thf)_3$.[350] Compounds **462** and **463** adopt heterocyclic structures, whereas the central Ga_4Si core of **464** consists of a C_3-symmetrical trigonal–bipyramidal geometry (Figure 36).



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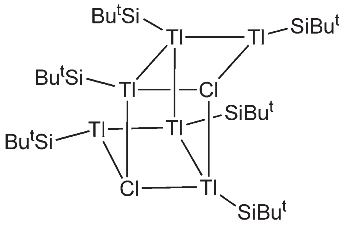

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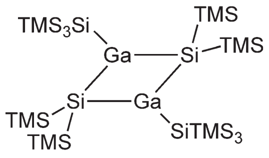
Figure 35 Structure of two novel tri- and hexathallanes.



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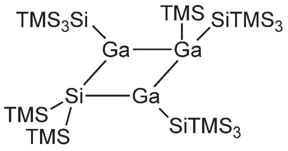

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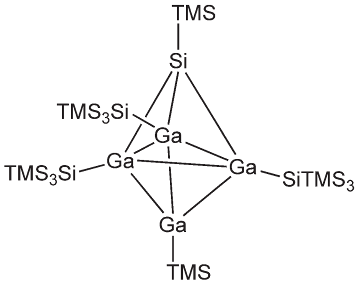

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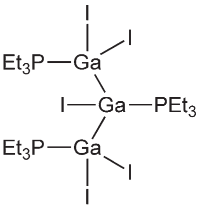
Figure 36 Structure of several silagalletanes.

3.07.4.4 Neutral and Anionic Compounds $[M_nR_m]^{x-}$ ($m < n$) with an Oxidation State between 0 and I

The clusters described so far have in common, that the number of metal atoms is less or equal than the number of substituents. However, there is a still growing number of both neutral and anionic clusters in which the number of metal atoms is larger than the number of substituents. As a consequence, these metal-rich clusters contain "naked" metal centers which are only bonded to other metal centers. Schnöckel referred these ones to as metalloid clusters. Several metalloid Al and Ga clusters were prepared by standard salt elimination reactions using metastable solutions of metal subhalides MX (M = Al, Ga; X = Cl, Br) as well as solutions of "GaI." Since the metal subhalides were found to play the key role for the successful synthesis of this particular class of compounds, they will be discussed first. (For excellent review articles see Refs: 273 and 274.)

Low-valent subhalides. Even though gallium and indium subhalides MX have been demonstrated in the last decade to be valuable starting reagents for the synthesis of low-valent metal clusters, there is only scarcely knowledge on their solid-state structures. (The structure of metal subhalides in solution not necessarily corresponds to that observed in the solid state.) This is in sharp contrast to donor-stabilized digallanes and diindanes of the general type $M_2X_4(donor)_2$, which have been structurally characterized in large numbers (see Section 3.07.4.1). Only a handful reports on the solid-state structures of gallium subhalides GaX, which of course are expected to be strongly dependent on the coordinating solvent, have been reported. The first compound, obtained from a metastabile GaX solution, was $Ga_5Cl_7(OEt_2)_5$ **465**.[351] Structure **465** was formed after crystallization of a $GaCl/Et_2O$ solution at −30 °C. Its central metal framework consists of a central Ga atom, that is bonded to three $GaCl_2(Et_2O)$ units and to a single $GaCl(OEt_2)_2$ group. Consequently, **465** can be described as a mixed-valent compound containing one Ga(0), one Ga(I), and three Ga(II) centers (av. oxidation state 1.4). The Ga–Ga bond distances differ slightly from about 242 pm (Ga(0)–Ga(II) bonds) to 245 pm (Ga(0)–Ga(I) bond). The formation of **465**, which decomposes above 0 °C, perfectly illustrates the tendency of gallium monohalides GaX to disproportionate into Ga(0) and Ga(II), which of course is the basic concept of metalloid cluster synthesis. Very recently, the Schnöckel group reported on the X-ray structures of four additional donor-stabilized Ga_5X_7 molecules ($Ga_5Br_7(thf)_5$ **466**, $Ga_5X_7(NHEt_2)_5$ (X = Cl **467**, Br **468**), $Ga_5Cl_7(NEt_3)_4$ **469**).[352] Each cluster adopts a structure similar to that of $Ga_5Cl_7(OEt_2)_5$ except for **469**, which features only four donor molecules and one bridging Cl atoms.

An even smaller compound, $Ga_3I_5(PEt_3)_3$ **470** (av. oxidation number 1.7), was obtained by treatment of a solution of GaI with PEt_3.[353] The compound features a Ga_3 chain (Ga–Ga–Ga bond angle 121.9°) with two terminal $GaI_2(PEt_3)$ moieties with a formal oxidation state II, whereas the central Ga atom carries one iodine and one donor molecule (Ga(I)). The Ga–Ga bond lengths (av. 245.6 pm) in **470** are similar to those observed in $Ga_5Cl_7(OEt_2)_5$.



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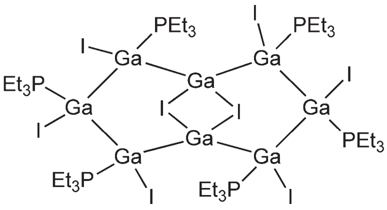

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Figure 37 Structures of two Lewis base-stabilized gallium subhalides **470** and **471**.

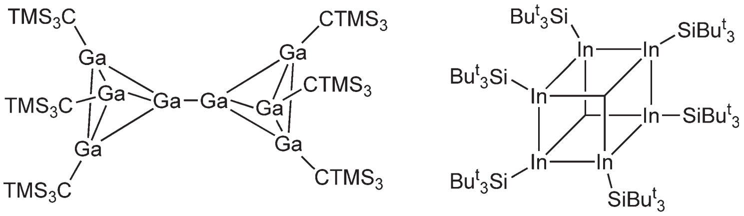
The first "real" GaI subhalide was crystallized from a GaI/PEt$_3$ solution at −50 °C. The rather unexpected product, Ga$_8$I$_8$(PEt$_3$)$_6$ **471**,[228] contains a planar Ga$_8$ heterocycle with four-coordinate Ga atoms. Six iodine atoms and six phosphane molecules are terminal bonded to six Ga centers, whereas the remaining two iodines form transannular bridges between the remaining Ga atoms. The Ga–Ga bond distances (av. 247 pm) are only slightly longer than those in **470** (Figure 37).

Co-condensation of GaBr and toluene/4-Bu^t-pyridine (donor) yielded Ga$_{10}$Br$_{10}$(donor)$_{10}$ **472**, which contains a central Ga$_6$ ring.[354] The average oxidation number of the Ga atoms in the cluster is I, but the electronic structure is better described as a mixed-valent compound (4 Ga(0), 2 Ga(I), 4 Ga(II)). Two of the Ga(0) centers are "naked" since they only bind two further Ga atoms. The Ga–Ga bond lengths within the six-membered ring range from 245.1 to 249.3 pm, whereas those to the terminal GaBr$_2$(donor) units are slightly shorter (av. 243.8 pm). According to DFT calculations, **472** is formed by reaction of two Ga$_5$Br$_7$ units with an excess of GaBr(donor) and subsequent elimination of GaBr$_3$(donor). This reaction is strongly exothermic by −135 kJ mol^{-1}. The GaBr$_3$(donor) molecules react with additional GaBr(donor) molecules with formation of Ga$_5$Br$_7$ as was previously demonstrated for the formation of Al$_5$X$_7$ species.[355] Interestingly, if 4-Bu^t-pyridine is replaced by the weaker electron donor THF, further reduction reactions of Ga$_{10}$Br$_{10}$(thf)$_{10}$ with GaBr(thf) occur with subsequent formation of additional Ga–Ga bonds. Finally, the first polyhedral gallium subhalide Ga$_{24}$Br$_{22}$(thf)$_{10}$ **473** was obtaioned.[356] This reaction is exothermic by −560 kJ mol^{-1}. Cluster **473** contains a central Ga$_{12}$ icosahedra with Ga–Ga bond distances ranging from 255 to 267 pm. Each Ga atom binds to an additional Ga atom by a 2c–2e bond (av. Ga–Ga 240 pm). The opposing apical Ga atoms of this outer Ga$_{12}$ shell each carry three Br atoms, with two of them shared with two neighboring Ga atoms. The other Ga atoms are each connected to two bromines. Structure **473** represents a metalloid Ga subhalide, which of course became available in larger numbers in form of organometallic derivatives as will be shown in the following section.

Metalloid clusters.[357] Metal subhalides MX generally tend to disproportionate into elemental metal (M(0)) and M(II) and M(III) species. This particular reaction pattern can be used for the synthesis of novel neutral and anionic metalloid clusters of the general type $[M_nR_m]^{x-}$ with more metal atoms than organic substutuents ($m < n$), "simply" by tracking the intermediately formed gallium subhalides by reaction with organometallics. As a result, kinetically stabilized metal cores are formed, whose structures often correspond to the structural subunits found for the elemental metal. Consequently, large structural variations were observed for metalloid gallium clusters since gallium is known to adopt seven different solid-state modifications.[357]

Metastable solutions of GaX (X = Cl, Br) as well as conventionally prepared "GaI" react with lithium or sodium organometallics in standard salt metathesis reactions with formation of M$_2$R$_4$ (Section 3.07.4.1) as well as neutral and anionic clusters of the type $[M_nR_m]^{x-}$ ($m \geq n$) (chapter 4.1). Moreover, metalloid clusters $[M_nR_m]^{x-}$ ($m < n$), which feature different types of metallic core structures, have been obtained. Their formation strongly depends on the reaction conditions, in particular the reaction temperature, and the (donor) solvent.

The smallest metalloid cluster of the desired type was obtained from the reaction of [(2,6-Tripp$_2$–C$_6$H$_3$)GaCl$_2$]$_2$ with K. Only two Ga atoms in the resulting square-planar Ga$_4$ cluster K$_2$[(2,6-Dipp$_2$–C$_6$H$_3$)$_2$Ga$_4$] **448** are bonded to an organic substituent (Section 3.07.4.3).[335] Larger metalloid Ga and In clusters containing six ([Ga$_6$(SiPh$_2$Me)$_8$]$^{2-}$ **474**), eight ([Ga$_8$(SiBu$^t_3$)$_6$] **475**,[358] [Ga$_8$(SiBu$^t_3$)$_6$]$^{2-}$ **476**,[358] [Ga$_8$(CTMS$_3$)$_6$] **477**,[359] [In$_8$(SiBu$^t_3$)$_6$] **478**,[360] [In$_8$(2,6-Mes$_2$–C$_6$H$_3$)$_4$] **479**[361])(Figure 38), nine ([Ga$_9$(SiTMS$_3$)$_6$]$^-$ **480**[318]), 10 ([Ga$_{10}$(SiTMS$_3$)$_6$] **481**,[259] [Ga$_{10}$(SiBu$^t_3$)$_6$]$^-$ **482**[259]), 11 ([Ga$_{11}$(2,6-Mes$_2$–C$_6$H$_3$)]$_4$ **483**[362]), 12 ([Ga$_{12}$(flu)$_{10}$]$^{2-}$ **484**,[363] [In$_{12}$(SiBu$^t_3$)$_8$] **485**[364]), 13 ([Ga$_{13}$(SiBu$^t_3$)$_6$]$^-$ **486**,[259] [Ga$_{13}$(SiTMS$_3$)$_6$]$^-$ **487**[365]), 16 ([Ga$_{16}$(μ_2-PBu$^t_2$)$_6$(PBu$^t_2$)$_4$] **488**[366]), 18 ([Ga$_{18}$(SiBu$^t_3$)$_8$] **489**[367]), 19 ([Ga$_{19}$(CTMS$_3$)$_6$]$^-$ **490**[368]), 22 ([Ga$_{22}$(SiBu$^t_3$)$_8$] **491**,[367] [Ga$_{22}$(SiTMS$_3$)$_8$] **492**,[369] [Ga$_{22}$(GeTMS$_3$)$_8$] **493**,[370]



477 **478**

Figure 38 Different structures of two M_8R_6 clusters.

$[Ga_{22}(NTMS_2)_{10}]^{2-}$ **494**[371]), and even 26 metal centers ($[Ga_{26}(SiTMS_3)_8]^{2-}$ **495**[372]) have been synthesized and structurally characterized. Moreover, three giant subvalent gallium clusters containing 51 ($[Ga_{51}(PBu^t{}_2)_{14}Br_6]^{3-}$ **496**[373]) and 84 Ga atoms $[Ga_{84}(NTMS_2)_{20}]^{x-}$ ($x = 3$ **497**,[374] 4 **498**[375]) have been isolated. Structures **497** and **498** represent the largest group 13 element metalloid clusters ever structurally characterized. The metalloid clusters, in particular the large Ga clusters, very often feature similarities to structural subunits of gallium modifications. These findings indicate that metalloid clusters are kinetically stabilized reaction intermediates of the disproportionation reaction of GaX toward elemental Ga.

The Ga_6 cluster $Ga_6(SiPh_2Me)_8]^{2-}$ **474** is somewhat special because it is the only compound that contains more organic substituents than metal atoms. However, it is also a metalloid cluster since it features two “naked” metal centers, whereas the remaining four each bind to two organic substituents. Interestingly, the Ga atoms adopt a ladder-like structure rather than a polyhedral structure. A comparable ladder-type arrangement of Ga atoms is observed in the solid-state structure of β-gallium. Many of the metalloid clusters described here (as well as neutral/anionic $[M_nR_n]$ cluster) exhibit structures of simple or fused deltahedra as observed in boron chemistry and the Wade–Mingos $(2n + 2)$ and Jemmis $(2n + 2m)$ electron-counting rules can be applied to most of them.[376] However, some structures based on fused deltahedra or supraicosahedral deltahedra such as $[In_8(SiBu^t{}_3)_6]$ **478**,[360] $[Ga_9Bu^t{}_9]$ **409**,[312] $[Ga_{22}R_8]$ ($R = SiBu^t{}_3$ **491**,[367] $SiTMS_3$ **492**,[369] $GeTMS_3$ **493**[370]) and $[Ga_{26}(SiTMS_3)_8]^{2-}$ **495**[372] are precedenceless in boron chemistry, indicating an increased structural diversity in gallium cluster chemistry compared to boron.

The Ga_8 cluster $[Ga_8(CTMS_3)_6]$ **477**,[359] which is an intermediate of the formation of $[Ga_{19}(CTMS_3)_6]^-$ **490**,[368] features probably the most surprising Ga arrangement. It contains two Ga_4 tetrahedra, which are connected via a Ga–Ga single bond (361.4(2) pm). The Ga–Ga bond distances within the Ga_4 tetrahedra (260.5(1)–264.8(1) pm) are significantly shorter than those in $[GaCTMS_3]_4$ **383** (av. 268.3 pm). The central Ga_2 moiety only shows metal–metal bonds to surrounding Ga atoms. Therefore, **477** can be interpreted as the first model compound for a metal atom contact in the form of a nano-metal wire.[377] In contrast, the In_8 clusters $[In_8(SiBu^t{}_3)_6]$ **478**[360] and $[In_8(2,6\text{-}Mes_2\text{–}C_6H_3)_4]$ **479**[361] adopt cubane-like geometries. Compound **478** is surrounded by six organic substituents, adopting a distorted octahedral arrangement, whereas the central metal core of **479** is stabilized by only four substituents. The In–In bond distances range from 277.0(1) to 330.3(1) pm **478** and 285.7(4) to 296.6(4) pm **479**, which is significantly shorter than those observed in elemental indium (325–338 pm).

$[Ga_{12}(flu)_{10}]^{2-}$ **484**[363] and $[In_{12}(SiBu^t{}_3)_8]$ **485**[364] both contain 12 metal centers, but their structures differ significantly. The metal atoms of **484** form an almost regular icosahedron with ten fluorenyl ligands bound to ten Ga atoms and two “naked” Ga centers. The Ga–Ga bond distances range from 258.9 to 268.4 pm. However, even though the geometrical arrangement is comparable to that in $[B_{12}H_{12}]^{2-}$, the bonding situation differs significantly. In **484**, the metal core is held together by only 26 electrons compared to 28 for the (closo-type) borane. According to DFT calculations, the framework molecular orbitals of **484** are more diffuse, indicating a more metalloid character compared to the borane. In contrast, the metal atoms in **485**[364] adopt an elipsoid-like polyhedral structure. The bulky $SiBu^t{}_3$ groups are bonded to the terminal In atoms (2 × 4), whereas the remaining four In atoms carry no substituents. The particular geometrical arrangement of the 12 In atoms in **485**, which can be described as a *conjuncto*-indane, was also observed in elemental indium.

The structurally characterized Ga_{18}, Ga_{22}, and Ga_{26} clusters as mentioned before each contain a shell of eight organic ligands, which stabilize the metalloid core. In each cluster, the eight Ga atoms, which bind to the organic substituents, form a square antiprism. In contrast, the metallic frameworks of the clusters differ significantly. In $[Ga_{18}(SiBu^t{}_3)_8]$ **489**,[367] the Ga atoms form a polyhedral cluster (Ga–Ga 250–300 pm), which shows a structural arrangement as was observed in β-Ga. In contrast, the Ga_{22} clusters $[Ga_{22}R_8]$ ($R = SiBu^t{}_3$ **491**,[367] $SiTMS_3$ **492**,[369] $GeTMS_3$ **493**[370]) contain a central Ga atom, that is surrounded by 13 Ga atoms. The average Ga–Ga bond distance between the central Ga atom and the Ga_{13} shell of 293.5 pm is longer than the average "innershell" Ga–Ga bond lengths (av. 284.3 pm). The metal core in $[Ga_{26}(SiTMS_3)_8]^{2-}$ **495** contains a central Ga atom, that is surrounded by a distorted square prism of eight Ga atoms (Ga–Ga 278.5–286.6 pm). Three of the four faces of this prism are capped by one Ga atom. The remaining one is capped by a Ga_2 unit, which shows a short Ga–Ga distance of 260.9 pm, thus yielding a "cuboctahedral" environment for the central Ga atom. A similar arrangement was observed in the Ga(III) high-pressure modification.

Even larger metalloid Ga clusters, $[Ga_{51}(PBu^t{}_2)_{14}Br_6]^{3-}$ **496**[373] and $[Ga_{84}(NTMS_2)_{20}]^{x-}$ ($x = 3$ **497**,[374] 4 **498**[375]), were obtained from reactions of GaBr with $LiPBu^t{}_2$ and $LiNTMS_2$, respectively. (Supply of structural plots of both clusters by Prof. H. Schnöckel is gratefully acknowledged.) The clusters contain 20 ligand-bearing Ga atoms as well as 31 and 64, respectively, naked metal atoms. The cluster framework of **496** consists of a central Ga atom, that is surrounded in a cuboctahedral fashion by 12 Ga centers (Ga–Ga 276.3–292.2 pm). Ga_5 units cap the six square planes of the cuboctahedron. One plane of the resulting square antiprismatic moiety is capped by a $GaPBu^t{}_2$ unit. Compounds **497** and **498** (Figure 39) represent the largest structurally characterized metalloid clusters. They consist of a central Ga_2 unit, which is surrounded by 32 Ga atoms, forming a rugby ball-shaped geometry with an average Ga–Ga bond distance of 275.6 pm. The Ga–Ga bond lengths observed in the Ga_2 hantles (234 pm) are very short. The Ga_{32} subunits consist of two icosahedral Ga_{11} moieties (Ga–Ga 261.2–281.4 pm), which exhibit some structural similarities to the icosahedral substructure of δ-gallium. They are connected through a puckered Ga_{10} ring. The remaining 30 Ga atoms cover the rugby ball unit in a meandering way with a medium Ga–Ga bond distance of 275.6 pm. The novel Ga_{84} clusters **497** and **498** (Figure 40) not only show fascinating structural features, but are also very interesting due to their electronic properties since they show metallic conductivity[378] and even superconductivity.[379]

3.07.5 Organometallics Containing Heteroatomic Groups of Groups 15 and 16

3.07.5.1 Introduction

The interest in compounds containing regular 2e–2c bonds between group 13 metals and elements of groups 15 and 16, respectively, has continued throughout the last decade. These studies have been motivated by fundamental questions concerning the synthesis, structure, and reactivity of group 13/15 compounds, which are basically of pure academic interest. Of particular interest has been the search for compounds, which feature unusual bonding situations. Consequently, the synthesis of multiple-bonded species and of quasi(anti)aromatic complexes has been studied in detail. In addition, the interest in novel "single source precursor" for the deposition of semiconducting

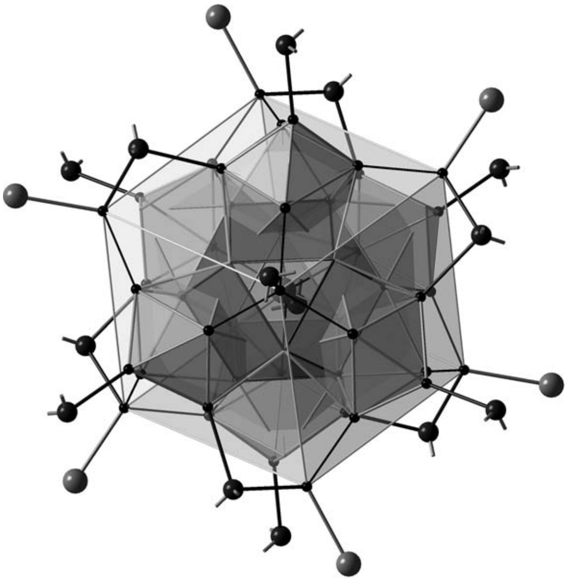


Figure 39 Structure of the Ga_{51}-cluster **496**.

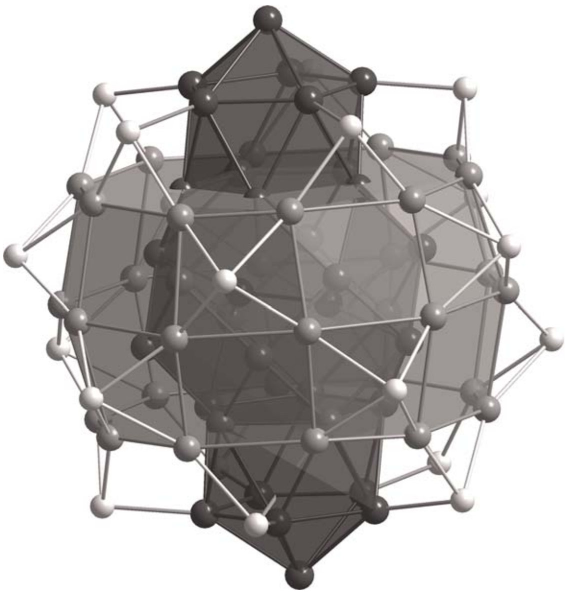


Figure 40 Structure of the largest metalloid group 13 element cluster **498** containing 84 Ga atoms.

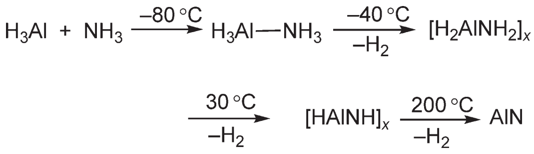
III–V and III–VI material films,[380–384] which exhibit potential applications in opto- and micro-electronic devices, by MOCVD processes has led to the synthesis of novel heteroatomic complexes including the heavier elements of groups 15 (Sb, Bi) and 16 (Se, Te). These have been only scarcely known before, but are now available due to the exploration of novel synthetic strategies.

3.07.5.2 Group 13–15 Complexes (N, P, As, Sb, and Bi)

An early study by Wiberg *et al.* almost 50 years ago perfectly illustrates the full range of group 13/15 chemistry.[385] The reaction of AlH_3 and NH_3 initially yields the Lewis acid–base adduct $H_3Al–NH_3$ (type I) followed by stepwise elimination of methane and subsequent formation of aminoalanes $[R_2AlNH_2]_x$ (type II) and iminoalanes $[RAlNH]_x$ (type III). Finally, AlN forms at higher temperature (Figure 41).

This reaction scheme has been generally applied in group 13/15 chemistry, and numerous compounds of types I, II, ands III, in particular amine adducts[75,75a–75c] and amides have been synthesized. (Lewis acid–base adducts of the types $R_3M–ER'_3$ and $H_xMR_{3-x}–ER'_3$ (R, R′ = alkyl, aryl) have already been described in Section 3.07.2, whereas the chemistry of group 13 amides has recently been reviewed.[387]) Unfortunately, complexes containing the heavier elements of group 15, Sb and Bi, are not available by this reaction pathway. Sb–H and Bi–H moieties in general feature a different reactivity since they are rather hydridic than protic in nature. However, tremendous improvements on the synthesis of this specific class of compounds have been made in the last decade due to the development of novel reaction pathways. In the following, the different types of compounds (Lewis acid–base adducts, heterocycles, clusters) are summarized.

Lewis acid–base adducts $R_3M–EH_xR_{3-x}$ ($x = 1, 2, 3$). Adducts of the type $R_3M–EHR'_2$ (R, R′ = H, alkyl, aryl), which are initially formed according to the Wiberg scheme, have been isolated at relatively low temperatures in

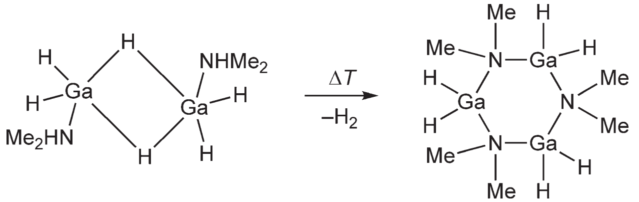


$$H_3Al + NH_3 \xrightarrow{-80\,°C} H_3Al—NH_3 \xrightarrow[-H_2]{-40\,°C} [H_2AlNH_2]_x \xrightarrow[-H_2]{30\,°C} [HAlNH]_x \xrightarrow[-H_2]{200\,°C} AlN$$

Figure 41 Reaction scheme for the reaction of alane AlH_3 and NH_3.

order to prevent the elimination of H_2 or RH. This particular class of compounds is almost exclusively limited to gallane and indane adducts of primary amines ($Bu^t_3Ga–NH_2CC(Me)_2CH_2NH_2$ **499**,[388] $Bu^t_3Ga–NH_2CC(Me)_2CH_2NH_2–GaBu^t_3$ **500**,[388] *o*-$OMe–C_6H_4$-$CH_2NH_2–GaMe_3$ **501**,[389] $Me_3Ga–NH_2Bu^t$ **502**,[390] $MeO(CH_2)_3NH_2–GaMe_3$ **503**,[391] $Me_3Ga–NH_2(CH_2)_2NH_2–GaMe_3$ **504**,[392] $Me_3In–NH_2Bu^t$ **505**[390]) and secondary amines ($Me_3Ga–NH(CH_2)_4$ **506**,[393] $Me_3M–NH(Bz)_2$ (M = Ga **507**, In **508**,[394] $H_3Ga–NH(Me)_2$ **509**[395]). In contrast, comparable adducts of the heavier group 15 elements are almost unknown.[396] Of particular interest is $[H_3Ga–NH(Me)_2]_2$ **510**, which was isolated as crystalline solid at −70 °C. Adduct **510** loses H_2 at higher temperature with subsequent formation of trimeric dimethylamidogallane $[H_2GaNMe_2]_3$ **511** (Figure 42).[395] Compound **510**, which is a liquid at ambient temperature, adopts an unsymmetrical dimeric, H-bridged structure with five-coordinate Ga atoms in the solid state. The Ga–H bond distances to the bridging H atoms differ significantly (150(3), 287(5) pm), indicating only weak Ga· · ·H interactions. Comparable findings were observed for alane and gallane adducts. In contrast, alkyl-substituted adducts $R_3M–ER'_3$ (R, R′ = alkyl, aryl) typically show the central atoms in tetrahedral environments (see Section 3.07.2).

Monomeric and heterocyclic compounds $[R_2MEH_2]_x$. Monomeric $R_2M–ER'_2$ compounds have received considerable attention due to their formal double bonding character, resulting from dative π-interactions of the electron lone pair of the group 15 element and the empty *p*-orbital at the group 13 metal. Unfortunately, these monomers tend to stabilize intermolecularly by formation of head-to-tail adducts, resulting in the formation of four- and six-membered heterocycles. However, monomeric species can be kinetically stabilized by use of sterically demanding substituents. Several monomeric gallium and indium amides ($Bu^t_2GaN(SiPh_3)Ada$ (Ada = adamantyl) **512** (For an excellent review on multiple bonding in main group element compounds, see Ref: 298a),[397] $Bu^t_2GaN(SiPh_3)Bu^t$ **513**,[397] $Tripp_2GaN(H)Dipp$ **514**,[397] $Tripp_2GaNPh_2$ **515**,[397] $Mes^*_2GaN(H)Ph$ **516**,[398] $Mes^*(Cl)GaN(H)Ph$ **517**,[398] $Mes^*(Cl)GaNTMS_2$ **518**,[399] $Me_2InNC_4Me_4$ **519**,[400] $Bu^t_2InN(SiPh_3)Dipp$ **520**[401]), phosphides (tmp_2GaPRR' (R = H, R′ = Mes **521**, Bu^t **522**; R, R′ = Bu^t **523**,[402] $Mes_2GaPBu^t_2$ **524** (Figure 43),[402] $Bu^t_2GaP(SiPh_3)TMS$ **525**,[403] $Bu^t_2GaP(SiPh_3)Tripp$ **526**[403]) and arsenides ($Bu^t_2GaAs(SiPh_3)CH(TMS)_2$ **527**[403]) have been structurally characterized in the last decade. In contrast, no monomeric Tl-containing derivative as well as group 13 metal stibides and bismuthides in general have been prepared, to date. Structural, spectroscopic and computational data of the



510 **511**

Figure 42 Structures of the dimeric amine-gallane adduct **510** and the aminogallane **511**.

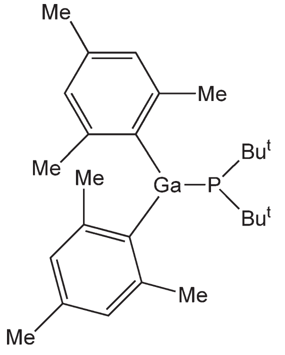


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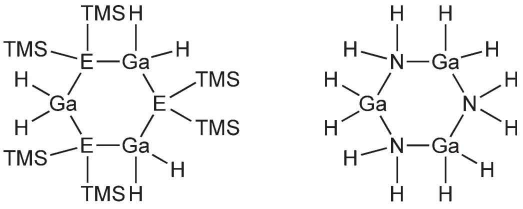
Figure 43 Structure of a monomeric phosphinogallane.

monomeric compounds clearly revealed the absence of any double-bonding character. Planar coordination geometry at both atoms, which is an essential requirement for effective π-bonding, is generally not observed due to the significantly larger inversion barriers of the heavier group 15 elements P, As, Sb, and Bi. Only amides exhibit in same cases a planar coordination sphere at the N center, but even they show small rotation barriers around the M–N bond as well as only marginally shorter M–N bond distances, indicating no strong π-bonding.

Among base-free monomeric compounds, a handful donor-stabilized monomeric species of the general type donor-$MR_2ER'_2$, in which the Lewis-acidic group 13 metal is either intramolecularly ($MeGa(C_5Me_4\text{-}2\text{-}SiMe_2NBu^t)$ **528**,[404] $Me_2M(2,5\text{-}CH_2NMe_2\text{–}pyrrole)$ (M = Ga **529**, In **530**)[405]) or intermolecularly (dmap–$GaMe_2ETMS_2$ (E = P **531**, As **532**),[406] dmap–$GaEt_2SbTMS_2$ **533**,[407] quin-GaH_2NTMS **534**[170]) stabilized by a Lewis base, have been synthesized. The dmap-stabilized compounds have been successfully introduced as main group element ligands for transition metal complexes.[406]

Heterocyclic complexes $[R_2MER'_2]_x$ have been synthesized in much larger number in the last decade. The ring size of the complexes (four- vs. six-membered rings) depends on the interplay of the atomic radii of the central atoms and the steric demand of the organic substituents. Large substituents strongly favor the formation of four-membered rings, whereas small substituents typically yield six-membered heterocycles.[408] Numerous four-membered amidogallanes and -indanes (Ga: $[H_2GaNR_2]_2$ (R = Et **535**,[409] $(CH_2)_5$ **536**,[410] $H/CH_2CMe_2CH_2NMe_2$ **537**[411]), $[Me_2GaN(H)R]_2$ (R = Bz **538**,[412] allyl **539**,[413] $SiEt_3$ **540**[414]), $[Cy_2GaN(H)R]_2$ (R = Ph **541**,[415] Bu^t **542**[415]), $[Me_2GaNR_2]_2$ (R = Cy **543**,[416] Ph **544**,[417] Bz **545**,[418] $Si(H)Me_2$ **546**,[419] Ph/TMS **547**[420]), $[Me_2GaNR]_2$ (R = $(C_2(H)_2Me_2)$ **548**,[393] $[(CH_2)_4]_2$ **549**[393]), $[Et_2GaNR_2]_2$ (R = Bu^i **550**,[416] Cy **551**[416]), $[Bu^t(R)GaNEt_2]_2$ (R = H **552**, Cl **553**)[421], $[Bu^t{}_2GaNMe_2]_2$ **554**,[422] $[(Ph(Me_2)CCH_2)_2GaN(H)R]_2$ (R = Ph **555**, Bu^t **556**)[423], $[R_2GaN(H)Bu^t]_2$ (R = Pr^i **557**,[424] Bu^t **558**,[425] Bz **559**,[128] Mes/Cl **560**[424]), $[Cl_2GaN(H)R]_2$ (R = Bu^t **561**,[426,427] $SiMe_2Ph$ **562**[428]); In: $[Me_2InN(H)R]_2$ (R = Pr^i **563**,[429] Bu^t **564**,[430] Bz **565**,[412] 2-Ph-C_6H_4 **566**[431]), $[Me_2InN(Me)TMS]_2$ **567**,[432] $[Bu^t{}_2InNR_2]_2$ (R = Et **568**, Bu **569**)[433]), phosphidogallanes and -indanes (Ga: $[R_2GaPTMS_2]_2$ (R = Me **570**,[434] Et **571**,[435] Bu **572**,[436] $TMSCH_2$ **573**,[437] *neo*-Pent **574**,[144] *neo*-Pent/Cl **575**,[144] *neo*-Pent/Br **576**,[144] Cl **577**,[438] Br **578**,[439] I **579**[440]), $[Bu^t{}_2GaP(H)Bu^t]_2$ **580**,[441,441a] $[R_2GaPBu^t{}_2]_2$ (R = Et **581**,[442] vinyl **582**,[443] $CH_2C(H)MeEt$ **583**[444]), [*neo*-$Pent_2GaPR_2]_2$ (R = Et **584**, Cy **585**[445]; In: $[Bu^t{}_2InP(H)TMS]_2$ **586**,[446] $[R_2InPTMS_2]_2$ (R = Me **587**,[408] Et **588**,[447] *neo*-Pent **589**,[448] *neo*-Pent/Me **590**,[448] Ph **591**,[449] R/CH_2TMS (R = Me **592**, Cl **593**)[450]), $[R_2InPBu^t{}_2]_2$ (R = *neo*-Pent **594**,[451] $CH_2C(H)MeEt$ **595**,[444] Bz **596**,[442] allyl **597**,[442] vinyl **598**,[442] *neo*-Pent **599**,[452] R/Cl (R = Pr^i **600**, CH_2TMS **601**)[453]), [*neo*-$Pent_2InPR_2]_2$ (R = Et **602**,[454] Pr^i **603**[455])), and arsenidogallanes and -indanes (Ga: $[R_2GaAsTMS_2]_2$ (R = Me **604**,[456,408] Et **605**,[435,457] I **606**[440]), $[R_2GaAsBu^t{}_2]_2$ (R = allyl **607**,[442] Bz **608**,[442] vinyl **609**,[442] vinyl/Cl **610**,[442] Pr^i/Cl **611**[458]); In: $[R_2InAsBu^t{}_2]_2$ (R = $(CH_2)_4$ **612**,[459] Bz **613**,[458] Cl **614**[460]), $[R_2InAsTMS_2]_2$ (R = Me **615**,[408] Et **616**,[447] Ph **617**,[449] *neo*-Pent **618**,[461] CH_2TMS **619**,[462] R/CH_2TMS (R = Ph **620**, Me **621**)[450]) have been structurally characterized. X-ray structure analyses unexceptionally show the central group 13/15 elements in distorted tetrahedral environments. Compared to monomeric compounds of the type $R_2MER'_2$, the central M–E bond distances within the heterocycles are elongated, which most likely result from the higher coordination number (4 vs. 3). In addition, a few six-membered group 13 amides (Ga: $[H_2GaNR_2]_3$ (R = H 622,[463,463a] Me 623[395]), $[Bu^t{}_2GaNH_2]_3$ 624[464]), phosphides (Ga: $[H_2GaPR_2]_3$ (R = Cy **625**,[465] TMS 626[466]), [*neo*-$Pent(Cl)GaPPh_2]_3$ 627,[467] $[Me_2GaPR_2]_3$ (R = Me/Ph **628**,[468] TMS **629**[469]); In: $[H_2InPCy_2]_3$ **630**,[470] $[Bu^t{}_2InPH_2]_3$ **631**,[446] $[R_2InPPh_2]_3$ (R = Me **632**,[471] Pr^i **633**,[472] Bz **634**[472]), [*neo*-$Pent_2InP(H)Ph]_3$ **635**[454]), and arsenides (Ga: $[H_2GaAsTMS_2]_3$ 636[466]) have been prepared in the last decade. The isolation and structural characterization of H-substituted derivatives such as $[H_2GaETMS_2]_3$ (E = P 626, As 636),[466] $[Bu^t{}_2InPH_2]_3$ **631**,[446] and $[H_2GaNH_2]_3$ 622,[463,463a] the probably most interesting compound, deserves particular attention since these are very reactive compounds which typically undergo further reactions with elimination of H_2 or RH. They were also successfully used for the synthesis of nanocrystalline materials such as GaN,[473,473a] GaP[466] and GaAs (Figure 44).[466]

Heterocyclic amido-, phosphido-, and arsenidogallanes and -indanes have a long-standing history in main group chemistry. In contrast, the corresponding heterocycles $[R_2MER'_2]_x$ containing the heaviest elements of group 13 (Tl) and group 15 (Sb, Bi) remained almost completely unknown. (Cowley *et al.* first synthesized heterocyclic stibinogallane and -indanes.[474,474a,474b]) Standard organometallic reaction types such as H_2 and alkane elimination reactions, which were successfully used for the synthesis of group 13/15 compounds containing the lighter congeners, completely failed, most likely due to the less acidic properties of the E–H group (E = Sb, Bi). In addition, salt elimination reactions very often occurred under reduction of the stibides and bismuthides, respectively, leading to the formation of elemental Sb and Bi. However, in the last decade alternate reaction pathways such as dehalo- and dehydrosilylation reactions, which are also valuable synthetic methods for the synthesis of phosphido- and arsenidogallanes and -indanes, have been established as general reaction pathways for the synthesis of the desired heterocycles.



E = P **626**, As **636** **622**

Figure 44 Structures of heterocyclic amino-, phosphino- and arsinogallanes **622**, **626**, and **627**.

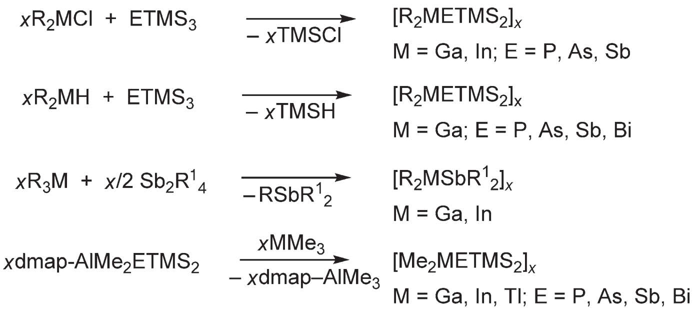


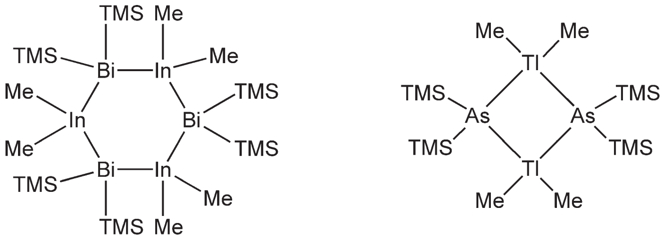
Figure 45 Established reaction pathways for the synthesis of group 13/15 complexes of the type $[\mathrm{R_2MER'_2}]_x$.

In addition, novel reaction types such as the distibine cleavage reaction[475] and a novel metathesis reactions using dmap-stabilized Al-pentele compounds of the type dmap–$\mathrm{AlMe_2ETMS_2}$ (E = P, As, Sb, Bi)[476] have been developed (Figure 45). (The group 13/15 chemistry of the heavier homologs of group 15 was recently reviewed.[477,477a,477b])

Several group 13-stibides (Ga: $[\mathrm{R_2GaSbTMS_2}]_2$ (R = Et **637**,[435,457] $\mathrm{Bu^t}$ **638**[478]), $[\mathrm{Bu^t{}_2GaSbEt_2}]_2$ **639**,[475] $[\mathrm{Me_2GaSbR_2}]_3$ (R = Me **640**,[479] $\mathrm{Pr^i}$ **641**,[479] TMS **642**[480]), $[\mathrm{Bu^t{}_2GaSbMe_2}]_3$ **643**[475]; In: $[\mathrm{R_2InSbTMS_2}]_2$ (R = $\mathrm{Bu^t}$ **644**,[481] $\mathrm{CH_2TMS}$ **645**[64]), $[\mathrm{R_2InSbTMS_2}]_3$ (R = Me **646**,[408] Et **647**[482]), $[\mathrm{Me_2InSbR_2}]_3$ (R = Me **648**,[479] $\mathrm{CH_2TMS}$ **649**[483])) have been structurally characterized. As was found for the lighter group 15 homologs, they either adopt dimeric or trimeric structures in the solid state, depending on the steric bulk of the organic substituents. In solution, the formation of a temperature- and concentration-dependent equilibrium between four- and six-membered rings was observed for $[\mathrm{Et_2GaSbTMS_2}]_2$ **637**. According to NMR spectroscopic studies, **637** adopts at 65 °C a trimeric structure ($x = 3$), whereas at lower temperatures, the formation of the dimeric moiety is favored ($x = 2$).[457] The M–Sb bond distances within the heterocycles are significantly shorter compared to the Lewis acid–base adducts as described in Section 3.07.2.

In addition, the first group 13-bismuthides (Ga: $[\mathrm{Me_2GaBiTMS_2}]_3$ **650**[484]; In: $[\mathrm{Me_2InBiTMS_2}]_3$ **651**[476]) and Tl-containing heterocycles ($[\mathrm{Me_2TlPTMS_2}]_2$ **652**,[476] $[\mathrm{Me_2TlAsTMS_2}]_2$ **653**,[476] $[\mathrm{Me_2TlSbTMS_2}]_3$ **654**[485]) have been structurally characterized (Figure 46). They have to be prepared at low temperatures due to their limited thermal stability in solution. Structure **651** for instance decomposes in solution above −30 °C within a couple of minutes. Comparable findings were reported for the thallanes **652–654**.

Monomeric, heterocyclic, and cage-like complexes $[\mathrm{RMER'}]_x$. Complexes of the type $[\mathrm{RMER'}]_x$ are almost exclusively limited to derivatives of the lighter group 15 elements (N, P). They were typically obtained from alkane elimination, salt elimination, and dehydrosilylation reactions. However, the synthesis of low-valent organometallics of the type $[\mathrm{MR}]_x$ and $\mathrm{M_2R_4}$ (Sections 3.07.4.1 and 3.07.4.2) has led to the development of novel reaction pathways. For instance, the unusual $[(\mathrm{TMS_3CGa})_3\mathrm{P_4}]$ **420** cluster was obtained from the reaction of $[\mathrm{GaCTMS_3}]_4$ **383** with $\mathrm{P_4}$.[486] Its formation occurs through insertion reactions of three $\mathrm{TMS_3CGa}$ monomers into three P–P bonds of the $\mathrm{P_4}$ tetrahedron, which is favored due to the ring strain of the $\mathrm{P_4}$ molecule. The cage-like structure of **420** is similar to that of $[\mathrm{P_7}]^{3-}$ or $\mathrm{P_4Se_3}$. In contrast, the reaction of **383** with the cyclotriphosphane $[\mathrm{PBu^t}]_3$ yielded the monoinsertion product $[\mathrm{TMS_3CGa(PBu^t{}_3)}]$ **655**.[487] Even in the presence of a large excess of **383**, no further insertion reaction was observed. Structure **655** contains a non-planar



651 **653**

Figure 46 Structures of the six-membered bismuthinoindane **651** and the four-membered arsinothallane **653**.

four-membered ring with the P atoms in pyramidal environments (sum of bond angles 296.5–306.2°). The Ga–P bond distances (av. 236.3 pm), which are relatively short since the central Ga and P centers are only three coordinate, are comparable to those observed in **420** (av. 235.6 pm). The same holds for the P–P bond distances (221.7 pm **655**; 218.1 pm **420**).

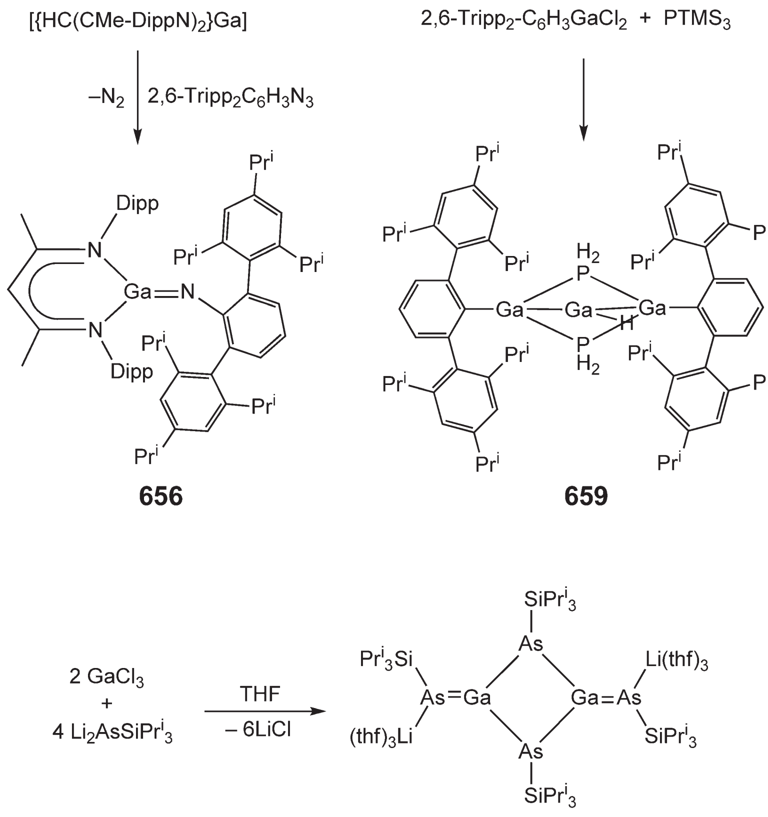
Even more interesting are reactions of low-valent compounds with organoazides RN_3. These yielded so far unknown monomeric gallium and indium imides, featuring M═N double bonding character. $[\{HC(MeCDippN)_2\}Ga{=}N\text{-}2,6\text{-}Tripp_2C_6H_3]$ **656**[488] and $(2,6\text{-}Dipp_2\text{–}C_6H_3)M{=}NAr'$ (M = Ga **657**, In **658**;[489] $Ar' = 2,6\text{-}[2,6\text{-}Me_2\text{-}4\text{-}Bu^t\text{-}C_6H_2]_2C_6H_3$) were obtained by reaction of sterically encumbered azides RN_3 with monomeric $[\{HC(CMeDippN)_2\}Ga]$[285] **387** and dimeric M_2Ar_2 (M = Ga **392**, In **393**),[293,294] respectively. They exhibit *trans*-bent, almost planar, CMNC cores with the shortest Ga–N (170.1(3) pm,[489] 174.2(3) pm[488]) and In–N bond distances (192.8(3) pm[489]) ever observed. Structure **656** shows a slightly longer Ga–N bond length (174.2(3) pm) due to the higher coordination number of the Ga atom (3 vs. 2). The M–N bonding in these remarkable compounds can be interpreted as an interaction between the triplet form of the nitrene Ar′N and the monovalent M(I) species, even though for the latter one the triplet form is higher in energy than the singlet form. According to theoretical calculations, double-bonding character within the novel compounds is clearly present but relatively weak.

The reaction of $2,6\text{-}Tripp_2\text{–}C_6H_3GaCl_2$ **176** with $PTMS_3$ was expected to proceed with dehalosilylation yielding $[2,6\text{-}Tripp_2\text{–}C_6H_3GaPTMS]_x$. Surprisingly, the rather unexpected compound $[(2,6\text{-}Tripp_2\text{–}C_6H_3Ga)_2(GaH)(PH_2)_2]$ **659** was formed.[490] Structure **659** contains a nonlinear, asymmetric Ga_3 chain (Ga–Ga–Ga 69.7(1)°; Ga–Ga: 251.5(2), 277.8(2) pm) with a central Ga–H group and two terminal $2,6\text{-}Tripp_2\text{–}C_6H_3Ga$ moieties, which are are bridged by two PH_2 groups. The mechanism for the formation of **659** is still unclear.

Reducing the steric bulk of the substituents rather yielded dimeric or trimeric heterocyclic compounds, as was shown for the reaction of Cp^*Ga and $(2,6\text{-}Me_2\text{–}C_6H_3)N_3$. The resulting $[Cp^*GaN(2,6\text{-}Me_2\text{–}C_6H_3)]_2$ **660**[156] forms a four-membered ring in the solid state. Dimeric as well as trimeric compounds $[RMER']_x$ ($x = 2$, 3) of the heavier group 15 elements (P–Bi) are only scarcely known in the literature. To date, only $[Bu^tGaPMes^*]_2$ **661**[491] and $[(2,4,6\text{-}Ph_3\text{–}C_6H_2GaPCy)]_3$ **662**[492] have been structurally characterized. Therefore, the synthesis of $[Li(thf)_3]_2[Pr^i{}_3Si(As)GaAs(SiPr^i{}_3)]_2$ **663** by reaction of $GaCl_3$ and $Li_2AsSiPr^i{}_3$ by Hänisch is remarkable.[493] Structure **663** features a planar Ga_2As_2 ring with essentially planar-coordinate Ga atoms, whereas the As atoms adopt a pyramidal (sum of bond angles 295.4°) environment. In addition, and even more interesting, **663** contains two terminal Ga–As bonds, which are significantly shorter (231.8(1) pm) than the heterocyclic ones (247.3(1), 243.6(1) pm). The bond angular sum of the terminal As atom of 343.2° and the small torsion angle of 14.6° point to the presence of dative $(p\text{-}p)\pi$ overlap, as was confirmed by computational calculations (Figure 47).

Four-membered heterocycles have also been stabilized by coordination of an external Lewis basic donor, resulting in the formation of heterocycles of the type $[(donor)RMER']_2$. A few complexes featuring central GaP ($[(Me(Bu^t)_2P)ClGaPTMS]_2$ **664**),[447] GaAs ($[(Me(Bu^t)_2P)ClGaAsTMS]_2$ **665**),[447] and GaSb cores ($[(Ph(Pr)_2P)ClGaSbSiPr^i{}_3]_2$ **666**[494]) have been structurally characterized. Interestingly, **666** undergoes a condensation reaction with elimination of two phosphines and subsequent formation of $[(Ph(Pr)_2P)_2(ClGa)_4(SbSiPr^i{}_3)_4]$ **667**. The central framework of **667** consists of three annealed four-membered rings, which adopt a chair-like structure. The Ga–Sb bond distances in **667** range from 261.8(1) pm, which is the shortest Ga–Sb bond observed, to date, to 271.7(1) pm, a typical value for monomeric and heterocyclic stibinogallanes of the type $[R_2GaSbR'_2]_x$.

Compound **667** adopts a rather unexpected structure in the solid state since the formation of a heterocubane-type structure, as was observed for $[MeGaNR]_4$ ($R = Bu^t$ **668**,[495] TMS **669**[496]), $[PhGaNPh]_4$ **670**,[497] $[MesGaNC_6F_5]_4$



656 **659**

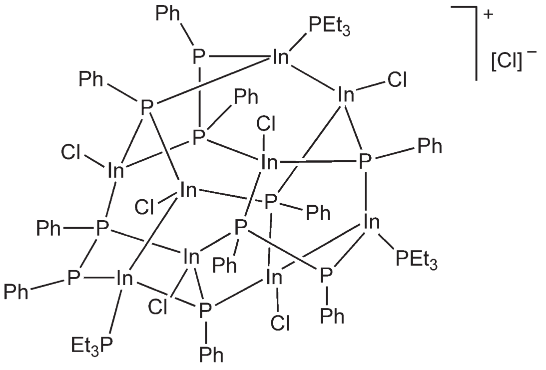
663

Figure 47 Synthesis and structures of novel group 13/15 compounds featuring double bonding character.

671,[498] [RGaPBu^t]$_4$ (R = Pr^i **672**, Mes **673**)[499], [Mes(H)PGa(MesGa)$_3$(PMes)$_4$] **674**,[500] [MeMNC$_6$F$_5$]$_4$ (M = Ga **675**, In **676**),[501] [Me(thf)InN(4-F-C$_6$H$_4$)]$_4$ **677**,[502] [RInNBu^t]$_4$ (R = Me **678**,[503] Cl **679**,[504] Br **680**,[504] I **681**[504]), [Pr^{i}InPSiPh$_3$]$_4$ **682**,[505] [EtInPSiPr$^i_3$]$_4$ **683**,[506] and [MesInPMes]$_4$ **684**,[472] is more typical in group 13/15 chemistry. The heterocubanes each contain four-coordinate group 13/15 atoms and consequently show longer M–E bond distances than the monomeric and (base-free) heterocyclic derivatives with three-coordinate central atoms. Structure **677** is somewhat special since it contains five-coordinate In atoms due to the presence of thf donors. Consequently, the In–N bond distances differ more (213.6(5)–227.9(5) pm) than those of the base-free pentafluorophenyl analog **676**[501] (216.7(1)–222.7(1) pm).

If the steric demand of the substituents is further reduced, hexamers such as [MeGaNR]$_6$ (R = Bu^i **685**,[507] 4-F-C$_6$H$_4$ **686**[502]), [EtGaNEt]$_6$ **687**,[508] [EtInPSiMe$_2$C(Me$_2$)Pr^i]$_6$ **688**,[506] {[MeInAsBu^t]$_6$Me}[Li(dme)$_3$] **689**,[509] {[ClInAsBu^t]$_6$Cl$_2$}[Li(thf)$_4$]$_2$ **690**[460] were formed, which typically adopt hexagonal prismatic arrangements. In addition, heptamers ([PhGaNMe]$_7$ **691**[497]) and larger oligomers such as [(MeIn)$_6$(Me$_2$In)$_2$(AsBu^t)$_6$(OH)$_2$] **692**[509] and [(MeIn)$_9$(AsBu^t)$_8$(OH)$_2$] **693**,[509] which were formed due to the presence of small amounts of water, have been prepared. In addition, the remarkable phosphine-stabilized In$_9$P$_{10}$ cluster [(InCl)$_6$(InPEt$_3$)$_3$(PPh)$_{10}$Cl] **694** was obtained from the reaction of InCl$_3$ and PhPTMS$_2$ in the presence of PEt$_3$.[510] Structure **694** is formed by redox reactions with subsequent formation of P–P and In–In bonds. Structure **694** contains four six-membered In$_3$P$_3$ rings as well as three In$_3$P$_2$ and three In$_2$P$_3$ five-membered heterocycles. Six Cl atoms are terminal bonded to In centers whereas the remaining Cl anion occupies a position in the center of the cluster (Figure 48).

Di and tripentelanes and donor-stabilized derivatives (donor)-R$_x$M(ER$'_2$)$_{3-x}$ (x = 0–2). Neutral di- and tripentelanes of the general type R$_x$M(ER$'_2$)$_{3-x}$ (R, R$'$ = H, alkyl, aryl, silyl) are almost exclusively limited to amido derivatives R$_x$M(NR$'_2$)$_{3-x}$. (Compounds containing the group 13 metal center embedded into a macrocyclic ligand system are not considered here.) Several diamides RM(NR$'_2$)$_2$ (Ga: [HGa(NMe$_2$)$_2$]$_2$ **695**,[511] quin-GaH(NTMS$_2$)$_2$ **696**,[170]



694

Figure 48 Structure of a large In–P cluster with P–P and In–In bonds.

quin-GaH(NHDipp)$_2$ **697**,[170] MeGa(2-NBz-py)$_2$ **698**,[512] tmp$_2$GaSiTMS$_3$ **699**,[513] MesGa(NHPh)$_2$ **700**,[398] PhGa(tmp)$_2$ **701**,[514] [XGaN(TMS)CH$_2$C(Me$_2$)CH$_2$NTMS]$_2$ (X = Cl **702**, Br **703**)[515]; In: MeGa(2-NBz-py)$_2$ **704**,[512] [Mes*In(NTMS$_2$)$_2$]$_2$ **705**[399]) and triamides M(NR′$_2$)$_3$ (Ga: Ga(NR$_2$)$_3$ (R = TMS **706**,[398,496,516] Cy **707**[517]), py-Ga(NHR)$_3$ (R = Dipp **708**,[518] Bu^t **709**[516]); In: In(NHMes*)$_3$ **710**,[518] In(NR$_2$)$_3$ (R = TMS **711**,[401] Cy **712**[519]), In(tmp)$_3$ **713**,[520] py-In(NPh$_2$)$_3$ **714**,[521] dmap–In(N(Bu^t)SiHMe$_2$)$_3$ **715**,[521] Et$_2$O–In{N(Ph)TMS}$_3$ **716**,[521] (py)$_2$In(NHDipp)$_3$ **717**[518]) have been synthesized by standard organometallic reactions. The transamination reaction of [In(NEt$_2$)$_3$]$_2$ with N(CH$_2$CH$_2$NSiMe$_3$H)$_3$ also yielded the first structurally characterized azaindatrane.[522,523] In addition, cluster-type compounds such as [(PhGa)$_4$(NHBu^i)$_4$(NBu^i)$_2$] **718**, which adopts an adamantane-like structure, and [(PhGa)$_7$(NHMe)$_4$(NMe)$_4$] **719**[524] have been structurally characterized.[524] Of particular interest are the syntheses of the polymeric gallium imide [Ga(NH)$_{3/2}$]$_x$ **720** by transamination reaction of the gallium trisamide [Ga(NMe$_2$)$_3$]$_2$ with either gaseous or liquid NH$_3$,[525] and of indium trisamide In(NH$_2$)$_3$ **721** by reaction of InI$_3$ and 3 equiv. of KNH$_2$ in liquid NH$_3$ at 25 °C.[526] Structures **720** and **721** are probably the most ideal precursor for the synthesis of metal nitrides due to the lack of any metal–carbon bond. The ammonothermal conversion of **720** into cubic GaN has recently been demonstrated.[527]

Diamides either form monomeric or dimeric aggregates as was observed for monoamides. In contrast, triamides typically are monomeric in the solid state with only a very few exceptions, most likely due to steric shielding of the large amido groups. Only [Ga(NHBu^t)$_3$]$_2$ **722** was found to adopt a dimeric structure similar to that of [Ga(NMe$_2$)$_3$]$_2$ **723**[528] with a central non-planar Ga$_2$N$_2$ ring.[516] Donor-stabilized derivatives of the type donor-M(NR$_2$)$_3$ typically show the central metal atom in (distorted) tetrahedral coordination spheres. However, if the donor is part of a relative rigid tridentate ligand system, the metal center is only slightly displaced from the trigonal plane in the direction of the apical substituents, as was found in ClGa[(N(R)CH$_2$CH$_2$)$_2$NR′] (R, R′ = Me **724**, Pr^i **725**, TMS **726**).[529,529a]

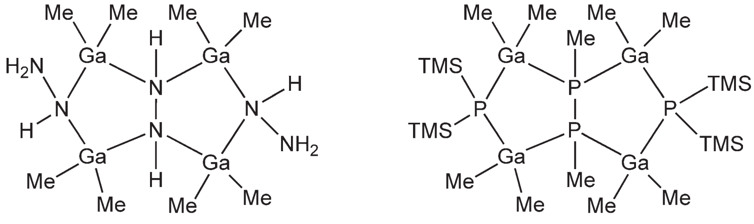
Di- and triphosphides (Ga: RGa(PBu$^t_2$)$_2$ (R = Bu^t **727**, Mes **728**, Cl **729**),[402] [*neo*-Pent(PPh$_2$)Ga(μ-PPh$_2$)]$_2$ **730**,[530] Ga(PHMes*)$_3$ **731**[399]; In: [Cl(PBu$^t_2$)In(μ-PBu$^t_2$)]$_2$ **732**,[531] [R(PPr$^i_2$)In(μ-PPr$^i_2$)]$_2$ (R = Pr^i **733**, Bu^t **734**[532]) as well as the corresponding arsenides (Ga: Ga(AsTMS)$_3$ **735**[533]) are only scarely known and comparable thallanes are completely unknown. Diphosphides adopt monomeric or dimeric structures in the solid state as was observed for diamides. The triphosphides M(PBu$^t_2$)$_3$ (M = Ga **736**, In **736a**) have recently been shown to serve as single source precursor for the synthesis of GaP and InP nanoparticles, respectively.[534]

Interesting cluster-type complexes have been prepared by reaction of MR$_3$ with chelating ligands. [(*neo*-Pent)In-(μ-(NH)$_2$C$_6$H$_4$)]$_4$ **737**, featuring a tetrameric In$_4$N$_8$ cluster with approximately tetrahedral symmetry, was formed from the reaction of 1,2-(NH$_2$)$_2$–C$_6$H$_4$ with In(*neo*-Pent)$_3$.[535] Structure **737** contains five-coordinate indium atoms, which adopt a square-pyramidal coordination geometry. In contrast, the reactions of GaMe$_3$ with 1,2-(NH$_2$)$_2$–C$_6$H$_4$ yielded the six-membered ring {(Me$_2$Ga)$_3$[(μ-NH)$_2$–(C$_6$H$_4$)(μ-NH)(C$_6$H$_4$NH$_2$)]} **738**. The Ga atoms in **738** are four coordinate.[536] In contrast, reactions of the corresponding diphosphines 1,2-(PH$_2$)$_2$–C$_6$H$_4$ and 1,2-(P(H)Bu^t)$_2$–C$_6$H$_4$ with 2 equiv. GaMe$_3$ gave the eight-membered tetrametallic heterocycles {(Me$_2$M)$_4$[(μ-PR)$_2$(C$_6$H$_4$)]$_2$} (R = H **739**,[536] Bu^t **740**[537]).

Hydrazine adducts, heterocycles, and cage-like oligomers. Alkylgallium hydrazides have generated considerable interest recently due to their potential application to serve as precursor for the generation of GaN (see Refs: 538, 538a, and 538b, and references cited therein). They were synthesized by standard organometallic reactions between group 13 trialkyls and dialkyl halides with hydrazines and lithium hydrazides (salt elimination, H_2 and alkane elimination reactions), which already have been found applicable for the synthesis of group 13 amides and imides.[539] The reactions also proceed stepwise with the initial formation of a hydrazine adduct, which were isolated in the form of the mixed alkyl/halide adducts $Me(Cl)_2Ga–NH_2NHBu^t$ **741**,[540] $Bu^t_2(Cl)In–NH_2NHBu^t$ **742**,[541] $(Me_2InCl)_2(NH_2NHPh)_2$ **743**,[541] and $(Me_2InCl)_4(NH_2NHPh)_2$ **744**.[541] In addition, adducts of trialkylgallanes GaR_3 ($R = Me$, Et, Pr^i) have been spectroscopically characterized,[542] whereas those of trialkylindanes and -thallanes are unknown, to date. Only the lithium hydrazide–$InMe_3$ adduct $([Me_3M\{N(Li)TMSN(H)Bu^t\}]_2$ ($M = Ga$ **745**, In **746**)[540]) has been structurally characterized. In addition, the reaction of Me_2InCl with *tert*-Butyl hydrazine yielded the anionic compound $[Me_2In(NH_2NHBu^t)_2][Me_2InCl_2]$ **747**.[541] On heating, as-formed adducts typically undergo alkane elimination reactions, leading to the formation of heterocycles of the general type $[R_2MNR'NR''_2]_x$. Several heterocyclic hydrazinogallanes $([Pr^i_2GaN(H)NMe_2]_2$ **748**,[542] $[H_2GaN(H)NMe_2]_2$ **749**,[543] $[R_2GaN(H)NPh_2]_2$ ($R = Me$ **750**,[544] Et **751**[545]), $[Ph(Me_2NNH)Ga(\mu\text{-}NHNMe_2)]_2$ **752**[511]), which were also obtained from salt eliminiation reactions, have been structurally characterized. In contrast, heterocyclic hydrazinoindanes are unknown, to date. Only the trishydrazide $In(NTMSNMe_2)_3$ **753**[546] has been structurally characterized. Galliumhydrazides typically form four-membered Ga_2N_2 heterocycles with two exocyclic N–N bonds. (Cowley *et al.* proposed a trimeric structure for $[Me_2GaN(H)NMe_2]_3$ based on mass spectroscopic studies. Unfortunately, no single crystal X-ray structure was obtained.) In contrast, $[(Me_2Ga)_4(HNNH_2)_2(HNNH)]$ **754** (Figure 49),[540] which was obtained from the reaction of $GaMe_3$ and N_2H_4 in refluxing toluene, adopts a bicyclic ring structure with a central N_2H_2 unit. In addition, reactions of 2,3-diazabutadienes and $H_3Ga–NR_3$ at low temperatures yielded the dimeric gallium hydrazonide $[H_2GaN(Pr^i)N{=}CMe_2]_2$ **755** containing a six-membered Ga_2N_4 heterocycle.[547] Only one C=N double bond has been reduced (hydrogallation reaction), whereas analogous reactions with base-stabilized alanes $R_3N–AlH_3$ (hydroalumination reaction) yielded both the mono- [548] and the bisaddition product.[549]

Further heating of heterocyclic gallium hydrazides finally resulted in the formation of higher oligomeric compounds. For instance, $[Me_2GaN(H)NHR]_2$ ($R = Ph$ **756**,[550] Bu^t **756a**[542]) reacts in boiling toluene with elimination of methane and subsequent formation of tetrameric $[MeGaN(H)NR]_4$ ($R = Ph$ **757**, Bu^t **758**). In addition, heterocyclic hydrazides react with an additional amount of hydrazine with formation of cage-like compounds such as $Ga_4[N(H)NMe_2]_8[NNMe_2]_2$ **759**, which was prepared by reaction of $[H_2GaN(H)NMe_2]_2$ with H_2NNMe_2.[543]

It should further be noted that a very few diphosphane complexes have been synthesized. The simple Lewis acid–base adduct $Me_3Ga–PMe_3$ was found to react with $PTMS_3$ in a rather unexpected way with formation of $[(Me_2Ga)_2(PTMS_2)_2(MePPMe)]$ **760** (Figure 49).[551] The reaction mechanism is still not understood, but the structure of the novel phosphinogallane, which also contains to fused five-membered Ga_2P_3 rings, is similar to that of $[(Me_2Ga)_4(HNNH_2)_2(HNNH)]$ **754**. In addition, $(tmp_2Ga)_2(PBu^t)_2$ **761**[402] has been prepared by reaction of tmp_2GaCl and $K_2[P_2Bu^t_2]$. Structure **761** contains a central diphosphine moiety with a P–P bond distance of 225.4(1) pm, which is typical for P–P bonds. The tmp_2Ga units (Ga–P 242.3(21) pm) adopt a transoid orientation.



754 **760**

Figure 49 Structures of diphosphine and hydrazine complexes featuring fused five-membered Ga_2E_3 rings.

3.07.5.3 Group 13–16 Complexes (O, S, Se, and Te)

Heteronuclear complexes containing elements of group 16 have continued to be an active research area in group 13 chemistry in the last decade. As was observed for group 13/15 complexes, the interest in novel structures and chemical properties of such compounds has stimulated several research groups to develop general pathways for this particular class of compounds. For instance, group 13 metal hydroxides, alkoxides, and oxides have been prepared in order to develop structural models for methylalumoxane (MAO), which is an essential co-catalyst in homogeneous olefin polymerization, and to understand its role in this industrially important reaction type. In addition, the interesting physical properties (semiconductors) of binary III–VI materials containing the heavier metals of group 16 (S, Se, Te) have forced several groups to synthesize this specific class of compounds and to investigate their capability to serve as single source precursors for III–VI materials in solution-based as well as in gas-phase deposition reactions. Group 13/16 complexes were typically synthesized by standard organometallic reactions comparable to those applied for the synthesis of group 13/15 complexes. Depending on the molar ratios of the reagents and the reaction conditions, different types of acyclic, heterocyclic, and cage-like compounds were obtained (Figure 50).

Monomers and heterocycles of the type $[R_2MER']_x$. The reaction of MR_3 (R = H, alkyl, aryl) with cyclic and acyclic ethers yielded the Lewis acid–base adducts $R_3M–OR'_2$, whereas analogous reactions of MR_3 with EH_2 and R′EH (E = O, S, Se, Te) typically yielded heterocyclic or cage-like compounds of the general types $[R_2MER']_x$ and $[RME]_x$, respectively. The initially formed Lewis acid–base adducts are almost completely unknown due to their lability toward the elimination of RH. Only one water adduct, $Mes_3Ga–OH_2$ **762**, has been isolated and structurally characterized, to date.[552] Adduct **762**, which was obtained by controlled hydrolysis of Mes_3Ga dissolved in THF at low temperature, is stable in solution only below 0 °C. At higher temperatures, mesitylene elimination occurs with subsequent formation of dimeric gallium hydroxide $[Mes_2GaOH]_2$ **763**.[552] The elimination of RH is typically observed in reactions of gallium triaryls GaR_3 with water. However, Raston *et al.* demonstrated that also intramolecular biaryl coupling might occur.[553] Structure **762** exhibits a relatively short Ga–O bond distance (204.7 pm) compared to ether adducts $Mes_3Ga–OR_2$, which most likely results from less sterical strain of the small water molecule. The Ga–O bond distance as observed in $[Mes_2GaOH]_2$ (194.9(2) pm) is significantly shorter. The same general trend was observed for group 13/15 compounds (Section 3.07.5.2).

Dialkyl and diaryl metal hydridochalcogenides typically dimerize or trimerize with formation of four-membered $[R_2MOH]_2$ (Ga: R = Pr^i **764**,[554] Mes **763**,[552] 2,6-Mes_2–C_6H_3 **765**,[29] 2,6-Mes_2–C_6H_3/Me **766**,[29] $CHTMS_2$ **767**[555]; In: $CHTMS_2$ **768**[134]), $[Bu^t{}_2GaSH]_2$ **769**[556]) and six-membered heterocycles $[R_2MOH]_3$ (Ga: R = Me **770**,[557,558] Bu^t **771**,[464,559] Ph **772**,[560] Me/$CTMS_3$ **773**[561]; In: R = Me/$CTMS_3$ **774**,[562] Pr/$CTMS_3$ **775**[563]). The same trends were observed for the corresponding chalcogenolates $[R_2MER']_x$. A large number of four-membered heterocyclic metal alkoxides (Ga: $[H_2GaOBu^t]_2$ **776**,[564] $[Me_2GaOR]_2$ (R = Cy **777**,[565] $CH(Me)CH_2NMe_2$

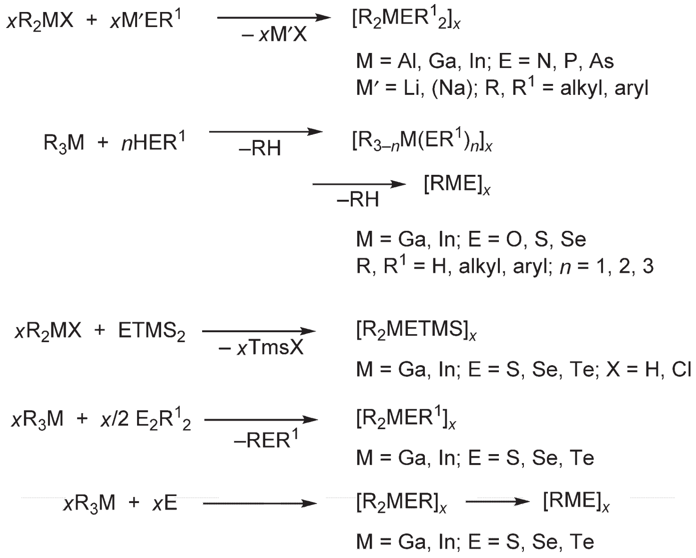


Figure 50 General reaction pathways for the synthesis of group 13/16 complexes.

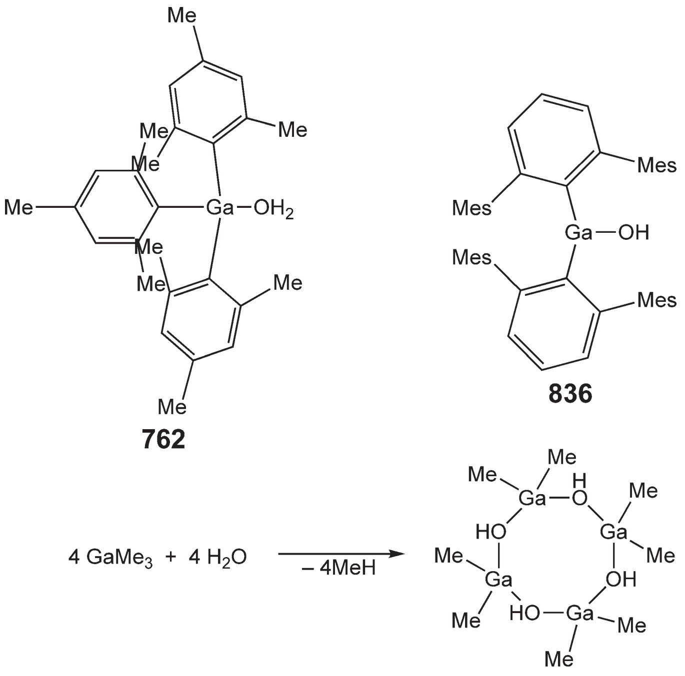
778,[566] $CH(Me)CH_2OMe$ **779**,[391] CH_2CH_2OMe **780**,[391] $CH_2(Me)$-(2-OMe–C_6H_4) **781**,[567] $CH(Ph)CH(NMe_2)_2$ **782**[568]), $[Et_2GaO(2,6\text{-}Ph_2\text{–}C_6H_3)]_2$ **783**,[569] $[Bu^t{}_2GaOR]_2$ (R = $CH(CF_3)_2$ **784**,[570] Me **785**,[571] Pr **786**,[571] $CHEt_2$ **787**,[571] Bu^t **788**,[572] Pent **789**,[571] Hex **790** (Hex = hexyl),[571] Ph **791**[571]), $[(TMSCH_2)_2GaOCH_2TMS]_2$ **792**,[573,573a] $[Bz_2GaOR]_2$ (R = Bz **793**,[574] Bu^t **794**[575]); In: $[Bu^t{}_2InOMe]_2$ **795**,[446] $[R_2InOBu^t]_2$ (R = TMS_2N **796**,[134] Cp **797**,[576] TMS_2N/Me **798**[577]), $[R_2InOTMS]_2$ (R = CH_2TMS **799**,[573] Ph **800**[578])) and thiolates (Ga: $[Et_2GaS(SiPh_3)]_2$ **801**,[442] $[Bu^t{}_2GaSPh]_2$ **802**,[579] $[Bz_2GaSBu^t]_2$ **803**[575]; In: $[Pr^i{}_2InS(pTol)]_2$ **804** (pTol = *para*-tolyl),[580] $[Bu^t{}_2InSR]_2$ (R = *cy*-Pent **805**,[581] Cy **806**,[581] 3-6-Me_2–C_6H_3 **807**,[581] $SnCy_3$ **808**,[581] Bu^t **809**[582]), [*neo*-Pent$_2$InS(Ph)]$_2$ **810**,[583] $[Mes_2InSR]_2$ (R = Bu^t **811**,[584] amyl **812**,[584] $SiPh_3$ **813**[584])) have been structurally characterized. Moreover, quite a few selenolates (Ga: $[Ph_2GaSeMe]_2$ **814**,[585] $[(TMSCH_2)_2GaSeCH_2TMS]_2$ **815**,[583] $[Bz_2GaSeBu^t]_2$ **816**[575]; In: $[Bu^t{}_2InSeBu^t]_2$ **817**,[582] [*neo*-Pent$_2$InSe(*neo*-Pent)]$_2$ **818**,[583] $[Mes_2InSeR]_2$ (R = Ph **819**,[584] Mes **820**[584])) and tellurolates (Ga: $[TMS_3C(Me)GaTeMe]_2$ **821**,[586] $[Bz_2GaTeBu^t]_2$ **822**[575]; In: $[Mes_2InTeR]_2$ (R = Pr **823**,[584] Ph **824**[584])) have been prepared within the last decade. These alkoxides and thiolates were typically prepared by reaction of MR_3 with $R'EH$ (E = O, S), whereas selenolates and tellurolates were obtained by insertion reactions of elemental Se and Te into the metal–C bond of metal triorganyls. In addition, a very few six- ($[Me_2InSR]_3$ (R = Bu^t **825**,[581] $SiPh_3$ **826**[584]), $[Bu^t{}_2InS(4,6\text{-}Me_2\text{–pyrimidine})]_3$ **827**[581]) and eight-membered heterocycles ($[Me_2GaOH]_4$ 828,[558] $[Me_2InS(2,6\text{-}Me_2\text{–}C_6H_3)]_4$ **829**,[581] $[Me_2TlS(4\text{-}CF_3\text{-}6\text{-Me-pyrimidine})]_4$ **830**[587]), which are precedenceless in group 13/15 chemistry, have been synthesized. The isolation of 828, obtained from the reaction of $GaMe_3$ with wet crown ether, is remarkable because metal hydroxides containing small ligands have a strong tendency to undergo consecutive condensation reactions.

The degree of oligomerization typically depends on the steric demand of the organic substituents as was observed for group 13/15 heterocycles $[R_2MER'_2]_x$ (Section 3.07.5.2). Consequently, monomeric compounds ($Bu^t_2GaOCPh_3$ **831**,[588] tmp_2GaOPh **832**,[514] $(TMS_2CH)_2GaOC_6F_5$ **833**,[589] $Mes^*{}_2GaSMe$ **834**,[590] $(TMS_2CH)_2GaTeSiTMS_3$ **835**[591]) are only accessible by use of bulky substituents, which kinetically stabilize the electron-deficient, three-coordinate metal center. Of particular interest is the monohydroxide $(2,6\text{-}Mes_2C_6H_3)_2GaOH$ 836,[29] which was obtained from hydrolysis of the corresponding monohydride $(2,6\text{-}Mes_2C_6H_3)_2GaH$ **141**. Compound 836 represents the only monomeric gallium monohydroxide, that has been structurally characterized, to date. Interestingly, hydrolysis of $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ **166** and $(2,6\text{-}Mes_2C_6H_3)_2GaMe$ **37**, respectively, occurred with cleavage of one Ga–terphenyl bond and subsequent formation of $(2,6\text{-}Mes_2C_6H_3)Ga(OH)X$ (X = Me **837**, Cl **838** (Figure 51).

As was found for group 13/15 compounds, monomeric compounds of the desired type can also be electronically stabilized by intermolecular coordination of a Lewis base. Several donor-stabilized alkoxides (Ga: donor–$Ga(Bu^t)_2OPh$ (donor = pyrazine **838**,[592] py **839**[593]), 1,4-dioxane–$(Bu^t{}_2Ga\text{–donor})_2$ (donor = py **840**, 4-Me–py **841**, 3,5-Me_2–py **842**)[593]), thiolates (quin–$Ga(H_2)SBu^t$ **843**[594]), and selenolates (Ga: (4-Me–py)–$Ga(Mes)_2SeMes$ **844**[583]) have been structurally characterized. In addition, intramolecular-stabilized monomers have been prepared by use of chelating ligands such as N-salicylideneaminato (see Refs: 595, 595a–595c, and references cited therein) and others (see Refs: 596, 596a–596c, and references cited therein). The M–O bond distances of the donor-stabilized derivatives are significantly elongated compared to those obtained for donor-free monomeric compounds, which results from the higher c.n. (4 vs. 3).

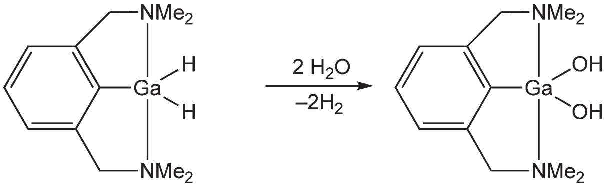
Monomers and heterocycles of the type $[RM(EH)_2]_x$. Bishydridochalcogenides of group 13 metals are almost unknown, to date. Only a very few bishydroxides such as the tetrameric $[(Bu^t{}_3Si)(HO)GaOH]_4$ **845**,[303] which was obtained from hydrolysis of the heterocubane $[Bu^t{}_3SiGa]_4$ 401, and the hexameric cluster $[LiOH]_2[TMS_3SiGa(OH)_2]_6$ **846**[597] have been structurally characterized. However, the most interesting compound of this specific type is $2,6\text{-}(Me_2NH_2C)_2\text{–}C_6H_3Ga(OH)_2$ 847, which was formed by controlled hydrolysis of the corresponding dihydride.[110] Compound 847 represents the only structurally characterized monomeric bishydroxide. Both amine sidearms of the organic substituent intramolecularly stabilize the Ga center, yielding a five-coordinate metal center (Figure 52). The unit cell of 847 consists of two $2,6\text{-}(Me_2NH_2C)_2\text{–}C_6H_3Ga(OH)_2$ layers, which are formed due to interactions between two Ga–OH moieties of neighboring molecules. These two layers sandwich a layer of water molecules by hydrogen bonding. Consequently, the hydrophilic hydroxide groups point toward the water layer, whereas the hydrophobic aromatic rings point away. The average Ga–O bond distance to the terminal OH groups (182.4(8) pm) is rather short compared to those of bridging OR groups, most likely due to the lower c.n. of the O center (2 vs. 3).

Monomers, heterocycles, and clusters of the type $[RME]_x$. Organometallic chalcogenides $[RME]_x$ have been synthesized by several synthetic approaches. Organometalloxanes $[RMO]_x$ such as $[Mes_9Ga_9O_9]$ 848,[598] $[(MeIn)_5(OBz)_8O]$ **849**,[599] and mixed hydroxide/oxide clusters such as $[(TMS_3C)_4Ga_4(OH)_4O_2]$ **850**,[561] $[Mes_6Ga_6(OH)_4O_4]$ **851**,[552,553,600] $[Me_{12}Ga_{12}(OH)_6O_8]$ **852**,[601] $[Bu^t{}_{12}Ga_{12}(OH)_4O_8]$ **853**[602] have been prepared by controlled hydrolytic cleavage of M–C bonds of MR_3 as well as by condensation reactions of metal hydroxides $[R_2MOH]_x$. Clusters containing the heavier chalcogenides (E = S, Se, Te) have been prepared by insertion reactions of elemental



762 **836** **828**

Figure 51 Structures of the water–gallane adduct **762** and two gallium hydroxides **828** and **836**.

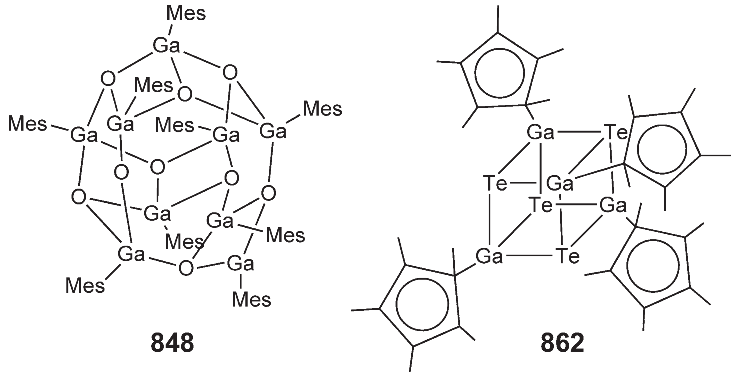


847

Figure 52 Synthesis and structure of the intramolecularly stabilized dihydroxygallane **847**.

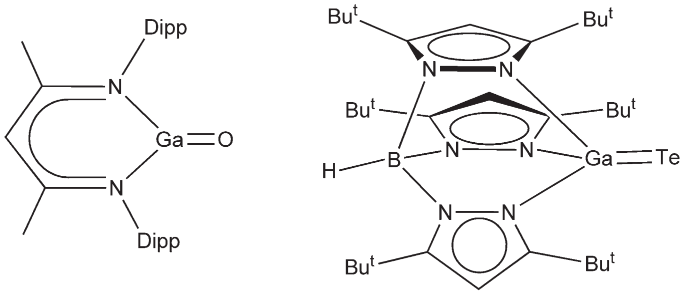
chalcogens into the M–C bond of metal triorganyls, resulting in the formation of tetrameric ($[\mathrm{TMS_3CGaS}]_4$ **854**,[586] $[\mathrm{Bu^tGaS}]_4$ **855**,[603] $[\mathrm{EtMe_2CGaE}]_4$ (E = Se **856**, Te **857**),[603] $[\mathrm{Et_2MeCGaE}]_4$ **858**,[604] $[\mathrm{Et_3CGaE}]_4$ (E = S **859**, Se **860**),[605] $[\mathrm{Cp^*GaE}]_4$ (E = Se **861**,[606] Te **862**[607])) or higher oligomeric complexes ($(\mathrm{PrNH_2})[\mathrm{Bu^tGaS}]_6$ **863**[608]) (Figure 53).

In contrast, only a very few dimeric complexes such as the donor-stabilized derivatives $[\mathrm{Mes(4\text{-}picoline)GaSe}]_2$ **864**[583] and $[(\mathrm{Cy_3P})\mathrm{ClGaSe}]_2$ **865**[609] as well as the azaallylgallium chalcogenides $[(\mathrm{TMS_2C(Ph)C(TMS)N)GaE}]_2$ (E = S **866**, Se **867**, Te **868**)[610] are known. The latter have been obtained either from the reaction of $[(\mathrm{TMS_2C(Ph)C(TMS)N)GaH_2}]_2$ with elemental sulfur or by dehalosilylation reaction of $[(\mathrm{TMS_2C(Ph)C(TMS)N)}$ $\mathrm{GaCl_2}$ with $\mathrm{ETMS_2}$ (E = Se, Te). In addition, base-stabilized trimers of the general type $[\mathrm{donor(X)GaE}]_3$ (X = Cl: E = S **869**, Se **870**; Br: E = S **871**, Se **872**)[611,611a,611b] have been structurally characterized. The synthesis of low-valent compounds $\mathrm{M_2R_4}$ and $[\mathrm{MR}]_x$ also opened alternative preparative approaches for the synthesis of group 13/16 complexes, since redox reaction with elemental chalcogens typically occur under less drastic reaction conditions. Consequently, novel monomeric ($[\mathrm{Tp^{Bu^t_2}}]\mathrm{GaE}$ (E = S **873**,[612] Se **874**,[613] Te **875**[613]),[614] $[\mathrm{Tp^{Bu^t_2}}]\mathrm{InSe}$ **876**[615]), dimeric ($\{\mathrm{HC[MeCDippN]_2}\}\mathrm{GaE}$ (E = O **877**, S **878**)[616]), and also tetrameric metal chalcogenides ($[\mathrm{Bu^t_3SiGaO}]_4$ **879**,[303] $[\mathrm{TMS_3CGaE}]_4$ (E = S **880**, Se **881**,[617] Te **882**)[617], $[\mathrm{TMS_3CInE}]_4$ (E = O **883**,[618] S **884**,[619] Se **885**,[281,617] Te **886**[619]),



848 **862**

Figure 53 Structure of the organogalliumoxide **848** and telluride **862**.



887 **875**

Figure 54 Structures of two complexes featuring Ga=E double bonding character.

$[\mathrm{Bu^t{}_3SiInSe}]_4$ 887[218]) have been prepared (Figure 54). The monomeric derivatives $[\mathrm{Tp^{Bu^t_2}}]\mathrm{GaE}$ are of particular interest since they belong to the very rare compounds containing heavier *p*-block elements, which exhibit multiple bonding.[620] They show the shortest M–E bond distances (Ga–S 209.3(2) pm, Ga–Se 221.4(1) pm, Ga–Te 242.2(1) pm, In–Se 237.6(1) pm) ever observed. Interestingly, the reaction of $[\mathrm{Tp^{Bu^t_2}}]\mathrm{In}$ **388** with sulfur did not yield $[\mathrm{Tp^{Bu^t_2}}]\mathrm{InS}$ as was observed for the Ga analog, but the novel tetrasulfido complex $[\mathrm{Tp^{Bu^t_2}}]\mathrm{In}(\eta^2\text{-}\mathrm{S}_4)$ 888.[621]

3.07.5.4 Ternary Clusters

Mimicking naturally occurring zeolites and developing novel zeolite-like structural architectures is a fascinating research field that has seen an increasing interest over the last decade. Among classical alumosilicates, which are typically prepared by sol–gel chemical routes, the synthesis of novel metallophosphates was investigated in detail. The discovery of a new group of alumophosphate-based molecular sieves by Flanigan in 1982 represents a milestone in this particular research field.[622] Since then, several group 13 element phosphates have been prepared, mostly under hydrothermal conditions in the presence of structure-directing organic templates.

In an attempt to better understand the mechanism of the formation of group 13 metalla silicates and -phosphates microporous materials and to discover novel structures with improved chemical and physical properties, precursor-based chemical methods, often referred to as "soft-chemical routes," have seen an increasing interest. Consequently, the synthesis of novel heterocyclic and cage-like complexes, which mimic structural architectures known as "secondary builing units" (SBUs) in zeolites, has been the preparative goal of several research groups. The control of the precursor structure on a molecular scale might give access to novel zeolite-type materials in the future ("bottom-up" approach). In the following, the progress, made in the synthesis of metal siloxanes and metal phosphates, will be summarized.

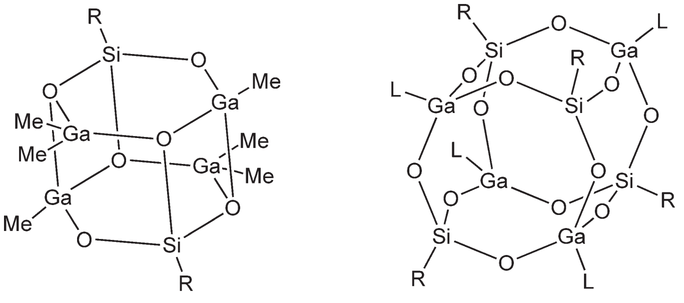
Metal siloxanes. Silandiols and silantriols of the general type $R_xSi(OH)_{4-x}$ ($x=2$, 3)[623] were successfully used as building blocks for the synthesis of heterocyclic ($x=2$) or cage-like metallasiloxanes containing Si–O–M frameworks. (Reactions of monosilanols and group 13 organometallics are long known in group 13 chemistry. They yielded metallasiloxanes of the general type $R_xM\ (OSiR_3)^{3-x}$, which are better described as simple alkoxides rather than silicates.) Among reactions with transition metal complexes, reactions of silanediols $R_2Si(OH)_2$, disilanols $HOSi(R_2)XSi(R_2)OH$ ($X=O$, $(CR_2)_n$), silanetriols $RSi(OH)_3$, and trisilanols, mainly silasesquioxanes $[R_3Si_7O_9(OH)_3]$, with group 13 metalorganics MR_3 have been investigated in detail. In particular, reactions of alanes R_xAlH_{3-x} ($x=1$–3) have been studied,[624] yielding novel heterocyclic and cluster-type complexes.

Even though numerous reactions of silandiols and disilanols with transition metal and main group element complexes have been reported,[625] reactions with organometallic gallanes and indanes have only scarcely been investigated. Only within the last decade, some progress has been made. Reaction of $Ph_2Si(OH)_2$ with $LiGaMe_4$ yielded a novel lithium galloxane $Li_2(Li(thf)_2)_2[Ph_2SiO_2GaMe_2]_2[Ph_2SiO_2GaMe(OH)]_2$ **889**.[626] The tetraanionic galloxane core consists of a central $Ga_4Si_4O_8$ 16-membered ring system, which mimics the single-8-ring (S8R) secondary building unit of zeolites. $[Bu^tOGaH_2]_2$ was found to react with different amounts of di- and trisiloxandiols $HO(Ph_2)Si$–$(OSiPh_2)_x$–OH ($x=1$, 2) with elimination of H_2 and subsequent formation of different types of cyclosiloxanes.[627] More recently, the lithium indium siloxane $[MeIn\{(OPh_2Si)_2O\}_2$-μ-$\{Li(thf)_2\}_2]$ **890** has been prepared by reaction of $Li[InMe_4]$ and $[HO(Ph_2)Si]_2O$.[628] The central MeIn unit binds to two $(Ph_2Si)_2O$ moieties, yielding a five-coordinate In atom.

Stable silantriols, which became available only within the last decade,[629] and trisilanols have been receiving an increasing interest due to the presence of three functional OH groups, which might allow the synthesis of three-dimensional frameworks.[630] Equimolar reactions of $RSi(OH)_3$ ($R=$ Dipp(TMS)N; Mes(TMS)N) with MMe_3 in THF yielded polyhedral gallio- and indiosiloxanes of the general type $[RSiO_3M(thf)]_4$ ($M=Ga$ **891**,[631] In **892**[632]) in high yields, whereas those in a 1 : 2 molar ratio gave drum-like compounds of the general type $[(Me_2M)(MeM)_2(O_3SiR)_2]$ ($M=Ga$ **893**,[631] In **894**[632]) (Figure 55). In addition, reactions with $Li[InMe_4]$ and $Na[InMe_4]$ resulted in the formation of different types of anionic indiosiloxanes.[632] It should also be noted that reaction of the isoelectronic trisaminosilane $[Dipp(Me_2Pr^iSi)N]Si(NH_2)_3$ afforded comparable cluster-type compounds containing Si–N–M frameworks.[633]

Reactions of incompletely condensed silsesquioxanes $R_7Si_7O_9(OH)_3$ ($R=Ph$, Cy) with $GaCl_3$ yielded monomeric and dimeric siloxanes containing one or two gallium atoms, whereas reactions with $Ga(CH_2TMS)_3$ resulted in the formation of a novel siloxane clusters consisting of six Ga centers.[634] Dimeric compounds were also obtained from the reaction of $Cy_7Si_7O_9(OH)_3$ and $Cy_7Si_7O_9(OTMS)_xOH)_{3-x}$ ($x=1$, 2) with TlOEt.[635] Very recently, reactions of $Cy_7Si_7O_9(OH)_3$ and $Cy_7Si_7O_9(OSiMePh_2)\ (OH)_2$ with $GaCl_3$ and $GaMe_3$, respectively, were investigated. Among mono- and dinuclear gallium silsesquioxanes, novel clusters containing three and four Ga centers have been obtained.[636]

Metal phosphinates, *phosphonates*, *phosphates*. The synthesis of molecular precursors for group 13 metal phosphate materials is almost limited to aluminum-based complexes (see Refs: 637, 637a–637d, and 638, and references cited therein). Only within the last decade, some complexes containing the heavier elements of group 13 elements (Ga, In) have been prepared. Reactions of diphenylphosphinic acid $Ph_2P(O)OH$ and MR_3 yielded metallophosphinates of the general type $[R_2MO_2PPh_2]_2$ ($M=Ga$, $R=Me$ **895**,[639] Et **896**,[640] Bu^t **897**;[641] $M=In$, $R=Et$ **898**[639]). The eight-membered ring structures mimic the simplest SBU in zeolite chemistry, a single-4-ring (S4R). Hydrolysis of



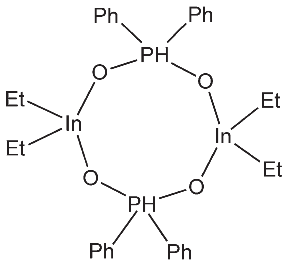
893 **891**

Figure 55 Structures of two organogalliumsiloxanes.

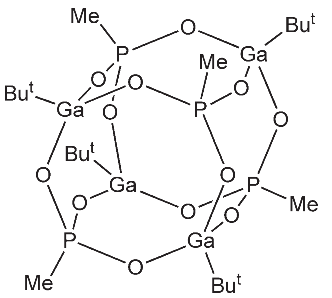
[$Me_2InO_2PPh_2$]$_2$ **899** in the presence of pyridine yielded [Me(HO)InO_2PPh_2]$_2$(4py), whereas **895** and **898** are hydrolytically stable.

Reactions of organophosphonates RP(O)(OH)$_2$ with group 13 metal organyls gave comparable eight-membered heterocycles such as [Bu$^t_2$GaO$_2$P(OH)R]$_2$ (R = H **900**,[642] Me **901**,[642] Bu^t **902**,[642] Ph **903**[643]). The hydroxyl group can be further derivatized by reaction with TMSNMe$_2$, yielding silylated derivatives [Bu$^t_2$GaO$_2$P(OTMS)R]$_2$ (R = H **904**, Me **905**, Bu^t **906**, Ph **907**).[642] Moreover, the reaction of [Bu$^t_2$GaO$_2$P(OH)Ph]$_2$ with GaBu$^t_3$ resulted in the formation of [Bu$^t_2$GaO$_2$P(OGaBu$^t_2$)Ph]$_2$ **908**.[644] Further heating of [Bu$^t_2$GaO$_2$P(OH)R]$_2$ in diglyme or solid-state pyrolysis at 250 °C resulted in condensation reaction, yielding cuboidal cage complexes of the general type [Bu^{t}GaO$_3$PR]$_4$ (R = Me **909**, Bu^t **910**, Ph **911**).[642] The central structural motif of these clusters, which were prepared in high yields, corresponds to a double-4-ring (D4R) structure. Comparable clusters were also formed from the reactions of RP(O)(OH)$_2$ with GaMe$_3$ (R = Me **912**, Et **913**, Bu^t **914**, Ph **915**) and InMe$_3$ (R = Me **916**, Et **917**, Bu^t **918**, Ph **919**).[645] However, due to the increased reactivity of MMe$_3$ compared to GaBu$^t_3$, the cage-type compounds were formed under much milder reaction conditions. Interestingly, [MeGaO$_3$PBu^t]$_4$ **910** reacts with NMe$_4$HF$_2$ with formation of monomeric [Bu$_4$N][MeGa{Bu^{t}P(OH)O$_2$}$_3$] **920**.[646] In additon, Roesky *et al*. reported on the reaction of LiGaMe$_4$ and Bu^{t}P(O)(OH)$_2$, yielding the remarkable lithium gallium phosphonate cluster Li$_4$[(MeGa)$_6$(μ_3-O)$_2$(Bu^{t}PO$_3$)$_6$] **921**, in which the Li ions are sandwiched by two dinegatively charged gallophosphonate bowls (Figure 56).

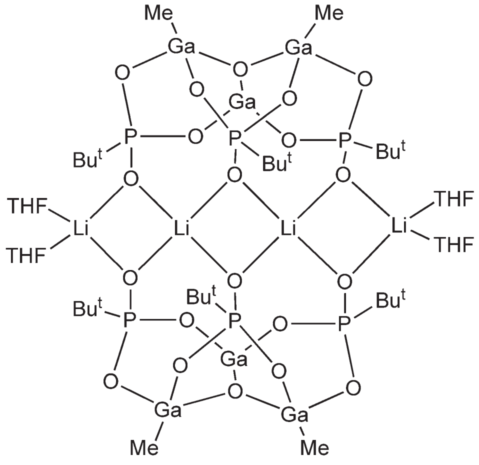
Molecular phosphates of group 13 metals are rare. The reaction of Bu$^t_3$Ga with H$_3$PO$_4$ yielded [Bu$^t_2$GaO$_2$P(OH)$_2$]$_2$ **922**,[642] which further reacts with TMSNMe$_2$ with subsequent formation of [Bu$^t_2$GaO$_2$P(OTMS)$_2$]$_2$ **923**. The corresponding dimethyl derivative [Me$_2$GaO$_2$P(OTMS)$_2$]$_2$ **924** has been obtained from the reaction of Me$_3$Ga and



898



909



921

Figure 56 Structures of novel organogallium- and -indiumphosphonates.

OP(OTMS)$_3$. This reaction initially yielded the corresponding adduct $Me_3Ga–OP(OTMS)_3$, which was then thermolyzed at 110 °C to give **924**.[647] Thermolysis of **922** in refluxing diglyme followed by reaction with $TMSNMe_2$ finally gave the tetrameric gallophosphate $[Bu^tGaO_3P(OTMS)]_4$ **925** in very high yield.[642] Structure **925** is readily hydrolyzed by moisture with formation of TMS_2O, whereas comparable cuboidal $Ga_4P_4O_{12}$ clusters $[Bu^tGaO_3PR]_4$ (R = Me **909**, Bu^t **910**, Ph **911**) are hydrolytically stable.

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3.08
d-Block Complexes of Aluminum, Gallium, Indium, and Thallium

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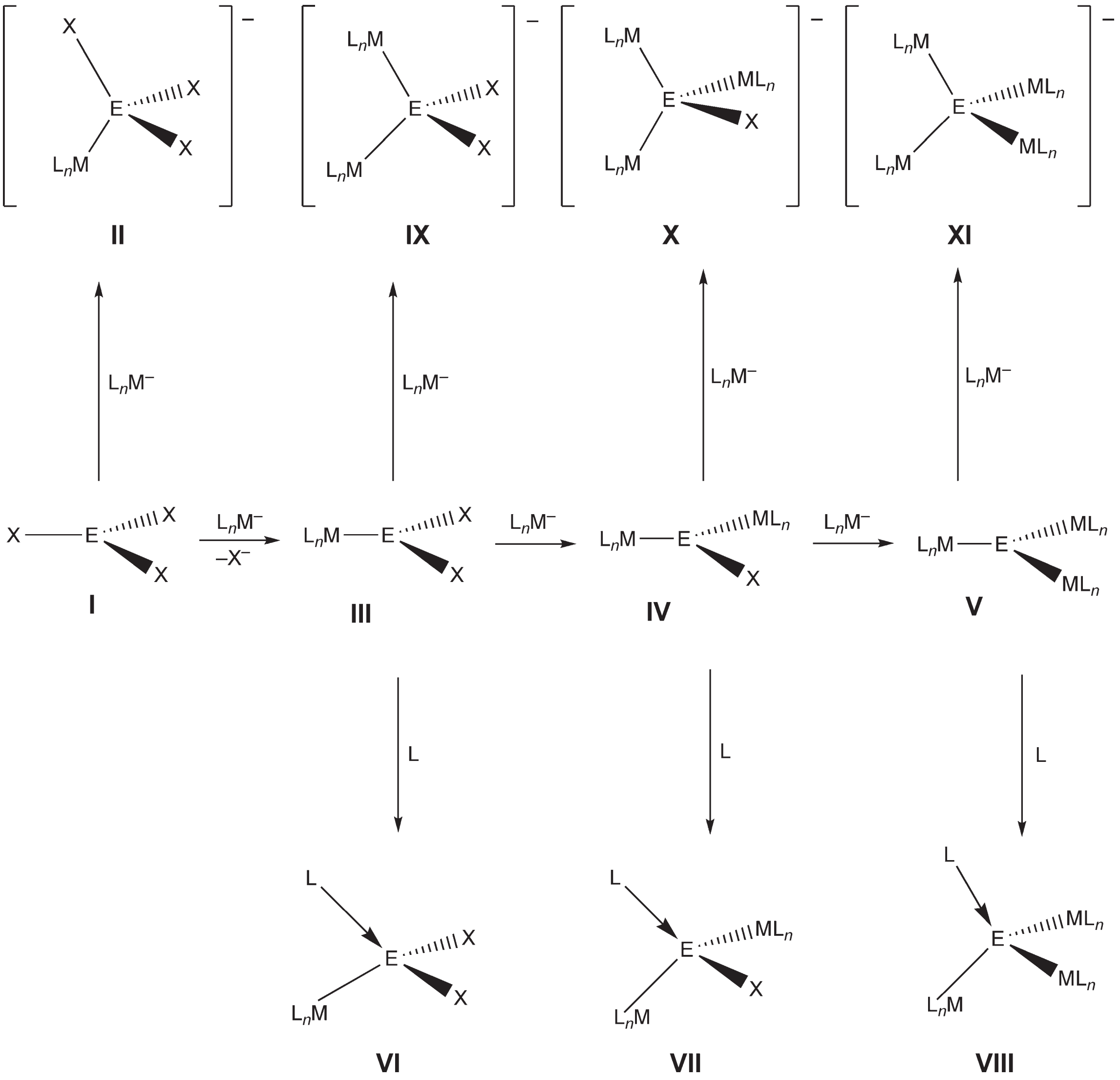
3.08.1 General Considerations

Transition metal adducts of the heaviest group 13 elements (Al, Ga, In, Tl) can be divided into various structural groups based upon simple Lewis structure arguments, where the trigonal-planar six-electron or eight-electron tetrahedral group 13 centers are created. Throughout this review, we will use E to designate a main group element, M a transition metal, and X a halide or pseudohalide. The most common group 13 element compounds EX_3 **I**, with trivalent E, can form simple Lewis acid–base compounds with electron-rich metal centers **II**



Scheme 1

(Scheme 1). In these cases, the metal center formally has an even electron count and is viewed as donating a lone pair of electrons to the group III element center. Often, these L_nM complexes are anionic, resulting in complex ions with an overall negative charge.

Alternatively, group 13 element fragments can bond to transition metals in a covalent linkage. The X^- anions on a central E^{3+} ion can be replaced with anionic organometallic fragments (Scheme 1). As with other inorganic and organometallic group 13 compounds, the tricoordinate metallated species are Lewis acids and can add donor ligands to give tetracoordinate, tetrahedral complexes that obey the octet rule. This "ligand" can also be an electron-donating metal fragment, usually anionic. In a further variation on this theme, the donor ligand L can be covalently attached to the ML_n fragment or to the X function. These structural concepts find a basis in experiment, where reaction of metal carbonyl anions with trivalent group 13 halide complexes is the most widely employed synthetic methodology. Much of the work in the past decade builds upon simple concepts already established in COMC II (1995). These synthetic studies have created an extensive library of chemical compounds.

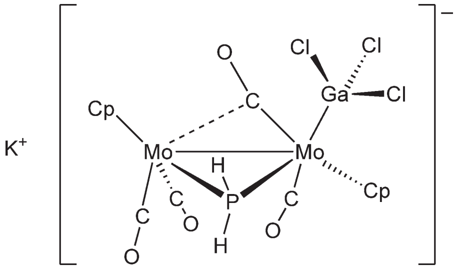
While a few compounds of group 13 complexes in which the group 13 atom was formally in the +1 oxidation state were reported in the previous edition, a tremendous amount of work has been done with such complexes since COMC II due to the ready availability of new reagents such as $\{ER\}_n$ (where R is a bulky organic or chelating nitrogen donor ligand), which have facilitated these studies. The simple Lewis structure of the E–R fragment places a lone pair of electrons on E, and almost all of the complexes reported to date can be conceptually derived as the E–R serving as a two-electron donor ligand to one or more transition metal fragments. The distinction between E^+ and E^{3+} compounds, however, is not always clear, and in some cases one can easily rationalize the structures as having a considerable amount of electron transfer from the E–R unit to the transition metal. The synthetic methodologies also overlap. For example, E–R coordinated to transition metal fragments can also arise from the reaction of REX_2 with metal carbonyl dianions, as will be illustrated below. These complexes have been the subject of recent reviews.[1,2]

For both classes of compounds, the chemistry of the group 13 trivalent and monovalent complexes proceeds similarly for Al, Ga, and In, and so these complexes will be treated together. Much of the chemistry of thallium compounds tends to be unique and will largely be handled separately.

3.08.2 Adducts of EX_3 with Transition Metal Complexes

In some cases, reactions of metal complexes, most often metal anions, with EX_3 or ER_3 lead to simple adduct formation (**II** in Scheme 1) rather than displacement of X or R. New structurally characterized complexes appearing in the past decade are found in Table 1.

In contrast to reactions of alkyl aluminum compounds, Cp^*IrH_2 ($Cp^* = C_5Me_5$ = pentamethylcyclopentadienyl) and $AlPh_3$ produce the simple adduct $Cp^*IrH_2(AlPh_3)$.[3] Similarly, $K[Cp_2Mo_2(CO)_4(\mu\text{-}PH_2)]$ reacts with $GaCl_3$ to produce $K[Cp_2Mo_2(CO)_4(\mu\text{-}PH_2)GaCl_3]$, **1**, which exhibits a polymeric structure in the solid state through $K^+\cdots Cl^-$ interactions.[4]

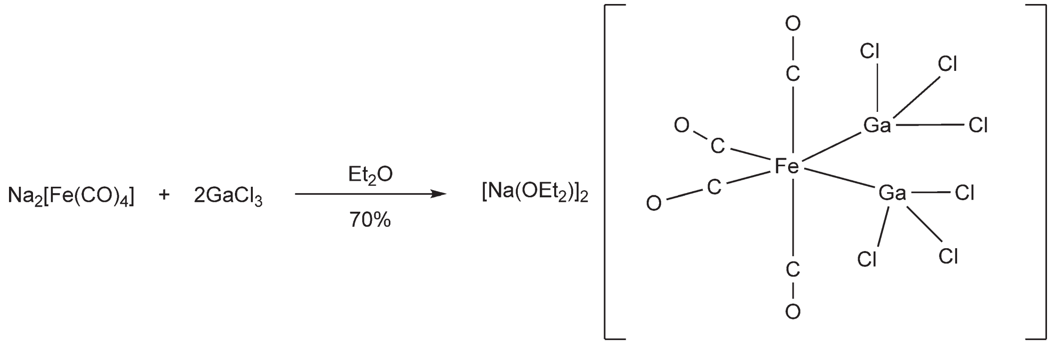


1

The double adduct **2** is formed when $[Fe(CO)_4]^{2-}$ reacts with $GaCl_3$ (Equation (1)). As with **1**, there are interactions between the Cl of the $GaCl_3$ units and the sodium cations, giving a polymeric structure in the solid state.[5] The Ga–Fe–Ga angle is 90.74(3)°.

Table 1 Adducts of the form L_nMEX_3

Compound	*E–M distance* (pm)	*References*
$Cp^*Ir(PMe_3)H_2(AlPh_3)$	268.4(2)	3
$K[Cp_2Mo_2(CO)_4(\mu\text{-}PH_2)GaCl_3]$	260.6(3)	4
$[Na(OEt_2)_2]_2[(CO)_4Fe\{GaCl_3\}_2]$	240.9(1) 241.1(1)	5
$[CpFe(C_6H_5Me)][Cp(CO)_2FeGaI_3]$	236.1(7)	6
$K[(CO)_4CoGaCl_3]$	237.99(18)	7
$[C(NMe_2)_3]_2[Fe(CO)_4InCl_3]$	251.7(2)	8

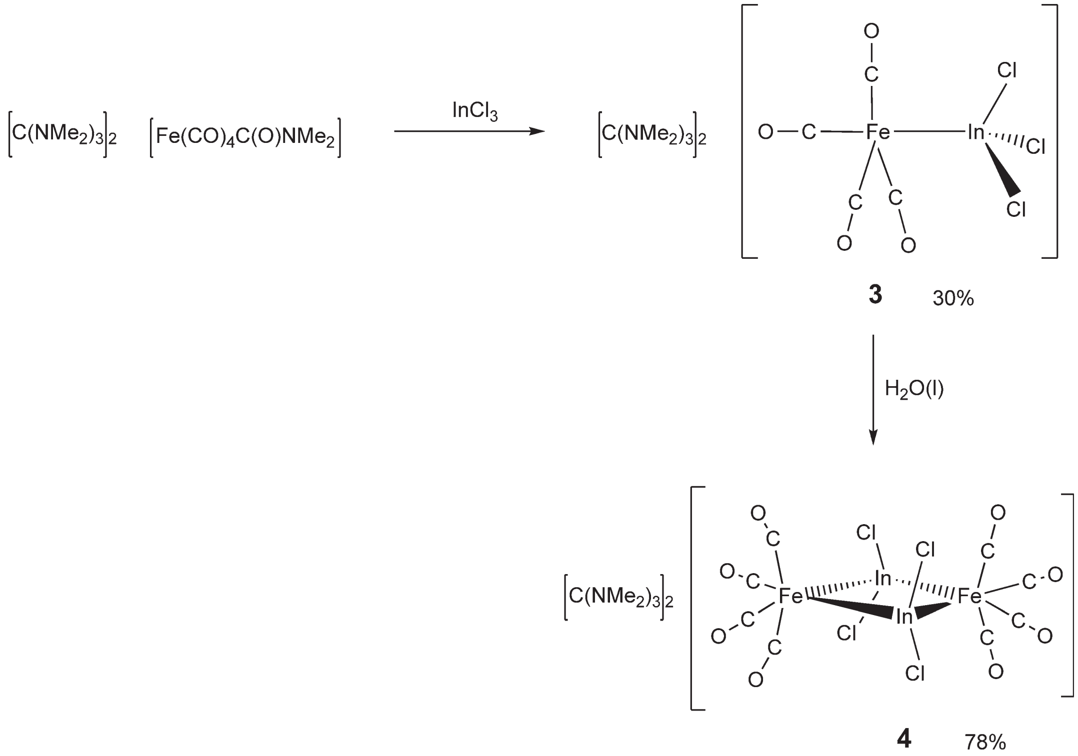


2

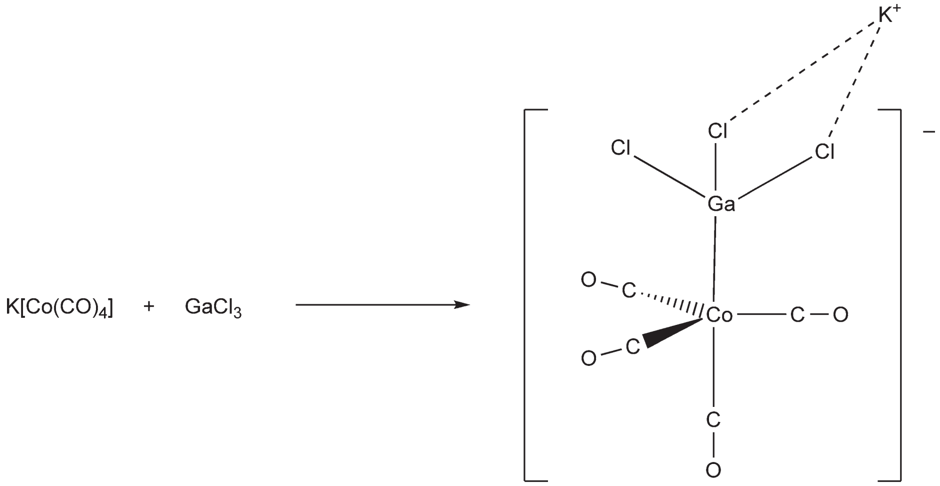
(1)

In contrast, $InCl_3$ produces a monoadduct **3** with $[Fe(CO)_4]^{2-}$ (Scheme 2). This adduct reacts with water to eliminate a chloride ion and produce $[C(NMe_2)_3]_2[Fe_2(CO)_8(\mu\text{-}InCl_2)_2]$ **4**, which can be viewed as a dimerization of two $[Fe(CO)_4InCl_2]^-$ units. The In–Fe distance in **3** (251.7(2) pm) is somewhat shorter than the Fe–In interactions in **4** (265.55(2) and 264.84(2) pm), as is usual for bridging versus terminal bonding.[9] DFT calculations indicate that **3** is best considered as an $InCl_3$ adduct of $Fe(CO)_4{}^{2-}$, but the compound has not been prepared by direct reaction of these two reagents. The compound $[CpFe(C_6H_5Me)][Cp(CO)_2FeGaI_3]$ is one product arising from the reaction of gallium(i) iodide with $[CpFe(CO)_2]_2$ in toluene (see Section 3.08.5).[6] The Fe–Ga distance is slightly shorter than observed in the $Fe(CO)_4$ derivative.

The anion $[Co(CO)_4]^-$ also forms the 1 : 1 adduct **5** with $GaCl_3$, also exhibiting $K^+\cdots Cl^-$ interactions in the solid state (Equation (2)) like (**1**).



Scheme 2



5

(2)

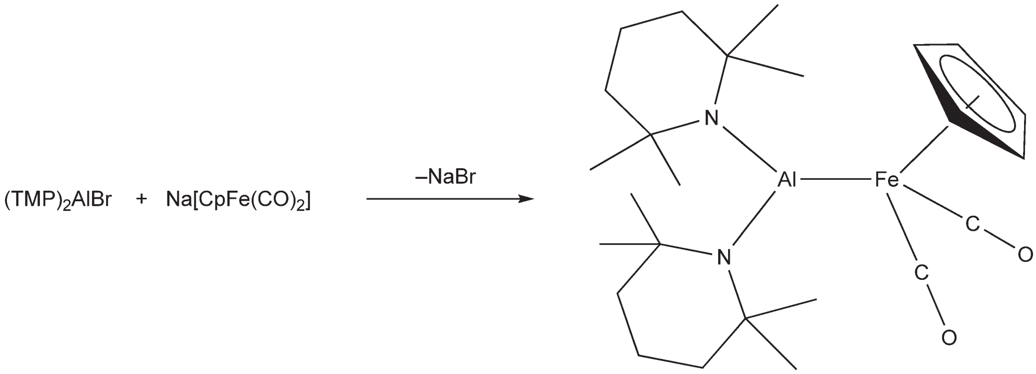
3.08.3 Reactions Beginning with Trivalent Group 13 Element Halides and Metal Carbonyl Monoanions

Successive reactions of metal carbonyl monoanions with EX$_3$ can lead to structure types **III** through **VIII** in Scheme 1, although these compounds may also be obtained from other, less obvious routes. Further options include replacing the X units with alkyl or aryl functions, which is usually achieved by starting with EX$_{3-x}$R$_x$.

3.08.3.1 Tricoordinate EX$_{3-x}$(ML$_n$)$_x$ and ER$_{3-x}$(ML$_n$)$_x$

This class of complexes represents the simplest derivatives of the trivalent EX$_3$ complexes, in which the E atom remains a six-electron center and adopts a trigonal-planar geometry. These are represented in Scheme 1 as **III–V**, and new compounds reported in the past decade are presented in Table 2. As formally "electron-poor" structures, these molecules can serve as Lewis acids, and may be employed to synthesize the other eight-electron structures seen in Scheme 1 **VI–XI**, and the corresponding organic derivatives where one or more X groups are replaced by R. The central group 13 element does not change oxidation number in these reactions.

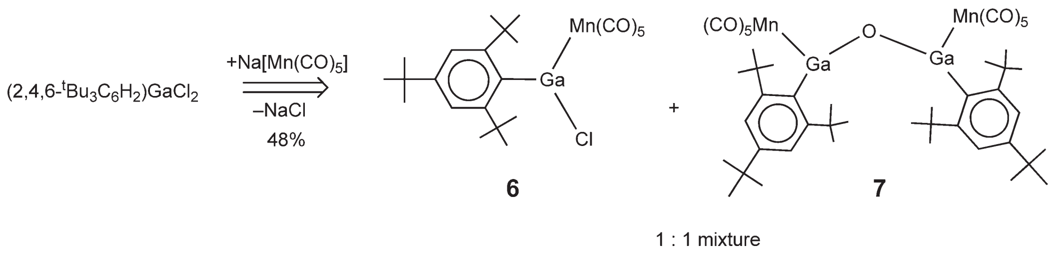
Examples of the simple salt metathesis reactions to produce metal-bound group 13 elements are given in Equations (3)–(16).[10–14,16,22] Compound **7** in Equation (4)[14] can be viewed as a hydrolysis product of **6**. Redistribution reactions can occur in these systems. For example, the reaction of Cp*GaCl$_2$ with Na[Mn(CO)$_5$] (Equation (5))[12] or recrystallization of GaCl$_2$(C$_6$H$_2$-2,4,6-^{t}Bu$_3$) gave Ga{Mn(CO)$_5$}$_3$.[12] Similarly, reaction of Cp*InCl$_2$ with K[CpFe(CO)$_2$] or K[CpW(CO)$_3$] yielded In(ML$_n$)$_3$.[13,14] The authors were ultimately able to isolate the bis-substituted GaMn$_2$ complex using an excess of the manganese carbonylate.[12]



(3)

Table 2 E–M bond distances for new crystallographically characterized trivalent complexes of the form $EX_{3-x}(ML_n)_x$ and $ER_{3-x}(ML_n)$

Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$Cp(CO)_2FeAl(tmp)_2$	245.0(1)	10
Gallium compounds		
$Cp(CO)_3MoGa(^tBu)_2$	273.76(5)	11
$Ga\{Mn(CO)_5\}_3$	255.4(1)	12
	255.8(1)	
	256.5(1)	
$(\eta^1\text{-}Cp^*)_2GaMn(CO)_5$	254.8(1)	13
$[(2,4,6\text{-}^tBu_3C_6H_2)\{Mn(CO)_5\}Ga]_2O$	253.0(3)	14
	253.6(4)	
$(2,4,6\text{-}^tBu_3C_6H_2)Ga\{Mn(CO)_5\}Cl$	249.5(4)	14
$[\{Cp^*(CO)_2Fe\}_2Ga][B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]$	227.2(1)	15
	226.6(1)	
$\{Cp^*(CO)_2Fe\}_2GaCl$	235.24(4)	15
$\{Cp(CO)_2Fe\}Ga(^tBu)_2$	241.7(1)	16
$\{Cp(CO)_2Fe\}_2Ga^tBu$	240.6(1)	16
	241.6(1)	
$\{Cp^*(CO)_2Fe\}_2Ga(mes)$	243.15(15)	17
$Cp^*(CO)_2FeGa(Cl)(Cp^*)$	233.55(10)	18
$[PPN]_2[MeGa\{Fe(CO)_4\}_2]$	241.58(6)	19
$(2,4,6\text{-}^tBu_3C_6H_2)Ga\{Co(CO)_4\}_2$	251.4(2)	14
	248.1(2)	
$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga\{Co(CO)_4\}_2$	260.2(16)	20
Indium compounds		
$(2,4,6\text{-}^tBu_3\text{-}C_6H_2)In\{Co(CO)_4\}_2$	265.0(1)	12
	261.2(1)	
$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}In\{Co(CO)_4\}_2$	267.4(1)	20
$(C_5H_4CH_2CH_2NMe_2)Ni(PMe_3)InI_2$	241.80(7)	21
$\{Cp(CO)_3Mo\}_2InN(SiMe_3)_2$	281.8(1)	22
	283.3(1)	
$\{Cp(CO)_3Mo\}In\{N(SiMe_3)_2\}_2$	279.4(1)	22
$\{Cp(CO)_3W\}_3In$	289.4(2)	13
	288.9(1)	
	286.8(2)	
Thallium compounds		
$Tl\{Co(CO)_4\}_3$	264.80(14)	23
	266.2(2)	
	266.03(14)	
$Tl\{Fe(CO)_2Cp\}_3$	263.9(2)–266.2(2)	23
$[BuNMe_3]_3[Tl\{Fe(CO)_4\}_3]$	269.40(12)	23



6 **7**

1 : 1 mixture

(4)

$$Cp^*GaCl_2 + Na[Mn(CO)_5] \Longrightarrow Ga\{Mn(CO)_5\}_3 \tag{5}$$

$$(\mathrm{Cp}^*)_2\mathrm{GaCl} + \mathrm{K[Mn(CO)_5]} \longrightarrow \underset{40\%}{(\eta^1\text{-}\mathrm{Cp}^*)_2\mathrm{GaMn(CO)_5}} + \mathrm{KCl} \tag{6}$$

$$\mathrm{GaCl_2(C_6H_2\text{-}2,4,6\text{-}{}^tBu_3)} + >2\mathrm{Na[Mn(CO)_5]} \xrightarrow{\mathrm{Et_2O}} \underset{82\%}{\mathrm{(2,4,6\text{-}{}^tBu_3\text{-}C_6H_2)Ga\{Mn(CO)_5\}_2}} + 2\mathrm{NaCl} \tag{7}$$

$$\mathrm{InBr_2(C_6H_2\text{-}2,4,6\text{-}{}^tBu_3)} + 2\mathrm{Na[Mn(CO)_5]} \xrightarrow{\mathrm{Et_2O}} \underset{71\%}{\mathrm{(2,4,6\text{-}{}^tBu_3\text{–}C_6H_2)In\{Mn(CO)_5\}_2}} + 2\mathrm{NaBr} \tag{8}$$

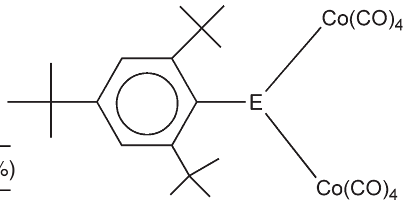
$$\mathrm{Na[CpFe(CO)_2]} + \mathrm{({}^tBu)_2GaCl} \xrightarrow[84\%]{-\mathrm{NaCl}} \mathrm{\{Cp(CO)_2Fe\}Ga({}^tBu)_2} \tag{9}$$

$$2\mathrm{Na[CpFe(CO)_2]} + \mathrm{{}^tBuGaCl_2} \longrightarrow \underset{60\%}{\mathrm{\{Cp(CO)_2Fe\}_2Ga{}^tBu}} + 2\mathrm{NaCl} \tag{10}$$

$$\mathrm{K[CpFe(CO)_2]} + \mathrm{GaI_3(excess)} \xrightarrow{-\mathrm{KI}} \mathrm{\{CpFe(CO)_2\}GaI_2} \tag{11}$$

$$3/n\ \mathrm{[\{Cp(CO)_2Fe\}GaCl_2]}_n + \mathrm{K} \longrightarrow \mathrm{\{Cp(CO)_2Fe\}_3Ga} + 2\mathrm{Ga} + 6\mathrm{KCl} \tag{12}$$

$$\mathrm{(2,4,6\text{–}{}^tBu_3\text{-}C_6H_2)EX_2} + 2\mathrm{Na[Co(CO)_4]} \xrightarrow{-2\mathrm{NaX}}$$



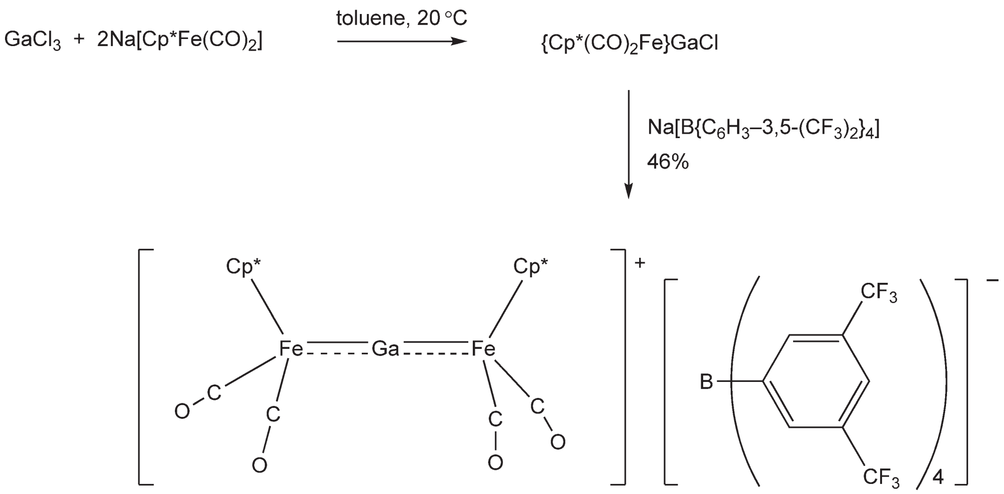
E	*X*	*Yield* (%)
Ga	Cl	32
In	Br	63

(13)

$$\mathrm{K[Cp(CO)}_x\mathrm{M]} + \mathrm{Cp^*InCl_2} \xrightarrow[\substack{\mathrm{M = Fe},\ x = 2\\ \mathrm{M = W},\ x = 3}]{} \mathrm{In\{M(CO)}_x\mathrm{Cp\}_3} \tag{14}$$

$$\mathrm{\{Cp(CO)_3Mo\}_2InCl} + \mathrm{LiN(SiMe_3)_2} \xrightarrow{-\mathrm{LiCl}} \mathrm{\{Cp(CO)_3Mo\}_2InN(SiMe_3)_2} \tag{15}$$

$$\mathrm{\{Cp(CO)_3Mo\}InCl_2} + 2\mathrm{LiN(SiMe_3)_2} \xrightarrow{-2\mathrm{LiCl}} \mathrm{\{Cp(CO)_3Mo\}In\{N(SiMe_3)_2\}_2} \tag{16}$$



[**8**]$^+$

Scheme 3

One exception to the three-coordinate, trigonal-planar structures of these adducts is the cation $[Ga\{Fe(CO)_2Cp^*\}_2]^+$ shown in Scheme 3.[15] The cationic complex $[\mathbf{8}]^+$ is produced by halide removal from $\{Cp^*(CO)_2Fe\}_2GaCl$ and can be thought of a Ga^{3+} ion ligated by two $[Cp(CO)_2Fe]^-$ groups. The Fe–Ga–Fe bond angle in $[\mathbf{8}]^+$ is 178.99(2)° as compared to that in $\{Cp^*(CO)_2Fe\}_2GaCl$, which has an angle of 138.90(3)°.[15] DFT calculations support significant π-backbonding from the Fe→Ga, which is also consistent with the relative orientation of the $Cp^*Fe(CO)_2$ units that maximizes overlap between the orthogonal *p*-orbitals on the Ga with *d*-orbitals on each metal fragment.[15] From Table 2, it can be seen that the Fe–Ga distances in $[\mathbf{8}]^+$ are considerably shorter (>10 pm) than those in other tricoordinate Ga–Fe compounds, supporting the Fe–Ga π-backbonding arguments. However, work on other E^+ derivatives suggests that forms with highly separated charge distributions can also explain the short distances (see Section 3.08.4).

3.08.3.2 Base-stabilized Trivalent Group 13 Element–Transition Metal Complexes

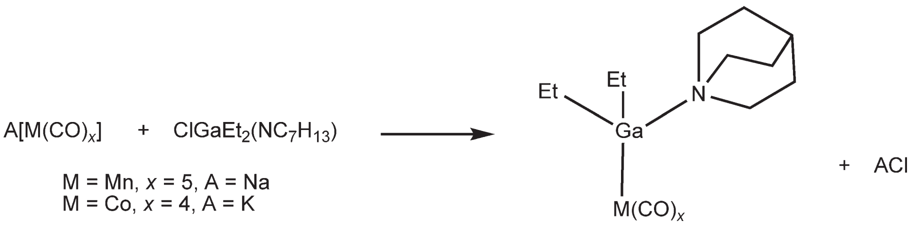
The Lewis-acidic group 13 elements can readily coordinate a variety of ligands to produce eight- or (in the case of Ga and In) ten-electron centers. The donor ligands can range from conventional basic ligands such as amines, phosphines, halide ions, hydroxide, or oxide ions. These fundamental structure types are found in Scheme 1 as structures **VI–XI**. As variations, the ligands may be internally bound to either the metal fragment or as part of an organic function attached to E. The Lewis acidity may also be satisfied by formation of dimers or higher oligomers through halide, hydroxide, or oxide bridges. A wide variety of base-stabilized metal-bound organogallium derivatives (Table 3) have been prepared from the metal carbonylate anions and the appropriate organogallium halide in yields of 80–95%.[24,25] Table 4 gives E–M bond distances for structurally characterized complexes in this class.

A variety of reactions forming ligand-stabilized complexes have been reported (Schemes 4[27] and 5[11], Equations (17)–(25)).[7,11,16,29,38] The complex $CpMo(CO)_3Ga(^tBu)_2$ shows intermolecular interactions between the Ga atom and the oxygen atoms of carbonyl ligands on adjacent molecules in the solid state and may be thought of as being weakly ligand stabilized.[11] The molecule adds MeCN to form a simple base-stabilized adduct (Equation (17)).[11] A unique, stabilized organogallium(III) species is produced from the reaction of a gallacyclopentadiene with $CpCo(C_2H_4)_2$ (Equation (25)).[38] In this case, the gallacyclopentadiene group binds to a CpCo fragment in a pentahapto fashion, producing a complex in which there is a Ga–Co bond of 270.6(2) pm. The gallium atom retains its three bonds to carbon.

Table 3 Base-stabilized trivalent group 13 element–transition metal complexes[24–26]

Compounds	*R, M, X, L*
Aluminum compounds	
$Cp(CO)_2FeAl(R)(CH_2CH_2CH_2NMe_2)$	$R = {}^iBu, CH_2CMe_3, BH_4, Br$
$(Me_3P)(CO)_3CoAl(R)(CH_2CH_2CH_2NMe_2)$	$R = {}^iBu, CH_2CMe_3, Br$
$Cp(CO)_2RuAl(Br)(CH_2CH_2CH_2NMe_2)$	
$Cp(CO)_2FeAlX_2L$	$X = Cl, L = THF$
	$X = H, L = THF$, quinuclidine
Gallium Compounds	
$Cp(CO)_xMGaCl_2(NMe_3)$	$M = Cr, Mo, W, x = 3$
	$M = Fe, x = 2$
	$M = Ni, x = 1$
$Cp(CO)_3MGaCl(CH_2CH_2CH_2NMe_2)$	$M = Cr, Mo, W$
$Cp^*M(CO)_3GaCl(CH_2CH_2CH_2NMe_2)$	$M = Mo, W$
$(CO)_5MnGaR_2L$	$R = H, Et, Cl, L = NMe_3$
	$R = Et, L = NC_7H_{13}$
$\{(CO)_5Mn\}_{2-x}GaCl_x(CH_2CH_2CH_2NMe_2)$	$x = 0, 1$
$\{(CO)_5Mn\}\{(CO)_5Re\}Ga(CH_2CH_2CH_2NMe_2)$	
$[Cp(CO)_2FeGa(O^tBu)_2]_2$	
$\{(CO)_4Co\}GaR_2(NMe_3)$	$R = H, Et, Cl$
$\{L(CO)_3Co\}Ga(CH_2CH_2CH_2NMe_2)(R)$	$R = Et, CH_2{}^tBu, H, Cl, L = CO$
	$R = Cl, L = PMe_3, PPh_3$
	$R = {}^tBu, L = PMe_3, PPh_3$
	$R = Me, L = PCy_3$
$\{(CO)_4Co\}Ga(CH_2CH_2CH_2NEt_2)({}^tBu)$	
$Cp(CO)NiGa(CH_2CH_2CH_2NEt_2)(R)$	$R = Me, {}^tBu$
$\{(CO)_4Co\}_2GaH(THF)$	
$(PMe_3)(CO)_3CoGaCl_2(NMe_3)$	

$$CpMo(CO)_3Ga({}^tBu)_2 + MeCN \longrightarrow CpMo(CO)_3Ga({}^tBu)_2(NCMe) \tag{17}$$



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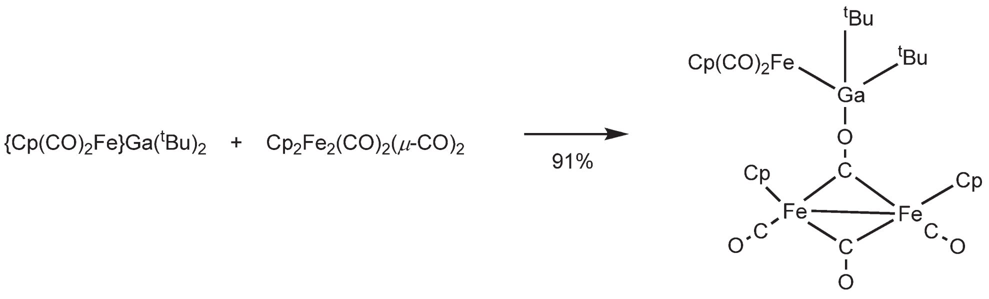

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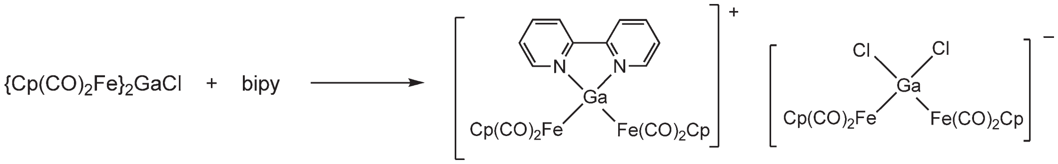
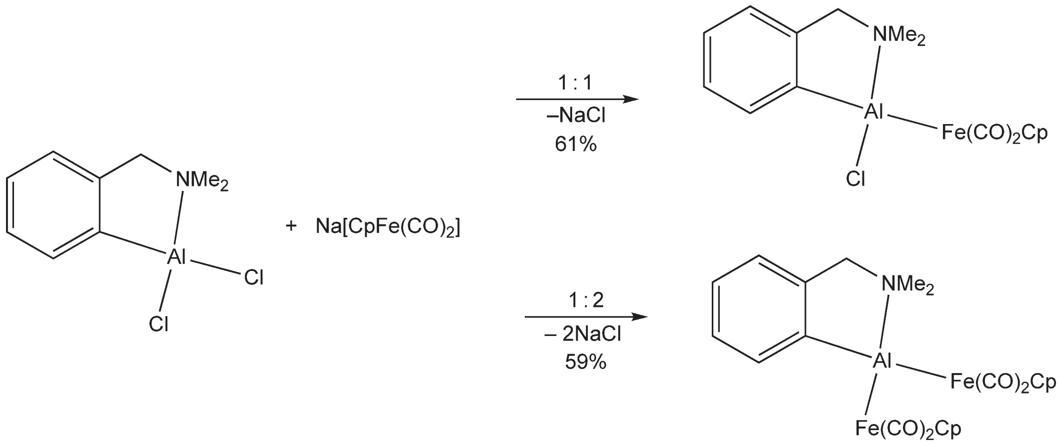


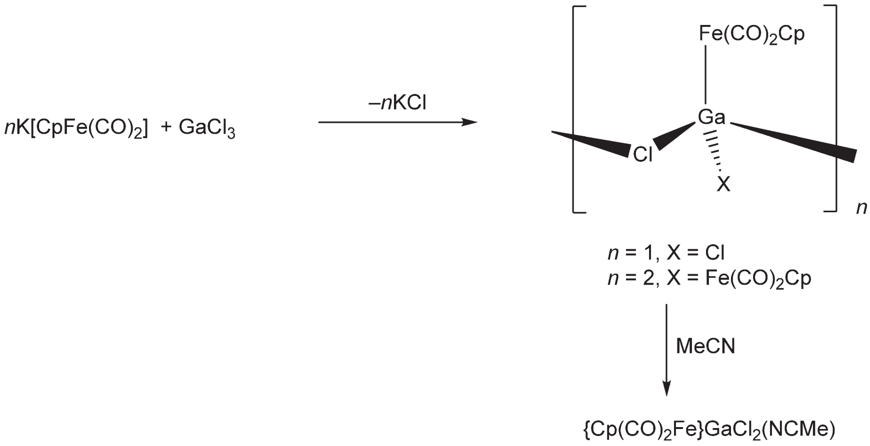
(20)

Table 4 E–M bond distances in new crystallographically characterized ligand-stabilized trivalent complexes

Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$\mathrm{Cp(CO)_2FeAl[(CH_2)_3NMe_2]({}^{i}Bu)}$	245.6(1)	26
$\mathrm{\{Cp(CO)_2Fe\}_2Al(C_6H_4CH_2NMe_2)}$	246.8(1)	27
	249.6(1)	
Gallium compounds		
$\mathrm{(CO)_5MnGaEt_2(NC_7H_{13})}$	266.67(7)	7
$\mathrm{\{(CO)_5Mn\}_2Ga(CH_2CH_2CH_2NMe_2)}$	262.63(5)	25
	267.92(4)	
$\mathrm{\{Cp(CO)_2Fe\}GaCl_2(THF)}$	231.7(1)	6
$\mathrm{\{Cp^*(GaCp^*)_2Fe\}GaCl_2(THF)}$	227.90(15)	18
	232.08(17)	
$\mathrm{\{Cp(CO)_2Fe\}GaCl_2(NMe_3)}$	236.18(3)	24
$\mathrm{\{Cp(CO)_2Fe\}_2GaCl(THF)}$	238.8(1)	6
$\mathrm{[\{Cp(CO)_2Fe\}GaCl_2]_2(dioxane)}$	231.64(9)	6
$\mathrm{[\{Cp(CO)_2Fe\}Ga(ClGaCl_3)(\mu\text{-}Cl)]_2}$	228.6(1)	11
$\mathrm{[\{Cp(CO)_2Fe\}_2Ga(\mu\text{-}Cl)]_\infty}$	236.54(7)	11
$\mathrm{K_2(OEt_2)_4FeO_2Br_8Ga_4\{Fe(CO)_2Cp\}_4}$	232.8(1) – 233.1(1)	6
$\mathrm{\{Cp(CO)_2Fe\}_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2}$	235.9(2)	11
	234.4(2)	
	234.0(2)	
$\mathrm{(CO)_4FeGa_3\{Si(SiMe_3)_3\}_3(OH)_4}$	248.36(12)	28
	248.98(12)	
$\mathrm{[\{Cp(CO)_2Fe\}_2Ga(bipy)][\{Cp(CO)_2Fe\}_2GaCl_2]}$		
cation	240.37(14)	29
	239.69(16)	
anion	242.34(13)	
	243.59(15)	
$\mathrm{\{Cp(CO)_2Fe\}(Cl)Ga(\mu\text{-}PPh_2)_2Fe(CO)Cp}$	238.5(2)	30
$\mathrm{\{Cp(CO)_2Fe\}Ga({}^{t}Bu)_2(\mu\text{-}OC)Fe_2(CO)_2(\mu\text{-}CO)Cp_2}$	244.1(1)	16
$\mathrm{K(OEt_2)_2Ga_2Cl_3\{Fe(CO)_2Cp\}_4}$	237.70(8)	6
	237.7(1)	
$\mathrm{(CO)_3(PMe_3)CoGaCl_2NMe_3}$	234.2(1)	7
$\mathrm{(CO)_4CoGaEt_2(NC_7H_{13})}$	258.67(10)	7
$\mathrm{(PPh_3)(CO)_3CoGa(Cl)(CH_2CH_2CH_2NEt_2)}$	237.78(4)	24
$\mathrm{(PPh_3)(CO)_3CoGa(Me)(CH_2CH_2CH_2NEt_2)}$	249.5(1)	24
$\mathrm{Ni(CO)(C_5H_4CH_2CH_2NMe_2)GaCl_2}$	227.9(7)	31
$\mathrm{Ru(CO)_3\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2}$	243.2(1)	32
	245.9(1)	
	247.8(1)	
$\mathrm{Ru_2(CO)_8\{GaCl_2(THF)\}_2}$	245.3(1)	32
Indium compounds		
$\mathrm{\{(CO)_4Co\}_2In(CH_2SiMe_3)(THF)}$	263.83(4)	33
$\mathrm{[\{Cp(CO)_3Mo\}InCl_2]_\infty}$	275.0(1)	34
$\mathrm{\{Cp(CO)_2Fe\}In(CH_2CH_2CH_2NMe_2)_2}$	263.9(1)	33
$\mathrm{\{Cp(CO)\ Ni\}In(CH_2CH_2CH_2NMe_2)_2}$	259.8(1)	33
$\mathrm{Cp(CO)NiInBr_2(quinuclidine)}$	246.3(1)	35
$\mathrm{Cp(Ph_3P)NiInBr_2(L)}$	244.65(9)	36
$\mathrm{[(PPh_3)(CO)_3Fe\{Si(OMe)_2(\mu\text{-}OMe)\}InCl_2(OPPh_3)]}$	260.0(1)	37
$\mathrm{[\{Si(OMe)_3\}(CO)_3Fe(\mu\text{-}dppm)InCl\{(C_5H_4Me)Mo(CO)_3\}]}$	268.0(1)	37
	284.3(1)	



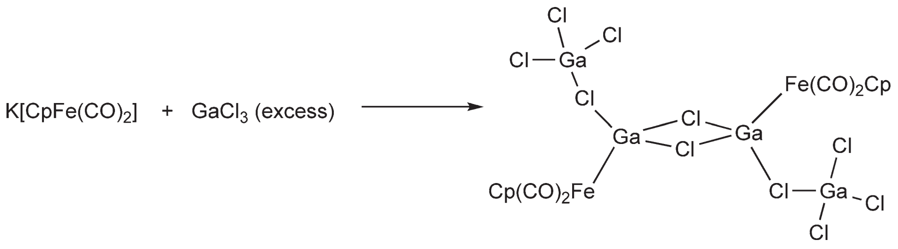
Scheme 4



Scheme 5

$$\{Cp(CO)_2Fe\}_2GaCl \quad + \quad L_2 \xrightarrow[-NaCl]{MeCN,\ NaBPh_4} [\{Cp(CO)_2Fe\}_2Ga(L_2)][BPh_4] \tag{21}$$

L_2	*Yield* (%)
N,*N*,*N*,*N*-tetramethylethylenediamine	31
1,10-phenanthroline	64
4-(dimethylamino)pyridine	62



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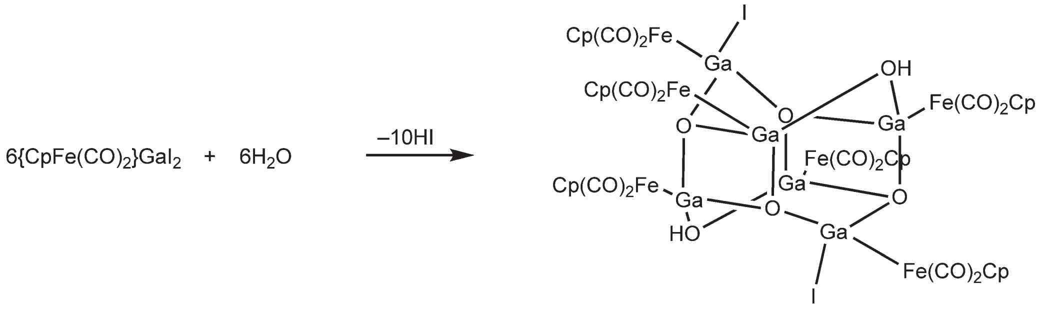

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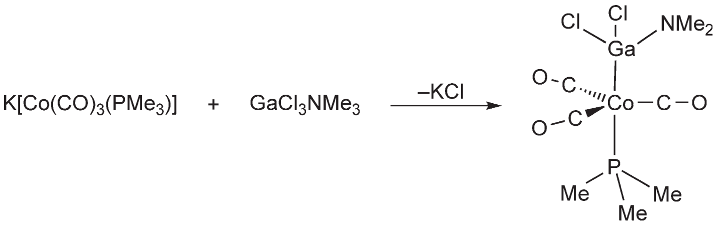

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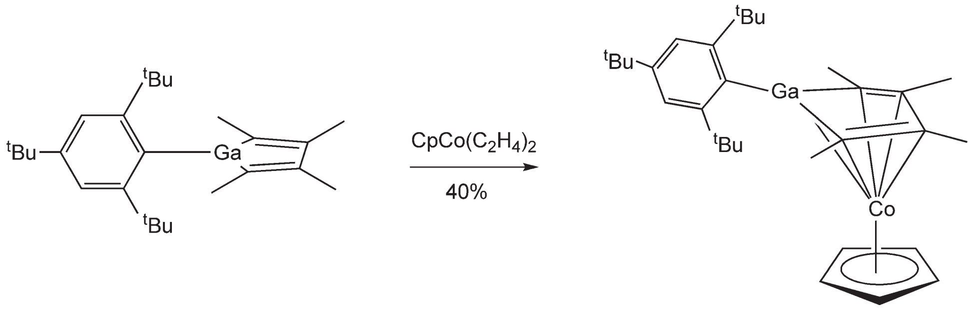
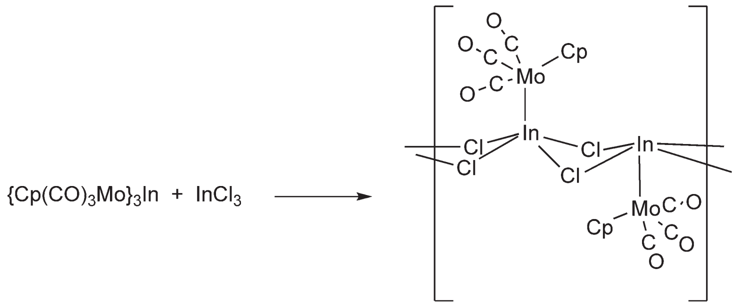


(25)

The variation in the Ga–M lengths in these compounds was found to be not due to solely steric factors,[7] but electronic influences are also important. The shortest M–Ga bonds are found for the most nucleophilic carbonyl metallate fragment and the most sterically unencumbered and most strongly electrophilic Ga units.[7] If TMEDA is present in a reaction similar to Equation (26), a compound thought to be $\{(CO)_4Co\}_2In(CH_2SiMe_3)(TMEDA)$ is isolated, but never in pure form.[33] If $ClInR_2$ (R = Me, ^{t}Bu) were employed instead, the product isolated was $In\{Co(CO)_4\}_3$. The redistribution reaction shown in Equation (27) produces a compound that is soluble in THF but crystallizes as a chain polymer 9 when hexane is added.[34] Equation (28)[35] is an alternate reaction methodology, in which In(I) and In(III) compounds are mixed in the presence of a metal–metal bonded dimer. Effectively, this produces an "In(II)" intermediate that can then reduce the metal–metal bond to end up with a product that contains In^{3+}. The mechanism is unclear as the reaction methodology also allows for insertion of the In(I) halide into the metal–metal bond, with subsequent redistribution with the In(III) halide.

$$Na[Co(CO)_4]\cdot 2THF \ + \ ClIn(CH_2SiMe_2)_2 \longrightarrow \{(CO)_4)Co\}_2In(CH_2SiMe_3)(THF) \qquad (26)$$



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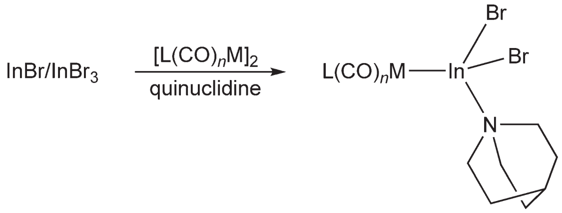
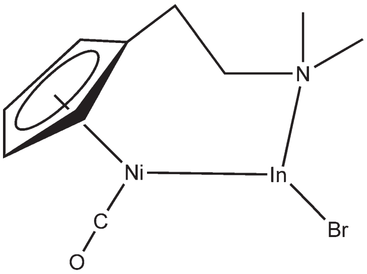
(27)



M	*L*	*n*
Fe	Cp	2
Ni	Cp	1
Co	CO	4

(28)

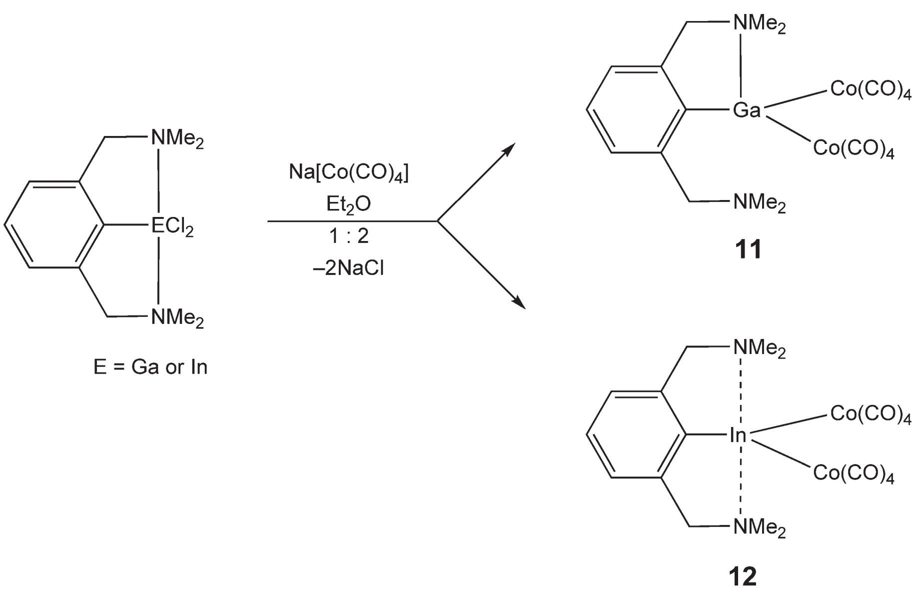
Structure **10**[31] illustrates an internally base-stabilized complex, in which the stabilizing unit is part of the added metal fragment. This contrasts to the other molecules in this section where the chelating function is part of the organic group attached to E.



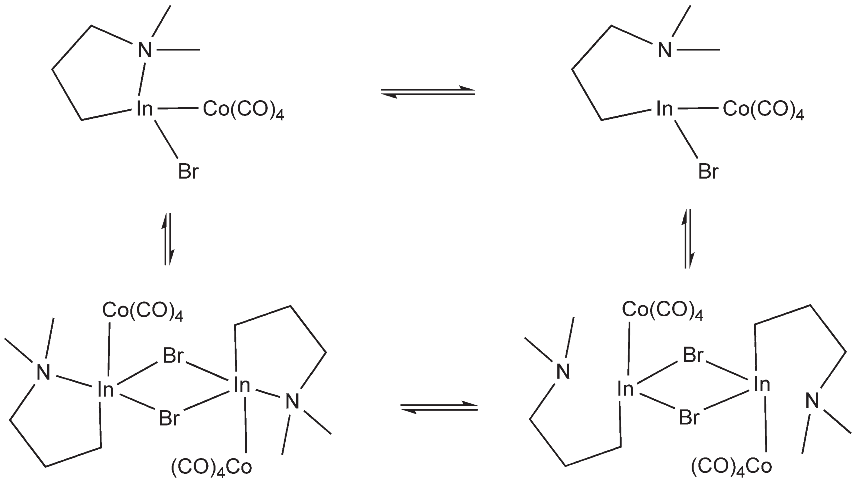
10

Scheme 6 illustrates the possibility that more than one internally coordinating chelating group may be present in a single molecule. For the smaller gallium atom, the coordination of two $Co(CO)_4$ units causes one of the NMe_2 arms to detach **11**, whereas both the NMe_2 remain bonded in the indium compound **12**, although they are bound weakly ($d_{In–N} = 270.2(5)$, 271.1(5) pm).[20] The indium compound is pseudo-trigonal bipyramidal. The $ClInCo_2$ grouping is nearly planar, but the N–In–N angle deviates considerably from linear at 143.1(2)°. The ^1H NMR spectrum for the gallium compound shows that the two NMe_2 units are equivalent on the NMR timescale, suggesting a "flip-flop" mechanism in which these two units switch back and forth in their coordination to the gallium center.

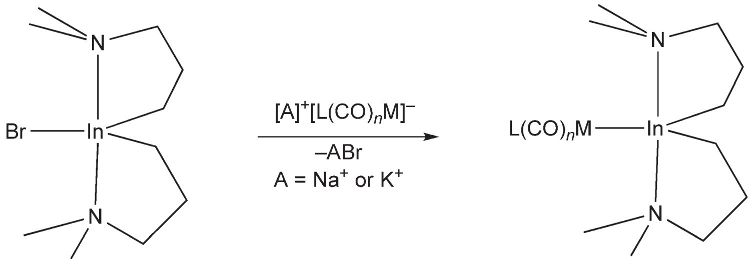
The use of multiple chelating arms was examined in yet another approach (Equation (29)),[33] in which the two arms are present in two separate organic functions attached to a central indium atom, **13**.[33] Direct metallation yields the exchange of the halide ion for the metal fragment giving **14**, but in the presence of InBr (Equation (30)),[35] a redistribution takes place to give a derivative containing only one organic group, **15**.[35] The two diastereotopic methyl groups of the NMe_2 unit in $\{(CO)_4Co\}In(Br)(CH_2CH_2CH_2NMe_2)$ equilibrate rapidly on the NMR timescale.[35] Involvement of species in which the NMe_2 unit dissociates from the indium atom were suggested, and the kinetics of the process implicated dimeric forms, such as those shown in Scheme 7,[35] as intermediates. Metallation of **13** with either $[Fe(CO)_4]^{2-}$ (Equation (31))[33] or $[CpM(CO)_3]^-$ (M = Mo, W) (Equation (32))[33] produces redistribution products directly.



Scheme 6



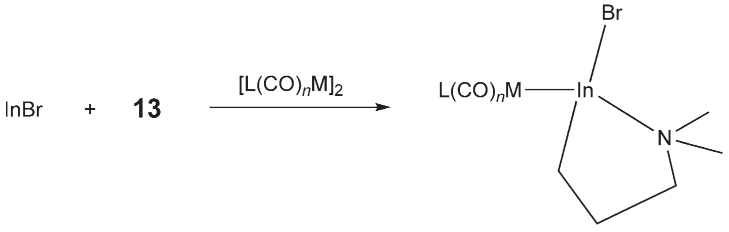
Scheme 7



13 **14**

M	*L*	*n*
Fe	Cp	2
Ni	Cp	1
Mn	CO	5
Re	CO	5
Co	CO	4

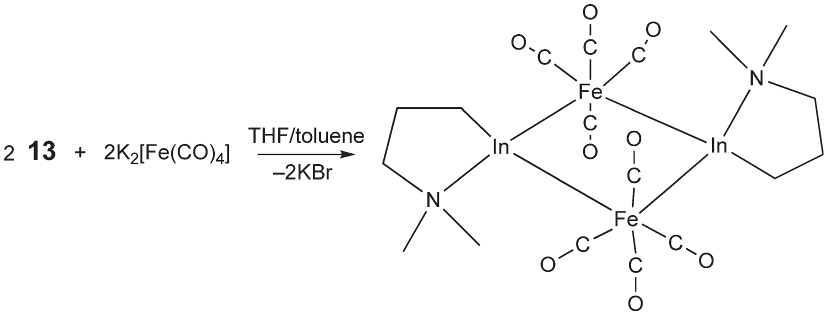
(29)



15

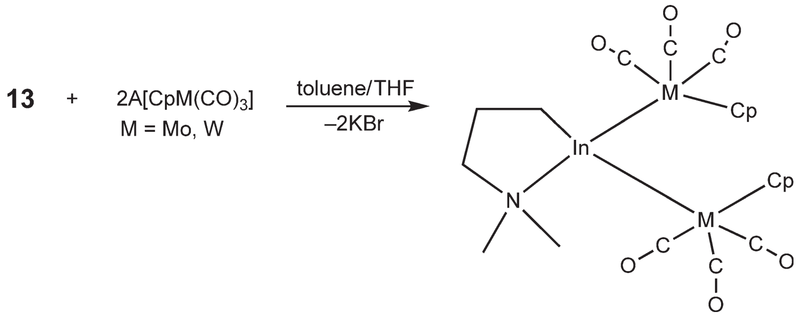
M	*L*	*n*
Fe	Cp	2
Ni	Cp	1
Co	CO	4

(30)



(~80–90%)

(31)

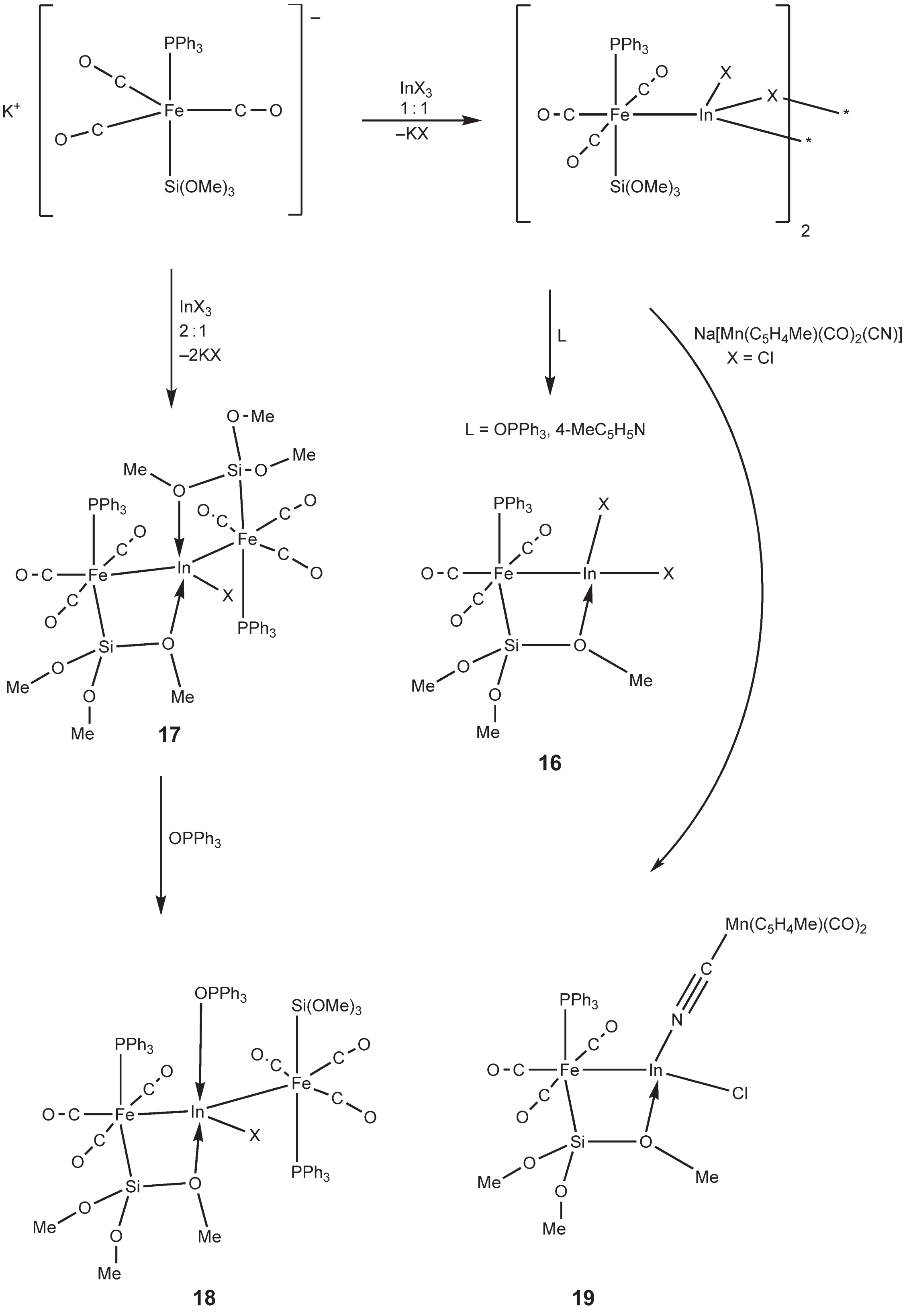


(32)

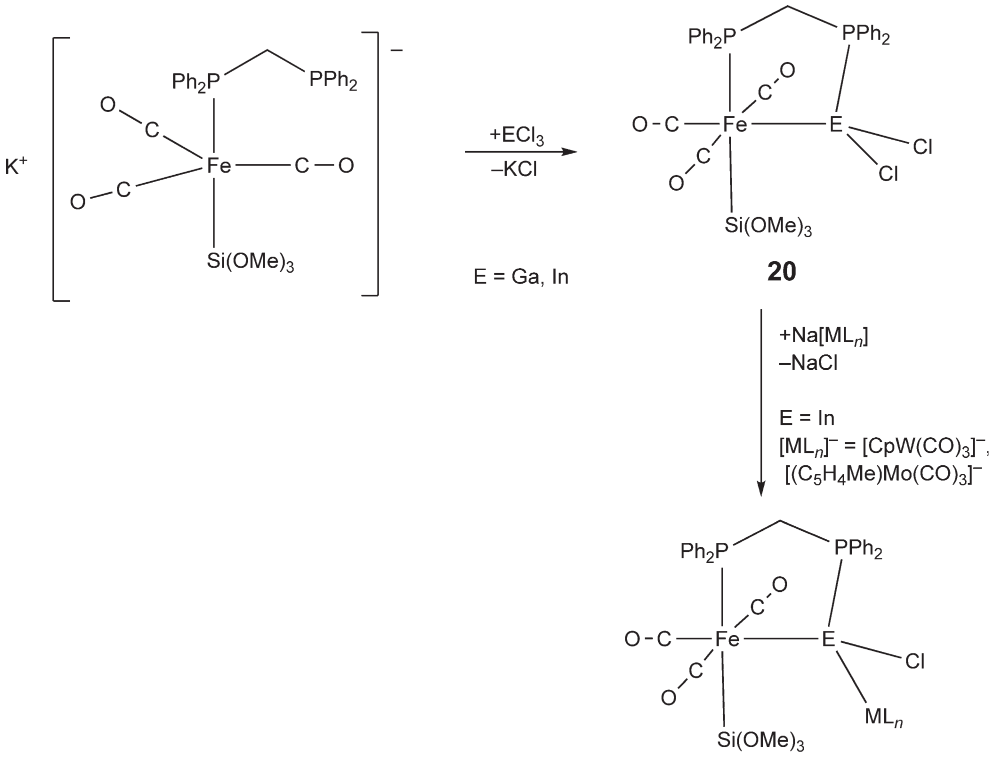
Schemes 8–10 represent another aspect of donor stabilization of the trivalent E atom. In these cases, a chelating ligand is used to stabilize the Fe–E bond. The chelating group can have a variety of forms such as an alkoxysilane (Scheme 8), a diphosphine (Scheme 9), or a phosphinopyridine (Scheme 10).[37] Use of $GaCl_3$ in place of InX_3 in Scheme 8 or $TlCl_3$ in Scheme 9 did not lead to formation of complexes with E–Fe bonds.[37] Compounds **16** and **17** illustrate that the internal stabilization can occur once or twice (cf. **15** and **14**). The chelating nature of an Si–O–R group is fairly weak and can be displaced by addition of a stronger ligand such as $OPPh_3$ **18**. Subsequent displacement of residual halide ions with metal carbonylates can also be achieved, although the production of **19** shows that the bonding to E is through the metal-bound cyanide ligand rather than direct attachment to the metal as in the conversion of **20** to **21** or **22** to **23**.

3.08.3.3 Reactions of Trivalent Group 13 Element Halides and Metal Carbonyl Monoanions Leading to Metal Cluster Products

Reaction of main group element halides with metal carbonyl anions can be complicated by more extensive redistribution/rearrangement processes, leading ultimately to cluster products. This is illustrated in Scheme 11.[5] It is fairly common for the heavier main group elements to lose organic fragments when treated with metal complexes. The Co–Co distances are insensitive to the counterion, being 258.8(1) and 256.2(1) in [K(toluene)$_2$][**25**] and 255.7(1) and 257.6(1) in [Li(THF)][**25**]. The Ga–Co distances in these two salts are also similar, with two being somewhat shorter than the others (239–240 vs. 244–245 pm).[5] The Co–Co distance in **24** is


K⁺
PPh3
Si(OMe)3
InX3
1 : 1
–KX
InX3
2 : 1
–2KX
L
L = OPPh3, 4-MeC5H5N
Na[Mn(C5H4Me)(CO)2(CN)]
X = Cl
OPPh3
Mn(C5H4Me)(CO)2
17
16
18
19

Scheme 8



20

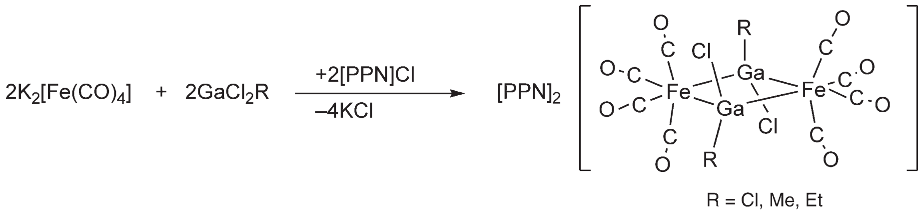
21

Scheme 9

slightly longer than in **25** (259.5(1) pm),[5] while the Ga–Co distances are similar, ranging from 241.9(1) to 244.8(1) pm. In general, the E–M distances are longer when involving metals that are bridged by the E atom than when the E atom is terminally bonded.

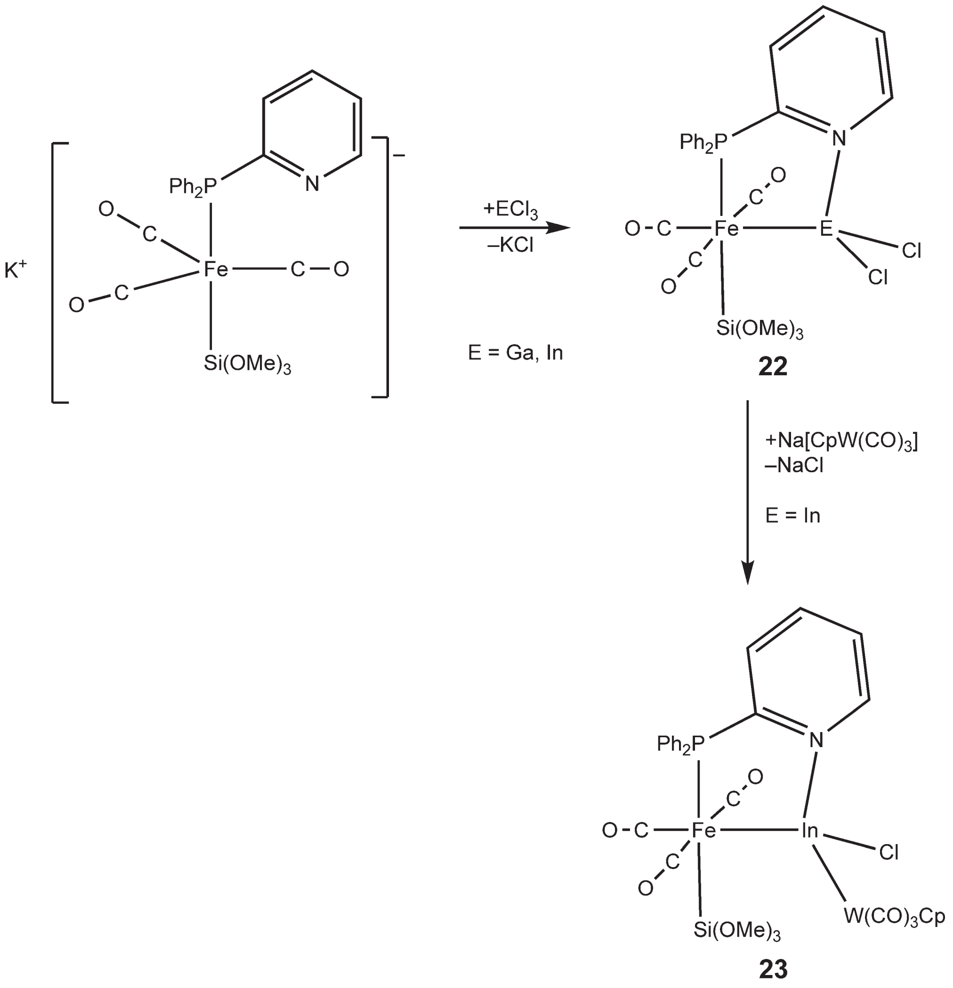
3.08.4 Reactions Beginning with Trivalent Group 13 Element Halides with Metal Carbonyl Dianions

In the reaction of group 13 element halides with metal carbonyl dianions, the analysis is more complex than observed for the reactions with metal monoanions. Upon addition of metal dianions to EX_3 or REX_2, either one or two halide ions may be eliminated. When only one halide ion is eliminated per added metal dianion, the complexes may still be viewed as E^{3+} derivatives (Equations (33)–(36)).[19] This may be controlled to some extent by the stoichiometry of the reaction. Comparison of Equations (33)[19] and (34)[19] shows that the electron demand at the main group element can be satisfied by coordination either to an electron-rich metal center **26** or formation of a halide bridge **27**. Ligand-stabilized forms may also be prepared in this fashion (Equation (36)).[19]

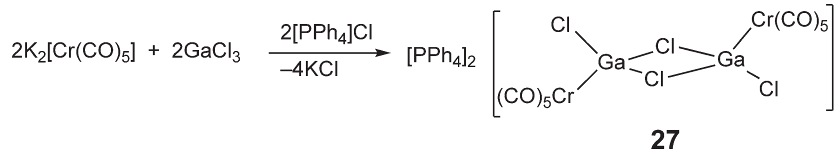


(33)

26



Scheme 10



27 (34)

$$2K_2[M(CO)_x] + RGaCl_2 \xrightarrow[-4KX]{+2[\text{cation}]X} [\text{cation}]_2[\{(CO)_x\cdot M\}_2GaR] \qquad (35)$$

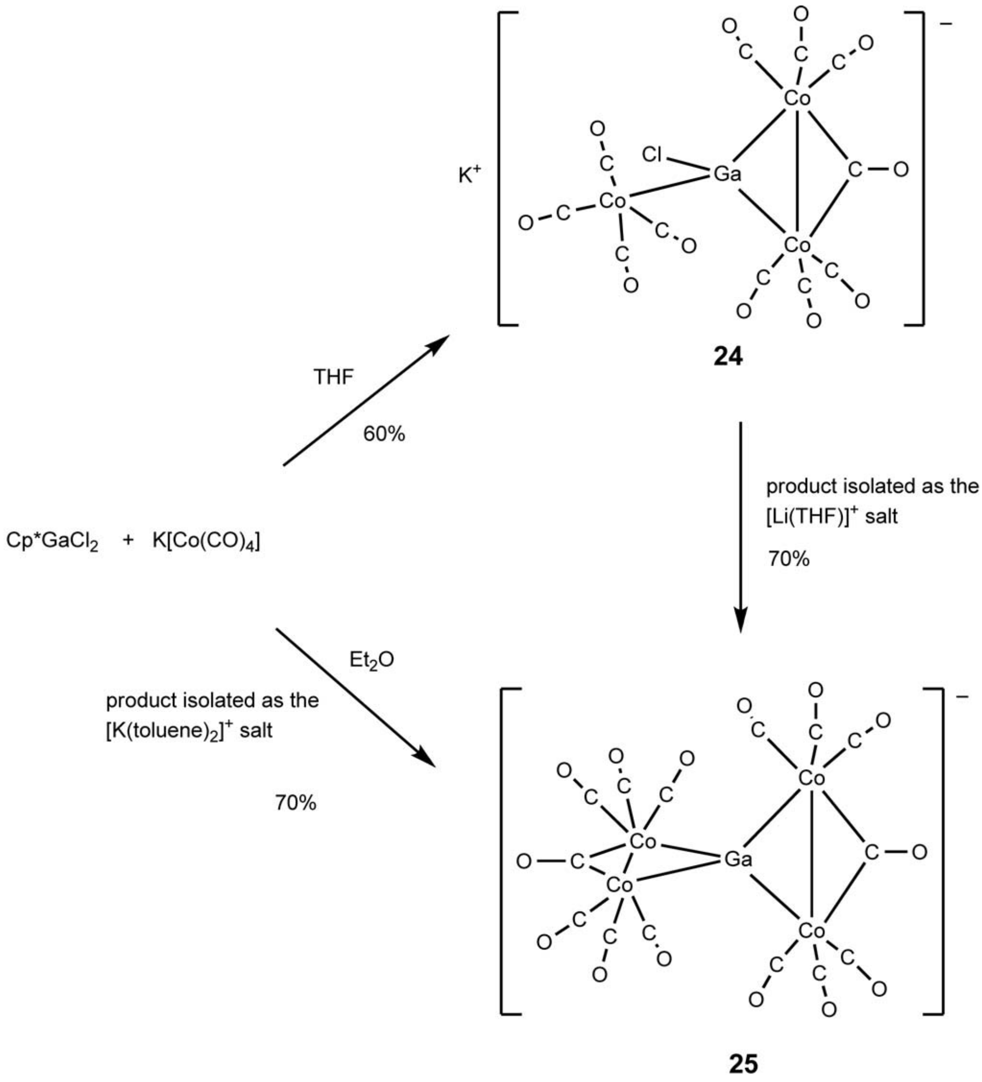
cation = PPN^+, $AsPh_4{}^+$ or $PPh_4{}^+$

M	*x*	*R*
Fe	4	Me
Cr	5	Me
Cr	5	Et

$$[\text{cat}]_2[L_nM] + GaCl(R)\{(CH_2)_3NMe_2\} \xrightarrow{-[\text{cation}]Cl} [\text{cation}][\{L_nM\}Ga(R)\{(CH_2)_3NMe_2\}] \qquad (36)$$

$[L_nM]^{2-} = [M(CO)_x(NO)_y]^{2-}$
cation = PPN^+, $PPh_4{}^+$, $AsPh_4{}^+$, or $K(THF)^+$

M	*x*	*y*	*R*
Fe	4	0	Cl, ^{t}Bu
Cr	5	0	Cl, ^{t}Bu, Me
Mn	3	1	^{t}Bu



Scheme 11

When two halide ions are eliminated upon addition of a single metal dianion, formally E^+ complexes result, which may be classified as several related groups of complexes (Tables 5–8). One can view these species as (i) a multiply bonded complex with backdonation from the electron-rich metal center onto the group 13 element, which is a reduction of the main group element fragment from 3+ to 1+, or (ii) one in which the charge separation remains largely intact with a highly polarized M^{2-}–E^{3+} bond (Scheme 12). The choice between these two extremes is discussed further below.

This point is not made clearer by the experimental methodologies as the same products can be obtained by treating metal carbonyl dianions with REX_2 or via substitution reactions carried out between neutral metal complexes and ER. As a consequence, the various structural types given in Tables 5–9 have been obtained by one or both of these approaches. More than one ER or EX fragment may be bonded to a single metal center (Table 6). As with the trivalent species, the group 13 element may be stabilized by the coordination of ligands (Table 7). For some chelating ligands, the coordination demand of the main group element is completely satisfied by a chelating ligand and no halide or organic function is present (Table 8). Some of these units afford cationic analogs to the ER and EX species (ER and EX vs. EL^+ where L is a bi- or tridentate chelating ligand).

Table 5 Compounds of monovalent E of the form RE–ML$_n$

Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$Cp^*AlFe(CO)_4$	223.1(3)	39
$Cp^*AlCr(CO)_5$	237.61(6)	40
Gallium compounds		
$Cp^*GaCr(CO)_5$	240.46(7)	41
$(\eta^5\text{-}2,5\text{-}{}^tBu_2H_2C_4P)GaCr(CO)_5$	239.0(1)	42
$Cp^*GaW(CO)_5$	256.6(1)	13
$Cp^*GaFe(CO)_4$	227.31(4)	41
$\{Cp^*(dppe)Fe\}GaFe(CO)_4$		
Ga–Fe(CO)$_4$	229.31(10)	43
Ga–Cp*Fe	224.79(10)	
$\{2,6\text{-}(2,4,6\text{-}{}^iPr_3H_2C_6)_2H_3C_6\}GaFe(CO)_4$	222.48(7)	44
Indium compounds		
$Cp^*InCr(CO)_5$	258.54(13)	45
$\{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}{}^iPr_3)_2\}InMn(CO)_2Cp$	241.02(9)	46

Table 6 Compounds with more than one monovalent ER group attached to a single ML$_n$ fragment

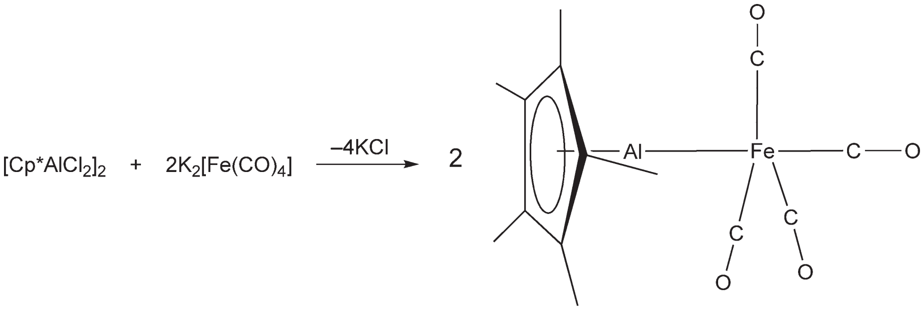
Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$Ni\{AlCp^*\}_3(\mu\text{-}H)Al(Ph)(Cp^*)\text{-}(\mu\text{-}H)$	216.88(11)–221.05(11) 229.12(11)	47
$Ni\{AlCp^*\}_3(H)SiEt_3$	218.0(7)–220.8(10) 220.8(10)	47
$(dcpe)Pt(AlCp^*)_2$	232.7(2), 233.5(2)	48
Gallium compounds		
cis-$(CO)_4Mo(GaCp^*)_2$	253.7(1), 255.4(1)	49
$(CO)_3Mo(GaCp^*)_3$	251.9(8)–252.3(8)	50
$(CO)_3W(GaCp^*)_3$	251.98(13)–252.21(12)	50
$Cp^*Fe\{GaCp^*\}_2\{GaCl_2(THF)\}$	227.90(15), 232.08(17)	18
$(dcpe)Pt(GaCp^*)_2$	235.5(2), 236.7(2)	48
$Pd(GaCp^*)_4$	236.68(7)	51
$Pt(GaCp^*)_4$	233.5(2)	51
$(dcpe)Pt\{GaC(SiMe_3)_3\}_2$	231.5(1), 231.8(1)	52
$Ni\{GaCp^*\}_4$	221.88(5)	49
$[NiGaC(SiMe_3)_3]_4$	217.00(4)	53
Indium compounds		
$[NiInC(SiMe_3)_3]_4$	231.0(1)	54
$Pt\{InC(SiMe_3)_3\}_4$	244.1(2)	55
$Cp^*Rh(InCp^*)_2(InCp^*Cl_2)$	252.2(3)–257.2(4)	56
$Cp^*Rh\{InC(SiMe_3)_3\}_2\{InC(SiMe_3)_3Cl_2\}$	256.17(7), 256.18(6) 262.44(6)	56
$(dcpe)Pt(InCp^*)_2$	255.6(1), 256.9(1)	52

Additionally, ER groups can also be bonded in bridging configurations in multimetallic compounds (Table 9). These complexes are most often encountered via substitution reactions. Reactions employing the substitution methodology will be discussed in Section 3.08.7.

Examples of the reactions of metal dianions with group 13 element halides that lead to elimination of two halide ions and formation of the formally reduced species are given in Equations (37)–(39).[39–44]

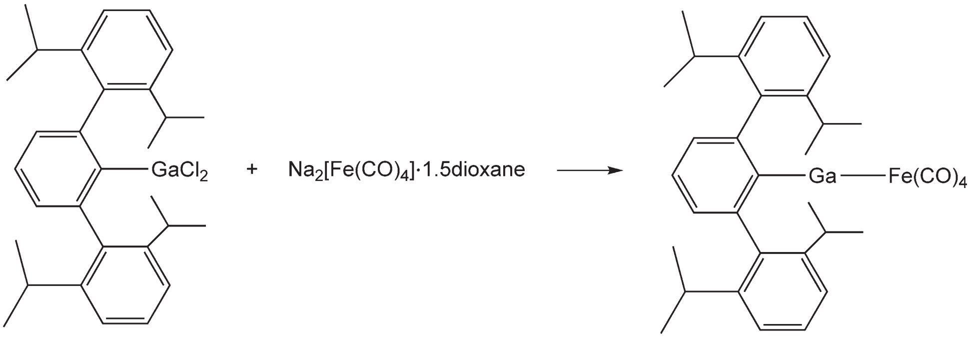
Table 7 Formally monovalent ligand-stabilized complexes of the form $\{L_nM\}E(X)(L')$

Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$(CO)_5CrAl(Cl)(TMPDA)$	248.2(1)	57
$(CO)_5WAl(Et)(TMEDA)$	267.0(1)	58
$(CO)_5WAl(Cl)(TMPDA)$	264.5(2)	58
$(CO)_5WAl(^tBu)(TMPDA)$	274.1(4)	57
Gallium compounds		
$(CO)_5CrGa(Me)(TMEDA)$	247.85(11)	59
$(CO)_5CrGa(Cl)(TMEDA)$	245.6(1)	58
$(CO)_4FeGa(Cl)(TMPDA)$	241.6(3)	57
$(CO)_4FeGa(I)(TMPDA)$	233.71(8)	57
$[(CO)_4FeGa(PMDETA)]I$	231.0(1)	57
$\{Fe(CO)_4\}Ga\{Fe(CO)_2Cp^*\}(bipy)$		
Ga–$Fe(CO)_4$	240.26(5)	43
Ga–Cp^*Fe	242.21(5)	
$Ru(CO)_3\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2$	243.2(1)	32
	245.9(1)	
Indium compounds		
$(CO)_4FeIn(Br)(TMPDA)$	249.68(18)	57
$(CO)_4FeIn(Br)(PMDETA)$	254.3(1)	57



28 (37)

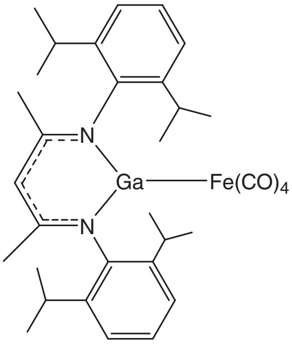
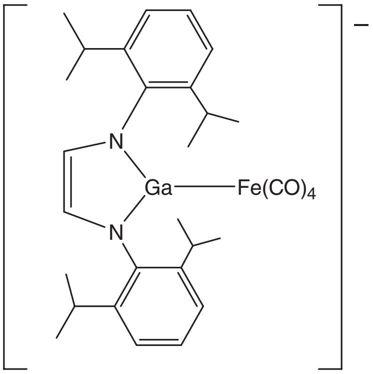
$$\text{Cp*GaCl}_2 \text{ or } (\text{Cp*})_2\text{GaCl} + \text{Na}_2[\text{W}_2(\text{CO})_{10}] \xrightarrow{-\text{NaCl}} \text{Cp*GaW(CO)}_5 \quad (38)$$

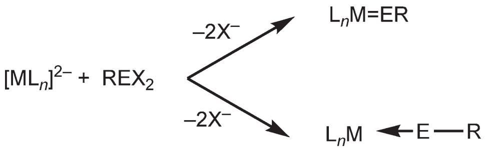


(39)

29
30%
+ 2NaCl + 1.5dioxane

Table 8 Monovalent chelated Ga^+ and In^+ complexes with transition metal fragments

Compound	*E–M distance* (pm)	*References*
Gallium compounds		
	228.51(3)	60
[K(TMEDA)]$^+$ 	230.68(8)	61
$HB(3,5\text{-}Me_2HC_3N_2)_3GaFe(CO)_4$	231.5(3)	62
$CpNi(GaN_2C_2H_2Ar_2)_2$	221.96(11)	63
$Ar = C_6H_3\text{-}2,6\text{-}{}^iPr_2$	221.54(11)	
$Ni(GaN_2C_2H_2Ar_2)_2(CN_2C_2Me_2)_2$	232.42(6)	63
$Ar = C_6H_3\text{-}2,6\text{-}{}^iPr_2$		
Indium compounds		
$HB(3,5\text{-}Me_2HC_3N_2)_3InFe(CO)_4{\cdot}1.5\ C_6H_6$	246.3(2)	64
$HB(3,5\text{-}Me_2HC_3N_2)_3InW(CO)_5$	278.3(2)	64



Scheme 12

Initial DFT calculations suggested the assignment of 28 as having Al^+ with a primarily σ-donation of the lone pair from Al to Fe. From the DFT calculations, the Al–Fe bond enthalpy was calculated to be 52.7 kcal mol^{-1}, a value that was considered to be overestimated, and a better value was thought to be closer to 50 kcal mol^{-1}.[39] This view was revised by later work that indicated that there was a large transfer of electron density from Al to Fe, so that an RAl^{2+} bound to $Fe(CO)_4{}^{2-}$ was deemed more appropriate.[41]

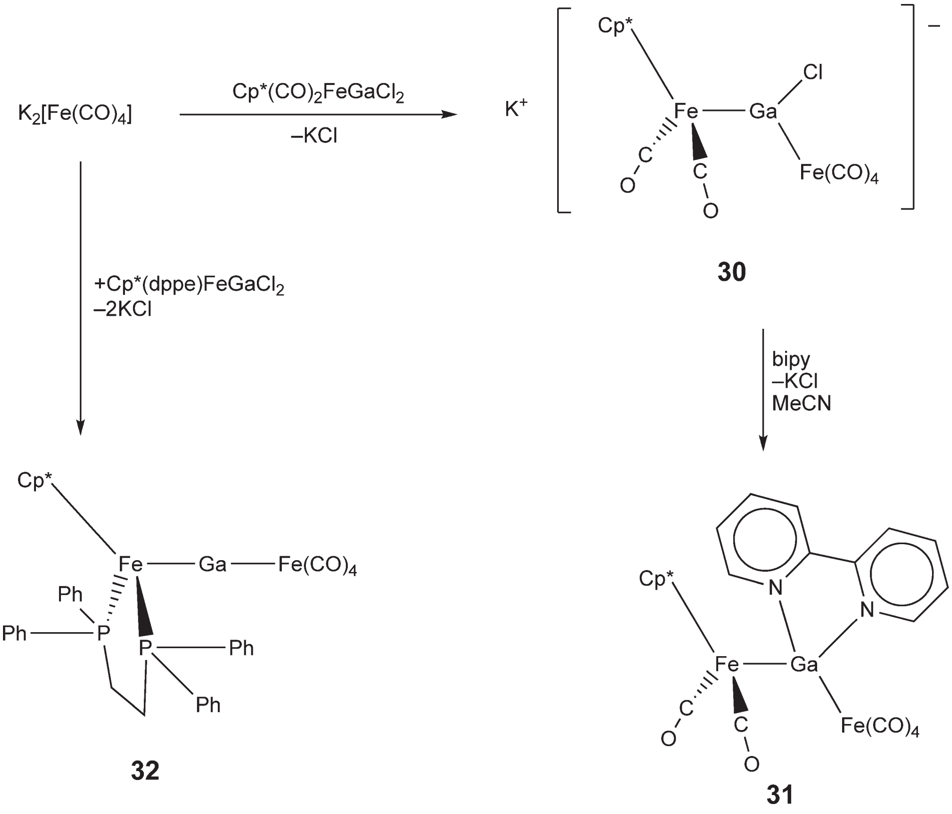
Table 9 Metal complexes with bridging ER units

Compound	*E–M distance* (pm)	*References*
Aluminum compounds		
$[Cp^*AlCo(CO)_3]_2$	236.9(3)–238.4(3)	65
$[(C_5Me_5)Ir(PMe_3)(\mu\text{-}AlEt)]_2$	245.6(1)–245.9(1)	3
$[CpNiAlCp^*]_2$	227.4(2)–228.3(2)	66
Galllium compounds		
trans-$\{Cp^*(CO)Fe\}_2(\mu\text{-}CO)(\mu\text{-}GaMes)$	231.47(9)	17
trans-$\{Cp(CO)Fe\}_2(\mu\text{-}CO)(\mu\text{-}GaMes)$	234.38(5)–234.89(6)	17
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GaCp^*)$	235.0(1)–238.3(1)	13
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}Ga\{Fe(CO)_2Cp\}$	233.2(2)	30
Fe_2	234.9(2)–237.0(2)	
$Fe_2(CO)_6(\mu\text{-}CO)[\mu\text{-}Ga\{Si(SiMe_3)_3\}]_2$	238.15–239.38(6)	28
$[Fe_2(CO)_6(\mu\text{-}CO)[\mu\text{-}Ga\{Si(SiMe_3)_3\}]_2][Na(THF)(Et_2O)_2Cl]$	244.1(2)–245.5(2)	28
$Fe_2(CO)_6[\mu\text{-}Ga\{Si(SiMe_3)_3\}]_3$	238.18(7)	28
$Fe_2(CO)_6(\mu\text{-}GaCp^*)_3$	240.1(3)–245.5(3)	41
$[\{(CO)_4Mn\}GaC(SiMe_3)_3]_2$	243.0(2), 253.0(2)	67
$Mo_2(CO)_6(GaCp^*)_3$	265.67(8)–267.96(8)	50
$[Na(triglyme)][HFe_3(CO)_9\{\mu_3\text{-}GaSi(SiMe_3)_3\}_2]$	242.3(2)–251.0(2)	28
$Fe_3(CO)_9(\mu\text{-}CO)\{\mu\text{-}GaC(SiMe_3)_3\}$	239.03(6)–240.29(6)	67
$[R_4Ga_4O(OH)_5]\ [Fe_3(CO)_9(\mu_3\text{-}GaR)_2\{\mu\text{-}GaFe(CO)_4\}]$		
μ_3	237.9(1)–254.7(1)	28
μ	244.6(1)–246.1(1)	
term.	228.9(1)	
$Co_2(CO)_6(\mu\text{-}GaCp^*)_2$	237.84(5)–239.59(5)	41
$Cp_2Ni_2\{\mu\text{-}GaC(SiMe_3)_3\}_2$	227.56(6)–227.89(6)	68
$Ni_4(CO)_6(\mu_3\text{-}GaCp^*)_2(\mu\text{-}GaCp^*)_2$		
μ_3	231.66(11)–283.21(13)	41
μ	229.33(11)–244.52(12)	
$Pt_2(\mu\text{-}GaCp^*)_3(GaCp^*)_2$		
term.	232.6(2)–233.2(1)	69
μ	245.0(1)–247.2(1)	
Indium compounds		
$Mn_2(CO)_8\{\mu\text{-}InC(SiMe_3)_3\}_2$	260.62(4)–266.51(4)	70
$Fe_2(CO)_8\{\mu\text{-}InR\}$	255.9(1)–257.4(1)	71
$Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}InR)_2$	256.36(5)–259.52(5)	71
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}InCH_2CH_2CH_2NMe_2)$	253.6(1)–263.03(4)	33
$Fe_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_3$	258.2(2)	72
$Co_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}InC(SiMe_3)_3\}$	257.03(6), 259.30(5)	73
$Co_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_2$	252.83(5)–254.05(6)	73
$Cp_2Ni_2\{\mu\text{-}InC(SiMe_3)_3\}_2$	243.8(1)–244.7(1)	68
$\{Cp(CO)Ni\}_2InC(SiMe_3)_3$	251.23(9)–252.01(10)	68
$Pd_3(InCp^*)_4(\mu\text{-}InCp^*)_4$		
term.	254–257	74
μ	258–261	

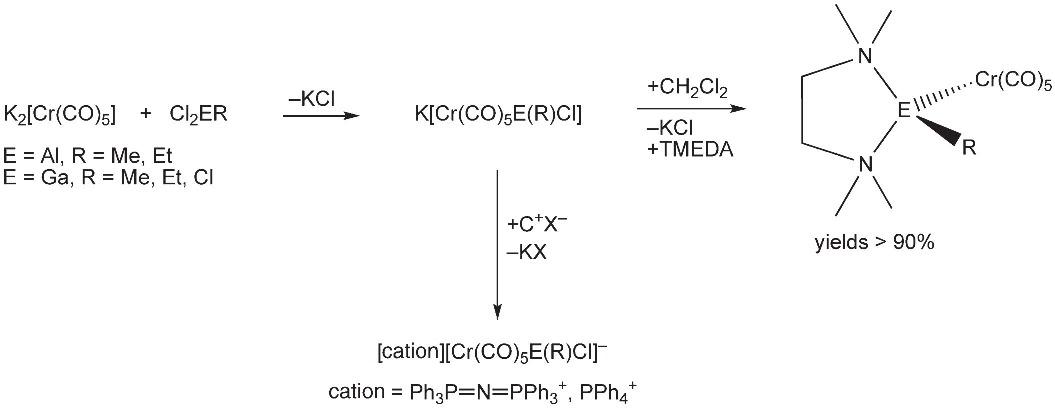
The reaction of $Na_2[Fe(CO)_4]\cdot 1.5$dioxane with the bulky aryl-substituted $\{2,6\text{-bis-}(2,4,6\text{-}^iPr_3H_2C_6)_2H_3C_6\}GaCl_2$ gave rise to a compound shown by X-ray diffraction to be **29**.[44] The same compound was obtained as a toluene solvate by treating $\{2,6\text{-bis-}(2,4,6\text{-}^iPr_3H_2C_6)_2H_3C_6\}Ga$ with $Fe(CO)_5$ in toluene in 72% yield.[60] The compound contains a linear C–Ga–Fe angle and a very short Ga–Fe distance that was originally interpreted as an Fe–Ga triple bond.[44] Others disputed that claim, arguing that the bond was in reality a single bond on the basis of DFT calculations.[75] A further, more extensive examination by yet another group came to the conclusion that neither the single bond nor the triple bond picture adequately portrayed the bonding in this compound.[76] The latter work compared **29** with $Cp^*GaFe(CO)_4$ and showed that the extent of π-backbonding from Fe to Ga and also the Fe–Ga bond dissociation energy was higher in the former compound, supporting a greater-than-one bond order. Although the authors left the exact nature of the bond order in question, they argued that the strongly ionic nature of the bond made both the single-bond and triple-bond pictures inaccurate extremes.

It did not prove possible to synthesize a substituent-free Ga complex with formula $\{Cp^*(CO)_2Fe\}\{Fe(CO)_4\}Ga$ (Scheme 13).[43] Addition of bipy to **30** resulted in halide elimation, but the main group element in the product **31** was coordinated by the bipy ligand. Upon addition of dppe, however, substitution of the carbonyl ligands occurred instead along with halide ion elimination to produce the substituent-free Ga complex **32**. It has a linear coordination environment (Fe–Ga–Fe angle = 176.01(4)°), and the Ga–Fe bond distances are much shorter than in those related adducts where donor ligands are also bound to the Ga atom.[43] The authors attributed the non-observation of the carbonyl derivative to a need for an electron-rich metal center to stabilize the Fe–Ga bond via π-backdonation.

An extensive series of ligand-stabilized compounds has been prepared starting with metal dianions and EX_3 or organo-group 13 halides (Scheme 14,[59] and Equations (40) and (41)).[57,58] Yields ranged from 92% to 98% for the Al and



Scheme 13



Scheme 14

Ga reactions.[58] In the case of alkyl complexes, 2 equiv. of R_2GaCl was employed, as redistribution produces GaR_3 as a byproduct. Calculations showed that the bonding is strongly of a donor/acceptor type with significant ionic contributions. Donor atoms attached to E increased the σ-donating ability toward the metal. π-Bonding was found to be minimal.[58]

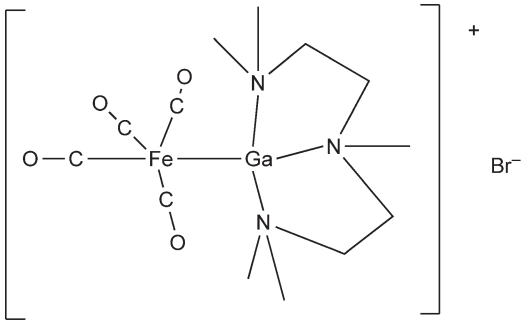
$$ECl_2R + K_2[M(CO)_n] + L \longrightarrow (CO)_nME(R)(L) + 2KCl \qquad (40)$$

E	*M*	*n*	*L*	*R*
Al	Cr	5	TMPDA	Cl
	Cr, Mo, W	5	TMEDA	Cl, Et
	W	5	TMPDA	Cl, ^{i}Bu
	Fe	4	TMPDA	Cl, ^{i}Bu
Ga	Cr	5	TMEDA	H, BH_4, Me
	Cr, Mo, W	5	TMEDA	Cl, Et
	Cr	5	$(THF)_2$, DME, bipy, ^{t}Bu-DAB, TMPDA	Cl
	Fe	4	TMEDA	Cl, Me, Et
	Fe	4	TMPDA	I, Me

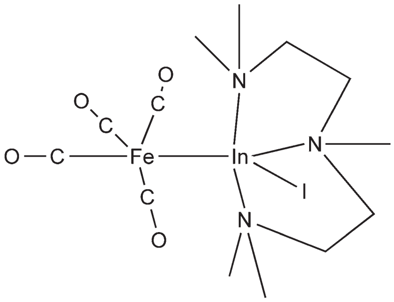
$$EBr_3 + K_2[Fe(CO)_4] + L \longrightarrow (CO)_4FeEBr(L) + 2KBr \qquad (41)$$

E = Ga, In; L = TMPEDA, PMDETA

In all these cases where L is a bidentate ligand, that ligand chelates the main group element in the final products. For the PMDETA ligand in Equation (41), the gallium product is ionic **33** but the halide remains attached to the main group atom in the indium derivative **34**.[57] Starting with the pyrazolyl borate complex, both halide and alkyl functions are lost to give a tetracoordinated Ga^+ or In^+ ion (**35** in Equation (42)).[62,64]

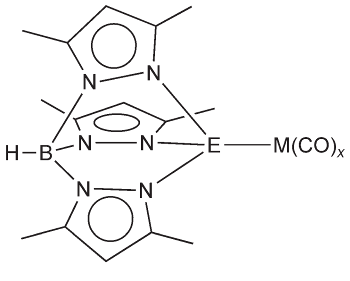


33



34

$$\{HB(3,5\text{-}Me_2HC_3N_2)_3\}EClMe + Na_2[M(CO)_x] \xRightarrow{-NaCl} \qquad (42)$$

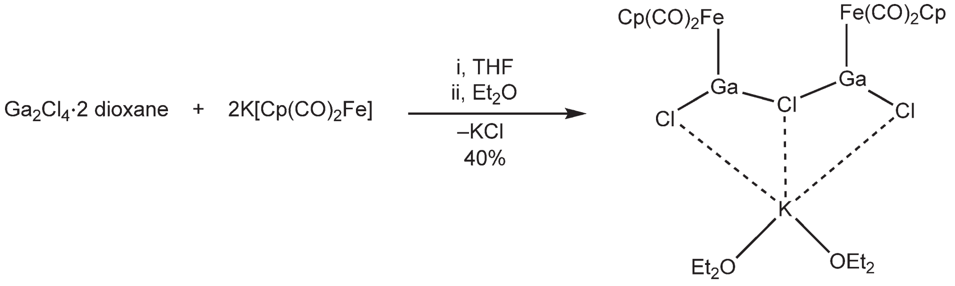


35

M	*x*	*E*	*Yield* (%)
Fe	4	Ga	33
Fe	4	In	95
W	4	In	33

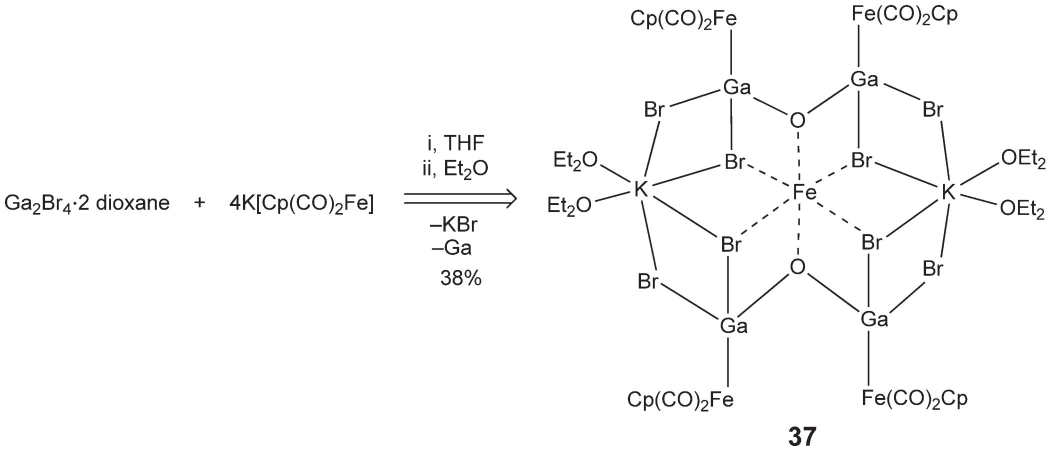
3.08.5 Reactions Beginning with Group 13 Elements and Reduced Group 13 Element Halides

The gallium(II) and indium(I) halides are known, and can be used as starting materials for reactions with metal carbonyl anions. The process illustrated in Equation (43)[6] retains gallium in a formal +2 oxidation state, while those that start with M–M bonded transition metal reagents (Equations (44)–(47),[6,32,36] Schemes 15–17)[6,21,31] are better viewed as based upon E^{3+}.[6,21,31] These reactions can be seen as arising from reduction of the metal dimers by the reduced main group element halides to give metal carbonyl anions attached to E^{3+}. In Equation (43),[6] **36** can be viewed as two $Cp(CO)_2FeGaCl$ groups that are stabilized by bonding to a bridging $[K(THF)_2]Cl$ group,[6] but compounds **37–44** are examples of base-stablized E^{3+} metal complexes. In the cluster compounds such as **45–48**, it is more difficult to assign formal oxidation numbers to the gallium centers. Some multiple bonding between the Rh atoms and the linear μ_2-Ga atoms was proposed based upon DFT calculations.



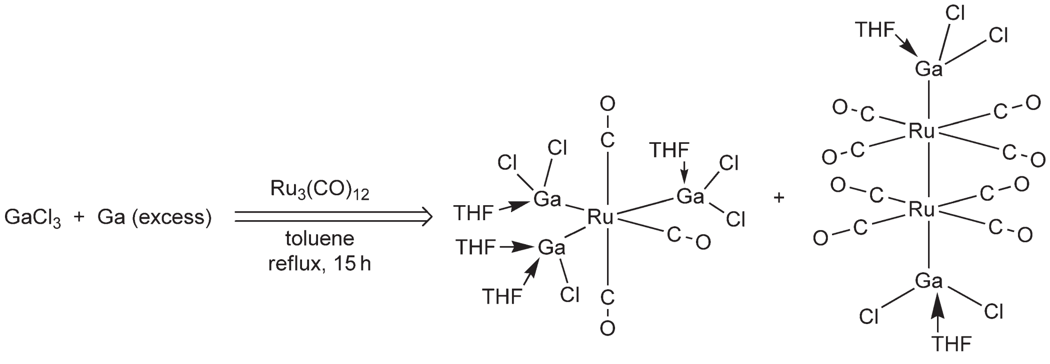
36

(43)



37

(44)



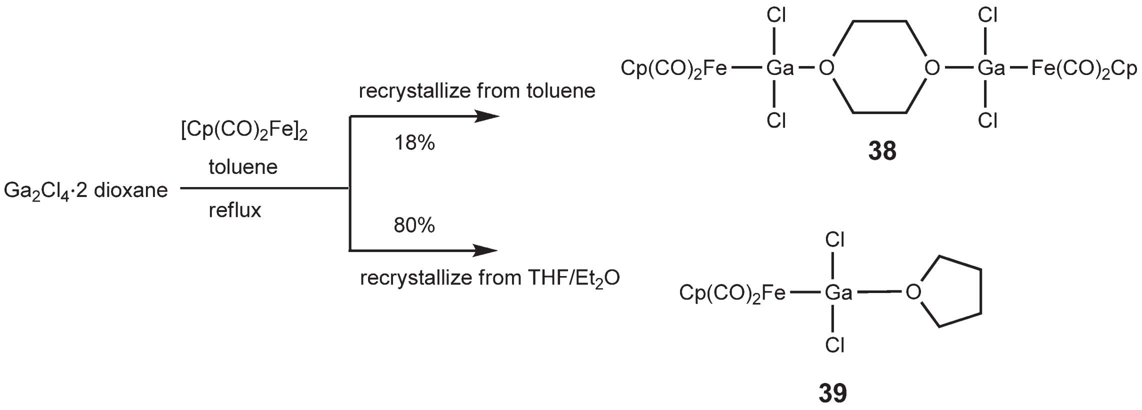
43 **44**

(45)

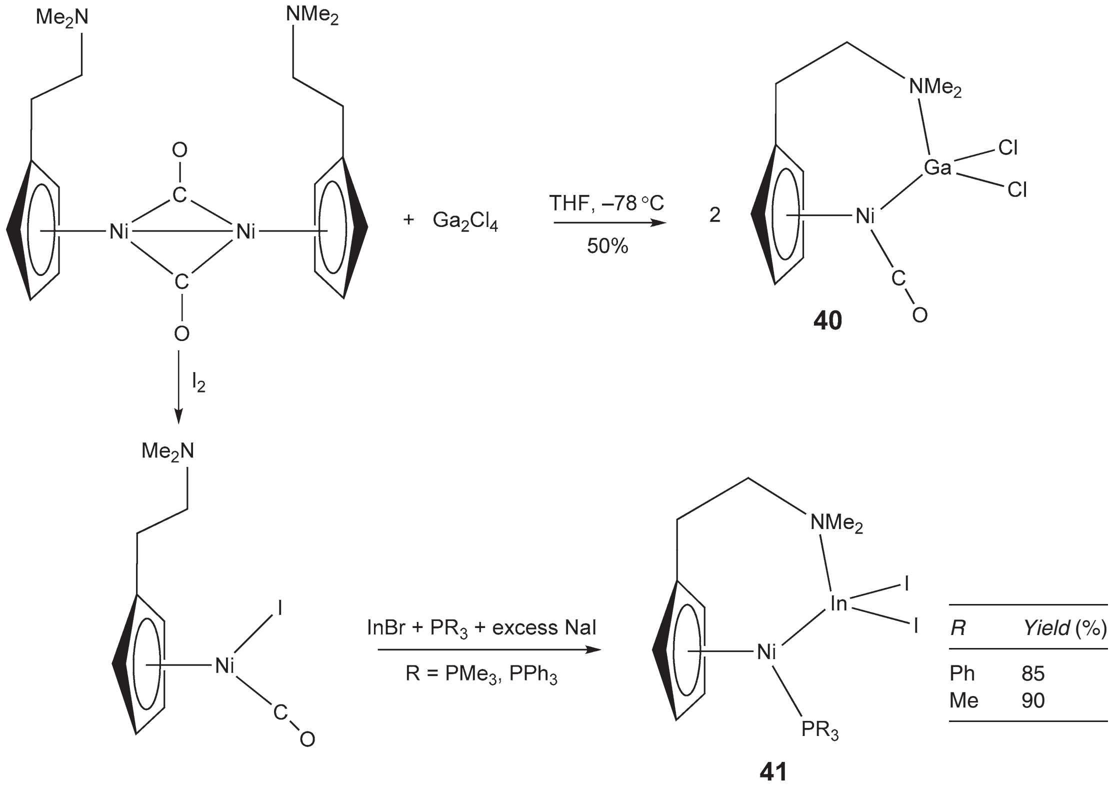
$$\mathrm{Cp(PPh_3)NiBr} + \mathrm{In} \xrightarrow[48\%]{\mathrm{Et_2O/THF}} \{\mathrm{Cp(PPh_3)Ni}\}_2\mathrm{InBr} \qquad (46)$$

$$\mathrm{Cp(PPh_3)NiBr} + \mathrm{InBr} + \mathrm{L} \xrightarrow{\mathrm{toluene/THF}} \mathrm{Cp(PPh_3)NiInBr_2(L)} \qquad (47)$$

L	*Yield* (%)
PPh_3	90
$O\ PPh_3$	87
NC_7H_{13}	80

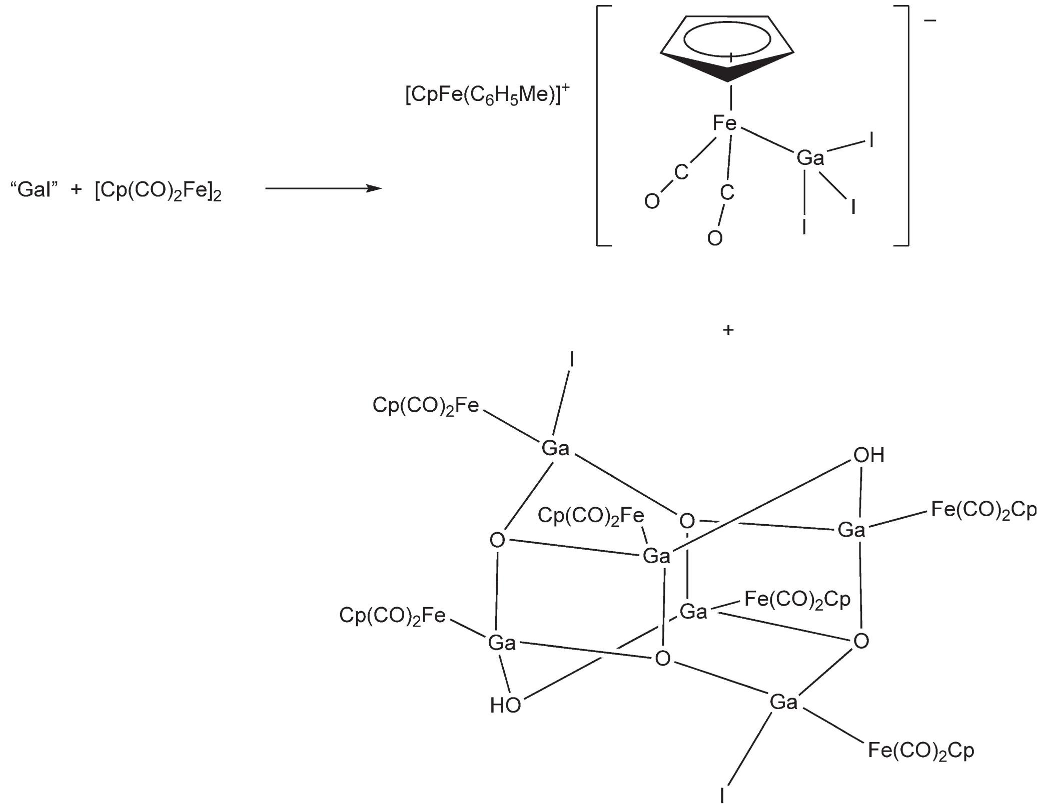


Scheme 15



R	*Yield* (%)
Ph	85
Me	90

Scheme 16

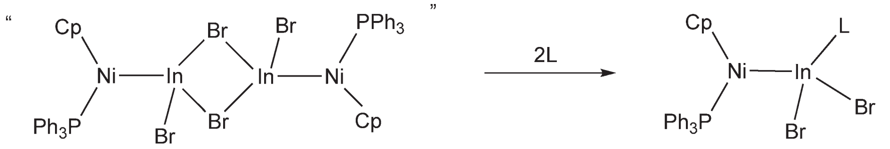


42

Scheme 17

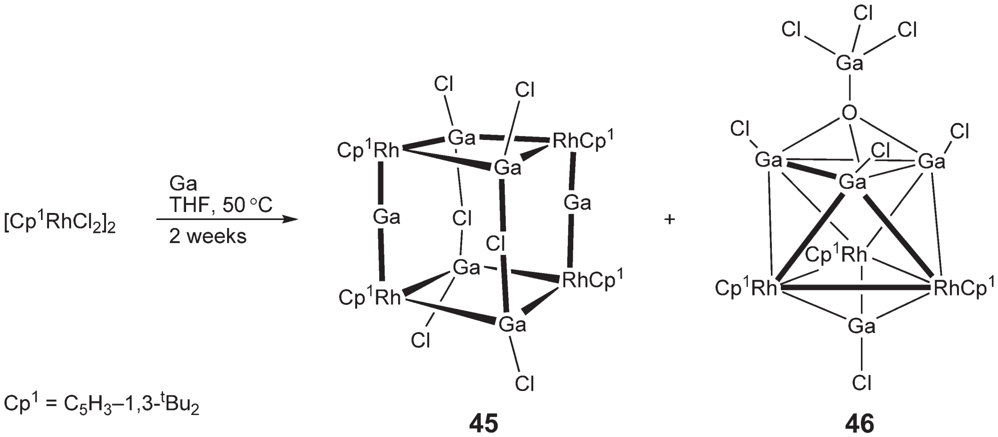
The reaction described in Equation (45) is believed to proceed through the intermediacy of Ga_2Cl_4, which has been observed to exist in several forms.[32] The reaction of $GaCl_3$ with Ga in toluene is similar to that used to prepare Ga_2Cl_4, which dissolved in dioxane to give the soluble (dioxane)Cl_2Ga–$GaCl_2$(dioxane) complex. Complex **43** contains gallium in both the +1 and +3 oxidation states. The Ru–Ru bond distance in **44** is 295.0(1) pm and the carbonyl ligands on the two ruthenium atoms are in an eclipsed geometry.

Indium metal will insert into the NiBr bond of Cp(PPh_3)NiBr as per Equation (46),[36] giving a simple trisubstituted, trivalent In^{3+} derivative. However, use of InBr in the presence of added ligands gives a base-stabilized product (Equation (47)). In the absence of added ligands, the product of the reaction of Cp(PPh_3)NiBr with InBr is [Cp(Ph_3P)$_2$Ni][$InBr_4$].[36] These reactions are thought to proceed via insertion of In into the Ni–Br bond to give the intermediate [Cp(Ph_3P)NiInBr(μ-Br)]$_2$ (Equation (48)), which was not isolated.



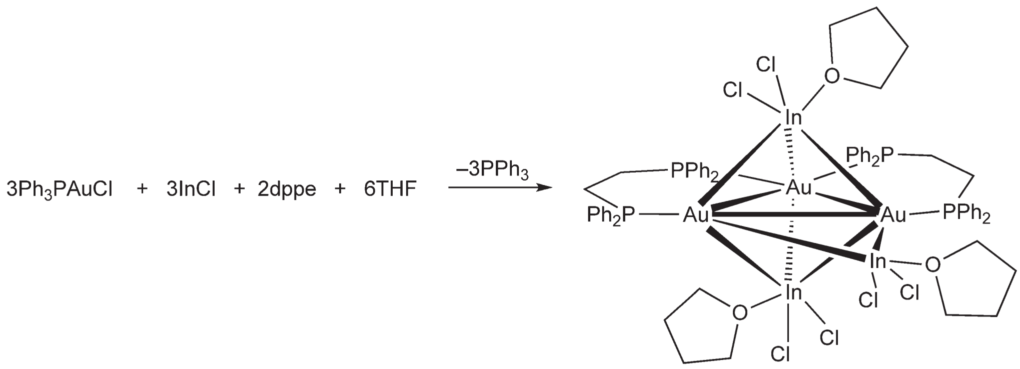
(48)

The Au–In cluster compounds **47 and 48** have the same cluster-core geometries. For the latter structure, there is an additional bridging Br^- ligand that serves the function of two of the THF ligands in **47**. If no dppe is present in this reaction, the product is [$InCl_2(THF)_2$]$_2$.[79] Like the Rh–Ga clusters **45 and 46**, the assignment of oxidation numbers to the Au and In atoms in these molecules is not straightforward. The DFT analysis suggested that two of the gold atoms are Au(0) and one is Au^+, while the oxidation states of all the In atoms appeared to be approximately the same, intermediate between +1 and +2 (Equation (49)–(51)).[77,79,80]



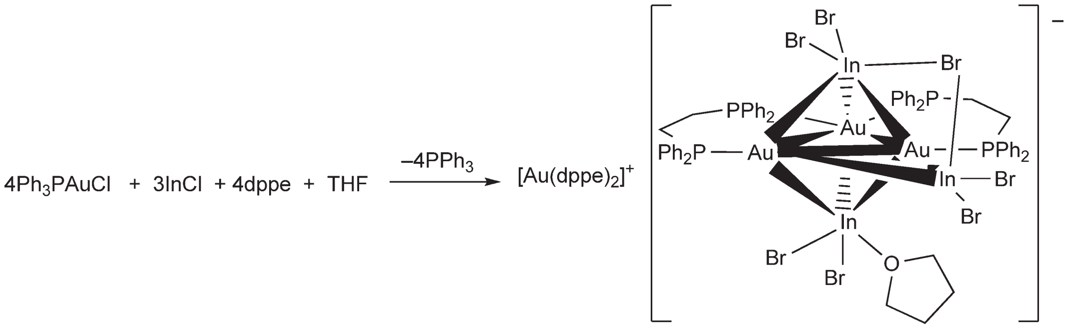
45 (~30%) **46** (~20%)

(49)



47

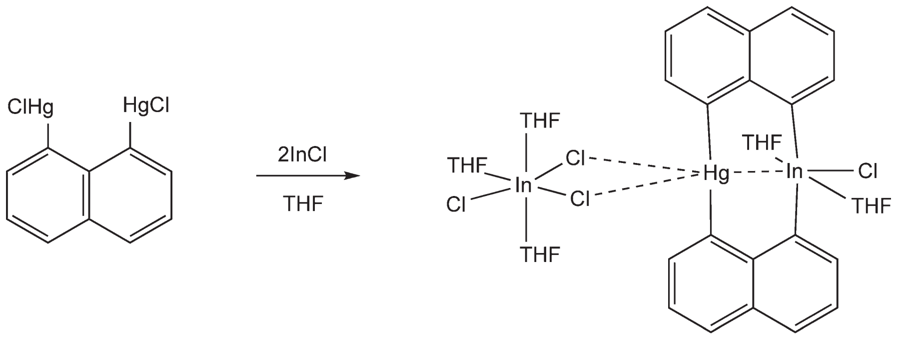
(50)



48

(51)

The reaction in Equation (52) carried out with InBr gave a similar product but without $InX_3(THF)_3$ attached, as in **49**. In the former compound, one of the THF ligands bridges between the In and Hg atoms. The In–Hg distances are long: 301.10(4) pm for the chloro derivative and 303.05(5) pm for the bromide, but they were still thought to represent a bonding interaction.[78]



49

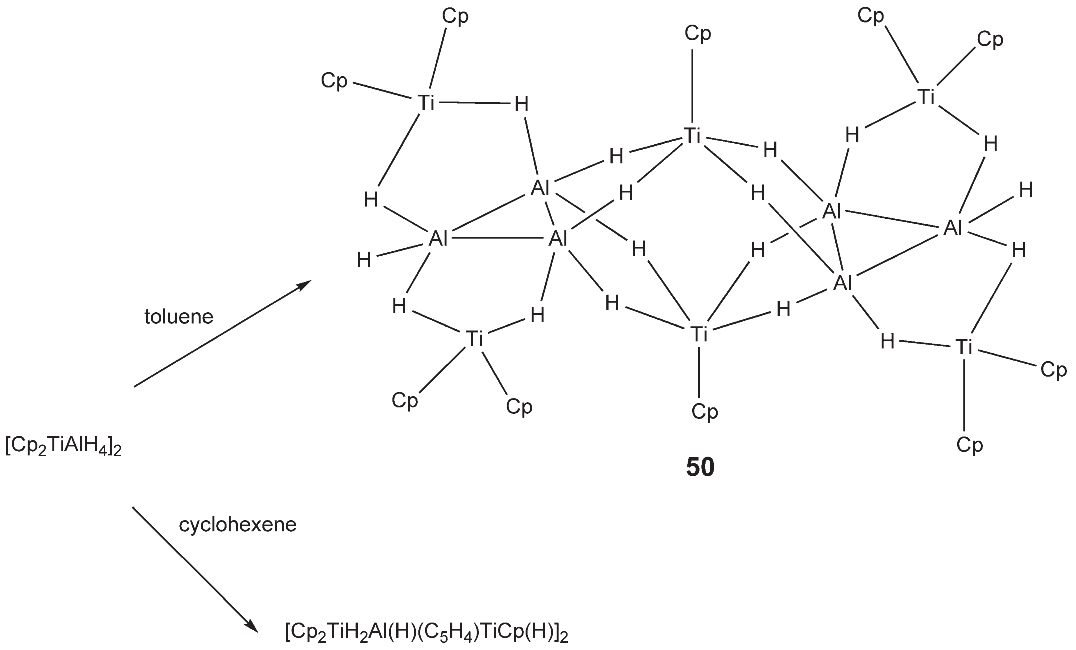
(52)

3.08.6 Related Compounds Derived from Reactions with Group 13 Element Hydrides and Alkyls

The compound $[Cp_2TiAlH_4]_2$ was found to transform in toluene solution to the complex aggregate $[(Cp_2Ti)_2(CpTi)Al_3(\mu\text{-}H)_8H]_2$ **50** (Scheme 18).[81] The complex was analyzed as having six Ti^{3+} groups attached through bridging hydride ligands to two reduced $Al_3{}^{3+}$ triangles. While there are not unsupported Ti–Al bonds in this molecule, there are 16 three-center two-electron Ti–H–Al bonds. The complex $[Cp_2TiAlH_4]_2$ was found to be an active catalyst for hydrogenation of 1-hexene, whereas the related compounds $Cp_2TiAlH_4(L)$ ($L = Et_2O$, THF, NR_3) are not. The compound $[Cp_2TiAlH_4]_2$ was found to be slightly less active toward the hydrogenation than $(Cp_2Ti)_2AlH_4Cl$ and $(Cp_2TiAlH_3OEt)_2$

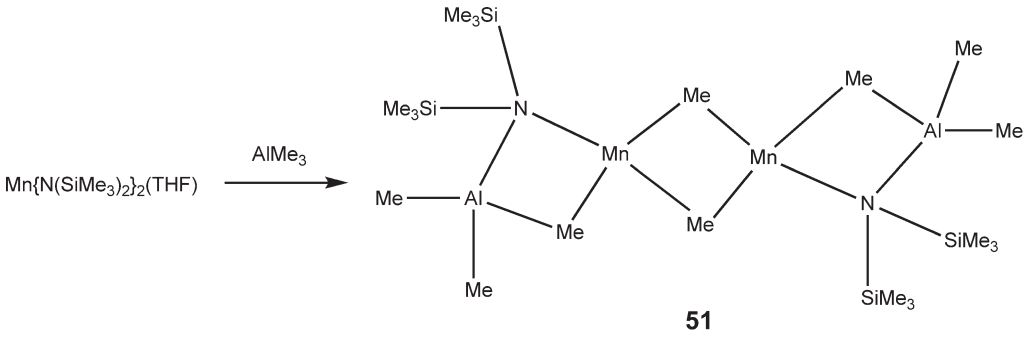
Three-center two-electron bonds are also created when $[Mn\{N(SiMe_3)_2\}_2(THF)]$ and $AlMe_3$ are reacted (Equation (53)).[82] The product is $[\{Mn(\mu\text{-}Me)[N(SiMe_3)_2AlMe_3]\}_2]$, **51**.[82]

Alkylaluminum hydrides react with metal hydrides to eliminate RH, and if the metal fragment is bonded to a cyclopentadienyl ring, H_2 may also be eliminated to produce a new aluminum–carbon bond, as illustrated in Equations (54)–(57).[11,84,83] The hydride-bridged Al–Mo bond in **52** is considerably longer than the direct Al–Mo interaction (294.4(2) vs. 263.6(2) pm).[83] A similar reaction with $(C_5H_4R)Co(C_2H_4)_2$ yields a mixture of **53**[82]

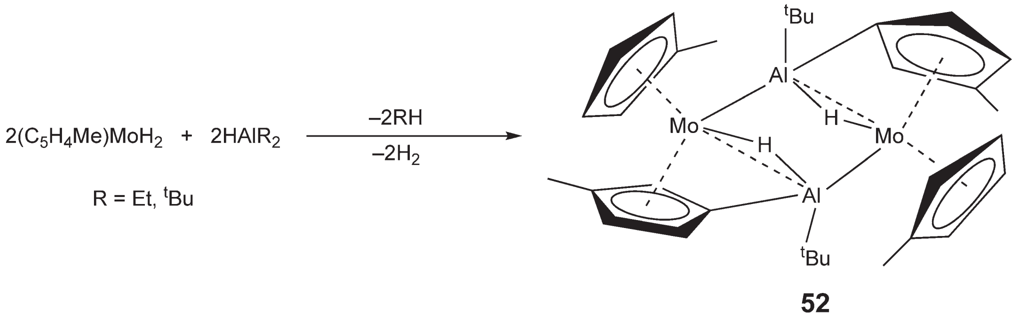


Scheme 18

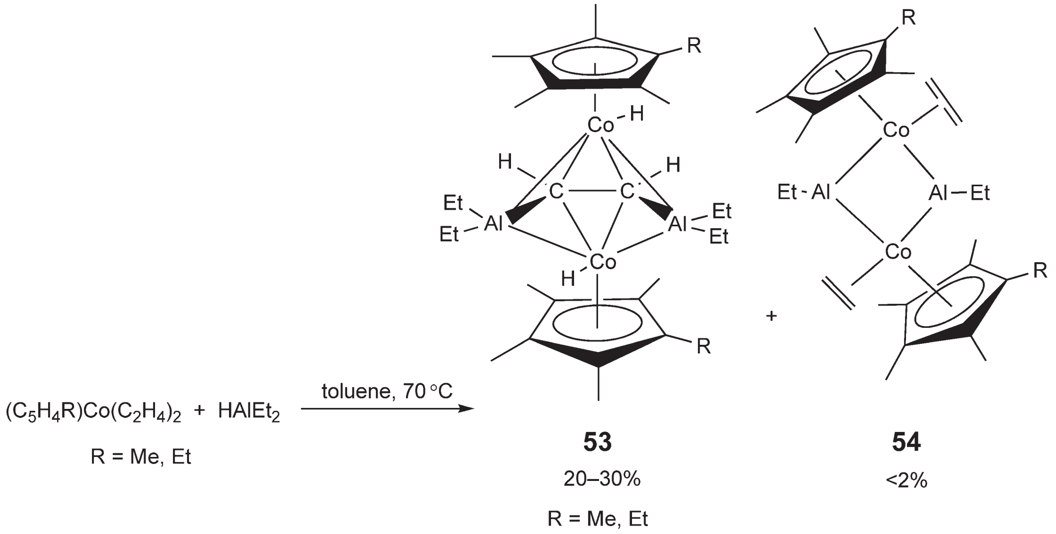
and **54**, both of which contain Co–Al bonds.[84] In **54**, the Co_2Al_2 core is planar, possessing crystallographically imposed inversion symmetry. The Co–Al bonds in **53** (259.1(2) and 260.4(1) pm) are longer than those in **54** (233.6(1) and 233.3(1) pm), as might be expected from more delocalized cluster bonding as compared to two-center two-electron bonds. Equations (56) and (57)[11] illustrate reactions between $CpMo(CO)_3H$ and organoaluminum and gallium reagents that have also been reported to lead to transition metal–group 13 element bonds.



(53)



(54)

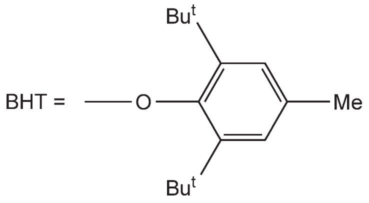


(55)

$$CpMo(CO)_3H \; + \; E(^tBu)_3 \longrightarrow Cp(CO)_3MoE(^tBu)_2 \; + \; {^tBuH} \qquad (56)$$

E = Al, Ga

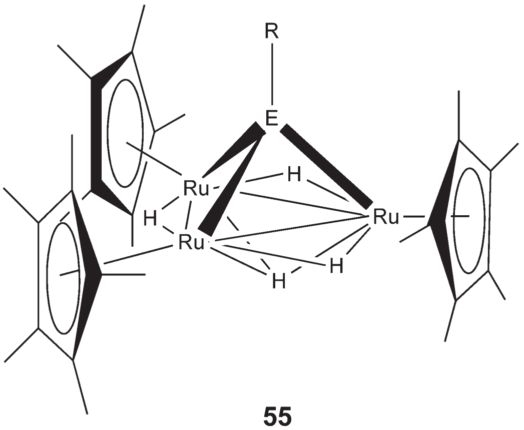
$$\mathrm{CpMo(CO)_3H} + \mathrm{HAl(BHT)_2(OEt_2)} \longrightarrow \mathrm{Cp(CO)_3MoAl(BHT)_2} + \mathrm{H_2} + \mathrm{Et_2O} \qquad (57)$$



The reaction of Cp^*IrH_2 and $AlEt_3$ contrasts with that of $AlPh_3$ mentioned in Section 3.08.2 where a simple adduct is formed. In the case of $AlEt_3$, ethane is eliminated to give a bridging alkylaluminum complex (Equation (58)).[3]

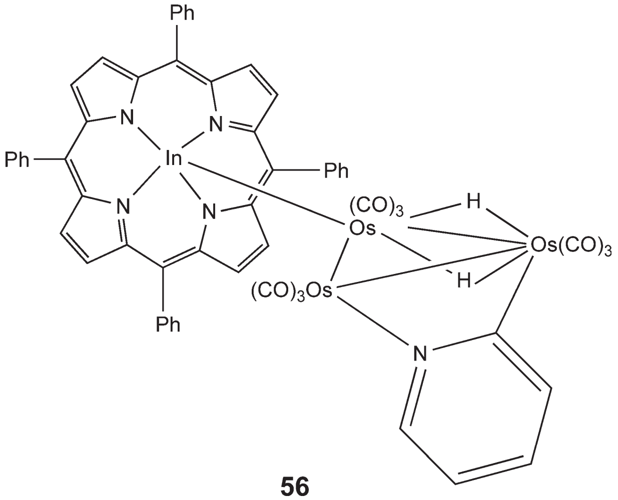
$$\mathrm{Cp^*IrH_2} + \mathrm{AlEt_3} \longrightarrow [\mathrm{Cp^*Ir(PMe_3)(\mu\text{-}AlEt)}]_2 + 2\mathrm{EtH} \qquad (58)$$

The triangular cluster $Cp^*_3Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ reacts with ER_3 (E = Al, R = Et, 70%; E = Ga, R = Me, 99%) with elimination of two R–H to produce $Cp^*_3Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)(\mu_3\text{-}ER)$, **55**.[85] In the gallium compound, the Ru–Ru bonds are all the same length at approximately 273 pm.



55

Tetraphenylporphyrin indium hydride (TPP)InH reacts with $H_2Os_3(CO)_{10}(NC_5H_5)$ in hot toluene to afford the cluster-bound indium–porphyrin complex $H_2Os_3(CO)_9(NC_5H_4)In(TPP)$, **56**.[86]



56

3.08.7 Complexes Derived by Ligand Substitution Reactions Using $(RE)_n$

As noted above, E–R ligands have a lone pair of electrons and the E atom is electron poor, giving rise to the possibility of backdonation from the metal into empty *p*-orbitals on the group 13 element. Regardless of the real extent of such backdonation, the situation remains similar to that encountered for CO bonding to transition metals; terminal as well as bridging carbonyls, both doubly and triply bridging varieties, can be formally replaced by E–R fragments. Even though CO and E–R fragments can adopt both terminal and bridging configurations, it will be seen that when both are present, it is generally the E–R fragment that will preferentially occupy the bridging sites. As with the terminal functions, E–R groups are most often introduced via simple substitution of CO or labile ligands.

3.08.7.1 Complexes with Terminal E-R and E-X Units

Equations (59)–(74)[40–42,45–49,51–55,60,61] and Schemes 19[63] and 20[50] illustrate reactions in which terminal RE ligands are introduced onto a single metal center (Table 5). These reactions are general for E = Al, Ga, and In, and more than one RE function may be appended to a given metal center (Table 6). As with the E^{3+} derivatives, the E^{+} complexes may also be stabilized by addition of a donor ligand, which in this case are chelating nitrogen bases (Table 7). These equations illustrate the diversity of functions that can be attached to E and the wide range of metal complexes that can be handled in this fashion. As illustrated in Equation (62), heteroelement cyclopentadiene analogs can also stabilize an E^{+} unit in both coordinated **57** and uncoordinated **58** forms. Groups other than bulky organic units can also function as the stabilizing units for Ga^{+} as seen in **59** and **60**, the latter also providing an anionic example of ligand-stabilized Ga^{+} (Equation (66), see also Table 8).[61] Table 10 provides a comparison of ^{27}Al NMR data for Al^{+} and Al^{3+} complexes. As can be seen, complexes with Al^{3+} have chemical shifts in the neighborhood of 200 ppm (range 156–214), while the Al^{+} compounds have higher field signals (–114 to +30 ppm).

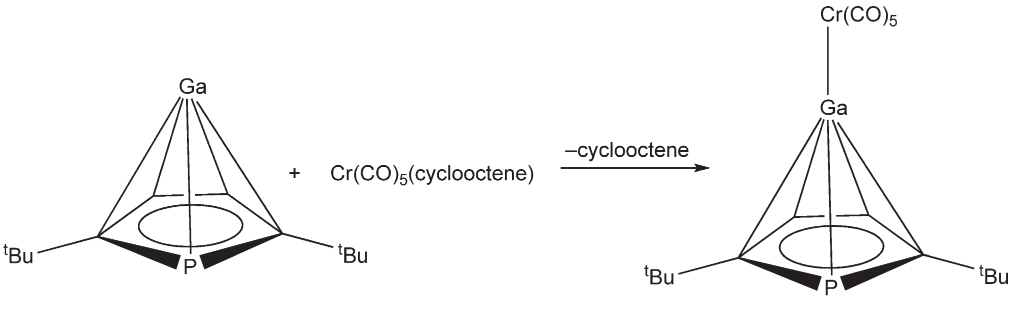
$$\mathrm{Cp^*Al} + \mathrm{Cr(CO)_5(COT)} \longrightarrow \mathrm{(CO)_5CrAlCp^*} \qquad (59)$$

$$\mathrm{ECp^*} + \mathrm{Cr(CO)_5(C_8H_{14})} \longrightarrow \mathrm{(CO)_5CrECp^*} + \mathrm{C_8H_{14}} \qquad (60)$$

E	*Yield* (%)
Ga	86
In	85

$$\mathrm{M(CO)_4(norbornadiene)} + \mathrm{2Cp^*Ga} \longrightarrow cis\text{-}\mathrm{M(CO)_4(GaCp^*)_2} \qquad (61)$$

$$\mathrm{M = Cr, Mo}$$

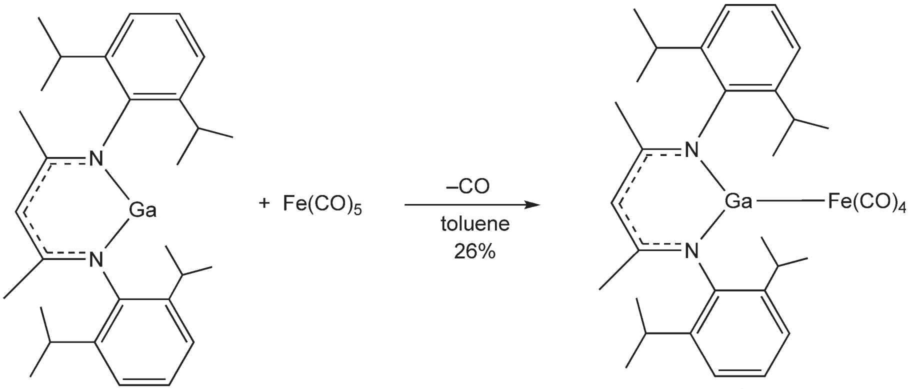


57 **58** (62)

$$\mathrm{InR} + \mathrm{CpMn(CO)_2(THF)} \longrightarrow \mathrm{CpMn(CO)_2InR} + \mathrm{THF} \qquad (63)$$

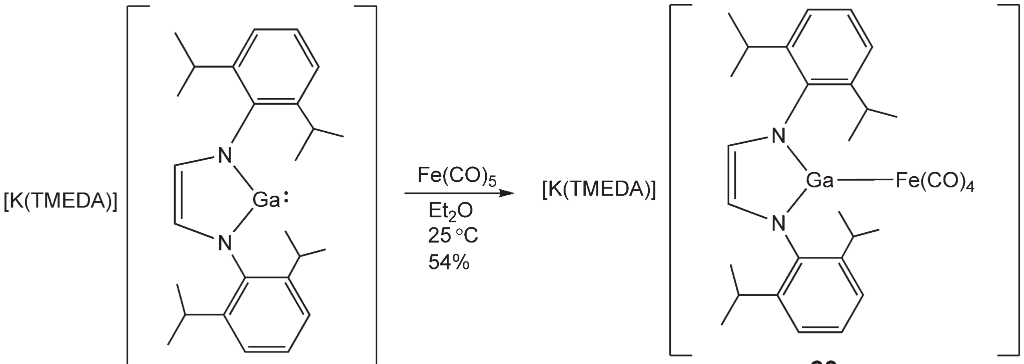
$$\mathrm{R = C_6H_3{-}2,6\text{-}(C_6H_2{-}2,4,6\text{-}{}^iPr_3)} \qquad 46\%$$

$$\mathrm{Fe_2(CO)_9} + \mathrm{GaCp^*} \longrightarrow \mathrm{Cp^*GaFe(CO)_4} \qquad (64)$$



59

(65)



60

(66)

$$Ni(COD)_2 + 4ER \xrightarrow{n\text{-hexane}} Ni(ER)_4 \qquad (67)$$

E	*R*	*yield* (%)
Ga	Cp	60
Ga	$C(SiMe_3)_3$	70
In	$C(SiMe_3)_3$	75

$$Ni(COD)_2 + 4AlCp^* \xrightarrow[90\%]{C_6H_6} Ni(AlCp^*)_3(\mu\text{-}H)Al(Ph)Cp^* \qquad (68)$$

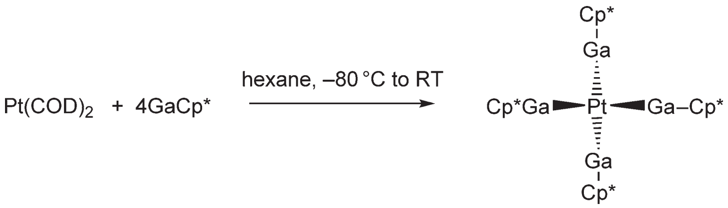
$$Ni(COD)_2 + 3AlCp^* + HSiEt_3 \xrightarrow[80\%]{} Ni(AlCp^*)_3(H)SiEt_3 \qquad (69)$$

$$Ni(AlCp^*)_3(H)SiEt_3 + L \longrightarrow Ni(AlCp^*)_3L \qquad (70)$$

L = GaCp*, PPh_3

$$Pd(TMEDA)Me_2 + ER \longrightarrow Pd(ER)_4 \qquad (71)$$

E = Ga, R = Cp*; E = In, R = $C(SiMe_3)_3$



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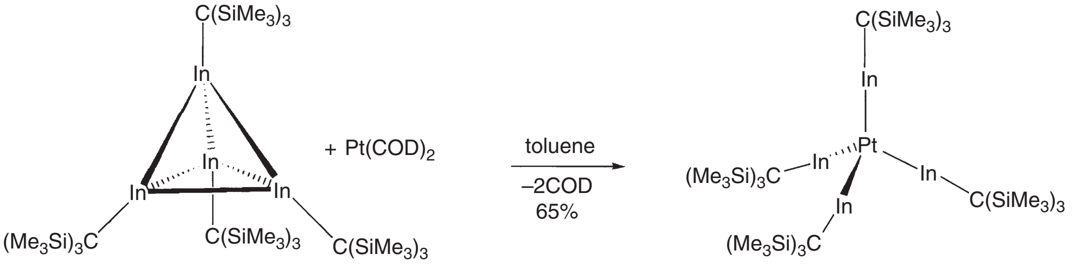

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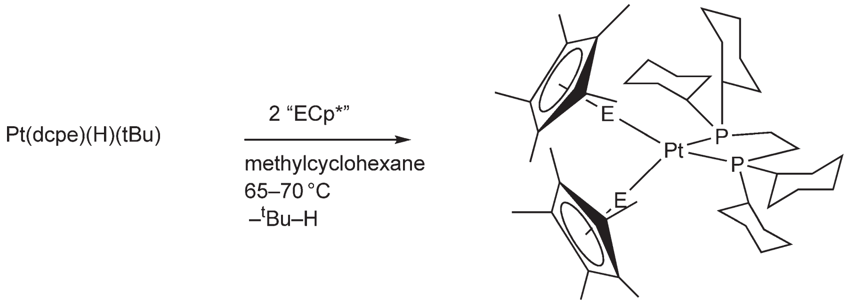


(74)

E = Al, R = Cp* (46%)
E = Ga, R = C(SiMe$_3$)$_3$ (49%); R = Cp* (50%)
E = In, R = Cp* (65%)

63

The Ni{ER}$_4$ compounds in Equation (67) are tetrahedral molecules.[53,54] Calculations were performed on the homologous series Ni{EMe}$_4$ for E = B, Al, Ga, In, and Tl.[53] The calculated bond lengths for the series were 176.4, 214.2, 221.0, 234.1, and 245.2 pm. For comparison, the actual distance observed in Ni{GaC(SiMe$_3$)$_3$}$_4$ was found to be 217.00(4) pm.[53] The calculations indicated strong π-backbonding from nickel to E.

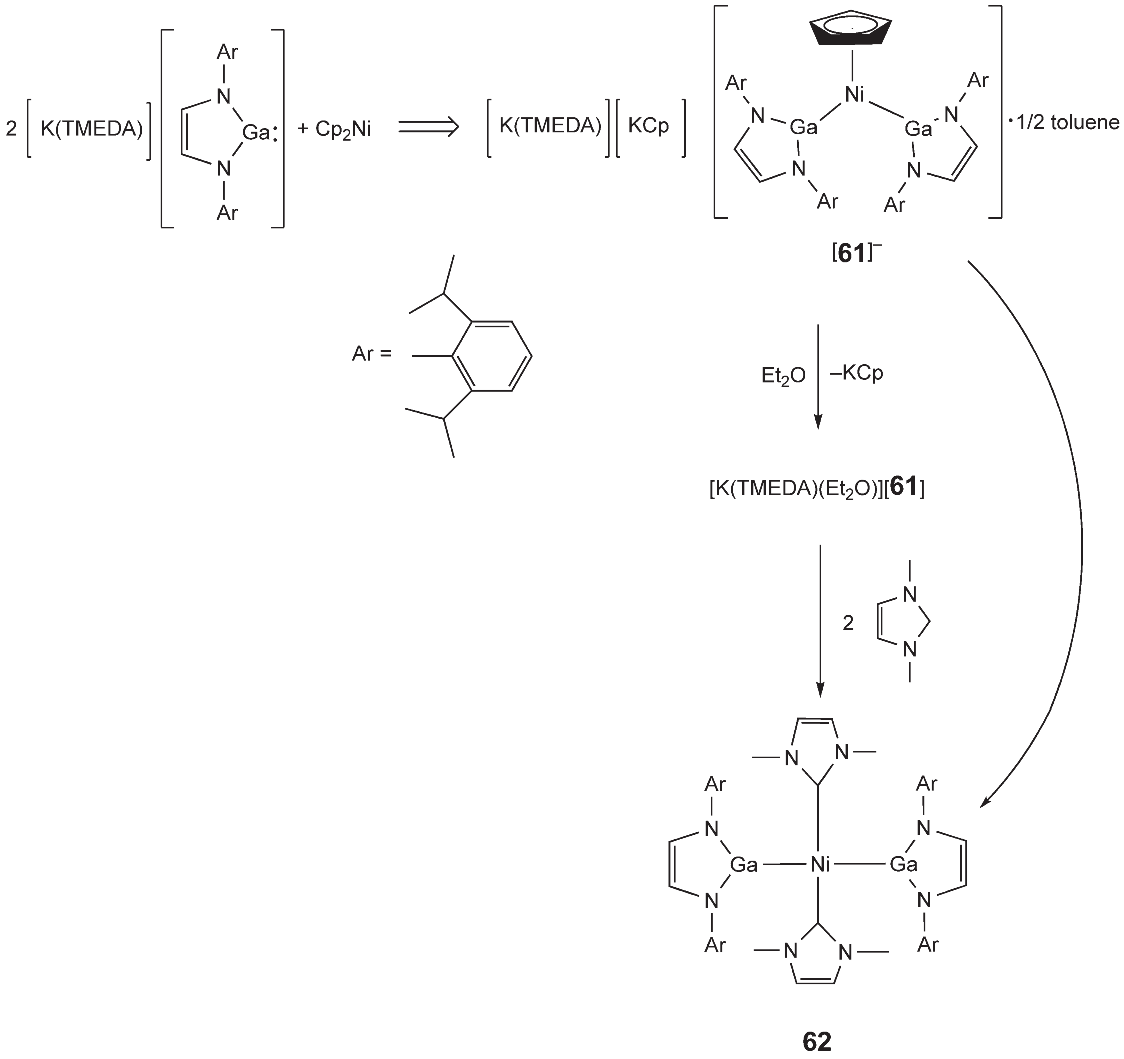
The reaction of Ni(COD)$_2$ with AlCp* in benzene (Equation (68)) differs from that reported to take place in hexane which leads to unreactive Ni{AlCp*}$_4$.[47] Similarly, reactions in the presence of HSiEt$_3$ result in oxidative addition across the Si–H bond (Equation (69))[47] to produce a reactive complex that can be used for further chemistry (Equation (70)).[47]

The Cp ligand in complex [**61**]$^-$ can be substituted by stabilized carbene units to give **62** in Scheme 19,[63] which is square planar.

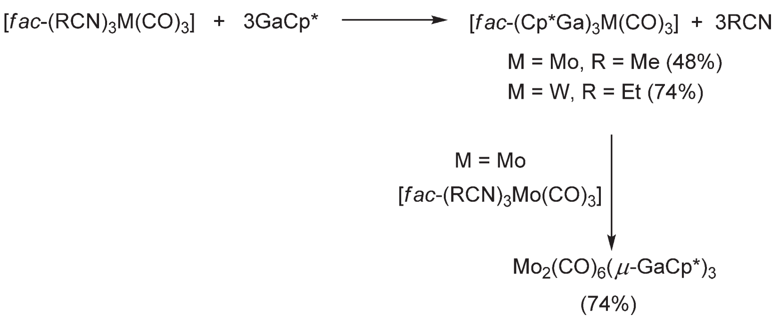
Platinum and palladium reagents also readily react with ER fragments to produce multiply substituted complexes (Equations (71)–(74)).[48,51,52,55] As with the Ni complexes described above, the M(GaCp*)$_4$ (M = Pd, Pt) compounds are tetrahedral. DFT calculations on the (H$_2$PCH$_2$CH$_2$PH$_2$)Pt(ECp)$_2$ (E = Al, Ga) (related to **63**) indicated that the Cp*E serves as a moderate σ-donor/π-acceptor with the M–E bond strength being highly dependent upon the ligands attached to M.[48]

3.08.7.2 Complexes with Bridging ER Units

As mentioned above, ER fragments can bridge between two or more metal centers. Examples are given in Table 9. Trisubstituted GaCp* complexes of Mo and W can be prepared from the tris(organonitrile)-substituted metal tricarbonyls, and the molybdenum compound reacts with a further equivalent of the metal tricarbonyl to afford a dinuclear derivative (Scheme 20).[50] Despite the short Mo–Mo distance in Mo$_2$(CO)$_6$(μ-GaCp*)$_3$ (276.61(6) pm), it is believed that there is not a direct Mo–Mo interaction. The bonding is better considered as having three three-center two-electron Mo$_2$Ga bonding interactions, with the short Mo–Mo distance being a consequence of the short Mo–Ga bonds.[50] Cyclopentadienyl-substituted metal carbonyls of molybdenum and tungsten also form dinuclear complexes, as illustrated in Equation (75).[50] Interestingly, the Cp* groups in **64** adopt η^1-configurations.



Scheme 19

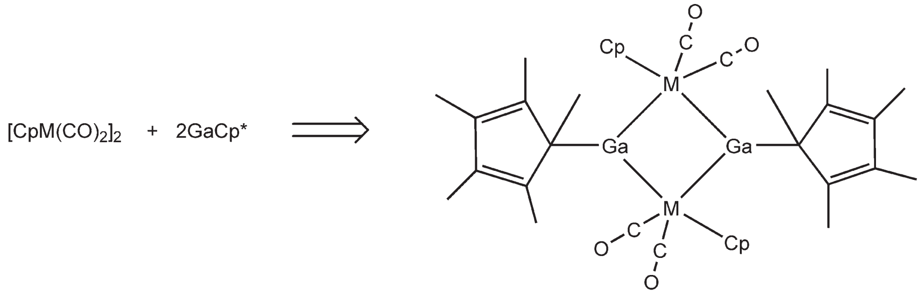


Scheme 20

Table 10 ^{27}Al NMR data

Compound	δ (ppm)	*References*
Compounds formally containing E^+		
$Cp^*AlFe(CO)_4$	−0.4	39
$Cp^*AlCr(CO)_5$	−26.1	40
$Ni\{AlCp^*\}_3(\mu\text{-}H)Al(Ph)(Cp^*)$[a]	−41.2	47
$Ni\{AlCp^*\}_3(H)SiEt_3$	−35.2	47
$[CpNiAlCp^*]_2$	30	66
$(dcpe)Pt(AlCp^*)_2$	−114.5	48
Compounds formally containing E^{3+}		
$Cp(CO)_2FeAl[(CH_2)_3NMe_2](^iBu)$	210	26
$Cp(CO)_2FeAl[(CH_2)_3NMe_2](CH_2{}^tBu)$	214	26
$Cp(CO)_2FeAl[(CH_2)_3NMe_2](BH_4)$	207	26
$\{Cp(CO)_2Fe\}Al(Cl)(C_6H_4CH_2NMe_2)$	186	27
$\{Cp(CO)_2Fe\}Al(Cl)(C_6H_4CH_2NMe_2)$	232	27
$(CO)_3(PMe_3)CoAl[(CH_2)_3NMe_2](^iBu)$	199	26
$(CO)_3(PMe_3)CoAl[(CH_2)_3NMe_2](CH_2{}^tBu)$	198	26
$Cp(CO)_2FeAl[(CH_2)_3NMe_2]Br$	197	26
$Cp(CO)_2RuAl[(CH_2)_3NMe_2]Cl$	192	26
$(CO)_3(PMe_3)CoAl[(CH_2)_3NMe_2]Br$	181	26
$Cp(CO)_2FeAlCl_2(THF)$	156	26
$Cp(CO)_2FeAlH_2(NC_7H_{13})$	221	26
$Cp(CO)_2FeAlH_2(THF)$	220	26
$Cp(CO)_2FeAl(TMP)_2$	212	10

[a] For Cp*Al fragments (presumably Cp*(Ph)Al group masked by probe signal).

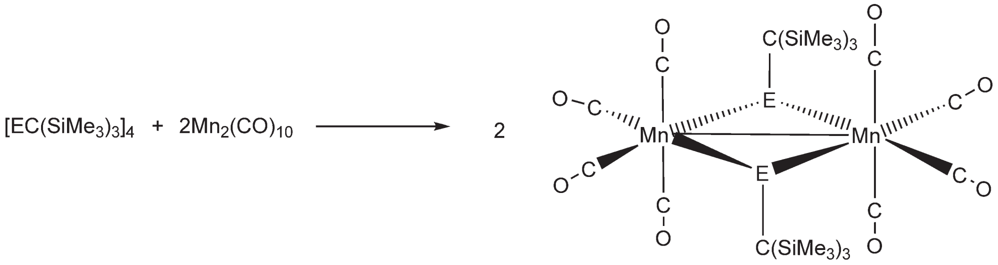


M = Mo, 50%; M = W , 41%

64

(75)

Decacarbonyl dimanganese reacts with tris(trimethylsilyl)methylgallium or -indium to produce bridged dimers (Equation (76)).[67,70] The Mn–Mn distances in **65** are long (313.70(6) pm in the In complex and 295.0(2) pm in the Ga compound) for Mn–Mn single bonds, consistent with the bonding occurring primarily through the bridging groups, as found for other molecules of this class.[67,70]



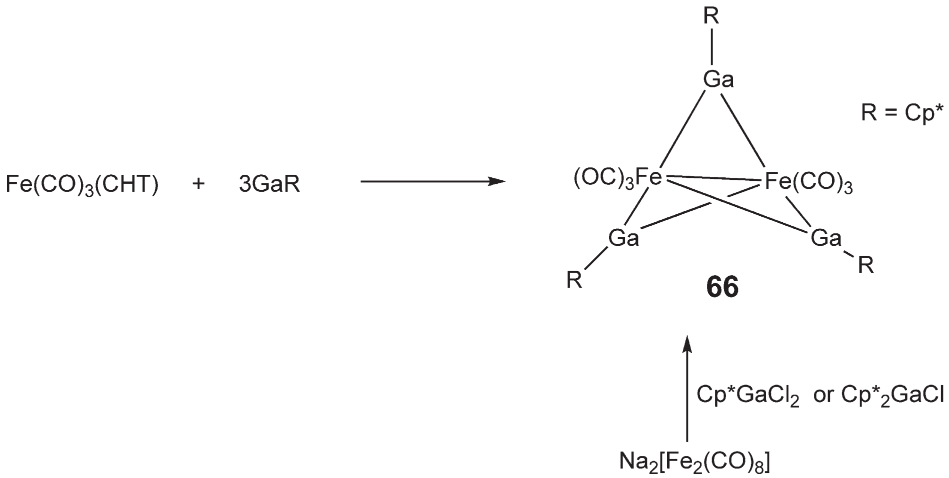
E = Ga, 17%; E = In, 63%

65

(76)

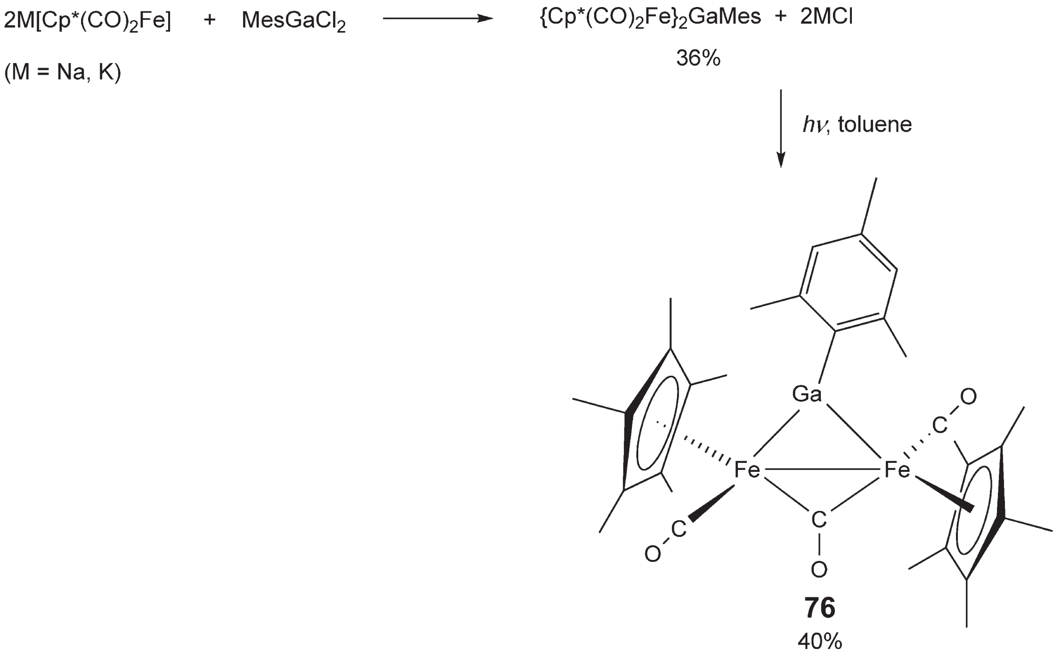
Iron derivatives of gallium and indium are now quite numerous (Equations (77)–(84),[28,41,65,67,71,72] Schemes 21–23).[13,17,41]

$$8\mathrm{Fe(CO)_3(COT)} + 3[\mathrm{InC(SiMe_3)_3}]_4 \longrightarrow \underset{60\%}{\mathrm{Fe_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_3}} + 8\mathrm{COT} \qquad (77)$$

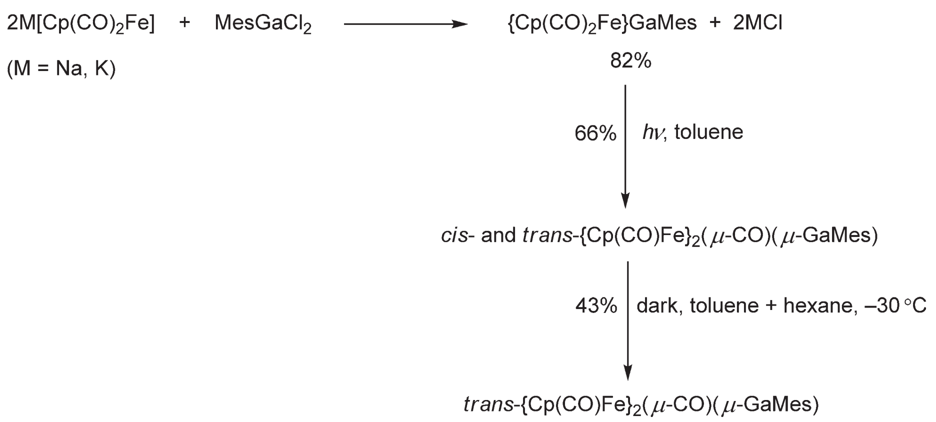


Scheme 21

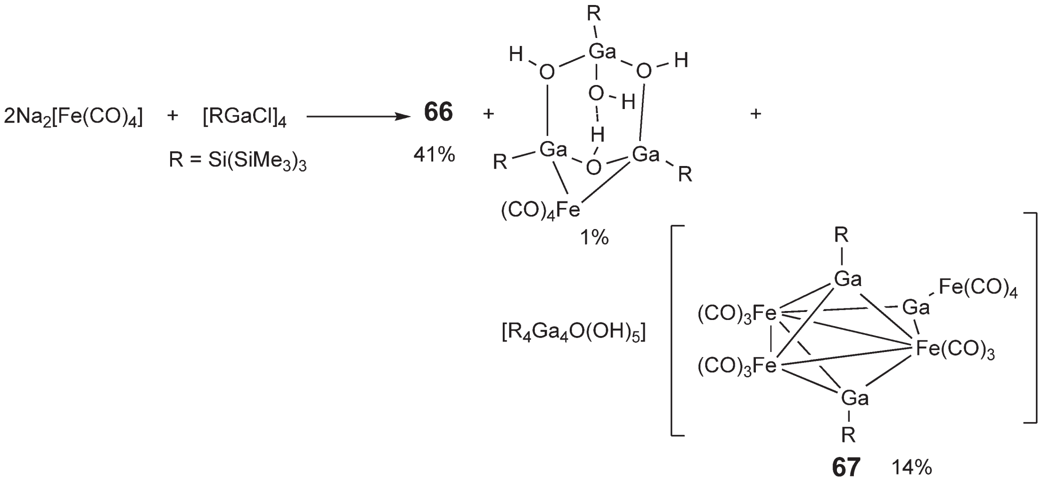
One gallium atom in 66 is not pentahapto bound to Cp*, but exhibits η^3/η^1-bonding.[41] The Fe–Fe distance is 290.8(6) pm. In addition to producing the structure 66, where $\mathrm{R = Si(SiMe_3)_3}$, trinuclear cluster 67 with one doubly bridging and two triply bridging GaR units is produced when $\mathrm{Na_2[Fe(CO)_4]}$ is treated with the reagent $[\mathrm{RGaCl}]_4$.



Scheme 22



Scheme 23



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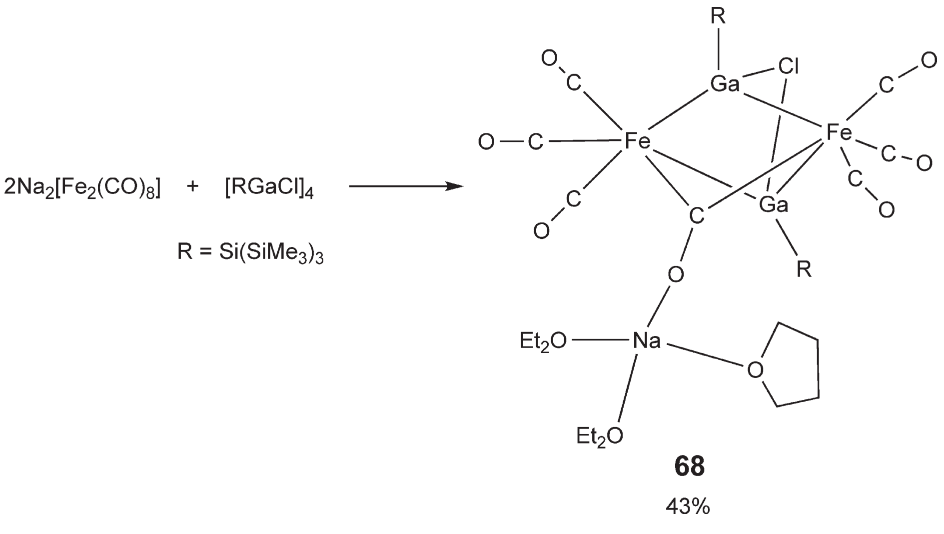

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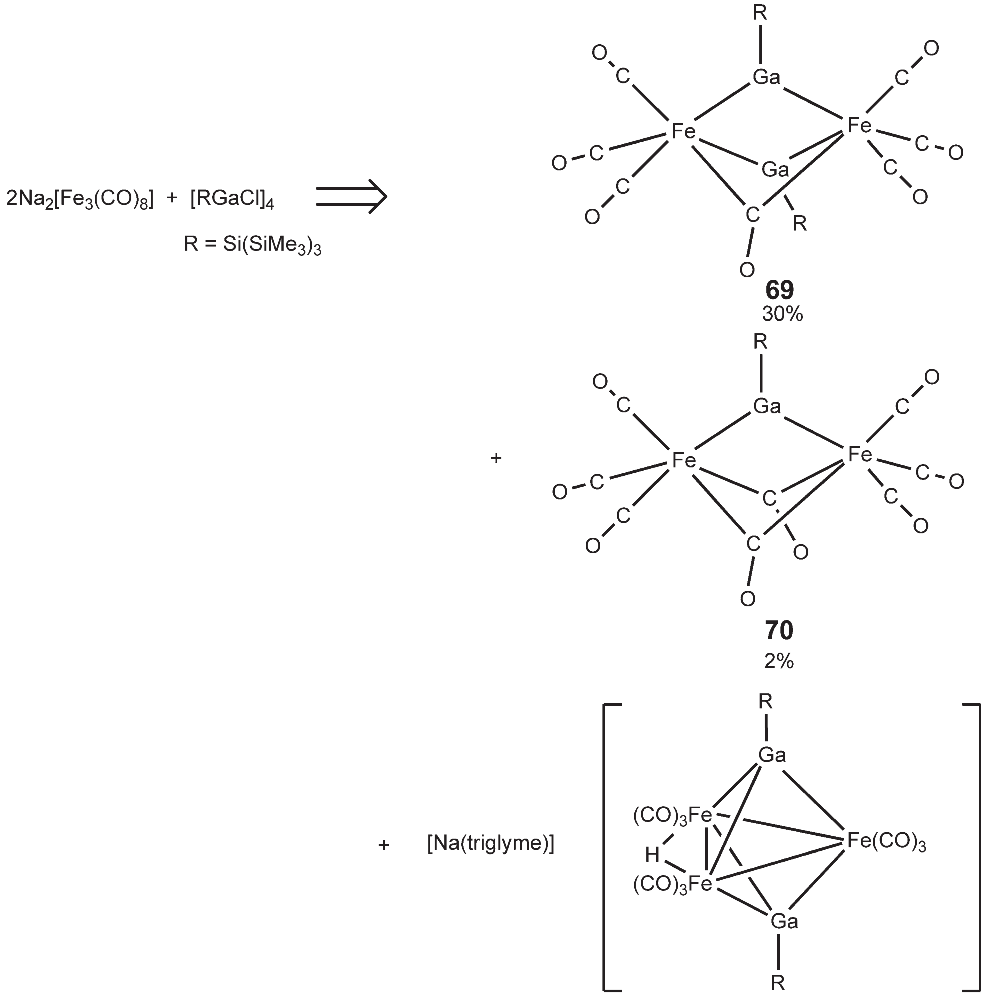
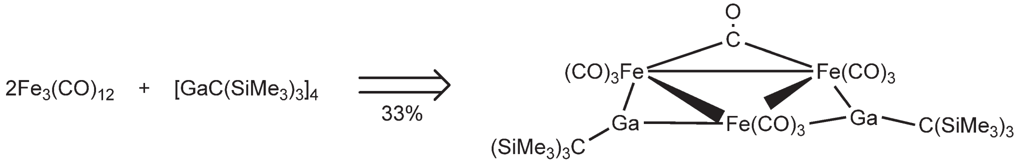


69 30%

70 2%

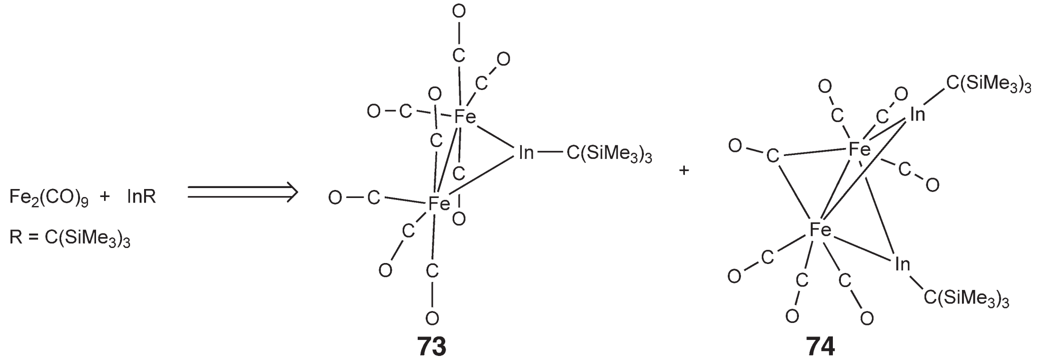
71 42%

(80)



72

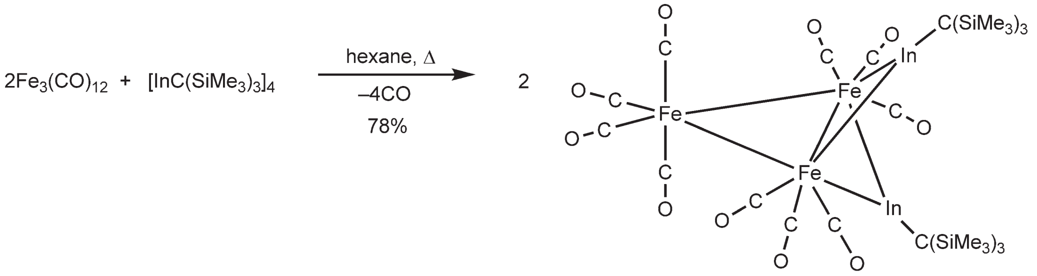
(81)



73 25%

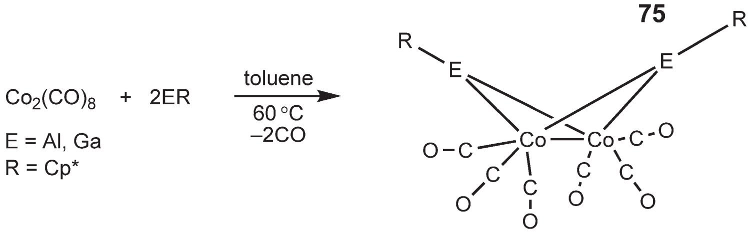
74 45%

(82)



(83)

75



(84)

77

The compounds **66**, **69**, and **70** form a homologous series of compounds with formula $Fe_2(CO)_6(\mu\text{-}CO)_{3-x}(\mu\text{-}GaR)_x$ ($x = 0$–3) of which $Fe_2(CO)_9$ may be viewed as the parent molecule. The nonacarbonyl diiron species has three bridging carbonyl ligands that can be successively replaced by other two-electron donor ligands, which in this case are the GaR units.[28] The Fe–Fe distances in this series and some related compounds are given in Table 11. It is clear that the Fe–Fe distance depends strongly upon the number of substitutions, as seen in Table 11. The bonding in these compounds is largely multicenter bonding with little direct Fe–Fe interaction expected, as supported by the very long Fe–Fe distances in the triply bridged compounds. This is consistent with findings in the related Fe–Tl compounds.[87]

Similarly, the triangular iron clusters **67** and **71** can be viewed as derivatives of $Fe_3(CO)_{12}$ in which three carbonyl ligands have been replaced by other two-electron donor ligands. In the case of **71**, two neutral GaR and one H^- ligand have replaced the three CO's, while in **67**, these ligands have been replaced by two neutral GaR and one anionic $\{Ga(CO)_4Fe\}^-$ fragments.[28] The Fe–Fe distances in these compounds are normal: 270.8(1), 269.7(1), and 274.9(1) pm for **67**, 267.2(2), 271.4(2), and 274.9(3) pm for **71**. In both cases, the longest Fe–Fe bonds are those that are bridged, either by $GaFe(CO)_4^-$ or H^-. The ^1H resonance for the hydride ligand appears at $\delta = -16.9$ ppm, which is consistent with signals for other doubly bridging hydride ligands.

Starting with $Fe_3(CO)_{12}$, another trinuclear complex is obtained having two doubly bridging GaR units (Equation (81)).[67] The Ga-bridged Fe–Fe bond distances in **72** are 277.85(7) and 276.51(7) pm, while the CO-bridged Fe–Fe bond is shorter at 266.61(8) pm.[67]

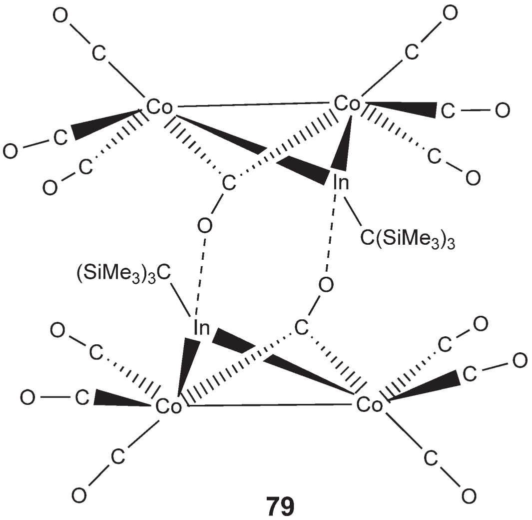
Indium-substituted di- and triiron carbonyl species can be accessed by substitution reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ (Equations (80) and (81)).[67] The Fe–Fe bond distances in **73** and **74** are 289.3(1) and 275.87(5) pm, respectively, while those in **75** are 286.7(1), 272.3(1), and 270.3(1) pm, with the longest being the one bridged by the two indium units.[71]

Table 11 Fe–Fe distances in $Fe_2(CO)_6(\mu\text{-}CO)_{3-x}(ER)_x$ complexes

Compound	*x*	d_{Fe-Fe} (pm)	*References*
$Fe_2(CO)_6(\mu\text{-}CO)_3$	0	254.0	88,89
$Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GaSi(SiMe_3)_3\}_2$	2	268.04(8)	28
$[Na(THF)(Et_2O)_2][Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GaSi(SiMe_3)_3\}_2(\mu\text{-}Cl)]$	2	267.9(2)	28
$Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_3$	3	287.6(2)	28
$Fe_2(CO)_6(\mu\text{-}GaCp^*)_3$	3	290.8(6)	41
$Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}InC(SiMe_3)_3\}_2$	2	275.87(5)	71
$Fe_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_3$	3	299.2(2)	72

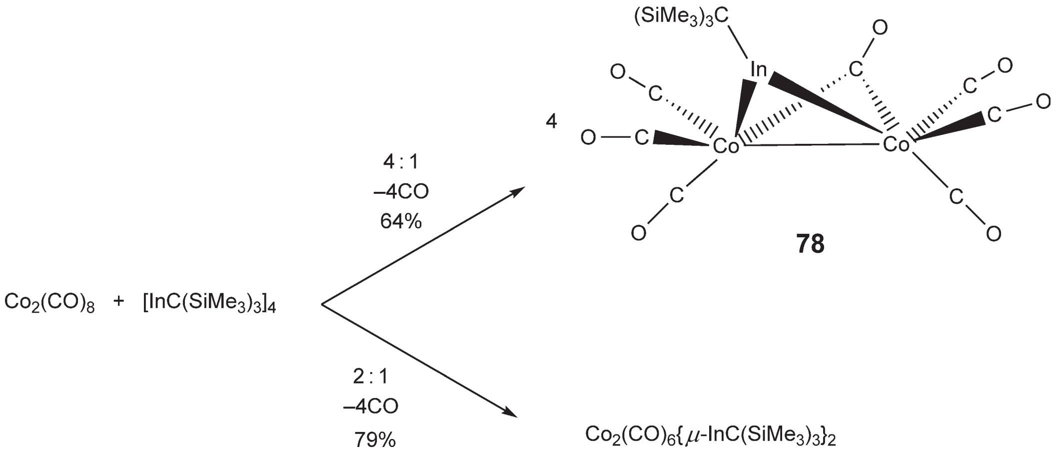
Cyclopentadienyl iron derivatives have also been prepared (Schemes 22 and 23) for both Cp and Cp*. A difference that is obvious upon comparing Schemes 22 and 23 is that the Cp* derivative favors the formation of the *trans*-complex, whereas a mixture of *cis*- and *trans*-forms is obtained in the case of Cp. The Fe–Fe bond distances in *trans*-$\{Cp^*(CO)Fe\}_2(\mu\text{-}CO)(\mu\text{-}Ga(mes))$ and *trans*-$\{Cp(CO)Fe\}_2(\mu\text{-}CO)(\mu\text{-}GaMes)$ are 270.22(11) and 265.26(6) pm, respectively.[17] For the *trans–cis* interconversion, the values were $\Delta H^{\ddagger} = 102(1)\,\text{kJ mol}^{-1}$, $\Delta S^{\ddagger} = 36(4)\,\text{J mol}^{-1}\,\text{K}^{-1}$, and $\Delta G^{\ddagger} = 91(2)\,\text{kJ mol}^{-1}$, while for the reverse process, the corresponding values were $105(2)\,\text{kJ mol}^{-1}$, $52(5)\,\text{J mol}^{-1}\,\text{K}^{-1}$, and $90(3)\,\text{kJ mol}^{-1}$, respectively. The small values of $\Delta S^{\ddagger}$ are consistent with a non-dissociative mechanism, which was also supported by the inertness of the complexes toward ligand substitution.

Group 13 element derivatives of the group 9 transition metals are also well represented in the literature. Simple substitution of $Co_2(CO)_8$ is achieved with either AlCp* or GaCp* (Equation (84)).[41,65] The Co–Co bond distance in **77** (E = Al) is 277.2(2) pm and the Al···Al distance is 312.1(3) pm. The bonding is polarized indicating a strong positive charge at Al, and this is reflected in the short Al–C bond distances.[65] The metals adopt a butterfly arrangement in which the $AlCo_2$ planes intersect at an angle of approximately 72°. For substitutions using $[InC(SiMe_3)_3]_4$, the stoichiometry controls the nature of the final product (Scheme 24).[73] The Co–Co bond distances are 256.81(5) pm in **78** and 280.14(6) pm in $Co_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_2$.[73] The compound **78** packs as dimers in the solid state with Lewis acid–base interactions between the bridging carbonyl ligands on one molecule with the indium center on the other **79**.



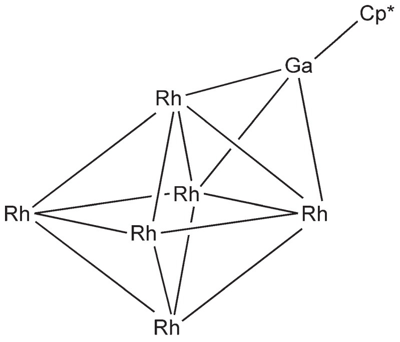
79

GaCp* can serve as a ligand in rhodium cluster compounds, effectively replacing up to four CO's in the parent $Rh_6(CO)_{16}$ cluster.[90] Direct reaction of $Rh_6(CO)_{16}$ and an excess of GaCp* led to the tri- and tetrasubstituted



Scheme 24

derivatives $Rh_6(CO)_{12}(\mu_3\text{-}CO)(\mu_3\text{-}GaCp^*)_3$ and $Rh_6(CO)_{12}(\mu_3\text{-}GaCp^*)_4$, but milder reaction conditions were needed to obtain the mono- and disubstituted compounds $Rh_6(CO)_{12}(\mu_3\text{-}CO)_3(\mu_3\text{-}GaCp^*)$ and $Rh_6(CO)_{12}(\mu_3\text{-}CO)_2(\mu_3\text{-}GaCp^*)_2$. These were prepared by a 1 : 1 reaction using the activated cluster $Rh_6(CO)_{15}(NCMe)$ in place of $Rh_6(CO)_{16}$.[90] For the mono-, di-, and trisubstituted compounds, structures were obtained and the metal cores are shown in 80–82. In all cases, the Ga atoms lay about 200 pm above the Rh_3 triangles to which they were attached,although the distances are slightly shorter in the trisubstituted compound. The Ga–Rh distances ranged from 256.80(7) to 263.09(7) pm in the monosubstituted compound.



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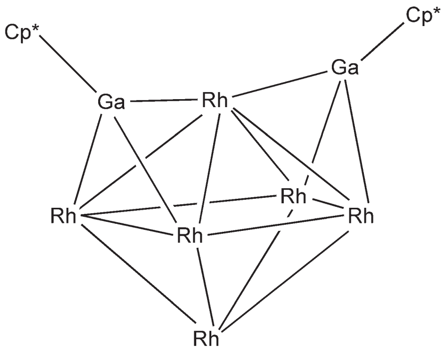

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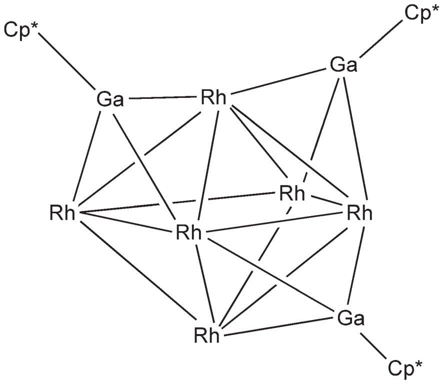
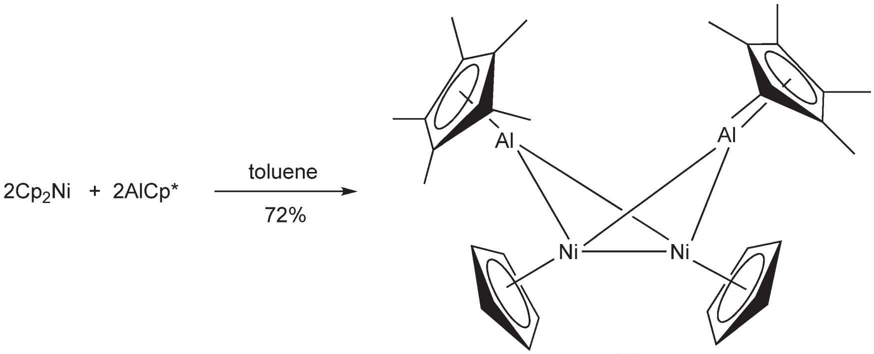


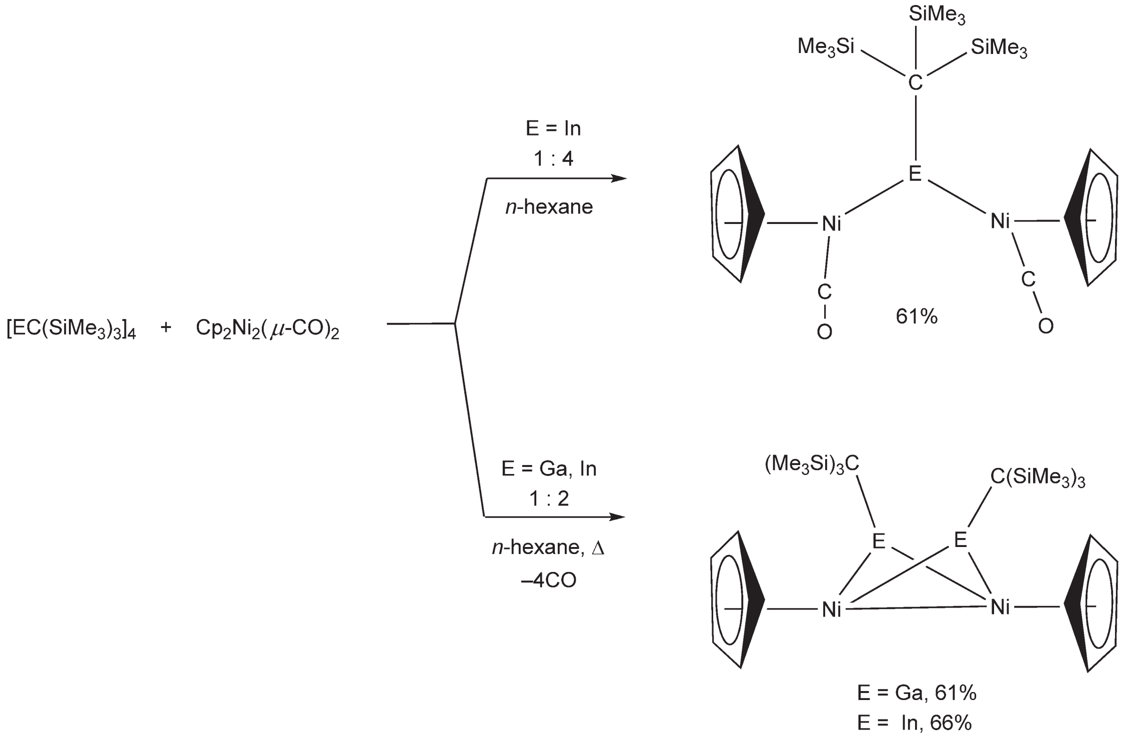
82

Cyclopentadienyl nickel dimers with bridging ER groups can be obtained either from nickelocene or from $Cp_2Ni_2(CO)_2$ (Equation (85),[66] Scheme 25).[68] For $Cp_2Ni_2\{EC(SiMe_3)_3\}_2$, the Ni–Ni bond distances are 244.85(7) pm for E = Ga and 249.1(1) pm for E = In.[68] A tetranuclear cluster is obtained when $GaCp^*$ is reacted with $Ni(CO)_4$ 84.[41]

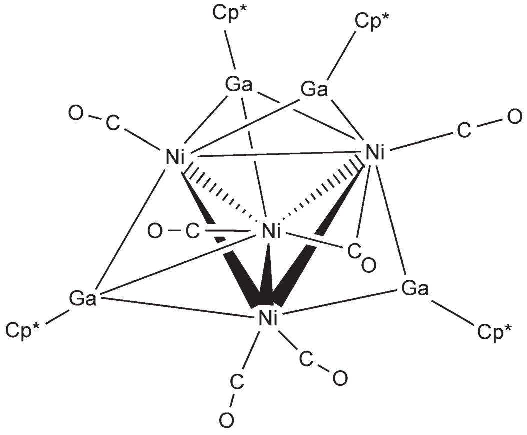


83

(85)



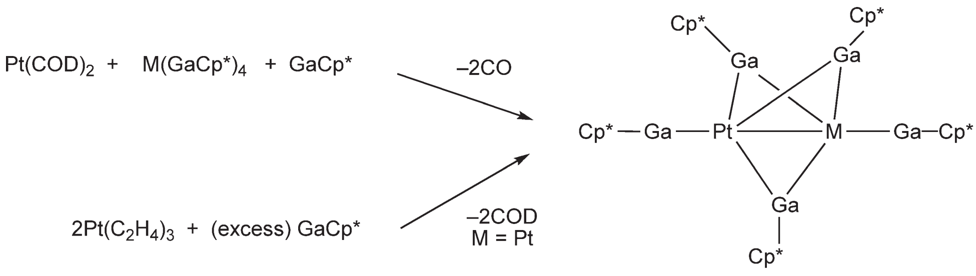
Scheme 25



84

Dinuclear compounds can also be created for Pd/Pt as indicated in Scheme 26. In the reaction using $Pt(COD)_2$ to form the dinuclear compounds, it is important to add the $Pt(COD)_2$ to $M(GaCp^*)_4$ first; presumably, an intermediate of the type $MPt(\mu\text{-}GaCp^*)_3(GaCp^*)(COD)$ is formed initially. Subsequent addition of the $GaCp^*$ gives the fully substituted $MPtGa_5$ compound. If the $Pt(COD)_2$ is not allowed to react with the $M(GaCp^*)_4$ compound first, the $Pt(COD)_2$ preferentially reacts with the $GaCp^*$ to give $Pt(GaCp^*)_4$. The Pt–Pt distance in 85 (M = Pt) is 258.2(1) pm.[69] The NMR data for 85 (M = Pt) were in agreement with the static structure but the data for the bimetallic Pd–Pt compound indicated fluxionality of the $GaCp^*$ units, presumably via movement onto and off the Pd atom.

Starting with $PdMe_2(TMEDA)$ and $InCp^*$, a tripalladium species (Equation (86))[74] that is completely ligated by $InCp^*$ units is formed. The Pd_3 arrangement is essentially linear (169.52(5)°) and each Pd atom is tetrahedrally coordinated by four indium atoms. The Pd–Pd distances are 277.62(14) and 277.47(14) pm.



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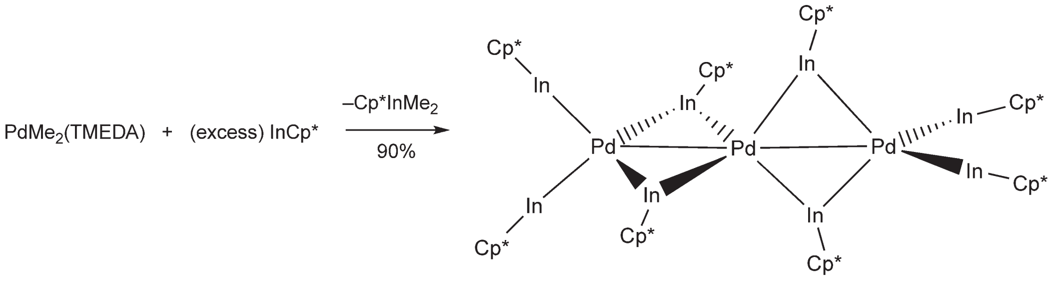
Scheme 26

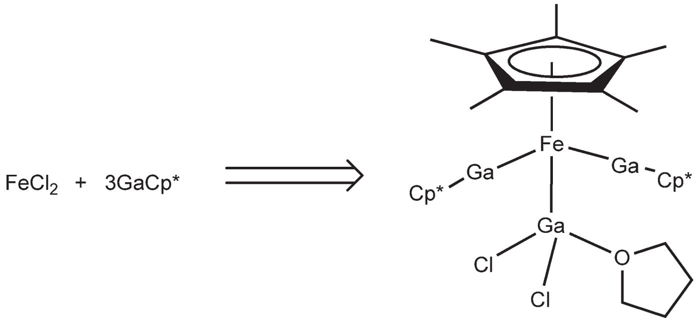


86

(86)

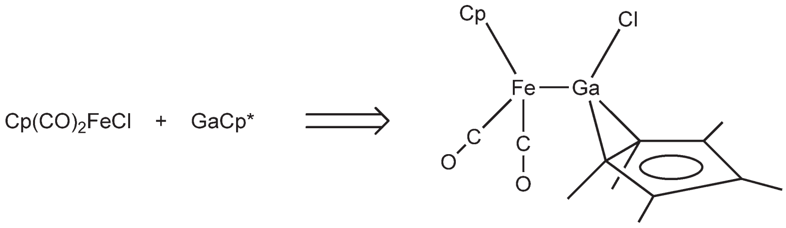
3.08.7.3 Complexes Formed by Reaction of ER with Transition Metal Halides

When ER fragments are treated with transition metal halides, most often insertion of the ER fragment into one or more M–X bonds occurs (Equations (87)[18] and (88)).[18]



87

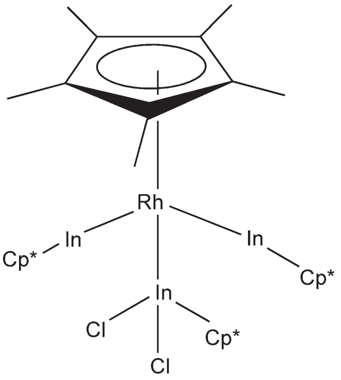
(87)



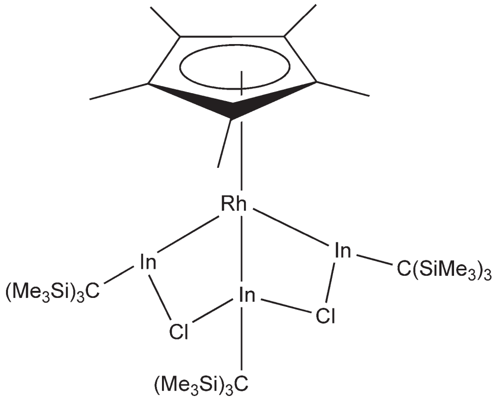
88

(88)

Reaction of $[Cp^*RhCl]_2$ with InR (R = $C(SiMe_3)_3$, Cp^*) produces $Cp^*Rh(InR)_2(InRCl_2)$ and the NMR data show fast exchange of the chloride ions between all three indium atoms in solution.[56] The solid-state structure of the R = Cp^* derivative shows the product to have the expected $Cp^*Rh(InR)_2 \rightarrow InCl_2R$ arrangement **89**, but the R = $C(SiMe_3)_3$ compound exhibits bridging chloride ions **90**, which presents a plausible pathway for chloride-ion scrambling.[56] Compound **89** shows variable coordination of the In atoms to the Cp^* rings. For the $InCl_2$ unit, the Cp^* is η^1-bound, while for the Cp^* units for the other two groups, one is η^3- and the other η^5-bound.



89



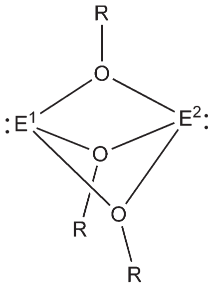
90

3.08.7.4 Complexes with $E(OR)_3E'$

A more specialized series of mixed $EE'(OR)_3$ ligands **91** having In^+ or Tl^+, and Sn^{2+} or Ge^{2+} have been synthesized. Structurally characterized examples are provided in Table 12. Metal carbonyl derivatives with metals attached to the indium atoms could be prepared in moderate to good yields, but coordinated thallium complexes were not reported.[91] Each main group element retains a lone pair of electrons that can be used to donate to an external metal center at one or both ends to form substituted metal carbonyl complexes **92** and **93**. Two such complexes can also be substituted onto a single metal center as in **94** and **95**. Addition of $M(CO)_6$ (M = Cr, Mo, W) or $Fe_2(CO)_9$ to the $In(\mu\text{-}O^tBu)_3E$ (E = Sn, Ge) selectively metallates at indium to produce the complexes in **92**. The symmetrically doubly metallated complexes can be obtained by simply using 2 equiv. of the metal carbonyl reagent, while the asymmetrically substituted complexes are obtained by treating the compounds **92** with the second metal carbonyl complex.

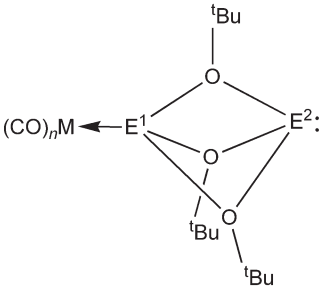
Table 12 Metal complexes of $E(\mu\text{-}OR)_3E'$

Compound	*E–M distance* (pm)	*References*
cis-$[Ge(\mu\text{-}O^tBu)_3In]_2Cr(CO)_4$	256.3(4)	91
$(CO)_4FeIn(\mu\text{-}O^tBu)_3SnCr(CO)_5$	242.0(9)	91
cis-$[(CO)_5CrSn(\mu\text{-}O^tBu)_3In]_2Cr(CO)_4$	257.1(3)	91
$(CO)_5MoIn(\mu\text{-}O^tBu)_3SnMo(CO)_5$	274.2(1)	91
$(CO)_5MoIn(\mu\text{-}O^tBu)_3SnCr(CO)_5$	273.4(2)	91
$(CO)_5MoIn(\mu\text{-}O^tBu)_3GeMo(CO)_5$	270.2(4)	91
cis-$[(CO)_5CrSn(\mu\text{-}O^tBu)_3In]_2Mo(CO)_4$	271.0(5)	91



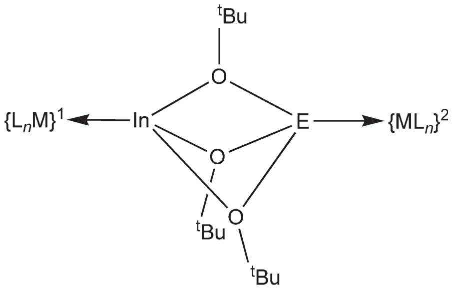
E^1 = In, Tl
E^2 = Sn, Ge

91



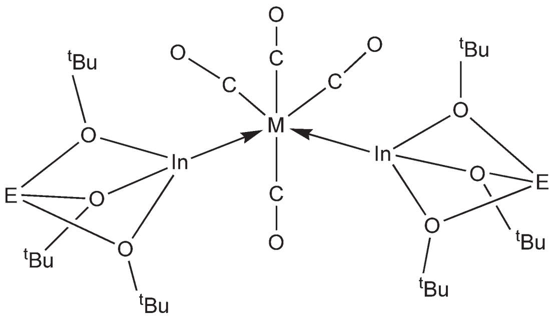
92

E^1	E^2	M	n
In	Sn, Ge	Cr, Mo, W	5
In	Sn	Fe	4



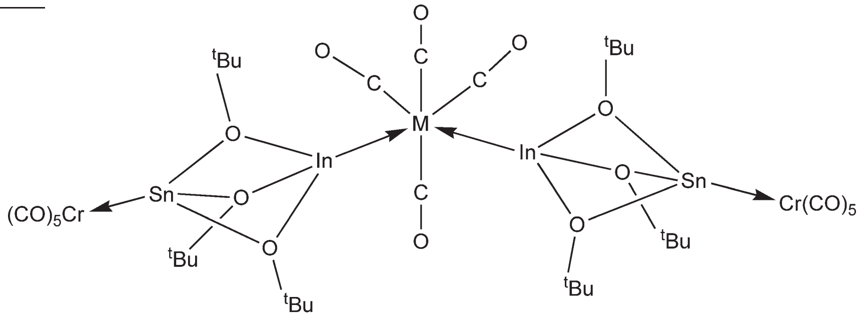
93

E	$\{ML_n\}^1$	$\{ML_n\}^2$
Sn	$Cr(CO)_5$, $Mo(CO)_5$	$Cr(CO)_5$, $Mo(CO)_5$
	$Fe(CO)_4$	$Cr(CO)_5$
	$Ni(CO)_3$	$Ni(CO)_3$
Ge	$Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$	$Cr(CO)_5$
	$Mo(CO)_5$	$Fe(CO)_4$, $Mo(CO)_5$
	$Fe(CO)_4$	$Fe(CO)_4$
	$Ni(CO)_3$	$Ni(CO)_3$



M	E
Cr	Ge
Cr, Mo, W	Sn

94



M = Cr, Mo

95

3.08.8 Reactions of Transition Metal–Group 13 Element Complexes with Main Group Element $SiMe_3$ Complexes

Cubane cluster complexes of the general formula $[\{L_nM\}EE'R]_4$ can be produced by treating metallated gallium or indium halides with trimethylsilyl chalcogenide or phosphorus reagents (Table 13, Equations (89)–(91),[30,92,93] structure 96.[30] Using $\{Cp(CO)_2Fe\}GaCl_2$ in place of $\{Cp(CO)_2Fe\}_2GaCl$ gave similar results but with larger

Table 13 Cubane clusters of the type $[\{L_nM\}EE'(R)]_4$

Compound	*E–M distance*(pm)	*References*
$[\{CpFe(CO)_2\}GaS]_4$	233.7(1)	92
$[\{CpFe(CO)_2\}GaSe]_4$	234.7(1)	92
$[\{CpFe(CO)_2\}GaTe]_4$	234.8(2), 235.7(2)	92
$[\{Cp(CO)_2Fe\}GaP(SiMe_3)_2]_4$	2.3771(14)–2.3838(14)	30
$[\{Cp(CO)_3Mo\}InP(SiMe_3)]_4$	278.1(2)–279.5(2)	93

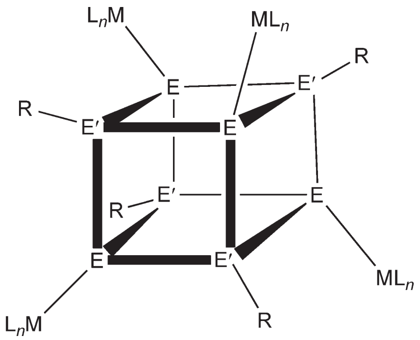
proportions of the cubane. In this reaction, the order of addition was found to be important. If $LiP(SiMe_3)_2$ is added to a solution of $\{Cp(CO)_2Fe\}_2GaCl$ at −78 °C, the major product is found to be the cyclic compound $[\{Cp(CO)_2Fe\}(Cl)GaP(SiMe_3)_2]_2$ **97** Similarly, when $\{Cp(CO)_2Fe\}_2GaCl$ is treated with $LiPPh_2$, the cyclic compound **98** is obtained. In contrast to other reactions in which Me_3SiCl is the byproduct, small amounts of $HP(SiMe_3)_2$ were found in the reaction solution.[30]

$$4\{Cp(CO)_2Fe\}GaCl_2 + 4E(SiMe_3)_2 \xrightarrow[20\,°C]{THF} [\{Cp(CO)_2Fe\}GaE]_4 + 8Me_3SiCl \tag{89}$$

E	*Yield* (%)
S	77
Se	74
Te	75

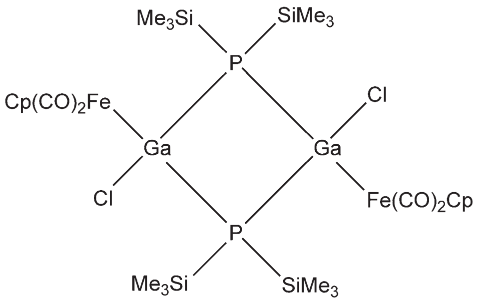
$$\underset{M = Li, Na, K}{\{Cp(CO)_2Fe\}_2GaCl + MP(SiMe_3)_2} \longrightarrow \underset{40\%}{\{Cp(CO)_2Fe\}GaFe_2(CO)_2(\mu\text{-}CO)Cp_2} + \underset{30\%}{[\{Cp(CO)_2Fe\}GaPSiMe_3]_4} \tag{90}$$

$$4Cp(CO)_3MoInCl_2 + 4P(SiMe_3)_3 \xrightarrow{THF} [\{Cp(CO)_3Mo\}InPSiMe_3]_4 + 8Me_3SiCl \tag{91}$$



96

E = Ga, E′ = S, Se, Te, R is a lone pair, $ML_n = Cp(CO)_2Fe$
E = Ga, E′ = P, R = $SiMe_3$, $ML_n = Cp(CO)_2Fe$
E = In, E′ = P, R = $SiMe_3$, $ML_n = Cp(CO)_3Mo$



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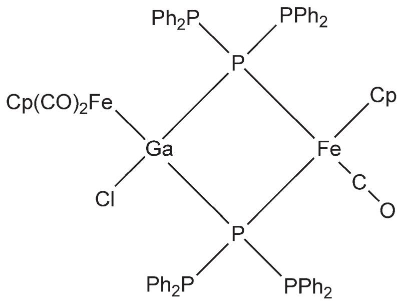

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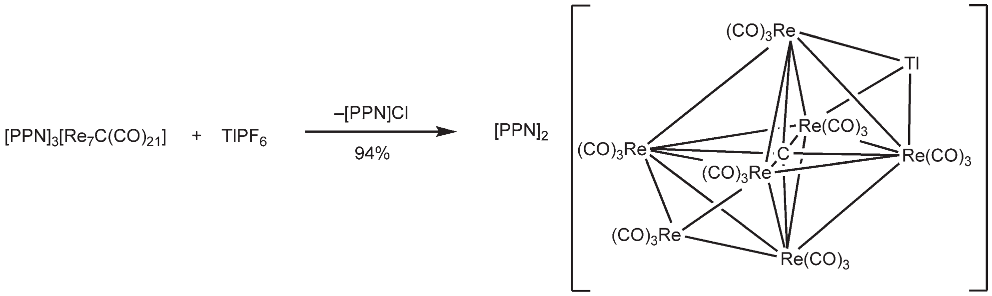
3.08.9 Complexes with Thallium

Thallium(I) salts have long been used in reactions with organic and organometallic halide complexes as a means of activating the halide by removal as insoluble TlX. However, the thallium ions proved not to be “innocent” bystanders, and numerous examples were reported in COMC (1995) where the metal-bound thallium complexes were formed. Deliberate reactions of thallium(I) and thallium(III) salts with metal carbonyl anions have yielded a variety of complexes of the form $Tl\{ML_n\}_3$. In the past decade, new examples of metal carbonyl derivatives of thallium have been prepared (see Table 2). In addition, the propensity for Tl^+ to form adducts with 16-electron noble metal complexes has been exploited.

3.08.9.1 Group 7–9 Metal Carbonyl Derivatives

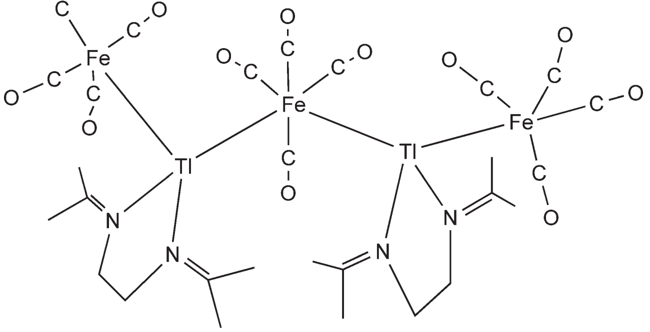
The only new report of a group 7 complex with thallium is the reaction of $[Re_7C(CO)_{21}]^{3-}$ ion with $TlPF_6$ (Equation (92)).[94] The thallium adds in a triply bridging fashion opposite to the capping $Re(CO)_3$ unit **99**.[94] The complex is stable in dichloromethane but dissociates in coordinating solvents. In acetone, infrared data indicated that the complex would be ~99% dissociated at concentrations of the cluster of about 10^{-4} M. Addition of halide ions to dichloromethane solutions causes a precipitation of the thallium(I) halide.



99

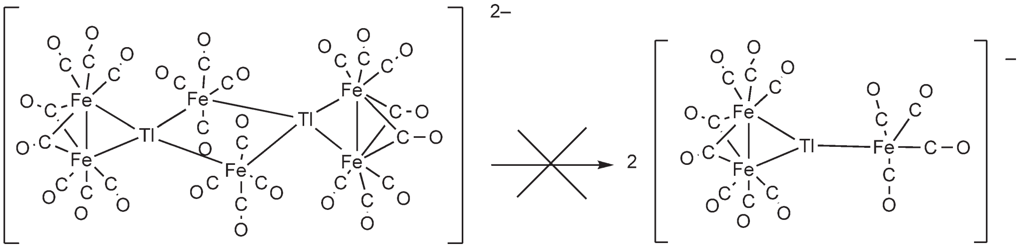
(92)

The complexes $Tl\{ML_n\}_3$ with $ML_n = Co(CO)_4$, $CpFe(CO)_2$, and $\{Fe(CO)_4\}^-$ have been structurally characterized and exhibit the expected trigonal-planar arrangement at the thallium center.[23] The previously prepared adduct $[Et_4N][(en)Tl\{Fe(CO)_4\}_2]$ was found to react with acetone and, upon apparent fortuitous oxidation, yielded the trinuclear complex **100**. Evidently, the acetone reacts with the coordinated ethylenediamine ligand to produce the thallium-bound diimine ligands.[23] The Tl–Fe distances fall into two distinct ranges – the shorter ones being those in which the Tl is bound to a terminal $Fe(CO)_4$ group (256.9(2) and 257.8(2) pm) and those to the bridging $Fe(CO)_4$ unit (270.0(2) and 274.9(2) pm).



100

Thallium NMR can be particularly useful because of the presence of two naturally occurring spin-(1/2) nuclei: ^{203}Tl and ^{205}Tl (30 : 70). The chemical shift range is also very large (~1,500 to ~6,800 ppm). Three-coordinate thallium generally gave signals in the region between 6,000 and 6,800 ppm, while four-coordinate thallium produced signals in the range of 4,400–5,800 ppm. Thallium NMR data for a variety of metal carbonylate derivatives of Tl were examined.[23] These included the mononuclear complexes Tl{ML$_n$}$_3$ (ML$_n$ = Co(CO)$_4$, CpFe(CO)$_2$, {Fe(CO)$_4$}$^-$, CpCr(CO)$_3$, CpMo(CO)$_3$) and tetraalkyl ammonium salts of [LTl{Fe(CO)$_4$}$_2$]$^-$ (L = bipy, en, phen, TMEDA, dien). For complexes containing more than one thallium atom, isotopomers may exhibit ^{203}Tl–^{205}Tl coupling, which can be structurally diagnostic. For example, of the possible dissociation equilibria for [Tl$_2$Fe$_6$(CO)$_{24}$]$^{2-}$,[95] [Tl$_2$Fe$_4$(CO)$_{16}$]$^{2-}$, and [Tl$_4$Fe$_8$(CO)$_{32}$]$^{4-}$ shown in Equations (93)–(95), the coupling patterns indicated that the process shown in Equation (93) does not occur, whereas those in Equations (94) and (95) do occur.



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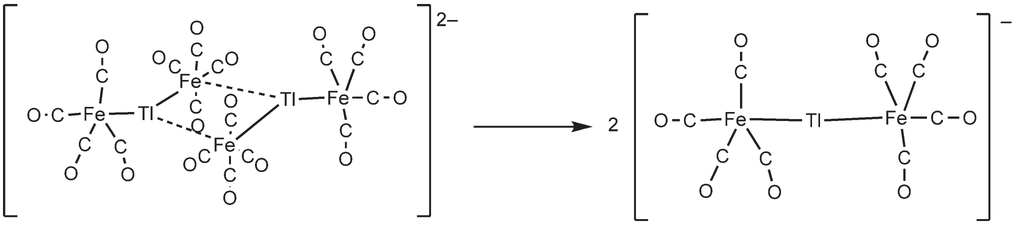

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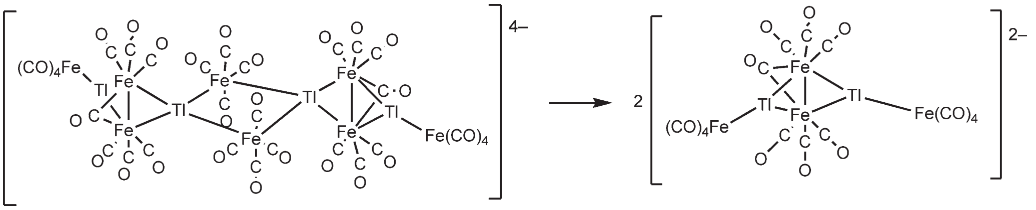
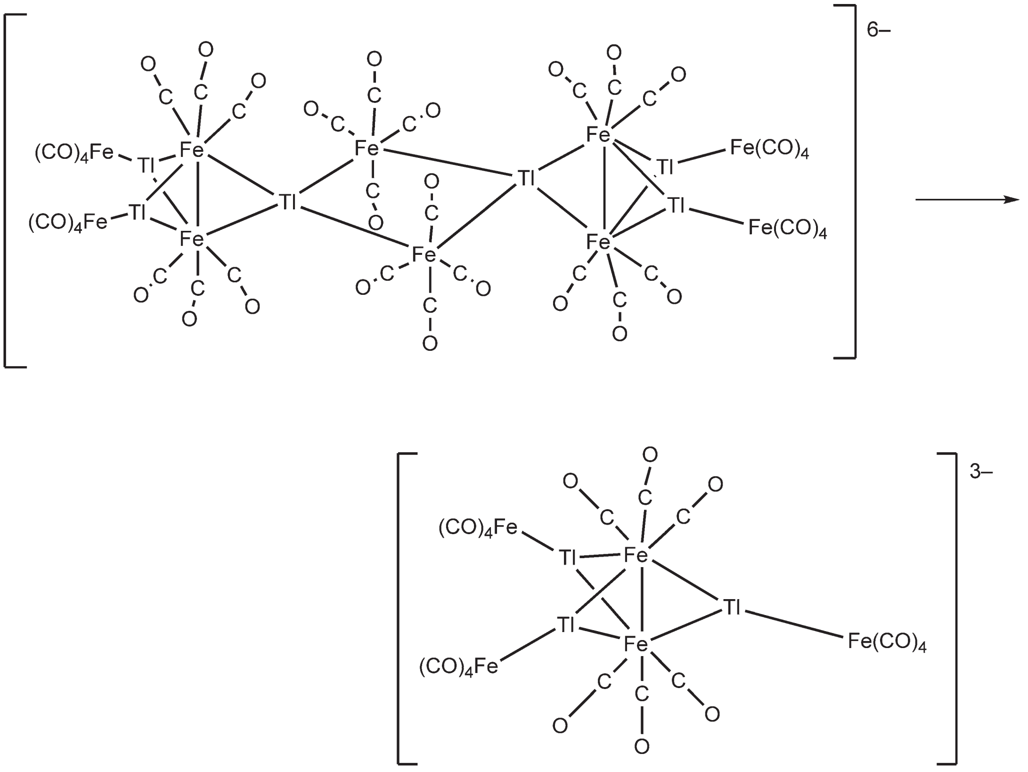


(95)

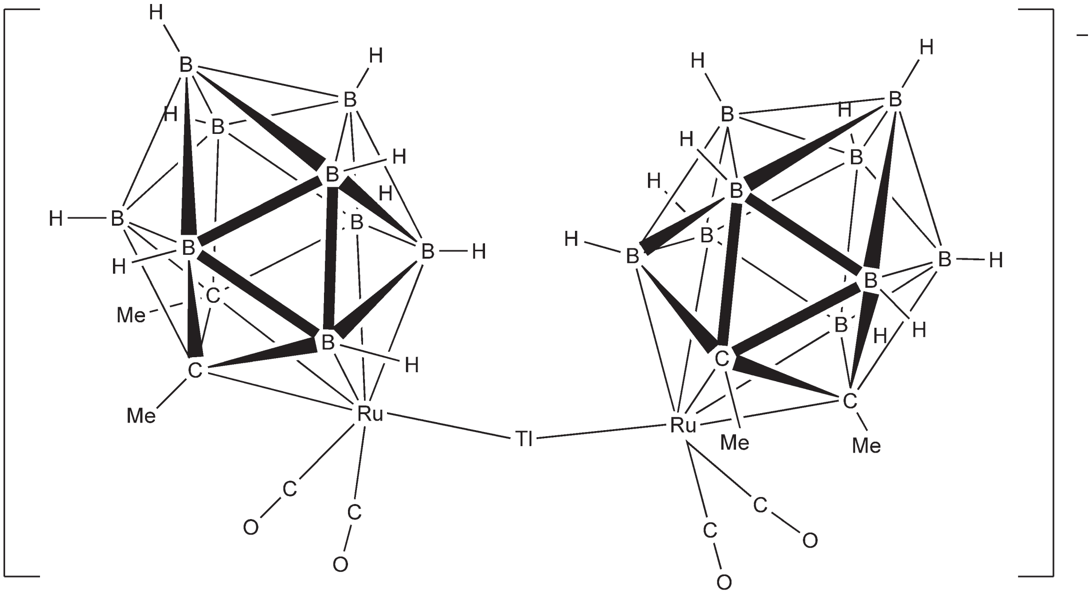
The monomeric compound [Fe$_2$(CO)$_6${μ-TlFe(CO)$_4$}$_3$]$^{3-}$ **101** was structurally characterized as the PPN$^+$ salt, contrasting with the earlier characterization of the [Et$_4$N]$^+$ salt that showed a dimer.[87] The monomer is isoelectronic with Fe$_2$(CO)$_9$ and a theoretical analysis of the bonding shows that the Fe–Fe interaction which varies through the entire series of [Fe$_2$(CO)$_6$(μ-CO)$_{3-x}${μ-TlFe(CO)$_4$}$_x$]$^{x-}$ (x = 0, 1, 2, 3) is consistent with three-center bonding. The Fe–Fe distances range from 252 pm in the nonacarbonyl to 311 pm in **101**. The Tl–Fe distances in **101** for the terminal Fe(CO)$_4$ units are again shorter (255.3(3) to 255.7(3) pm) than those to bridging Fe groups (260.9(3) to 266.4(3) pm) (Equation (96)).[87]

Reaction of RuBr(CO)$_3$(η^3-C$_3$H$_5$) with Tl[*closo*-1,2-Me$_2$-1,3,2-TlC$_2$B$_9$H$_9$] gave a mixture of (CO)$_3$Ru(*closo*-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$) and [Tl{Ru(CO)$_2$(*closo*-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)}$_2$]$^-$ **102**.[96] The [Et$_4$N]$^+$ salt of the latter could be isolated after addition of [Et$_4$N]Cl followed by column chromatography. The yields of these compounds were not reported. The Tl–Ru bond distance of 259.94(4) pm is short compared to the values in the previously reported [AsPh$_4$][{Ru$_6$C(CO)$_{16}$}$_2$(μ_4-Tl)].[97] The Tl–Ru–Tl angle is close to linear at 165.67(2)°.



(96)

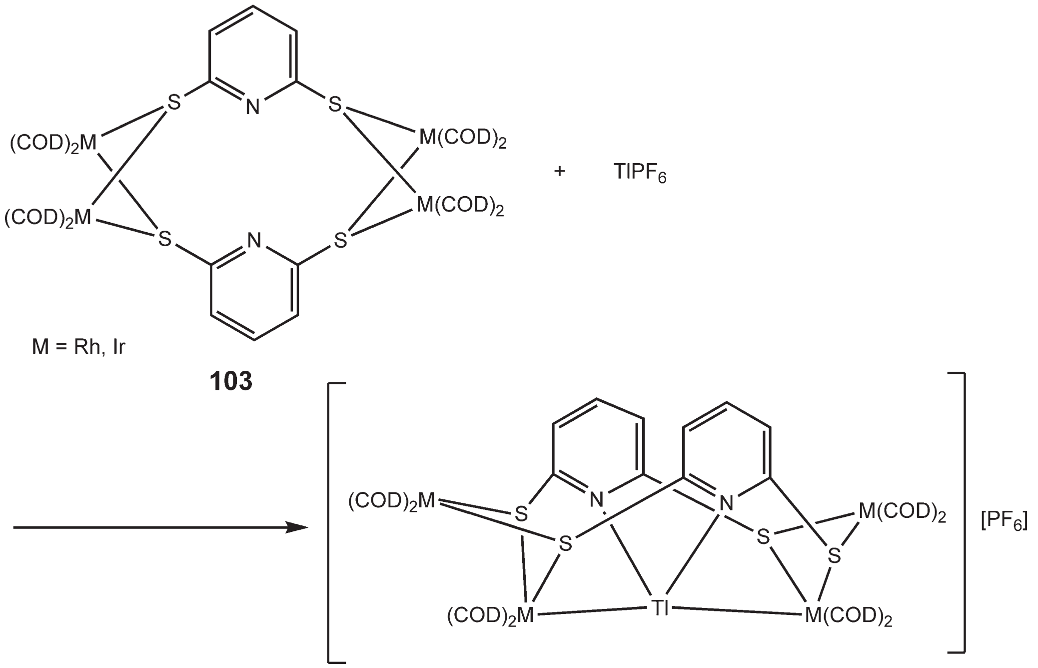
101



102

3.08.9.2 Thallium(I) Derivatives of Rhodium and Iridium Complexes

The assembly of two 2,6-pyridinedithiolate ligands with four $M(COD)_2^+$ (M = Rh, Ir) creates a macrocyclic complex **103** that reacts with $Tl[PF_6]$ to encapsulate the Tl^+ ion between the nitrogen atoms of the two pyridine units **104** and two of the M centers (Equation (97)).[98] The Rh–Tl distances are 276.86(9) and 277.06(9) pm.[98] Replacing the COD with stronger π-accepting ligands prevented the formation of the Tl^+ complexes.[98] The Rh–Tl–Th angle is 174.72(2)°. The thallium ion may be removed quantitatively by addition of LiCl to dichloromethane solutions of the complex. The ^{205}Tl chemical shift is observed at 2,926 ppm and is more in line with chemical shifts expected for Tl^{3+} than for Tl^+.

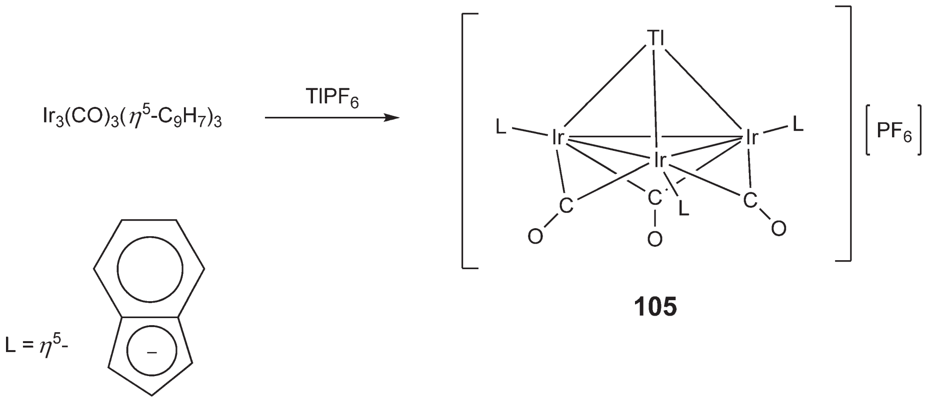


103

104

(97)

The trinuclear cluster $Ir_3(CO)_3(\eta^5\text{-}C_9H_7)_3$ adds a variety of electrophiles to the iridium triangle, and among these is $TlPF_6$ (Equation (98)).[99] The Ir–Ir distances in **105** are slightly longer than in the parent compound (271.18(9) vs. 267.2(6) pm), and the Tl–Ir distance (322.4(2) pm) is significantly longer than those observed in other molecules.[99]



105

(98)

3.08.9.3 Thallium(I) Derivatives of Nickel, Palladium, Platinum, and Gold Coordination Complexes

A wide variety of Ni, Pd, Pt, and Au coordination complexes will bind Tl^+, as seen in Table 14. Thallium(I) salts readily add to palladium, platinum, and gold centers in both mononuclear and cluster compounds; many of these compounds have been examined because of their luminescent properties which have been attributed to the presence of the transition metal–thallium bonds. These may be divided into two general classes: (i) complexes in which the transition metal is ligated primarily by chelating nitrogen- and/or phosphorus-based ligands, and (ii) aryl complexes of Pt and Au. The aryl compounds will be described in Section 3.08.9.3. Within the first class of compounds, there are two general structural types: complexes A in which two transition metals are held at an appropriate distance for Tl^+ bonding by a suitable bidentate spacer ligand, and complexes B in which the Tl^+ ion binds to a triangle of metal atoms as in the rhenium complex **99** or the iridium complex **105**. In some cases, a Tl^+ ion will bind to two triangles. Complexes of type A will be discussed first.

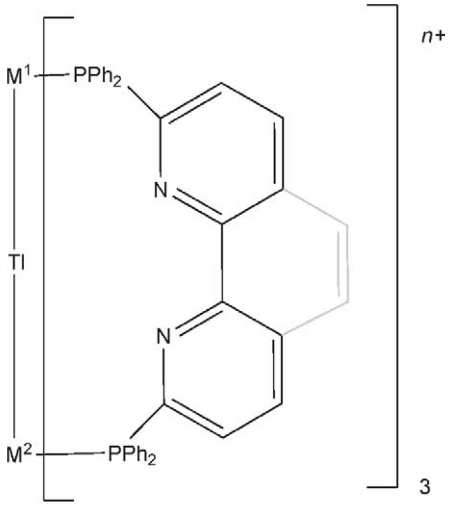
The combination of Pd(0), Pt(0), or Au^+ complexes with bis(diphenylphosphino)-substituted bipyridine or phenanthroline and $TlNO_3$ produced the Tl^+ encapsulated complexes **106**. The metal reagents used included $Pt(AsPh_3)_4$, $Pt(dba)_2$, $Pd_2(dba)_3$, and Au(THT)Cl.[100,102] The M–Tl–M angles are essentially linear, although the Pd–phenanthroline derivative shows the most distortion (160.62(3)°).[100] Related heterotrimetallic complexes were obtained when the Au(THT)Cl, TlO_2CMe, and either $Pt(dba)_2$ or $Pd_2(dba)_3$ were mixed in the presence of the substituted phenanthroline. The Pd and Pt compounds were isolated as the PF_6^- salts in 60–70% yields, and the Au_2 complex as a perchlorate salt.[101] The complexes containing Au show high energy π–π^* transitions with a broad low-energy band at about 400 nm. Excitation into the low-energy bands produced photoluminescence for the mixed Au–Pd and Au–Pt species, and an intense Stokes-shifted emission band for the Au_2 complex. This is in contrast to the Pd_2 and Pt_2 species, which showed no emission.

Partially encapsulated Tl^+ ions have been observed for the related doubly bridged compound **107**.[103] The transition metal fragment $[\{Me_2Pt\}_2(\mu\text{-}Ph_2PC_5H_3NPPh_2)_2]$ is first assembled and then treated with $TlClO_4$ to give the product in 60% yield. The Tl^+ ion was displaced by Cu^+ upon addition of $[Cu(MeCN)_4]ClO_4$ almost quantitatively.

The complexes $[\{Pt(DACH)(\mu\text{-}NHCO^tBu)_2\}_2In][ClO_4]_3$ (DACH = 1,2-diaminocyclohexane) and $[\{Pt(NH_3)_2(\mu\text{-}NHCO^tBu)_2\}_2In][ClO_4]_3$ (**108**)$^{3+}$ were prepared by addition of $PtL_2(\mu\text{-}NHCO^tBu)_2\cdot 2H_2O$ ($L = NH_3$ or $L_2 = DACH$) to $In(NO_3)_3\cdot 6H_2O$ in water. The products precipitated upon addition of $NaClO_4$. For the DACH derivative, the Pt–In–Pt angle is required to be 180° by crystallographically imposed symmetry, while that angle in the NH_3 compound is 174.81°.[110]

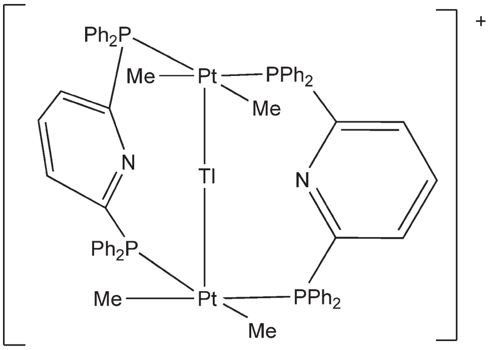
Table 14 Palladium, platinum, and gold coordination complexes that bind thallium

Compound	*M–T1 distance* (pm)	*References*
$[Pt_2(\mu\text{-}Ph_2P\text{-}phen\text{-}PPh_2)_3Tl][NO_3]$	279.07(9), 279.19(9)	100
$[Pt_2(\mu\text{-}Ph_2P\text{-}bipy\text{-}PPh_2)_3Tl][NO_3]$	279.53(2)	100
$[Pd_2(\mu\text{-}Ph_2P\text{-}phen\text{-}PPh_2)_3Tl][NO_3]$	279.14(6)	100
$[Pd_2(\mu\text{-}Ph_2P\text{-}bipy\text{-}PPh_2)_3Tl][NO_3]$	276.78(6)	100
$[AuPd(\mu\text{-}Ph_2P\text{-}bipy\text{-}PPh_2)_3Tl][PF_6]_2\cdot 3\ C_6H_6$		
Pd	279.6(14)	101
Au	281.1(9)	
$[AuPt(\mu\text{-}Ph_2P\text{-}phen\text{-}PPh_2)_3Tl][PF_6]_2$		
Pt	277.12 (6)	101
Au	290.00(6)	
$[Au_2(\mu\text{-}Ph_2P\text{-}phen\text{-}PPh_2)_3Tl][ClO_4]_3$	291.09(5), 291.71(5)	102
$[Tl\{Me_2Pt\}_2(\mu\text{-}Ph_2PC_5H_3NPPh_2)_2][ClO_4]$	279.61(7), 280.90(7)	103
$[Pt\{PPh_2(C_5H_4N)\}_3Tl][NO_3]$	288.88(5)	104
$[Pt\{PPh_2(C_5H_4N)\}_3Tl][MeCO_2]$	286.53(4)	104
$[Pt_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)(\mu_3\text{-}Tl)\{MeC({=}O)CHC({=}O)^tBu\}(H_2O)][PF_6]_2$	289.1(3)–294.7(1)	105
$[Pt_3(\mu\text{-}dppm)_3(\mu_3\text{-}CO)(\mu_3\text{-}Tl)\{MeC({=}O)CHC({=}O)^tBu\}(CF_3CO_2)][PF_6]$	286.7(1)–293.5(1)	105
$[\{(CO)_3(PEt_3)_3Pd_3\}_2(\mu_6\text{-}Tl)]$	282.0(1)–311.9(1)	106
$[\{(CO)_3(PEt_3)_3Pt_3\}_2(\mu_6\text{-}Tl)]$	288.1(1)–312.7(1)	106
$[\{Pt_3(CO)_3\}_2(\mu\text{-}dppp)_3(\mu_6\text{-}Tl)][PF_6]$	286.0(3)–299.2(3)	107,108
$[Tl_2Pd_{10}(CO)_9(PEt_3)_9][PF_6]_2$	284.31(7)–304.22(7)	109



M^1	M^2	n
Pd, Pt	Pd, Pt	1
Au	Pd, Pt	2
Au	Au	3

106



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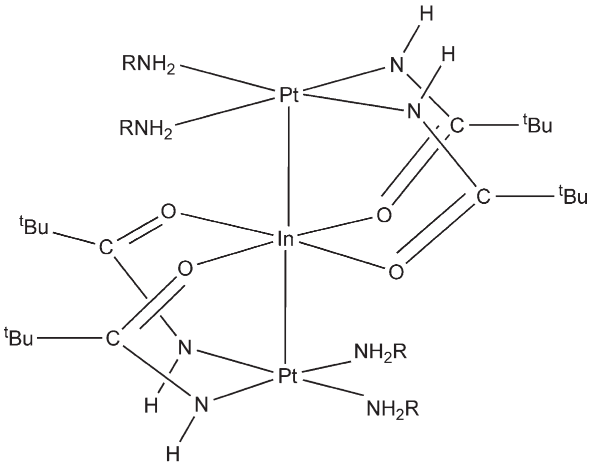


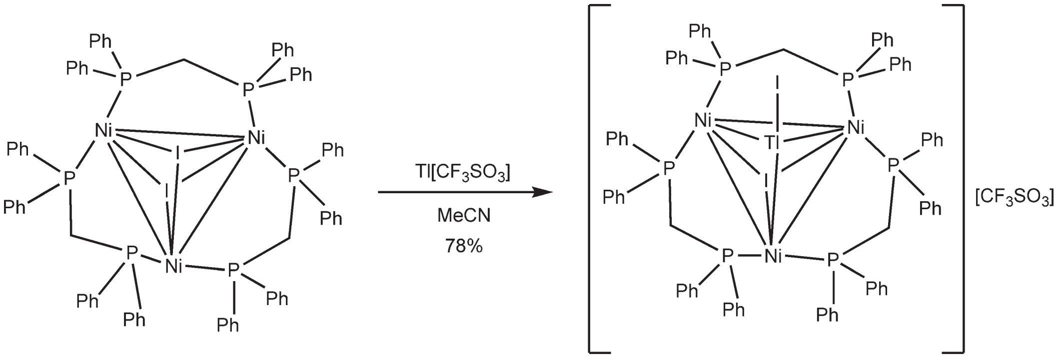
108

The compound Pt{PPh_2(Ar)}$_3$ (Ar = Ph, C_5H_4N) adds TlX (X = NO_3^-, $MeCO_2^-$) to produce [Pt{$PPh_2(C_5H_4N)$}$_3$-Tl]X.[104] The NMR data indicate that the Pt–Tl bond is maintained in solution, and the X-ray data for the two $PPh_2(C_5H_4N)$ complexes show relatively short Pt^0–Tl^+ bonds. For the acetate compound, the anion remains coordinated to thallium.

3.08.9.4 Complexes with Thallium(I) Capping a Triangular Array of Metal Atoms

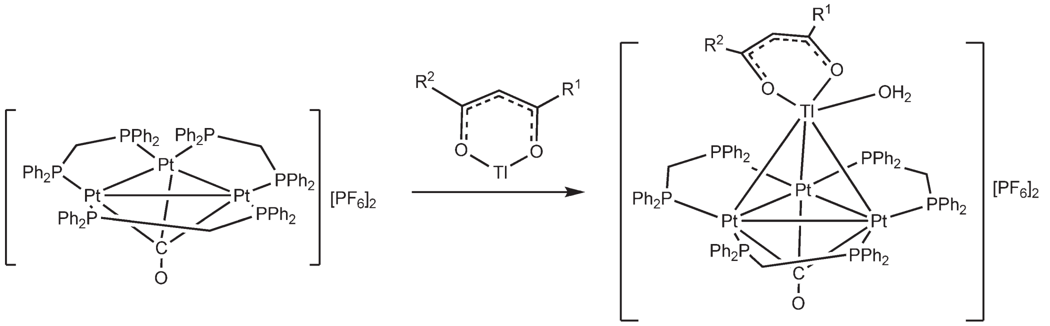
As with the Ir cluster complexes described above, binding to a triangular M_3 face is a very stable arrangement for a Tl^+ ion, and binding two such units to give trigonal prismatic or trigonal anti-prismatic configurations is also well precedented.

As indicated in Equation (99),[111] Tl^+ will insert into the Ni–I bonds of the neutral cluster compound $Ni_3(\mu$-dppm$)_3(\mu_3$-I$)_2$ **109** to give the cationic cluster compound $Ni_3(\mu$-dppm$)_3(\mu_3$-I$)(\mu_3$-TlI) **110**.[111] The Ni–Ni distances range from 249.1(3) to 252.0(3) pm and are comparable to those found in the starting compound $Ni_3(dppm)_3I_2$ and its oxidized form $[Ni_3(dppm)_3I_2]^+$ (average values: 249(2) and 251.8(13) pm, respectively), but are much longer than found in the electron-precise 48-electron cluster cation $[Ni_3(dppm)_3(\mu_3$-I$)(\mu_3$-CO$)]^+$. These longer distances were rationalized as a depopulation of an Ni_3 $d\pi$-bonding level resulting from the inertness of the Tl electron pair.



109 **110** (99)

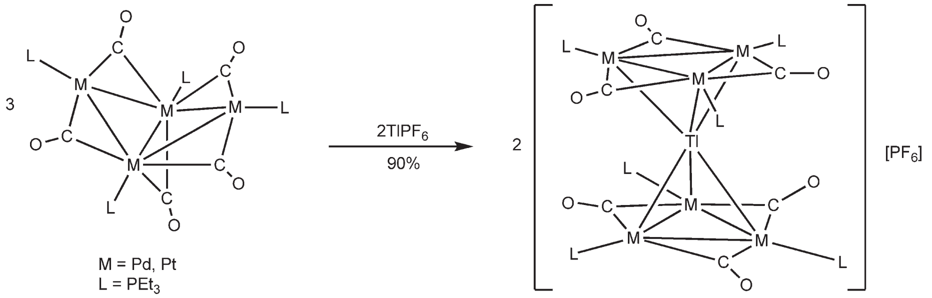
A series of new compounds was prepared as per Equation (100)[105] by the addition of thallium diketonates to $[Pt_3(\mu$-dppm$)_3(\mu_3$-CO$)][PF_6]_2$ **111**.[105] The yields of **112** ranged from 58% to 98%. The thallium ions are easily displaced by $X^- = Cl^-, Br^-, I^-, SnCl_3^-$ to produce $[Pt_3(\mu$-dppm$)_3(\mu_3$-X$)][PF_6]$. If trifluoroacetate is added instead, an equilibrium is established in which the trifluoroacetate ion displaces the water on the Tl^+ ion.



111 **112** (100)

$R^1 = R^2$ = Me, Et, CF_3, ^tBu
R^1 = Me, R^2 = CF_3, ^tBu, Ph

In $[\{(CO)_3(PEt_3)_3Pt_3\}_2(\mu_6$-Tl$)]$ **113** (Equation (101)),[106] the multinuclear NMR data support retention of the Pt_3TlPt_3 unit in solution. The Pd analog is not stable under N_2 and converts into the higher nuclearity complex $[Tl_2Pd_{12}(CO)_9(PEt_3)_9][PF_6]_2$,[106] whose cluster core geometry is shown in **114**. This molecule was also prepared by reaction of $TlPF_6$ with $Pd_{10}(CO)_{10}(PEt_3)_6$ and $Au(PPh_3)Cl$,[109] and the two thallium atoms were initially misassigned as gold atoms. It can also be prepared from $TlPF_6$ and $Pd_4(CO)_5(PEt_3)_4$ with or without the presence of $Au(SMe_2)Cl$. The cluster can be thought of as three Pd_5 trigonal bipyramids linked in a ring, alternating such that an apical Pd atom of one unit is an equatorial atom in the next **114**. This core has a threefold axis, and the thallium ions sit on the axis such that each Tl^+ is bonded to six Pd atoms **115**. The Tl–Pd distances range from 284.3 to 304.2 pm.



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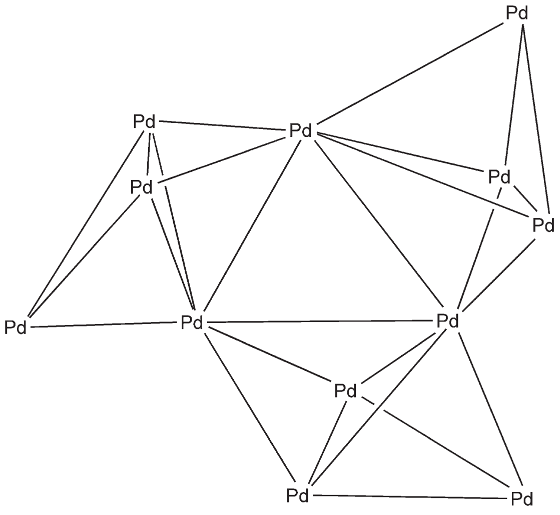
113



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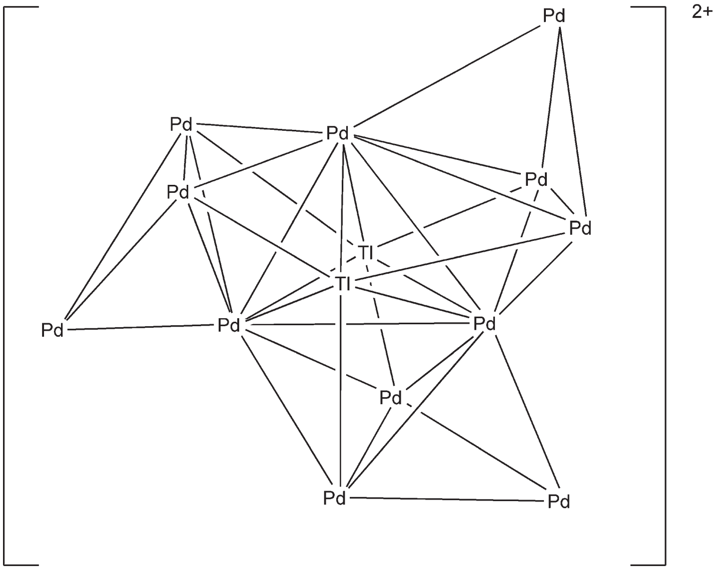

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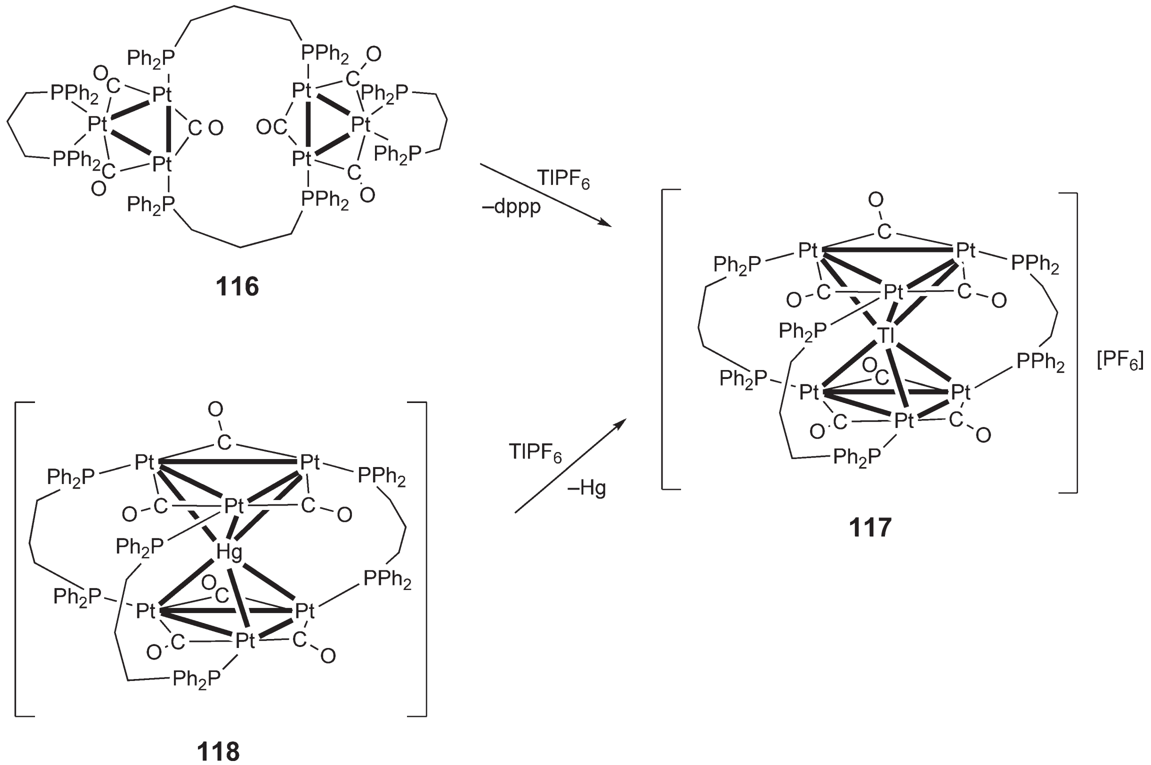

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117

118

Scheme 27

[{$Pt_3(\mu\text{-}CO)_3$}$_2(\mu\text{-dppp})_2(\eta^2\text{-dppp})_2$] **116** reacts with $TlPF_6$ to encapsulate the Tl^+ ion giving [{$Pt_3(\mu\text{-}CO)_3$}$_2(dppp)_3(\mu_6\text{-}Tl)$][$PF_6$] **117** as given in Scheme 27.[107,108] The Tl^+ ion will also displace Hg from the related Hg-encapsulated cluster **118**. The cluster has a geometry that is intermediate between trigonal prismatic and trigonal antiprismatic about the Tl^+ ion. The Pt–Tl distances are shorter by about 20 pm than those found in the cationic cluster $[Pt_3(CO)_3(PCy_3)_3(\mu_3\text{-}Tl)]^+$.

3.08.9.5 Thallium Adducts of Arylplatinum and -gold Complexes

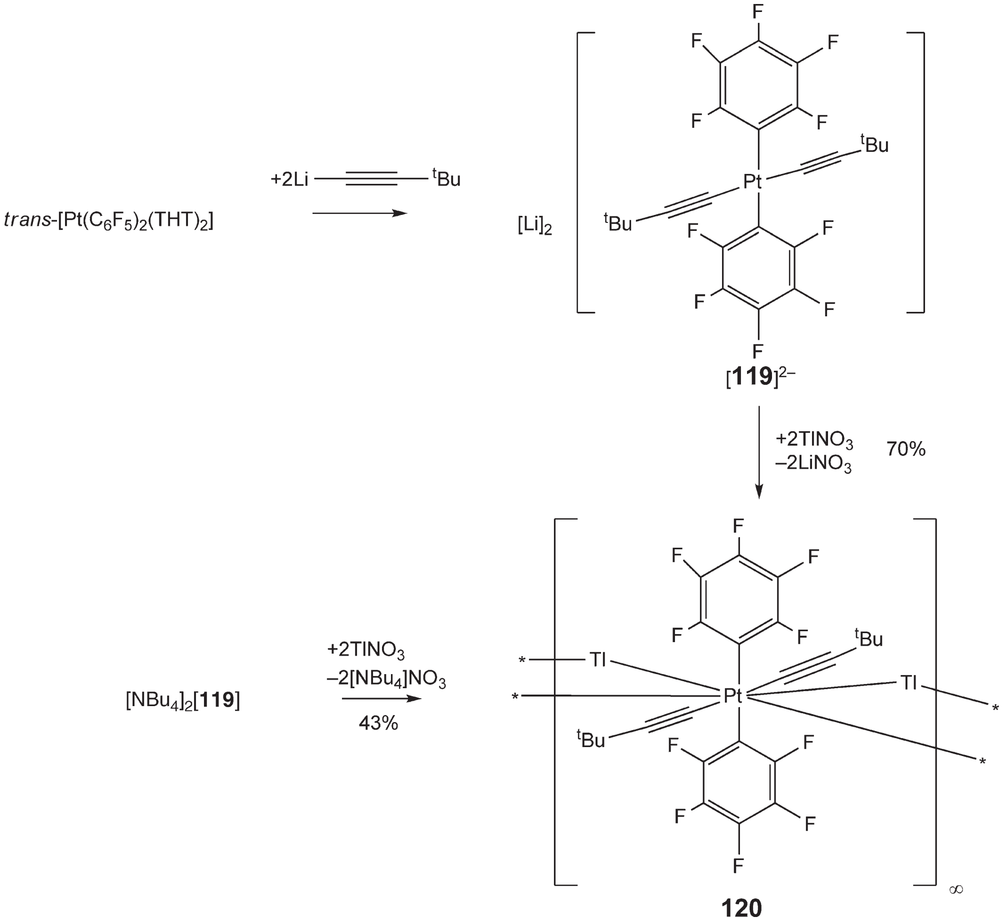
3.08.9.5.1 Platinum aryl complexes

Several arylplatinum complexes of Tl^+ have been reported (Table 15). The anionic *trans,trans*-diarylplatinum bis(acetylide) complex $[\mathbf{119}]^{2-}$, either as Li^+ or $NBu_4{}^+$ salts, reacts with $TlNO_3$ to produce a chain polymer **120**, in which successive Pt atoms are bridged to each other by two Tl^+ ions (Scheme 28).[112] The compound is an acetone solvate, and there also appear to be weak Tl···F interactions in the solid-state structure. Upon irradiation ($\lambda = 441$ nm), the complex exhibits an intense emission with a maximum at 678 nm. The luminescence is attributed to MLCT transitions.

A related compound in which the aryl groups and acetylide functions are both in *cis*-arrangement has been prepared in 84% yield starting with *cis*-$[(C_6F_5)_2Pt(THT)_2]$. Again, the compound is an acetone solvate, but the intermolecular

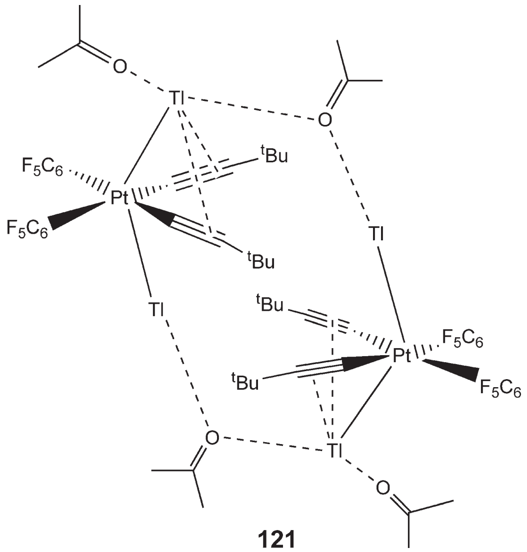
Table 15 Thallium(I) complexes of arylplatinum complexes

Compound	*M–Tl distance* (pm)	*References*
trans,trans,trans-$[Tl_2Pt(C_6F_5)_2(C_2{}^tBu)_2(acetone)_2]_n$	313.5(1), 378.5(1)	112
trans,cis,cis-$[Tl_2Pt(C_6F_5)_2(C_2{}^tBu)_2(acetone)_2]_2$	299.21(5), 302.74(6)	113
cis-$[(C_6F_5)_2Pt(PPh_3)(\mu\text{-}MeCO_2)Tl]$	299.4(1)	114
$[(C_6F_5)_3Pt(\mu\text{-}O_2CMe)Tl]_2$	288.4(1)	114
$[NBu_4]_2[Tl\{Pt(C_6F_5)_4\}_2]$	269.8(1), 270.8(1)	115



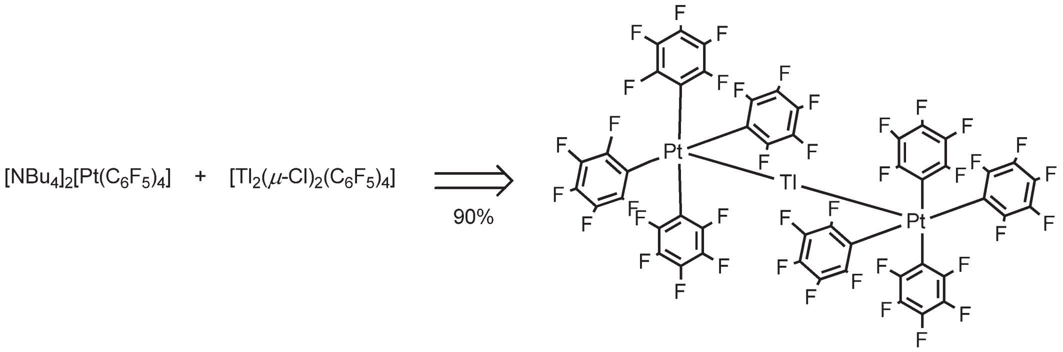
Scheme 28

interactions produce dimeric units rather than a polymer in the solid state **121**.[113] This complex also shows weak Tl···F interactions. Adding 1 equiv. of LiCl to **121** causes the precipitation of TlCl and formation of the mixed salt *cis*-$LiTlPt(C_6F_5)_2(C_2{}^tBu)_2$, but that compound has not yet been structurally characterized. Both **121** and this mixed species exhibit intense yellow luminescence.



121

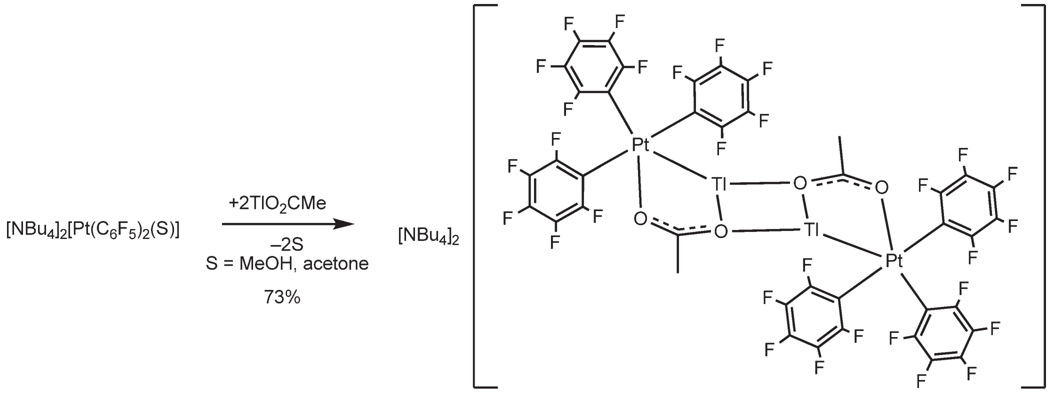
The reaction in Equation (102)[115] produces a paramagnetic compound in which a Tl^{2+} ion bridges between two $[Pt(C_6F_5)_4]^{2-}$ groups (Structure **122**).[115] The Pt–Tl–Pt angle is 179(1)°. The Pt–Tl distances are considerably shorter than those in the related Tl^+ Pt/C_6F_5 complexes mentioned above.



(102)

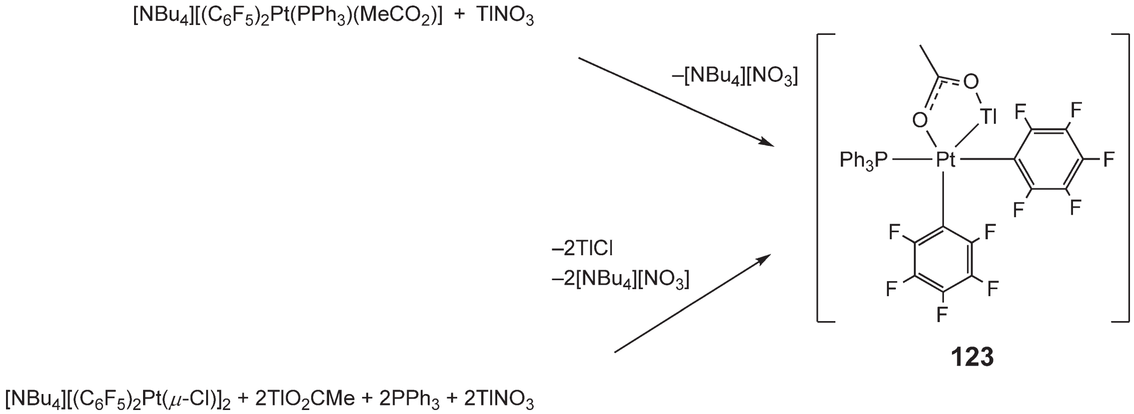
122

Two additional Tl–Pt–C_6F_5 complexes have been prepared (Scheme 29[114] and Equation (103)).[114] These are *cis*-$[(C_6F_5)_2Pt(PPh_3)(\mu\text{-}MeCO_2)Tl]$ **123** and $[(C_6F_5)_3Pt(\mu\text{-}O_2CMe)Tl]_2$ **124**, the latter having the shortest reported Tl^+–Pt^{2+} bond.[114] As with the other compounds in this class, these are strongly luminescent and the luminescence is attributable to the presence of the Pt–Tl bonds.



(103)

124

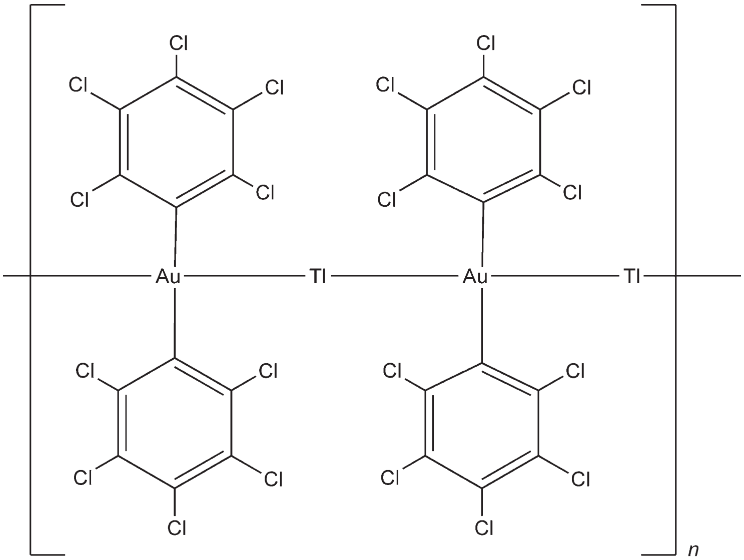


123

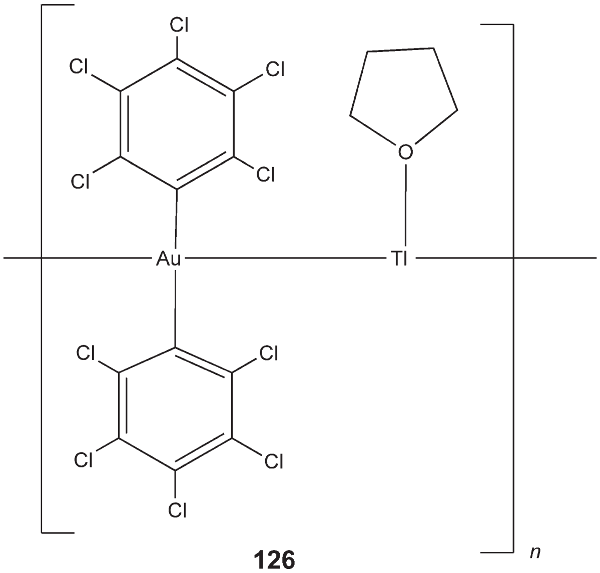
Scheme 29

3.08.9.5.2 Gold aryl complexes

A number of C_6F_5 and C_6Cl_5 gold complexes have been treated with thallium salts to produce Tl–Au bonded complexes which are luminescent (Table 16).[116–123] The luminescent properties of gold–heteroatom compounds have been recently reviewed.[124] These compounds are generally made by adding an anionic arylgold complex to a suitable thallium salt, usually in the presence of a donor ligand, which may also be the solvent. In the absence of added ligands, the reaction of $[NBu_4][Au(C_6Cl_5)_2]$ with $TlPF_6$ leads to a one-dimensional polymer of linear chains with alternating Tl^+ and $Au(C_6Cl_5)_2^-$ ions **125**.[121,123] The solid-state structure exhibits large holes, and this may be related to the change of color the solid undergoes upon exposure to the vapor of a number of organic molecules (THF, THT, 2-fluoropyridine, pyridine, acetone, MeCN, Et_3N, acetylacetone).[121,123] This color change is reversible upon heating the solid to ca. 100 °C. As detailed below, the addition of donor molecules in solution leads to complexes in which the donors coordinate to the thallium atoms. In one case, crystals of an adduct were obtained after exposure of solid **125** to an organic vapor. This resulted in the partially solvated complex $[\{Tl(THF)_{0.5}\}\{Au(C_6Cl_5)_2\}]_n$, **126**.[122] Interestingly, the other crystalline adducts do not lose their Tl-bound organic ligands upon exposure to vacuum.



125

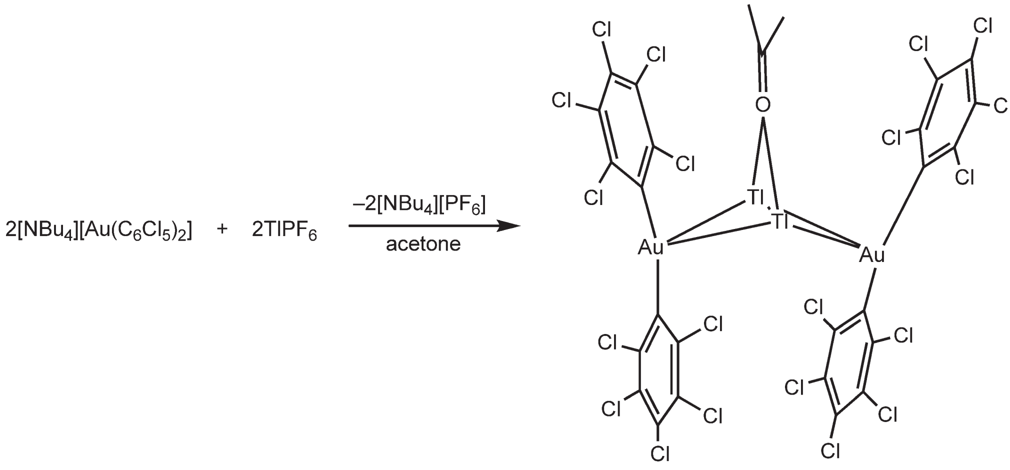


126

Table 16 Thallium adducts with arylgold complexes

Compound	*E–M distance* (pm)	*References*
$[\mathrm{TlAu(C_6Cl_5)_2\}_2]_\infty}$	297.26(5), 304.44(5)	121
$[\mathrm{Tl(OPPh_3\}_2Au(C_6F_5)_2]_\infty}$	303.58(8), 308.62(8)	116
$\mathrm{(C_6Cl_5)_2Au_2Tl_2(OCMe_2)}$	303.3(6)–318.8(6)	117
$\mathrm{[Au(C_6F_5)_2]_2[Tl(4,4'\text{-}bipyridine)]_2}$	301.61(2)	118
$\mathrm{[Au(C_6F_5)_2]_2[Tl(L)][Tl(L)_{1/2}(THF)]}$ L = 4,4′-bipyridine	303.23(4)–305.40(4)	118
$\mathrm{[AuTl(\eta^6\text{-}C_7H_8)(C_6Cl_5)_2]_2(\mu\text{-}dioxane)}$	289.35(3)	120
$\mathrm{[Au(C_6Cl_5)_2]_2[Tl(OPPh_3)][Tl(OPPh_3)(THF)]}$	305.29(3)–332.05(3)	119
$\mathrm{[Au(C_6Cl_5)_2]_2[Tl(OPPh_3)][Tl(OPPh_3)(acetone)]}$	309.37(3)–327.05(4)	119
$\mathrm{[Tl\{Au(PhCH_2N_2C_3H_2)_3\}_2][PF_6]}$	297.11(7)–304.33(7)	125

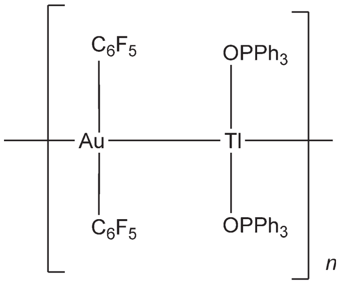
The related reaction shown in Equation (104)[117] leads to a butterfly arrangement with two thallium ions bridging between two gold atoms, **127**. Here, the Tl–Tl distance is 360.27 pm and is thought to contribute significantly to the physical properties of the complex. The compound shows solvent-dependent luminescent behavior in solution as well as in the solid state.



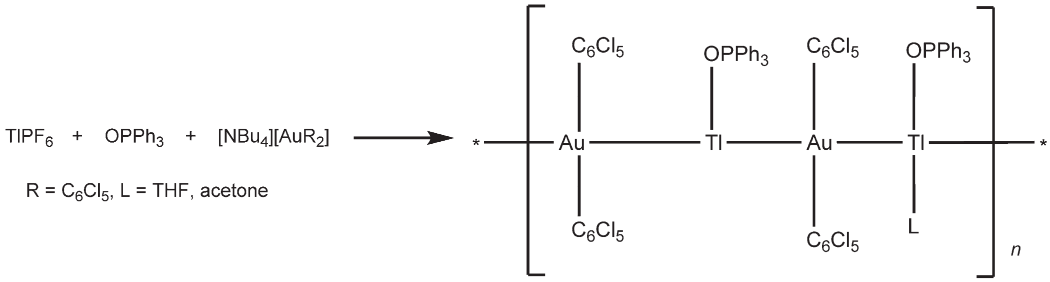
127

(104)

Addition of $\mathrm{Li[Au(C_6F_5)_2]}$ to $\mathrm{TlNO_3}$ in the presence of $\mathrm{OPPh_3}$ in acetone at −78 °C produces the chain polymer **128** in about 40% yield.[116] The complex $\mathrm{[NBu_4][Au(C_6F_5)_2]}$ could also be used for this synthesis.[119] The gold atoms are square planar and the thallium atoms are trigonal bipyramidal with a vacant coordination site. Using the $\mathrm{C_6Cl_5}$ gold complex instead, an $\mathrm{OPPh_3}$ adduct is also formed (Equation (105)),[119] but the $\mathrm{Tl^+}$ ions alternate between being three- and four-coordinate **129**, with only one $\mathrm{OPPh_3}$ ligand attached to each.



128

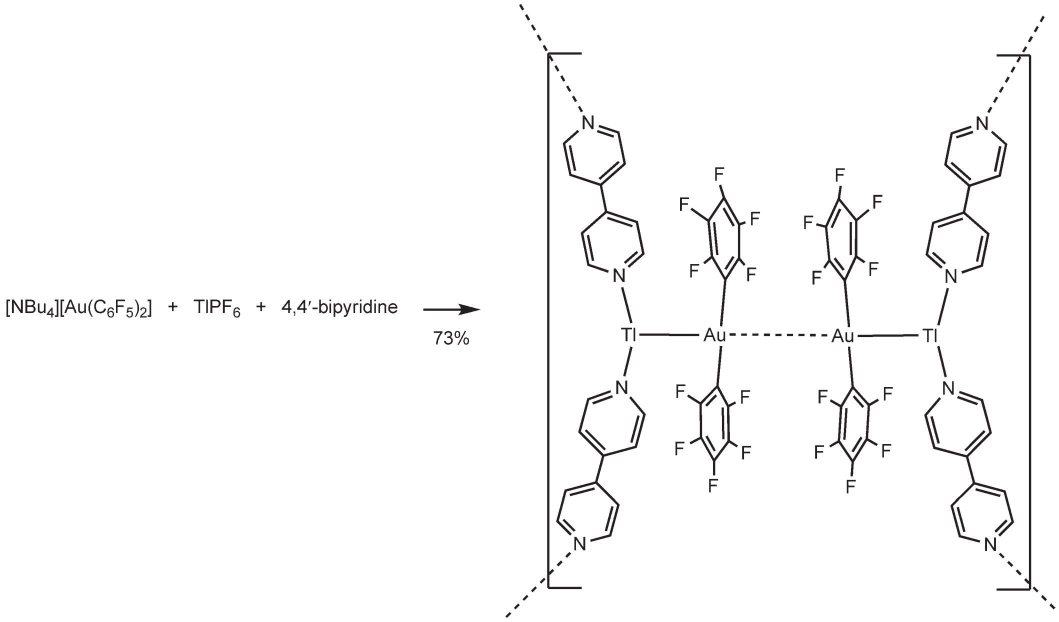


(105)

129

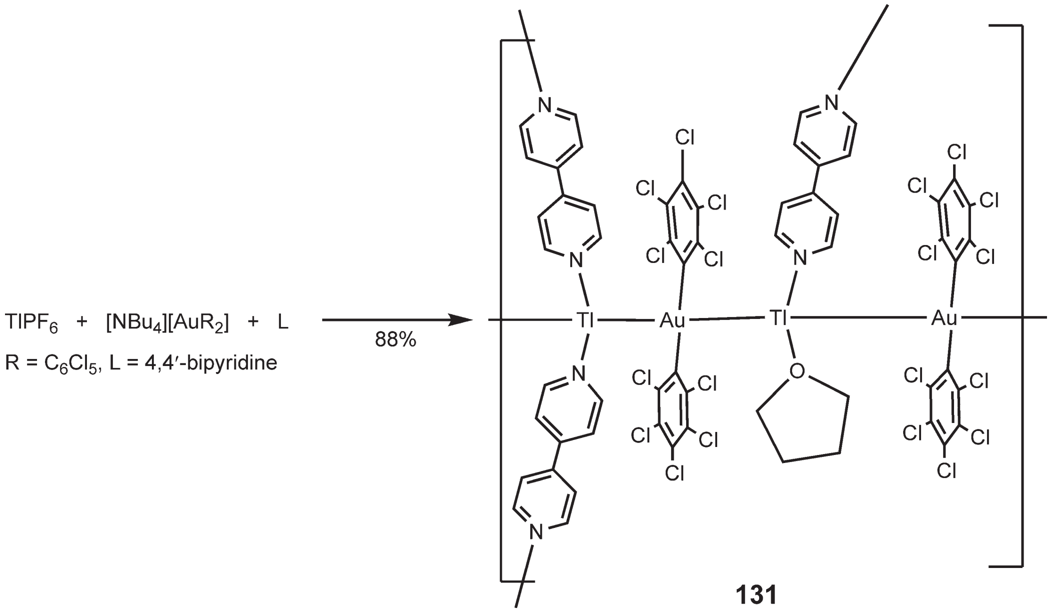
The difference in structures adopted upon switching between C_6F_5 and C_6Cl_5 is observed for other ligand sets as well. Employing 4,4′-bipyridine in Equation (106)[118,122] with the C_6F_5 gold reagent, **130** is obtained. The structure of $[Au(C_6F_5)_2][Tl(4,4'\text{-bipyridine})]_2$ is complex in the solid state, showing Au–Au interactions. Each 4,4′-bipyridine ligand is bonded to two thallium atoms, so that the overall structure is polymeric through the bipyridine ligands, with no Tl–Tl interactions. The NMR data suggest that the complex exists as its ionic components in solution. For the C_6Cl_5 compound (Equation (107)), the Au and Tl atoms alternate in a one-dimensional polymeric chain **131**, with links between the chains formed via coordination of both ends of the 4,4-bipyridine ligands.[118,122]

When dioxane is added to $[Au(C_6Cl_5)_2Tl]_\infty$ (Equation (108)),[120] a simple dimer results in which the Au–Tl groups are connected via a dioxane bridge between the two thallium atoms **132**.[120] The thallium atom is coordinated in a π-fashion to the toluene which served as the solvent of the reaction. The Tl(I) ion does not exhibit a stereochemically active lone pair, and the blue luminescence was attributed to an Au→Tl charge transfer transition.



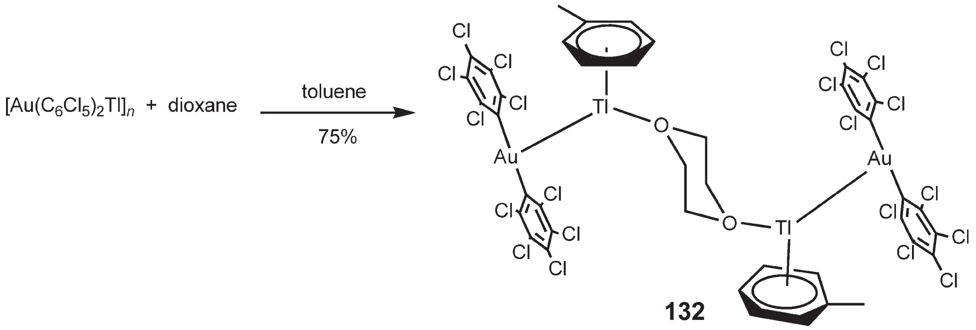
(106)

130



131

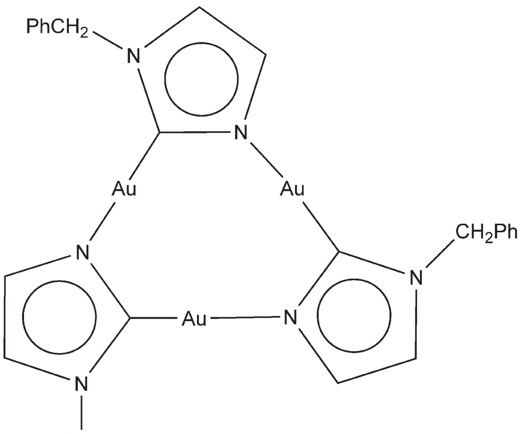
(107)



132

(108)

In addition to these arylgold complexes, related cyclic trinuclear gold coordination compounds 133 will also bind thallium. Two of these ring structures will sandwich a Tl^+ ion upon addition of $TlPF_6$ in a fashion similar to triangular Pt_3 complexes (cf. compounds 113 and 117). The thallium-coordination geometry is a distorted trigonal prism. For this compound, the luminescence observed is thermochromic with a blue emission at ambient temperature and a green emission at 77 K. The latter emission also changes with the wavelength of irradiation, being green upon irradiation by 420 nm light and yellow when using 475 nm radiation.



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3.09
Oligosilanes

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3.09.1 Introduction

3.09.1.1 Advances

Even after more than 100 years of history, organosilicon chemistry is arguably still one of the most significant and diverse research areas of chemistry. The last ten years have witnessed tremendous advances and breakthroughs. Significant new applications in organic synthesis and medicinal chemistry have been developed. For instance, environmentally benign organosilanes have been utilized in cross-coupling reactions as genuine alternatives to traditional Suzuki and Stille cross-coupling reactions based on boron and tin reagents. Functionalized organosilanes have been used for the stereoselective introduction of (masked) hydroxyl groups. Biologically active organosilanes, including unnatural amino acids, protease inhibitors associated with diseases, such as hypertension and HIV, and fragrances have been developed. The kinetic stabilization of reactive species including low-coordinated silyl cations and radicals, (conjugated) disilenes and disilynes has been achieved for the first time. Novel routes for the preparation of polysilanols including incompletely condensed silsesquioxanes have been found, and applications thereof for the synthesis of catalytically active metallasiloxanes have been developed. Hydrogen-rich silanes and silazanes have been utilized as molecular volatile precursors for Si/C, Si/C/N, and Si/C ceramic materials. Silyl anions have been employed for the preparation of well-defined open-chain, branched, dendritic and cyclic oligosilanes. Hypervalent silicon complexes have been instrumental in understanding fundamental aspects of chemistry often in comparison with organic chemistry.

3.09.1.2 Review Literature

The vigorous research activity is reflected in a number of monographs, books, and reviews. In two volumes of *The Chemistry of Organic Silicon Compounds* edited by Zvi Rappoport and Yitzhak Apeloig and published in 1998 and 2001, a large number of subjects were covered comprehensively.[1,2] A monograph *Silicon in Organic, Organometallic and Polymer Chemistry* by Michael A. Brook covers all facets of silicon chemistry including references up to the year 2000.[3] An edited book was published in 1996 entitled *Tailor-made Silicon-Oxygen Compounds – From Molecules to Materials* by Robert Corriu and Peter Jutzi.[4] An edited book *Silicon Chemistry (From the Atom to Extended Systems)* by Peter Jutzi and Ulrich Schubert summarizes the research activities of several groups supported by the German science-funding body *Deutsche Forschungsgemeinschaft* (DFG) under the program entitled *Specific Phenomena in Silicon Chemistry*.[5] The proceedings of the *Munich Silicon Days* held in 1994, 1996, and 1998 and its successor, the *European Silicon Days*, held in 2001 and 2003, were published in four volumes of *Organosilicon Chemistry – From Molecules to Materials*, giving a decisive overview of up-to-the-minute developments.[6–11] Several reviews have been published as journal papers, and these will be referred to at appropriate points in this chapter.

3.09.2 Silicon–Carbon Compounds

3.09.2.1 Fundamental Reactions and Precursor Chemistry

More than 60 years after its simultaneous discovery by Rochow and Müller, the direct reaction of copper-activated silicon with alkyl chlorides is arguably still the most important industrial process for the preparation of basic organosilanes. An inspiring historic account highlighting the significance of this seminal work has been given by Seyferth.[12] A comprehensive review on the subject has been written by Jung and Yoo.[13] The most recent work associated with the direct process is concerned with the role of metallic promoters, such as Zn and Cd, as well as mechanistic aspects.[14]

Precursor chemistry, the development of synthetic routes leading to simple organosilanes with various functional groups, continues to attract considerable attention. Schmidbaur *et al.* have prepared hydrogen-rich silylethenes, silyl acetylenes, silyl arenes, and silyl pyridines, which are of great interest as precursors for the chemical vapor deposition (CVD) of silicon carbide thin films and for the preparation of polysilanes by dehydropolymerization reactions.[15–26] Jung *et al.* have extensively studied Friedel–Crafts type alkylation reactions of benzene derivatives and ferrocene with functionalized organochlorosilanes and recently reviewed the subject.[27] The same group has also investigated Lewis acid-catalyzed rearrangement reactions of vinyl- and allylsilanes,[28–31] and extended the scope of Benkeser-type dehydrochlorinative coupling reactions to non-activated alkyl halides.[32–34] Similar dichlorosilylene transfer reactions have been employed by other groups for the preparation of functionalized chlorosilanes.[35] The synthesis of multifunctional (chloromethyl)silanes has been extended,[36] and new routes for the preparation of (lithiomethyl)silanes[37] and (aminomethyl)silanes[38–40] have been reported. (Carbonylmethyl)silanes (α-silyl carbonyl compounds) have been prepared by the rhodium-catalyzed carbenoid insertion of α-diazo carbonyl compounds into the Si–H bonds of triorganosilanes, R_3SiH (R = alkyl, aryl).[41–45] The hydrosilylation reaction, first reported more than 50 years ago by Sommer *et al.*, has been comprehensively covered in a monograph[46] and more recent reviews by Marciniec[47–49] and others[50–53] reporting on practical as well as mechanistic aspects of the addition of silicon hydrides to unsaturated hydrocarbons. Besides the traditional radical initiators and late transition metals, new catalytic systems, such as Lewis acids,[54–56] lanthanoid complexes,[57–70] and immobilized catalysts,[71,72] have been developed. Mechanistic studies and the influence of the reaction pathway on regio- and stereoselectivity have been studied.[73–124] For the traditional hydrosilylation reactions using H_2PtCl_6 as catalyst, the Chalk–Harrod mechanism has been widely accepted. Consistent with this mechanism, the hydrosilylation occurs with a stereochemistry that is complementary to those of radical hydroboration reactions. Recently, Glaser and Tilley provided evidence for a new type of hydrosilylation mechanism in which a ruthenium silylene complex plays a major role.[125,126] In these reactions, the stereochemical outcome is analogous to those of radical hydroboration reactions. Brookhart *et al.* and Widenhoefer have also provided strong evidence to suggest that a different mechanism is operative for electrophilic catalysts, which promote the C–Si bond formation prior to coupling of the C–H bond.[127,128] Enantioselective hydrosilylation of olefins can be achieved when chiral transition metals are used.[129–139] The most powerful catalysts are Pd complexes with axially chiral ligands derived from 1,1′-binaphthol (BINOL) delivering enantioselectivities of more than 99% ee. Recently, Oestreich and Rendler have reported the enantioselective hydrosilyation of a Si-centered H-silane with an achiral catalyst.[140]

3.09.2.2 Optically Active Organosilanes

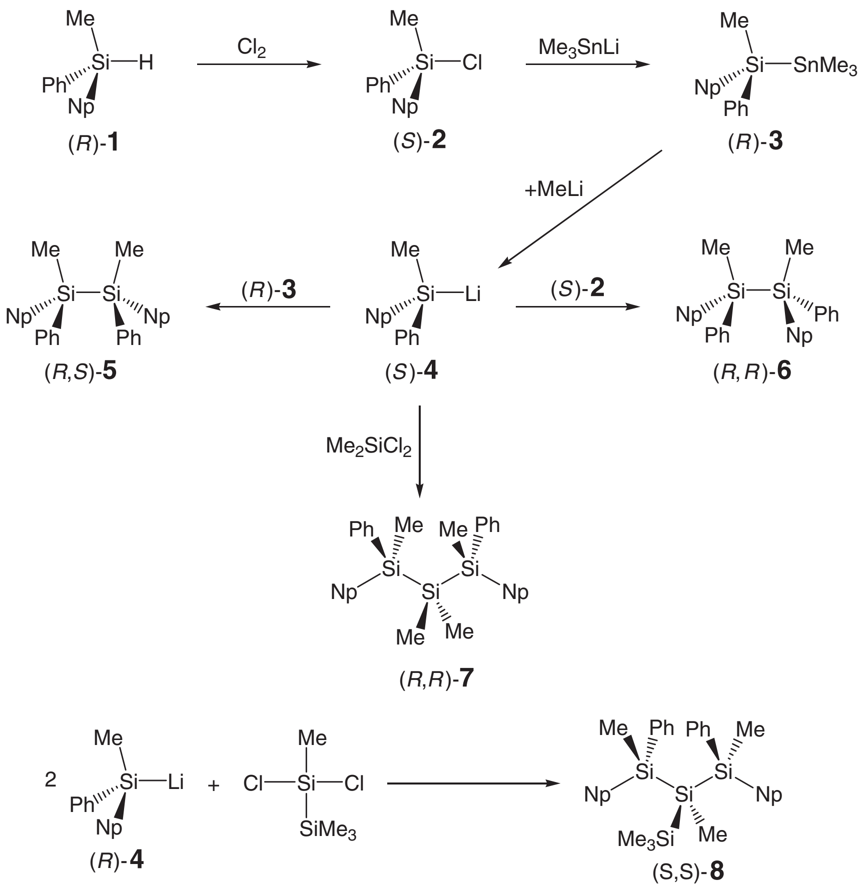
Corriu summarized seminal work on chiral silicon chemistry in 1982.[141] Applications of carbon- and silicon-centered optically active organosilanes in organic synthesis are numerous, and have been comprehensively covered by Chan and Wang in 1992 and Fleming *et al.* in 1997.[142,143] Many of these applications are based on a small number of well-defined chiral organosilanes, such as the crystalline (1-naphthyl)methylphenylsilane NpMePhSiH **1**, which were originally prepared by Sommer *et al.* in a racemic form and subsequently resolved into the enantiomers.[144–146] Kawakami *et al.* have prepared the enantiomerically pure disilanes **5** and **6** as well as the trisilanes **7** and **8** starting from a configurationally stable chlorosilane **2** and the stannasilane **3**, which has been converted into the lithium silanide **4** and reacted with some chlorosilanes, such as Me_2SiCl_2 and $(Me_3Si)MeSiCl_2$ (Scheme 1).[147–152]

Recently, Schaumann *et al.*[153,154] and Bienz *et al.*[155,156] have developed dependable routes for the resolution of racemic functionalized organosilanes with Si-centered chirality using chiral auxiliaries, such as binaphthol (BINOL), 2-aminobutanol, and phenylethane-1,2-diol (Scheme 2). For instance, the successive reaction of BINOL with butyllithium and the chiral triorganochlorosilanes RPhMeSiCl (R = *i*-Pr, *n*-Bu, *t*-Bu) affords the BINOL monosilyl ethers **9–11**, which can be resolved into the pure enantiomers (*S*)-**9–11** and (*R*)-**9–11**, respectively. Reduction with $LiAlH_4$ produces the enantiomerically pure triorgano-H-silanes (*S*)- and (*R*)-RPhMeSiH (**12**, R = *i*-Pr; **13**, *n*-Bu; **14**, *t*-Bu), respectively (Scheme 2). Tamao *et al.* have used chiral amines to prepare optically active organosilanes.[157]

Kawakami *et al.* have prepared optically active bifunctional 1,3-dimethyl-1,3-diphenyldisiloxanes.[158,159] Strohmann *et al.* have prepared enantiomerically enriched Si-centered silyllithium compounds, which react stereospecifically with triorganochlorosilanes.[160–162] In solution, slow racemization of the silyllithium compounds takes place, which, however, can be circumvented by transmetallation with $MgBr_2$. Oestreich *et al.* prepared new Si-centered cyclic silanes adopting the strategies developed by Corriu and Sommer.[163] Bienz *et al.* have developed enantioselective routes for the preparation of C-centered chiral allenylsilanes.[156,164–166]

3.09.2.3 Biologically Active Organosilanes

Efforts in bioorganosilicon chemistry are motivated by the prospects of finding biologically active organosilicon drugs, more potent agrochemicals, active and selective biocatalysts, and even sophisticated fragrances.[167] Organosilanes are inherently unnatural, but not intrinsically toxic. The fact that silicon is the element that resembles carbon the most, and the thermodynamic and kinetic stability of the Si–C bond, make organosilanes ideal candidates for bioisosteristic replacements. In recent years, a number of unnatural α-amino acids having silicon atoms in α-, β-, and γ-position have been reported. Starting from α-trialkylsilyl-α-diazoacetates **15** and **16**, Bolm and Drauz *et al.* have prepared (protected) racemic α-trialkylsilyl-substituted α-amino acids **17** and **18**, which have been resolved by chiral chromatography (Scheme 3).[168] The silylated diazoacetates **15** and **16** are available from the reaction of the parent diazoacetates with silyl triflates in the presence of a base.[169–171]

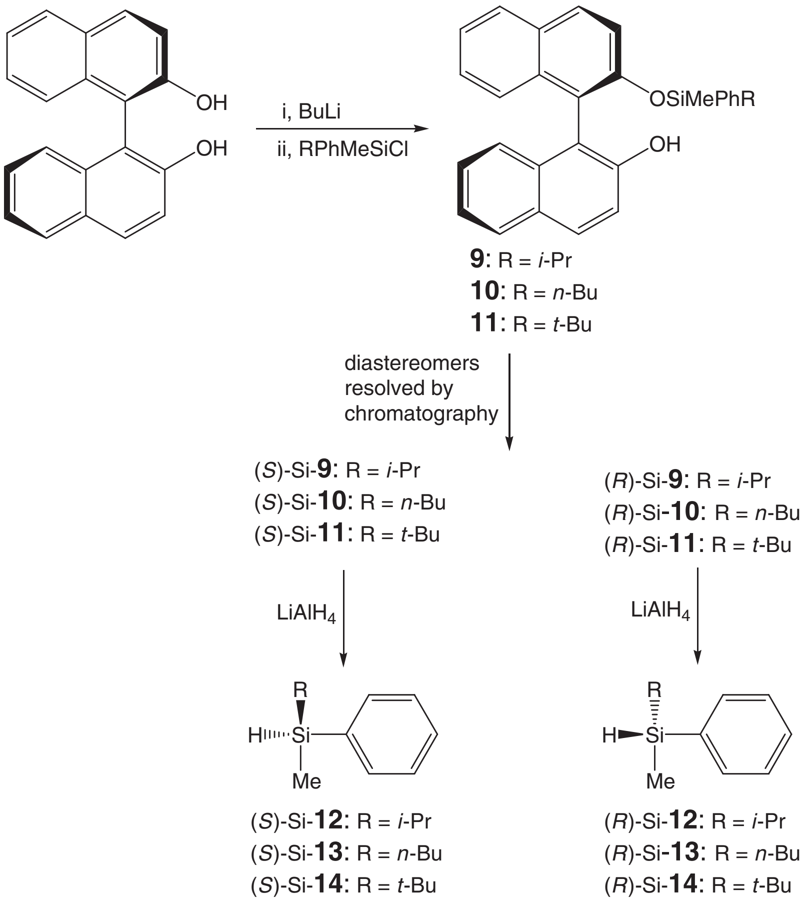


Scheme 1

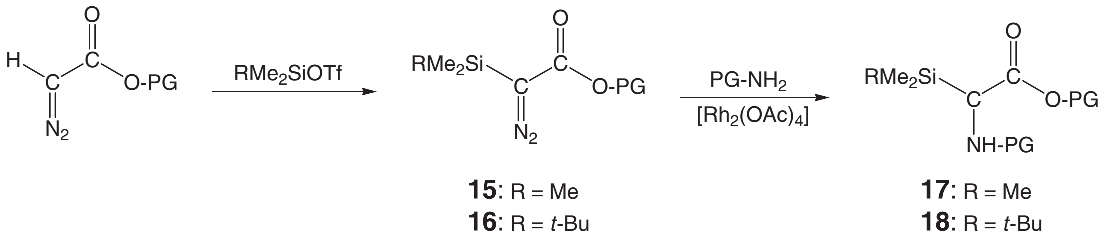
The amino acid **17** can be regarded as a derivative of *tert*-leucine, one of the most important unnatural amino acids.[172] A dipeptide has been successfully prepared from **18**.[168] In a similar fashion, α-trialkylsilyl-substituted α-hydroxy acids have been prepared.[173] The stability of α-trialkylsilyl-substituted α-amino acids has been investigated.[174] The stereoselective synthesis of trimethylsilylalanine **19**, the most simple β-trialkylsilyl-substituted α-amino acid, was achieved in 1993 by Weidmann, who applied Schöllkopf's procedure,[175,176] using the bis-lactim ether of a cyclic dipeptide containing D-valine (Scheme 4).[177] Tacke *et al.* and Cavelier *et al.* have adopted a similar route for the preparation of other β-trialkylsilyl substituted α-amino acids, including $RMe_2SiCH_2C(NH)_2COOH$ (**20**, R = Ph; **21**, R = vinyl; **22**, R = CH_2Cl, **23**, R = CH_2SH; **24**, R = CH_2NH_2)[178–182] and 3-dimethylsilylproline **25**,[183,184] which have found application as surrogates of tyrosine and proline and as GnRH anatagonists for controlled ovarian stimulation during assisted reproduction, respectively.

Sibi *et al.* have disclosed an alternative route to prepare protected enantiomerically pure β-trialkylsilyl-substituted α-amino acids, $RPh_2SiCH_2C(NH)_2COOH$ (**26**, R = Me; **27**, R = Ph; **28**, R = *t*-Bu), using an electrophilic alaninol synthon and triorganosilyl cuprates.[185] A number of racemic β-trialkylsilyl-substituted α-amino acids have also been prepared by other routes[186] and subsequently resolved into pure enantiomers by enzymatic technologies.[187,188] Oligopeptides incorporating β-trialkylsilyl-substituted α-amino acids have been reported.[182,184,189] Tacke *et al.* have further reported the synthesis of the β-dialkylhydroxysilyl-substituted α-amino acid $HOMe_2SiCH_2C(NH)_2COOH$ **29** that could be grafted on a silica surface by an HCl-induced phenyl group cleavage of **20** (Figure 1).[179] Amino acids functionalized by silanol groups show great promise for new hybrid materials which may find applications in the healthcare industry.[190]

Bienz *et al.* have prepared functionalized α-amino acids containing Si that are derivatives of serine and methionine.[191] Saturated and unsaturated γ-trialkylsilyl-substituted α-amino acid derivatives **30–35** have been prepared stereoselectively by Reginato *et al.*[192,193] The synthetic approach involves a silylcupration of chiral-protected 4-ethynlyloxazolidine (Scheme 5).

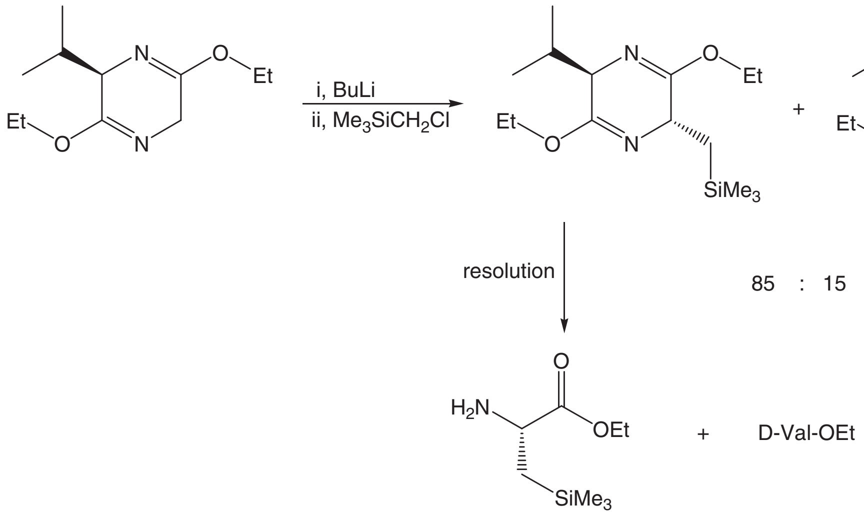


Scheme 2



Scheme 3

The synthesis of an optically active δ-silylvinyl α-amino acid[194] and a sila-substituted α-amino acid has been disclosed.[195] Besides amino acids containing Si atoms, the bioisosterism of other pharmacologically important silicon substances that are associated with hypertension, HIV, and cancer has been investigated. Sieburth *et al.* have studied a silicon analog **37** of the potent ACE inhibitor **36**, which has found applications as a medicine to treat high blood pressure (hypertension) and congestive heart failure (Scheme 6).[196–201] Although the biological mechanism is not understood in detail, the disilanol moiety of **37** is believed to form stronger hydrogen bonds with the receptor site than the hydrated ketone group of **36**. Sieburth *et al.* have also developed a silicon analog **39** of an HIV-1 protease inhibitor **38** that functions in a similar way. Tacke *et al.* have prepared a disilicon analog **41** of bexarotene **40**, an RXR-selective retinoid, which is used to treat skin lesions of cutaneous T-cell lymphoma (CTCL) in patients who have not responded to or not tolerated other therapies.[202] The exact mechanism of bexarotene **40** interactions is unknown, but



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Scheme 4

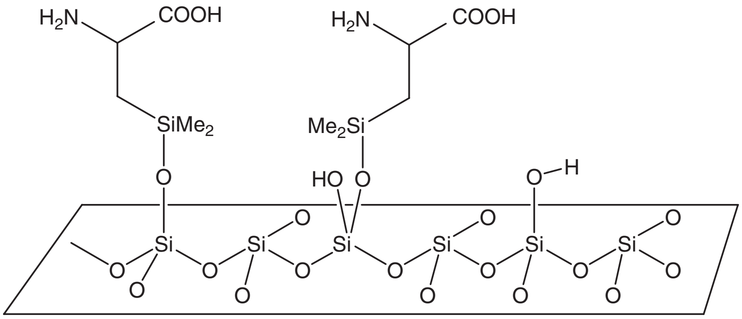
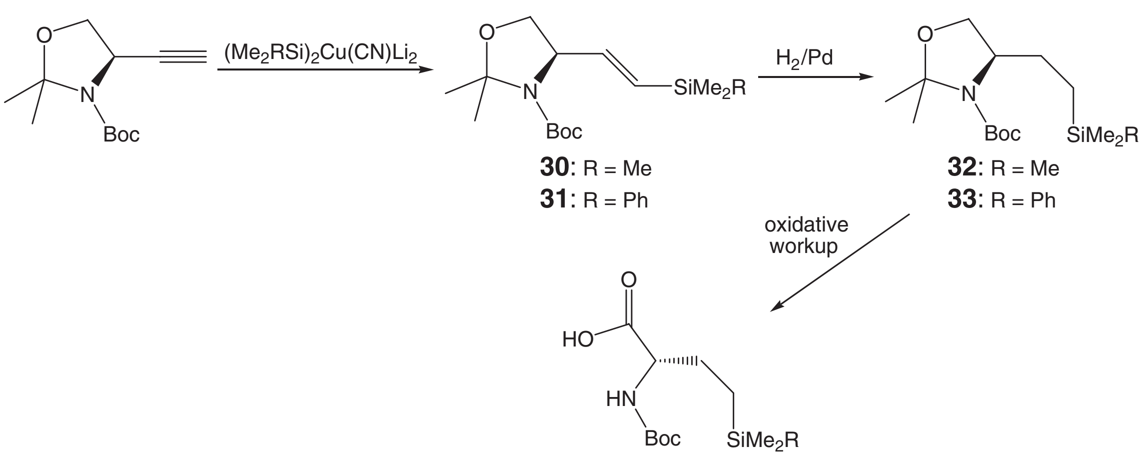
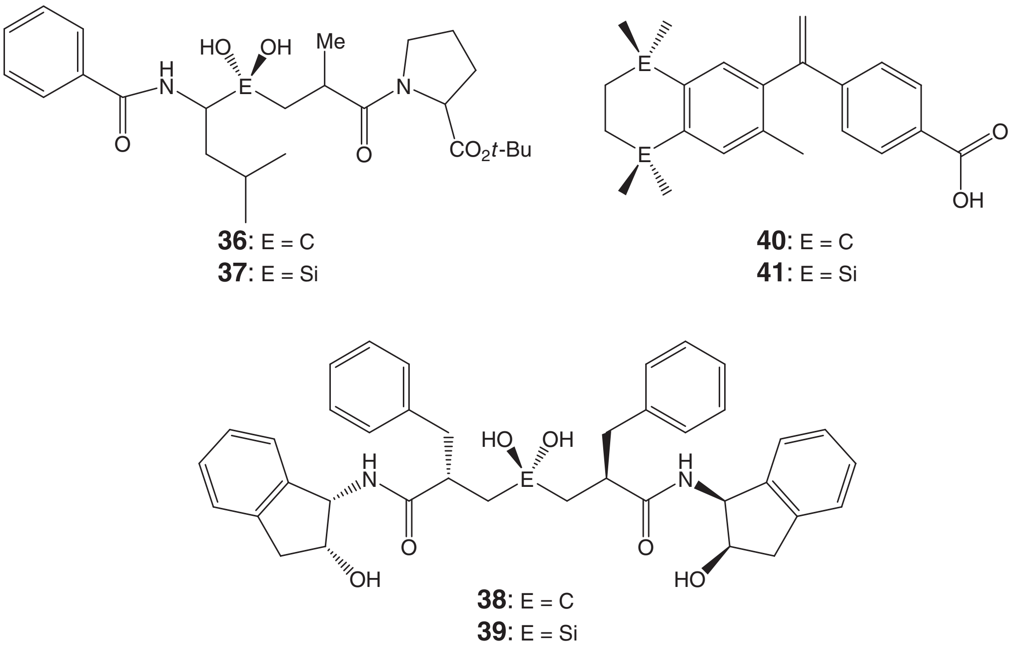


Figure 1



34: R = Me
35: R = Ph

Scheme 5



36: E = C
37: E = Si

40: E = C
41: E = Si

38: E = C
39: E = Si

Scheme 6

it is believed to inhibit the growth of tumor cells. Most silicon analogs of drugs studied so far are antagonists, but it has been shown that disilabexarotene **41** lacks a detrimental effect on the biological activity in terms of its activating target genes through the XRX receptor.

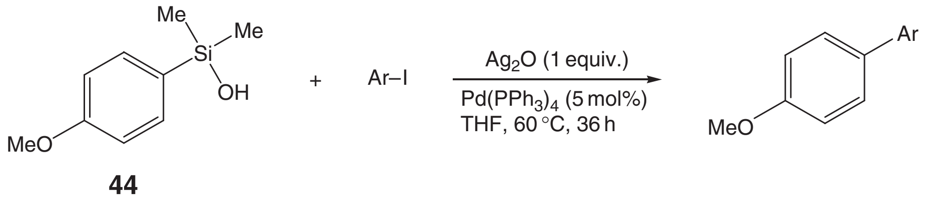
Tacke *et al.* have also studied the bioisosterism of fragrance materials and reported the synthesis of silamajantol, hydroxymethyldimethyl(3-methylbenzyl)silane **42**, which shows drastically different sensory characteristics compared to the parent majantol, 2,2-dimethyl-3-(3-methylphenyl)propanol **43**, an important perfume ingredient.[203,204]

3.09.2.4 Selected Applications in Organic Synthesis

Applications of organosilanes have been covered in a book by Brook[3] and in a number of reviews in 2004. Miura and Hosomi have reviewed silicon reagents used in organic synthesis.[205,206] In 1995, Langkopf and Schinzer described how organosilanes have been employed in the synthesis of natural products.[207] Organosilanes controlling the stereochemistry of organic reactions have been reviewed by Fleming *et al.* in 1997.[143] Silicon-tethered reactions have been covered by Bols and Skrydstrup in 1995.[208] Chan and Wang, Landais *et al.*, and Kobayashi *et al.* have reviewed applications of allylsilanes in organic synthesis in 1995 and 2004.[209–211] The silylcupration of C–C double and triple bonds and applications thereof in organic synthesis have been summarized by Barbero and Pulido in 2004.[212] C–C bond formation reactions mediated by silicon Lewis acids have been reviewed by Dilman and Ioffe in 2003.[213]

3.09.2.4.1 Cross-coupling reactions

Novel Pd-catalyzed cross-coupling reactions for the formation of C–C bonds based on functionalized organosilanes have been developed and reviewed extensively by Denmark *et al.*[214,215] The Si-based cross-coupling reagents have the advantage that they are environmentally benign and generally cheaper than those based on B and Sn reagents, which are commonly used for Suzuki–Miyaura and Stille–Migita–Kosugi cross-coupling reactions. Whereas the first generation of Si reagents used hypervalent organofluorosilicates, the second generation of Si reagents included more readily available and air-stable organosilanols, -siloxanes, and alkoxysilanes.[216–224] For cross-coupling reactions based on hypervalent organofluorosilicates, see Section 6.3. For instance, Mori *et al.* have found that *p*-methoxyphenyldimethylsilanol **44** can be coupled with aryl iodides in the presence of the catalyst $Pd(PPh_3)_4$ and the promoter Ag_2O to give the corresponding unsymmetric biphenyls (Scheme 7). Very few homocoupled products were found under these conditions. Notably, tetrabutylammonium fluoride (TBAF) was ineffective as promoter.



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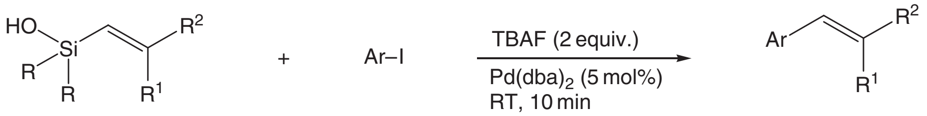
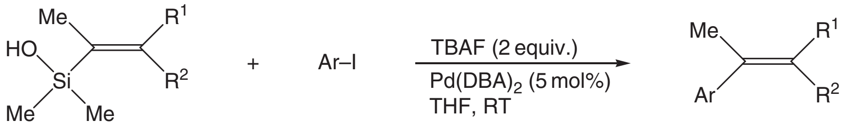
Scheme 7



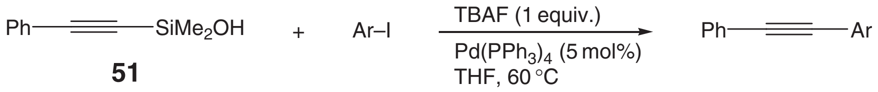
45: R = Me; R^1 = n-C$_5$H$_{11}$; R^2 = H (Z)
46: R = Me; R^1 = H; R^2 = n-C$_5$H$_{11}$ (E)
47: R = i-Pr; R^1 = n-C$_5$H$_{11}$; R^2 = H (Z)
48: R = i-Pr; R^1 = H; R^2 = n-C$_5$H$_{11}$ (E)

Scheme 8



49: R^1 = CH$_2$OTHP; R^2 = H (E)
50: R^1 = H; R^2 = CH$_2$OTHP (Z)

Scheme 9



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Scheme 10

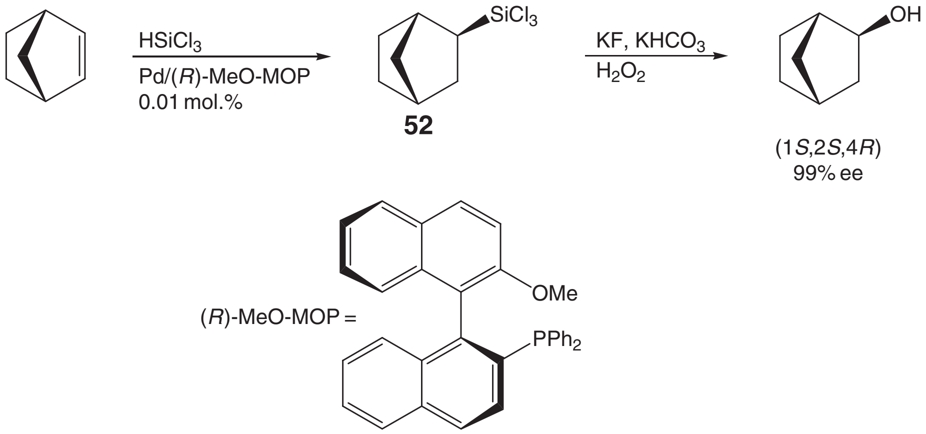
According to Denmark *et al.*, the cross-coupling of alkenylsilanols **45–48** with aryl iodides is effectively catalyzed by Pd(DBA)$_2$ in the presence of the promoter TBAF giving styrol derivatives (Scheme 8).

Similarly, the cross-coupling of sterically hindered alkenylsilanols **49** and **50** with aryl iodides works well under mild conditions (Scheme 9).

At slightly elevated temperatures, the cross-coupling of the alkynylsilanol **51** with aryl iodides is also possible in the presence of Pd(dba)$_2$ and TBAF (Scheme 10).

3.09.2.4.2 Masked hydroxyl groups

Jones and Landais[225] as well as Tamao[226] have summarized methodical oxidation reactions of the Si–C bond that give rise to formation of alcohols. The more general Tamao-type oxidation reaction entails the use of hypervalent silicon species in which the Si–C bonds are activated, and is particularly useful for the selective transformation of functional groups. Other reaction types may be used prior to the Tamao oxidation. The combination of hydrosilylation reaction of an olefin with a chlorosilane, followed by a Tamao-type oxidation using KF and H_2O_2, will transform



Scheme 11

a C–C double bond into an *anti*-Markovnikov alcohol. Consequently, this reaction sequence provides an alternative for the most commonly used oxidative hydroboration.[227] For instance, the enantioselective hydrosilylation of norbornene with $HSiCl_3$ in the presence of a chiral palladium catalyst provides the chiral *exo*-2-(trichlorosilyl)norbornane **52**, whose Tamao-type reaction produces the chiral *exo*-norbornanol with up to 99% ee (Scheme 11).[228]

Yoshida *et al.* have introduced (2-pyridyldimethylsilyl)methyllithium as hydroxymethylating reagent.[229–231] Since sterically hindered silyl groups are often resistant to oxidation with H_2O_2/KF, Woerpel introduced a more powerful oxidation procedure based on the reagent *t*-BuOOH/CsOH/Bu_4NF.[232] Recently, Itami *et al.* have reported the Si–C bond scission by supercritical water yielding hydrocarbons and siloxanes.[233]

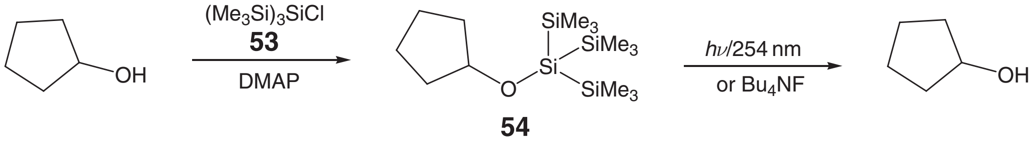
3.09.2.4.3 Novel protecting groups for alcohols

Silyl protecting groups are the "gold standard" for the protection of alcohols.[234] Novel photochemically removable protection groups for alcohols have been developed by Brook *et al.*[235] and Pirrung *et al.*[236] For instance, cyclopentanol can be reacted with tris(trimethylsilyl)chlorosilane **53** in the presence of a mild base to yield the protected silyl ether **54**. The protection group can be removed conveniently upon UV irradiation or by the use of Bu_4NF (Scheme 12).

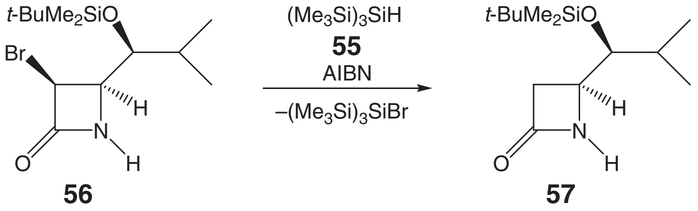
3.09.2.4.4 Reducing agents

Applications of tris(trimethylsilyl)silane, $(Me_3Si)_3SiH$ **55**, as a free radical-based reducing agent in organic synthesis, originally introduced as an alternative to Bu_3SnH by Chatgilialoglu,[237] have been reviewed extensively.[238,239] The utility of $(Me_3Si)_3SiH$ **55** is demonstrated best by the reduction of the α-bromo cycloamide **56** containing a number of functional groups that are incompatible with alternative reducing agents. The free-radical reduction induced by $(Me_3Si)_3SiH$ **55** occurs selectively at the activated α-carbon of the carbonyl group to give the cycloamide **57** leaving the oxo functionalities intact (Scheme 13).

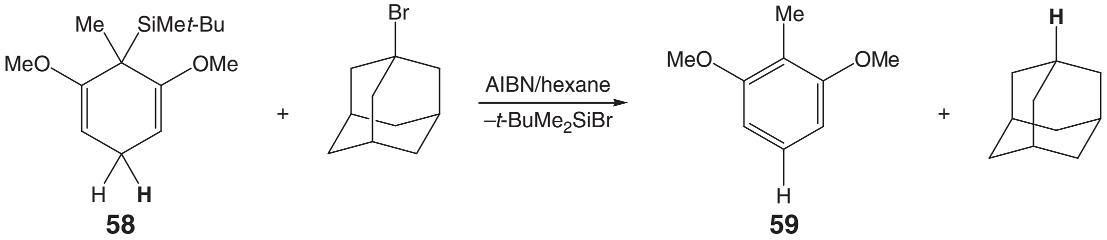
The reagent $(Me_3Si)_3SiH$ **55** has been further used for free-radical hydrosilylation reactions.[240,241] The reactivity of the Si–H bond in $(Me_3Si)_3SiH$ **55** is greatly enhanced by the three triorganosilyl groups when compared with simple triorganosilanes, R_3SiH (R = alkyl, aryl). A major drawback of $(Me_3Si)_3SiH$ **55** is its limited air stability.[242] Studer and Amrein have introduced silylated 1,4-cyclohexadienes as an alternative source of tris(triorganosily)silyl radicals, which may find applications as free radical-based reducing agents and in hydrosilylation reactions.[243,244]



Scheme 12



Scheme 13



Scheme 14

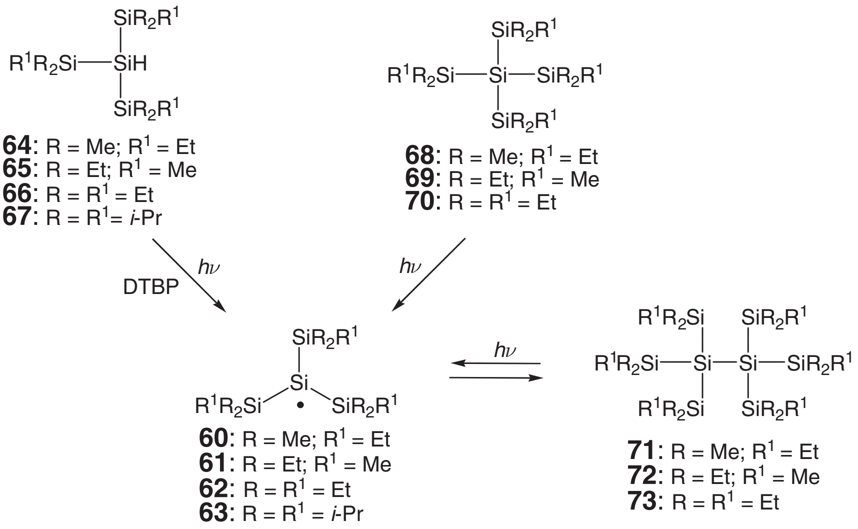
Silylated 1,4-cyclohexadienes, such as **58**, are accessible by the Birch reduction of resorcin dimethyl ether and subsequent one-pot silylation–methylation. The reduction of bromo adamantane with **58**, occurs readily in the presence of the radical initiator AIBN, with the driving force being the aromatization leading to **59** (Scheme 14).

It is well known that the comparatively inert Si–H bonds of triorganosilane R_3SiH (R = alkyl, aryl) can be activated by transition metal complexes. Chatgililaloglu *et al.* have used Et_3SiH in palladium-catalyzed dehalogenation reactions, which occur with the involvement of free radicals.[245]

3.09.2.5 Silyl Radicals, Silyl Cations and Silyl Anions

The interest in silicon-centered radicals dates back to the 1940s and has initially focused on their role as short-lived intermediates in organic synthesis. Our knowledge on silyl radicals was extensively reviewed in 1995 by Chatgilialoglu.[246] A brief review on the structures of stable Si-centered radicals and heavier group 14 congeners was given by Lee and Sekiguchi in 2005.[247] The first persistent silyl radicals $[(R_2R^1Si)_3Si]$ (**60**, R = Me, R^1 = Et; **61**, R = Et, R^1 = Me; **62**, R = R^1 = Et; **63**, R = R^1 = *i*-Pr) with life spans up to days and weeks at room temperature have been obtained by irradiation of $(R_2R'Si)_3SiH$ (**64**, R = Me, R^1 = Et; **65**, R = Et, R^1 = Me; **66**, R = R^1 = Et; **67**, R = R^1 = *i*-Pr), $(R_2R^1Si)_4Si$ (**68**, R = Me, R^1 = Et; **69**, R = Et, R^1 = Me; **70**, R = R^1 = Et) and $(R_2R^1Si)_3SiSi(SiR^1R_2)_3$ (**71**, R = Me, R^1 = Et; **72**, R = Et, R^1 = Me; **73**, R = R^1 = Et), respectively (Scheme 15).[248–250] The stabilization of radicals **60–63** can be attributed to the electronic nature and the bulk of the triorganosilyl substituents. The decay of the silyl radicals **60–62** partly leads to the formation of the disilanes **71–73** (Scheme 15). On the basis of ESR spectroscopy, it has been concluded that the tris(trisilyl)silyl radicals **60–63** are planar, unlike simple triorganosilyl radicals, such as the chiral α-naphthylphenylmethylsilyl radical [NpPhMeSi], which retains its configurational stability prior to reacting with CCl_4.[246]

The first isolable silicon-centered radicals, namely $[(t\text{-}Bu_2MeSi)_3Si]$ **74** and *cyclo*-$[t\text{-}Bu_2Si(SiMe t\text{-}Bu_2)_3]$ **75**, have been prepared and fully characterized by Sekiguchi *et al.* in 2001 (Schemes 16 and 17).[251,252] The synthesis of $[(t\text{-}Bu_2MeSi)_3Si]$ **74** was achieved by the reaction of $(t\text{-}Bu_2MeSi)_2SiBr_2$ **76** with 2 equiv. of $t\text{-}Bu_2MeSiNa$.[252] Apparently, the first equivalent leads to the formation of the transient silylene $(t\text{-}Bu_2MeSi)_2Si$ **77**, whose oxidative addition to the second equivalent of $t\text{-}Bu_2MeSiNa$ provides the sodium tris(triorganosilyl)silanide $Na[Si(SiMe t\text{-}Bu_2)_3]$ **78**. The selective reduction of **78** with $GeCl_2$ gave rise to formation of $[(t\text{-}Bu_2MeSi)_3Si]$ **74**.[252] An X-ray structure analysis of **74** confirmed the planar geometry around the central Si atom. Interestingly, the reduction of $(t\text{-}Bu_2MeSi)_2SiBr_2$ **76** with sodium has produced an entirely different product, namely the disilene $(t\text{-}Bu_2MeSi)_2SiSi(SiMe t\text{-}Bu_2)_2$ **79** (Scheme 16).[253] Reduction of the latter with *tert*-butyllithium gave rise to the first well-defined disilene radical anion, namely $Li[(t\text{-}Bu_2MeSi)_2SiSi(SiMe t\text{-}Bu_2)_2]$ **80**.[253] Notably, the higher group 14 congeners of the silyl radical **74**,



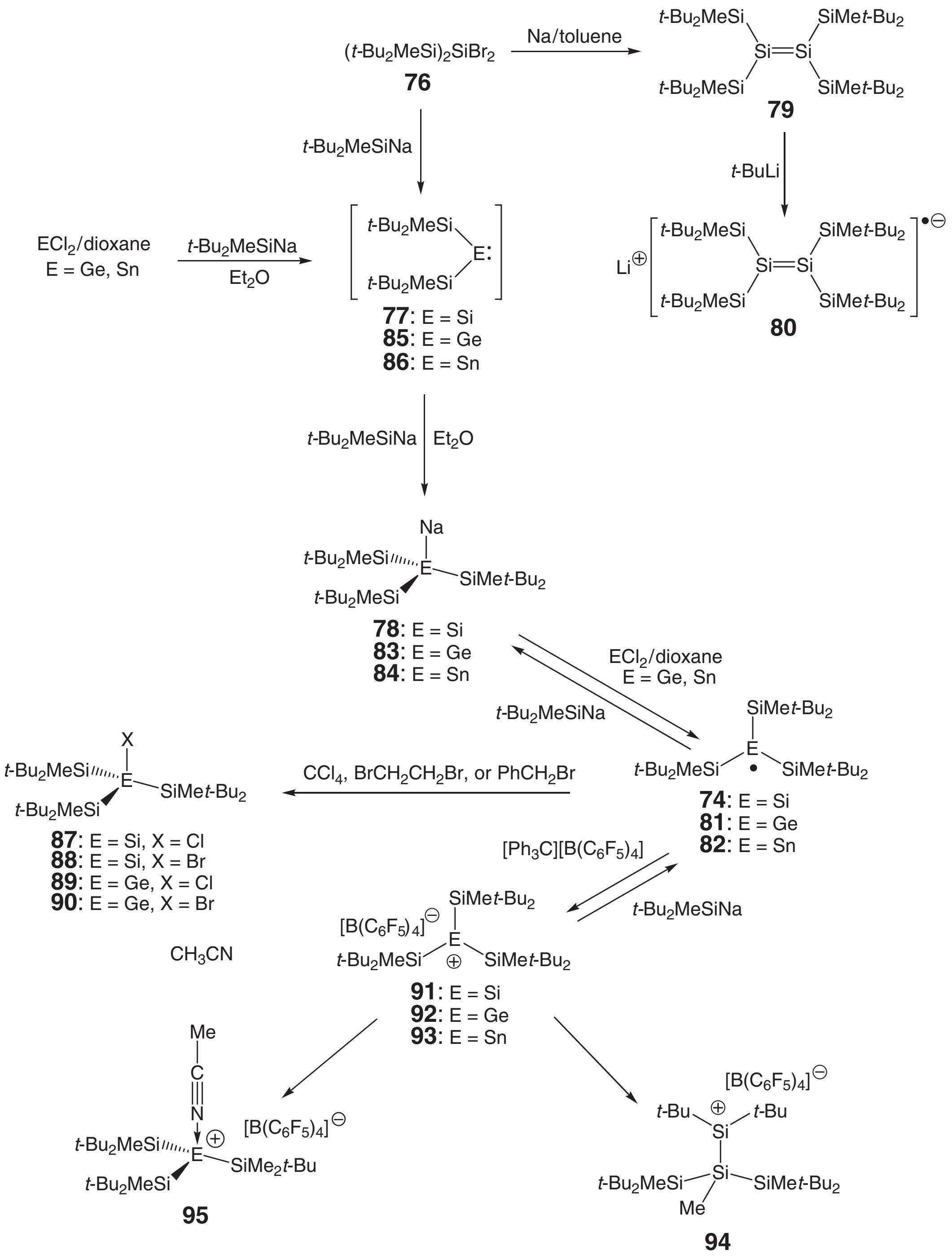
Scheme 15

namely tris(triorganosilyl)germane and -stannane [(t-$Bu_2MeSi)_3E$] (**81**, E = Ge; **82**, E = Sn), have been obtained in two steps by the reaction of $GeCl_2$ and $SnCl_2$ with 3 equiv. of t-$Bu_2MeSiNa$, yielding $Na[E(SiMe$$t$-$Bu_2)_3]$ (**83**, E = Ge; **84**, E = Sn) (via the transient germylene **85** and stannylene **86**), followed by the reduction with $GeCl_2$ and $SnCl_2$, respectively (Scheme 16).[254,255]

Despite their stability, the tris(triorganosilyl)-substituted radicals **74** and **81** readily abstract halogen atoms from activated carbon halides, such as CCl_4, $BrCH_2CH_2Br$, and $PhCH_2Br$, affording (t-$Bu_2MeSi)_3EX$ (**87**, E = Si, X = Cl; **88**, E = Si, X = Br; **89**, E = Ge, X = Cl; **90**, E = Ge, X = Br) (Scheme 16).[252] The oxidation of tris(triorganosilyl)-substituted radicals **74, 81**, and **82** involving a single-electron transfer (SET) to $[Ph_3C][B(C_6F_5)_4]$ has resulted in the corresponding cations, namely [(t-$Bu_2MeSi)_3E][B(C_6F_5)_4]$ (**91**, E = Si; **92**, E = Ge; **93**, E = Sn) (Scheme 16). The tricoordinate tris(triorganosilyl) cation **91** has proved to be unstable with respect to a Wagner–Meerwein-type rearrangement (1,3-methyl migration) to give the new silylium ion **94**, which further decomposed. However, [(t-$Bu_2MeSi)_3E][B(C_6F_5)_4]$ **91** could be stabilized as Lewis acid/Lewis base adduct [(t-$Bu_2MeSi)_3E(NCMe)][B(C_6F_5)_4]$ **95** with acetonitrile.[256]

The cyclotetrasilenyl radical *cyclo*-[t-$Bu_2Si(SiMe$$t$-$Bu_2)_3$] **75** has been prepared in three steps (Scheme 17).[251] The first step involves a reductive co-coupling of t-$Bu_2MeSiSiBr_3$ **96** and (t-$Bu_2MeSi)_2SiBr_2$ **97** with sodium, thus providing a rare example of a cyclotrisilene [(t-$Bu_2MeSi)_2Si(SiSiMe$$t$-$Bu_2)_2$] **98**,[257] whose reaction with $[Et_3Si(C_6H_6)][B(C_6F_5)_4]$ has afforded the homocyclotrisilenylium ion **99**.[258] Reduction of the latter with either t-Bu_3SiNa or potassium graphite has yielded the cyclotetrasilenyl radical [t-$Bu_2Si(SiMe$$t$-$Bu_2)_3$] **75**, whereas the reaction with methyllithium gave rise to the formation of a rare example of a tetrasilacyclobutene [(t-$Bu_2Si)${(t-$Bu_2MeSi)MeSi}(SiMe$$t$-$Bu_2)_2$] **100** (Scheme 17).[259] It is noteworthy that the cation **99** and the radical **75** are stabilized by conjugation with the Si–Si double bond. The subsequent reaction of the cyclotetrasilenyl radical **75** with lithium and $BrCH_2CH_2Br$ has produced the cyclotetrasilane anion **101** and the neutral dibromo cyclotetrasilane **102**, respectively (Scheme 17).

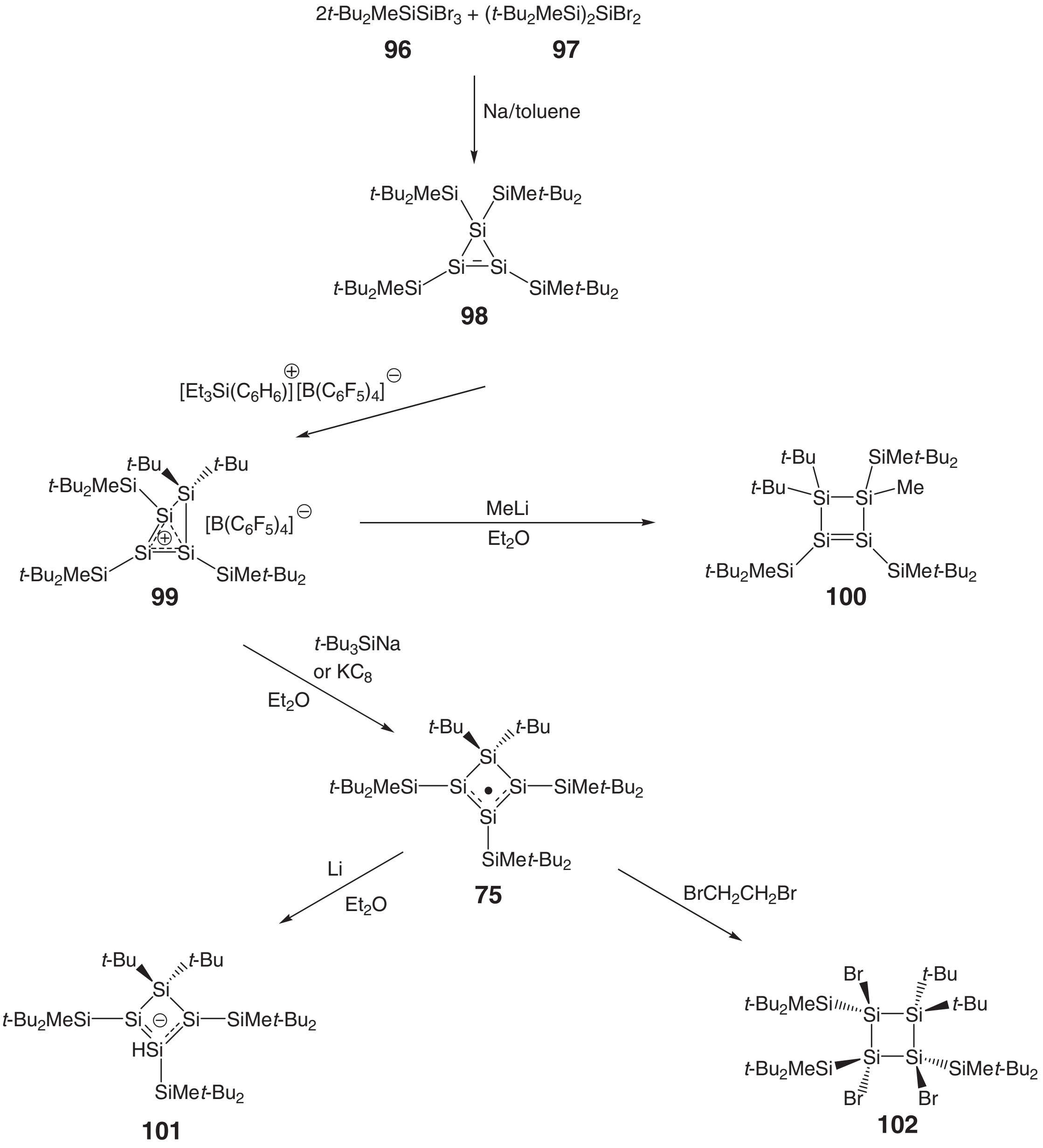
Tricoordinate silyl cations (silylium ions) $[R_3Si]^+$, the silicon congeners of carbo cations (carbenium ions), have been long sought-after species, a fact that is well documented in a number of reviews on the subject matter.[260,261] In 1997, Lambert and Zhao reported the preparation of $[Mes_3Si][B(C_6F_5)_4]$ **103**, a compound that fulfilled all spectroscopic criteria required for a truly three-coordinated silylium ions.[262] In 2000, Reed *et al.* succeeded in the preparation of $[Mes_3Si][H\text{-}CB_{11}Me_5BBr_6]$ **104** and its full characterization by X-ray diffraction, revealing that the coordination number at the silicon atom was indeed 3.[263] The preparation of **104** was made possible by the judicious choice of a sterically demanding and electron-poor organic substituent and a non-coordinating counterion, and involved the reaction of allyltrimesitylsilane $Mes_3SiAllyl$ **105** with the icosahedral triethylsilyl carborane $Et_3Si(HCB_{11}Me_5BBr_6)$ under the strict exclusion of donor solvents (Scheme 18). By contrast, the preparation of tetra- or pentacoordinate silylium ions is much less challenging. Reed *et al.* have reported on the tetracoordinate-hydrated triorganosilyl cation



Scheme 16

[t-$Bu_3Si(OH_2)$][H-$CB_{11}Me_5BBr_6$] **106**, which can be rationalized in two canonical forms, namely a Lewis acid–Lewis base adduct of the silylium ion and water, and, alternatively, a protonated silanol (Scheme 18).[264]

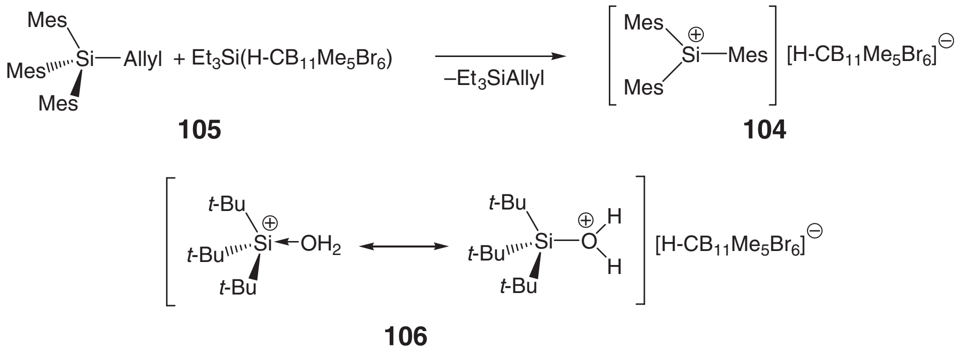
The chemistry of decamethylsilicocene $(Me_5C_5)_2Si$ **107**, the first haptobonded silylene, was reviewed in 2003 by Jutzi.[265] The most interesting feature of decamethylsilicocene derivatives is the ability to switch between σ- and η-bonding. For instance, the oxidative addition of GaX_3 ($X = Cl$, Br) to $(Me_5C_5)_2Si$ **107** has readily afforded the diorganodihalosilanes $(Me_5C_5)_2SiX_2$ (**108**, $X = Cl$; **109**, $X = Br$) having Si–C σ-bonds (Scheme 19).[266] Most interestingly,



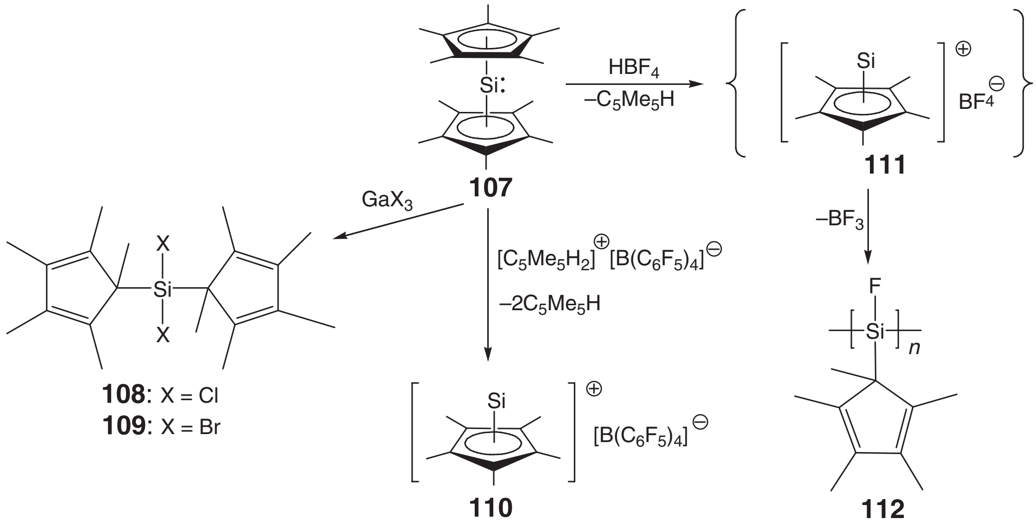
Scheme 17

the reaction of $(Me_5C_5)_2Si$ **107** with the proton-transfer reagent $[Me_5C_5H_2][B(C_6F_5)_4]$ has yielded the unique salt $[(Me_5C_5)Si][B(C_6F_5)_4]$ **110** containing a pentahapto (η^5)-bonded pentamethylcyclopentadienylsilyl cation, which can be regarded as being a derivative of the silyliumylidene cation HSi^+ (Scheme 19).[267] The protonation of **107** with HBF_4 presumably affords an analog **110**, namely $[(Me_5C_5)Si]BF_4$ **111**, which, however, decomposes to give the polymer **112**.

Unlike silyl radicals and silylium ions that have been elusive for a long time, silyl anions (silanides) are well known since the pioneering work of Gilman *et al.* in the 1960s. Two literature reviews on silyl anions by Lickiss and Smith as well as Tamao appeared in 1995.[268,269] Many structural elucidations and reactivity studies of silyl anions have been undertaken recently. A number of alkaline silanides,[270–272] earth alkali silanides,[273] as well as transition metal silanides,[270,274] have been prepared and fully characterized. Sekiguchi *et al.* have reported X-ray structures of lithium silanides and provided evidence for intramolecular Li···Ph interactions.[275] A review on the synthesis and structures of metal silanides has been given by Lerner in 2005.[276] A versatile method for the preparation of potassium



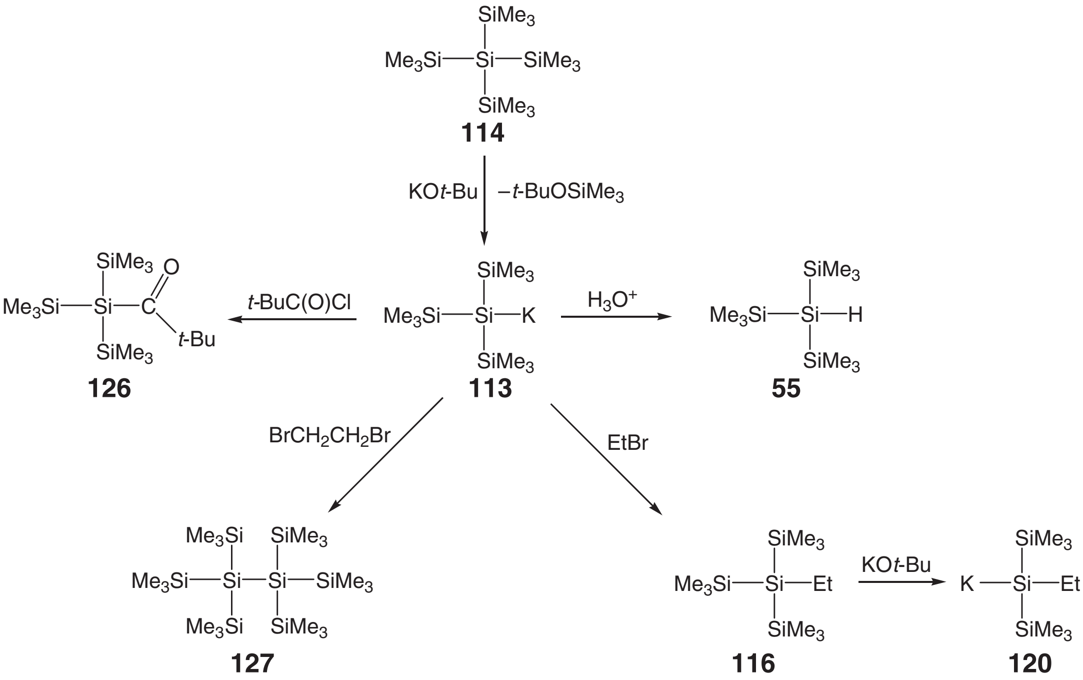
Scheme 18



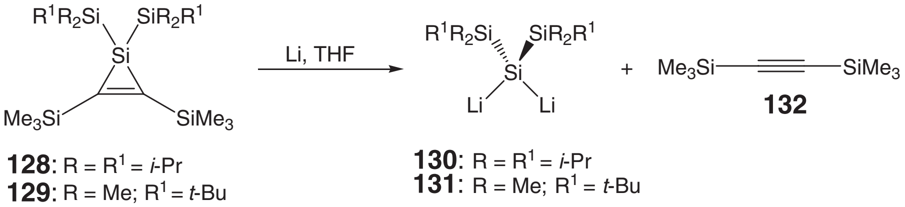
Scheme 19

tris(trimethylsilyl)silanide $KSi(SiMe_3)_3$ **113** and similar silyl-substituted potassium silanides and applications thereof in organometallic synthesis have been developed by Marschner.[277] It involves the reaction of tetrakis(trimethylsilyl)silane $(Me_3Si)_4Si$ **114** with KO*t*-Bu, which quantitatively provides $K[Si(SiMe_3)_3]$ **113** and *t*-BuOSiMe$_3$ (Scheme 20). Organotris(triorganosilyl)silanes $R(Me_3Si)_3Si$ (**115**, R = Me; **116**, R = Et; **117**, R = Ph; **118**, R = OMe) react similarly, albeit less readily, with KO*t*-Bu to give the corresponding potassium silanides $K[Si(Me_3Si)_2R]$ (**119**, R = Me; **120**, R = Et; **121**, R = Ph; **122**, R = OMe).[277,278] In the absence of a crown ether, compound **122** dimerizes to form the disilyl anion $K[Si(SiMe_3)_2Si(SiMe_3)_2OMe]$ **123**. Similarly, the reaction of $(Me_3Si)_3SiF$ **124** with KO*t*-Bu affords $K[Si(SiMe_3)_2Si(SiMe_3)_2F]$ **125**.[279] Compounds **122–125** have been fully characterized (as their crown ether adducts). Silyl anions are important intermediates in organosilicon chemistry. Thus, the metathesis reaction of $K[Si(SiMe_3)_3]$ **113** with *t*-BuC(O)Cl, $BrCH_2CH_2Br$, and EtBr has produced *t*-BuC(O)Si(SiMe$_3$)$_3$ **126**, $(Me_3Si)_3SiSi(SiMe_3)_3$ **127**, and $EtSi(SiMe_3)_3$ **117**, respectively. Simple protolysis of $K[Si(SiMe_3)_3]$ **113** provides easy access to $(Me_3Si)_3SiH$ **55** (Scheme 20).[277] Furthermore, $K[Si(SiMe_3)_3]$ **113** has been used to prepare compounds with Si–M bonds (M = Zr, W, Mo, Cr).[280] For applications of silyl anions at preparing oligosilanes, see Section 5.1.

The unexpected formation of the first bis(triorganosilyl)silyl dianions has been reported by Sekiguchi *et al.* in 1999. Thus, the reaction of 1,1-bis(triorganosilyl)-2,3-bis(trimethylsilyl)silacyclopropenes **128** and **129** with lithium provided the dilithiosilanes $Li_2[Si(R_2R^1Si)_2]$ (**130**; R = R^1 = *i*-Pr; **131**, R = Me, R^1 = *t*-Bu) with the only byproduct being bis(trimethylsilyl) acetylene $Me_3SiCCSiMe_3$ **132** (Scheme 21).[281,282] For reactions of silyl dianions at preparing unsaturated silanes, see Section 5.2.



Scheme 20

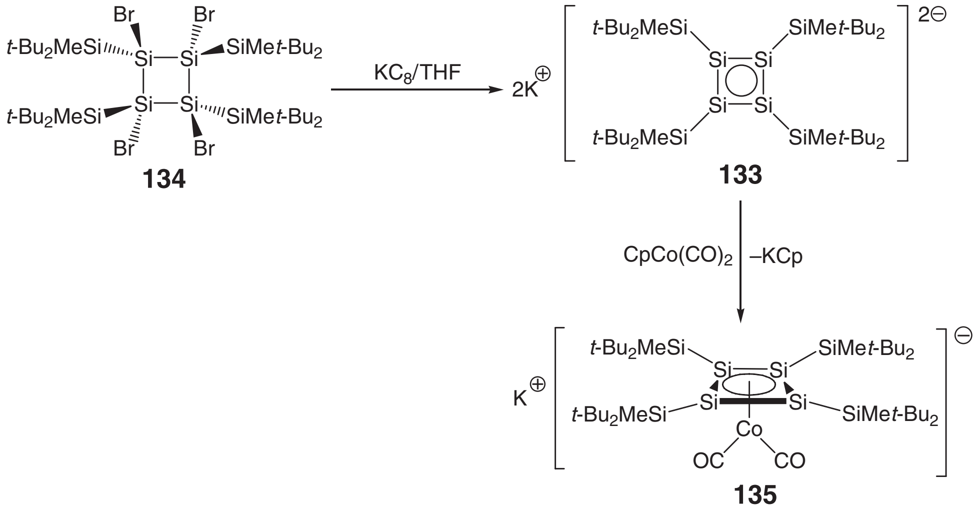


Scheme 21

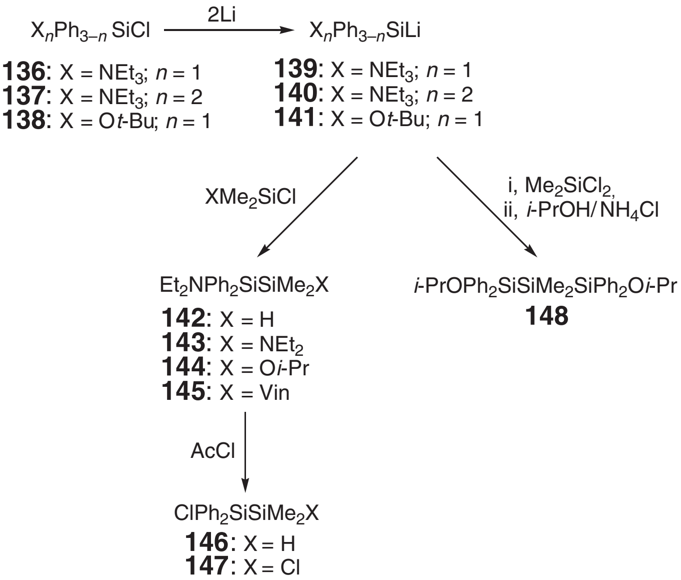
The first dipotassium tetrasilacyclobutadiene dianion $K_2[Si(SiMe\textit{t}\text{-}Bu_2)]_4$ **133**, a silicon analog of the aromatic (6π-electron) cyclobutadiene dianion, has been prepared from the tetrabromo cyclotetrasilane **134** and KC_8 by Sekiguchi *et al.* in 2004 (Scheme 22).[283] A unique transition metal complex, namely potassium [tetrakis(di-*tert*-butylmethylsilyl)tetrasilacyclobutadiene]dicarbonylcobalt $K[\eta^4\text{-}(\textit{t}\text{-}Bu_2MeSiSi)_4Co(CO)_2]$ **135** containing tetrahapto (η^4)-bonded tetrasilacyclobutadiene ligand has been obtained by the reaction of **133** and $CpCo(CO)_2$ (Scheme 22).[284]

The chemistry of functionalized stable silyl anions, first communicated in 1992,[285] has been substantially extended by Tamao *et al.*[286–291] and other groups.[292–294] The treatment of (amino)- and (alkoxy)phenylsilyl chlorides, such as $X_nPh_{3-n}SiCl$ (**136**, X = Et_3N, $n = 1$; **137**, X = Et_3N, $n = 2$; **138**, X = *t*-BuO, $n = 1$), with lithium provides easy access to the corresponding lithium (amino)- and (alkoxy)phenylsilanides $X_nPh_{3-n}SiLi$ (**139**, X = Et_3N, $n = 1$; **140**, X = Et_3N, $n = 2$; **141**, X = *t*-BuO, $n = 1$) (Scheme 23). Compounds **139** and **140** containing amino groups show little or no silylenoide character and can be stored for longer periods of time without decomposition. The coupling of **139** and **140** with functionalized dimethylchlorosilanes XMe_2SiCl (X = H, NEt_2, O*i*-Pr, Vin) and Me_2SiCl_2, followed by reactions with nucleophiles, such as acetyl chloride or isopropanol, leads to the formation of unsymmetric di- and trisilanes, $Et_2NPh_2SiSiMe_2X$ (**142**, X = H; **143**, X = NEt_2; **144**, X = O*i*-Pr; **145**, X = Vin), $ClPh_2SiSiMe_2X$ (**146**, X = H; **147**, X = Cl) and *i*-$PrOSiPh_2SiMe_2SiPh_2O$*i*-Pr **148**, containing various functional groups (Scheme 23).[285,289,290] The X-ray structure of Ph_2NPh_2SiLi **149**, an analog of **136**, was determined as the THF solvate.[287]

It is interesting to note that (alkoxy)phenylsilanides, such as *t*-$BuOPh_2SiLi$ **141**, show a more pronounced silylenoide character than comparable (amino)phenylsilanides, and undergo self-condensation at 0 °C.[291] An unstable



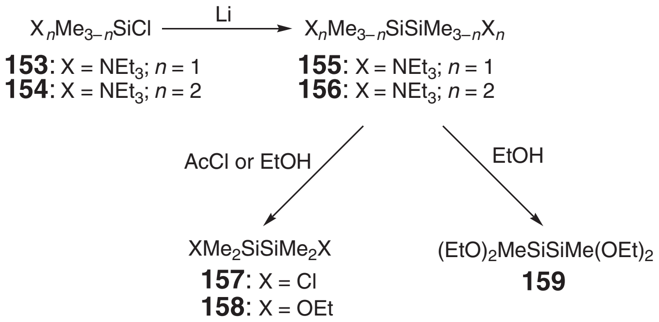
Scheme 22



Scheme 23

bromo silylenoid Tbt(Dip)SiLiBr **150** has been postulated by Tokitoh *et al.* (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Dip = 2,6-diisopropylphenyl).[295,296] Recently, the synthesis and reactivity of the first halo silylenoids $TsiX_2SiLi$ (**151**, X = Cl; **152**, X = Br) that are stable at room temperatures have been reported by Lee *et al.* (Tsi = $(Me_3Si)_3C$).[297] The treatment of (amino)methylsilyl chlorides, such as $X_nMe_{3-n}SiCl$ (153, X = Et_3N, $n = 1$; 154, X = Et_3N, $n = 2$), with lithium provides symmetric (amino)methyldisilanes $X_nMe_{3-n}SiSiMe_{3-n}X_n$ (155, X = Et_3N, $n = 1$; 156, X = Et_3N, $n = 2$), which can be transformed into the corresponding (chloro)- and (ethoxy)-methyl disilanes $X_nMe_{3-n}SiSiMe_{3-n}X_n$ (157, X = Cl, $n = 1$; 158, X = OEt, $n = 1$; 159, X = OEt, $n = 2$) upon reaction with acetyl chloride and ethanol (Scheme 24).[286]

More recently, Kira *et al.* have published a new route to the preparation of hydrido(trialkylsilyl)silyllithiums, such as $(t\text{-}BuMe_2Si)_2SiHLi$ **160**,[298] which show promise as versatile starting materials in organometallic synthesis.



Scheme 24

3.09.2.6 Silylenes and Silenes

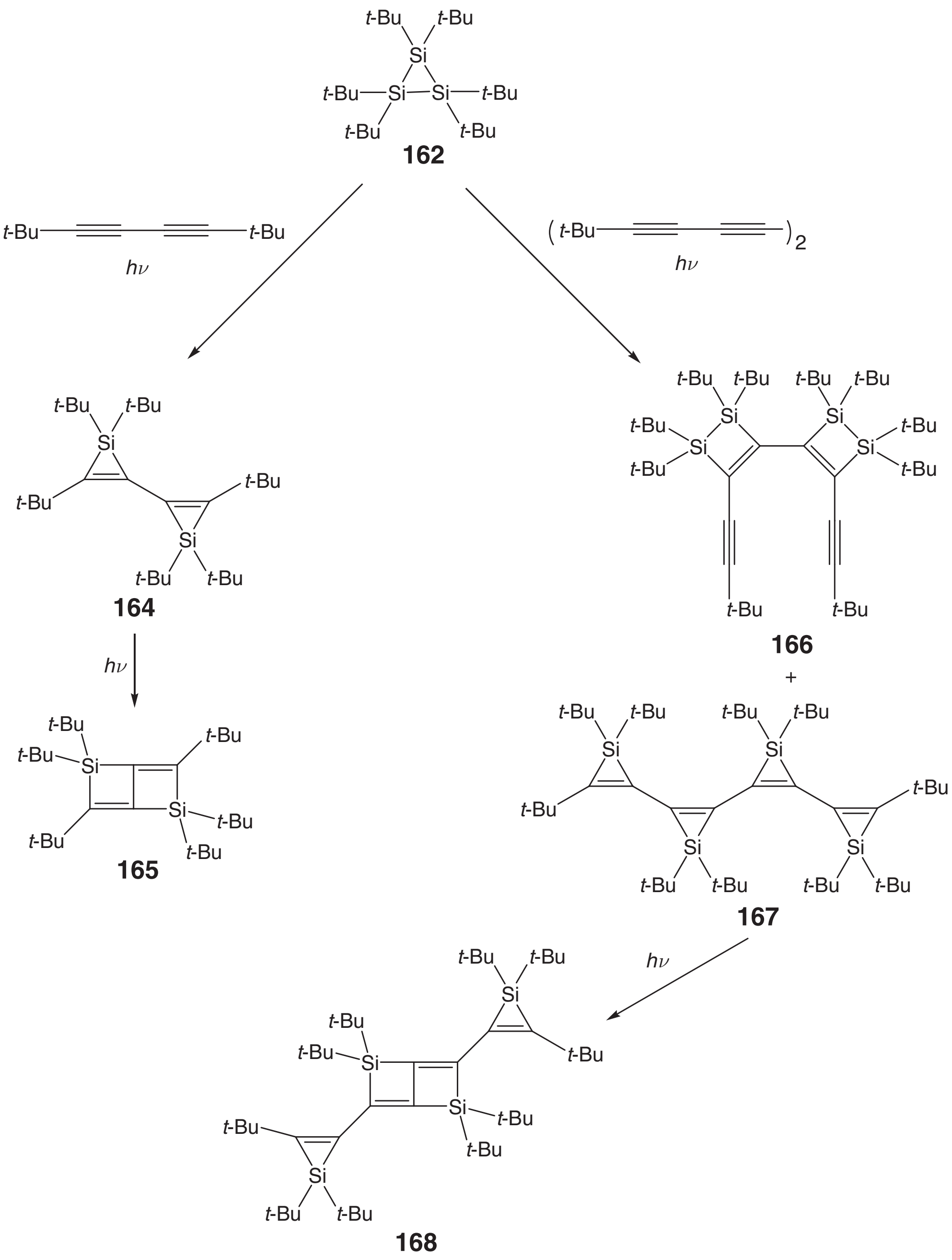
Divalent silylenes, silicon congeners of carbenes, are well-established reactive intermediates, whose chemistry has been reviewed by Weidenbruch in 1995, by Gasper and West in 1998, and by West *et al.* in 2000.[299–301] Chemistry related to the first stable silylene containing two σ-Si–C bonds has been reviewed by Kira *et al.* in 2004.[302] Di-*tert*-butylsilylene *t*-Bu_2Si **161**, one of the most studied transient silylenes, can be generated either photochemically from the cyclotrisilane (*t*-$Bu_2Si)_3$ **162**[303] or thermally from 1,1-di-*tert*-butyl-*trans*-2,3-dimethyl-1-silacyclopropane **163**.[304,305] The reactivity of silylenes toward olefins and acetylenes has been the focus of most recent work in this area. The reaction of silylenes with buta-1,3-diynes and octa-1,3,5,7-tetraynes has been studied by Weidenbruch *et al.*[306,307] The photochemical reaction of (*t*-$Bu_2Si)_3$ **162** with 1,4-di-*tert*-butyl-1,3-diyne has yielded the bis(silacyclopropene) **164**, which upon prolonged radiation underwent rearrangement into the bicyclic compound **165** (Scheme 25). The analogous reaction with 1,8-di-*tert*-butyl-1,3,5,7-tetrayne has furnished two products, a C–C-linked bis(disilacyclobutene) derivative **166** with therminal alkylnyl groups and a quatersilirene **167**. Upon prolonged radiation, the latter rearranges partly into the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene derivative **168** having terminal silirene groups (Scheme 25).[306,307]

Novel thermal and metal-catalyzed di-*tert*-butylsilylene **161** transfer reactions have been reported by Woerpel *et al.*[308–312] The transfer reactions required the inital preparation of cyclohexene-derived silacyclopropanes **169–171**, which has been achieved by trapping of di-*tert*-butylsilylenoid, generated from *t*-Bu_2SiCl_2 and lithium, with cyclohexenes (Scheme 26).[305] It is noteworthy that these reactions occur with remarkably high diastereoselectivities when 2-substituted cyclohexenes are used. The silacyclopropanation of **169** with functionalized cyclopentenes under thermal conditions (115 °C) has provided *trans*-silacyclopropanes, such as **172**, with diastereoselectivities up to 96 : 4, whereas no silacyclopropanes were obtained from the direct reaction of the same cyclopentenes with *t*-Bu_2SiCl_2 in the presence of lithium (Scheme 26).[308]

The silacyclopropanation of acyclic and cyclic alkenes with **169**, catalyzed by AgOTf, occur at room temperature or even below to yield new cyclosilapropanes **173–177**. In the case of chiral β-pinene, the silacyclopropanation occurs enantioselectively (dr > 95 : 5) (Scheme 26).[312] Mechanistic studies have been undertaken, which suggest that silyl silver complexes play an important role in the catalytic cycle of the silylene transfer.[310]

Like carbenes, silylenes in principle may exist with a singlet or a triplet ground state. As early work has shown that all investigated silylenes possess a singlet ground state: it has been suggested that triplet silylenes may be obtainable when extremely bulky substituents are employed. It was argued that repulsion between the bulky substituents would favor large C–Si–C bond angles, which in the extreme case of 180° would result in two bonding *sp*-hybrid orbitals and two degenerate non-bonding *p*-orbitals for which Hund's rule would dictate a triplet ground state.[313] In 2001, Jiang and Gasper revealed conclusive evidence that the silylene *t*-$Bu_3SiSiSi$*i*-Pr_3 **178** obtained by photolysis reacted with various trapping agents from a triplet ground state.[314] In 2003, Sekiguchi and Akiyama proved by ESR spectroscopy that the related silylene *t*-$Bu_3SiSiSi$*t*-Bu_3 **179** exists in the triplet ground state.[315]

Following a number of stable Si–N silylenes[301] and the stable hapto bonded silylene decamethylsilicocene $(Me_5C_5)_2Si$ **107**,[265] Kira *et al.* have described the preparation of the first stable sigma-bonded dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)cyclopenta-1-silylene $[H_2C(SiMe_3)_2C]_2Si$ **180** in 2001 (Scheme 27).[302] The synthesis of **180** started with the reaction of 1,1-bis(trimethylsilyl)ethene **181** with lithium, affording a transient radical anion **182**, which undergoes dimerization to form the dilithiated species **183**.[316] The reaction of **183** with $SiBr_4$ yields the diorganodibromosilane **184**, whose reduction with KC_8 provides the silylene **180** (Scheme 27).[317] It is worth mentioning that Marciniec *et al.* have developed a novel synthetic route to prepare 1,1-bis(silylethenes), such as

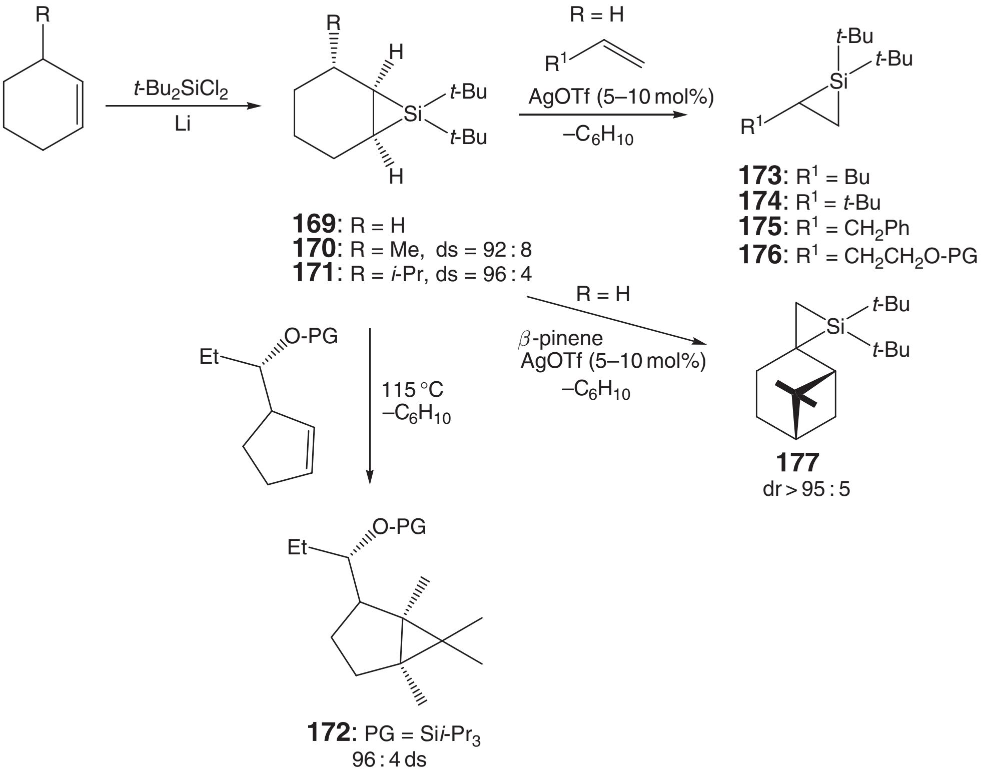


Scheme 25

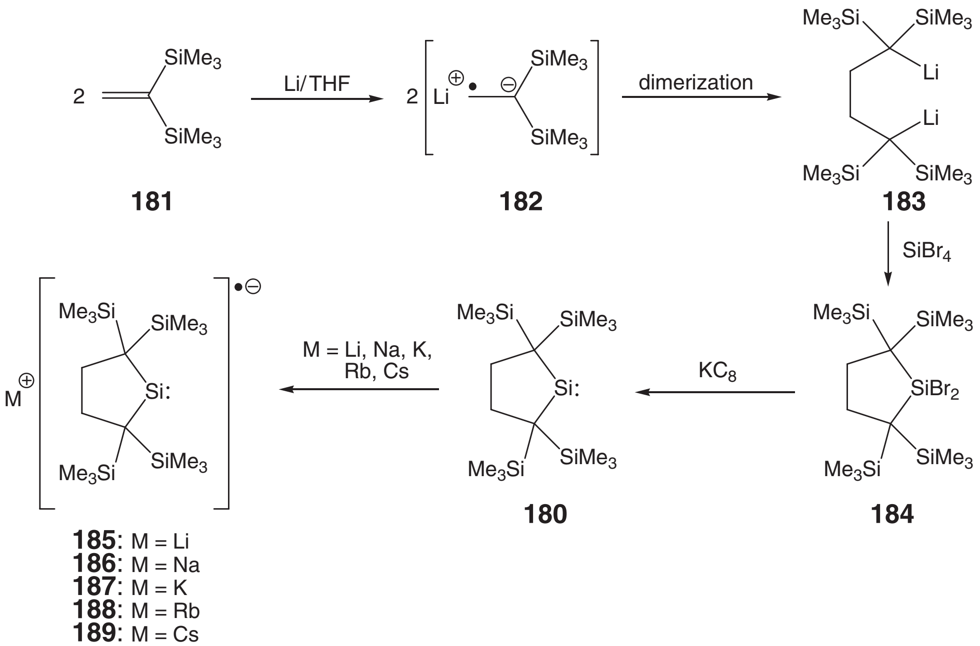
181.[318] Reduction of the silylene 180 with alkali metals gives rise to formation of the divalent silyl radical anions $M[H_2C(SiMe_3)_2C]_2Si$ (185, M = Li; 186, M = Na; 187, M = K; 188, M = Rb; 189, M = Cs) (Scheme 27).[317]

The reactivity of the silylene $[H_2C(SiMe_3)_2C]_2Si$ 180 has been extensively studied by Kira *et al.* (Schemes 28 and 29).[319–325] Thus, the reaction of 180 with $CHCl_3$ and CCl_4 occurs via oxidative addition and formation of the dichlorosilane $[H_2C(SiMe_3)_2C]_2SiCl_2$ 190, whereas the reaction with CH_2Cl_2 affords the methylene-bridged product 191 analogous to 190 (Scheme 28).

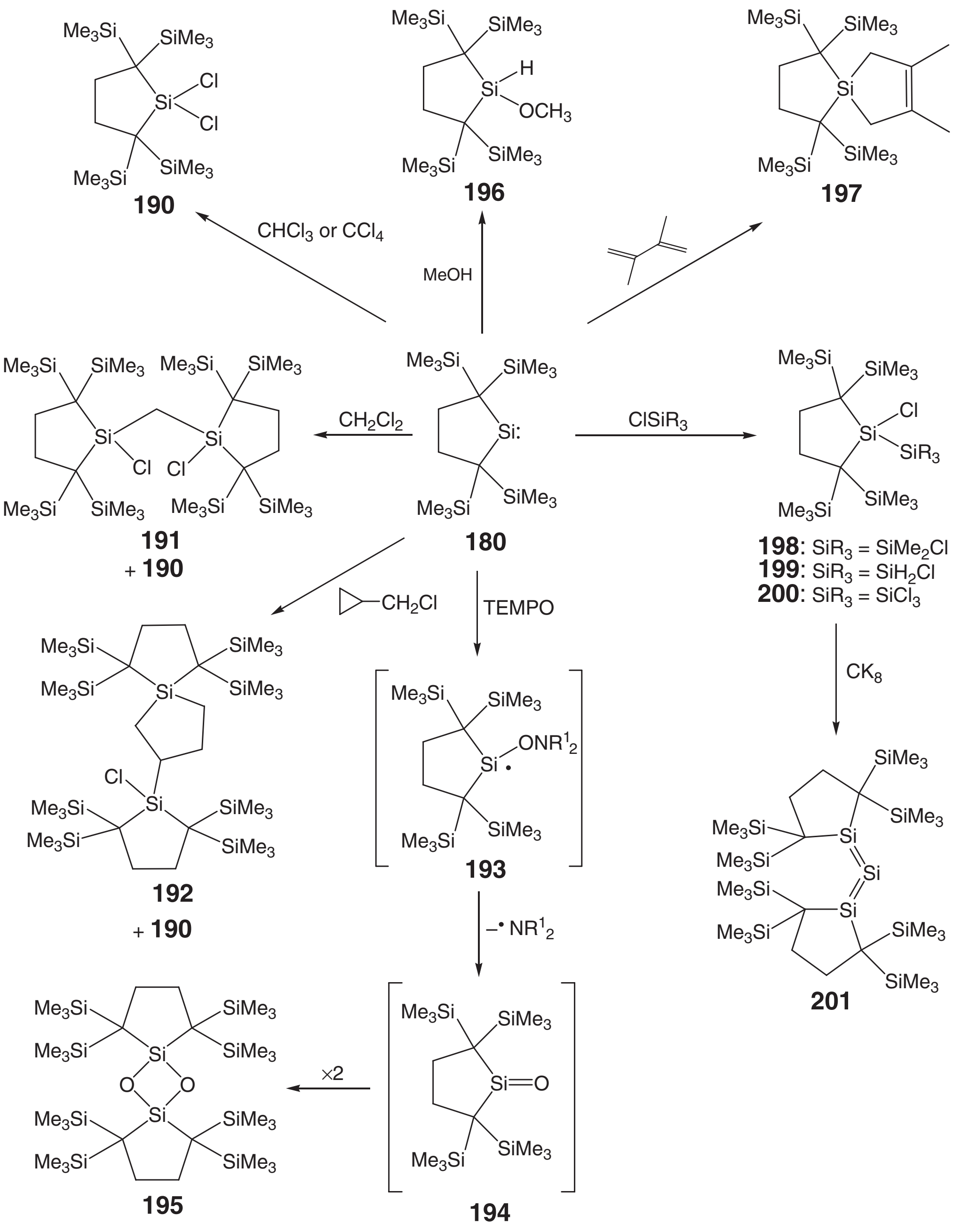
The reaction of $[H_2C(SiMe_3)_2C]_2Si$ 180 with cyclopropylmethyl chloride proceeds via ring opening and formation of product 192 containing a spirocyclic Si atom, whose formation can be attributed to a radical-reaction pathway



Scheme 26

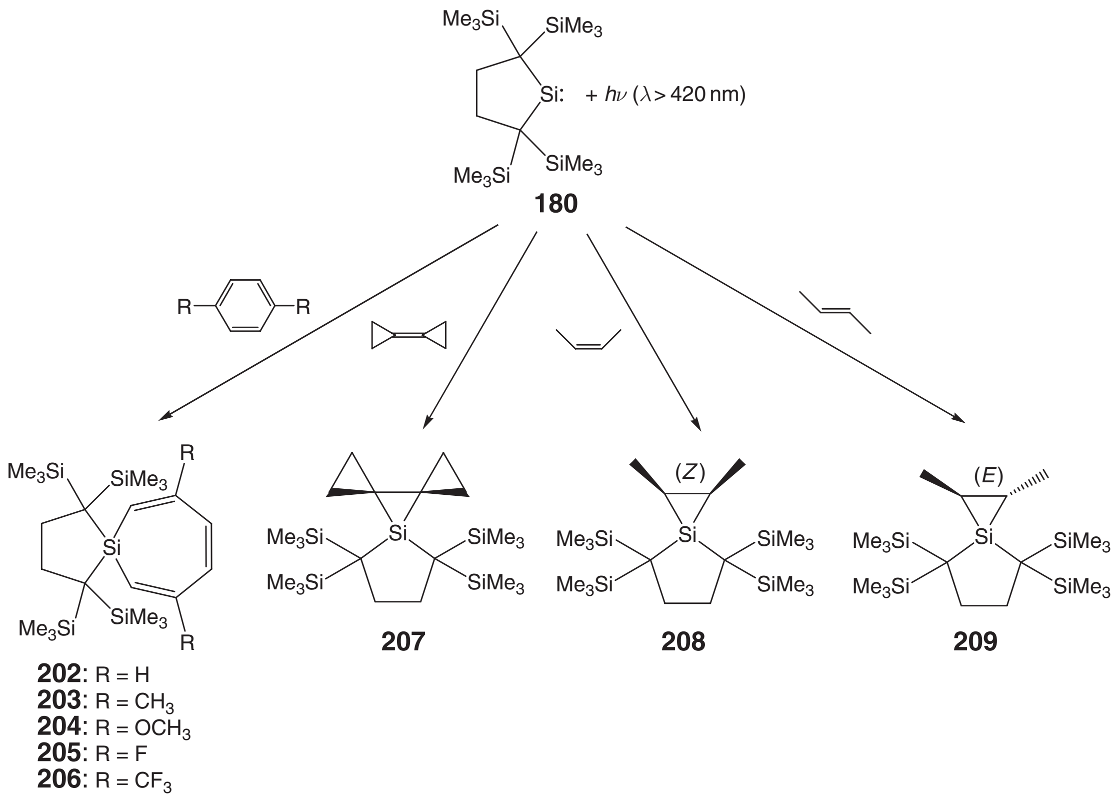


Scheme 27

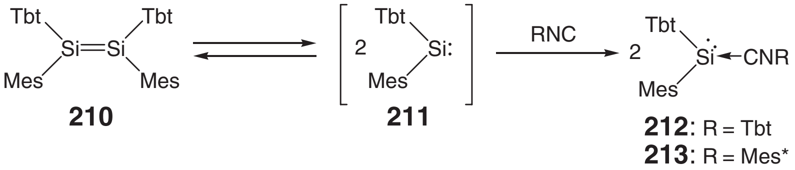


Scheme 28

(Scheme 28). The reaction of **180** with the stable nitroxoide radical 2,2,6,6,-tetramethylpiperidine *N*-oxide (TEMPO) presumably progresses via the formation of two intermediates **193** and **194**, and eventually yields the cyclodisiloxane **195** (Scheme 28). The oxidative addition of methanol to **180** has provided the tetravalent compound $[H_2C(SiMe_3)_2C]_2Si(H)OMe$ **196**, while the cycloaddition of **180** with 1,3-butadiene gives the spirocyclic product **197** (Scheme 28). The reaction of $[H_2C(SiMe_3)_2C]_2Si$ **180** with the chlorosilanes Me_2SiCl_2, H_2SiCl_2, and $SiCl_4$ has produced a number of chlorodisilanes $[H_2C(SiMe_3)_2C]_2Si(Cl)SiR_3$ (**198**, $SiR_3 = SiMe_2Cl$; **199**, $SiR_3 = SiH_2Cl$; **200**, $SiR_3 = SiCl_3$). The reduction of $[H_2C(SiMe_3)_2C]_2Si(Cl)SiCl_3$ **200** with potassium graphite allowed the preparation of the first stable silaallene $[H_2C(SiMe_3)_2C]_2SiSiSi[C(SiMe_3)_2H_2C]$ **201**, containing formally an *sp*-hybridized Si atom



Scheme 29



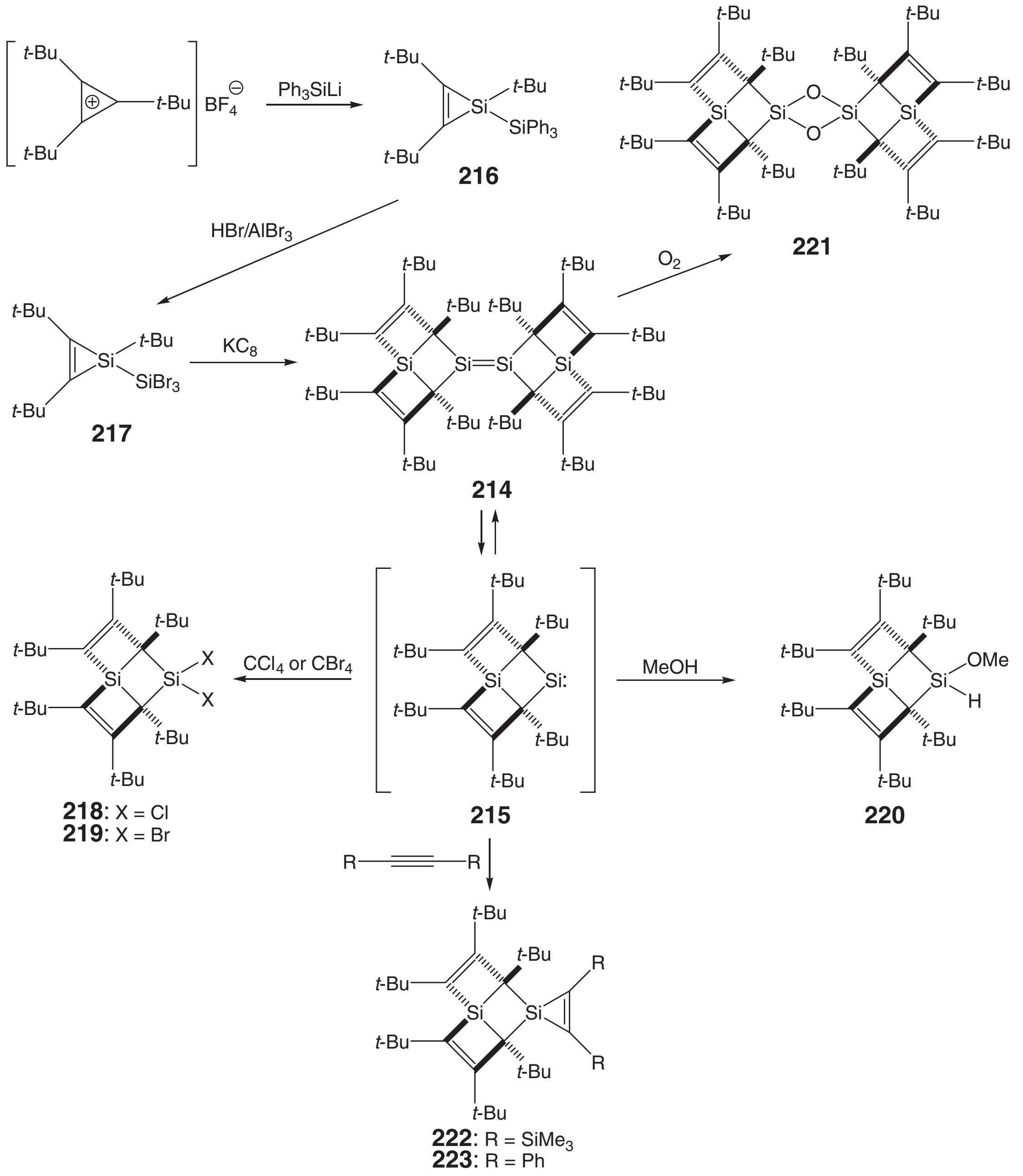
Tbt = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$
Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

Scheme 30

(Scheme 28). The chemistry of heavier group 14 allene analogs has been the subject of a recent review by Eichler and West.[326] The photoreaction of [HC$_2$(SiMe$_3$)$_2$C]$_2$Si **180** (from a singlet excited state) with benzene derivatives proceeds via insertion into a (formal) C–C single bond and results in a series of silacycloheptatrienes **202–206**, whereas a cycloaddition takes place in the photoreaction of **180** with bicyclopropylidene, *cis*- and *trans*-2-butene providing the silacyclopropane derivatives **207–209** (Scheme 29).

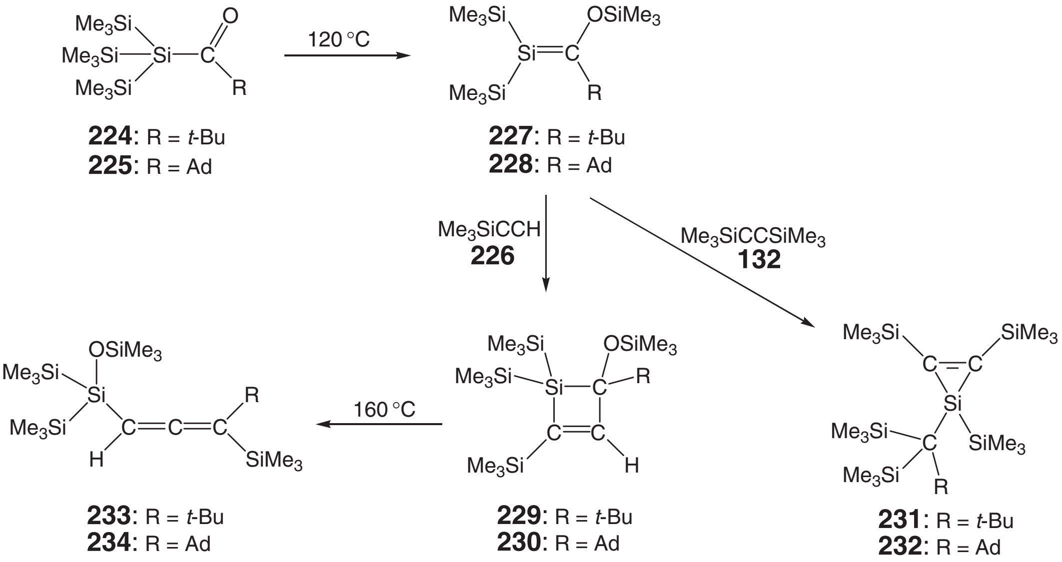
Tokitoh *et al.* have synthesized a sterically hindered disilene TbtMesSiSiMesTbt **210** that is kinetically stable but thermally labile, thus providing the corresponding silylene TbtMesSi **211**, whose reaction with isocyanides bearing bulky substituents has resulted in the formation of the first stable silylene isocyanide complexes TbtMesSiCNR (**212**, R = Tbt; **213**, R = Mes*) (Scheme 30).[327]

Recently, Tsutsui and Sakamoto have reported on a lattice-framework disilene **214**, whose reactivity may be explained best by a thermal equilibrium to the corresponding silylene **215** (Scheme 31).[328–330] The lattice-framework disilene **214** is accessible in three steps starting from tri-*tert*-butylcyclopropenyium tetrafluoroborate [*t*-Bu$_3$C$_3$][BF$_4$], which upon reaction with lithium triphenylsilanide has provided tri-*tert*-butyl-3-(triphenylsilyl)cyclopropene **216**. The exhaustive cleavage of phenyl groups using HBr/AlBr$_3$ has yielded the corresponding



Scheme 31

tribromosilane **217**, whose reduction with KC_8 has resulted in the formation of the lattice-framework disilene **214** (Scheme 31).[328–330] The reaction of the disilene **214** with CCl_4, CBr_4, MeOH, and substituted acetylenes proceeds via the formation of the transient silylene **215** and yields the tetravalent silanes **218–220** (Scheme 31). The oxidation of disilene **214** with O_2 gives the four-membered cyclodisiloxane ring **221** (Scheme 31). The cycloaddition of the disilene **214** with the acetylene derivates PhCCPh and $Me_3SiCCSiMe_3$ **132** provides the silacyclopropenes **222** and **223**, respectively (Scheme 31).

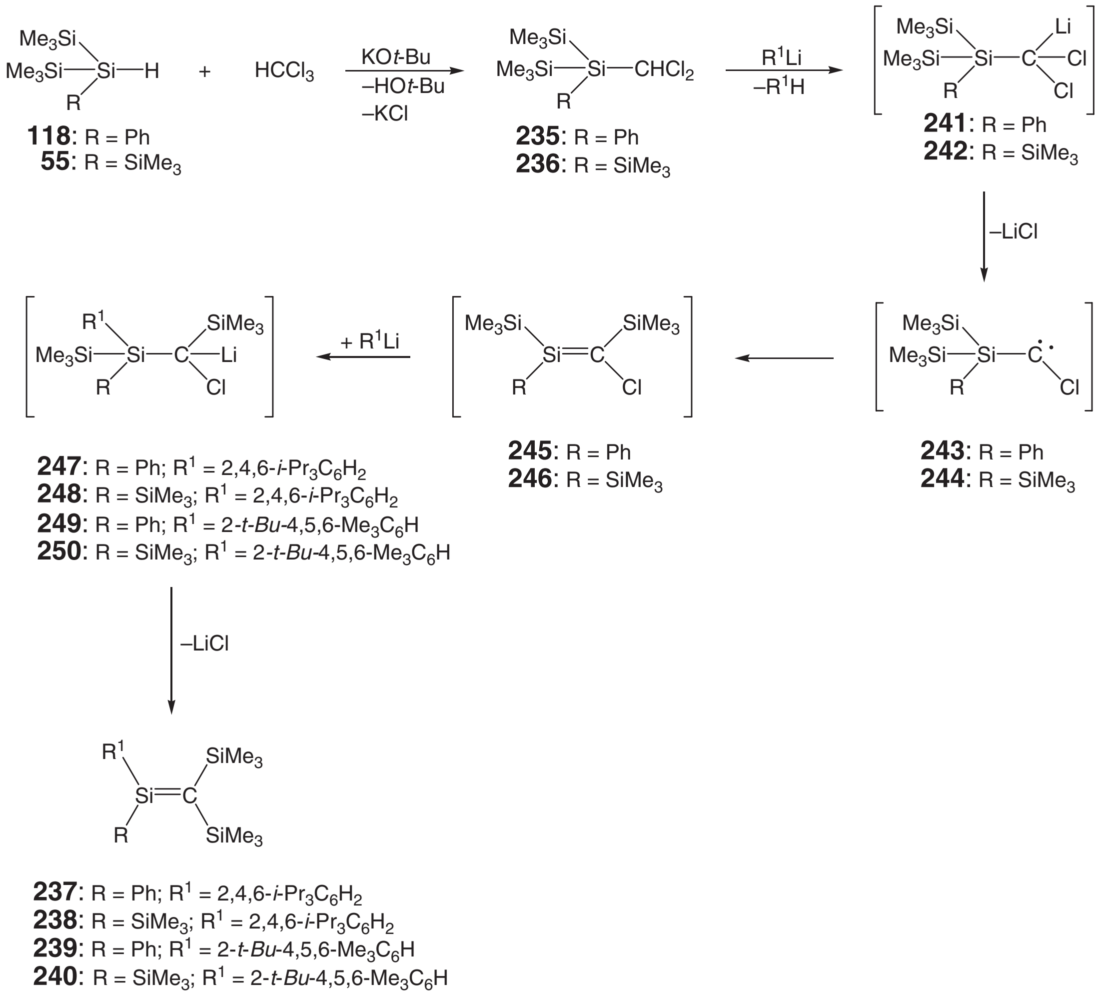


Scheme 32

Silenes (silaethenes), compounds having Si–C double bonds, were first described in 1981, and since then, their chemistry has been substantially developed. Recent extensive reviews on the subject are available by Leigh and Morkin[331] and Lerner.[332] In a series of publications, Ishikawa *et al.* have studied the co-thermolysis of acyltris(trimethylsilylsilanes), thus providing the corresponding silene intermediates with olefins and acetylenes.[333–340] For instance, the reaction of pivaloyl- and adamantoyltris(trimethylsilylsilanes) **224** and **225** with trimethylsilyl acetylene **226** and bis(trimethylsilyl) acetylene **132** at 120 °C proceeds via the initial formation of the silenes **227** and **228**, which undergo cycloaddition with the C–C triple bonds yielding the silacyclobutene derivatives **229** and **230**, and silacyclopropene derivatives **231** and **232**, respectively (Scheme 32). At 160 °C, the silacyclobutene derivatives **229** and **230** undergo a rearrangement into the sila-substituted allene derivatives **233** and **234** (Scheme 32).

Employing acyltris(trimethylsilylsilanes), Azarifar has photochemically generated silenes and studied their reactivity toward hydrazines and ureas.[341] In a series of publications, Ohshita *et al.* have investigated the reaction of acyltris(trimethylsilylsilanes) and tris(trimethylsilyl)silane carboxylates toward organolithium reagents and lithium silanides, which has led to silenes and precursors thereof.[342,343] Similar chemistry has been reported by Oehme *et al.*, who have studied the base-induced elimination of trimethylsilanolate from hydroxyalkyltris(trimethylsilyl)silanes providing transient silenes.[344–347] Notably, the acid-induced arrangement of hydroxyalkyltris(trimethylsilyl)silanes has also been studied.[348,349] More recently, Oehme *et al.* have reported on the synthesis of stable and transient silenes starting from dichloromethyloligosilanes.[350,351] The required dichloromethyloligosilanes $(Me_3Si)_2RSiCHCl_2$ (**235**, R = Ph; **236**, R = $SiMe_3$) have been obtained by treatment of the H-silanes $(Me_3Si)_2RSiH$ (**118**, R = Ph; **55**, R = $SiMe_3$) with the dichlorocarbene CCl_2, generated *in situ* from KO*t*-Bu and $CHCl_3$ (Scheme 33). For the synthesis of the silenes $RR^1SiC(SiMe_3)_2$ (**237**, R = Ph, R^1 = 2,4,6-*i*-$Pr_3C_6H_2$; **238**, R = $SiMe_3$, R^1 = 2,4,6-*i*-$Pr_3C_6H_2$; **239**, R = Ph, R^1 = 2-*t*-Bu-4,5,6-Me_3C_6H; **240**, R = $SiMe_3$, R^1 = 2-*t*-Bu-4,5,6-Me_3C_6H), the dichloromethyloligosilanes $(Me_3Si)_2RSiCHCl_2$ (**235**, R = Ph; **236**, R = $SiMe_3$) have been treated with 2 equiv. of a bulky organolithium reagent R^1Li (R^1 = 2,4,6-*i*-$Pr_3C_6H_2$, 2-*t*-Bu-4,5,6-Me_3C_6H). Notably, the first equivalent is responsible for the deprotonation and lithiation of the α-carbon atom of **235** and **236** leading to the transient formation of the carbenoid **241** and **242**. The subsequent 1,1-lithium chloride elimination gives rise to the transient silylchlorocarbene **243** and **244**, which undergoes rearrangement into the chloro silene **245** and **246** via a 1,2-Si,C shift of a trimethylsilyl group. The nucleophilic addition of the second equivalent of the organolithium reagent, R^1Li, to the Si–C double bonds, affords new carbenoids **247–250**, which react under 1,1-lithium chloride elimination to form the silenes $RR^1SiC(SiMe_3)_2$ (**237**, R = Ph, R^1 = 2,4,6-*i*-$Pr_3C_6H_2$; **238**, R = $SiMe_3$, R^1 = 2,4,6-*i*-$Pr_3C_6H_2$; **239**, R = Ph, R^1 = 2-*t*-Bu-4,5,6-Me_3C_6H; **240**, R = $SiMe_3$, R^1 = 2-*t*-Bu-4,5,6-Me_3C_6H) (Scheme 33). For related hypercoordinate silenes of **237–240**, see Section 6.6.

Recently, Sakamoto *et al.* have reported on the synthesis of the first stable 4-silatriafulvenes, which contain Si–C double bonds that are significantly less polar than those of previously described silaethenes.[352–354] The

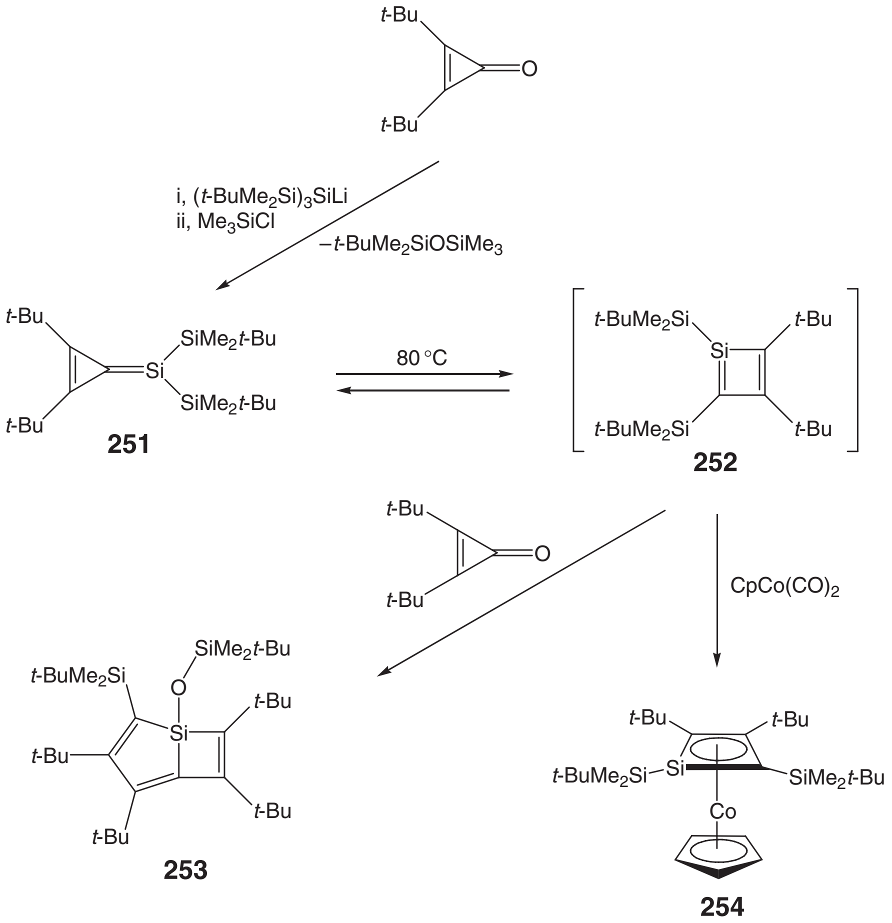


Scheme 33

4-silatrifulvene **251** is accessible via the sila-Peterson reaction of di-*tert*-butylcyclopropenone with lithium tris(*tert*-butyldimethylsilyl)silanide and Me_3SiCl (Scheme 34). At 80 °C, the 4-silatrifulvene **251** reversibly rearranges into the silabutadiene derivative **252**, which in the presence of di-*tert*-butylcyclopropenone forms the sila-bicyclic compound **253**. In the presence of η^5-cyclopentadienyldicarbonylcobalt, the silabutadiene derivative **252** furnishes a rare example of a cobalt silacyclobutadiene complex, namely (η^5-cyclopentadienyl)[η^4-1,2-bis(*tert*-butyldimethylsilyl)-3,4-di-*tert*-butyl-1-silacyclobutadiene]cobalt **254** (Scheme 34).

3.09.2.7 Silyl Acetylenes, Silyl Ketenes, and Silols

Although silyl-substituted acetylenes are a well-established class of compounds, they have attracted considerable attention in recent years owing to applications in material science and organometallic synthesis. For instance, rigid polymers based on conjugated acetylene units possess photoluminescent and electroluminescent properties, which make them potentially useful for light-emitting electroluminescent devices, especially for large-area light-emitting displays. Incorporation of silicon atoms into the polymer backbones is expected to lower the ionization energy compared to pure carbon chains.[355] Corriu has reported the use of alkynylsilanes as pre-ceramics for the preparation of silicon carbides.[356] Takahashi *et al.* have described the zircononene-mediated intramolecular C–C-bond formation of two alkynyl groups in bis(alkynyl)silanes yielding silacyclobutene derivatives.[357]



Scheme 34

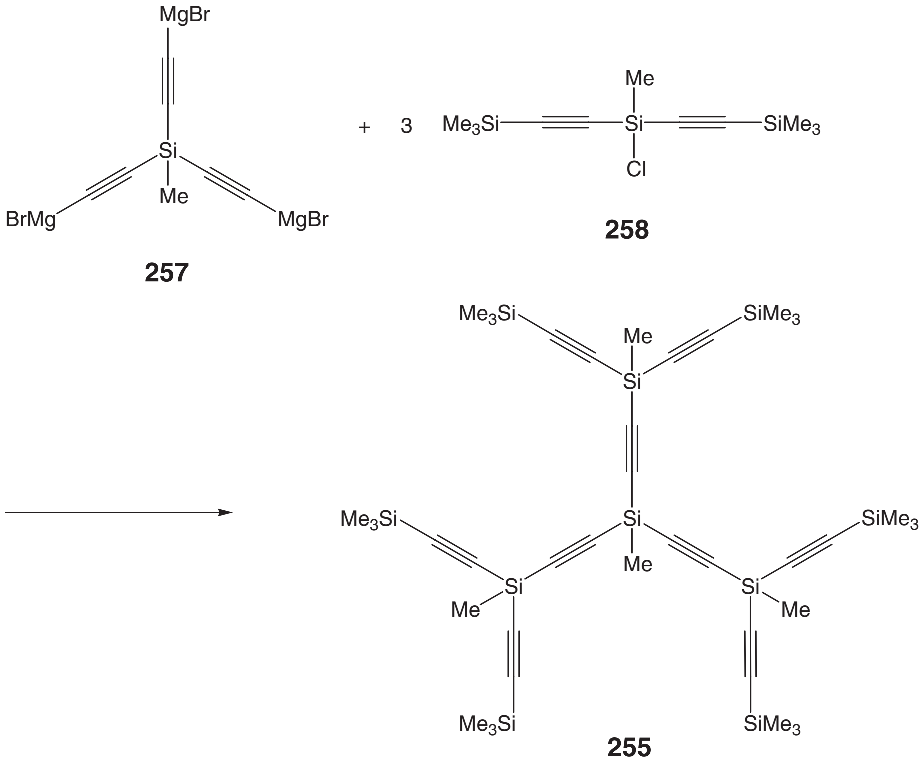
In 1999, Sekiguchi *et al.* prepared the first silyl acetylene dendrimers **255 and 256** with up to 22 Si atoms and 21 acetylene units (Schemes 35 and 36).[358] The preparation of **255** and **256** has been achieved by the reaction of the triple Grignard reagent **257** with the trisila diyne **258** and the heptasila hexayne **259**, respectively.

Novel oligoacetylenic silanes **260–263** have been prepared and their molecular and electronic structures explored (Scheme 37).[359] The synthetic approach involves lithiation of the acetylenes Me_3SiCCH **226** and PhCCH using BuLi prior to reaction with the chlorosilanes Ph_2SiCl_2 and $(Me_3Si)_2SiBr_2$. The treatment with $CaCO_3$/MeOH cleaves one trimethylsilyl group of **260** and leads to the formation of **262**. The reaction of **262** with butyllithium and Ph_2SiCl_2 provides **263** having four acetylene units. The spectroscopic investigations indicate that conjugation is operative through Si.

Marschner *et al.* have developed new synthetic routes to prepare alkynyl oligosilanes **264–268** containing tris-(trimethylsilyl)silyl groups, which were transformed into their corresponding silyl anions **269–271** that may serve as versatile building blocks for more extended rigid scarefolds (Scheme 38).[360] A number of symmetric tetraalkynyldisilanes have been prepared by Roesky *et al.*[361]

Using 1,4-dilithiobutadiyne and *i*-$Pr_2ClSiSiCl$*i*-Pr_2, Matsumoto *et al.* have prepared *cyclo*-[(disilanylene)(butadiyne)]s **272–274** that contain 12-, 18-, and 24-membered rings, and consist of alternating sequences of disilane and butadiyne units (Scheme 39).[362]

The synthesis of novel triorganosilyl-substituted ketenes and bisketenes has been described by Tidwell *et al.*[363–368] The gas-phase pyrolysis of simple silaalkynyl ethers $R_2R^1SiCCOEt$ (**275**, $R=R^1=Me$; **276**, $R=R^1=i\text{-}Pr$; **277**, $R=Me$, $R^1=Ph$; **278**, $R=Me$, $R^1=t\text{-}Bu$) at 115 °C affords triorganosilyl-substituted ketenes $R_2R^1SiCHCO$ (**279**, $R=R^1=Me$; **280**, $R=R^1=i\text{-}Pr$; **281**, $R=Me$, $R^1=Ph$; **282**, $R=Me$, $R^1=t\text{-}Bu$) as stable products (Scheme 40). The reaction of bis(triorganosilyl) acetylenes $Me_2RSiCCSiRMe_2$ (**283**, $R=Me$; **284**, $R=Ph$) with trichloroacetyl chloride in the presence of Zn powder provides the bis(triorganosilyl)-substituted dichlorocyclobutenone **285 and**



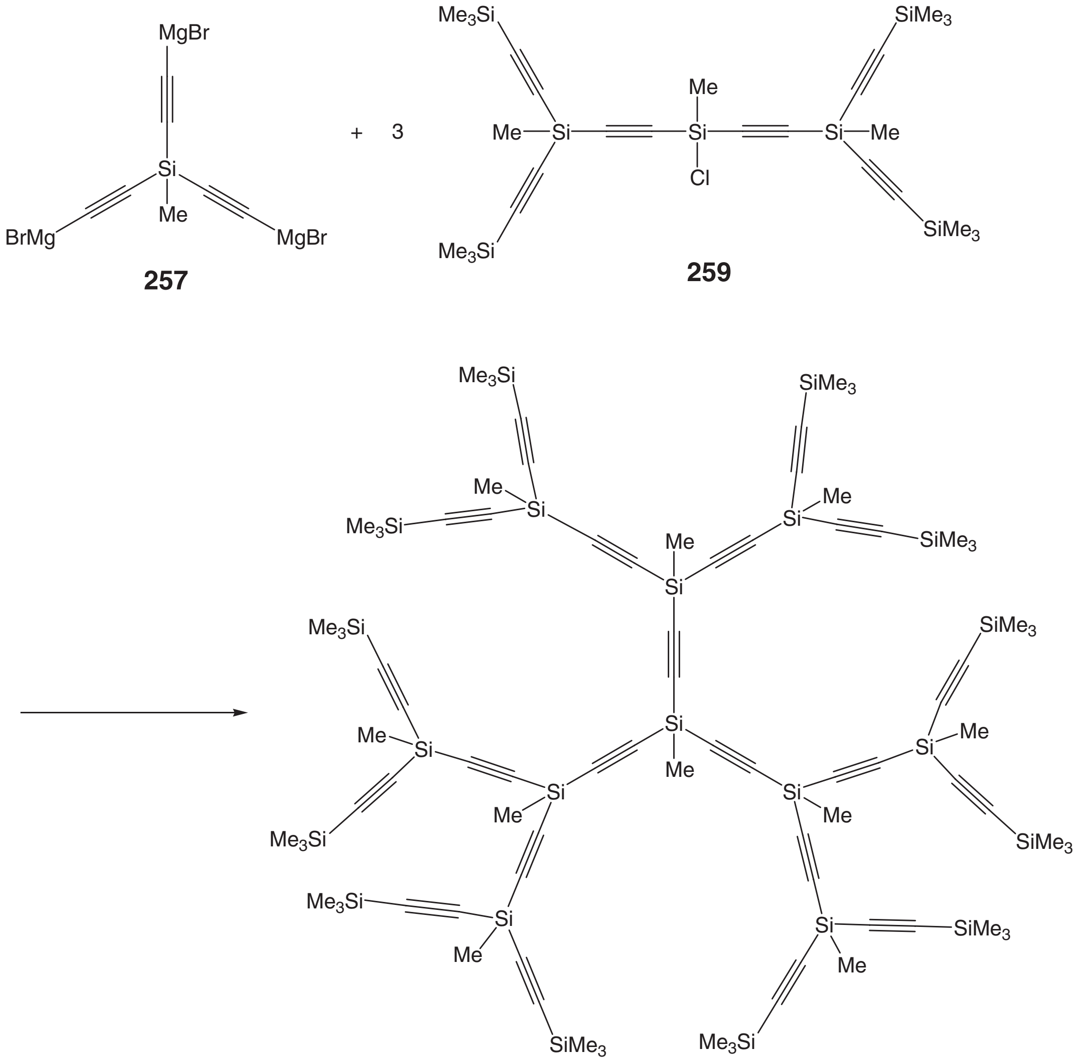
Scheme 35

286, whose subsequent reaction with AgO_2CCF_3 gave rise to the corresponding bis(triorganosilyl)-substituted cyclobutendione 287 and 288. Thermolysis of 287 and 288 affords the bis(triorganosilyl) bisketenes 289 and 290 (Scheme 40).

The bromination and hydrolysis of ketenes and bisketenes have been studied. The reaction of the bis(ketene) 289 with bromine has yielded the dibromo fumarate derivative 290, whose *trans*-configuration has been confirmed by X-ray crystallography (Scheme 41).[366] The hydrolysis of the dibromo fumarate derivative 291 first provided the dibromo derivative (5*H*)-furanone 292. The prolonged reaction with water afforded the maleic anhydride 293. The methanolysis of the dibromo fumarate derivative 290 has resulted in the formation of an isomeric mixture of dimethyl 2,3-bis(trimethylsilyl)fumarates, of which the *trans*-isomer 294 dominates over the *cis*-isomer 294 (Scheme 41). The hydrolysis of the bisketene 289 has produced a mixture of bis(triorganosilyl)-substituted succinic anhydrides, of which the *trans*-isomer 295 dominates over the *cis*-isomer 296 (Scheme 41).[366] Substitution reactions of $(Me_3Si)_3SiLi$ with ketenes have been reported.[369]

Although silols, silacyclopentadienes, are well established since the pioneering work of Braye and Hübel in 1959, their unique electronic structure has stimulated much research in recent years.[370] The most notable feature of silols is their high electron-accepting property, associated with their low-lying LUMOs. Potential applications of silols span a wide range, including electron-transporting materials, electroluminescent (EL) devices, and electronic sensors. A general review on silols by Yamaguchi and Tamao is available.[371] More specialized reviews on (aromatic) silol anions and polymeric silols have been written by Saito and Yoshioka in 2005 and by Dyer *et al.* in 2003.[372,373]

Silols containing phenyl groups are synthesized best starting from diphenylacetylene and lithium, which affords 1,4-dilithio-1,2,3,4-tetraphenylbutadiene that readily react with the chlorosilanes $SiCl_4$, Me_2SiCl_2, Ph_2SiCl_2, and $PhSiCl_3$ to produce the silols 297–300 (Scheme 42). Silols containing methyl groups, such as 301, are accessible upon metallation of 1,4-diiodo-1,2,3,4-tetramethylbutadiene providing the corresponding dilithio compound that may be reacted with chlorosilanes, such as $SiCl_4$ (Scheme 42). The 2,5-dilithiated 1,1-bis(diethylamino) silol 302 is available by the reduction of bis(phenylethynyl)silane 303 with lithium naphthalenide (Scheme 42). The subsequent reaction of 302 with trimethylchlorosilane and dimethyl sulfate provides access to the 1,1-bis(diethylamino) silols 304 and 305, having trimethylsilyl and methyl groups in vicinal positions (Scheme 42).



257

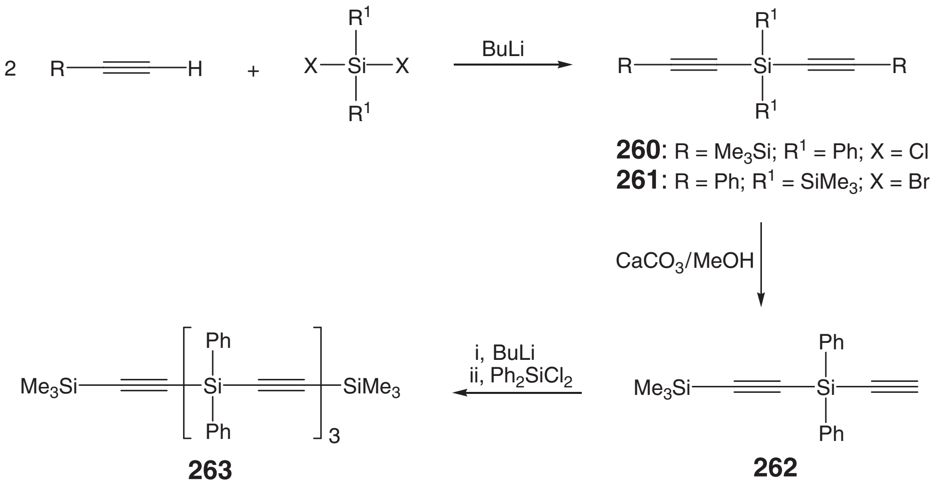
259

256

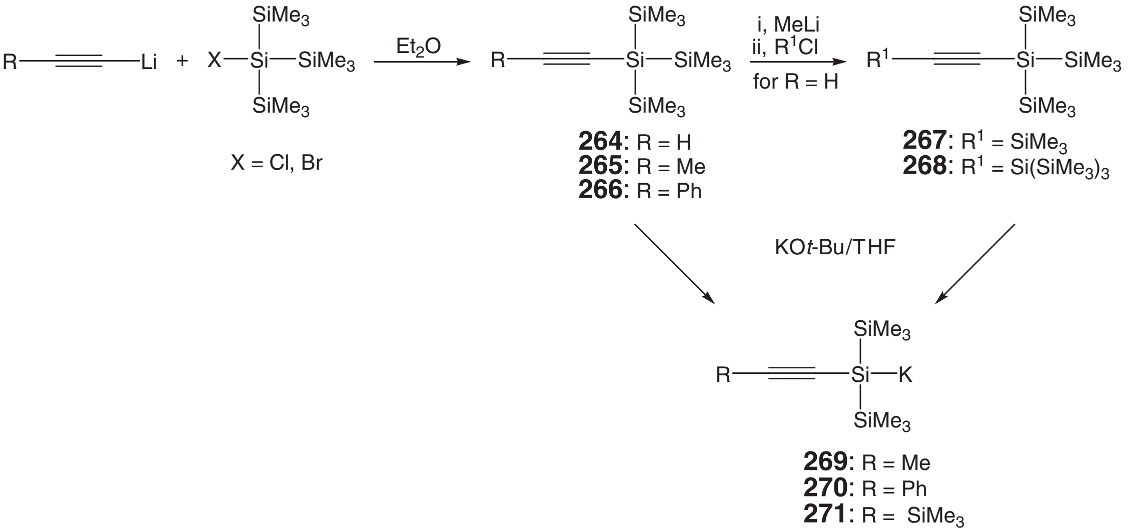
Scheme 36

The 1,1-bis(diethylamino) silols **304 and 305** are excellent precursors for the synthesis of other 1,1-difunctionalized silols (Scheme 43).[374] The reaction of **304 and 305** with EtOH/$AlCl_3$ and HCl produces the silols **306** and **307** containing ethoxy groups or chlorine atoms attached to the silicon. The 1,1-dichloro silols **308 and 309** have been converted into the corresponding 1,1-difluoro silols **310 and 311** with ZnF_2. Hydrolysis of **309 and 311** yields the fluorosilanol **312** and the silanediol **313**, respectively (Scheme 43).

The perphenylated 1,1-dichloro silol **297** is also a versatile starting material for the preparation of new silol derivatives (Scheme 44). The reaction of **297** with the metallated acetylene derivatives PhCCLi and HCCMgBr provides access to the silols **314 and 315** containing ethynyl groups, whereas the careful hydrolysis with $NaHCO_3$ affords the silandiol **316**.[375] Reduction of **297** with $LiAlH_4$, sodium (short reaction time), and lithium (long reaction time) gives rise to formation of the dihydride **317**, the polysilole **318** having terminal chlorine atoms,[376] and the dilithium disilanide **319**, respectively.[377–379] The silole dianions are believed to be aromatic. The negative charge of **319** is partly distributed over the delocalized π-electron system, explaining the high electron-accepting property and the partial silylenoide character of the silicon atom. The catalytic dehydrocoupling of **317** using H_2PtCl_6 and $RhCl(PPh_3)_3$ gives access to low molecular weight polysilols **320** having terminal hydrogen atoms (Scheme 44).[380]



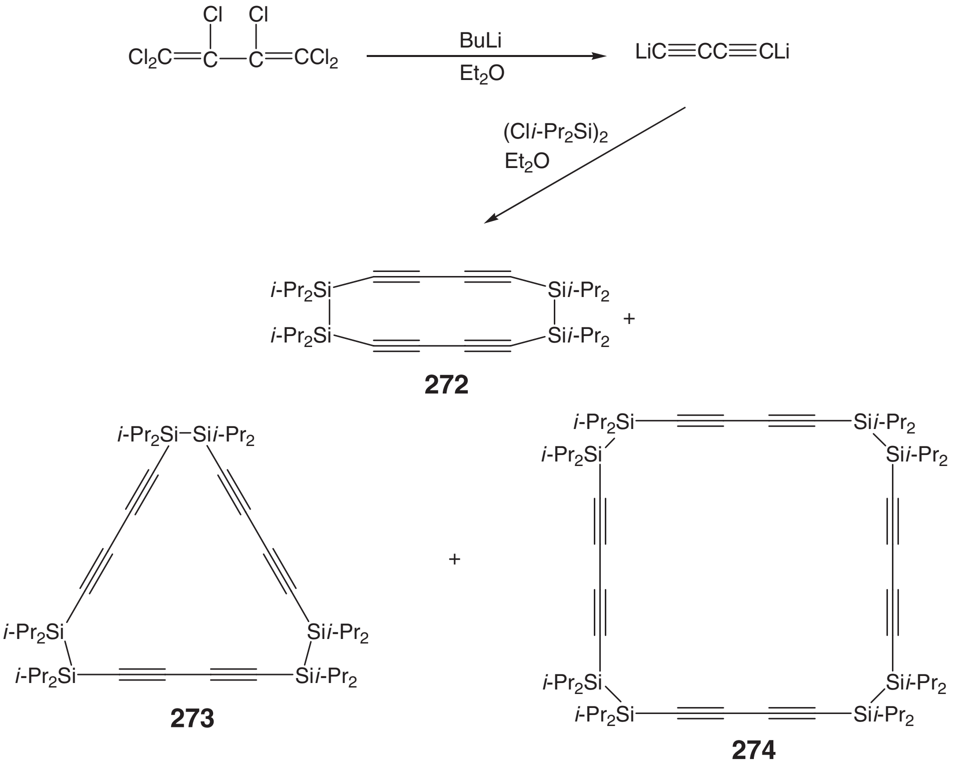
Scheme 37



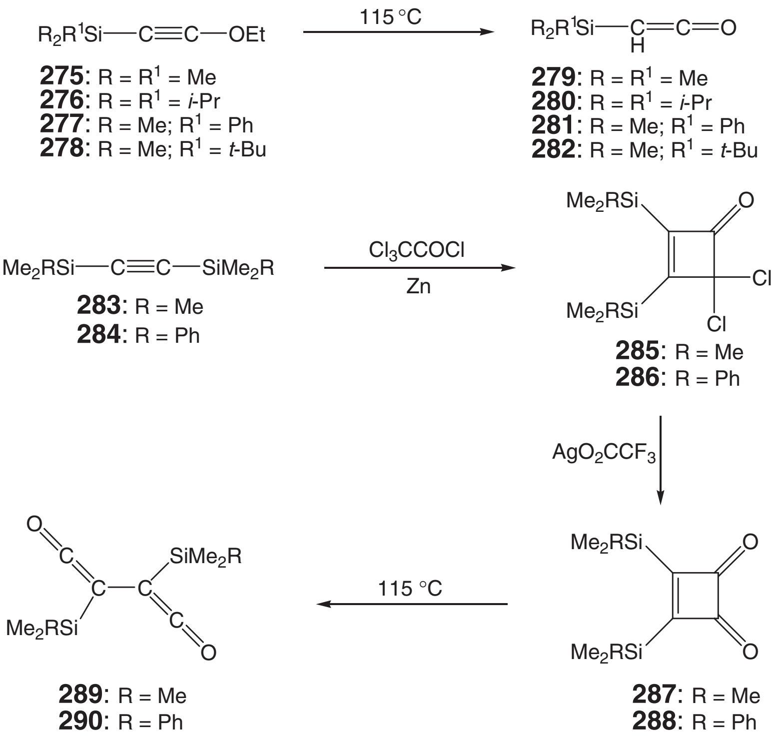
Scheme 38

Being closely related to silols and their dianions, the synthesis of dichloro silaindene and dichloro silafluorene and their corresponding silaindenyl and silafluorenyl dianions have been reported by Boudjouk *et al.*[381] and West *et al.*[382,383] The route leading to silafluorene derivatives involves the reaction of 1,2-dibromobenzene with butyllithium giving 2,2′-dibromo biphenyl, whose reaction with butyllithium and SiCl$_4$ provides the dichloro silafluorene **321** and spirocyclic compound **322** as side-product (Scheme 45).[382,383] Reduction of the dichloro silafluorene **321** with potassium produces the polysilafluorene **323** at mild conditions and the dipotassium silafluorenyl **324** at harsher conditions, respectively (Scheme 45).[382,383] The reaction of **324** with Me$_3$SiCl yields the trisilane **325**. In an attempt to crystallize **324** as a crown ether adduct, a unique diradical dianion has been obtained.[382,383]

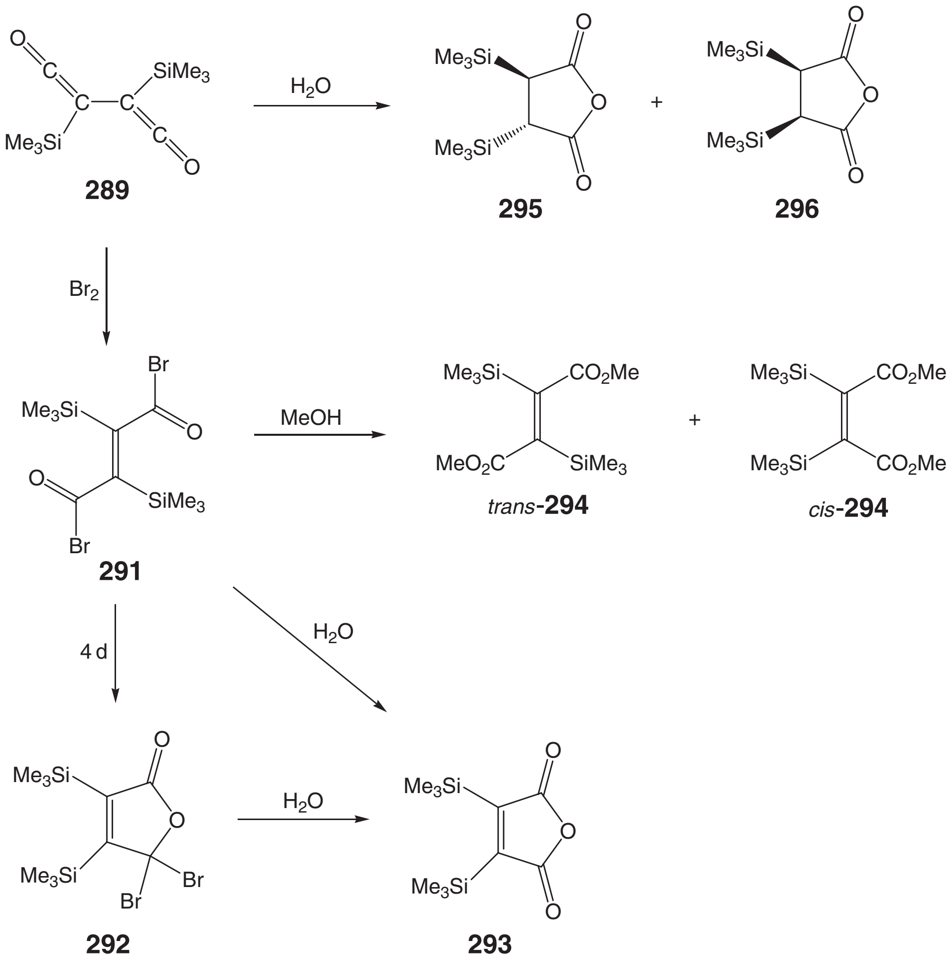
In general, the annelation of π-conjugated frameworks is an effective way to achieve the enhancement of conjugation and the decrease of the HOMO–LUMO gap. The novel bis- and tetrakis-silicon-bridged stilbenes **326** and **327** possessing extended π-conjugated frameworks and silole units have been developed by Yamaguchi and Tamao *et al.* (Scheme 46).[384] Compounds **326** and **327** are accessible by the intramolecular reductive cyclization of the silylated phenylacetylenes **328** and **329**, with lithium naphthalenide and show interesting fluorescence properties in the visible range upon UV irradiation (Scheme 46).[385] Ladder oligo(phenylene–vinylene)s **330** and **331** containing



Scheme 39



Scheme 40

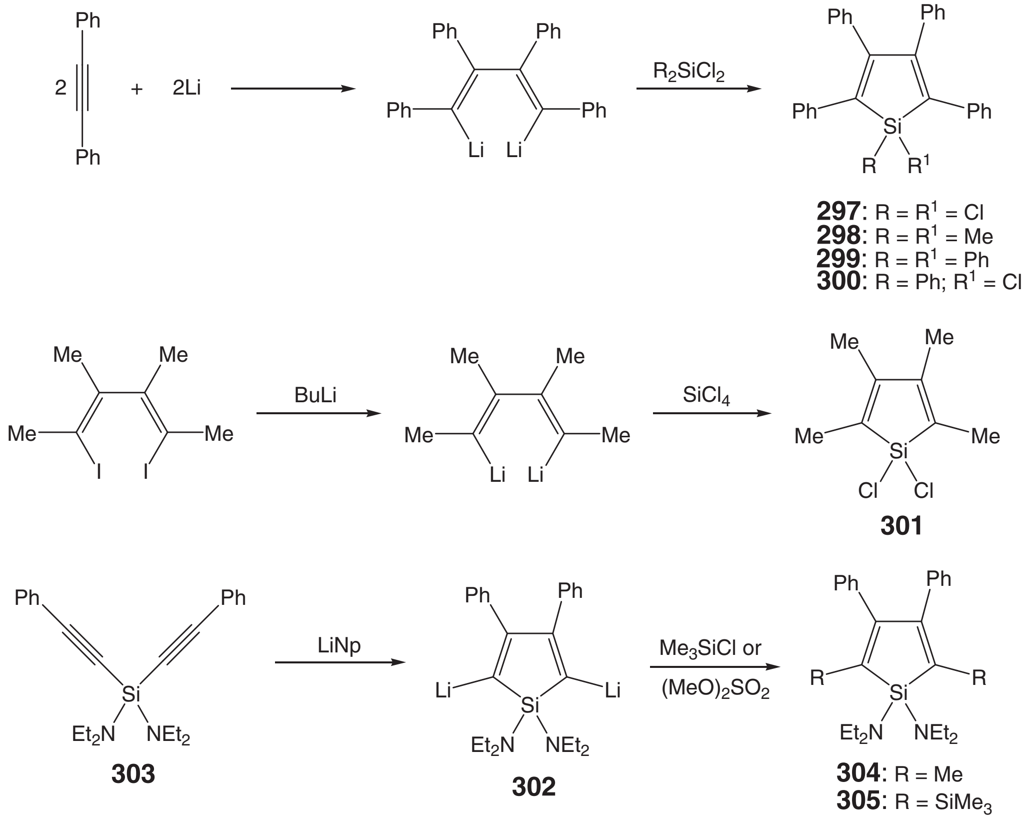


Scheme 41

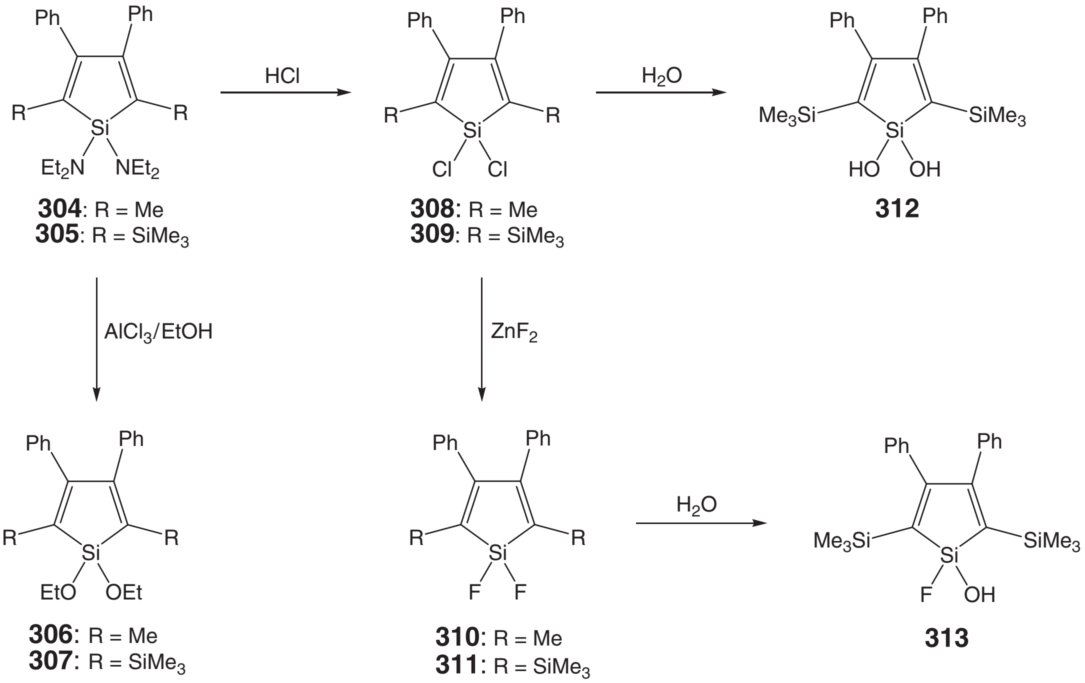
fewer silicon atoms than **326** and **327** have been prepared by Yamaguchi *et al.* in two steps. Thus, the 1,4-bis(phenyl–ethynyl)benzenes **332** and **333**, each containing two silicon atoms, have been subject to intramolecular reductive coupling using lithium naphthalenide, yielding the bis(silaindenyl) derivatives **334** and **335**, whose intramolecular Friedel–Crafts cyclization have provided the ladder oligo(phenylene–vinylene)s **330** and **331** (Scheme 47).[386]

3.09.2.8 Sila-aromatic Compounds

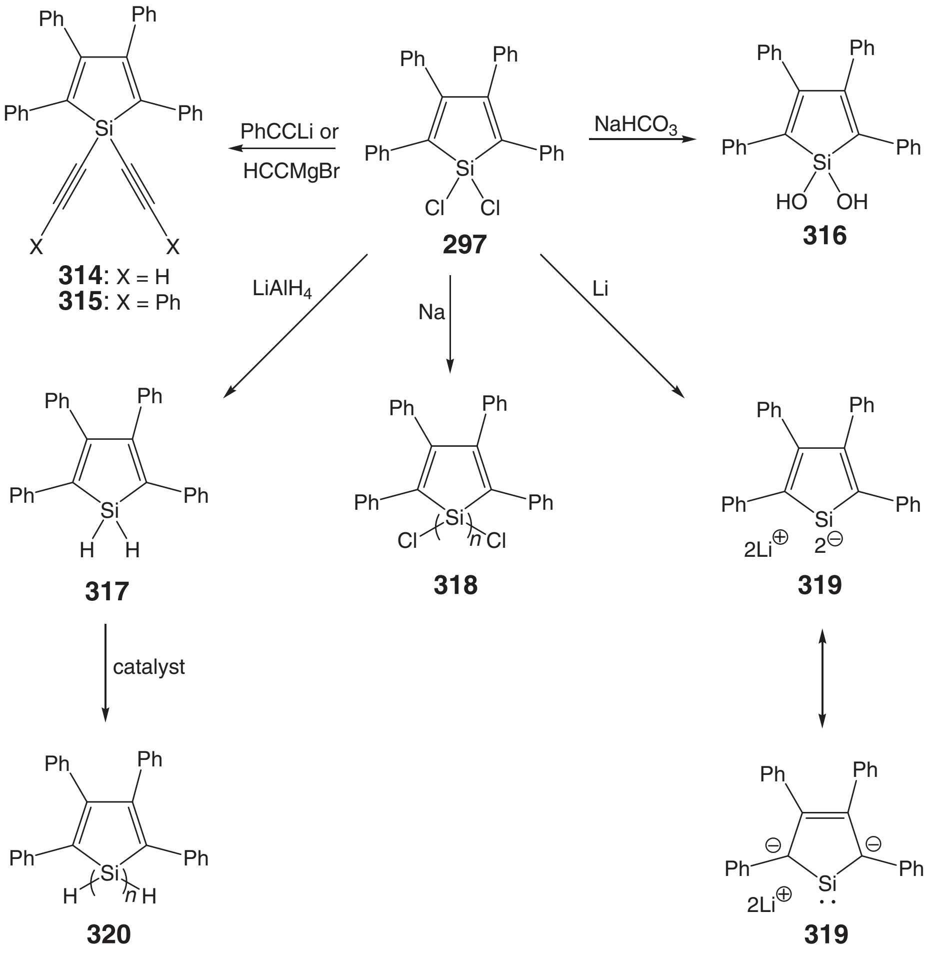
Significant advances have been made in the field of sila-aromatic compounds. These have been covered in two recent reviews by Tokitoh.[387,388] The first stable silabenzene **336** derivative containing formally an sp^2-hybrized Si atom has been obtained by Tokitoh *et al.* (Scheme 48). It is accessible upon the reaction of the chloro silacyclohexadiene **337**, containing a bulky substituent attached to the silicon with *tert*-butyl lithium.[389,390] The silabenzene **336** possesses a fully delocalized π-electron-ring system; however, the reaction with most reagents leads to products lacking aromaticity. Thus, the reaction of **336** with phenylacetylene, styrol and benzophenone has produced bicycle[3,3,3]octane derivatives **338–340** containing Si atoms at bridgehead positions (Scheme 48).The reaction of **336** with mesityl isocyanate, 1,3-dimethyl-1,3-butadiene, sulfur, and selenium has afforded bicyclic silacyclohexadiene derivatives **341–344** (Scheme 48). The hydrolysis and methanolysis of **336** gave rise to mixtures of monocyclic silacyclohexadiene oxo compounds **345–348** (Scheme 48). By contrast, the aromaticity remains intact in the reaction of **336** with the acetonitrile adducts of [M(CO)$_3$] (M = Cr, Mo) yielding the first η^6-silabenzene–M(CO)$_3$ complexes **349** and **350** (Scheme 48).[391]



Scheme 42



Scheme 43



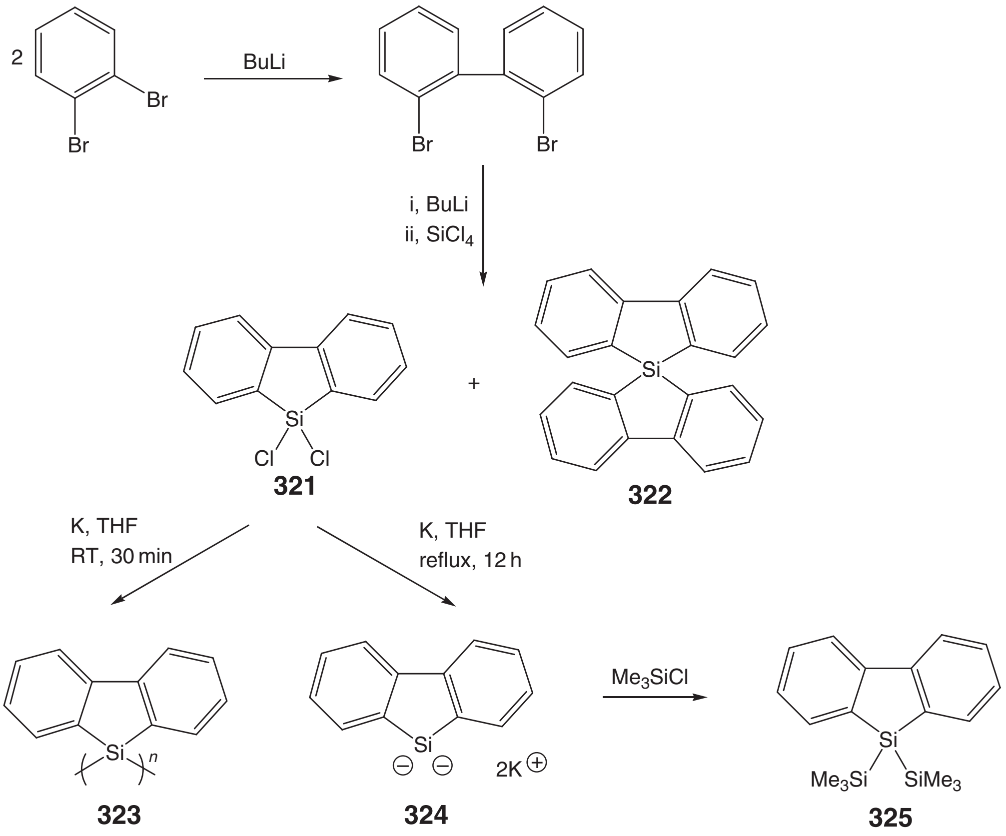
Scheme 44

Besides the silabenzene **336**, a number of sila-aromatic naphthaline and anthracene derivatives **351–353** have been synthesized and their reactivity studied (Figure 2).[392–395]

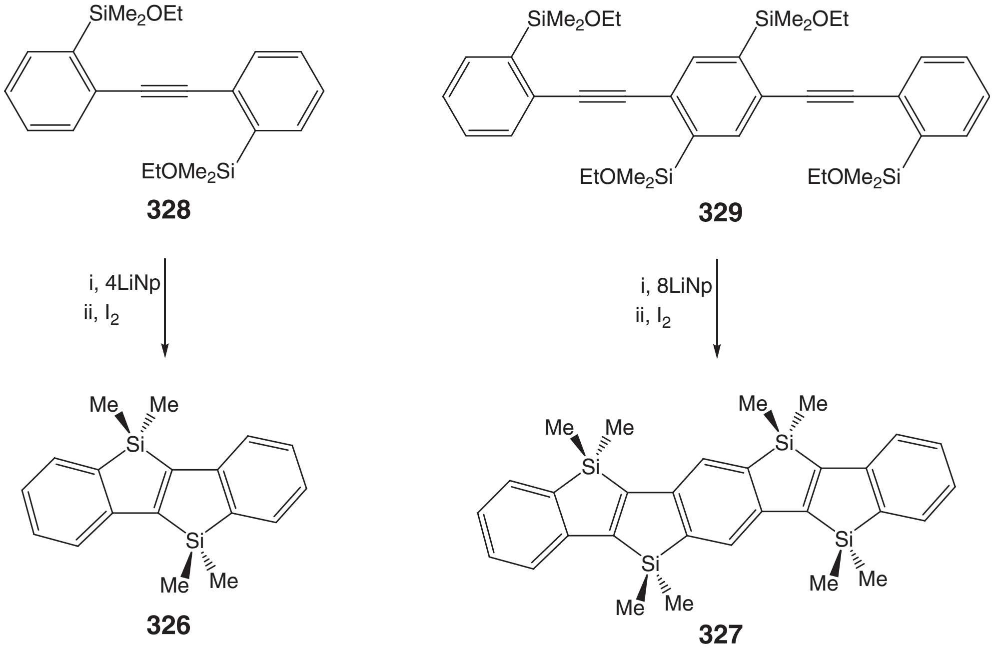
3.09.3 Silicon–Nitrogen Compounds

3.09.3.1 Silyl Amines, Silyl Hydrazines, and Iminosilanes

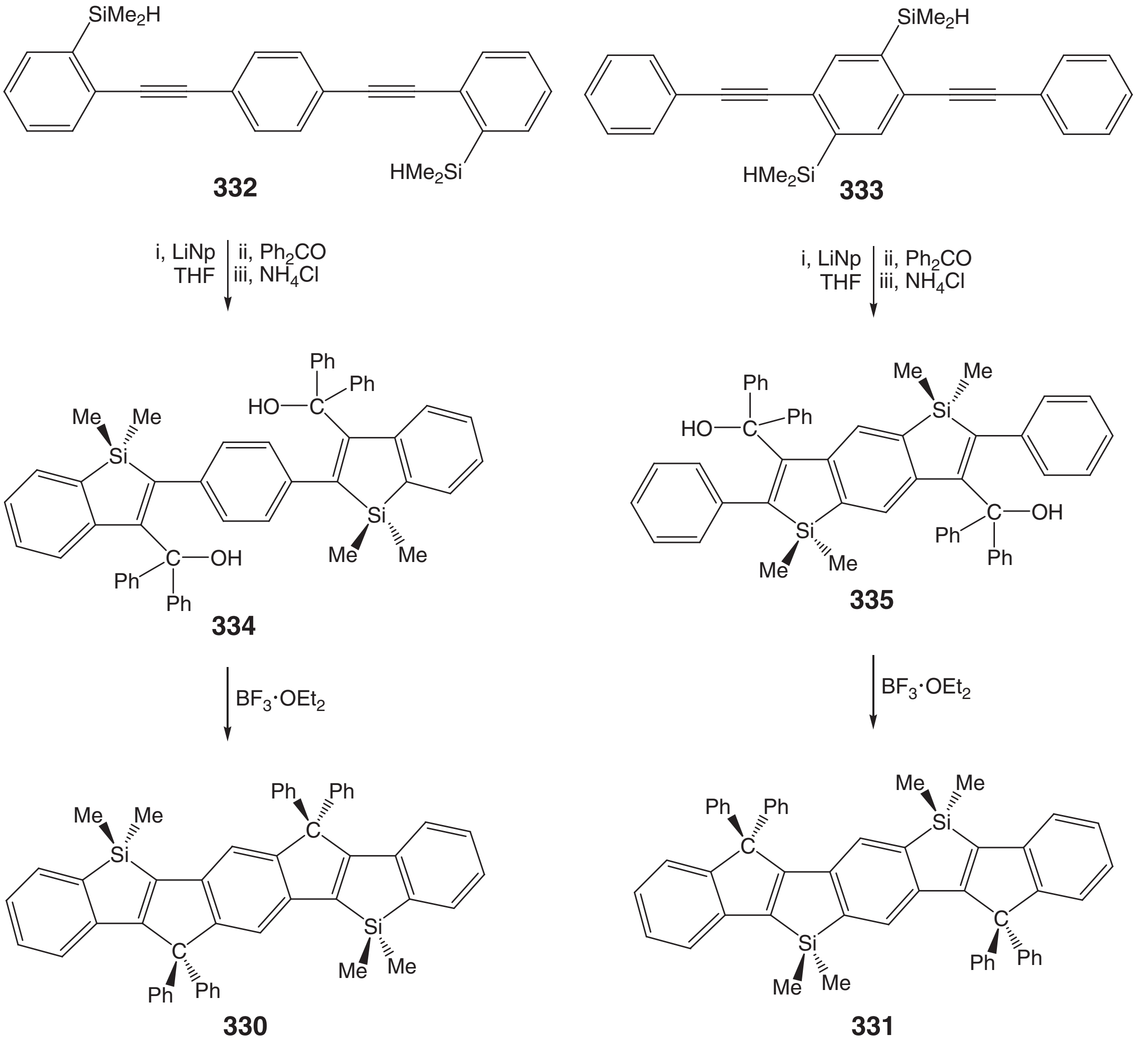
The chemistry of silazanes, compounds that contain Si–N bonds, was pioneered by Aylett, Bailey, Wannagat, West, and others in the 1960s.[396] During the 1980s, the renewed interest in this chemistry stemmed from the potential of often poorly characterized (poly)silazanes to serve as precursors for the preparation of Si/N and Si/C/N ceramics. A comprehensive review of the precursor chemistry and related material science aspects was written by Dunogues *et al.* in 1995.[397] The chemistry of compounds with Si–N bonds was reviewed by Klingebiel *et al.* in 2001.[398] Recently, efforts have been directed toward the ammonolysis of organotrichlorosilanes (in the presence of Na) providing molecular silazanes including rings and cages. Power *et al.* have achieved the isolation of a monosilazane 2,4,6-$R_3C_6H_2Si(NH_2)_3$ (**354**, R = Me; **355**, R = Ph), and using bulky terphenyl and mesityl substituents (Scheme 49).[399] Roesky *et al.* have reported that the ammonolysis of the less bulky organotrichlorosilanes $(Me_3Si)_2HCSiCl_3$, $PhSiCl_3$, $EtSiCl_3$, $MeSiCl_3$ provides the disilazane $[(Me_3Si)_2HCSi(NH_2)_2]_2NH$ **356**, the cyclotrisilazane $[PhSi(NH_2)NH]_3$ **357**, and the hexameric silazane cages $[(RSi)(NH)_{1.5}]_6$ (**358**, R = Me; **359**, R = Et), respectively (Scheme 49).[400,401]



Scheme 45



Scheme 46

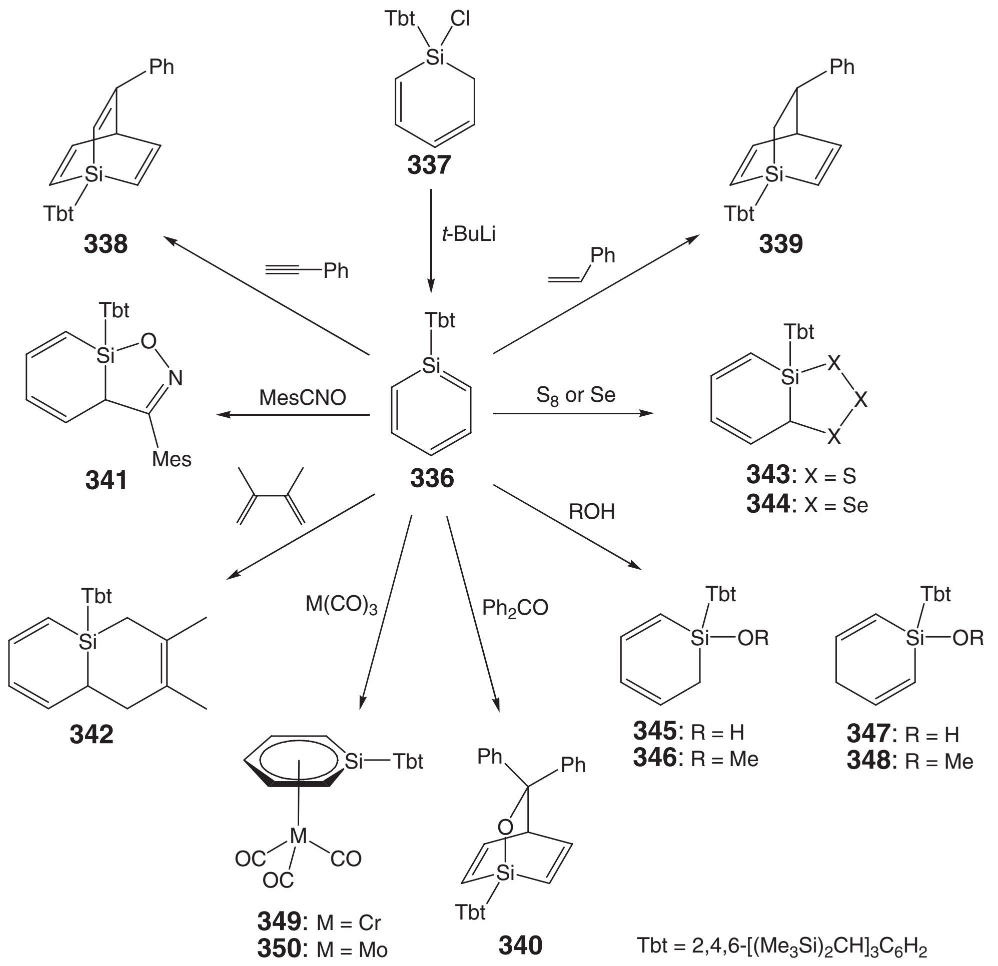


Scheme 47

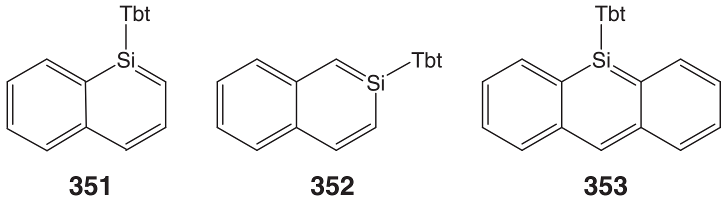
Routes to the stepwise synthesis of functionalized silazanes have been developed by Klingebiel *et al.* For instance, di-*tert*-butylmethylsilylamine $t\text{-}Bu_2MeSiNH_2$ **360** reacts with butyllithium to give rise to the formation of the tetrameric lithium derivative $[t\text{-}Bu_2MeSiNHLi]_4$ **361**, which has proved to be a versatile precursor for reactions with halosilanes. Depending on the stoichiometry applied, **361** reacts with SiF_4 and $SiCl_4$ to form halo-silazane products $(t\text{-}Bu_2MeSiNH)_4Si$ **362**, $(t\text{-}Bu_2MeSiNH)_3SiF$ **263**, $(t\text{-}Bu_2MeSiNH)_2SiX_2$ (**364**, X = F; **365**, X = Cl), and $(t\text{-}Bu_2MeSiNH)SiX_3$ **366**, X = F; **367**, X = Cl), respectively (Scheme 50). The reaction of **361** with the bis(trimethylsilyl)-methylene-bridged bis(trifluorosilane) $(Me_3Si)_2C(SiF_3)_2$ has provided the cyclic product **368** and the open-chain product **369**, respectively (Scheme 50).[402]

The lithiation of the difluoro trisilazane $(t\text{-}Bu_2MeSiNH)_2SiF_2$ **364** with 1 equiv. of butyllithium has provided the stable lithium difluoro silylamide **370**. Upon heating of **370**, lithium fluoride elimination occurs, and the symmetric four-membered cyclodisilazane **371** containing exocyclic fluorine atoms and di-*tert*-butylmethylsilylamide groups forms. The reaction of the lithium difluoro silylamide **370** (Scheme 51) with Me_3SiCl has yielded the difluoro tetrasilazane $(t\text{-}Bu_2Me_2Si)(Me_3Si)NSiF_2(NHSiMe t\text{-}Bu_2)$ **372**. The reaction of **372** with methyllithium has produced the lithium difluoro amide **373**, whose structure has been elucidated by X-ray diffraction (Scheme 51).[402]

The reaction of the bis(trimethylsilyl)methylene-bridged bis(difluoro disilazane) $(Me_3Si)_2C[SiF_2(NHSiMe t\text{-}Bu_2)]_2$ **369** with 2 equiv. of methyllithium has produced the bis(trimethylsilyl)methylene-bridged bis(lithium difluoro



Scheme 48

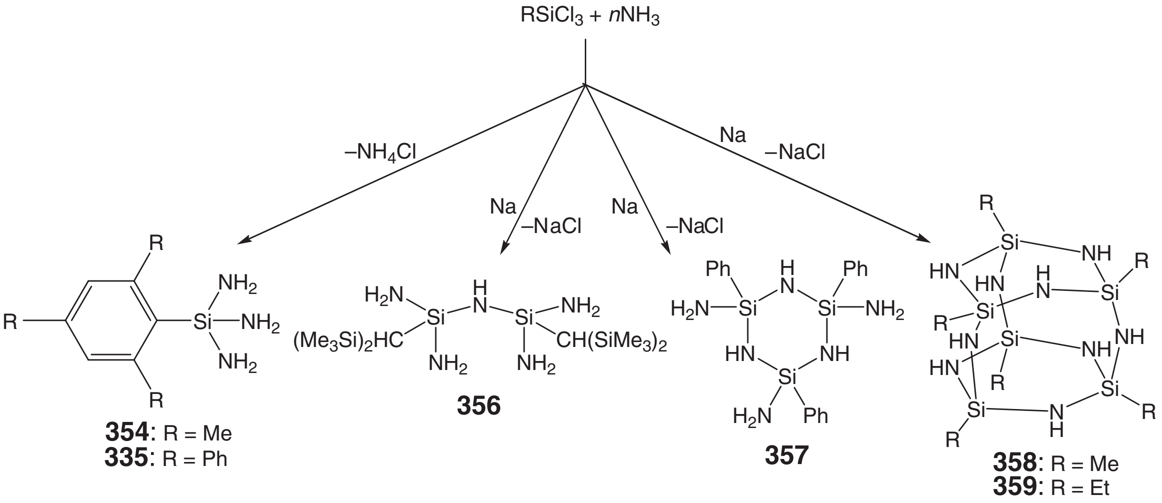


Tbt = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$

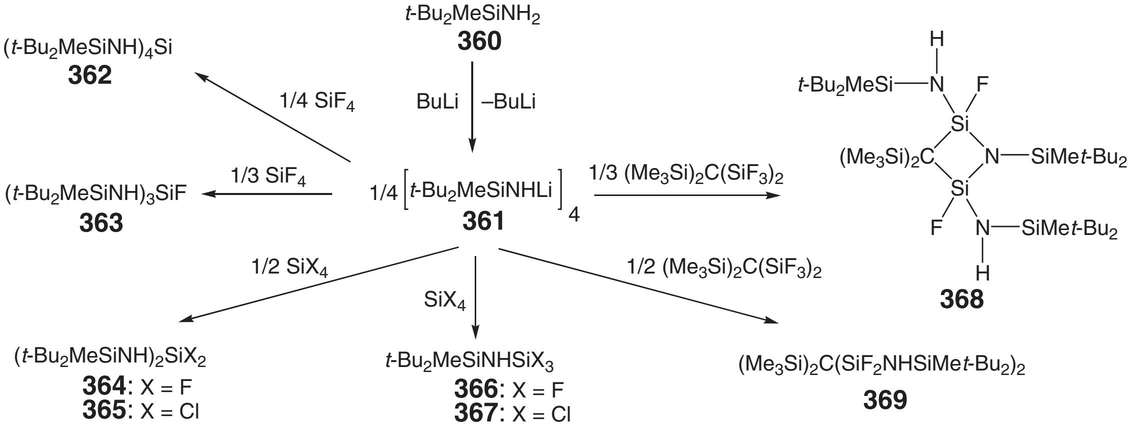
Figure 2

silylamide) $(Me_3Si)_2C[SiF_2(NLiSiMe$*t*-$Bu_2)]_2$ **374**. In the presence of THF, **374** gives rise to lithium fluoride elimination and formation of the unsymmetric cyclic product **375** (Scheme 52).[402]

The lithiation of the unsymmetric disilazane *t*-$Bu_2MeSiNHSiCl_3$ **367** with 2 equiv. of butyllithium has provided the 1,3-bis(triorganosilyl)-2,2,4,4-tetrachlorocyclodisilazane **376**, whose reduction with $LiAlH_4$ has resulted in the formation of 1,3-bis(triorganosilyl)cyclodisilazane **377** containing two cyclic SiH_2 moieties (Scheme 53).[403] The reaction of **376** with an excess of ammonia has exclusively provided the *trans*-1,3-bis(triorganosilyl)-2,4-dichloro-2,4-di(amino)cyclodisilazane **378** (Scheme 53).[404]



Scheme 49

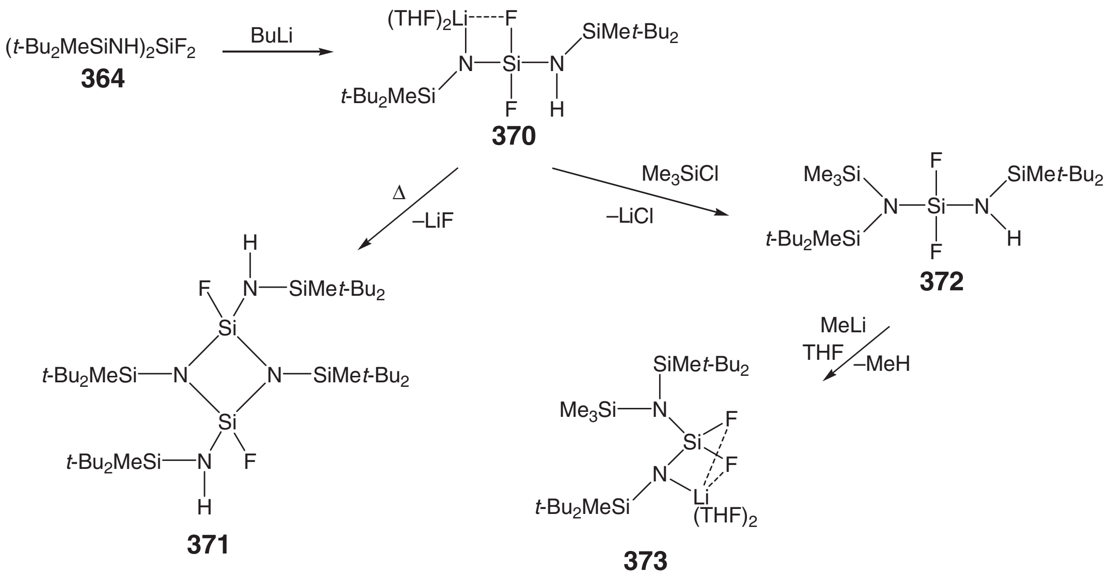


Scheme 50

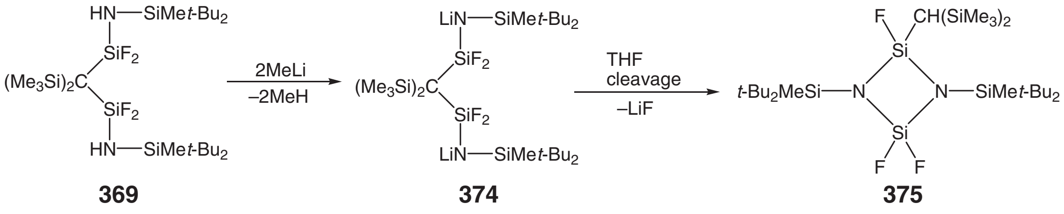
By contrast, the preparation of the 1,3-bis(dimethylchlorosilyl)cyclodisilazane 379 can be achieved in one step by the condensation of the cyclotetrasilazane $(Me_2SiNH)_4$ 380 with Me_2SiCl_2 (Scheme 54).[405] The reduction of 379 with sodium has given rise to formation of the polycyclodisilazane 381, an interesting precursor for SiN-based ceramics (Scheme 54).[405]

With the aim of preparing dendritic silazanes, Xiao and Son have developed novel routes for the synthesis of cyclodisilazanes and branched silazanes.[406] Their approach involves the lithiation of the trisilazane $(RMe_2Si)_2NSiMe_2NH_2$ (382, R = H; 383, R = Me) at the reactive NH_2 group, prior to reaction with Me_2SiCl_2, and Me_2SiHCl and Me_3SiCl, yielding the 1,3-bis(silyl)cyclodisilazanes 384 and 385, and the 2,4-bis(silyl)trisilazanes 386 and 387, respectively (Scheme 55). Chlorination of 386 with BCl_3 affords the tetrachloro 2,4-bis(silyl)trisilazane 388 (Scheme 55).[406]

The chemistry of silylhydrazines, compounds that contain the Si–N–N linkages, was reviewed in 1996 by Bode and Klingebiel.[407] In general, difficulties in preparing single compounds are often encountered due to the possibility of isomers, for example, *N*,*N*-bis(triorganosilyl)hydrazines and *N*,*N*′-bis(triorganosilyl)hydrazines. For instance, dilithiated hydrazine LiHNNHLi reacts with 2 equiv. of $PhMe_2SiCl$ to form a mixture of $(PhMe_2Si)HNNH(SiMe_2Ph)$ 389 and $(PhMe_2Si)_2NNH_2$ 390 (Scheme 56). Nevertheless, the reaction of this mixture with 1 and 2 equiv. of butyllithium produces single products, namely the dimeric $(PhMe_2Si)_2NNHLi$ 391 and the trimeric $(PhMe_2Si)LiNNLi(SiMe_2Ph)$ 392, respectively, whose reaction with *i*-Pr_2SiF_2, $MeSiF_3$, and



Scheme 51



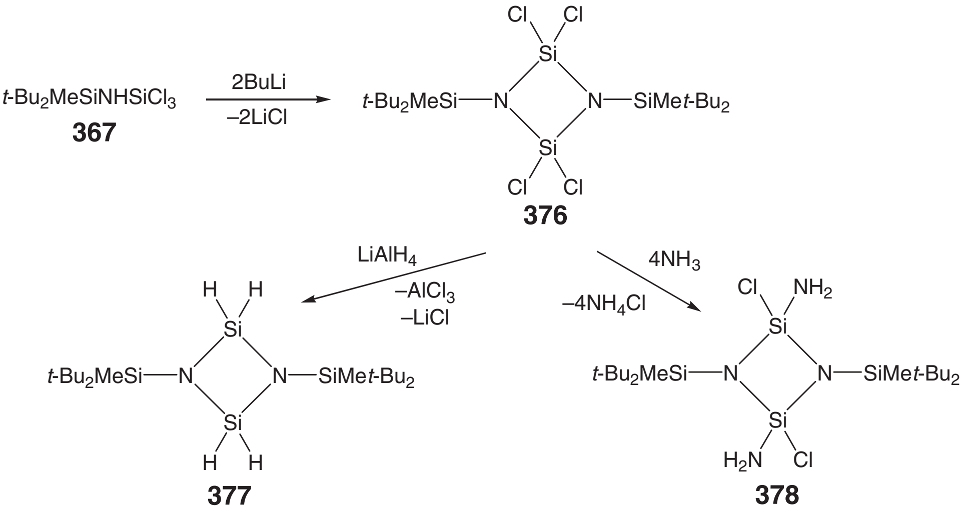
Scheme 52

SiF_4 gives rise to the formation of the fluorosilyl hydrazines ($(i\text{-}Pr_2FSi)HNN(SiMe_2Ph)_2$) **393** and $(PhMe_2Si)(RF_2Si)NN(SiMe_2Ph)(SiF_2R)$ (**394**, R = Me; **395**, R = F), respectively (Scheme 56).

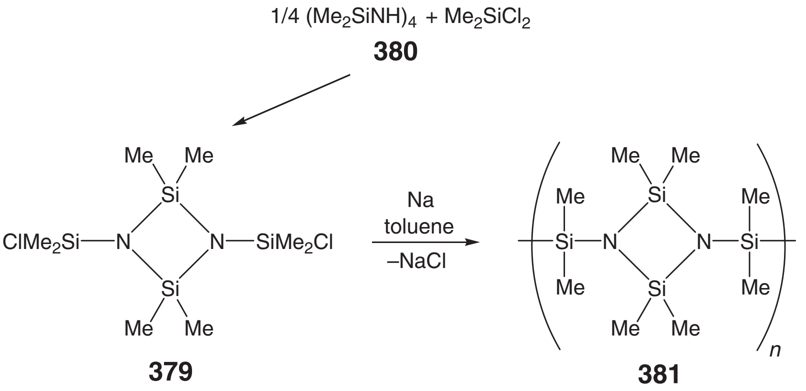
Recently, Klingebiel *et al.* have demonstrated that silylhydrazines can be synthesized stepwise using carefully selected auxiliary bases and bulky substituents, which suppresses formation of isomeric mixtures.[408,409] Thus, the reaction of $t\text{-}BuPh_2SiCl$ with hydrazine in the presence of triethylamine affords only the monosubstituted product, $(t\text{-}BuPh_2Si)HNNH_2$ **396** (Scheme 57). As in the case of organic hydrazines, **396** reacts with acetone under condensation to form a Schiff base product **397**. The lithiation of **396** with BuLi selectively provides $(t\text{-}BuPh_2Si)HNNHLi$ **398**, whose subsequent reaction with $t\text{-}BuPh_2SiCl$ gives the *N*,*N*′-bis(triorganosilyl)hydrazine $(t\text{-}BuPh_2Si)HNNH(SiPh_2t\text{-}Bu)$ **399** as single isomer (Scheme 57). The dilithiation of **399** with BuLi affords $(t\text{-}BuPh_2Si)LiNNLi(SiPh_2t\text{-}Bu)$ **400**, which has been reacted with SiF_4 to yield the tetrasilyl hydrazine $(t\text{-}BuPh_2Si)(F_3Si)NN(SiF_3)(SiPh_2t\text{-}Bu)$ **401** containing six Si–F bonds (Scheme 57).

Following a similar approach, the first bis(triorganosilyl) diazene **402** that is stable at room temperature could be obtained.[410] Thus, the reaction of $(t\text{-}Bu_2MeSi)HNNH(SiMet\text{-}Bu_2)$ **403**, an analog of **399**, with 2 equiv. of BuLi has provided $(t\text{-}Bu_2MeSi)LiNNLi(SiMet\text{-}Bu_2)$ **404**, whose oxidation with bromine has led to the formation of the diazene $t\text{-}Bu_2MeSiNNSiMet\text{-}Bu_2$ **402** (Scheme 58). Recently, the stepwise synthesis of cyclic and open-chain silyl hydroxylamines has been reported by Klingebiel *et al.*[411–414] For hypervalent silyl hydroxylamines, see Section 6.8.

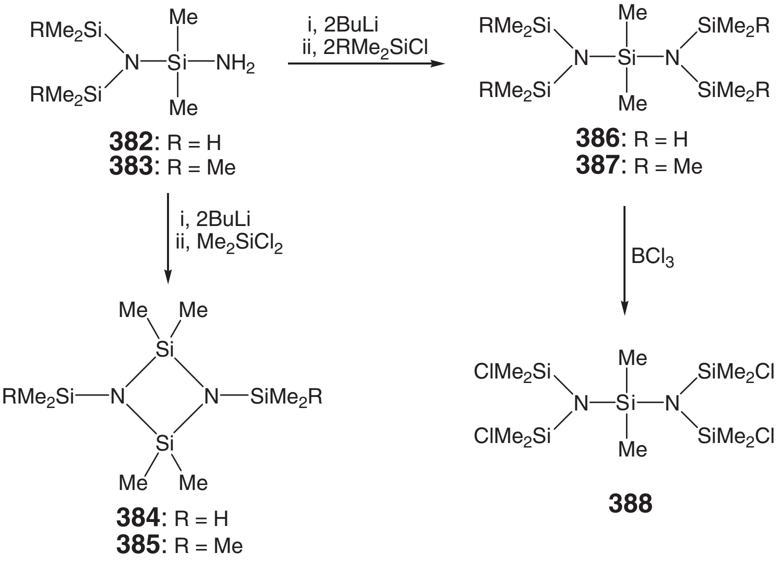
The chemistry of iminosilanes, compounds consisting of Si–N double bonds, has been extensively reviewed by Klingebiel *et al.*[415,416] In general, the stabilization of iminosilanes requires the use of sterically demanding substituents at both the Si and the N atoms of the double bond to prevent cyclooligomerization. The synthesis of iminosilanes begins by setting up aminosilane precursors with two functional groups at the N and the Si atoms, which



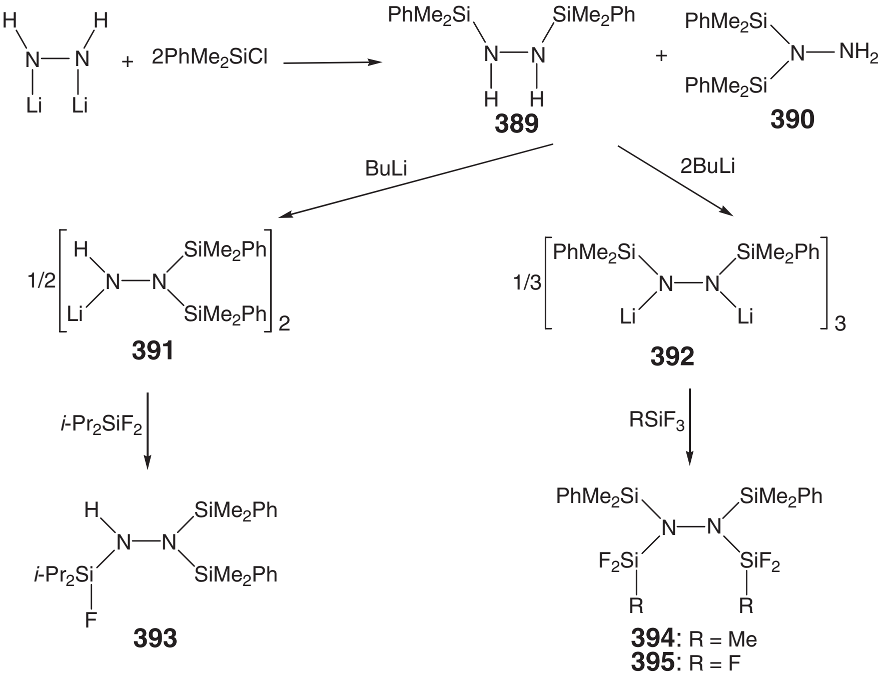
Scheme 53



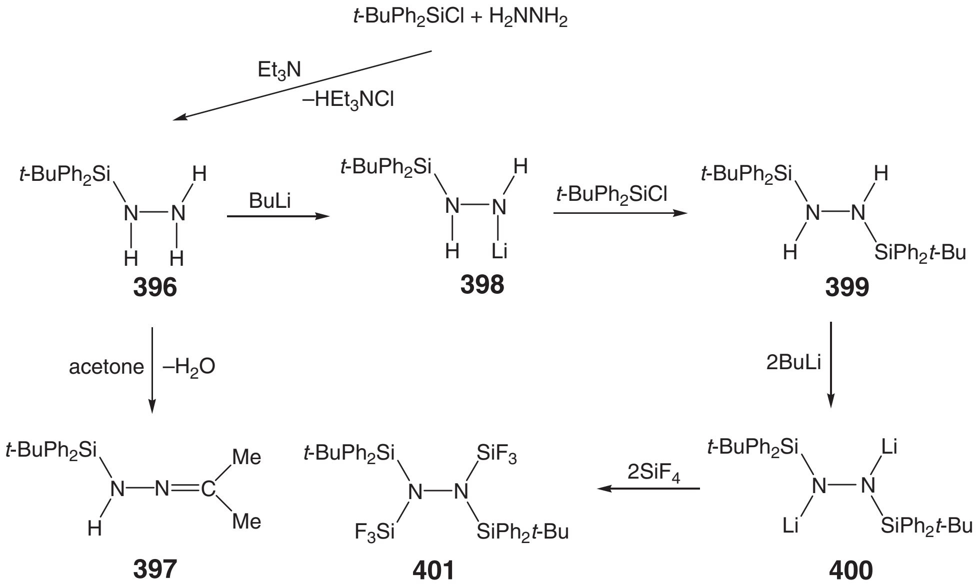
Scheme 54



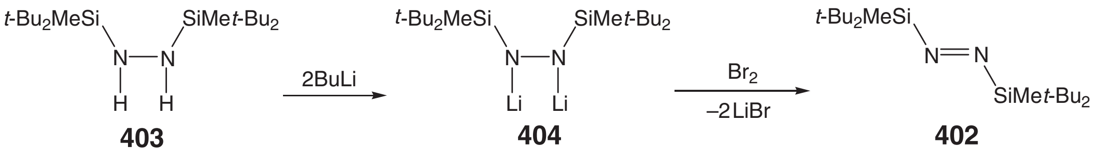
Scheme 55



Scheme 56



Scheme 57

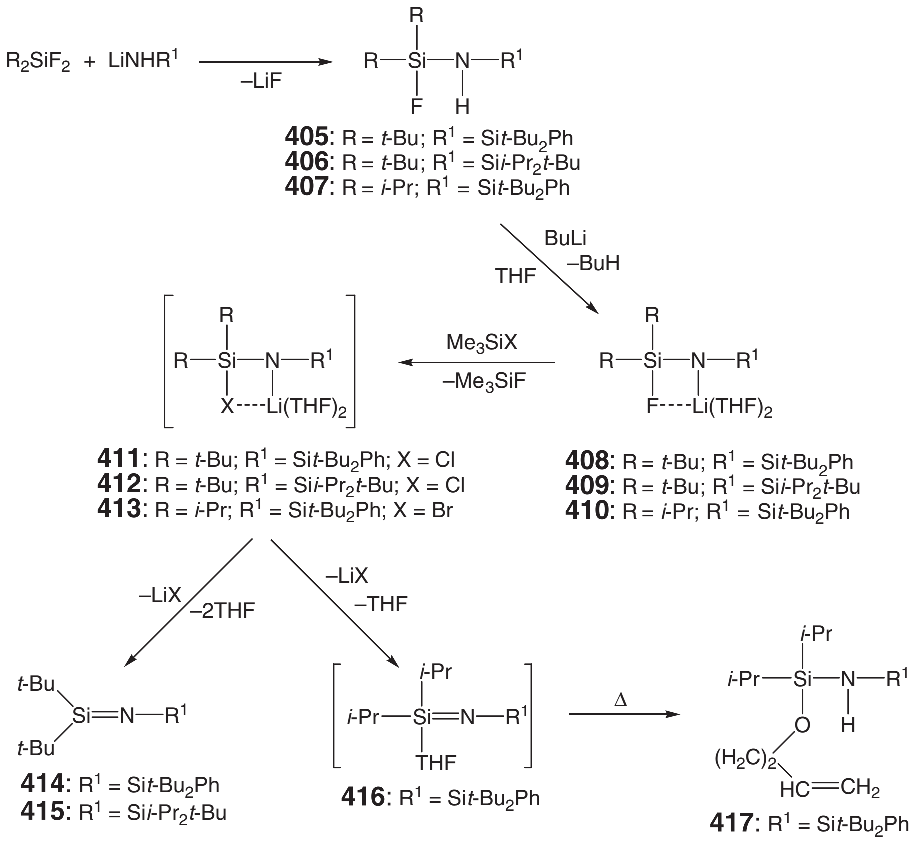


Scheme 58

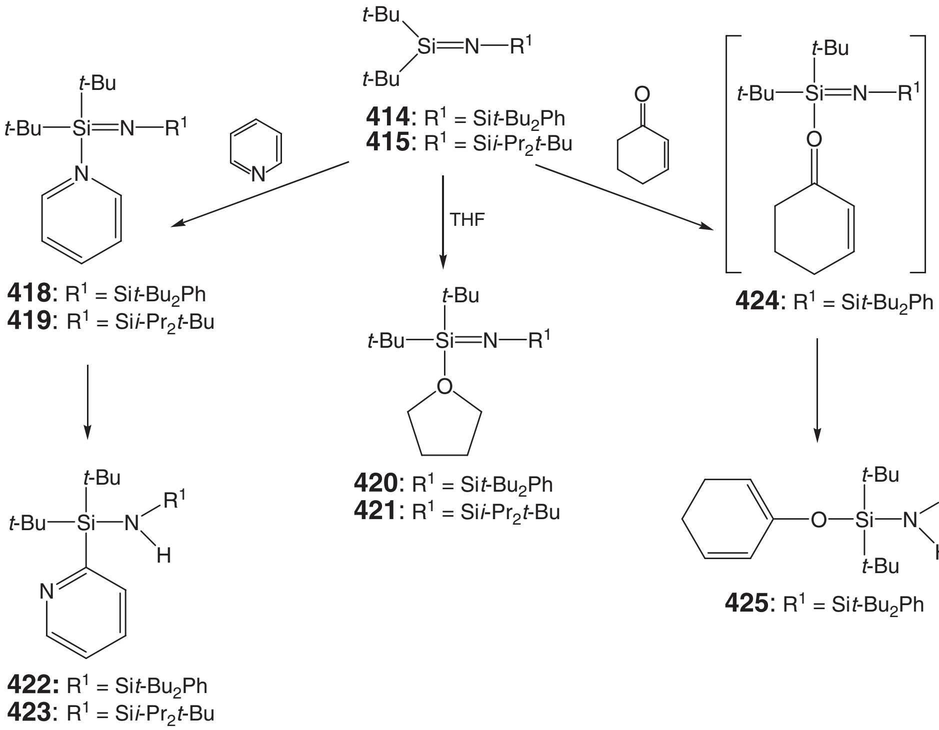
are susceptible to elimination reactions.[417] The reaction of the diorganodifluorosilanes *i*-Pr_2SiF_2 and *t*-Bu_2SiF_2 with the lithium (triorganosilyl) amides LiNH(SiPh*t*-Bu_2) and LiNH(Si*i*-Pr_2*t*-Bu) has provided the bis(silyl) amines R_2(F)SiN(H)R^1 (**405**, R = *t*-Bu, R^1 = SiPh*t*-Bu_2; **406**, R = *t*-Bu, R^1 = Si*i*-Pr_2*t*-Bu; **407**, R = *i*-Pr, R^1 = SiPh*t*-Bu_2) containing one Si–F bond and one N–H bond (Scheme 59). Lithiation of **405–407** with butyllithium results in the stable lithium bis(silyl) amides R_2(F)SiN(Li)R^1 (**408**, R = *t*-Bu, R^1 = SiPh*t*-Bu_2; **409**, R = *t*-Bu, R^1 = Si*i*-Pr_2*t*-Bu; **410**, R = *i*-Pr, R^1 = SiPh*t*-Bu_2) as THF adducts, which apparently show no propensity to undergo intramolecular lithium fluoride elimination. Interestingly, the lithium bis(silyl) amides **408–410** react with Me_3SiCl and Me_3SiBr via halide exchange rather than substitution to form gaseous trimethylfluorosilane and the intermediate lithium bis(silyl) amides R_2(X)SiN(Li)R^1 **411–413** containing Si–X (X = Cl, Br) bonds, which readily undergo lithium halide elimination. In two cases, these elimination reactions have produced stable iminosilanes *t*-Bu_2SiNR^1 (**414**, R^1 = Si*t*-Bu_2Ph; **415**, R^1 = Si*i*-Pr_2*t*-Bu) having three-coordinate Si atoms. In one case, an iminosilane THF adduct **416** is presumably formed, which induces ring opening of THF to give the stable aminosiloxane **417** (Scheme 59).[417]

The reactivity of the iminosilanes *t*-Bu_2SiNR^1 (**414**, R^1 = Si*t*-Bu_2Ph; **415**, R^1 = Si*i*-Pr_2*t*-Bu) toward complexation by Lewis bases has been studied in greater detail. With both pyridine and THF, the iminosilanes form stable adducts **418–421**, which undergo rearrangement into the 2-pyridyl-di-*tert*-butysilylaminosilanes **422** and **423** (Scheme 60).[417] The reaction of the iminosilanes *t*-Bu_2SiNSi*t*-Bu_2Ph **414** with cyclohexenone apparently occurs more readily with formation of the transient adduct **424**, which is rapidly transformed into the silyl enolate **425** (Scheme 60).

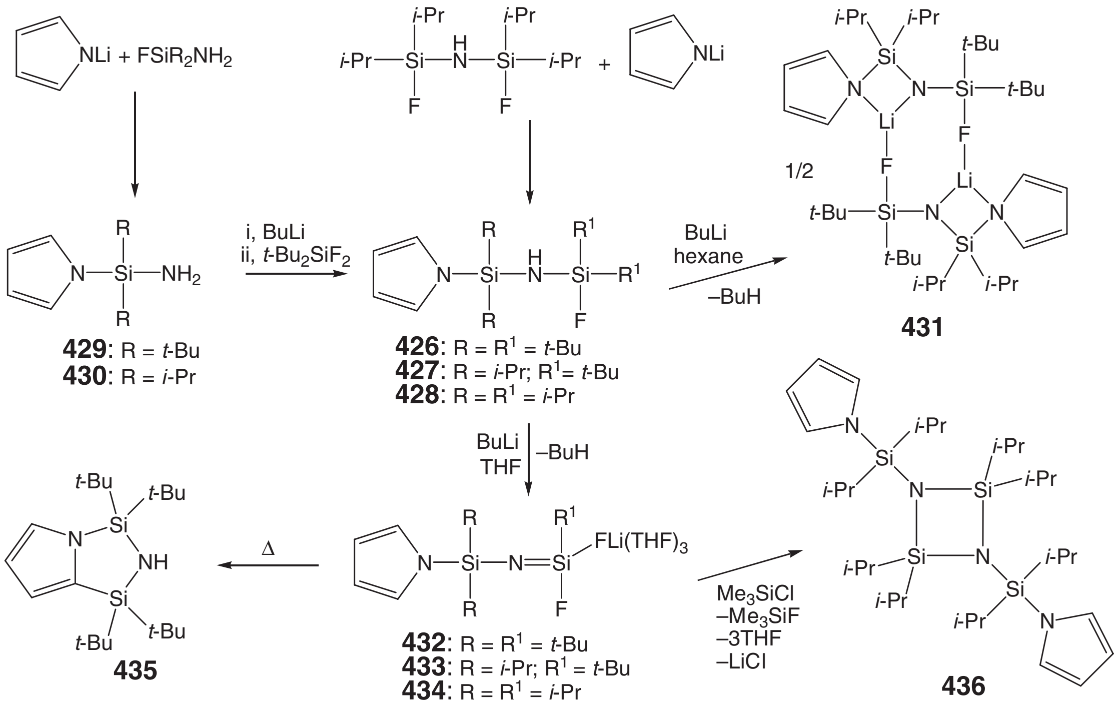
Klingebiel *et al.* have further investigated fluorosilyl(pyrolyl)silylamines $R_2(C_4H_4N)Si(H)NSi(F)R^1_2$ (**426**, R = R^1 = *t*-Bu; **427**, R = *i*-Pr, R^1 = *t*-Bu; **428**, R = R^1 = *i*-Pr) and their potential to serve as precursors for the preparation of iminosilanes.[418] The fluorosilyl(pyrolyl)silylamines **426–428** are accessible via two different routes (Scheme 61). The reaction of lithiated pyrrol with the aminodiorganofluorosilanes *i*-Pr_2SiFNH_2 and *t*-Bu_2SiFNH_2 gives rise to the diorganobis(amino)silanes $R_2(C_4H_4N)SiNH_2$ (**429**, R = *t*-Bu; **430**, R = *i*-Pr), which react with butyllithium and



Scheme 59



Scheme 60



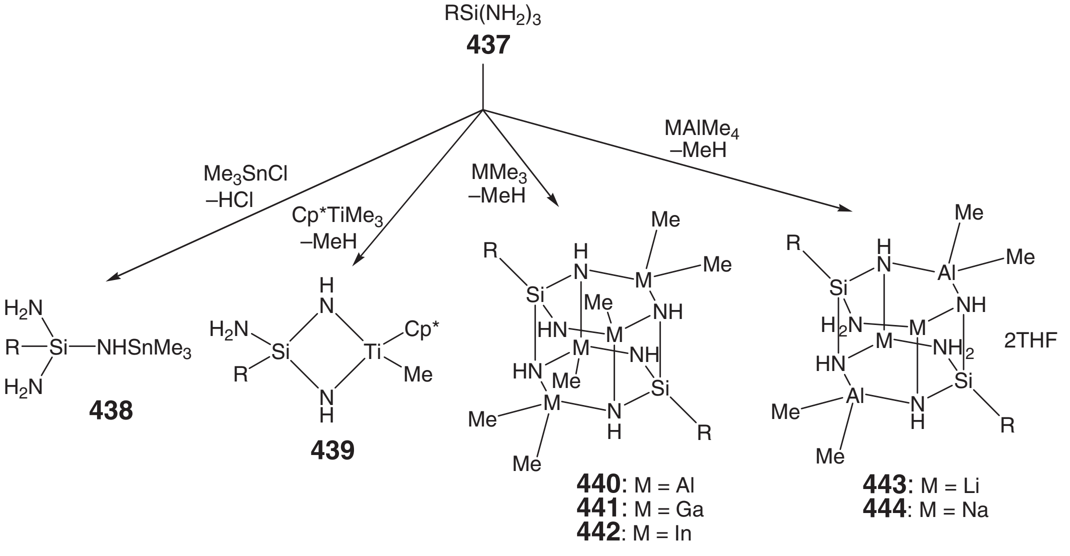
Scheme 61

t-Bu_2SiF_2 to give the fluorosilyl(pyrolyl)silylamines **426 and 427**. Alternatively, the reaction of bis(fluorodiisopropylsilyl)amine, *i*-$Pr_2(F)SiNHSi(F)$*i*-Pr_2, with 1 equiv. of the lithiated pyrrol provides the fluorosilyl(pyrolyl)silylamine **428** (Scheme 61).[418] The reaction of the fluorosilyl(pyrolyl)silylamine *i*-$Pr_2(C_4H_4N)Si(H)NSi(F)$*t*-Bu_2 **427** with BuLi in hexane has provided a dimeric product **431**, whereas the reaction of the fluorosilyl(pyrolyl)silylamines $R_2(C_4H_4N)Si(H)NSi(F)R^1{}_2$ (**426**, R = R^1 = *t*-Bu; **427**, R = *i*-Pr, R^1 = *t*-Bu; **428**, R = R^1 = *i*-Pr) with BuLi in THF gives the monomeric iminosilane lithium fluoride adducts $R_2(C_4H_4N)SiNSiR^1{}_2LiF$ (**432**, R = R^1 = *t*-Bu; **433**, R = *i*-Pr, R^1 = *t*-Bu; **434**, R = R^1 = *i*-Pr) that are stabilized by THF. The thermally induced lithium fluoride elimination of **432** leads to the formation of the bicyclic product **435** (Scheme 61).[418] The reaction of *i*-$Pr_2(C_4H_4N)SiNSi$*i*-Pr $_2LiF$ **434** with Me_3SiCl occurs via halide exchange and lithium chloride elimination to form the 1,3-bis(silyl)cyclodisilazane **436** (Scheme 61).

3.09.3.2 Metallasilazanes

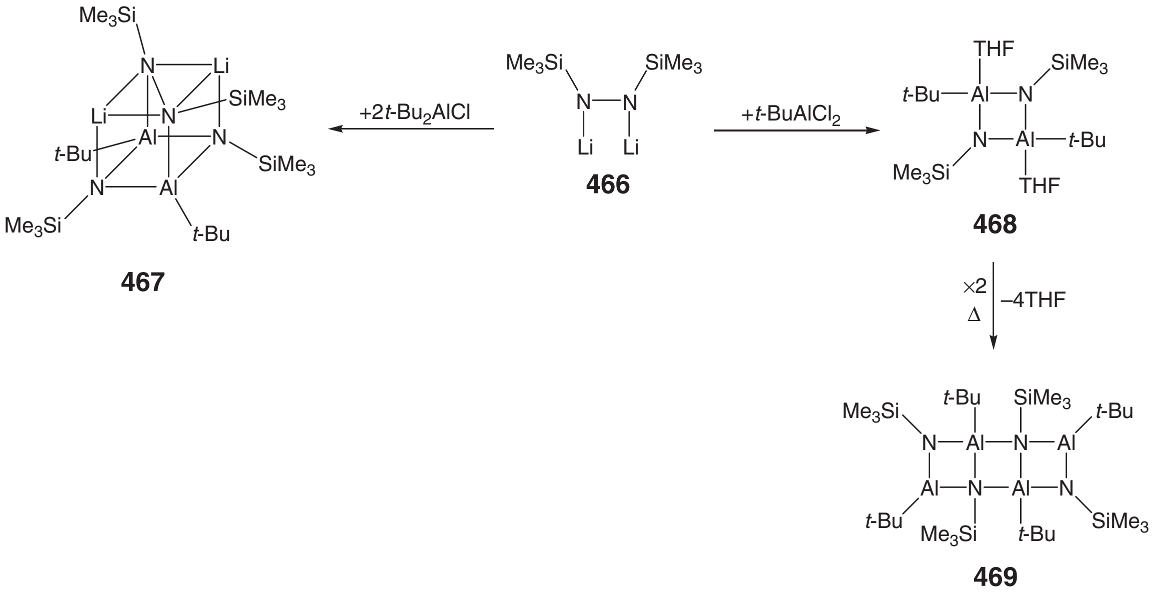
Over the years there was an apparent interest to use amino- and hydrazinosilanes as ligands for metal complexes. The use of the bis(trimethylsilyl)amide group $(Me_3Si)_2N$ and related silylamide ligands for the synthesis of low-coordinated electrophilic main group elements, transitions metals, and lanthanides is well established and has been reviewed extensively.[419,420] More recently, molecular metallasilazanes with more sophisticated aminosilicate ligands have been prepared and structurally characterized by Roesky *et al.*[421–424] The reaction of *i*-$Pr_2C_6H_3NSiMe_3Si(NH_2)_3$ **437**, an analog of **354** and **355**, with organometallic precursors, such as Me_3SnCl, Cp^*TiMe_3, MMe_3 (M = Al, Ga, In), and $MeAlMe_4$ (M = Li, Na) gives rise to the formation of well-defined molecular metallasilazanes $RSi(NH_2)_2(NHSnMe_3)$ **438**, $RSi(NH_2)(NH)_2TiCp^*Me$ **439**, $[(RSi)(NH)_3(MMe_2)(MMe)]_2$ (**440**, M = Al; **441**, M = Ga; **442**, M = In) and $[(RSi)(NH)_2(NH_2)(Me_2Al)M]_2$ (**443**, M = Li; **444**, M = Na), respectively (R = 2,6-*i*-$PrC_6H_3N(SiMe_3)$) (Scheme 62).

Veith *et al.* have prepared a number of difunctionalized disilazanes $XSiMe_2NHSiMe_2X$ (**445**, X = OC_4H_3; **446**, X = OPh, **447**, X = $OSiMe_3$; **448**, X = NMe_2; **449**, X = SC_4H_3) by replacing the chlorine atoms in $ClSiMe_2NHSiMe_2Cl$ **450** with anionic ligands, and have converted them with BuLi into the corresponding lithium amides $Li_2[XSiMe_2NSiMe_2X]_2$ (**451**, X = OC_4H_3; **452**, X = OPh, **453**, X = $OSiMe_3$; **454**, X = NMe_2; **455**, X = SC_4H_3), all of which were fully characterized.[425] The same group has also investigated the solid-state dynamic behavior of $Li_2[$*t*-$BuOSiMe_2NSiMe_2O$*t*-$Bu]_2$ **456**, an analog of **452**, and the related compound $Li_4[$*t*-$BuNSiMe_2OSiMe_2N$*t*-$Bu]_2$ **457** by solid-state NMR spectroscopy and X-ray crystallography.[426] Compound **457** has been obtained by lithiation of *t*-$BuHNSiMe_2OSiMe_2NH$*t*-Bu **458**, which is accessible by the reaction of $(ClSiMe_2)_2O$ with LiNH*t*-Bu. The reaction of the trichlorotetrasiloxane *t*-$BuSi(OSiMe_2Cl)_3$ **459** with



R = 2,6-*i*-$PrC_6H_3N(SiMe_3)$

Scheme 62



Scheme 63

LiNH*t*-Bu provided a new tripodal siloxazane ligand *t*-BuSi(OSiMe$_2$NH*t*-Bu)$_3$ **460** that has been deprotonated and converted into some metal complexes M$_3$[*t*-BuSi(OSiMe$_3$NH*t*-Bu)$_3$] (**461**, M = Li; **462**, M = Na; **463**, M = Cu).[427] Stalke *et al.* have conducted experimental and theoretical charge-density measurements on cyclotetrasilazane (Me$_2$SiNH)$_4$ **380** and related metal complexes [(THF)$_2$Li$_2$(NSiMe$_2$NHSiMe$_2$)$_2$] **464** and [(THF)$_2$LiAl(NSiMe$_3$)$_4$]$_2$ **465**.[428]

The reactivity of dilithium bis(trimethylsilyl) hydrazide (Me$_3$Si)LiNNLi(SiMe$_3$) **466**, being an analog of **399** and **404**, toward *tert*-butylaluminum chlorides has been studied by Uhl *et al.*[429] The reaction of **466** with *t*-Bu$_2$AlCl occurs with partial cleavage of the N–N bonds and provides the cubic cage **467**. The reaction of **466** with *t*-BuAlCl$_2$ proceeds with lithium chloride elimination and formation of the four-membered Al$_2$N$_2$ heterocycle **468**, which upon heating rearranges into the tricyclic Al$_4$N$_4$ hetereocycle **469** (Scheme 63).

Notably, the reaction of an isomeric mixture of 1,1-(Me$_3$Si)$_2$(NH)$_2$ **470** and 1,2-(Me$_3$Si)$_2$(NH)$_2$ **471** with *t*-Bu$_2$AlCl (in the absence of alkali metals) affords the fully characterized Lewis acid–Lewis base adducts *t*-Bu$_2$AlCl·NH$_2$NHSiMe$_3$ **472** and N$_2$H(SiMe$_3$)$_3$ **473**, respectively.[430]

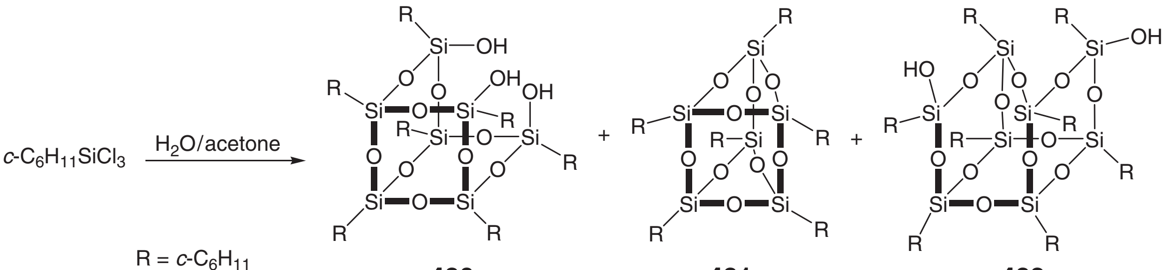
3.09.4 Silicon–Oxygen Compounds

3.09.4.1 Silanols and Siloxanes

The role of organosilanols as starting materials for the synthesis of siloxanes and metallasiloxane cannot be overstated. Recent times have witnessed significant advances in the preparation of polysilanols, and a number of reviews by Lickiss,[431,432] Roesky *et al.*,[433] and Chandrasekhar *et al.*[434] give an account of this rapid development. Organosilanols are well known for their inherent tendency to undergo self-condensation to form siloxanes. In fact, silanols play an important role as intermediates in the sol–gel process and the preparation of silicone polymers.[435,436] However, the self-condensation of organosilanols can be circumvented by kinetic stabilization using bulky organic substituents. Presumably, the most shielded triorganosilanol yet reported is the bowl-shaped compound [3,5-(2,5-Me$_2$C$_6$H$_4$)C$_6$H$_3$]$_3$SiOH **474** containing *m*-terphenyl moieties that prevent condensation even under the most extreme conditions.[437] One of the most labile triorganosilanols is the archetypical Me$_3$SiOH **475**, whose X-ray structure has been published only recently.[438] Self-condensation of exposed organosilanols can be prevented to some extent when heat, strong acids and bases are avoided during their preparation. Arguably, one of the best methods to prepare the most labile silanols, such as Me$_2$Si(OH)$_2$ **476**, is the mild hydrolysis of chlorosilanes using stoichiometric amounts of water and weakly basic amines, such as HCl scavenger.[439] In this way a number of monoorganotrisilanols $RSi(OH)_3$ (**477**, R = *t*-Bu;[440] **478**, R = Me_5C_5; **479**, R = $Me_3SiC_5H_4$[441,442]) have been prepared. An excellent alternative way to prepare exposed organosilanols is the oxygenation of organo-H-silanes using homogeneous transition metal-based catalysts (M = Cu,[443] Cr,[444] Rh,[445] Re,[446,447] Ru[448]) whereby H_2O and/or O_2 serve as oxygen source. Immobilized transition metal catalysts based on Ru[449] and Pd[450] on hydroxoapatite and carbon supports that can be easily separated from the silanols have been also reported. When the oxidation is carried out in alcohols rather than water, the oxygenation of organo-H-silanes provides alkoxysilanes.[451–453] In the beginning of the 1990s, Feher and Budzichowski published a series of landmark papers on incompletely condensed silsesquioxane cages $[RSiO_{1.5}]_n$ ($n = 4$–8) containing siloxanol groups, which literally opened the door to a new field of chemistry.[454] In a now classic experiment, these researchers showed that the careful hydrolysis of cyclohexyltrichlorosilane $c\text{-}C_6H_{11}SiCl_3$ in aqueous acetone leads to the formation of two main products, namely, the heptasiloxanetriol $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **480** and silesquioxane hexamer $(c\text{-}C_6H_{11}Si)_6O_9$ **481**, along with smaller amounts of the octasiloxanediol $(c\text{-}C_6H_{11}Si)_8O_{10}(OH)_2$ **482**, which could be separated by fractional crystallization and prepared on a multigram scale (Scheme 64). Incompletely condensed silsesquioxanes have been shown to be soluble model compounds for silica surface silanol sites and serve as starting materials for metallasioxanes and hybrid inorganic–organic polymers, commonly referred to as POSS materials.[454,455]

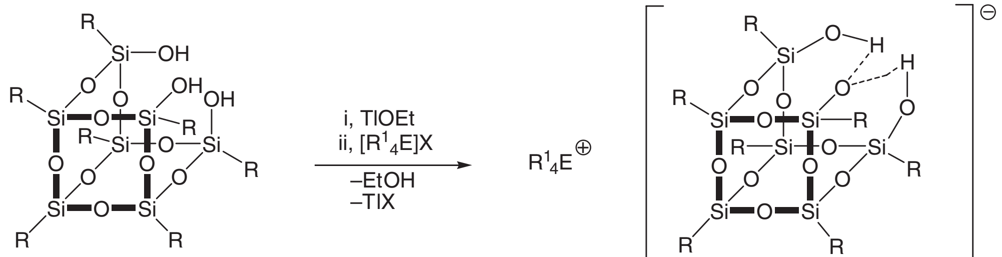
Variation of the organic group has shown that only a very few other organotrichlorosilanes $RSiCl_3$ (e.g., R = $c\text{-}C_5H_9$, norbornyl) can provide similar hydrolysis products, whereas the majority of $RSiCl_3$ (R = alkyl, aryl) produce either molecular silsesquioxane cages or ill-defined resinous polymers.[456,457] The reactivity of the heptasiloxanetriol $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **480** has been the subject of numerous studies. The deprotonation of **480** with TlOEt/$[R^1{}_4E]X$ ($[R^1{}_4E]X$ = $[Bu_4N]Br$, $[Bu_4P]Cl$, $[Ph_4P]Cl$) gives rise to the formation of monosiloxanolate anions $[R^1{}_4E][(c\text{-}C_6H_{11}Si)_7O_{10}(OH)_2]$ that were isolated as crystalline solids with various counterions (**483**, $[R^1{}_4E]$ = $[Bu_4N]$; **484**, $[R^1{}_4E]$ = $[Bu_4P]$; **485**, $[R^1{}_4E]$ = $[Ph_4P]$) (Scheme 65).[458,459]

The reaction of the heptasiloxanetriols $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **480** and $(c\text{-}C_5H_9Si)_7O_9(OH)_3$ **486** with $R^1{}_2R^2SiX$ (R^1,R^2 = alkyl, aryl; X = Cl, OTf) in the presence of a base has given rise to selective formation of monosubstituted



480 **481** **482**

Scheme 64

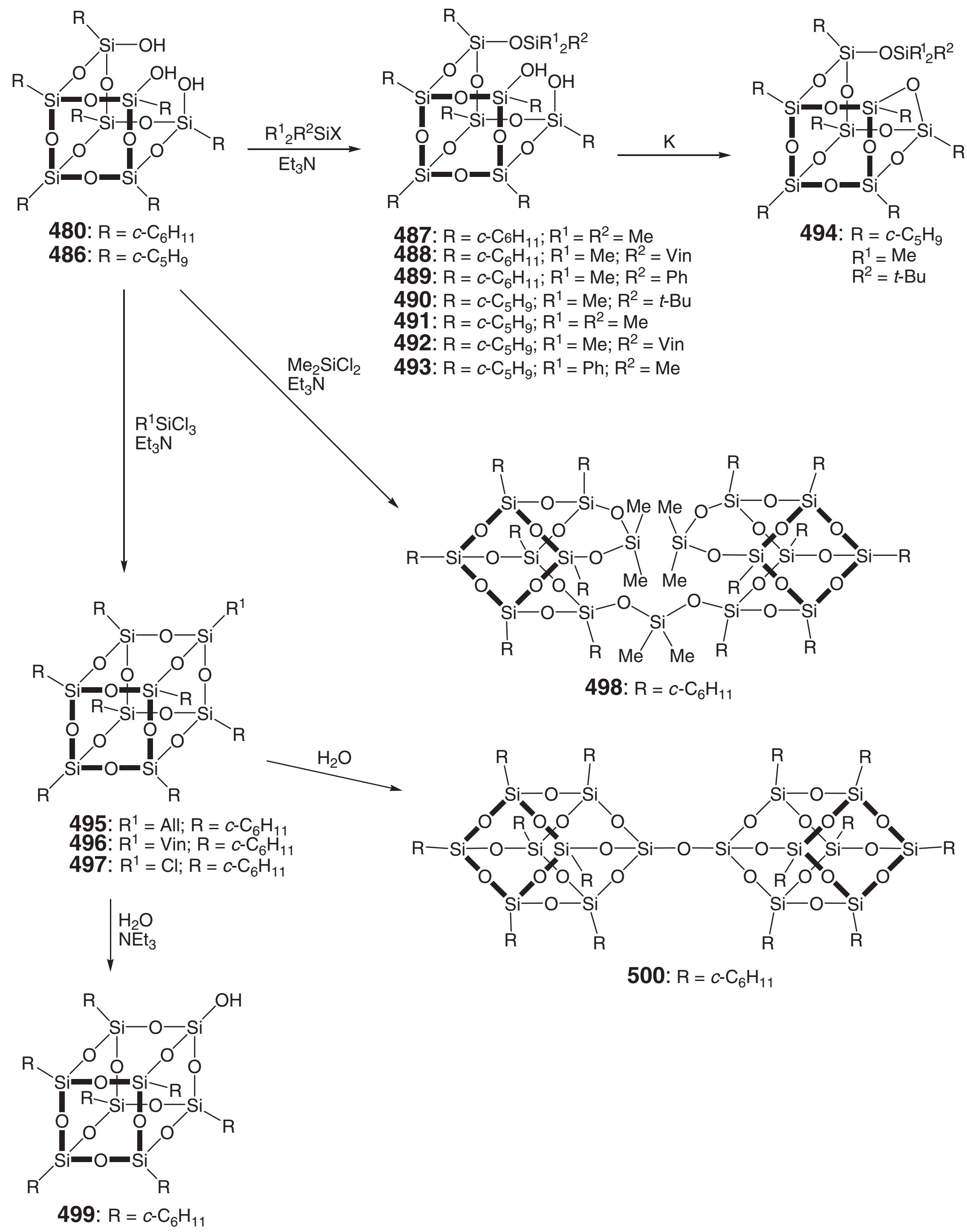


480

$[R^1{}_4E]X$ = $[Bu_4N]Br$, $[Bu_4P]Cl$, $[Ph_4P]Cl$
R = $c\text{-}C_6H_{11}$

483: $R^1{}_4E$ = Bu_4N
484: $R^1{}_4E$ = Bu_4P
485: $R^1{}_4E$ = Ph_4P

Scheme 65



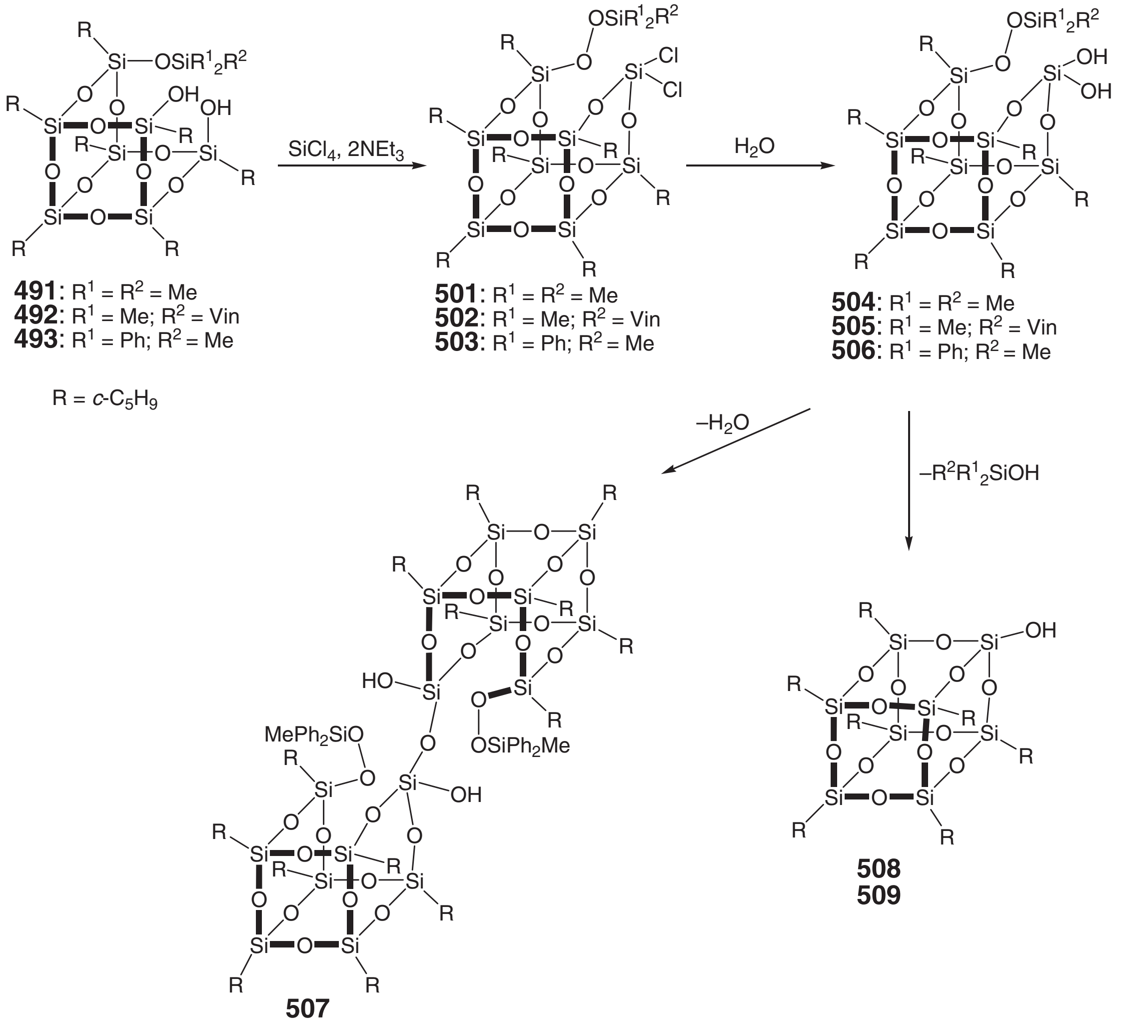
Scheme 66

siloxandiols ($(c\text{-}C_6H_{11}Si)_7O_9(OH)_2(OsiR^1{}_2R^2)$ (487, $R^1 = R^2 = Me$; 488, $R^1 = Me$, $R^2 = Vin$; 489, $R^1 = Me$, $R^2 = Ph$)[460,461] and $(c\text{-}C_5H_9Si)_7O_9(OH)_2(OsiR^1{}_2R^2)$ (490, $R^1 = Me$, $R^2 = t\text{-}Bu$; 491, $R^1 = R^2 = Me$; 492, $R^1 = Me$, $R^2 = Vin$; 493, $R^1 = Ph$, $R^2 = Me$) (Scheme 66).[462–465] Reduction of 490 with K has provided the completely condensed silesquioxane cage $(c\text{-}C_5H_9Si)_7O_{10}(OSiMe_2t\text{-}Bu)$ 494 that incorporates a strained six-membered ring.[463]

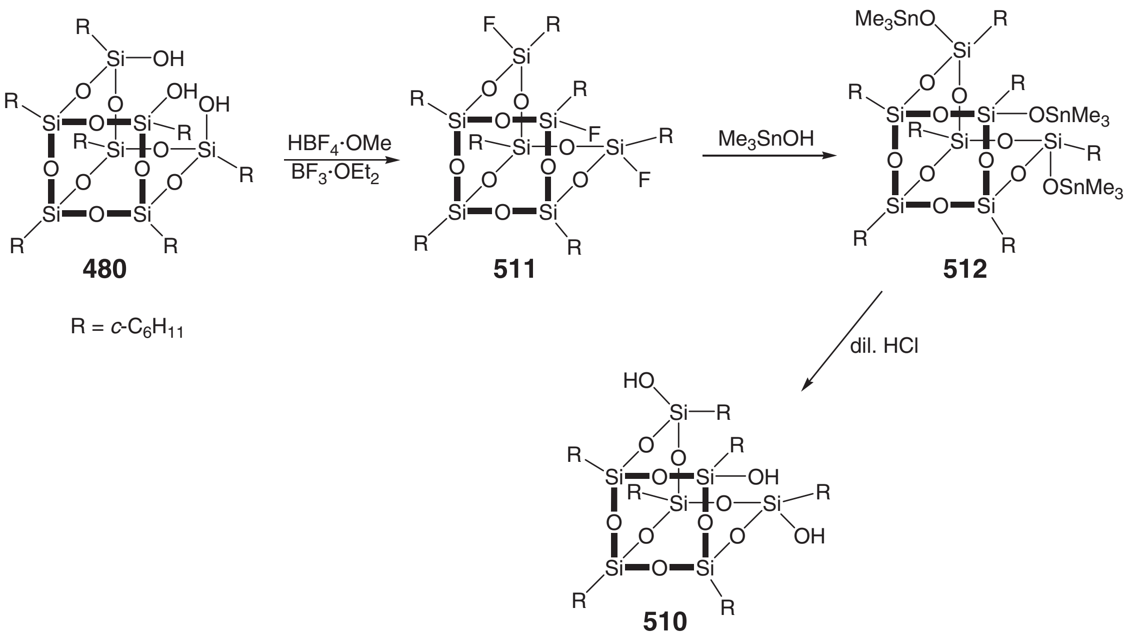
Reaction of heptasiloxanetriols $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **480** with Me_2SiCl_2 and R^1SiCl_3 has afforded unsymmetrically substituted silsesquioxane octamer cages $(c\text{-}C_6H_{11}Si)_7(R^1Si)O_{12}$ (**495**, $R^1 = $ All; **496**, $R^1 = $ Vin, **497**, $R^1 = $ Cl) [466,467] and the product **498** containing two fused octamer cages.[467] The chloro silsesquioxane **497** has been hydrolyzed in the presence and absence of triethylamine providing the corresponding silanol **499** and the siloxane **500**, respectively, whereas the ammonolysis has afforded amino and iminosilsesquioxanes.[468] Silesquioxane cages containing disilene units have been reported.[469]

The siloxandiols $(c\text{-}C_5H_9Si)_7O_9(OH)_2(OSiR^1{}_2R^2)$ (**491**, $R^1 = R^2 = $ Me; **492**, $R^1 = $ Me, $R^2 = $ Vin; **493**, $R^1 = $ Ph, $R^2 = $ Me) have been reacted with $SiCl_4$ to give the dichloro-substituted products (**501**, $R^1 = R^2 = $ Me; **502**, $R^1 = $ Me, $R^2 = $ Vin; **503**, $R^1 = $ Ph, $R^2 = $ Me), whose controlled hydrolysis has given new disilanols (**504**, $R^1 = R^2 = $ Me; **505**, $R^1 = $ Me, $R^2 = $ Vin; **506**, $R^1 = $ Ph, $R^2 = $ Me). Subsequent condensation of water and elimination of Me_3SiOH and $Me_2VinSiOH$ provides new silanol cages **507–509**, which have found applications as supports for homogeneous catalysts (Scheme 67).[465]

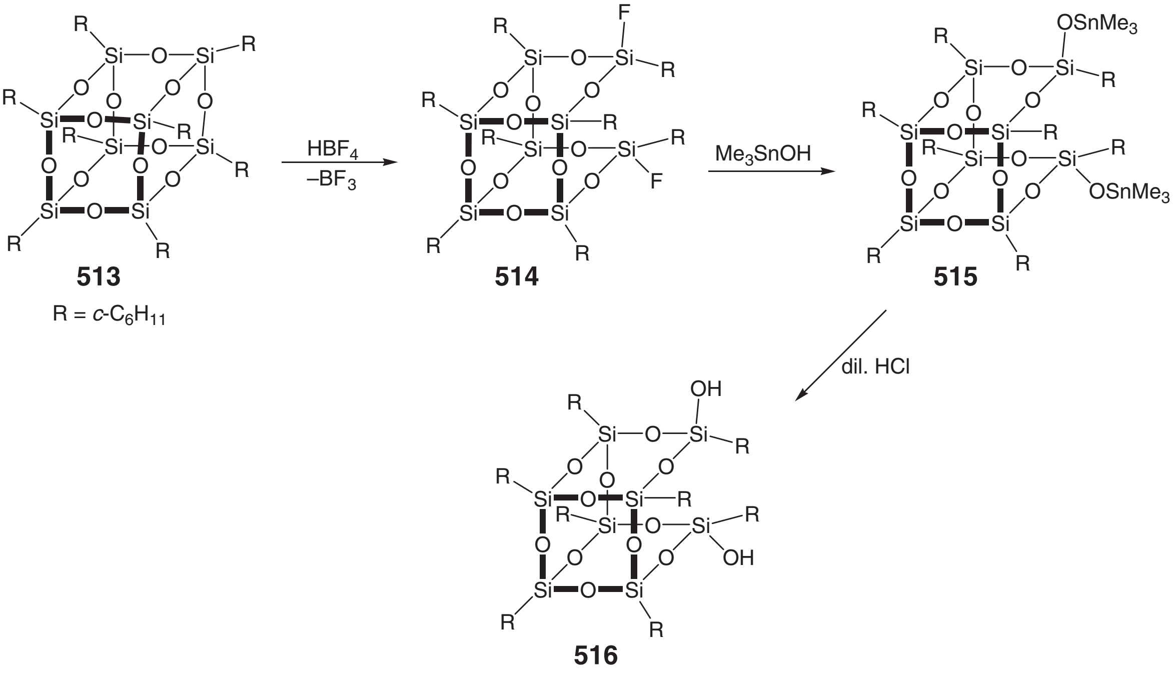
A constitutional isomer of the heptasiloxanetriol $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **480** has been prepared. The conversion of **480** in two steps using the auxiliary reagents HBF_4 and Me_3SnOH provided the isomer $(c\text{-}C_6H_{11}Si)_7O_9(OH)_3$ **510** via the isolated intermediates **511** and **512** containing F and Me_3Sn groups (Scheme 68).[470]



Scheme 67



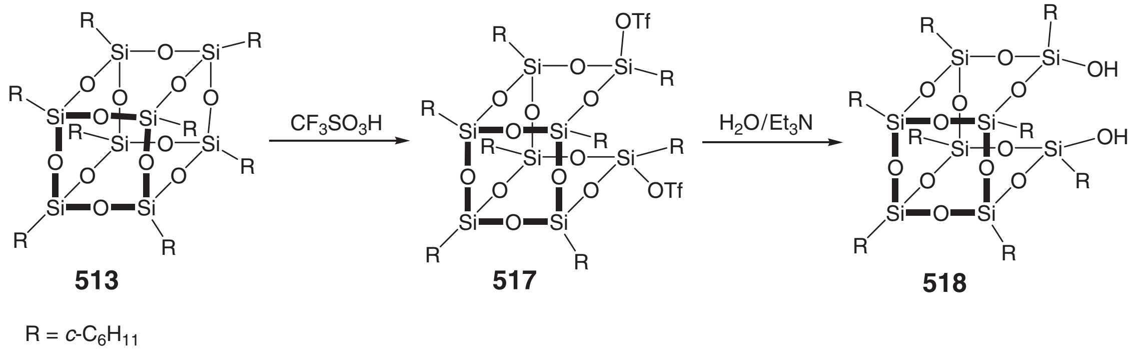
Scheme 68



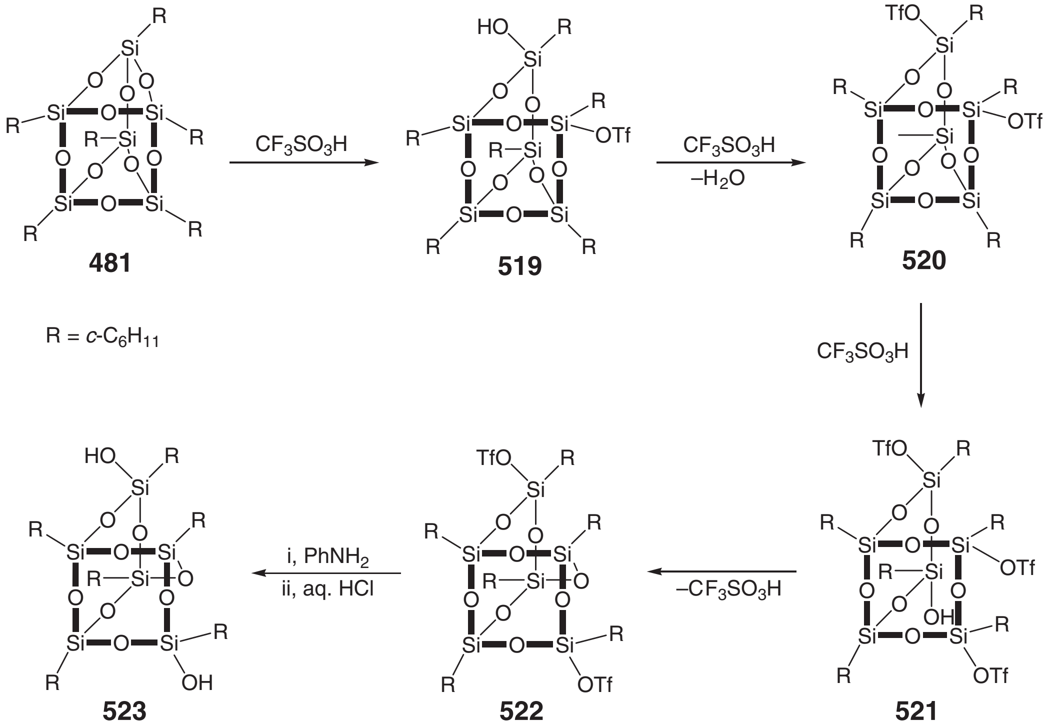
Scheme 69

A similar reaction sequence starting from the completely condensed silsesquioxane octamer cage ($(c\text{-}C_6H_{11}Si)_8O_{12}$ **513** affords the isolated intermediates **514** and **515**, eventually providing the octasiloxanediol ($(c\text{-}C_6H_{11}Si)_7O_{10}(OH)_2$ **516** (Scheme 69).[471]

Cleavage of the silsesquioxane octamer cage ($(c\text{-}C_6H_{11}Si)_8O_{12}$ **513** with triflic acid produces a triflate intermediate that has been converted into the octasiloxanediol ($(c\text{-}C_6H_{11}Si)_7O_{10}(OH)_2$ **518**, a constitutional isomer of **516** (Scheme 70).[472,473]



Scheme 70

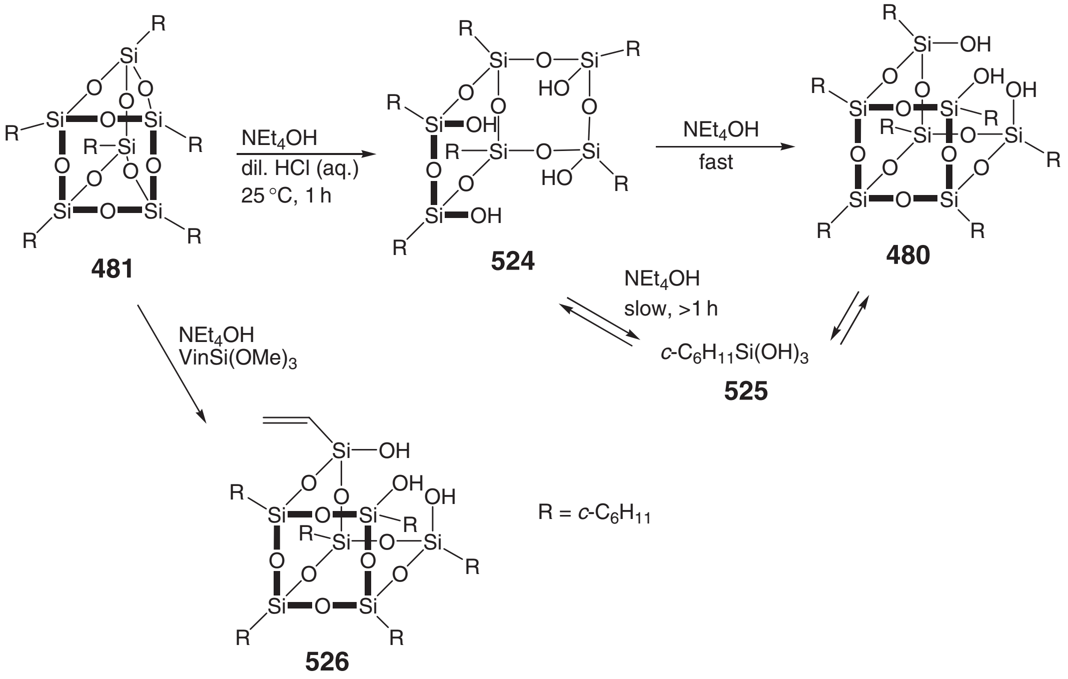


Scheme 71

The silsesquioxane hexamer cage (*c*-$C_6H_{11}Si)_6O_9$ **481** is even more susceptible to acid and base cleavage reactions owing to the strain present in the six-membered rings.[474,475] Reaction of the silsesquioxane hexamer cage (*c*-$C_6H_{11}Si)_6O_9$ **481** with triflic acid leads to the formation of a series of cleavage and rearrangement products **519–522**, which after neutralization with aniline have yielded the hexasiloxanediol **523** (Scheme 71).[474,476]

The silsesquioxane hexamer cage (*c*-$C_6H_{11}Si)_6O_9$ **481** reacts with NEt_4OH under scission of two siloxane linkages to give the product **524**, which quickly rearranges into the heptasiloxanetriol (*c*-$C_6H_{11}Si)_7O_9(OH)_3$ **480** (Scheme 72). ^{29}Si NMR studies revealed the intermediate presence of *c*-$C_6H_{11}Si(OH)_3$ **525**. When the reaction of **481** with NEt_4OH is repeated in the presence of $VinSi(OMe)_3$, the unsymmetric heptasiloxanetriol **526** is obtained. This can be regarded as a derivative of **480**, in which one of the cyclohexyl substituents has been formally replaced by a vinyl group (Scheme 72).[475,477]

A different strategy for the preparation of silsesquioxanes containing silanol groups has been put forward by Matasumoto *et al.*, which involves the stepwise formation of siloxane linkages and the use of protection groups. In this



Scheme 72

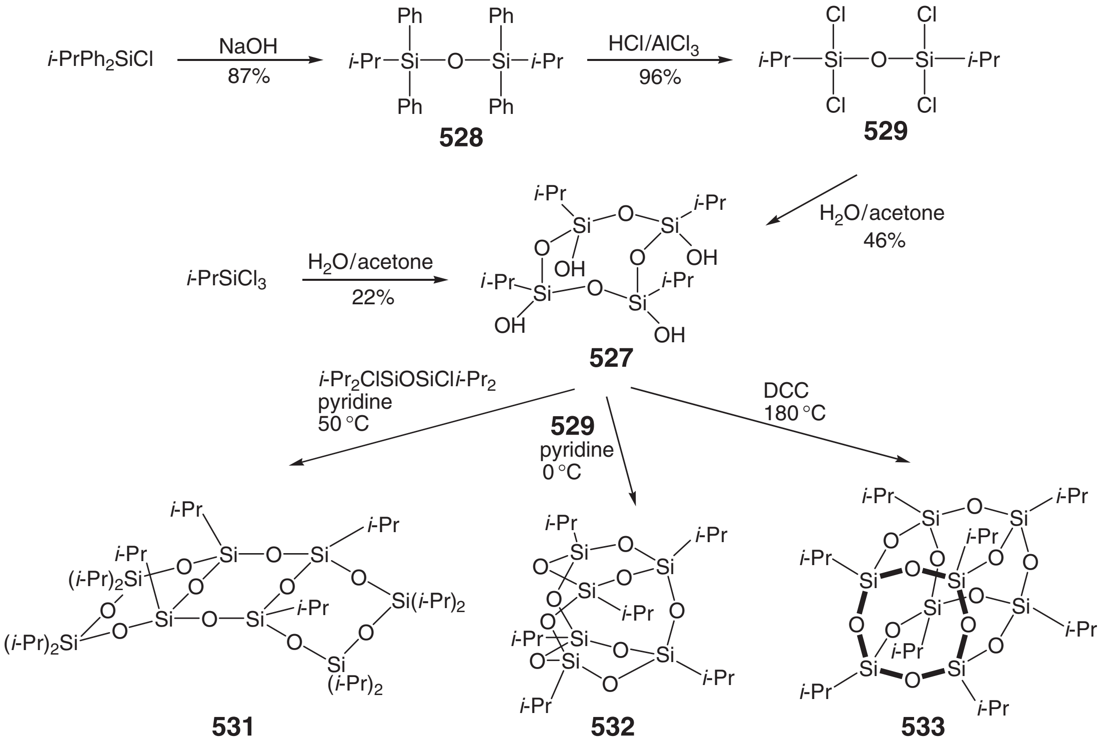
way, an interesting new tetrahydroxycyclotetrasiloxane, namely, *all-cis*-[*i*-Pr(OH)SiO]$_4$ **527**, has been obtained in three steps via the intermediates *i*-PrPh$_2$SiOSiPh$_2$*i*-Pr **528** and *i*-PrCl$_2$SiOSiCl$_2$*i*-Pr **529**, (Scheme 73). *all-cis*-[*i*-Pr(OH)SiO]$_4$ **527** is also obtained in low yield by the direct hydrolysis of *i*-PrSiCl$_3$ in acetone/water.[478,479] Co-crystals of **527** and *i*-Pr$_2$Si(OH)$_2$ have revealed a supramolecular tube-like structure.[480] A more labile analog of **527** with phenyl groups, namely *all-cis*-[*c*-PhSi(OH)SiO]$_4$ **530** has been reported by Feher *et al.*[481] The co-condensation of *all-cis*-[*i*-Pr(OH)SiO]$_4$ **527** with *i*-Pr$_2$ClSiOSiCl*i*-Pr$_2$ and *i*-PrCl$_2$SiOSiCl$_2$*i*-Pr **529** has yielded a long sought-after ladder-type siloxane **531** and the silsesquioxane hexamer cage (*i*-PrSi)$_6$O$_9$ **532**, respectively (Scheme 73).[478,479,482] Self co-condensation of *all-cis*-[*i*-Pr(OH)SiO]$_4$ **527** at elevated temperatures provided the silsesquioxane octamer cage (*i*-PrSi)$_8$O$_{12}$ **533**.

Even larger ladder-type siloxane structures with up to five fused eight-membered rings can be obtained by similar routes. Thus, co-condensation of *all-cis*-[*i*-Pr(OH)SiO]$_4$ **527** with *i*-PrPhClSiOSiClPh*i*-Pr **534** has given a tricyclic ladder siloxane **535** which has been converted into the tetrachloro derivative **536** using HCl/AlCl$_3$. Mild hydrolysis provided a new siloxanetetraol **534**, whose co-condensation with *i*-PrPhClSiOSiClPh*i*-Pr provided the pentacyclic ladder siloxane **538** (Scheme 74).[483]

A similar strategy was also applicable for the synthesis of six- and eight-membered siloxanol-ring systems. Hydrolysis of *i*-PrRSiCl$_2$ (R = Ph, *o*-Tol) with ZnO and KOH provided the six-membered siloxane rings as a mixture of two constitutional isomers *cis-trans*-(*i*-PrRSiO)$_3$ (**539**, R = Ph; **540**, R = *o*-Tol) and *cis-cis*-(*i*-PrRSiO)$_3$ (**541**, R = Ph; **542**, R = *o*-Tol) which were separated by preparative HPLC. Subsequent reaction with HCl/AlCl$_3$ and hydrolysis of the chloro intermediates yielded the same product for both isomers, namely *cis-cis*-[*i*-Pr(OH)SiO]$_3$ **543**, implying that isomerization occurs under these conditions (Scheme 75).[484]

The base hydrolysis of *i*-PrRSiCl$_2$ (R = Ph, *p*-Tol) gave rise to formation of eight-membered siloxane rings which have been obtained as a mixture of four constitutional isomers, *cis-trans*-(*i*-PrRSiO)$_4$ (**544**, R = Ph; **545**, R = *p*-Tol), *cis-cis*-(*i*-PrRSiO)$_4$ (**546**, R = Ph; **547**, R = *p*-Tol), *all-trans*-(*i*-PrRSiO)$_4$ (**548**, R = Ph; **549**, R = *p*-Tol) and *all-cis*-(*i*-PrRSiO)$_4$ (**550**, R = Ph; **551**, R = *p*-Tol), respectively. These were separated by preparative HPLC. Reaction with HCl/AlCl$_3$, followed by hydrolysis of the chloro intermediates, afforded the corresponding siloxanol rings *cis-trans*-(*i*-Pr(HO)SiO)$_4$ **552**, *cis-cis*-[(*i*-Pr(HO)SiO)]$_4$ **553**, *all-trans*-[*i*-Pr(HO)SiO)]$_4$ **554**, and *all-cis*-[(*i*-Pr(HO)SiO)]$_4$ **555** which are configurationally stable (Scheme 76).[485]

Matasumoto *et al.* have also reported a new family of silanols and siloxanes derived from thexyltrichlorosilane ThexSiCl$_3$ **556** (Thex = 1,1,2-trimethypropyl).[486,487] Depending on the applied conditions, the hydrolysis of **556** has afforded either ThexSi(OH)$_3$ **557** or Thex(OH)$_2$SiOSi(OH)$_2$Thex **558**, both of which provide the silsesquioxane



Scheme 73

hexamer $(ThexSi)_6O_9$ **559** upon self-condensation with DCC. The co-condensation of **558** with $Ph_2(OH)SiOSi(OH)Ph_2$ yielded four different bicyclic siloxane products **560**, **561**, **562**, and **563**, depending on the temperature and the desiccant used (Scheme 77).[486,487]

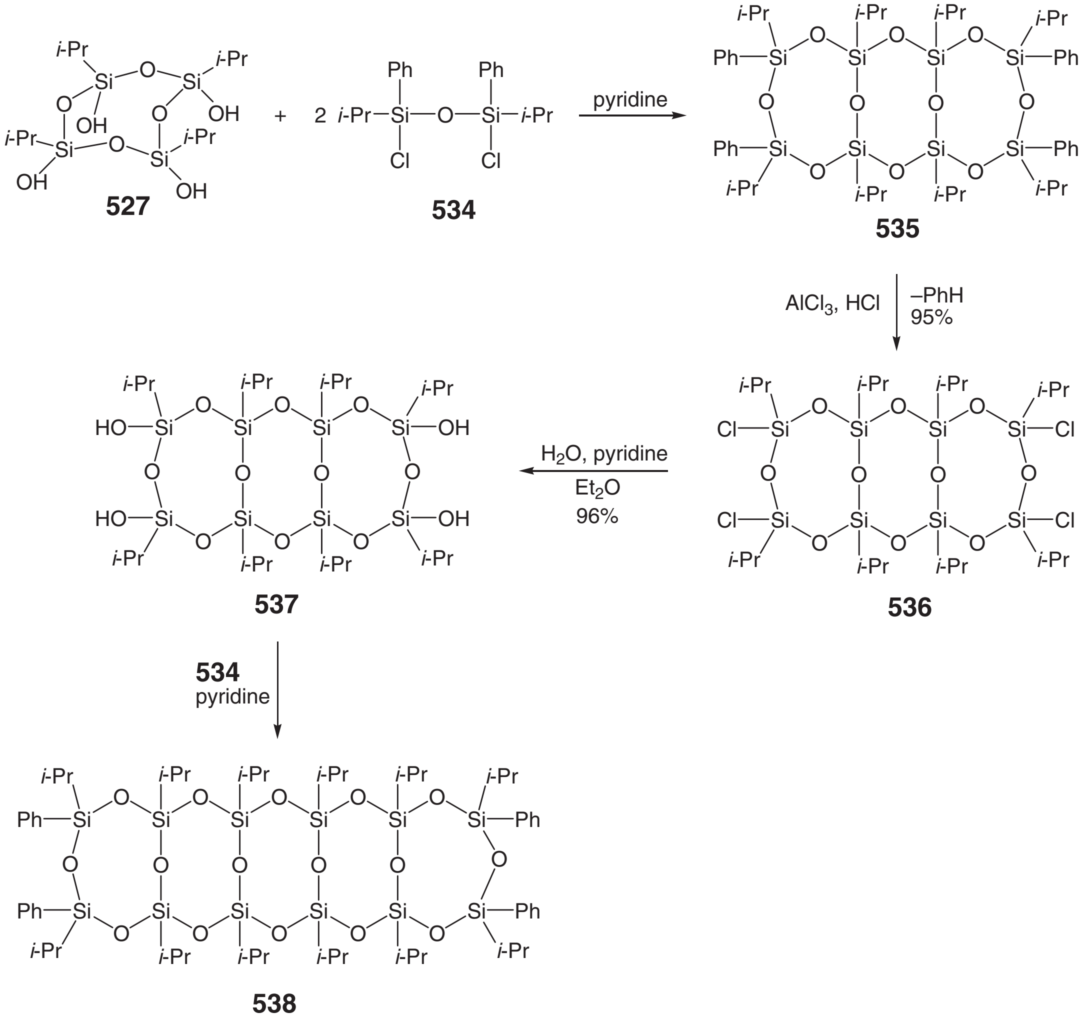
Similarly, the controlled hydrolysis of $TipSiCl_3$ **564** (Tip = 2,4,6-triisopropylphenyl) has afforded the products $TipSi(OH)_3$ **565**, $TipCl_2SiOSiCl_2Tip$ **566**, and $Tip(OH)_2SiOSi(OH)_2Tip$ **567**. The condensation of **565**–**567** at different conditions has provided new discrete molecular siloxanols **568**, **569**, and **570**, containing three to five Si atoms (Scheme 78).[488]

Stereoregular siloxanol-ring systems including *all-cis*-$[Ph(OH)SiO]_4$ **527**, *all-cis*-$[Ph(OH)SiO]_6$ **572**, and *tris-cis-tris-trans*-$[Ph(OH)SiO]_{12}$ **573**, as well as their sodium and trimethylsilyl derivatives, have been obtained by the careful hydrolysis of metallasiloxane cages by Shchegolikhina *et al.*[489–491] Roesky *et al.* and Chandrasekhar *et al.* have published on a great number of silanols, -diols and -triols having Si–N bonds from bulky aromatic amines.[492–497] Malisch *et al.* have described a number of discrete silanols and siloxanes bonded directly to transition metals, such as Fe, W, and Ru,[498–504] whereas Pannell *et al.*, Manners *et al.*, and Lorenz *et al.* have reported silanols derived from ferrocene.[505–509] For instance, the reaction of dilithiated ferrocene with $SiCl_4$ gave the spirocyclic tetraorganosilane **574**. The subsequent reaction with HCl leads to the formation of diferrocenedichlorosilane **575**, whose hydrolysis has provided the diferrocenesilanediol **576** (Scheme 79). Corriu *et al.* have prepared the first phenylene-bridged bis(silanoltriol) 1,4-$[(HO)_3Si]_2C_6H_4$ **577** for applications in sol–gel chemistry.[510,511]

The self-organization of polysilanols in the presence of other hydrogen bond acceptors has been studied by several groups.[512–516] Several other publications have dealt with the stepwise synthesis of siloxane and siloxanol chains.[450,517–522] Recent work on fully condensed siloxane rings and silsesquioxane cages involves the "non-aqueous hydrolysis" of chlorosilanes[523–526] as well as mechanistic and structural studies.[527–532]

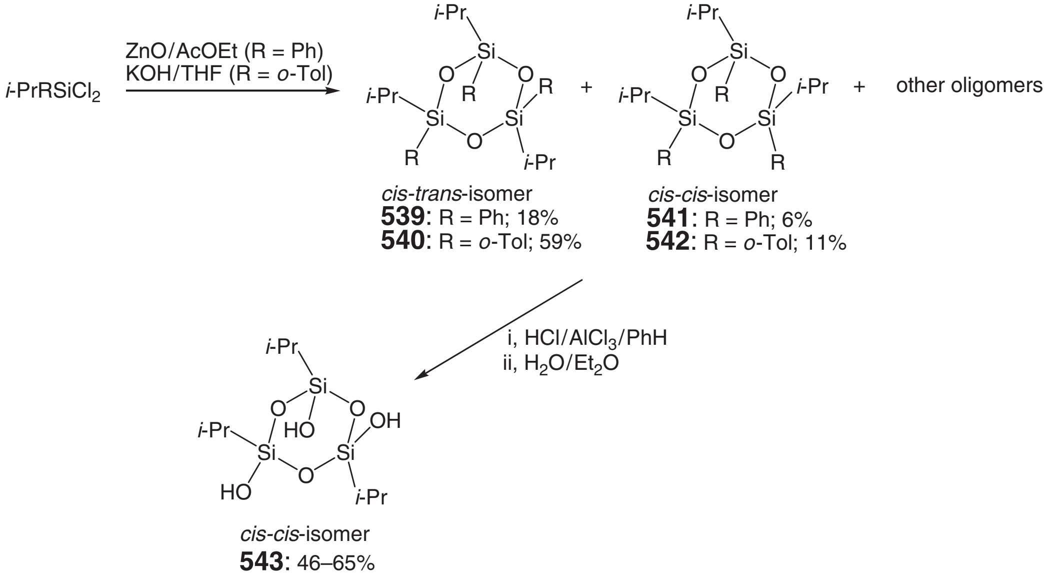
3.09.4.2 Metallasiloxanes

In recent years, great efforts have been devoted toward the preparation of well-defined metallasiloxanes, compounds having Si–O–M linkages (M = *s*-, *p*-, *d*- and *f*-block elements). In general, these efforts are motivated by the prospect

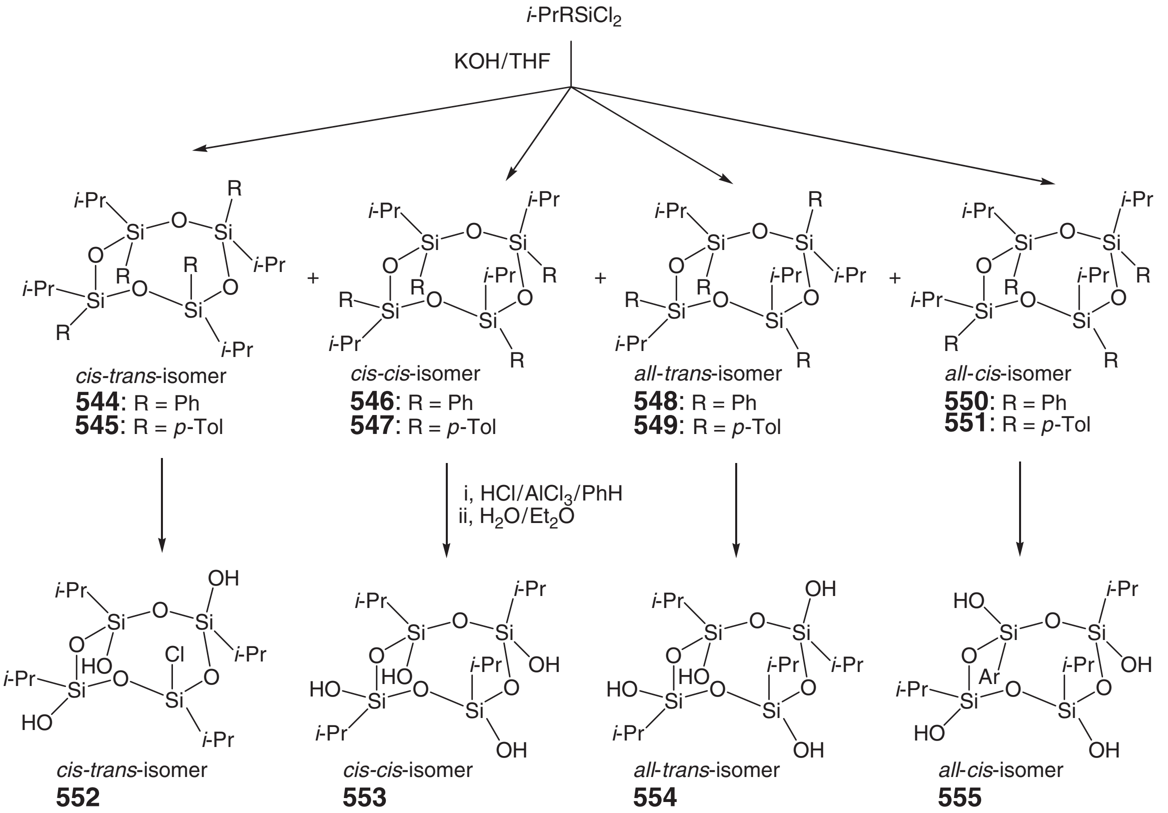


Scheme 74

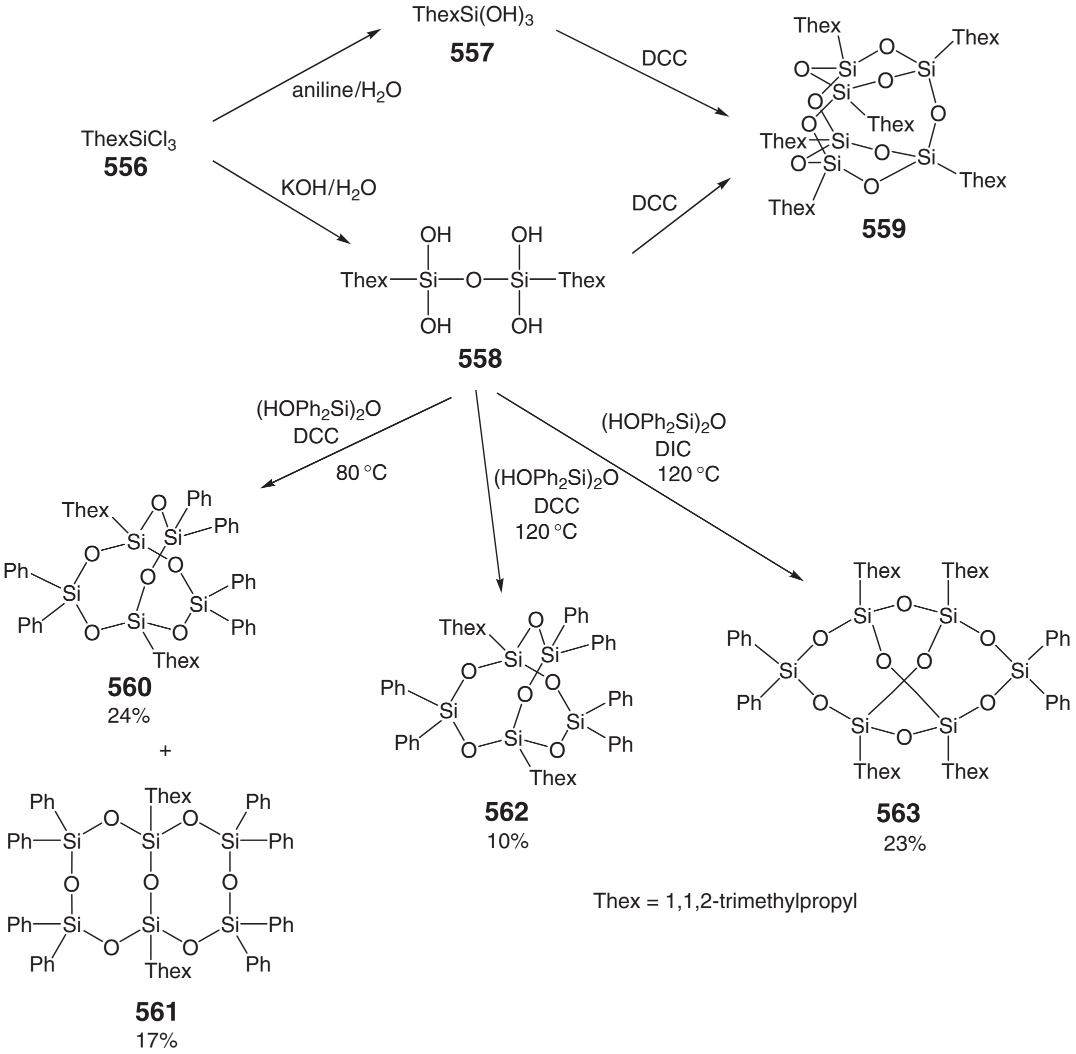
of finding novel structures and by potential applications in material science and catalysis. The great majority of metallasiloxanes has been prepared utilizing readily available silanols and appropriate organometallic or inorganic metal precursors. A great number of reviews on the subject reflect the rapid development of the field in recent years. In 1996 and 2004, Roesky *et al.* reviewed metallasiloxanes derived from silantriols and related silesquioxane cages.[433,533] In 1999, King and Sullivan summarized metallasiloxanes derived from main group and transition metals and diorganosilanoldiols and related siloxanols.[534] In 2000, Edelmann *et al.* published a comprehensive review dealing with metallsiloxanes of early transition metals and *f*-block elements.[535] A review by Beckmann and Jurkschat covers work on stannasiloxane rings and polymers.[536] In 2004, Abbenuis *et al.* reported on the progress in the field of metallasiloxanes derived from incompletely condensed silsesquioxanes and applications thereof in catalysis.[537,538] The most recent review on metallasiloxanes by Lorenz and Edelmann includes species derived from incompletely condensed silsesquioxanes.[539] Over the years, a large number of fully characterized alkali and earth alkai metal silanolates and siloxanolates have been published.[540–548] Wolczanski *et al.* have prepared low-coordinate early transition metal complexes using the *t*-Bu$_3$SiO (silox) ligand.[549–565] Driess *et al.* have described zinc siloxanolates, such as (MeZnOSiMe$_3$)$_4$ **578**, having polyhedral structures (Figure 3).[566–569] Sita *et al.* prepared a polyhedral tin(II) oxo silanolate cluster Sn$_6$O$_4$(OSiMe$_3$)$_4$ **579** by heating Sn(OSiMe$_3$)$_3$ **580** at 180 °C.[570] Mehring *et al.* obtained the bismuth oxo silanolate cluster Bi$_{22}$O$_{26}$(OSiMe$_2$*t*-Bu)$_{14}$ **581** by the controlled hydrolysis of Bi(OSiMe$_2$*t*-Bu)$_3$ **582**.[571] Veith *et al.* have reported a number of multinuclear aluminosiloxanes, such as the pentacyclic compound **583**, which is accessible by the reaction of Ph$_2$Si(OH)$_2$ with [*t*-BuAlH$_2$]$_2$. The reactivity of the Al–OH groups has



Scheme 75

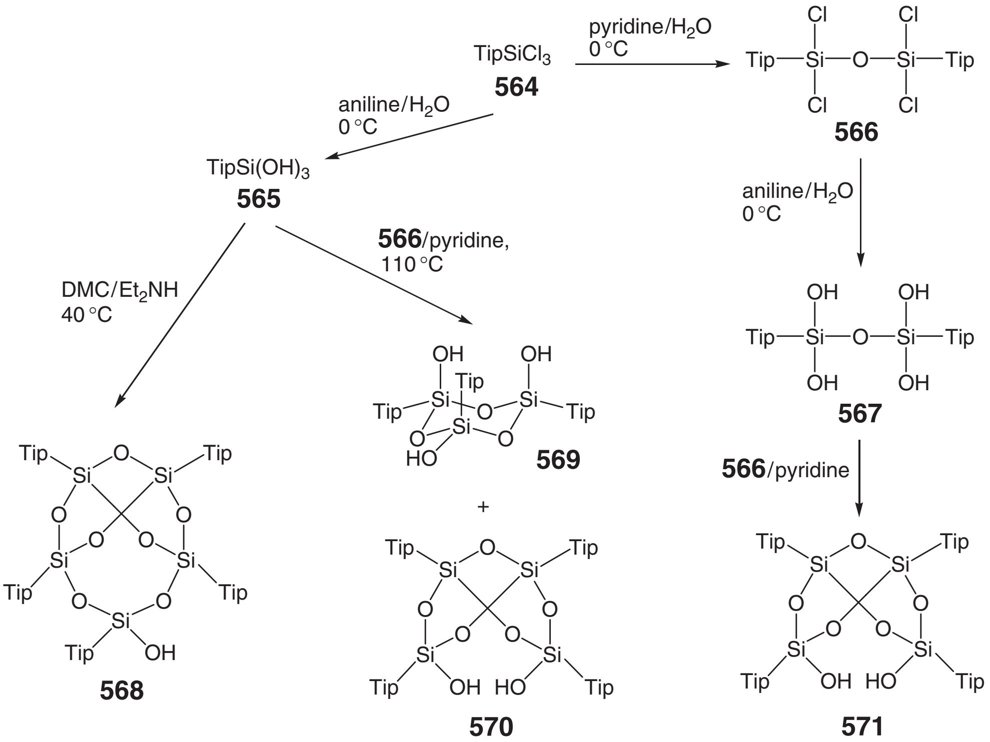


Scheme 76

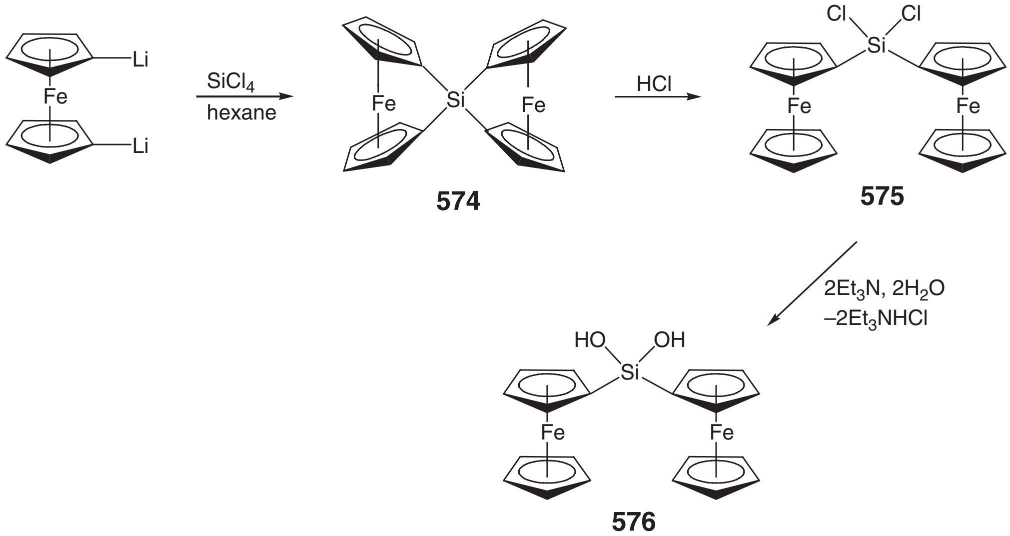


Scheme 77

been probed in a number of reactions.[572,573] Metallasiloxane rings incorporating metals such as Al, B, Ga, Sn, Ti, W have been prepared by several groups.[509,574–583] Acyclic metallasiloxanes based on V, Mo, and W have been assessed by Bregeault *et al.* on their potential to serve as oxidation catalysts[584–587] Potentially chelating tetraorganodisiloxanediols have been utilized to synthesize metallasiloxanes of lanthanides and actinides, such as Eu, Gd, Ln, Sm, Sc, U, Nd, and Yb, which often contain six-membered ring units.[588–590] Very few metallasiloxanes containing disilane units and five-membered ring structures are also known.[591–593] Boro silicate cages have been reported by Spalding *et al.*[594,595] Duchateau *et al.* and Collins *et al.* have described silsesquioxanes modified by organoboranes and zirconocene, which have been utilized as models of heterogenous catalysts for the olefin polymerization.[596–601] Maschmeyer *et al.* and Abbenhuis *et al.* have prepared titanium silsesquioxane clusters, such as **584**, that show potential as epoxidation catalysts.[602,603] Edelmann *et al.* and other groups have prepared metallasilsesquioxanes incorporating metals such as Li, B, Al, In, Sn, Ti, Zr, Hf, W, V, Ta, Fe, Cu, Sc, Y, La, Ce, Yb and Sm.[456,465,467–469,604–624] Roesky *et al.* have prepared polyhedral metallasiloxanes derived from the aminosilantriol (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)Si$(OH)_3$ **585** incoorporating metals, such as Sn, Zn, Fe and Co.[492,496,497,625–650] Tilley *et al.* have described metallasiloxenes derived from (*t*-BuO)$_3$SiOH **586** and related siloxanols incorporating metals, such as B, Bi, Sn, V, Mo, Ti, Zr, Hf and Cu.[651–667] Metallasiloxenes derived from (*t*-BuO)$_3$SiOH **586** have been used as single-source precursors for mixed metal-oxide ceramic materials.



Scheme 78

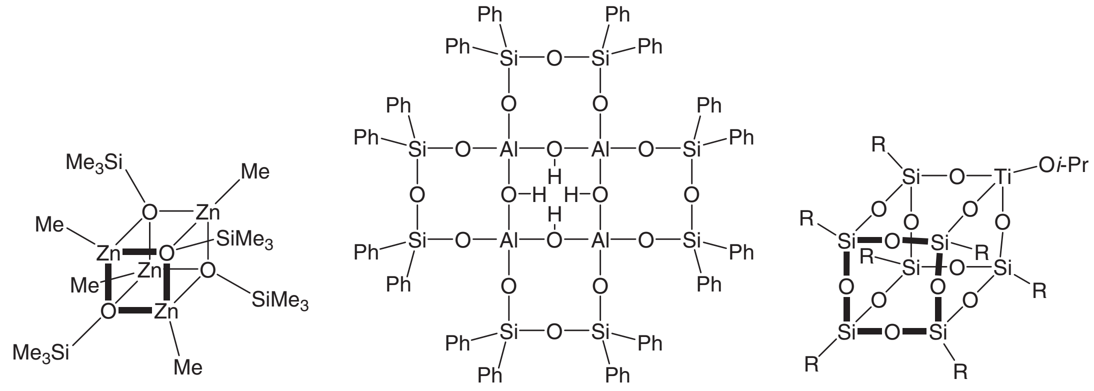


Scheme 79

3.09.5 Silicon–Silicon Compounds

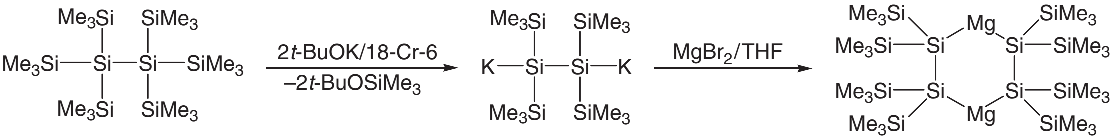
3.09.5.1 Oligosilanes

Several reviews dealing with the progress in the field of saturated oligosilanes have been published.[299,668–672] One of the most prominent methods for the formation of Si–Si bonds involves the dehydrocoupling of hydrosilanes catalyzed by transition metals. A comprehensive review by Corey in 2004 covers all aspects of this chemistry.[673] The most



578 **583** **584**

Figure 3



127 **587** **588**

Scheme 80

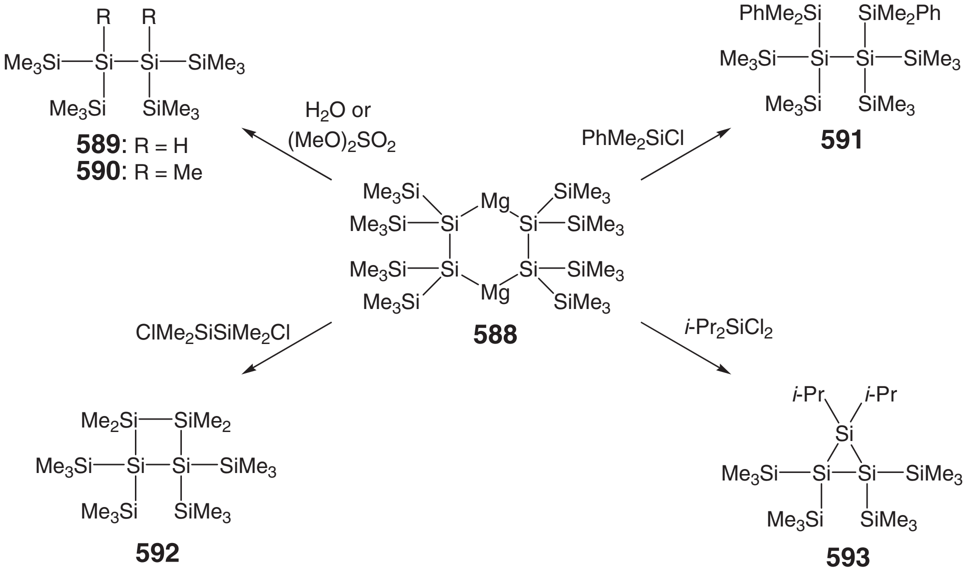
recent work in the field entails the search for new catalysts as well as mechanistic studies. Corriu *et al.* and Marschner *et al.* have utilized $Cp_2M(OPh)_2$ and Cp_2MF_2 (M = Ti, Zr) as catalysts for the dehydropolymerization of silanes since they are air stable as opposed to many commonly used catalysts, for example, Cp_2ZrMe_2.[674,675] Rosenberg *et al.* have used Wilkinson's catalyst $(Ph_3P)_3PhCl$ for dehydrogenative couplings, including even dialkylsilanes R_2SiH_2 (R = alkyl) usually react very sluggishly. The same authors suggested the removal of hydrogen gas from the reaction mixture in order to drive the reaction to completion.[676,677]

Oligosilane anions have been extensively used by Marschner *et al.* to build up larger oligosilane aggregates and heteroatom derivatives. For instance, the reaction of the octasilane $(Me_3Si)_3SiSi(SiMe_3)_3$ **127** with 2 equiv. of potassium *tert*-butoxylate in the presence of a crown ether provides the dipotassium silanide $K(Me_3Si)_2SiSi(SiMe_3)_2K$ **587**, whose transmetallation with $MgBr_2$ gives rise to formation of the six-membered Mg_2Si_4 heterocycle **588** which exists as THF adduct (Scheme 80).[678]

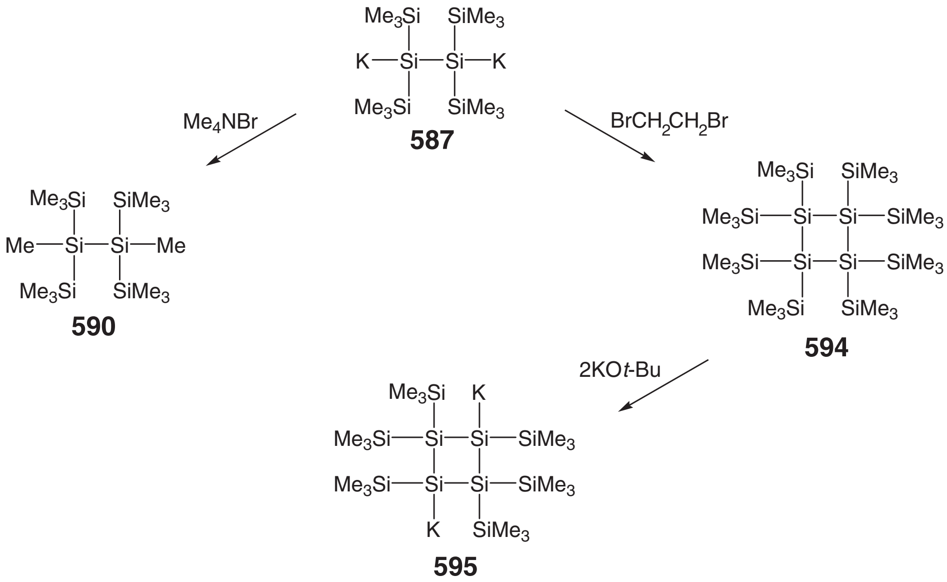
The six-membered Mg_2Si_4 heterocycle **588** is a versatile starting material for the preparation of open-chain and cyclic oligosilanes. The hydrolysis of **588** and the reduction of **588** with dimethyl sulfate afford the hexasilanes $R(Me_3Si)_2SiSi(SiMe_3)_2R$ (**589**, R = H; **590**, R = Me), whereas the coupling reaction of **588** with $PhMe_2SiCl$ gives a new hexasilane $(PhMe_2Si)(Me_3Si)_2SiSi(SiMe_3)_2(SiMe_2Ph)$ **591**, respectively (Scheme 81).[678] The coupling reaction of **588** with $ClMe_2SiSiMe_2Cl$ and $i\text{-}Pr_2SiCl_2$ provides the four-membered cyclooctasilane $[Me_2SiSi(SiMe_3)_2]_2$ **592** and the three-membered cycloheptasilane $i\text{-}Pr_2Si[Si(SiMe_3)_2]_2$ **593**, respectively (Scheme 81).[678]

The hexasilane $Me(Me_3Si)_2SiSi(SiMe_3)_2Me$ **590** can also be prepared by the reaction of the dipotassium silanide $K(Me_3Si)_2SiSi(SiMe_3)K$ **587** with tetramethylammonium bromide (Scheme 82). Reaction of **587** with ethylene bromide has yielded the symmetric four-membered cyclooctasilane $[(Me_3Si)_2Si]_4$ **594**, whose reaction with 2 equiv. of KO*t*-Bu produces a novel cyclic dipotassium disilanide **595** (Scheme 82).[678]

The reaction of the open-chain decasilane $(Me_3Si)_3SiMe_2SiMe_2SiSi(SiMe_3)_3$ **596** with 2 equiv. of KO*t*-Bu also occurs with remarkable selectivity and affords the dipotassium silanide $K(Me_3Si)_2SiMe_2SiMe_2SiSi(SiMe_3)_2K$ **597**, whose reaction with dimethyl sulfate and water gives rise to formation of the octasilanes $R(Me_3Si)_2$-$SiMe_2SiMe_2SiSi(SiMe_3)_2R$ (**598**, R = Me; **599**, R = H) (Scheme 83). It is worth mentioning that Matsumoto *et al.* have obtained an analog of **597**, namely, $K[(i\text{-}Pr_2)Si]_4K$ **600**, by cleavage of the four-membered cyclotetrasilane $(i\text{-}Pr_2Si)_4$ with potassium.[679] The coupling reaction of **597** with the organoelement chlorides Me_2ECl_2 (E = Si, Sn), $TMPD\text{–}BCl_2$ (TMPD = 2,2,6,6-tetramethylpiperidiinyl), Et_2PNCl_2, and Cp_2ECl_2 (E = Zr, Hf) has made possible



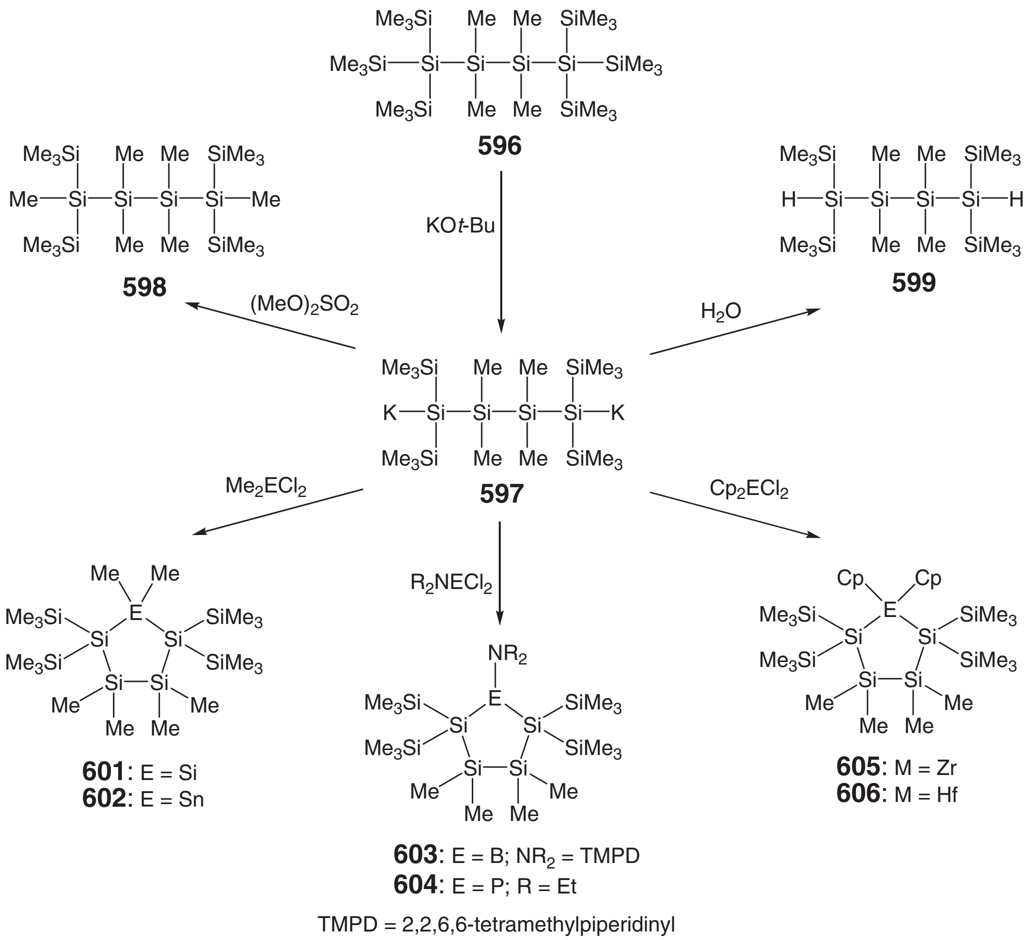
Scheme 81



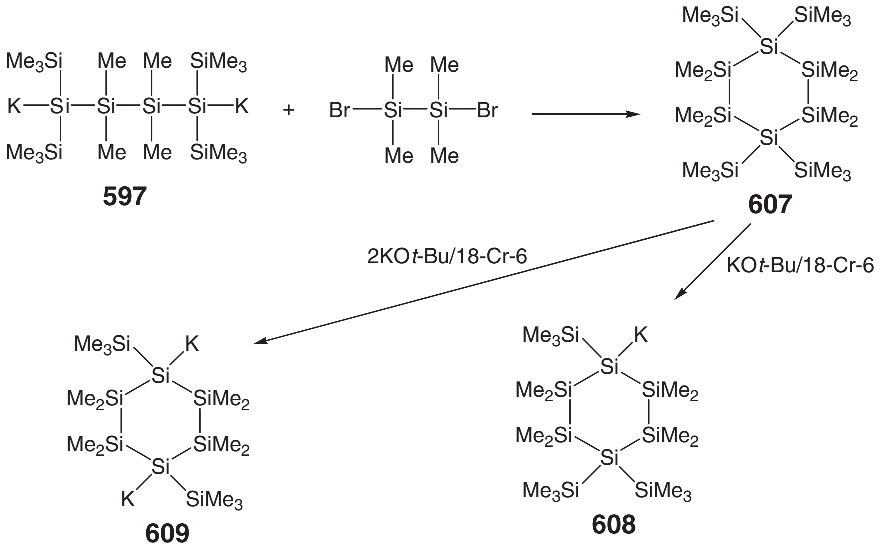
Scheme 82

the preparation of five-membered ESi_4 heterocylces $Me_2E[Si(SiMe_2)_2SiMe_2]_2$ (**601**, E = Si; **602**, E = Sn), $R_2NE[Si(SiMe_2)_2SiMe_2]_2$ (**603**, E = B, NR_2 = TMPD; **604**, E = P, R = Et) and $Cp_2E[Si(SiMe_2)_2SiMe_2]_2$ (**605**, E = Zr; **606**, E = Hf), respectively (Scheme 83).[680] The reaction of the dipotassium silanide $K(Me_3Si)_2SiMe_2SiMe_2SiSi(SiMe_3)_2K$ **597** with dibromo disilane $BrMe_2SiSiMe_2Br$ has provided access to the six-membered cyclodecasilane $(Me_3Si)_2Si(SiMe_2SiMe_2)_2Si(SiMe_3)_2$ **607**, which has been utilized to prepare the corresponding cyclooligosilane anion $K(Me_3Si)Si(SiMe_2SiMe_2)_2Si(SiMe_3)_2$ **608** and the dianion $K(Me_3Si)Si(SiMe_2SiMe_2)_2Si(SiMe_3)K$ **609** by varying the amount of KO*t*-Bu used (Scheme 84).

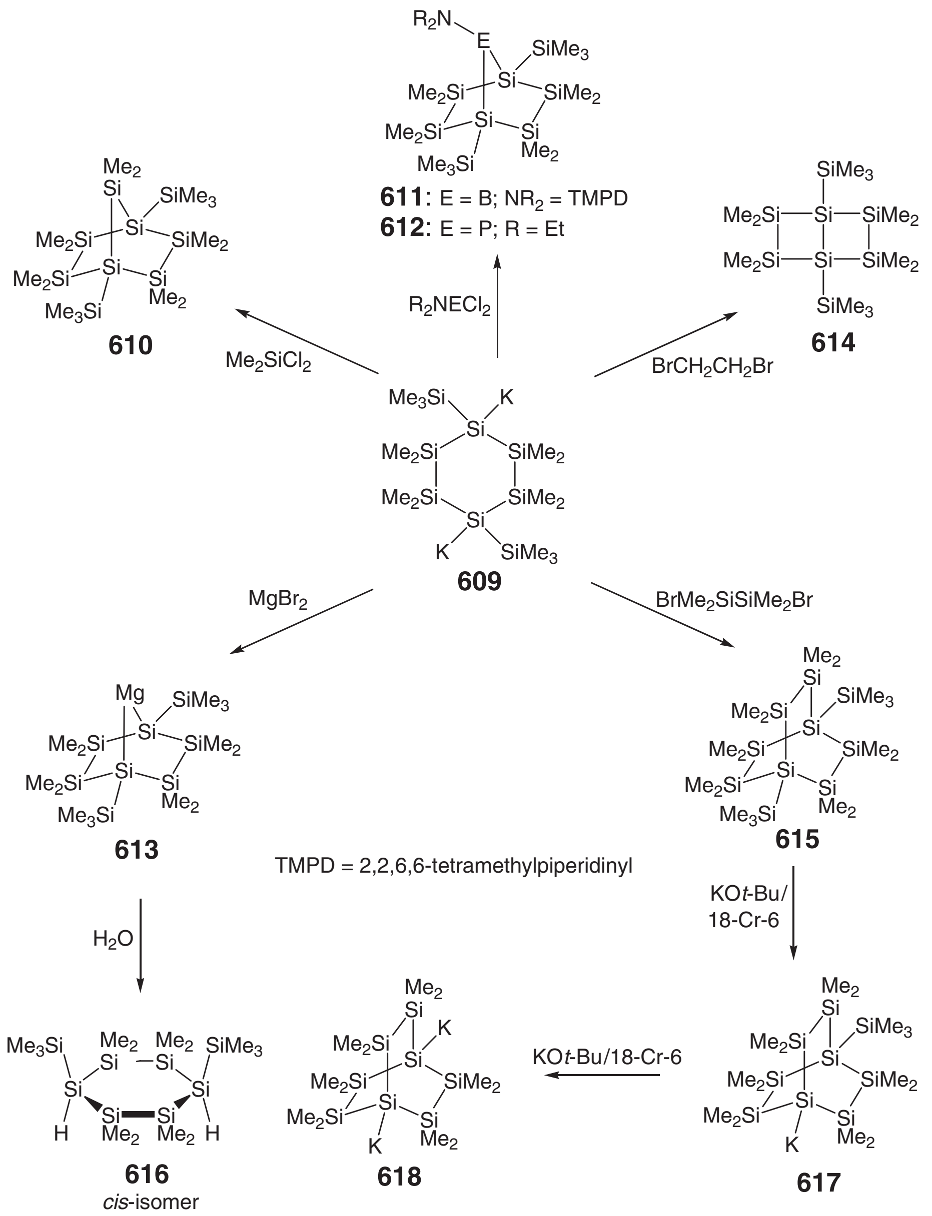
The chemistry of cyclooligosilanes was reviewed by Hengge and Janoschek in 1995.[672] The most commonly studied cyclooligosilanes include five- and six-membered rings $(R_2Si)_5$ (R = Me, Ph) and $(R_2Si)_6$ (R = Me, Ph).



Scheme 83



Scheme 84

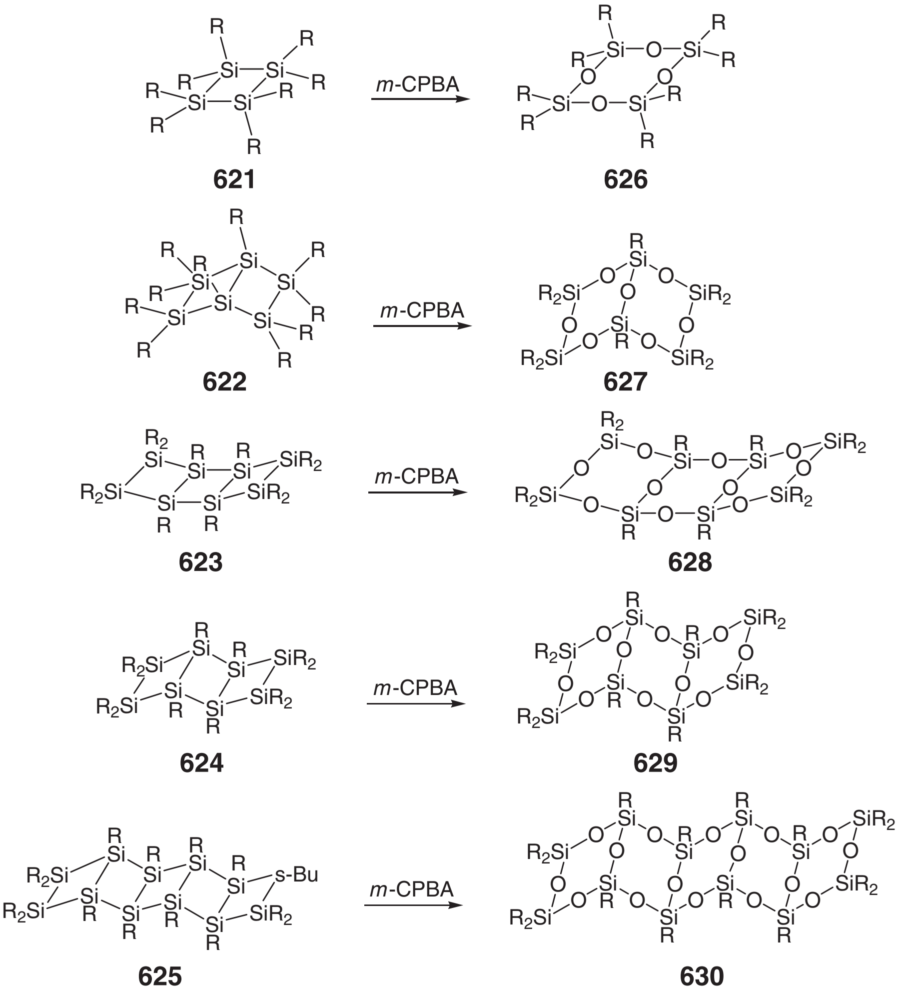


Scheme 85

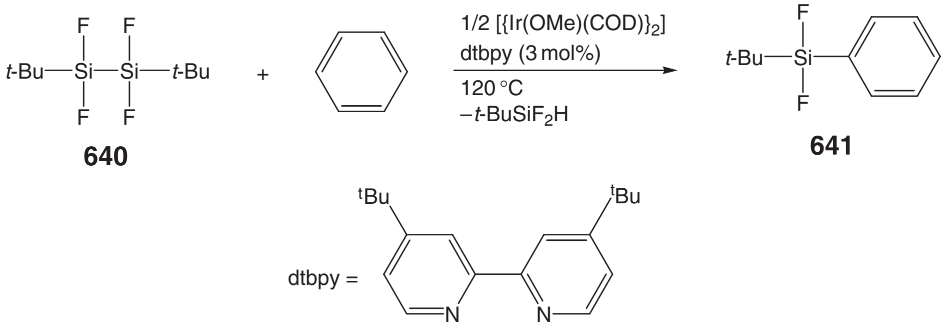
The functionalization of these cyclooligosilanes is often cumbersome and accompanied by unwanted ring cleavage as well as substantial amounts of byproducts. The approach developed by Maschner *et al.* even allows the preparation of bicyclooligosilanes and related heterocycles.[681] Thus, the reaction of the dipotassiocyclooligosilane $K(Me_3Si)Si(SiMe_2SiMe_2)_2Si(SiMe_3)K$ **609** with Me_2SiCl_2, TMPD–BCl_2, Et_2NPCl_2, $MgBr_2$, $BrCH_2CH_2Br$, and $BrMe_2SiSiMe_2Br$, respectively, affords the bicyclooligosilanes **610–615** containing 8–10 Si atoms (Scheme 85).

The hydrolysis of the $MgSi_6$ heterobicycle **613** has resulted in the exlusive formation of six-membered cyclooctasilane **616** having a *cis*-configuration (Scheme 85). The bicyclodecasilane **615** has been employed for the preparation of the corresponding bicyclononasilane anion **617** and the bicycloctasilane dianion **618** upon treatment with KO*t*-Bu. Notably, the attack of the reagent occurs selectively under substitution of the trimethylsilyl groups attached to the bridgehead Si atoms (Scheme 85). At elevated temperatures, dodecamethylcyclohexasilane $(Me_2Si)_6$ **610** has been converted by the action of KO*t*-Bu into the related undecamethylcyclohexasilanyl anion $KMeSi(SiMe_2SiMe_2)_2SiMe_2$ **619**,[682] which has been utilized by Maschner *et al.* for the preparation of oligosilanes with up to 24 silicon atoms.[678]

Recently, even oligosilanes having adamantane structures have been synthesized, which can be regarded as smallest piece of the α-silicon modification.[683,684] Functionalized derivatives of dodecamethylcyclohexasilane $(Me_2Si)_6$ **610** have been studied by Stüger *et al.* as model compounds for siloxenes, which are under investigation due to their photoluminescence properties.[685] The undecamethylcyclohexasilanyl anion $KMeSi(SiMe_2SiMe_2)_2SiMe_2$ **619** has been further used to prepare $Me_2Si(SiMe_2SiMe_2)_2SiMeSiH_3$ **620**, which has been subject to transition metal-catalyzed dehydropolymerization studies.[686] A number of oligomethylene-bridged bis(silyl) dianions has been reported.[687,688] Moreover, Apeloig *et al.* and Marschner *et al.* have used silyl anions to prepare branched polysilanes.[689–691] Structural and spectroscopic studies on short-chain, branched, and dendritic oligosilanes have been conducted by Lambert *et al.*,[692,693] Krempner *et al.*,[694,695] Obata and Kira,[696] and Baumgartner *et al.*[697,698] Attempts have been made to correlate UV spectroscopic properties, associated with the σ-conjugation of the Si–Si bonds, with the chain conformations observed by X-ray crystallography. However, the conformational flexibility in solution precluded a reliable interpretation. The first systematic studies on the conformational dependence of the UV absorption have been undertaken by Tamao *et al.* who applied rigid cyclooligosilanes, which are locked into a particular conformation.[699–701] Ladder oligosilanes are accessible via the reductive coupling of appropriate chlorosilanes. Two detailed reviews on the synthesis, structure, and spectroscopic properties of ladder oligosilanes have been given by Matsumoto *et al.* in 2000 and 2003[702,703] The oxidation of ladder oligosilanes **621–625** using *m*-chloroperbenzoic acid (*m*-CPBA) occurs affording the corresponding ladder polysiloxanes **626–630** (Scheme 86). The insertion of O atoms into the Si–Si bonds occurs without degradation of the structural framework. Mechanistic studies suggest that Si–O bonds may activate adjacent Si–Si bonds, which lead the authors to propose a domino oxidation effect.[704]



Scheme 86



Scheme 87

Further information on the oxidation of oligosilanes is available. For instance, the electrochemical and chemical oxidation of cyclooligosilanes giving cyclosiloxanes has been studied by Becker *et al.*[705–709] The oxidation of octasilacubanes, such as (t-BuMe$_2$SiSi)$_8$ **631**, has been studied by Matsumoto *et al.*[488,710] The air oxidation of polysilanes H[Ph(H)Si]$_n$H **632** has been thoroughly investigated by Chatgilialoglu *et al.*[711]

Over the years, numerous efforts have been directed to the functionalization of oligosilanes. Based on an early communication by Bassindale and Stout,[712] Uhlig has developed routes for the selective cleavage of phenyl and amino groups in oligosilanes using triflic acid. The silyl triflates may be transformed into a variety of useful other groups.[713–718] A straightforward example for a selective p-tolyl group cleavage is the synthesis of 1,2-disilanediyl bis(triflate), (TfO)H$_2$SiSiH$_2$(OTf) **633**, by reaction of (p-Tol)H$_2$SiSiH$_2$(p-Tol) **634** with 2 equiv. of triflic acid. Schmidbaur *et al.* have demonstrated that 1,2-disilanediyl bis(triflate) **633** is a very versatile building block for the synthesis of hydrogen-rich disilanes.[21,719–722] Corey *et al.* have studied the reaction of oligosilanes H(PhMeSi)$_n$H (**635**, $n = 2$; **636**, $n = 3$; **637**, $n = 4$) with triflic acid and provide evidence for rearrangement processes.[723,724] Similar observations have been made by Krempner *et al.*, who have reported that the tetrasilane [Ph(Me$_3$Si)$_2$SiMe$_2$Si]$_2$ **638** undergoes a skeletal rearrangement upon reaction with triflic acid yielding the unsymmetric product TfO(Me$_3$Si)$_2$SiMe$_2$Si(Me$_3$Si)$_2$SiMe$_2$SiOTf **639**.[725] Roewer *et al.* have studied the mild and selective reduction of oligosilanes containing multiple chlorine atoms using triorganotin hydrides, such as Bu$_3$SnH.[726–728] Roewer *et al.* and Herzog *et al.* have also reported that the chlorosilanes can be converted into the corresponding alkoxy-substituted silanes using trialkyl orthoformates.[729,730] Moreover, Herzog *et al.* have converted (branched) chlorosilanes into the related chalcogenides and studied their polyhedral structures.[731–740] Routes leading to di- and oligosilanes containing two functional groups with different reactivities have been explored by Roesky *et al.*,[741] Stüger *et al.*,[742,743] and Böhme *et al.*[744,745]

The activation of Si–Si bonds by transition metal complexes and addition to unsaturated organic compounds has been the subject of two comprehensive reviews in 1999 and 2000 by Suginome and Ito.[51,746] Photoinduced Si–Si bond cleavage reactions have been summarized by Kako and Nakadaira in 1999.[747] More recently, Ishiyama and Miyaura *et al.* have described the Ir(I)-catalyzed C–H silylation benzene derivatives by disilenes. According to their work, benzene reacts with t-BuF$_2$SiSiF$_2t$-Bu **640**[748] to form t-BuPhSiF$_2$ **641** and gaseous t-BuSiF$_2$H (Scheme 87).[749]

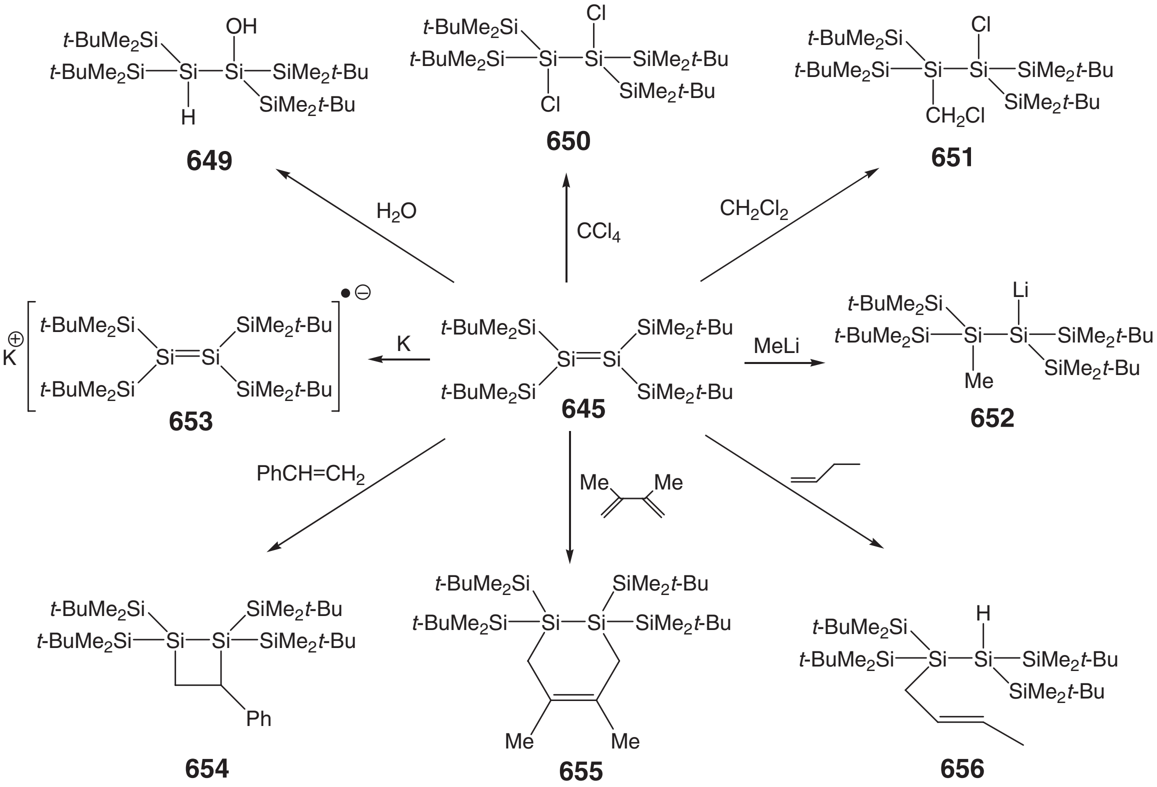
Denmark and Kallemeyn have described the mild palladium-catalyzed insertion of 1,2-diethoxy-1,1,2,2,-tetramethyldisilane EtOMe$_2$SiSiMe$_2$OEt into aryl bromides RBr affording aryldimethylsilyl ethers RMe$_2$SiOEt and Me$_2$SiBrOEt in high yields.[750] Williams and Tanaka *et al.* have reported on the palladium- and platinium-catalyzed reaction of carbonyl and imine compounds with disilanes.[751]

3.09.5.2 Disilenes

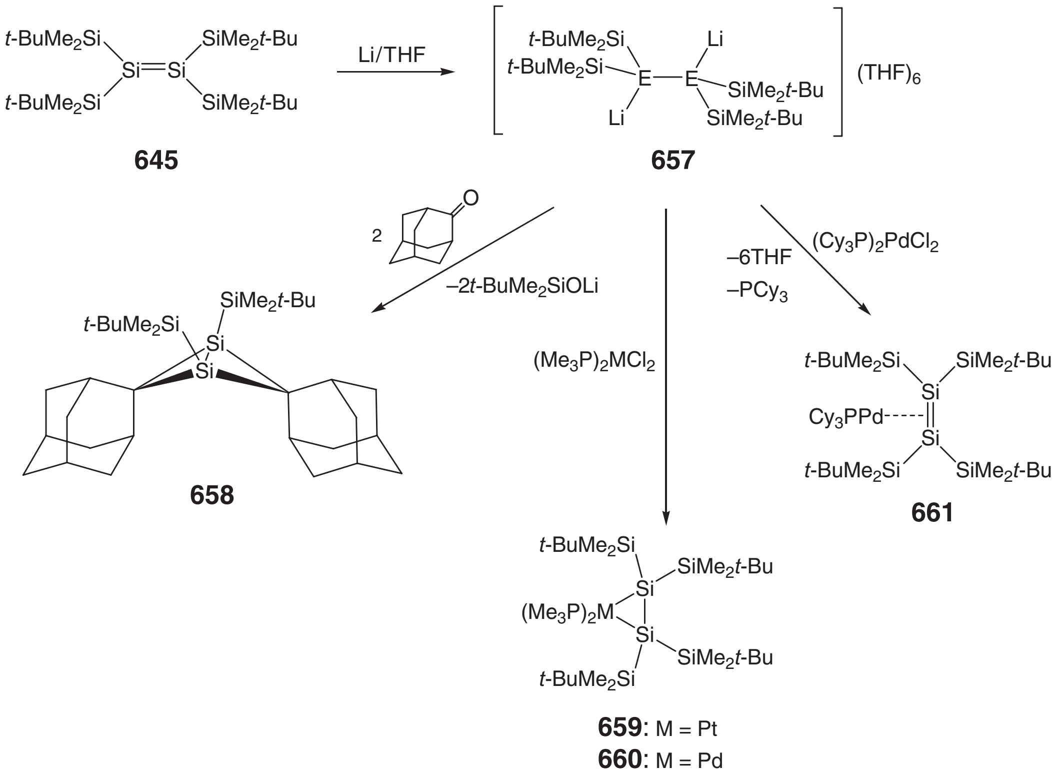
Disilenes (disilaethenes), compounds having Si–Si double bonds, have been known since the description of the full characterization of Mes$_2$SiSiMes$_2$ **642** by West *et al.* in 1981.[752] Since then, several reviews on disilenes have documented the rapid development of the field.[753–755] In 1994, Kira and Sakurai *et al.* published the first well-defined tetrakis(trialkylsilyl)disilenes (R$_3$Si)$_2$SiSi(SiR$_3$)$_2$ (**643**, R$_3$Si = i-Pr$_2$MeSi; **644**, R$_3$Si = i-Pr$_3$Si; **645**, R$_3$Si = t-BuMe$_2$Si),[756] which are accessible by the reduction of (i-Pr$_2$MeSi)SiBr$_2$ **646** with sodium, the reduction of (i-Pr$_3$Si)$_2$SiBr$_2$ **647** with lithium naphthalide, and by the photolysis of the three-membered cyclohexasilane [(t-BuMe$_2$)$_2$Si]$_3$ **648**,[757] respectively. Structural and spectroscopic properties of **643–648** have been compared to those of Mes$_2$SiSiMes$_2$ **642**.[756] Reactivity studies on tetrakis(trialkylsilyl)disilenes has been conducted using (t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$ **645**. The reaction of **645** with H_2O, CCl_4, CH_2Cl_2, and MeLi proceeds via oxidative addition to the Si–Si double bonds and yields the functionalized open-chain hexasilanes X(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$Y (**649**, X = H, Y = OH; **650**, X = Y = Cl; **651**, X = CH$_2$Cl, Y = Cl; **652**, X = Me, Y = Li).[758,759] In general, disilenes have rather low-lying LUMOs when compared to ethenes, which suggests that the reduction of Si–Si double bonds should be thermodynamically more feasible than those of C–C double bonds (Scheme 88). The reduction of **645** with potassium indeed occurs via a single-electron transfer (SET) to form the radical anion K[(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$] **653**, an analog of Li[(t-Bu$_2$MeSi)$_2$SiSi(SiMet-Bu$_2$)$_2$] **80** (Scheme 16).[253] With styrol and 1,3-dimethyl-1,3-butadiene, **645** reacts via cycloaddition and formation of four- and six-membered heterocycles **654 and 655** contaning disilane units (Scheme 88).[758] The reaction of **645** with 1-butene proceeds via addition of a terminal C–H bond to the Si–Si double bond affording the alkene **656** (Scheme 88). Unlike the reduction with potassium, the reaction of **645** with lithium leads to the formation of tetrakis(*tert*-butyldimethylsilyl)dilithiodisilane Li(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$Li **657**, whose reaction with adamantone provides synthetic access to the first 1,3-disilabicyclo[1.1.0]butane **658** (Scheme 89).[760]

The reaction of tetrakis(*tert*-butyldimethylsilyl)dilithiodisilane Li(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$Li **657** with (Me$_3$P)$_2MCl_2$ (M = Pt, Pd) and (Cy$_3$P)$_2$PdCl$_2$ yields novel side-on transition metal–disilene complexes, which have been formulated as metallacycle in the case of (Me$_3$P)$_2$M(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$ (**659**, M = Pt; **660**, M = Pd) and as π-complex in case of Cy$_3$PPd(t-BuMe$_2$Si)$_2$SiSi(SiMe$_2$$t$-Bu)$_2$ **661**, respectively (Scheme 89).[761] In a similar fashion, Maschner *et al.* have reacted the dianionic compound K[(Me$_3$Si)$_2$SiSi(SiMe$_3$)$_2$] **587** with Cp$_2$HfCl$_2$ and obtained a side-on transition metal–disilene complex Cp$_2$Hf(Me$_3$Si)$_2$SiSi(SiMe$_3$)$_2$ **662**.[762] The nature of bonding between the disilene unit and the metal has been rationalized by two contributing resonance structures, namely a π-complex and a disilylene complex.

The reduction of t-BuMe$_2$SiSiBr$_2$X (**663**, X = Cl; **664**, X = Br) with sodium in toluene, carried out at room temperature (X = Cl) and under reflux conditions (X = Br), has provided two different products, namely the



Scheme 88

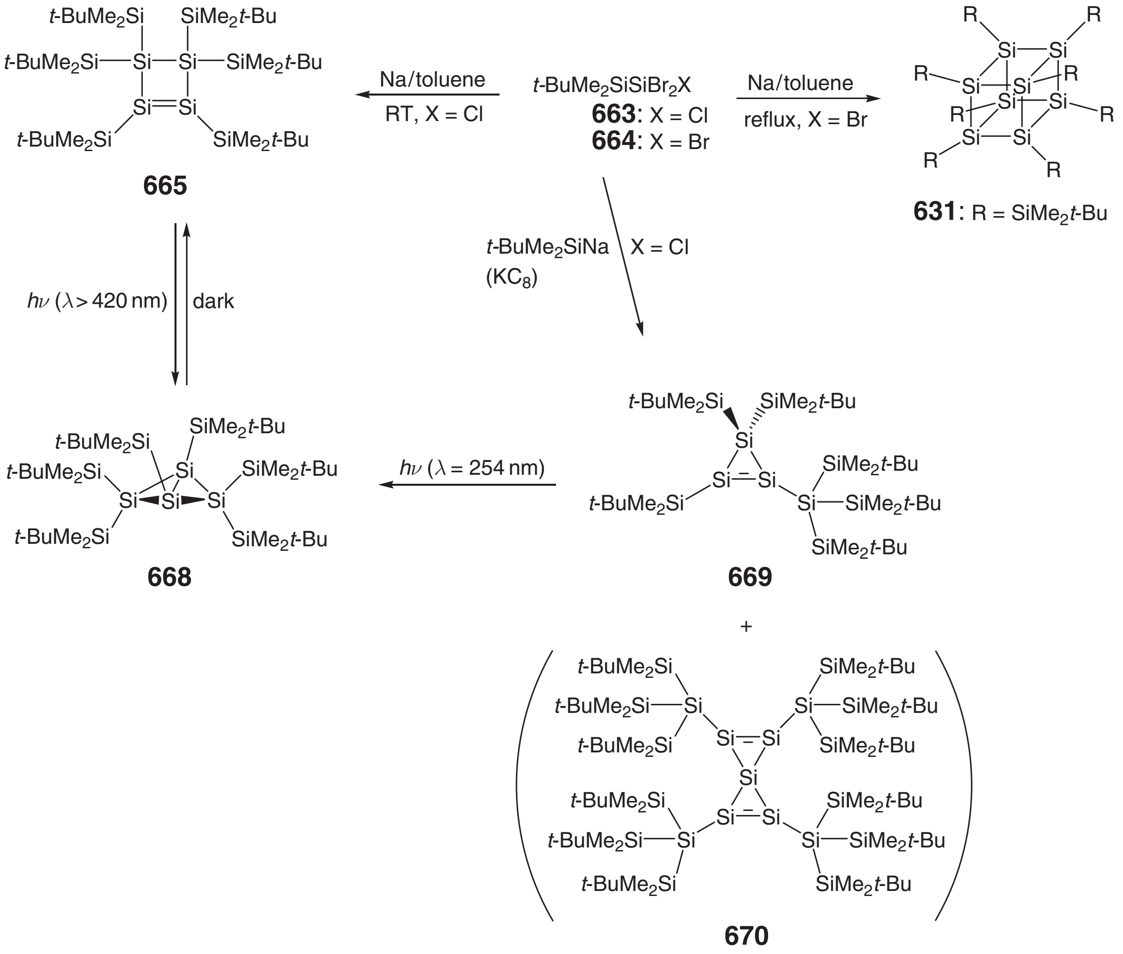


Scheme 89

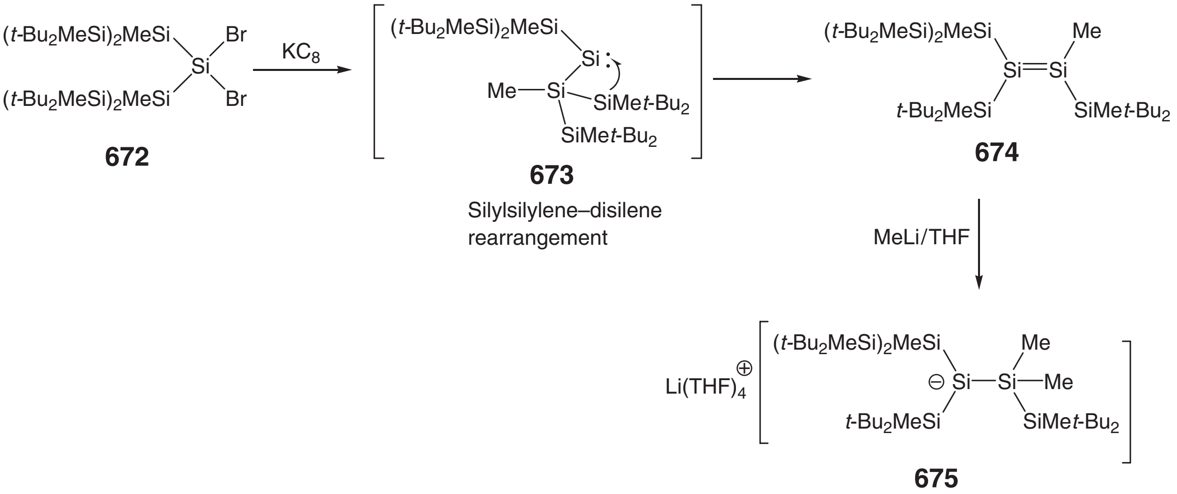
tetrasilacyclobutene $[(t\text{-BuMe}_2\text{Si})_2\text{SiSi}(\text{SiMe}_2t\text{-Bu})]_2$ **665**[763] and the octasilacubane $(t\text{-BuMe}_2\text{SiSi})_8$ **631**, respectively (Scheme 90).[488,764]

The tetrasilacyclobutene $[(t\text{-BuMe}_2\text{Si})_2\text{SiSi}(\text{SiMe}_2t\text{-Bu})]_2$ **665**, also accessible by the reaction of $(t\text{-BuMe}_2\text{Si})\text{Br}_2\text{SiSiBr}_2(\text{SiMe}_2t\text{-Bu})$ **666**, $(t\text{-BuMe}_2\text{Si})_2\text{SiBr}_2$ **667**, and lithium naphthalenide, is the first compound having an endocyclic Si–Si double bond.[763] Later, an analog of **665**, namely, $[(t\text{-Bu}_2\text{Si})\{(t\text{-Bu}_2\text{MeSi})\text{MeSi}\}(\text{SiMe}t\text{-Bu}_2)_2]$ **100**, has been prepared (Scheme 17). Although thermally very stable, the tetrasilacyclobutene $[(t\text{-BuMe}_2\text{Si})_2\text{SiSi}(\text{SiMe}_2t\text{-Bu})]_2$ **665** rearranges upon irradiation ($\lambda = 420\,\text{nm}$) into the isomeric tetrasilabicyclobutane **668**. In the dark, **668** slowly converts back to form **665** (Scheme 90).[765] Mechanistic considerations propose that an isomeric open-chain tetrasilabutadiene might be a conceivable key intermediate of the rearrangement process. The reduction of $t\text{-BuMe}_2\text{SiSiBr}_2\text{Cl}$ **663** with $t\text{-BuMe}_2\text{SiNa}$ gives rise to formation of another constitutional isomer of **665** and **668**, namely, the first cyclotrisilene, $(t\text{-BuMe}_2\text{Si})_2\text{SiSi}(\text{SiMe}_2t\text{-Bu})\text{SiSi}(\text{SiMe}_2t\text{-Bu})_3$ **669**, which contains an exocyclic $(t\text{-BuMe}_2\text{Si})_3\text{Si}$ group.[766,767] Later, an analog of **669**, namely, the cyclotrisilene *cyclo*-$[(t\text{-Bu}_2\text{MeSi})_2\text{Si}(\text{SiSiMe}t\text{-Bu}_2)_2]$ **98**, has been prepared (Scheme 17). Upon radiation ($\lambda = 254\,\text{nm}$), the cyclotrisilene $(t\text{-BuMe}_2\text{Si})_2\text{SiSi}(\text{SiMe}_2t\text{-Bu})\text{SiSi}(\text{SiMe}_2t\text{-Bu})_3$ **669** undergoes rearrangement into the tetrasilabicyclobutane **668** and some unidentified side-products (Scheme 90).[767] When the reduction of $t\text{-BuMe}_2\text{SiSiBr}_2\text{Cl}$ **663** was repeated with potassium graphite, KC_8, the cyclotrisilene **669** was obtained as major product along with small amounts of the first *spiro*-pentasiladiene $[(t\text{-BuMe}_2\text{Si})_3\text{SiSi}]_4\text{Si}$ **670** (Scheme 90).[768] Brief summaries of the chemistry on disilenes containing $t\text{-BuMe}_2\text{Si}$ groups have been given in a personal account by Kira in 2004 and in an award account by Iwamoto in 2005.[769,770] Very recently, Iwamato *et al.* have described a bicyclic disilene $\text{Me}_2\text{Si}[(\text{Me}_3\text{Si})_2\text{Si}]_2\text{SiSi}[\text{Si}(\text{SiMe}_3)_2]\text{SiMe}_2$ **671** containing two fused five-membered rings, which has been regarded as a model for a silicon surface.[771]

Sekiguchi *et al.* have developed novel routes for the preparation of unsymmetric disilenes. The reduction of the heptasilane $[(t\text{-Bu}_2\text{MeSi})_2\text{MeSi}]_2\text{SiBr}_2$ **672** with potassium graphite, KC_8, proceeds under initial formation of the corresponding silylsilylene intermediate **673**, which undergoes rearrangement to give the first methyl-substituted disilene $[(t\text{-Bu}_2\text{MeSi})_2\text{MeSi}](t\text{-Bu}_2\text{MeSi})\text{SiSiMe}(\text{SiMe}t\text{-Bu}_2)$ **674** (Scheme 91).[772] The regioselective addition of



Scheme 90



Scheme 91

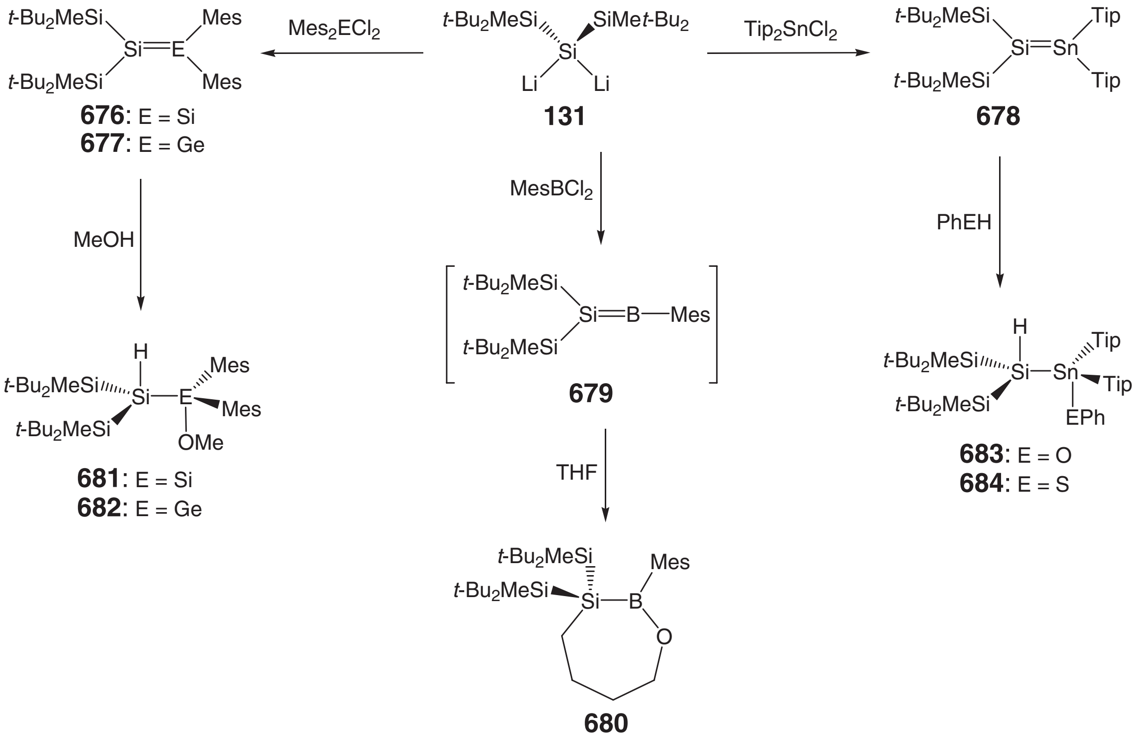
MeLi to [(t-$Bu_2MeSi)_2MeSi$](t-Bu_2MeSi)SiSiMe(SiMet-Bu_2) **674** has yielded the disilyl anion (as THF adduct), Li[(t-$Bu_2MeSi)_2MeSi$](t-Bu_2MeSi)$SiSiMe_2$(SiMet-Bu_2) **675**, an analog of **652** (Scheme 91).

A more rational approach of preparing unsymmetric disilenes involves the use of the dianion (t-$Bu_2MeSi)_2SiLi_2$ **131** (Scheme 21). The reaction of (t-$Bu_2MeSi)_2SiLi_2$ **131** with Mes_2SiCl_2 and (t-$Bu_2MeSi)_2SiBr_2$ **76** provides the disilenes (t-$Bu_2MeSi)_2SiSiMes_2$ **676** and (t-$Bu_2MeSi)_2SiSi$(SiMet-$Bu_2)_2$ **79**, respectively (Scheme 92).[282]

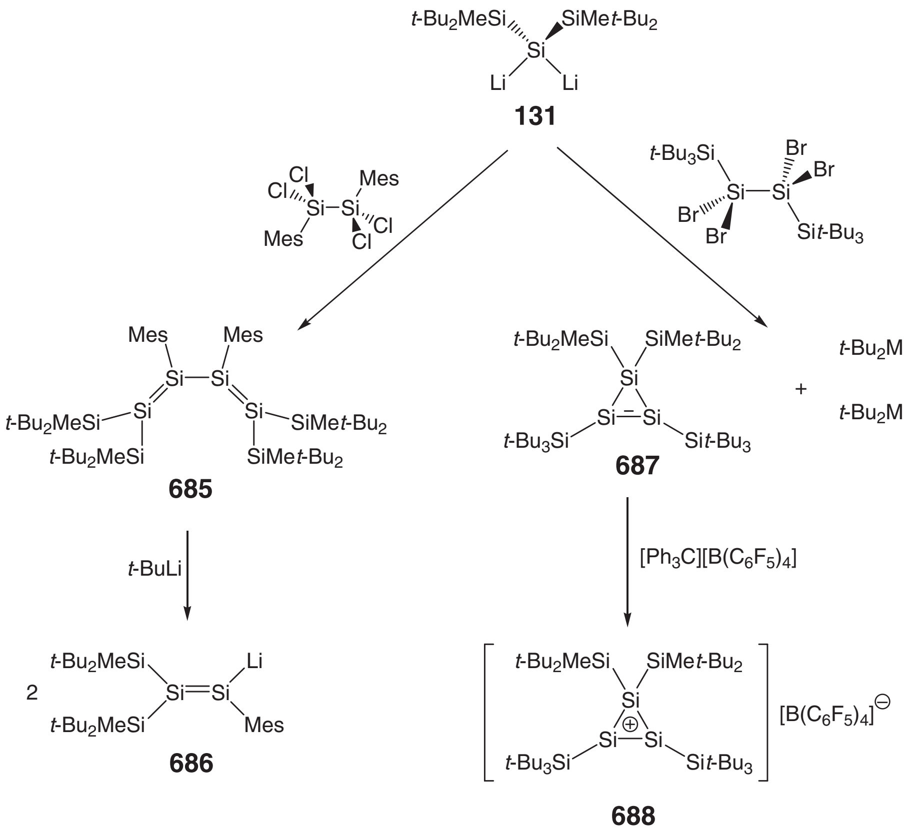
The chemistry of silametallenes, compounds having Si–E double bonds (E = group 14 element), is only poorly developed. The novel silagermene (t-$Bu_2MeSi)_2SiGeMes_2$ **677** and silastannene (t-$Bu_2MeSi)_2SiSnTip_2$ **678** have been prepared by the reaction of the dianion (t-$Bu_2MeSi)_2SiLi_2$ **131** with Mes_2GeCl_2 and Tip_2SnCl_2, respectively (Scheme 92).[282,773] The analogous reaction of (t-$Bu_2MeSi)_2SiLi_2$ **131** with $MesBCl_2$ has provided evidence for intermediate formation of the first borasilene (t-$Bu_2MeSi)_2SiBMes$ **679**, which, however, appears to cleave THF to produce the seven-membered C_4SiBO heterocycle **680** (Scheme 92).[774] The reaction of (t-$Bu_2MeSi)_2SiEMes_2$ (**676**, E = Si; **677**, E = Ge) with methanol occurs via addition to the Si–E double bond and gives the 1,2-difunctionalized products H(t-$Bu_2MeSi)_2SiEMes_2OMe$ (**681**, E = Si; **682**, E = Ge) (Scheme 92).[282] Similarly, the reaction of silastannene (t-$Bu_2MeSi)_2SiSnTip_2$ **678** with phenyl and thiophenyl has produced H(t-$Bu_2MeSi)_2SiSnTip_2EPh$ (**683**, E = O; **684**, E = S) (Scheme 92).[773]

The reactivity of the dianion (t-$Bu_2MeSi)_2SiLi_2$ **131** toward 1,1,2,2-tetrahalodisilanes has been studied by Sekiguchi *et al.*[775–777] The reaction of **131** with $MesCl_2SiSiCl_2Mes$ has provided the second example of a tetrasila-1,3-butadiene, (t-$Bu_2MeSi)_2$SiMesSiSiMesSi(SiMet-$Bu_2)_2$ **685**, a compound with two conjugated Si–Si double bonds (Scheme 93). The reaction of **685** with *tert*-butyllithium has given rise to the formation of Li[MesSiSi(SiMet-$Bu_2)_2$] **686**, a rare sila-analog of vinyllithium (Scheme 93).[775]

Interestingly, the analog reaction of the dianion (t-$Bu_2MeSi)_2SiLi_2$ **131** with (t-$Bu_3Si)Br_2SiSiBr_2Si$(t-Bu_3) has produced two entirely different products, namely the cyclotrisilene [(t-BuMeSi$)_2$Si[Si(Sit-Bu_3)]$_2$ **687** and the disilene (t-$Bu_2MeSi)_2SiSi$(SiMet-$Bu_2)_2$ **79**.[776] The oxidation of the cyclotrisilene **687** using $[Ph_3C][B(C_6F_5)_4]$ has afforded the cyclotrisilenylium ion, [(t-BuMeSi$)_2$Si[Si(Sit-Bu_3)]$_2$[B($C_6F_5)_4$] **688**, a persilaaromatic compound (Scheme 93).[776] Notably, the cyclotrisilene **687** is an analog of **98** and **669**.



Scheme 92

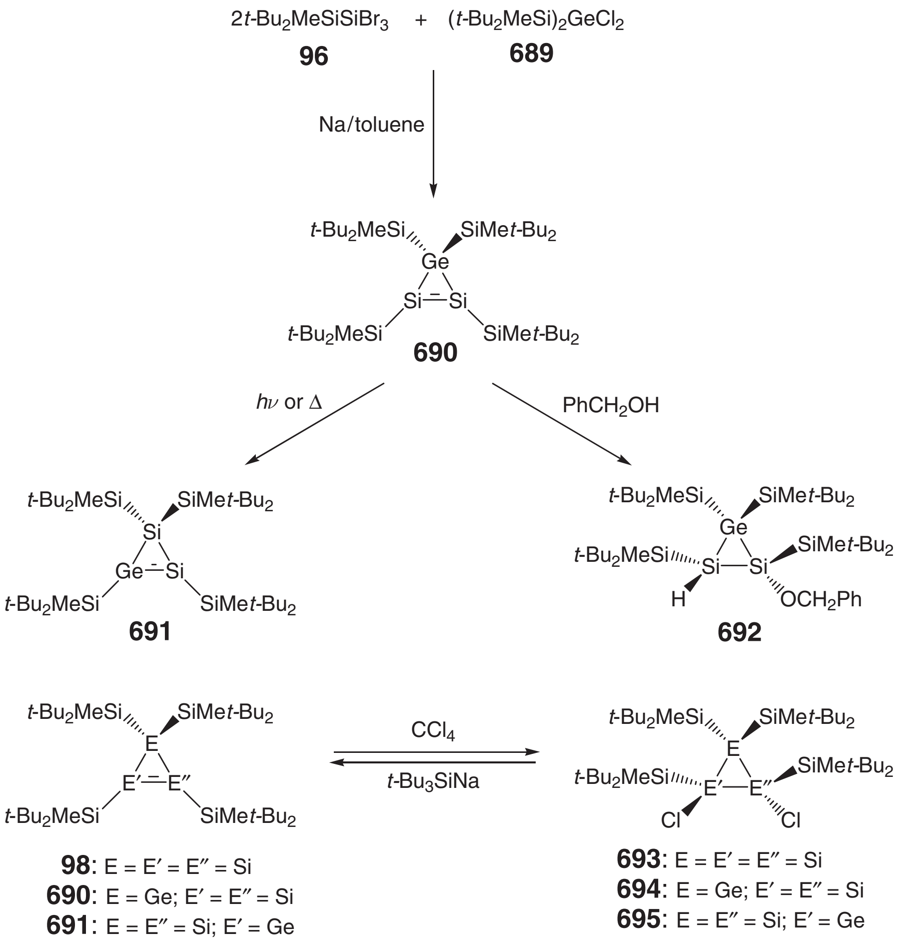


Scheme 93

The chemistry of heavy cyclopropene derivatives of group 14 elements has been reviewed in 2002 by Sekiguchi and Lee.[778] Analogous to the synthesis of cyclotrisilene [(t-$Bu_2MeSi)_2Si(SiSiMe$$t$-$Bu_2)_2$] **98** from t-$Bu_2MeSiSiBr_3$ **96** and (t-$Bu_2MeSi)_2SiBr_2$ **97** (Scheme 17),[257] the reductive co-coupling of t-$Bu_2MeSiSiBr_3$ **96** and (t-$Bu_2MeSi)_2GeCl_2$ **689** with sodium has provided the cyclogermadisilene [(t-$Bu_2MeSi)_2Ge(SiSiMe$$t$-$Bu_2)_2$] **690**, whose reactivity has been studied (Scheme 94).[779]

Most interestingly, the cyclogermadisilene [(t-$Bu_2MeSi)_2Ge(SiSiMe$$t$-$Bu_2)_2$] **690** can be converted photochemically or thermally to the isomeric cyclosilagermasilene [(t-$Bu_2MeSi)_2Si(SiSiMe$$t$-$Bu_2)(GeSiMe$$t$-$Bu_2)$] **691**, which involves a 1,2-trialkylsilyl group migration. The reaction of the cyclogermadisilene [(t-$Bu_2MeSi)_2Ge(SiSiMe$$t$-$Bu_2)_2$] **690** with benzyl alcohol proceeds via addition to the Si–Si double bond and affords the bifunctionalized cyclogermadisilane **692** (Scheme 94).[779] The reaction of the heavy group 14 cyclopropene derivatives **98, 690**, and **691** with CCl_4 affords the corresponding 1,2-dichloro-cyclopropane derivatives **693–695** (Scheme 94). The reverse reaction can be observed when compounds **693–695** are reacted with t-Bu_3SiNa (Scheme 94).[779] Very recently, Sekiguchi *et al.* have also reported on cyclosiladigermene [(t-$Bu_2MeSi)_2Si(GeSiMe$$t$-$Bu_2)_2$] **696**, which is related to the cyclogermadisilene **690** by an inverted Si/Ge ratio.[779]

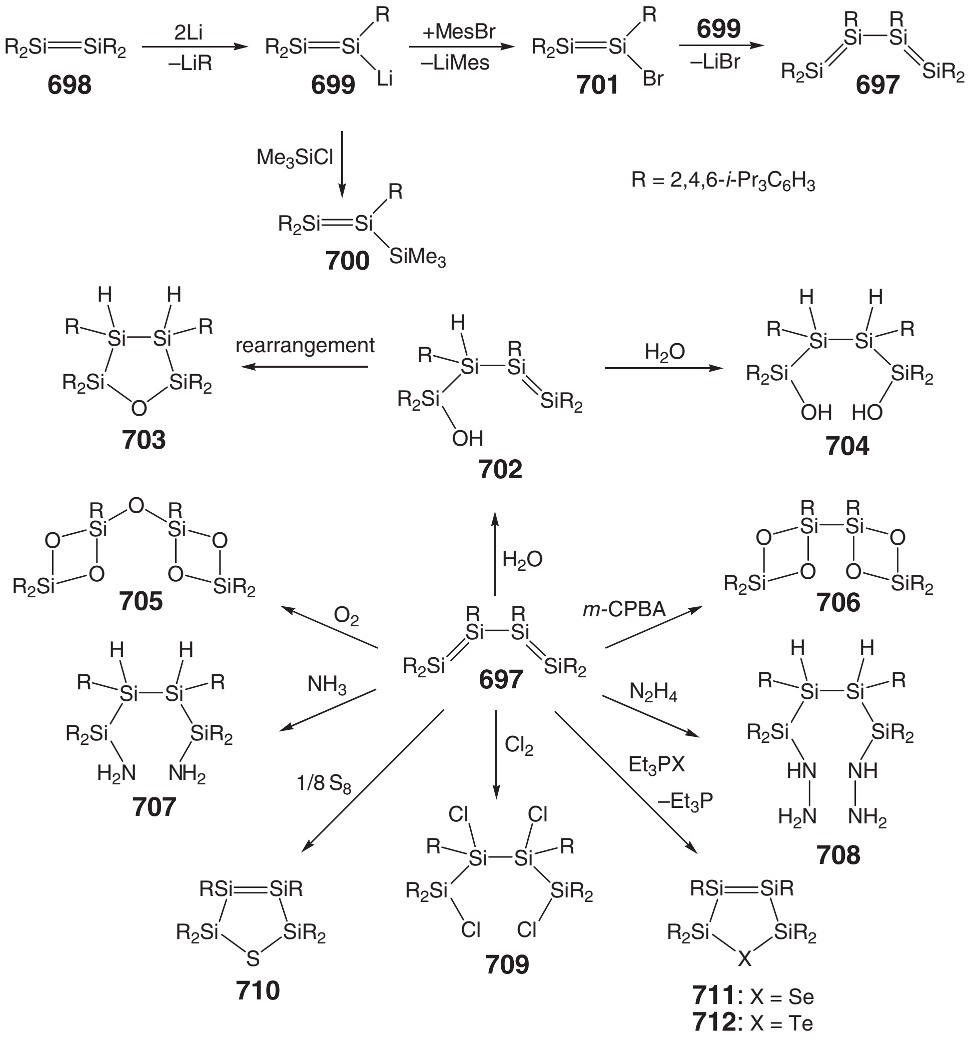
The first tetrasilabuta-1,3-diene, $Tip_2Si(Tip)SiSi(Tip)SiTip_2$ **697**, a compound with two conjugated Si–Si double bonds, was synthesized by Weidenbruch *et al.* in 1997 (Tip = 2,4,6-i-$Pr_3C_6H_2$).[780] The synthesis of **697** entails the reaction of the disilene $Tip_2SiSiTip_2$ **698** with lithium, which provides Li[$TipSiSiTip_2$] **699**, the first sila-analog of vinyllithium. The molecular structure of **699**, and its reaction with Me_3SiCl to give the new disilene $Tip_2SiSiTip(SiMe_3)$ **700**, were reported later by Scheschkewitz (Scheme 95).[781] The metal–halide exchange reaction of Li[$TipSiSiTip_2$] **699** and mesityl bromide affords the bromodisilene $Tip_2SiSiTipBr$ **701**, whose subsequent coupling reaction with **699** produces $Tip_2Si(Tip)SiSi(Tip)SiTip_2$ **697** (Scheme 95). The reactivity of the tetrasilabuta-1,3-diene **697** has been thoroughly studied.[782–785] The hydrolysis of **697** proceeds via the initial formation of the monosilanol $Tip_2Si(Tip)SiSiH(Tip)SiTip_2OH$ **702**, which, in the absence of more water, slowly rearranges into the symmetric Si_4O heterocycle $(Tip_2SiSiHTip)_2O$ **703**. With an excess of water, tetrasilabuta-1,3-diene **697** reacts to form the tetrasilane $HOTip_2Si(Tip)SiSi(Tip)SiTip_2OH$ **704** having two terminal hydroxyl groups (Scheme 95). The oxidation



Scheme 94

of the tetrasilabuta-1,3-diene **697** with dioxygen and *m*-CPBA results in the formation of two bis(cyclodisiloxanes) **705** and **706** being bridged by a siloxane and a disilane unit, respectively (Scheme 95). The addition of ammonia and hydrazine to the tetrasilabuta-1,3-diene **697** produces a tetrasilazane $(H_2N)Tip_2Si(Tip)HSiSiH(Tip)SiTip_2(NH_2)$ **707** and a tetrasilahydrazine $(H_2NHN)Tip_2Si(Tip)HSiSiH(Tip)SiTip_2(NHNH_2)$ **708**, which are involved in intramolecular hydrogen bonding (Scheme 95). The addition of chlorine to the tetrasilabuta-1,3-diene **697** affords the open-chain tetrachlorotetrasilane $ClTip_2Si(Tip)ClSiSiCl(Tip)SiTip_2Cl$ **709** (Scheme 95). The chalcogenolysis of the tetrasilabuta-1,3-diene **697** with elemental sulfur, triethylphosphine selenide, and triethylphosphine telluride proceeds under preservation of one Si–Si bond and formation of the chalcogenatetrasilacyclopentenes $[Tip_2Si(Tip)Si]_2X$ (**710**, X = S; **711**, X = Se; **712**, X = Te) (Scheme 95).

Wiberg *et al.* have studied the formation and reactivity of disilenes derived from the very bulky "supersilyl" t-Bu_3Si group (Scheme 96).[786–789] The metal–halide exchange of the 2,3-dibromo tetrasilanes $(t\text{-}Bu_3Si)(R)(Br)Si(R)(Br)Si(Si\textit{t}\text{-}Bu_3)$ (**713**, R = H; **714**, R = Me; **715**, R = Ph) with t-Bu_3SiNa has afforded the corresponding monosodium compounds $(t\text{-}Bu_3Si)(R)(Br)Si(R)(Na)Si(Si\textit{t}\text{-}Bu_3)$ (**716**, R = H; **717**, R = Me; **718**, R = Ph), which undergo sodium bromide elimination to give the disilenes $(t\text{-}Bu_3Si)(R)SiSi(R)(Si\textit{t}\text{-}Bu_3)$ (**719**, R = H; **720**, R = Me; **721**, R = Ph) (Scheme 96). The stability of the disilenes depends heavily on the nature of the substituent R. In the case of **719** (R = H) and **720** (R = Me), the disilenes could not be isolated due to their high reactivity, and their transient formation was deduced from trapping experiments with diphenylacetylene and anthracene yielding the [2 + 2] and [2 + 4] cycloadducts **722–724**, respectively (Scheme 96). In the absence of trapping reagents, the reactive disilenes **719** and **720** eventually form the hexasilane **725** and the monosodium compound **726**, which undergoes elimination to give a mixture of cyclotrisilanes and cyclotetrasilanes **727–729**, respectively (Scheme 96). However, the disilene **721** (R = Ph) possesses a higher stability than **719** and **720**, and consequently has been isolated.[787]

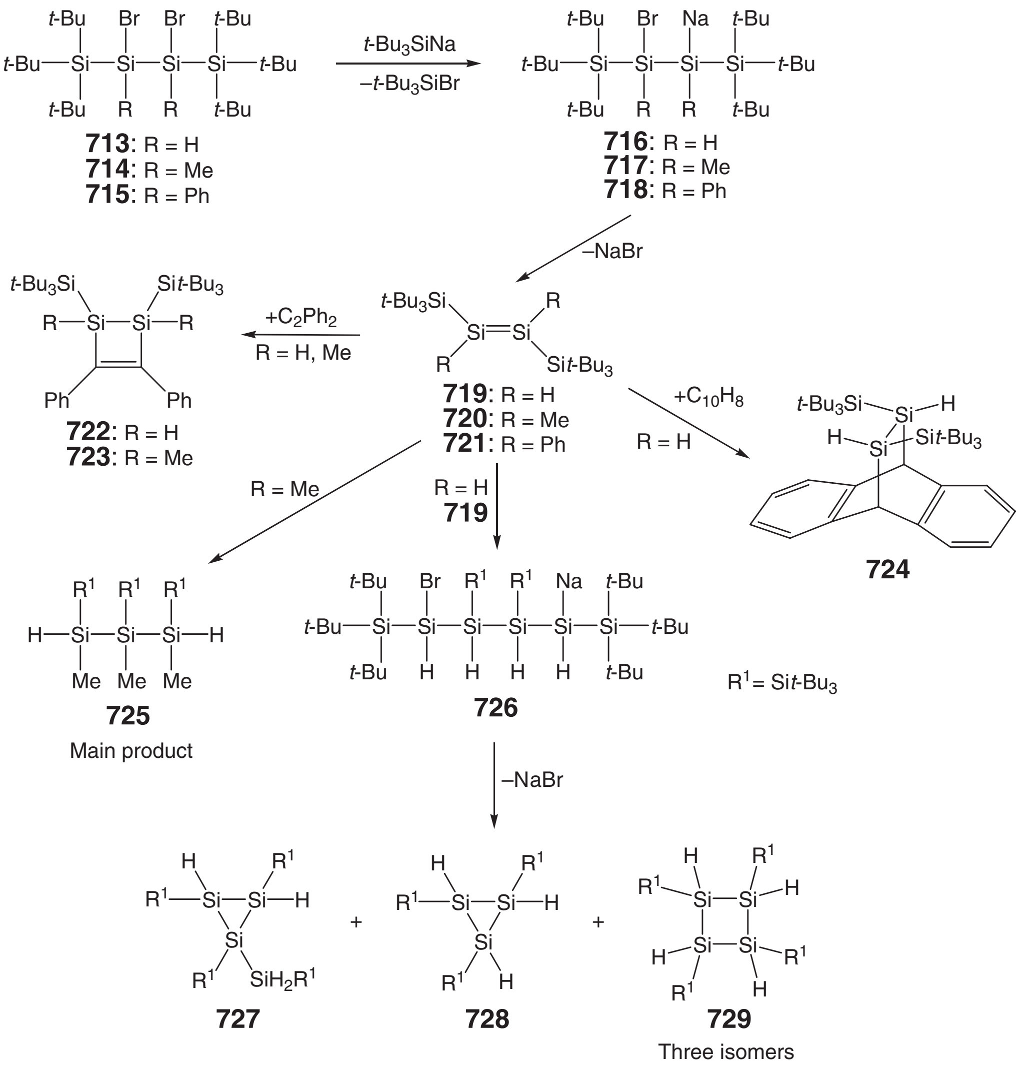


Scheme 95

However, at elevated temperatures, the disilene (*t*-Bu$_3$Si)(R)SiSi(R)(Si*t*-Bu$_3$) **721** undergoes isomerization to give the 1,2-disilyl benzene derivative **730**, which can be rationalized in terms of a C–H addition to the Si–Si double bond (Scheme 97).

With unsaturated compounds, the disilene **721** often undergoes [$2+n$] ($n=2$–4) cycloadditions (Scheme 97). Thus, the reaction of **721** with benzaldehyde and thiobenzophenone provides the four-membered Si$_3$X hetereocycles **731** (X = O) and **732** (X = S) ([2 + 2]-cycloadducts), whereas the reaction with benzophenone gives the bicyclic [2 + 4] cycloadduct **733** (Scheme 97). [2 + 3]-Cycloadditions take place in the reaction of the disilene **721** with carbon dioxide and their heavier group 16 congeners to give disilapropiolactone derivatives **734** and **735**, and the transient carbenes **736** and **737**, which dimerize to form the corresponding alkenes **738** and **739** (Scheme 97). Owing to the presence of allylic hydrogen atoms, the reaction of isobutene with **721** affords the ene product **740**, whereas a [2 + 4] addition takes place in the reaction of **721** with 2,3-dimethylbutadiene, giving the disilacyclohexene derivative **741** (Scheme 97). The reaction of the disilene **721** with Co$_2$(CO)$_8$ proceeds under CO elimination and affords the novel transition metal silyl complex **742** (Scheme 97). The addition of X$_2$, HX (X = Cl, Br), and water to the disilene (*t*-Bu$_3$Si)(Ph)SiSi(Ph)(Si*t*-Bu$_3$) **721** provides the 2,3-difunctionalized tetrasilanes X(*t*-Bu$_3$Si)(Ph)SiSi(Ph)(Si*t*-Bu$_3$)X (**743**, X = Cl; **744**, X = Br) and X(*t*-Bu$_3$Si)(Ph)SiSi(Ph)(Si*t*-Bu$_3$)H (**745**, X = Cl; **746**, X = Br; **747**, X = OH), respectively (Scheme 98).[787]

The chalcogenolysis of the disilene **721** with N$_2$O, S, Se, and Te results in formation of the three- and four-membered heterocyles **748–752** (Scheme 98). The addition of the isonitrile *t*-BuNC to the disilene **721** affords



Scheme 96

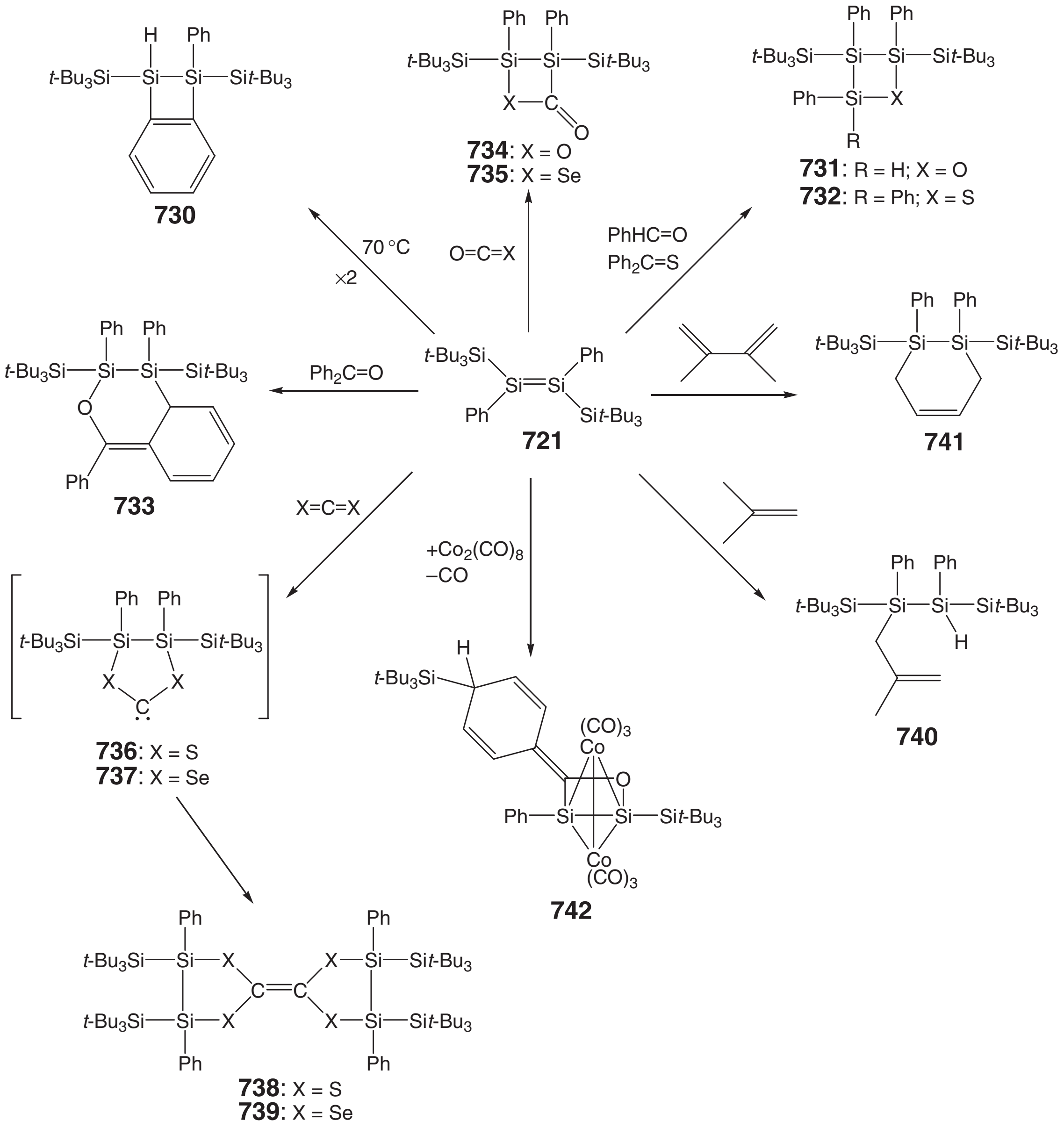
a thermolabile disilirane **753**, whose thermolysis produces the 2,3-dicyano tetrasilane NC(*t*-Bu_3Si)(Ph)SiSi(Ph)-(Si*t*-Bu_3)CN **754** along with the three-membered cyclotrisilane **755** (Scheme 98). The addition of trimethylsilyl azide to the disilene **721** produces the three-membered cycloazadisilirane **756** (Scheme 98).[787]

Recently, the first disilenes [(*t*-$Bu_3Si)_2$MeSi](X)SiSi(X)[SiMe(Si*t*-Bu_3)] (**757**, X = Cl; **758**, X = Br) containing halogen atoms at the (formally) sp^2-hybridized Si atoms have been isolated from the reaction of (*t*-$Bu_3Si)_2MeSiSiX_3$ (**759**, X = Cl; **760**, X = Br) with *t*-Bu_3SiNa.[790]

3.09.5.3 Disilynes

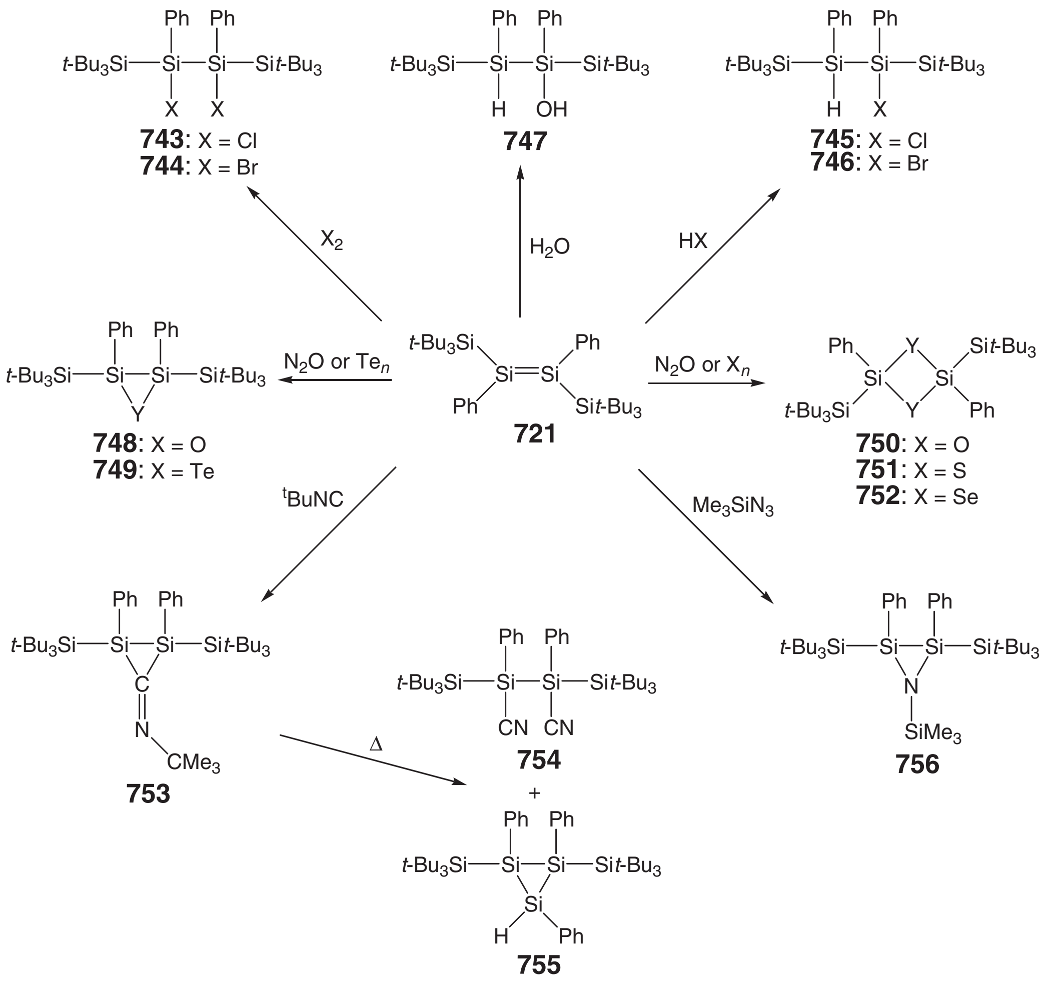
In recent years, several attempts have been made to prepare the first disilynes, compounds having Si–Si triple bonds,[791,792] until Sekiguchi *et al.* in 2004 succeeded in the isolation and full characterization of the first member of this compound class.[793] West *et al.* have studied the dehalogenation of 2,6-$Mes_2C_6H_3SiF_3$ **761** with sodium, which has afforded the bis(silafluorene) derivative **762**, whose formation may be rationalized in terms of two intramolecular insertion reactions of a bis(silylenoid) **763** into two C(sp^2)–C(sp^3) bonds (Scheme 99). [794]

In 1993, Wiberg *et al.* obtained the first tetrasilatetrahedrane (*t*-$Bu_3SiSi)_4$ **764** from the reduction of the 2,2,3,3-tetrabromo-tetrasilane *t*-$Bu_3SiBr_2SiSiBr_2Si$*t*-Bu_3 **765** with *t*-Bu_3SiNa (Scheme 100).



Scheme 97

The formation of (t-Bu$_3$SiSi)$_4$ 764 has been rationalized by the dimerization of the initially formed disilyne t-Bu$_3$SiSiSiSit-Bu$_3$ 766.[795] More recently, an analog of 764, namely, (R$_2$R^{1}SiSi)$_4$ 767, has been obtained similarly by the reduction of the 2,2,3,3-tetrabromo-tetrasilane R$_2$R^{1}SiBr$_2$SiSiBr$_2$SiR^{1}R$_2$ 768 with potassium graphite (R = CH(SiMe$_3$)$_2$, R^1 = Me), which presumably also involved the formation of a transient disilyne R$_2$R^{1}SiSiSiSiR^{1}R$_2$ 769 (Scheme 100).[796] The lack of stability of the intermediate disilynes 766 and 769 may be attributed to the insufficient shielding of the triple bonds by the substituents. The reduction of the 2,2,3,3-tetrabromo-tetrasilane R$_2$R^{1}SiBr$_2$SiSiBr$_2$SiR^{1}R$_2$ 770 having even bulkier substituents (R = CH(SiMe$_3$)$_2$, R^1 = i-Pr) with KC$_8$ has been indeed the key to the isolation of the first fully characterized disilyne R$_2$R^{1}SiSiSiSiR^{1}R$_2$ 771 (Scheme 100).[796] A few months earlier than Sekiguchi *et al.*, Wiberg *et al.* obtained another disilyne, namely, (t-Bu$_3$Si)$_2$MeSiSiSiSiMe(Sit-Bu$_3$)$_2$ 772, by the reduction of the dibromo disilene [(t-Bu$_3$Si)$_2$MeSi](Br)SiSi(Br)Si[Me(Sit-Bu$_3$)$_2$] 758, with t-Bu$_3$SiNa, which, however, could not be structurally characterized (Scheme 100).[790] The reactivity of the tetrasilatetrahedranes 764 and 767 has been studied by Wiberg *et al.* and Sekiguchi *et al.* The

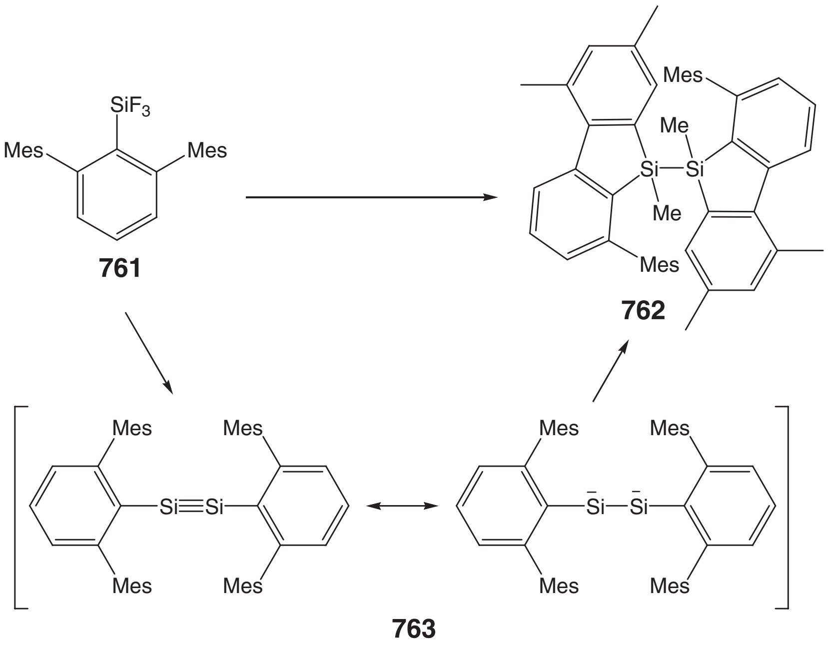


Scheme 98

iodation of the tetrasilatetrahedrane (t-$Bu_3SiSi)_4$ **764** with 1 equiv. of I_2 has provided the diiodo tetrasilacyclobutene derivative **773**, whose hydrolysis has afforded the first tetrasilatetrahedrane monoxide **774** (Scheme 100).[797] The oxidation of (t-$Bu_3SiSi)_4$ **764** with $[Ph_3C][(B(C_6F_5)_4]$ in the presence of accidental water has given rise to the protonated tetrasilatetrahedrane monoxide **775**. The deprotonation and formation of **774** has been achieved by the addition of triethylamine to **775** (Scheme 100).[798] The synthesis of a novel silicon cage anion, the tetrasilatetrahedranide $K[Si(SiSiMeDis_2)_3]$ **776** has been reported by Sekiguchi *et al.* in 2003.[799] Compound **776** is accessible by the reductive cleavage of one triorganosilyl group from $(SiSiMeDis_2)_4$ **767** with KC_8 ($Dis = CH(SiMe_3)_2$). Most interestingly, the reduction of the diiodo tetrasilacyclobutene derivative **773** with t-Bu_3SiNa has produced the entirely novel silicon cluster (t-$Bu_3Si)_6Si_8$ **777** (Scheme 100).[800] A somewhat related silicon cluster, namely, $(Tip_2Si)_2(TipSi)_2Si$ **778**, has been isolated from the reaction of $Li[TipSiSiTip_2]$ **699** with $SiCl_4$.[801] The reactivity of the disilyne **772** has been briefly investigated by Wiberg *et al.*[802] The addition of 2 equiv. of I_2 and BI_3 to the diiodo tetrasilacyclobutene derivative **773** has provided the pentaiodo tetrasilacyclobutane **779** and the cationic species **780**, respectively. The latter is structurally related to **775**. The methanolysis of **773** has afforded the bis(methoxy) tetrasilacyclobutene derivative **781**.

3.09.6 Hypercoordinated Silicon Compounds

The chemistry of hypercoordinated silicon compounds has continued to be an extremely active research field in recent years. Some of this interest is driven by the observation that many hypercoordinated silicon species possess a



Scheme 99

higher reactivity toward nucleophilic displacement reactions than their tetracoordinated counterparts. A number of synthetically very useful routes now actively utilize hypervalent silicon intermediates. Kinetic and thermodynamic studies on nucleophilic displacement reactions featuring pentacoordinated silicon intermediates have provided invaluable insights into inorganic reaction mechanisms, which have also been very useful in comparison with related carbon chemistry where pentacoordinated species are frequently postulated as being transition states. Most of the earlier work in this area has been covered in milestone reviews by Corriu *et al.* (1993)[803] and Holmes (1990, 1996).[804,805] More recent results were summarized by the reviews of Kost and Kalikhman (1998)[806] and Corriu *et al.* (1999).[807]

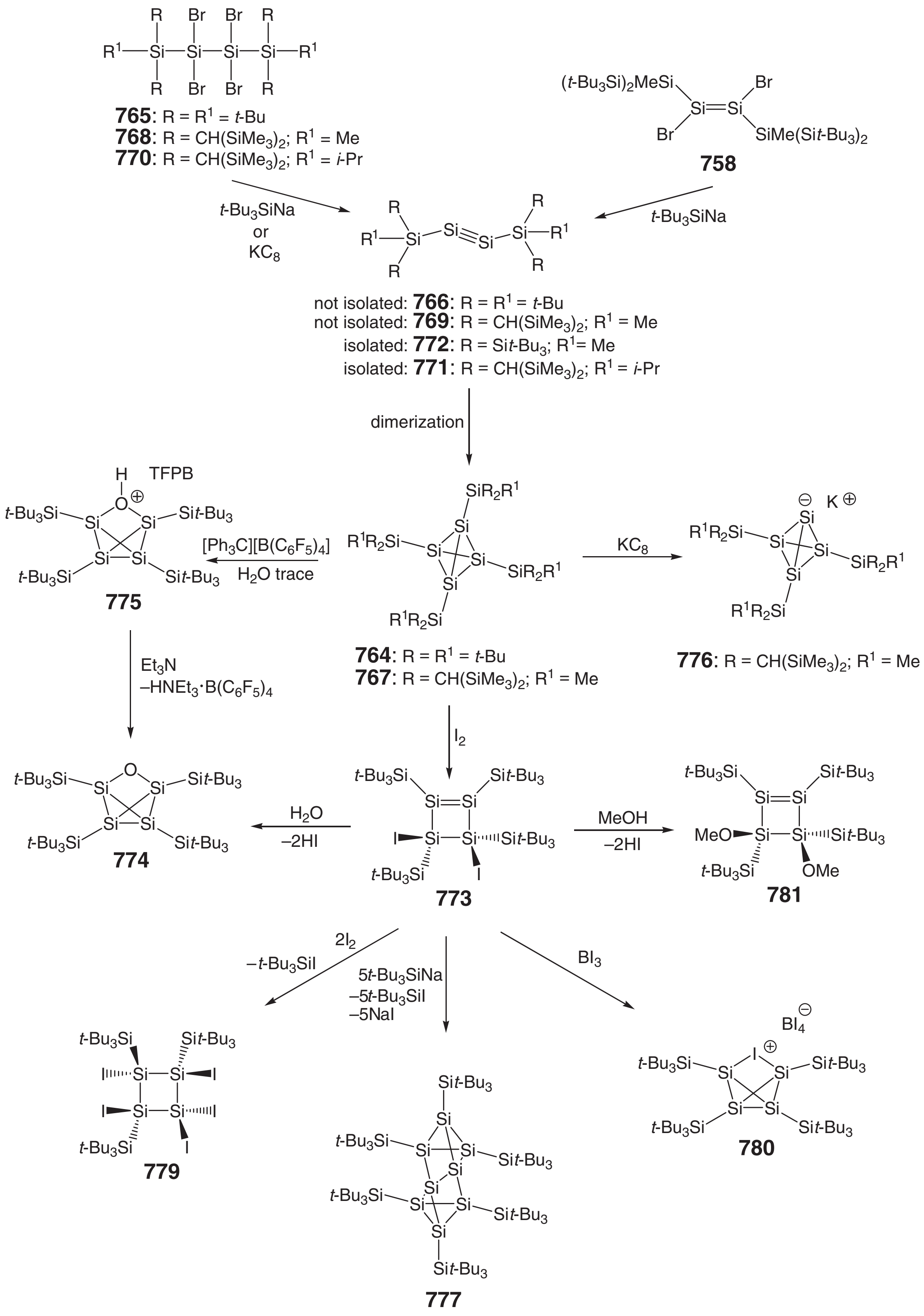
Many advances in the field have been achieved using the potentially intramolecularly coordinating ("built-in") ligands 2-(*N*,*N*-dimethylaminomethyl)phenyl and 8-dimethylamino-naphth-1-yl, which can be introduced to the silicon via nucleophilic displacement reactions using the corresponding lithium salts and appropriate chlorosilanes (Figure 4). However, recently some arguments have been put forward that question the nature of the hypercoordinated interactions provided by the rigid 8-dimethylamino-naphth-1-yl group.[808]

3.09.6.1 Intramolecularly Stabilized Silyl Cations

It is an intriguing idea to stabilize low-valent silicon species, such as silyl cations, silylenes, silenes, and disilenes using intramolecularly coordinating ligands. Corriu *et al.* succeeded in the preparation of the first hypervalent silyl cation $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6)_2\text{SiH}]^+1/2[\text{I}_8]^{2-}$ **782** by the reaction of the hexacoordinated diorganosilane $(8\text{-Me}_2\text{NC}_{10}\text{H}_6)_2\text{SiH}_2$ **783** with iodine (Scheme 101).[809] The positive charge at the silicon atom of **782** is stabilized by two intramolecularly coordinating 8-dimethylamino-naphth-1-yl ligands (av. Si···N = 2.07(2) Å).

Similarly, Belzner *et al.* obtained the trivalent siliconium cation $[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{SiH}][\text{O}_3\text{SCF}_3]$ **784** by the protonation of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{SiH}_2$ **785** with triflic acid (Scheme 102).[810] The strength of intramolecular Si···N coordination of **784** (av. 2.06(2) Å) seems to be comparable with that of compound **782**. The geometry of the silicon atoms in **782** and **784** is trigonal bipyramidal with the nitrogen atoms being situated in the axial positions.

With the compound $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{PhSi(H)(O}_3\text{SCF}_3)$ **786**, it was demonstrated that more than one built-in ligand is needed for the stabilization of trivalent silicon cations as, in this structure, the triflate anion is involved in the coordination to the silicon atoms.[810] The related Si–O bond distance of 1.951(1) Å is longer than the "standard" Si–O bond length (approx. 1.6 Å) and therefore compound **786** might be best described as contact ion pairs (Figure 5).


765: R = R¹ = t-Bu
768: R = CH(SiMe₃)₂; R¹ = Me
770: R = CH(SiMe₃)₂; R¹ = i-Pr
(t-Bu₃Si)₂MeSi
SiMe(Sit-Bu₃)₂
758
t-Bu₃SiNa or KC₈
t-Bu₃SiNa
not isolated: 766: R = R¹ = t-Bu
not isolated: 769: R = CH(SiMe₃)₂; R¹ = Me
isolated: 772: R = Sit-Bu₃; R¹= Me
isolated: 771: R = CH(SiMe₃)₂; R¹ = i-Pr
dimerization
TFPB
[Ph₃C][B(C₆F₅)₄]
H₂O trace
775
KC₈
764: R = R¹ = t-Bu
767: R = CH(SiMe₃)₂; R¹ = Me
776: R = CH(SiMe₃)₂; R¹ = Me
Et₃N
–HNEt₃·B(C₆F₅)₄
I₂
H₂O
–2HI
774
773
MeOH
–2HI
781
2I₂
–t-Bu₃SiI
5t-Bu₃SiNa
–5t-Bu₃SiI
–5NaI
BI₃
BI₄
779
777
780

Scheme 100

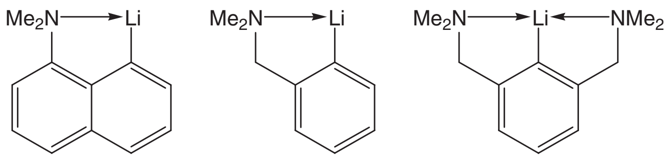
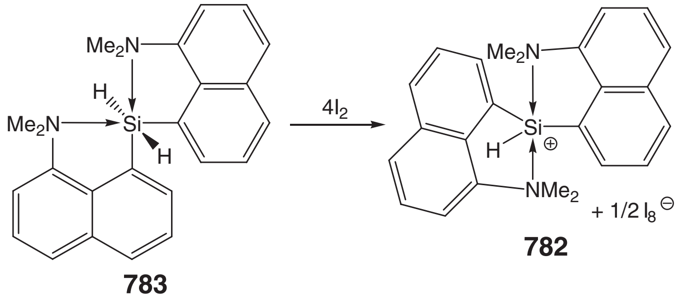
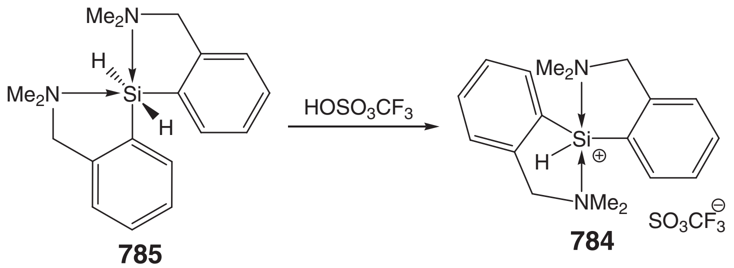


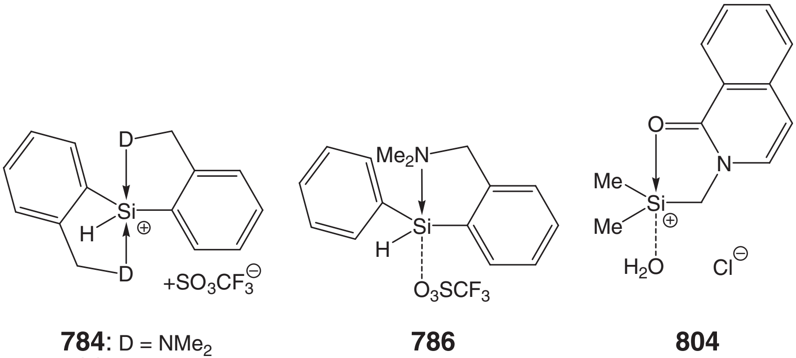
Figure 4



Scheme 101



Scheme 102

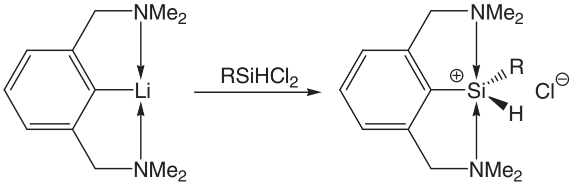


784: D = NMe_2
796: D = PMe_2
797: D = OMe
798: D = SMe

Figure 5

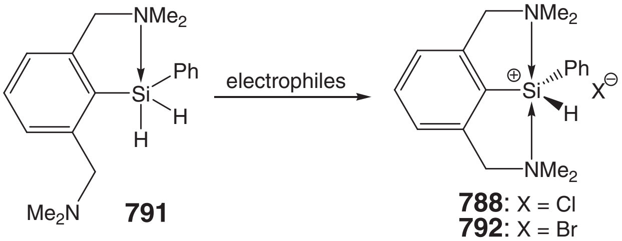
With the potentially bis-chelating 2,6-bis(*N*,*N*-dimethylaminomethyl)phenyl ligand, which can be attached to silicon via its lithium salt (Figure 4), Corriu *et al.* have prepared a number of trivalent silyl cations as their chloride salts **787–790** (Scheme 103).[811]

Alternatively, the pentacoordinated dihydrosilane **791** can be reacted with suitable electrophiles, such as I_2, PhCOCl, PhCOBr, $Ph_3C^+BF_4^-$, $CF_3SO_3SiMe_3$, to give the same trivalent siliconium cations having different



787: R = Me
788: R = Ph
789: R = $CHCH_2$
790: R = Cl

Scheme 103



791

788: X = Cl
792: X = Br
793: X = I
794: X = BF_4
795: X = O_3SCF_3

electrophiles = I_2, PhCOCl, PhCOBr, $Ph_3C^+BF_4^-$, $CF_3SO_3SiMe_3$

Scheme 104

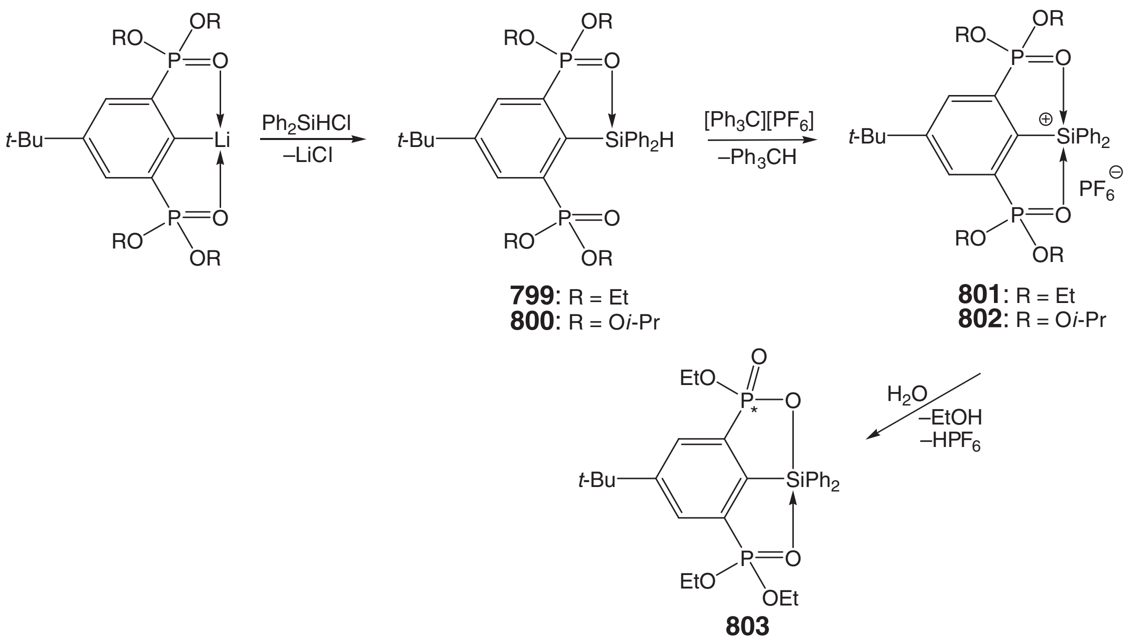
counterions **788, 792–795** (Scheme 104). In solution, the coordination number of the silicon atoms of **788, 792–795** depends on the coordinating strength of the counterion and the polarity of the solvent.[811]

Jutzi *et al.* have synthesized structural analogs of **784**, in which the NMe_2 groups were formally replaced by other donor groups, such as **796** (D = PMe_2) **797** (D = OMe), **798** (D = SMe).[812] The intramolecular Si···O coordination of **797** is documented by the short Si–O bond distances (av. 1.921(3) Å). It was also found that the stabilizing energy of the softer P and S ligands is smaller, whereas the covalent bond character of the Si···D bond is larger than in the harder N and O ligands. Recently, Jurkschat *et al.* applied their versatile *O,C,O*-coordinating pincer ligand to prepare intramolecularly coordinated triorganosilanes.[813,814] The reaction of the lithiated pincer ligand {4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}Li (R = Et, *i*-Pr) with Ph_2SiHCl afforded the [4 + 1]-coordinated triorganosilanes {4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}$SiPh_2H$ (**799**, R = Et; **800**, R = *i*-Pr), which were fully characterized (Scheme 105). The constrained geometry of the P=O groups resulted in secondary Si···O contacts of 2.918(2) and 2.7378(18) Å. Reaction of the Si–H bonds in {4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}$SiPh_2H$ (**799**, R = Et; **800**, R = *i*-Pr) with $[Ph_3C][PF_6]$ gave rise to the formation of [4 + 2]-coordinated triorganosiliconium hexafluorophosphates [{4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}$SiPh_2]^+[PF_6]^-$ (R = Et **801**, *i*-Pr **802**) (Scheme 105). Upon contact with moist air, compound **801** formed the [4 + 1]-coordinated benzoxasilaphosphole [1(*P*),3(*Si*)-P(O)(OEt)$OSiPh_2$-6-*t*-Bu-4-$P(O)(OEt)_2]C_6H_2$ **803**, which contains a chiral center at one phosphorus atom.[813] The intramolecular Si···O contacts in the triorganosilicon cation **802** and the benzoxasilaphosphole **803** of average 1.9269(14) and 2.614(2) Å, respectively, demonstrate the dramatically different Lewis acidities of the silicon atoms.[813,814]

Recently, a fully characterized hypercoordinated protonated quinoline silanol (counterion = chloride) **804** has been described. This can also be regarded as intramolecularly coordinated triorganosiliconium cation, in which a neutral water molecule fills the vacant position in the trigonal-bipyramidal geometry of the silicon atom (Figure 5).[815]

3.09.6.2 Zwitterionic Silicates

Tacke *et al.* have reported a new family of spirocyclic silicates adopting betaine-type structures of the general formula $X_4SiCH_2NR_2H$ (X = electronegative atoms or groups; R = organic groups) in which the silicon atoms are



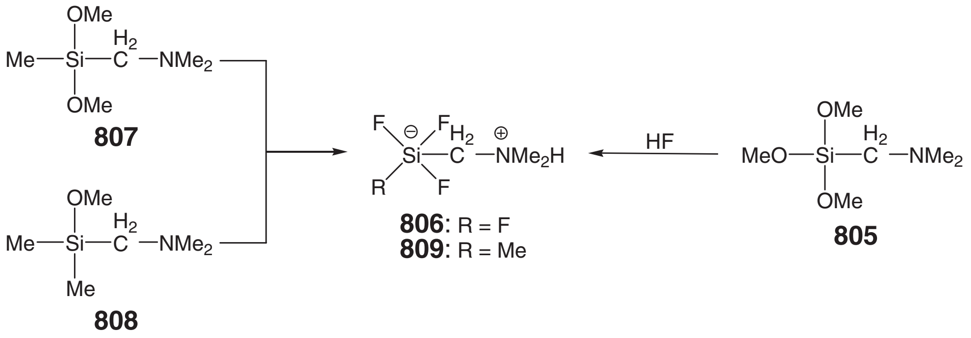
Scheme 105

pentacoordinated and formally carry a negative charge, whereas the nitrogen atoms are positively charged.[816] The hydrofluorination of dimethylaminomethyltrimethoxysilane, $Me_2NCH_2Si(OMe)_3$ **805**, affords the zwitterionic tetrafluorosilicate, $HMe_2NCH_2SiF_4$ **806**, whereas the same reaction of the dimethylaminomethylmethoxymethylsilanes $Me_2NCH_2SiMe(OMe)_2$ **807** and $Me_2NCH_2Si(OMe)Me_2$ **808** provides a single product, namely the zwitterionic methyltrifluorosilicate, $HMe_2NCH_2SiMeF_3$ **809** (Scheme 106).[816]

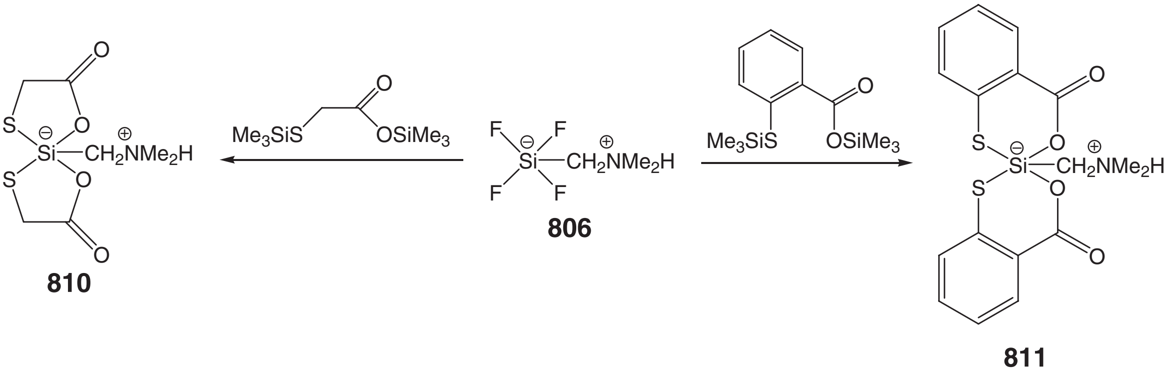
The reaction of the zwitterionic tetrafluorosilicate, $HMe_2NCH_2SiF_4$ **806**, with $Me_3SiSCH_2C(O)OSiMe_3$ and 1,2-$Me_3SiSC_6H_4C(O)OSiMe_3$ proceeds to form two O_2S_2C-coordinated spirocyclic silicates **810** and **811** and Me_3SiF as gaseous side-product (Scheme 107).[817]

Similarly, the zwitterionic methyltrifluorosilicate, $HMe_2NCH_2SiMeF_3$ **809**, reacts with some glycol derivatives to yield the O_4C-coordinated spirocyclic silicates **812–815** and Me_3SiF as gaseous side-product (Scheme 108).[818–820]

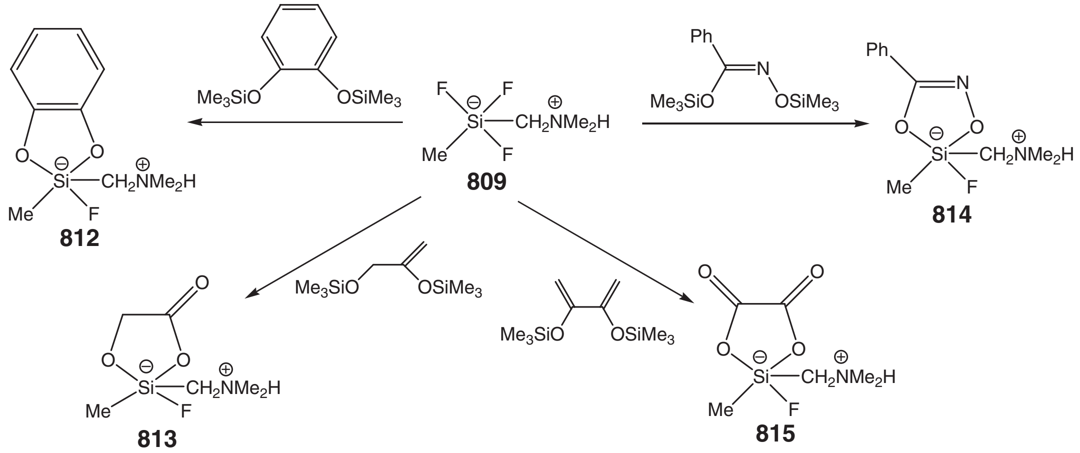
2,2,6,6-Tetramethylpiperidinomethyltrimehtoxysilane **816** and the corresponding 2,2,6,6-tetramethylpiperidinomethylsilane **817** are the precursors for another family of spirocyclic silicates **818–824**, which are accessible upon reaction with α-hydroxy acids, α-amino acids, *o*-benzene dithiol, and dithioglycol (Scheme 109).[821,822]



Scheme 106



Scheme 107



Scheme 108

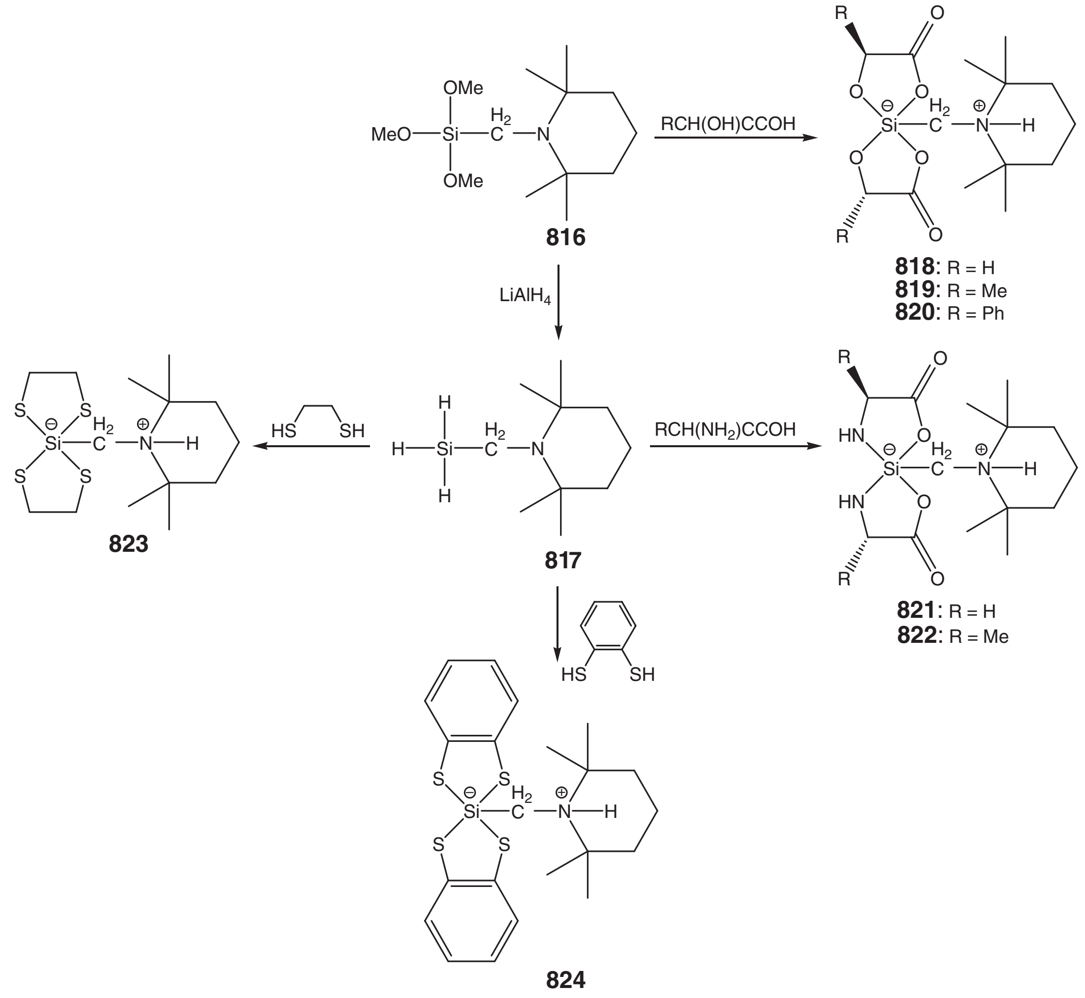
Compounds 818–820 are kinetically labile and undergo epimerization in solution. The rates of these epimerization processes were determined by kinetic measurements. Owing to the hydrolytic sensitivity of compounds 821 and 822, a conceivable role of bidentate amino acid ligands in the silicon biomineralization process has been denied.[821]

3.09.6.3 Hypercoordinated Fluorosilicate Anions

Although simple pentacoordinated triorganodifluorosilicate anions $[R_3SiF_2]^-$ and related materials are a well-established compound class,[803] their preparation is often accompanied by indestructible impurities.[823] Albanese *et al.* reported a facile synthesis, starting from triorganosilanes and hydrogen difluorides, that provides high yields of pure quaternary ammonium or phosphonium triorganodifluorosilicates $Q[R_3SiF_2]$ (825, $Q = Bu_4N$, $R = Ph$; 826, $Q = Bu_4N$, $R = Me$; 827, $Q = BzMe_3P$, $R = Ph$; 828, $Q = BzMe_3P$, $R = Me$) (Scheme 110).[824]

Application in organic synthesis of pentacoordinated triorganodifluorosilicate anions, such as $[Bu_4N][Ph_3SiF_2]$ 825, have been extended to palladium(0)-catalyzed cross coupling reactions (solvents: DMF, THF, dioxane) with arene halides (Scheme 111).[825] This method is tolerant to various palladium(0) catalysts and provides excellent yields of mainly heterocoupled products and only small amounts of homocoupled byproducts.

Another application of $[Bu_4N][Ph_3SiF_2]$ 826 involves the silicon–carbon bond cleavage of allyl-, benzyl-, and alkynylsilane derivatives 827–829.[826] Subsequent reactions of the generated carbanions with electrophiles (Scheme 112) and alkyl halides (Scheme 113) provide high yields of carbon–carbon coupled products.[827]



Scheme 109

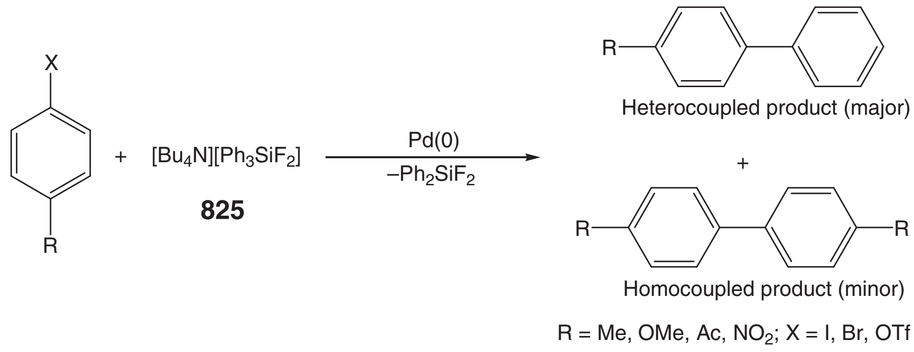
$$R_3SiH + Q^+HF_2^- \xrightarrow[-H_2]{RT} Q^+[R_3SiF_2]^-$$

Scheme 110

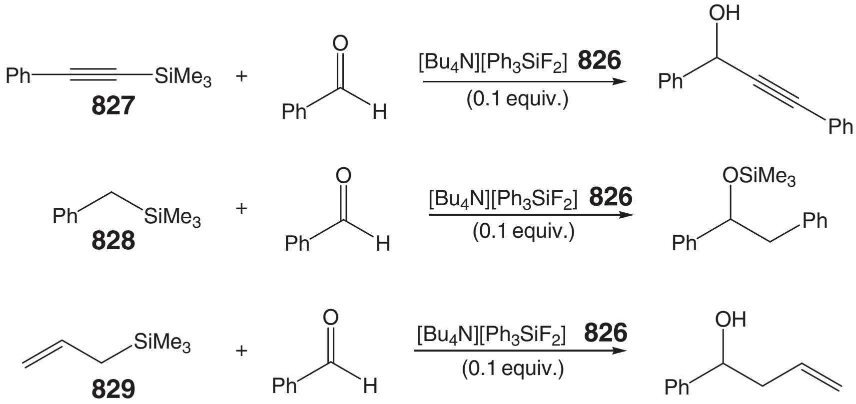
It has been well recognized that the hydrolysis of alkoxysilanes and chlorosilanes is effectively catalyzed when fluoride anions are present due to formation of hypercoordinated silicon intermediates.[803] More in-depth studies by Bassindale *et al.* showed that the reaction of $PhSi(OEt)_3$ with stoichiometric amounts of Bu_4NF surprisingly yields an encapsulation complex, namely tetrabutylammonium octaphenyloctasilsesquioxane fluoride **830**, in which the fluorine atom is situated inside the cubic siloxane cage (Scheme 114).[828] The Si···F distance of average 2.65 Å is shorter than the sum of van der Waals radii (3.57 Å), which renders the coordination number of the silicon atoms at [4 + 1].

Recently, Pietschnig *et al.* provided conclusive evidence for the increased reactivity of hypercoordinated fluorosilicates toward hydrolysis compared to their tetracoordinated counterparts. The sterically shielded terphenyl-substituted trifluorosilane 2,6-$Mes_2C_6H_3SiF_3$ **761** is entirely unreactive toward water,[794] whereas the corresponding alkali tetrafluorosilicate anions $M^+[2,6\text{-}Mes_2C_6H_3SiF_4]^-$ (**831**, M = Li; **832**, M = Rb) slowly reacted with water giving rise to the sequential hydrolysis products **833–835** (Scheme 115).[829] Interestingly, fine tuning of the reactivity was possible by using different alkali metals M = Li, Rb.

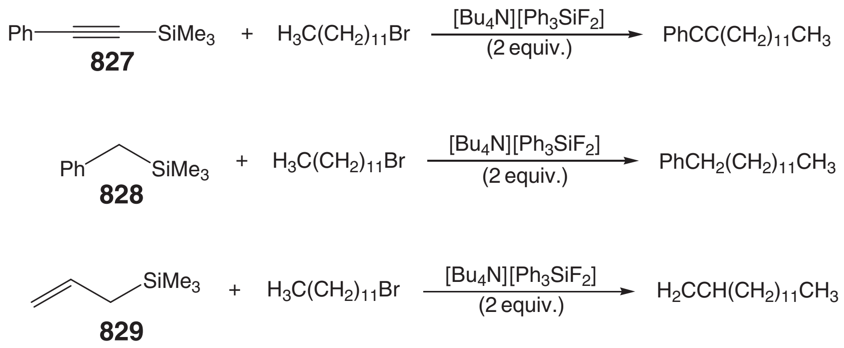
Photoswitching has allowed Kawashima *et al.* to control the configuration of the N–N double bond and the coordination number of potassium 18-crown-6 2-(phenylazo)phenyltetrafluorosilicates 836 and 837, which are accessible by the reaction of 2-(phenylazo)phenyltrifluorosilane 838 with KF/18-crown-6 (Scheme 116).[830] In the (*Z*)-form, the silicon atom of 837 is pentacoordinated, whereas in the (*E*)-form, one nitrogen atom of the azo group of 836 intramoleculary coordinates to the silicon atom, thus extending its coordination sphere to six ligands. Almost



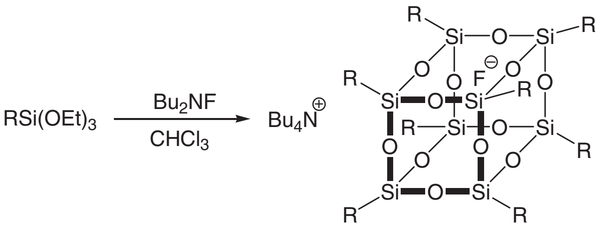
Scheme 111



Scheme 112

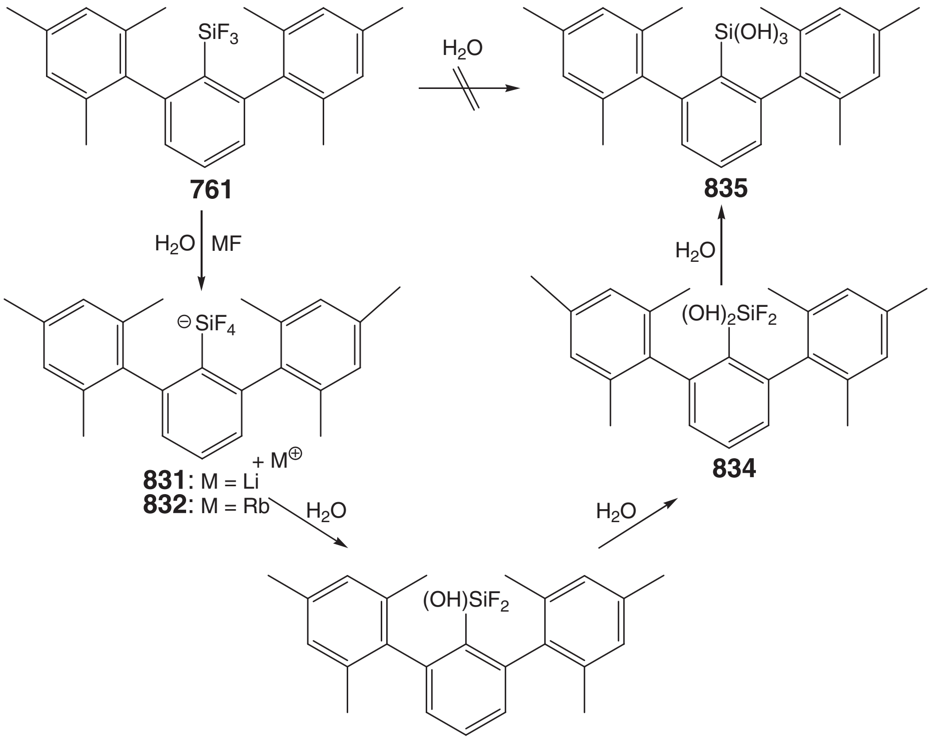


Scheme 113



830: R = Ph

Scheme 114



761

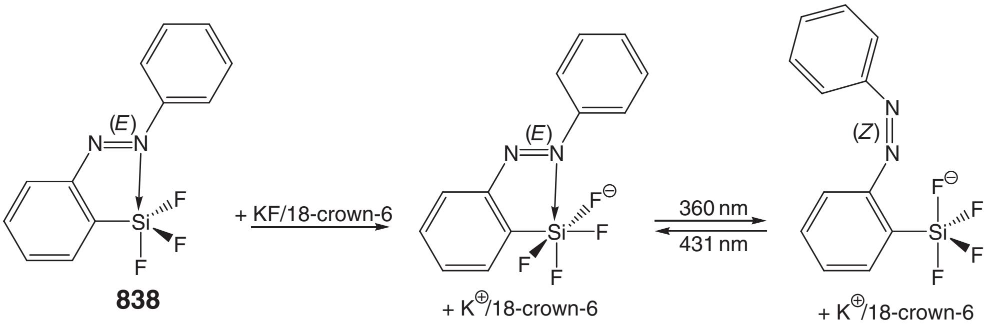
835

831: M = Li
832: M = Rb

834

833

Scheme 115

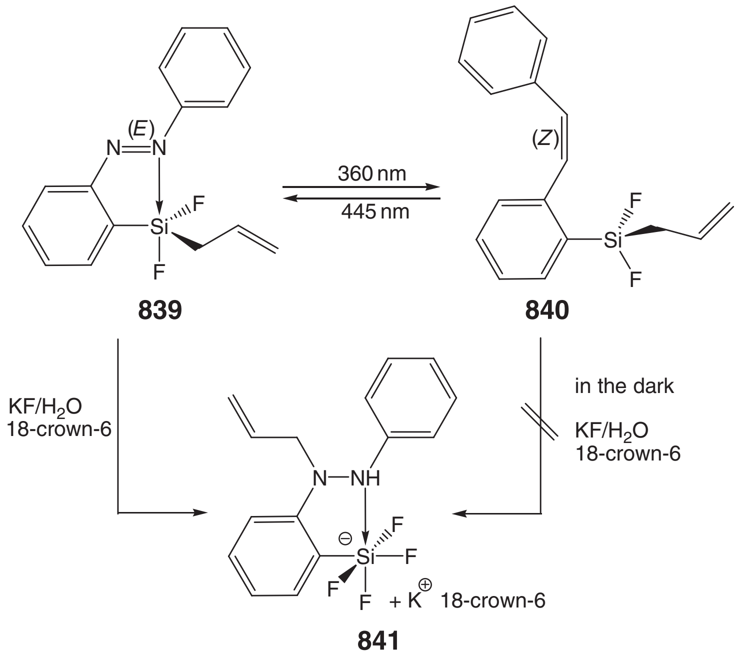


838

836

837

Scheme 116



Scheme 117

quantitative photoisomerization of the N–N double bond occurs upon radiation at $\lambda = 360$ and 431 nm, respectively. The molecular structures of both isomers of 836 and 837 have been confirmed by X-ray crystallography.[830]

Photoswitching of the coordination number of the silicon atom is also the key to control the reactivity of the allyl group in 2-(phenylazo)phenylallyldifluorosilane 839 and 840. Only the (*E*)-form 839 reacts with KF/H_2O/18-crown-6 to the corresponding allyhydrazine tetrafluorosilicate derivative 841 (Scheme 117). Apparently, the involvement of the azo group in the coordination of the silicon atom leads to an activation of the N–N double bond.[831]

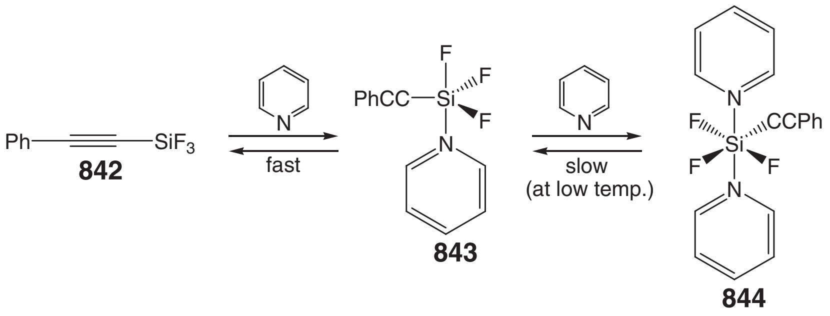
3.09.6.4 Hypercoordinated Silicon Complexes with Mixed Ligands

Nakash *et al.* have studied the reaction of phenylethynyltrifluorosilane 842 with mono- and bidentate nitrogen bases in solution using a combination of ^1H, ^{13}C, ^{15}N, ^{19}F, and ^{29}Si NMR spectroscopy, which gives rise to formation of neutral penta- and hexacoordinated silane complexes (Scheme 118).[832,833] At room temperature, pyridine and $PhCCSiF_3$ are in equilibrium with the pentacoordinated 1 : 1 complex 843. Only at low temperatures, a second equivalent of pyridine slowly coordinates to the silicon to selectively form one of three conceivable isomers, namely, the hexacoordinated 1 : 2 complex 844 having the two pyridine molecules in *trans*-position (Scheme 118).[832]

In the presence of the bidentate ligands, 2,2-bipyridyl and 1,10-phenanthroline, phenylethynyltrifluorosilane 842 is in equilibrium with the two possible isomers of the hexacoordinated 1 : 1 complexes 845 and 846, and 847 and 848, respectively. These have been also investigated by X-ray crystallography (Figure 6).[833]

Roewer *et al.* have used salene-type ligands for the preparation of neutral penta- and hexacoordinated silane complexes.[834–836] Interestingly, the reaction of the acid form of the salene ligand reacts with organotrichlorosilanes in the presence of diethylamine to form pentacoordinated enamine silane complexes 849–851, whereas the disodium salt of the salene ligand reacts with phenyltrichlorosilane providing the hexacoordinated chlorosilane complex 852 (Scheme 119).[834] The pentacoordinated complex 849 was also obtained when the hexacoordinated complex 852 was reacted with triethylamine (Scheme 119).

It has been shown also that salene ligands that lack β-hydrogen atoms next to the imine group will only afford hexacoordinated complexes.[834] The reaction of the salene ligand having phenyl groups with the diorganodichlorosilanes $PhRSiCl_2$ (R = Me, Et) exclusively provides the hexacoordinated complexes 853 and 854, which nevertheless show an enhanced reactivity and can be transformed into the pentacoordinated complexes 855 and 856 upon radiation with UV light (Scheme 120).[835] Most remarkably, this transformation entails the 1,3-migration of an alkyl



Scheme 118

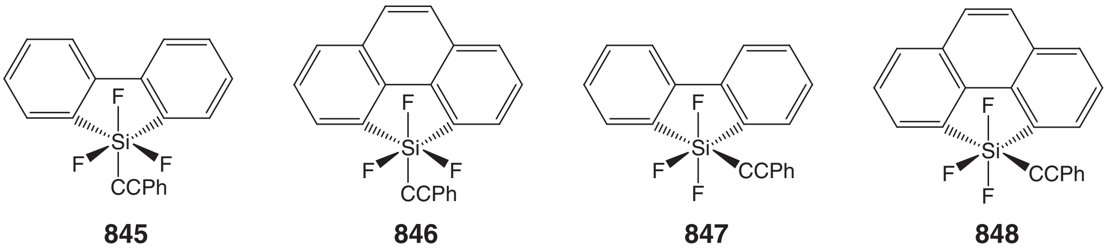
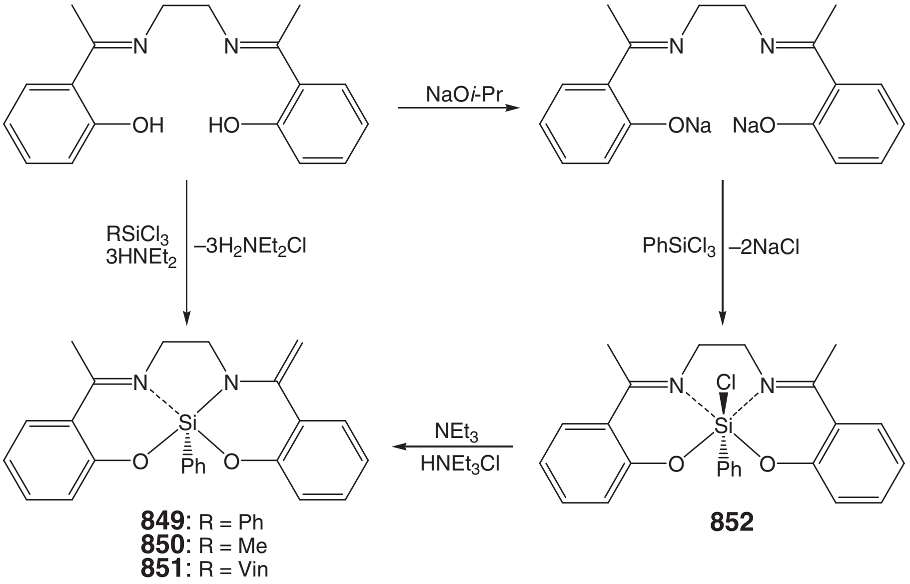


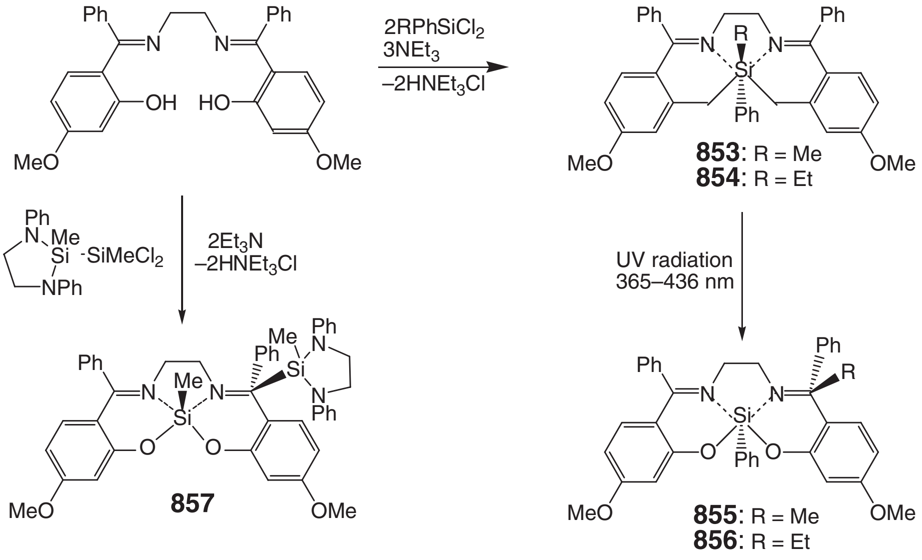
Figure 6



Scheme 119

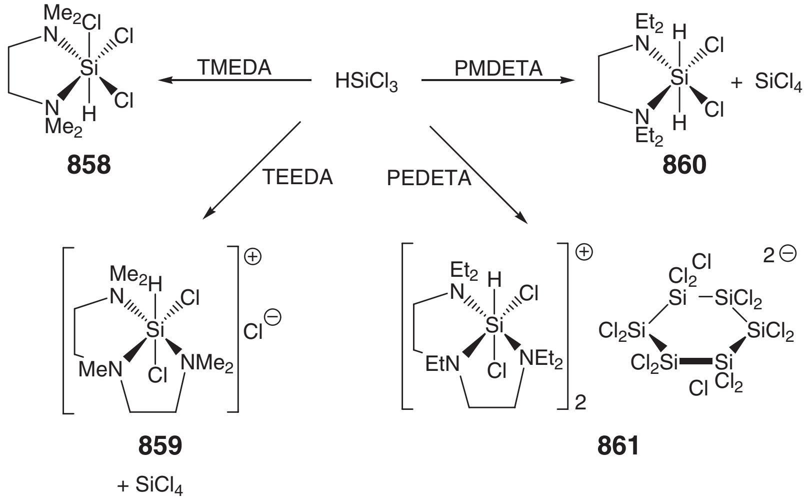
group (rather than a phenyl group) from silicon to the imine carbon. The reaction of the same salene ligand with 2-(dichloromethylsilyl)-2-methyl-1,3-diphenyl-1,2,3-diazasilolidine proceeded with a facile cleavage of the silicon–silicon bond in favor of the new bond to the imine carbon, yielding a pentacoordinated complex 857 (Scheme 120).[834]

Boudjouk *et al.* have investigated the reactivity of trichlorosilane toward ethylene-bridged di- and triamines.[837–839] With *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), $HSiCl_3$ forms the expected hexacoordinated complex (TMEDA)$SiHCl_3$ 858, whereas with *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA), a facile redistribution reaction takes place, which gives rise to the formation of the hexacoordinated complex (TEEDA)SiH_2Cl_2 859 and $SiCl_4$



Scheme 120

(Scheme 121).[837] With *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) and *N,N,N′,N′,N″*-pentaethyldiethylenetriamine (PEDETA), $HSiCl_3$ affords hexacoordinated cationic complexes $[(PMDETA)SiHCl_2]Cl$ **860**[838] and $[(PEDETA)SiHCl_2]_2[Si_6Cl_{14}]$ **861**, respectively (Scheme 121).[839] Most interestingly, compound **861** features a hitherto unknown hypercoordinate anion, which comprises an almost planar six-membered cyclohexasilane substituted by 12 chlorine atoms and two additional chlorine atoms situated on the sixfold axis of the ring. The associated Si···Cl distance of average 3.00 Å is significantly shorter than the sum of the van der Waals radii (3.90 Å), but longer than the "standard" covalent bond length (2.17 Å). Therefore, the coordination number of the six silicon atoms in the ring can be considered as [4 + 2].[839] The compounds $(TEEDA)SiH_2Cl_2$ **859** and $[(PEDETA)SiHCl_2]_2[Si_6Cl_{14}]$ **861** provide interesting opportunities for organosilicon synthesis. In the reaction with Grignard reagents, such as PhMgCl, $(TEEDA)SiH_2Cl_2$ **859** is a synthetic equivalent for the highly reactive H_2SiCl_2 gas and allows direct synthetic access to diorganosilanes, such as Ph_2SiH_2.[837] The cyclohexasilane dianion of $[(PEDETA)SiHCl_2]_2[Si_6Cl_{14}]$ **861** is a convenient precursor for the synthesis of other silicon-ring systems. The reaction of **861** with $LiAlH_4$ and MeMgBr proceeds with retention of the six-membered ring structure and gives rise to the formation of $(H_2Si)_6$ **862** and $(Me_2Si)_6$ **612**, respectively.[839]



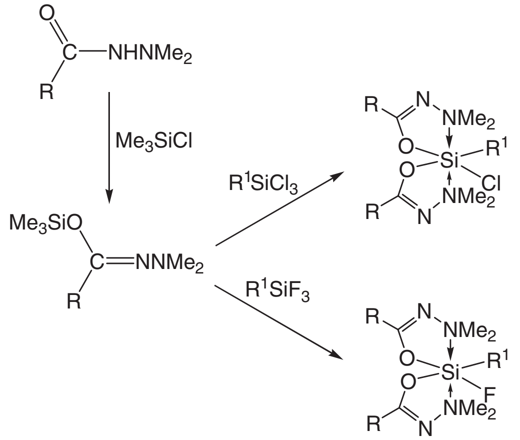
Scheme 121

3.09.6.5 Hypercoordinated Silicon Complexes with Ligands Derived from Hydrazine

Advances in the field of hydrazine-based hypervalent Si complexes have been reviewed by Kost and Kalikhman in 2004.[840] *O*-Trimethylsilyl-*N*,*N*-dimethylhydrazines are accessible by the reaction of 1,1-dimethyl-2-acylhydrazines with trimethylchlorosilane. The reaction of *O*-trimethylsilyl-*N*,*N*-dimethylhydrazines $(Me_3SiO)RCNNMe_2$ (R = Me, Ph, CH_2Ph, CF_3, PhMeCH, *t*-Bu) with trihalosilanes R^1SiCl_3 and R^1SiF_3 (R^1 = H, Me, *t*-Bu, Cl, CH_2Cl, Ph, *c*-Hex) has given a large number of chelate complexes 863–883 (Scheme 122).[841–854]

The most striking feature of 863–883 is their structural diversity in solution and the solid state. In solution, dynamic equilibria exist between penta- and hexacoordinated species, which have been probed by NMR spectroscopy (Scheme 123).

The chelate complexes 871 and 876 containing chloromethyl groups undergo irreversible rearrangement at elevated temperatures to give novel complexes 884 and 885 (Scheme 124). The rearrangement may be rationalized by an intramolecular substitution of the chlorine atom at the chloromethyl group by the nitrogen atom of one hydrazine ligand.

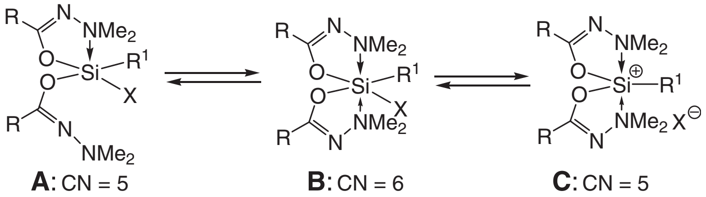


863: R = Me; R^1 = H
864: R = Me; R^1 = Me
865: R = Me; R^1 = *t*-Bu
866: R = Me; R^1 = Cl
867: R = Ph; R^1 = H
868: R = Ph; R^1 = Me
869: R = Ph; R^1 = *t*-Bu
870: R = Ph; R^1 = Cl
871: R = Ph; R^1 = CH_2Cl
872: R = CH_2Ph; R^1 = Ph

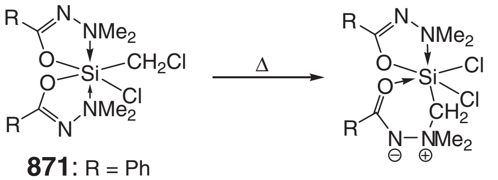
873: R = CF_3; R^1 = H
874: R = CF_3; R^1 = Me
875: R = CF_3; R^1 = Cl
876: R = CF_3; R^1 = CH_2Cl
877: R = CF_3; R^1 = c-*Hex*
878: R = PhMeCH; R^1 = Ph
879: R = *t*-Bu; R^1 = Ph
880: R = *t*-Bu; R^1 = *t*-Bu
881: R = *t*-Bu; R = *c*-Hex

882: R = CF_3; R^1 = Ph
883: R = CF_3; R^1 = Cl

Scheme 122



Scheme 123



871: R = Ph
876: R = CF_3

884: R = Ph
885: R = CF_3

Scheme 124

3.09.6.6 Intramolecularly Coordinated Di- and Oligosilanes, Silylenes and Silenes

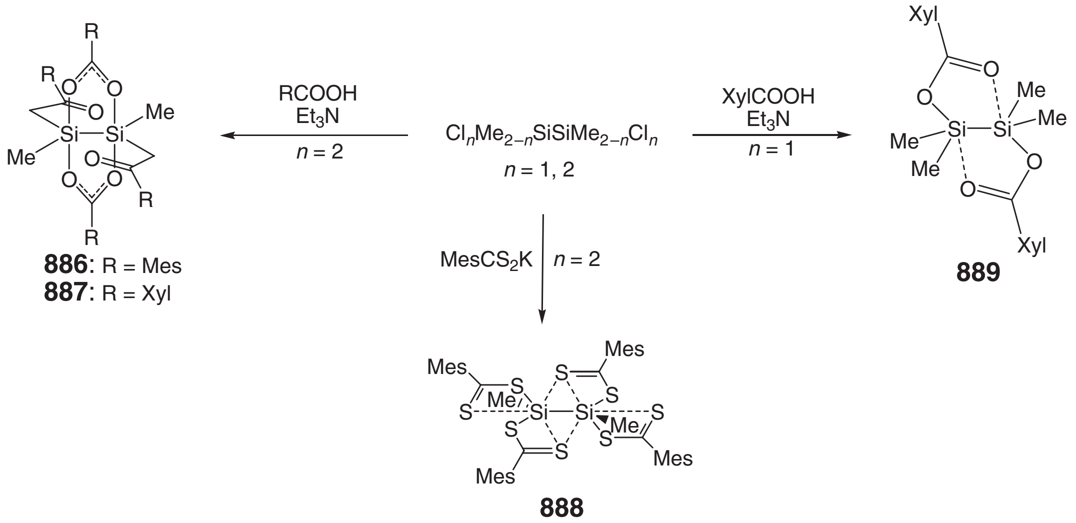
In the absence of electron-withdrawing ligands, disilanes possess only a little Lewis acidity; consequently, they show a limited propensity to form hypervalent complexes. Starting from the symmetric methylchlorodisilanes $ClMe_2SiSiMe_2Cl$ and $Cl_2MeSiSiMeCl_2$ as well as carboxylic acids and thiocarboxylic acids, Kawashima *et al.* have prepared rare examples of penta- and hexacoordinated disilene, namely compounds 886–889 (Scheme 125).[855,856]

Corey *et al.* have studied the epimerization of the diastereomeric difluorodisilanes $F(RMeSi)_2F$ (**890**, R = Ph; **891**, R = 4-FC_6H_4; **892**, R = 4-$MeOC_6H_4$; **893**, R = 4-MeC_6H_4), which in solution exist as a slowly interconverting mixture of *meso*- and *rac*-isomers. Upon slow evaporation, only the more symmetric *meso*-isomers crystallize out. ^{29}Si NMR studies have revealed that the *meso*-/*rac*-ratio remained unchanged after the cystallization, which is consistent with the slow equilibration process. When the pure *meso*-isomers are dissolved in organic solvents, the concentration of the *meso*-isomers decreases in favor of the *rac*-isomers until an equilibrium state has been reached. The addition of fluoride ions dramatically accelerated the equilibration reaction, pointing to the intermediate formation of hypervalent fluorosilicate.[857,858]

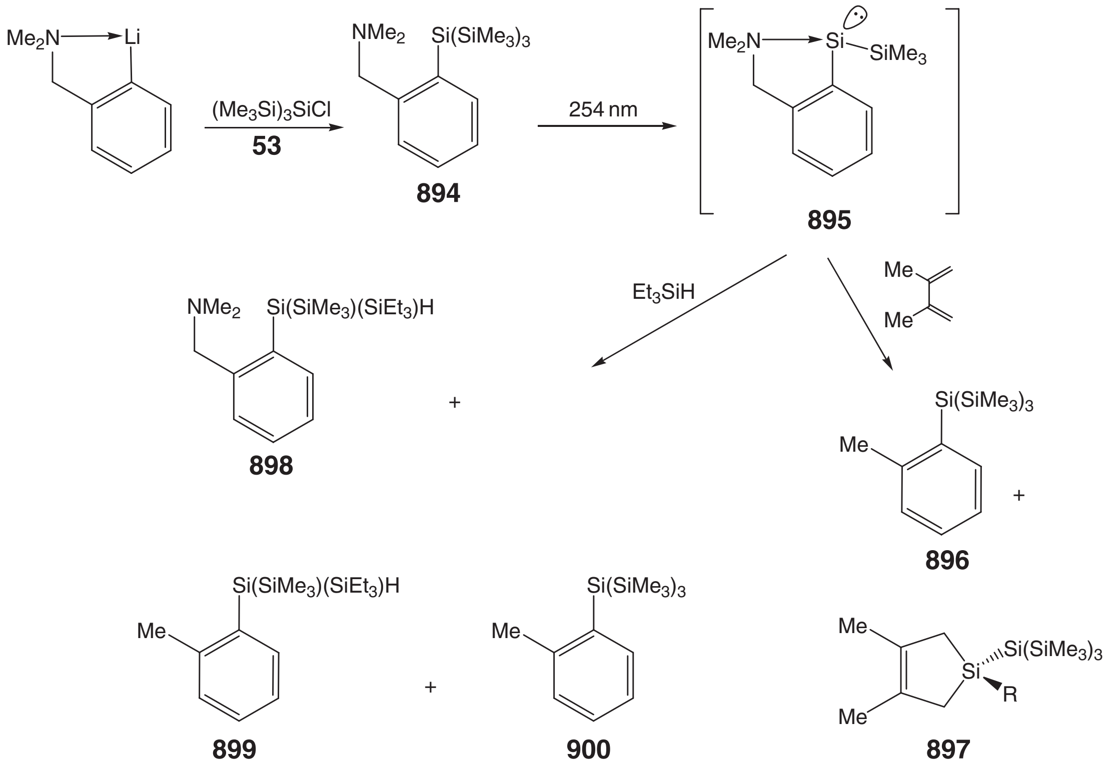
Corriu *et al.* have reported that the coupling reaction of 2-(*N*,*N*-dimethylaminomethyl)phenyllithium with $(Me_3Si)_3SiCl$ 53 affords 2-(*N*,*N*-dimethylaminomethyl)-1-[tris(trimethylsilyl)silyl]benzene 894. No evidence has been found that the intramolecular *N*-ligand coordinates to the silicon atom of 894. Upon UV irradiation, the trisilane forms a transient silyene 895, which has been trapped with 2,3-dimethyl-2,3-butadiene and triethylsilane to give the oligosilanes 896 and 897 as well as 898–900, (Scheme 126).[859] Apparently, the bulk on the two ligands is insufficient to provide kinetic stabilization of the silylene intermediate 895.

Tamao *et al.* have prepared disilanes and related compounds starting from 8-dimethylaminonaphth-1-yl lithium (Schemes 127 and 128).[860–865] The reaction of 8-dimethylaminonaphth-1-yl lithium with the disilene $Ph_2MeSiSiMeCl_2$ has provided the chlorodisilane 901, which has been reacted with EtOH and $LiAlH_4$ to give the ethoxydisilane 902 and the H-disilane 903, respectively. The latter have been used for the formation of the transient silylene 904, which has been trapped with unsaturated hydrocarbons. The thermolysis of 902 in presence of 2,3-dimethyl-1,3-butadiene and diphenylacetylene has delivered the trapping products 905 and 906, respectively.[861] When thermolysis of the H-disilane 903 in the presence of diphenylacetylene and the catalyst system $NiAc_2/Et_3P/DIBAL–H$ has resulted in different products, namley, the silole derivative 907 and the vinlysilane 908 (Schemes 127). A mechanism accounting on the different reaction pathways has been proposed.[862] More trapping experiments on transient silylenes have been conducted using other catalysts and intramolecularly coordinating ligands that contain S and Se donor atoms, respectively.[864,865]

Attempts have been made to prepare polysilanes containing the 8-dimethylaminonaphth-1-yl ligand.[863] The coupling reaction of 8-dimethylaminonaphth-1-yl lithium with $MeSiCl_3$ has given the dichlorosilane 909, whose mild reduction with Mg has surprisingly yielded the disilane 910 rather than the expected polysilane (Scheme 128). The formation of the disilane may be rationalized by the insertion of a transient silylene 904 into an Si–N bond of



Scheme 125



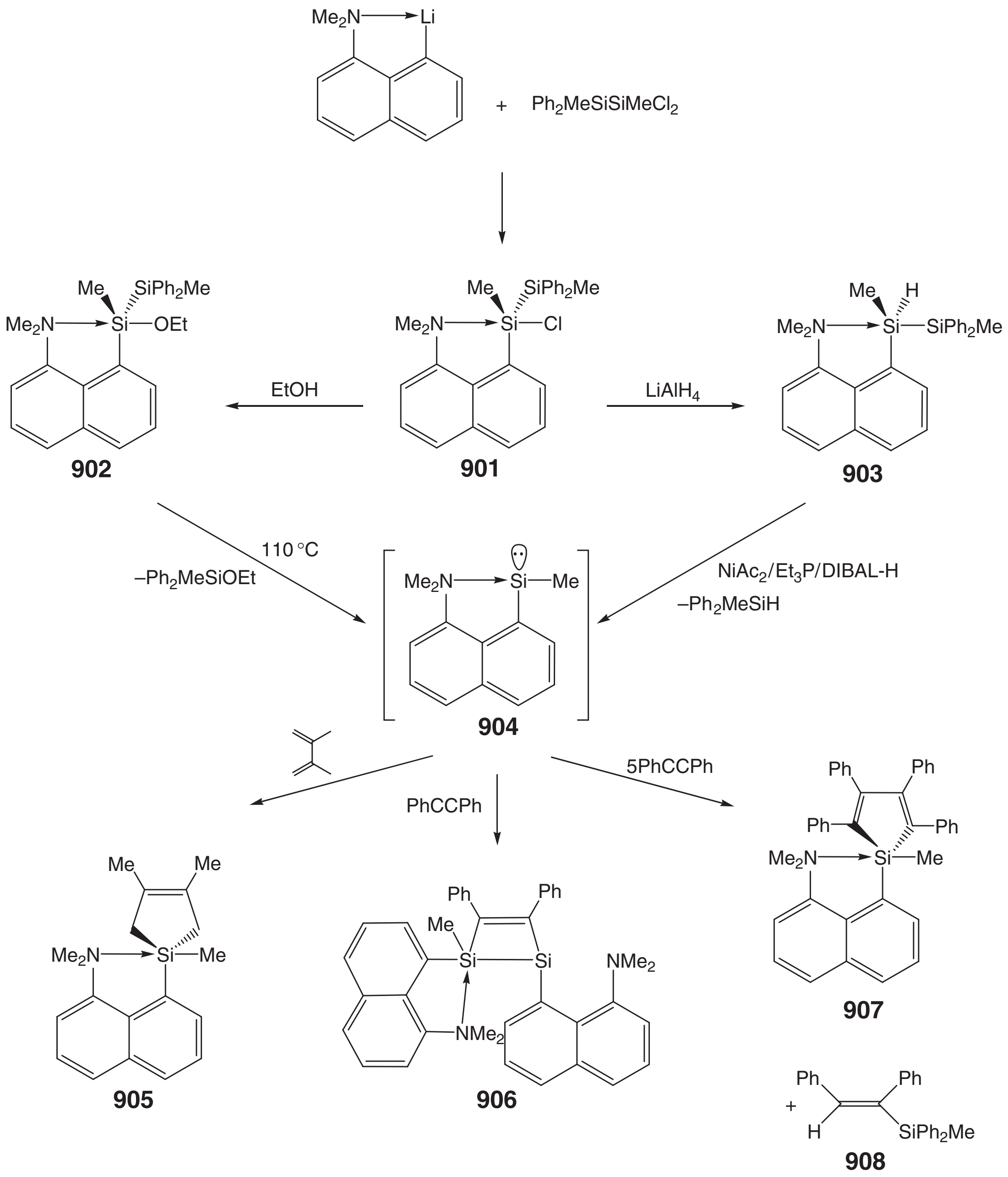
Scheme 126

another molecule. Alternatively, two silylene molecules **904** may have dimerized to form the corresponding disilene, which undergoes an intramolecular rearrangement process involving the addition of an Si–N bond to the Si–Si double bond (Scheme 128). The reaction of the disilane **910** with isopropanol occurs under substitution of the amino group and yields a 2 : 1 mixture of the *cis-* and *trans*-disilenes **911 and 912** (Scheme 128).[863]

Belzner *et al.* have studied the similar reduction of the bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]dichlorosilane R_2SiCl_2 **913** with Mg, which has given rise to the formation of the cyclotrisilane $(R_2Si)_3$ **914** ($R = 2\text{-}Me_2NCH_2C_6H_4$) (Scheme 129).[866] In the solid state, neither of the six 2-(*N*,*N*-dimethylaminomethyl)phenyl ligands is involved in intramolecular coordination to the silicon atoms, due to the lack of sufficient Lewis acidity. However, at elevated temperatures in solution, the trisilane is in equilibrium with the intramolecularly coordinated silylene R_2Si **915** (Scheme 129). The reaction of the cyclotrisilane **914** with lithium yields the dilithium disilanide **916**, whose quenching with H_2O and Me_3SiCl provides the disilene HR_2SiSiR_2H **917** and the tetrasilane $Me_3SiR_2SiSiR_2SiMe_3$ **918**, respectively ($R = 2\text{-}Me_2NCH_2C_6H_4$). Alcoholysis of the cyclotrisilane **914** with *t*-BuOH initially gives the trisilane $HSiR_2SiR_2SiR_2O$*t*-Bu **919**, which reacts with more *t*-BuOH to give the stable products HR_2SiSiR_2O*t*-Bu **920** and HR_2SiO*t*-Bu **921** (Scheme 129).[867]

Similarly, reduction of the [2-(*N*,*N*-dimethylaminomethyl)phenyl]mesityldichlorosilane $RMesSiCl_2$ **922** with Mg has provided the cyclotrisilane $(RMesSi)_3$ **923**, which is also involved in an equilibrium with the corresponding intramolecularly coordinated silylene RMesSi **924** in solution ($R = 2\text{-}Me_2NCH_2C_6H_4$) (Scheme 130). The reactivity of the cyclotrisilanes **923** can be rationalized best by taking into account the equilibrium with the silylene **924**. The reaction of **923** with 2,3-dimethyl-1,3-butadiene and trimethylsilyl acetylene **226** results in the formation of the cycloaddition products **925 and 926**, respectively, whereas the reaction of **923** with $RMesSiCl_2$ and *t*-BuOH gives dichlorodisilane ClMesSiSiMesCl **927** and RMesSiHO*t*-Bu **928** (Scheme 130) ($R = 2\text{-}Me_2NCH_2C_6H_4$).[867]

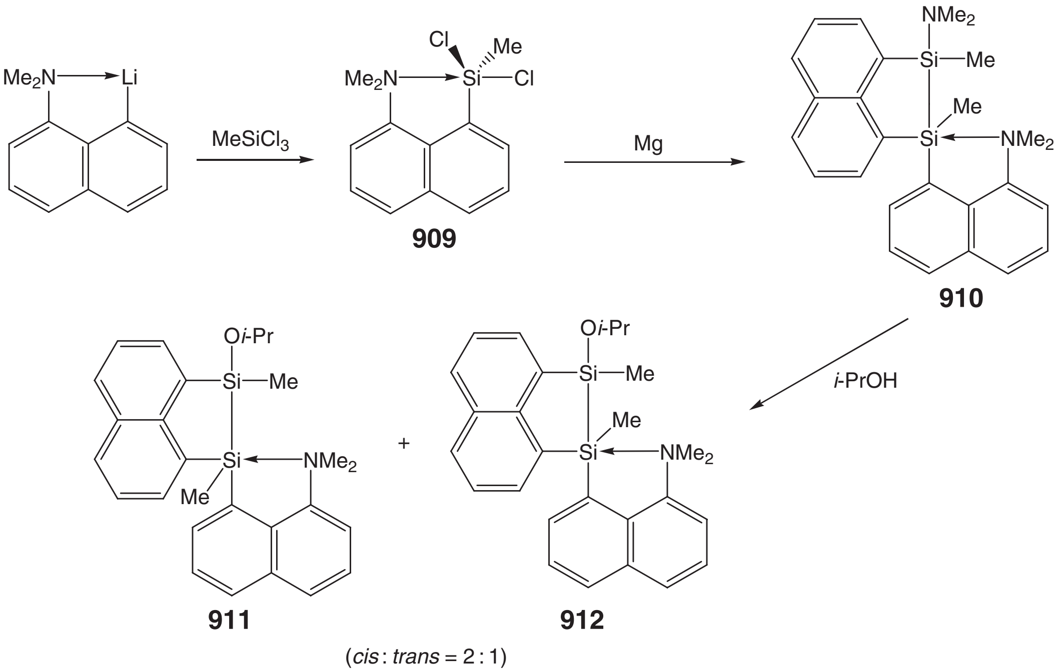
Intramolecularly coordinated silenes have been prepared by Oehme *et al.*[868–871] Adopting their general procedure for the synthesis of silenes (Scheme 33), 8-dimethylaminonaphth-1-yl lithium has been reacted with $(Me_3Si)_3SiCHCl_2$ yielding the disilene $(Me_3Si)RSiC(SiMe_3)_2$ **929** via the intermediates **930–933** (R = 8-dimethylaminonaphth-1-yl) (Scheme 131).



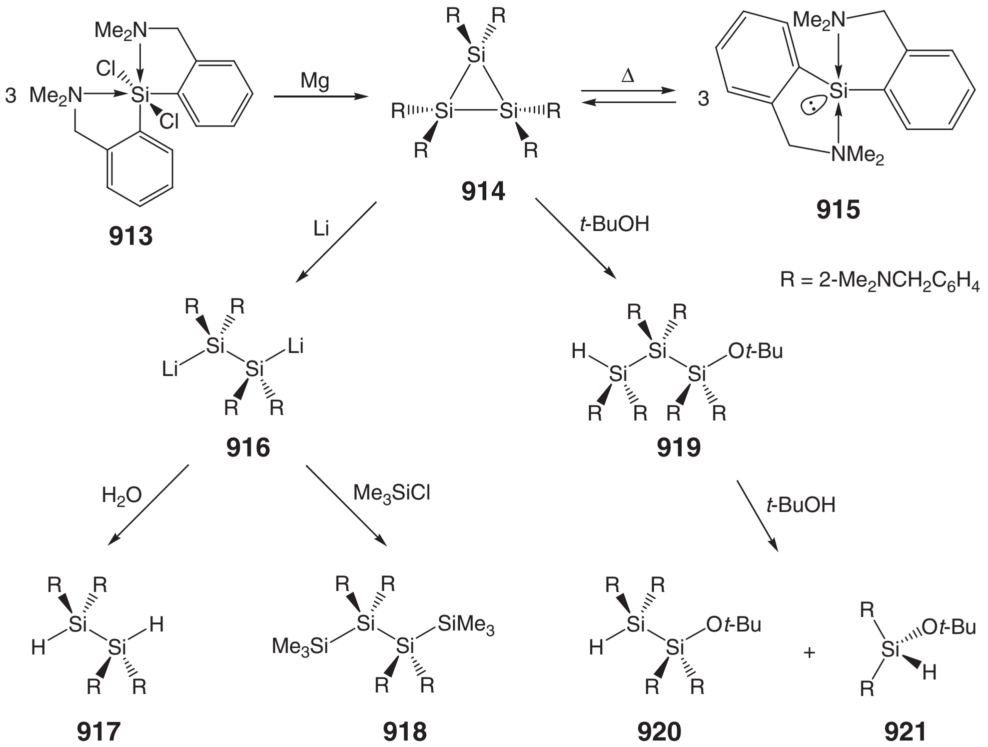
Scheme 127

In a similar way, 2-(*N*,*N*-dimethylaminomethyl)phenyllithium and 2,6-bis(*N*,*N*-dimethylaminomethyl)-phenyllithium (Figure 4) have been used to prepare the intramolecularly coordinated silenes 934 and 935 (Figure 7).

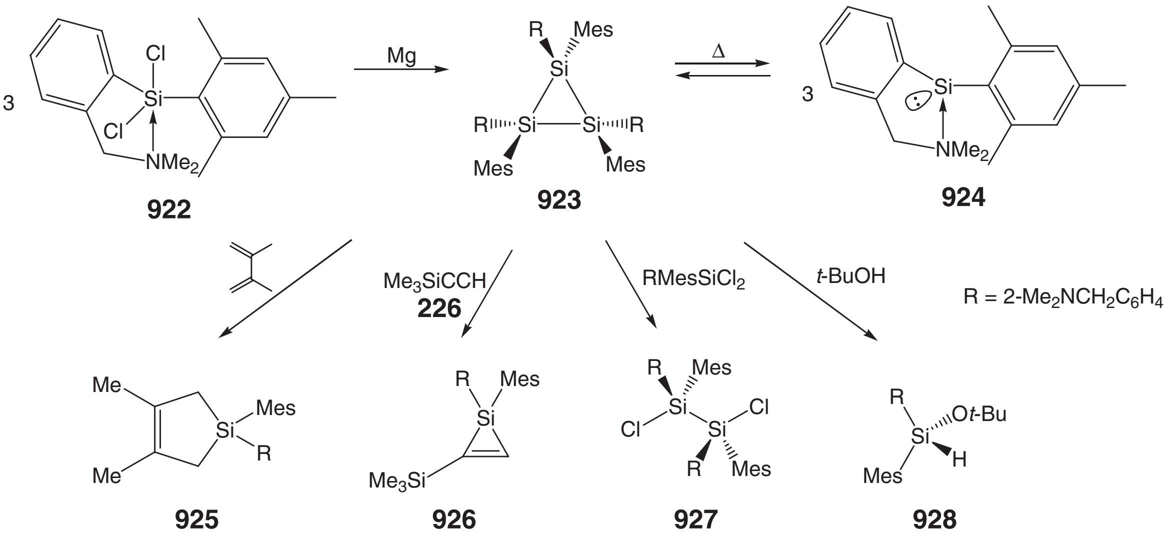
The reactivity of the intramolecularly coordinated silenes 929, 934, and 935 has been investigated. The hydrolysis and methanolysis of 929 proceed via formation of Si–O bonds and yield the products 936 and 937 (Scheme 132). The reaction of 929 with benzaldehyde can be regarded as sila-Wittig reaction, and proceeds via the initial formation of the cycloaddition product 938, which rearranges into the cyclodisiloxane $[R(Me_3Si)SiO]_2$ 939 (R = 8-dimethylamino-naphthyl-1-yl) and 1,1-bis(trimethylsilyl)-2-phenylethene 940 (Scheme 132). Methyl iodide catalyzes the isomerization of 929, which proceeds via addition to the Si–C



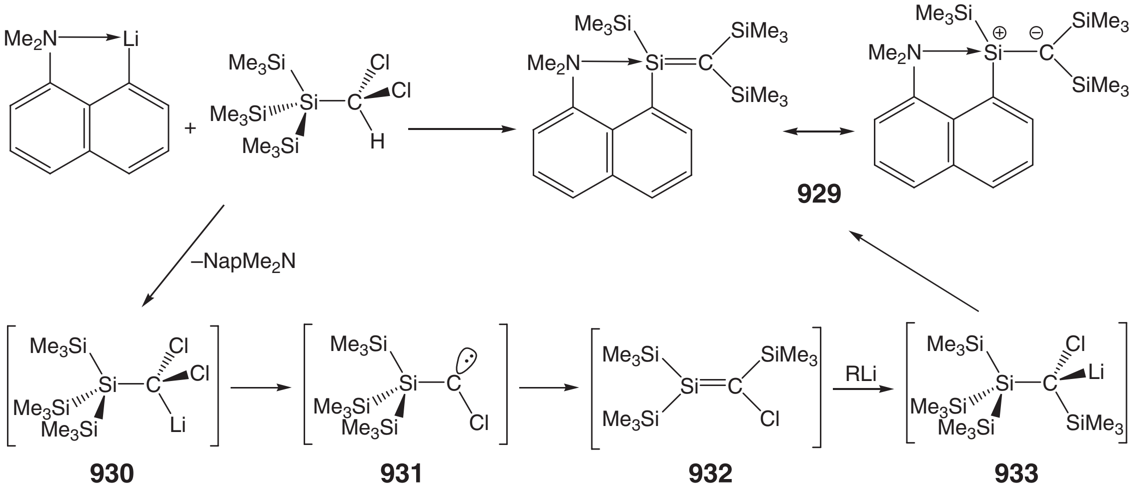
Scheme 128



Scheme 129



Scheme 130



Scheme 131

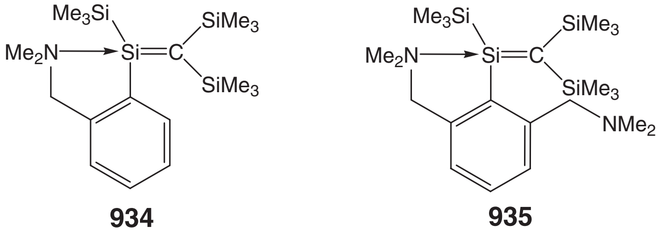
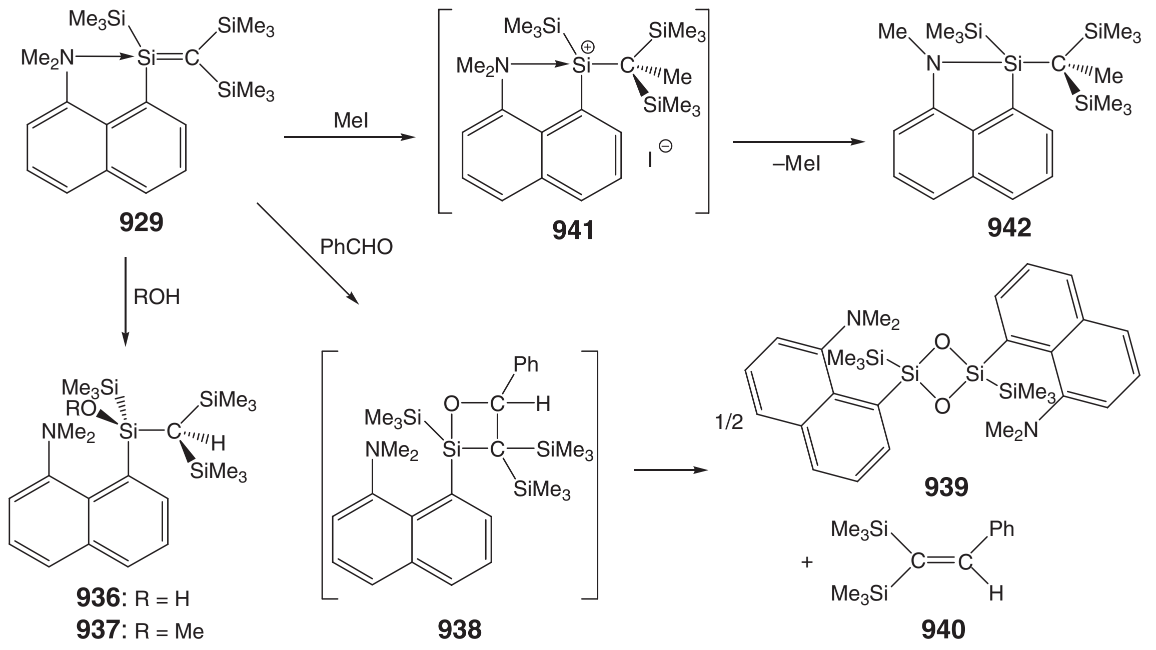


Figure 7



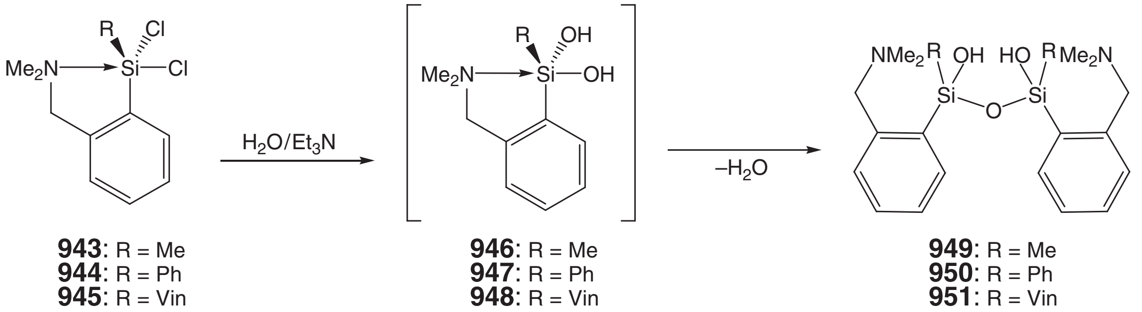
Scheme 132

double bond and the intermediate formation of the silyl cation **941**. The cation **941** rearranges via a 1,3-methyl shift to give the tetracoordinate silazane **942** (Scheme 132).

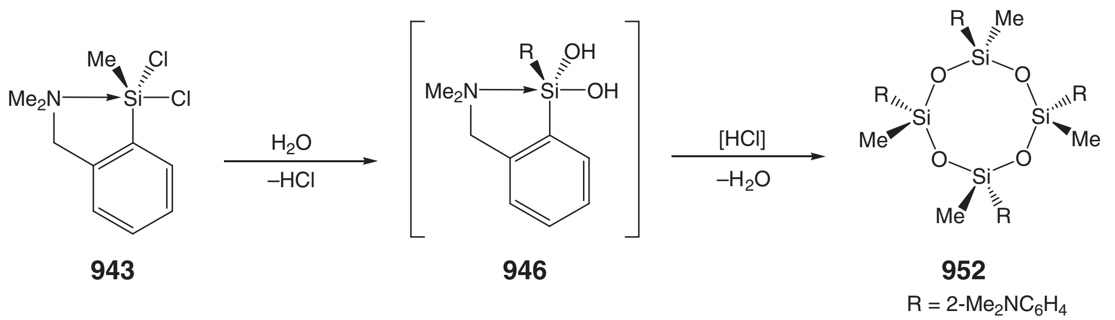
3.09.6.7 Intramolecularly Coordinated Silanols

The hydrolysis of (2-dimethylaminophenyl)organochlorosilanes has been studied by Lee *et al.* and Lang *et al.* (Schemes 133 and 134). The careful hydrolysis of (2-$Me_2NCH_2C_6H_4$)$RSiCl_2$ (**943**, R = Me; **944**, R = Ph; **945**, R = Vin) in the presence of triethylamine proceeds via initial formation of the silandiols (2-$Me_2NCH_2C_6H_4$)$RSi(OH)_2$ (**946**, R = Me; **947**, R = Ph; **948**, R = Vin), which undergo self-condensation to give diastereomeric mixtures of the disiloxanediols [(2-$Me_2NCH_2C_6H_4$)R(OH)Si]$_2$O (**949**, R = Me; **950**, R = Ph; **951**, R = Vin) (Scheme 133). The *meso*- and *rac*-isomers of **949–951** could be distinguished by their crystal forms and have been manually separated. In dry chloroform solutions, the *meso*- and *rac*-isomers of **949–951** are configurationally stable, but undergo epimerization when traces of moisture are present.[872,873] In the solid state, the amino groups are involved in hydrogen bonding with the silanol groups.

The hydrolysis of (2-$Me_2NCH_2C_6H_4$)$MeSiCl_2$ **943** in absence of a base also proceeds via formation of the silanoldiol **946**, which, catalyzed by HCl, undergoes complete condensation to give the eight-membered



Scheme 133



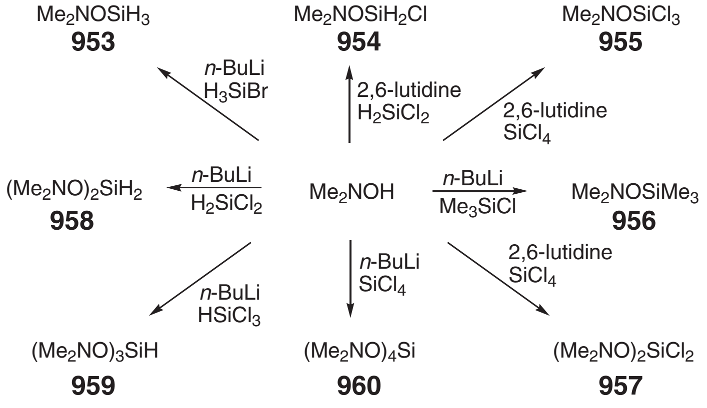
Scheme 134

cyclotetrasiloxane **952**. An X-ray structure analysis has revealed that the (2-dimethylaminophenyl) groups are not involved in intramolecular coordination to the Si atoms (Scheme 134).[874]

3.09.6.8 Intramolecular β-Donor–Acceptor Complexes

Mitzel *et al.* have studied the strong β-donor–acceptor bonds of *O*-hydroxyaminosilanes by X-ray crystallography and gas-phase electron diffraction. *O*-Hydroxyaminosilanes are accessible upon reaction of Me_2NOH with halosilanes using either *n*-BuLi or amines as proton scavengers (Scheme 135). As a result of the rather weak intramolecular N···Si coordination, this compound class shows [4 + 1] (Me_2NOSiH_3 **953**,[875] Me_2NOSiH_2Cl **954**,[876] $Me_2NOSiCl_3$ **955**,[877] $Me_2NOSiMe_3$ **956**),[878] [4 + 2] ($(Me_2NO)_2SiCl_2$ **957**,[879] $(Me_2NO)_2SiH_2$ **958**),[875] [4 + 3] ($(Me_2NO)_3SiH$ **959**[880]), and [4 + 4] ($(Me_2NO)_4Si$ **960**)[881] coordination geometries, depending on the number of dimethylaminohydroxy groups present.

Within the series of mono(hydroxyamino)silanes, the intramolecular Si···N coordination has been manifested experimentally in the gas phase by the Si···N distance and the N–O–Si angle of 2.453(1) Å/102.63(5)° (Me_2NOSiH_3 **953**),[875] 2.160(7) Å/87.1(9)° (*anti*-conformer of Me_2NOSiH_2Cl **954**),[876] 2.468(25) Å/104.7(11)° (*gauche*-conformer of Me_2NOSiH_2Cl **954**),[876] 2.473(12) Å/105.6(8)° ($Me_2NOSiCl_3$ **955**),[877] and 2.566(8) Å/107.9(6)° ($Me_2NOSiMe_3$ **956**), respectively (Figure 8).[878]



Scheme 135

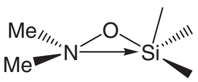


Figure 8

The experimentally obtained values are in excellent agreement with the results of *ab initio* calculations. Negative hyperconjugation was proposed to be one suitable model to describe the Si···N attraction as $n(\mathrm{n})$–$\sigma^*(\mathrm{Si})$ interaction.[878] Although the isomerization of Me_2NOSiH_3 **953** to the aminosilanol Me_2NSiH_2OH **961** is thermodynamically favored, it can be heated unchanged to about 100 °C.[875]

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3.10
Compounds with Bonds between Silicon and *d*-Block Metal Atoms

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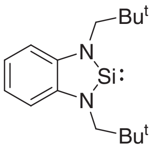
3.10.1 Introduction

The chemistry of compounds containing bonds between silicon and *d*-block metal atoms has expanded enormously over the past 20 years. In COMC (1982)[1] and COMC (1995),[2] short sections dealt with some of these compounds. However, the growth in the area demands a more detailed survey in this edition. Such active current research relates to *d*-block metal complexes involved in the catalyzed reactions of hydrosilanes or disilanes, and also the growing interest in organometallic precursors for materials. In parallel with these areas of research comes the isolation and characterization of a wide range of *d*-block metal silyl compounds, many with novel structures and properties. Applications of silicon-containing compounds (including transition metal complexes) in organic synthesis are covered in Volumes 9 and 10 of this edition. The aim of this chapter is to provide an overview of well-characterized complexes containing bonds between Si and *d*-block metals. A seminal review by Corey and Braddock-Wilking published in 1999[3] surveys the literature for the period 1981–1997, and contains ≈550 references; this work focuses on the reactions of hydrosilanes with metal complexes, which is one of the most important methods of preparing metal complexes containing M–Si bonds. In the light of the detailed coverage by Corey and Braddock-Wilking, this chapter will be mainly concerned with work published in or after 1997. In their conclusions, Corey and Braddock-Wilking[3] point to the fact that of the *d*-block metals, those in the Sc, Cu, and Zn triads are poorly represented among silyl derivatives. Since 1997, some progress has been made for these metals, but the bulk of M–Si bonds are formed for metals in groups 4–10, with a dominant number in group 8 where metal–silyl chemistry began.[4] In the past few years, significant progress has been made in the isolation of metal silylene complexes, that is, analogs of the much better established metal carbenes.

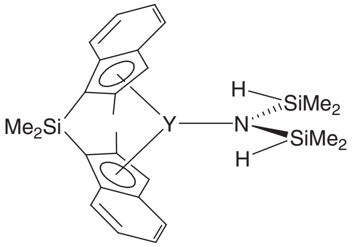
3.10.2 Group 3 Metals

New developments in group 3 chemistry of the M–Si bond center on yttrium, and are typically a part of the growing area of lanthanidocene chemistry. The thermally stable silylene **1** reacts with Cp_3Y with the formation of a Y–Si bond (structurally confirmed); variable-temperature $^{29}Si\{^1H\}$ NMR spectroscopic data show that the complex dissociates in solution.[5] A σ-bond metathesis route has been used for the formation of $Cp^*_2YSiH(SiMe_3)_2$. The synthesis involved the reaction of $Cp^*_2YCH(SiMe_3)_2$ with $(Me_3Si)_2SiH_2$, but the method was shown to be sensitive to the steric bulk of the precursors, suggesting that a four-center transition state is involved.[6]

Agostic Y–H–Si interactions feature in several reports. Treatment of $Y\{N(SiHMe_2)_2\}_3(THF)_2$ (THF = tetrahydrofuran) with $(C_9H_5\text{-}2\text{-}Me)_2SiMe_2$ gave the *ansa*-yttrocene **2** in almost quantitative yield. The solid-state structure of *rac*-**2** confirms that the Si–H bonds face the Y center ($Si\cdots Y = 3.082(1)$ Å), and the evolution of Y–H interactions are consistent with NMR spectroscopic data.[7,8] Silylamine elimination has also been used as a means of preparing $Cp^*Y\{N(SiHMe_2)_2\}_2$ and $Cp^*_2YN(SiHMe_2)_2$, as well as related species containing sterically demanding substituents on the cyclopentadienyl rings. As in **2**, Y–H–Si interactions are present, and the structural features of the $YN(SiHMe_2)_2$ units depend on the steric crowding of the C_5R_5 ligands.[9] Transacylation reactions between enolesters and chiral secondary alcohols are catalyzed by salen (H_2L) complexes of yttrium. Complexes of the type $(L\text{-}N,N',O,O')Y\{N(SiHMe_2)_2\}(THF)$ have been prepared and the solid-state structure of one member of the family determined. Again, an agostic Y–H–Si interaction is observed. The structural features of the catalyst are the basis for a mechanistic proposal for the transacylation process.[10]



1



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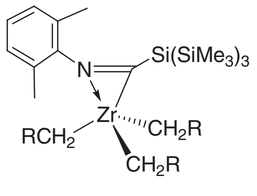
3.10.3 Group 4 Metals

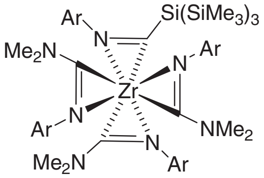
The chemistry of group 4 metal silyl compounds has developed significantly over the past decade. A new family of stable d^0-alkyl/silyl metal complexes $(Me_3ECH_2)_3MSi(SiMe_3)_3$ (E = C or Si; M = Ti or Zr) that do not involve anionic π-ligands (e.g., cyclopentadienyl) was reported in 1996,[11] with a preliminary report in 1994 of $(Me_3CCH_2)_3ZrSi(SiMe_3)_3$, $(Me_3CCH_2)_2Ta({=}CHCMe_3)Si(SiMe_3)_3$, and $(Me_3CCH_2)_2W({\equiv}CCMe_3)Si(SiMe_3)_3$, which represented the first silyl alkyl, and stable alkylidene and alkylidyne compounds of early *d*-block metals.[12] The complexes $(Me_3ECH_2)_3MSi(SiMe_3)_3$ were prepared by reactions of $(Me_3ECH_2)_3MCl$ with $LiSi(SiMe_3)_3(THF)_3$, and X-ray diffraction data for the Ti(IV) products have been described.[11] From reactions between $LiSi(SiMe_3)_3(THF)_3$ or $LiSiPh_2{}^tBu(THF)_3$ with $(Me_2N)_3MCl$ (M = Ti, Zr, Hf) or $(Me_2N)_2\{(Me_3Si)_2N\}ZrCl$, the complexes

$(Me_2N)_3MSi(SiMe_3)_3$ (M = Zr, Hf), $(Me_2N)_3TiSiPh_2Bu^t$, $(Me_2N)_3ZrSiPh_2Bu^t\cdot 0.5THF$, $(Me_2N)_3HfSiPh_2Bu^t\cdot nTHF$ ($n = 0.5$ or 1), and $(Me_2N)_2\{(Me_3Si)_2N\}ZrSiR_3$ ($SiR_3 = Si(SiMe_3)_3$, $SiPh_2Bu^t$) have been isolated and representative structures determined.[13] Early *d*-block metal–silicon bonds are very reactive and undergo insertions as illustrated by the reaction of $(Me_3ECH_2)_3ZrSi(SiMe_3)_3$ (E = C or Si) with 2,6-dimethylphenyl isocyanide (ArNC). The first equivalent of ArNC inserts into the Zr–Si bond to give **3**, and this is followed by insertion into the Zr–C bonds; no more than three ArNC can be inserted.[14] This work has been extended to the reactions of isocyanides with $(Me_2N)_3ZrSi(SiMe_3)_3$, $(Me_2N)_3ZrSiPh_2Bu^t(THF)_{0.5}$, and $(Me_2N)_2\{(Me_3Si)_2N\}ZrSi(SiMe_3)_3$. For example, $(Me_2N)_3ZrSi(SiMe_3)_3$ reacts instantaneously at room temperature with 4 equiv. of 2,6-dimethylphenyl isocyanide to give the product **4**.[15] When $Li(THF)_3SiPh_2Bu^t$ reacts with $(Me_2N)_3Zr(SiPh_2Bu^t)$, the product is the salt $[Li(THF)_4][(Me_2N)_3Zr(SiPh_2Bu^t)_2]$, which is thermally unstable in solution. The complex $(Me_2N)_3Ta\{Si(SiMe_3)_3\}_2$ results from treatment of $(Me_2N)_3TaCl_2$ with $Li(THF)_3Si(SiMe_3)_3$. During this reaction, the intermediate $(Me_2N)_3Ta\{Si(SiMe_3)_3\}Cl$ was isolated and structurally characterized.[16]



R = CMe3

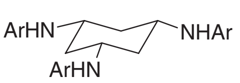
3



Ar = 2,6-Me2C6H4

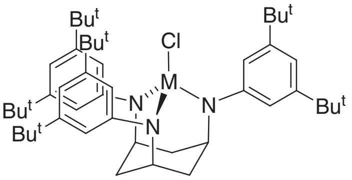
4

One means of accessing Zr or Hf silyl complexes which are free of π-ligands such as Cp^- is the reaction of a silyl anion with a group 4 metal tetrahalide. However, this strategy tends to suffer from side-reactions. One success has been the reaction of 2 equiv. of the tmen ($tmen = Me_2NCH_2CH_2NMe_2$) adduct of $KSi(SiMe_3)_3$ with $HfCl_4$ to give $(tmen)Cl_3HfSi(SiMe_3)_3$ (Hf–Si = 2.802(6) Å). The Si–Hf bond is cleaved by H_2O or H_2, and also inserts 2,6-dimethylphenyl isocyanide.[17] When the trilithium salt of ligand **5** reacts with $MCl_4(THF)_n$ (M = Ti, $n = 2$; M = Zr, $n = 0$), complex **6** is formed, with the solid-state structure being confirmed for the zirconium complex. A range of related complexes has also been studied.[18]



Ar = 3,5-Bu$^t_2$C$_6$H$_4$

5

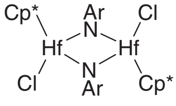


M = Ti, Zr

6

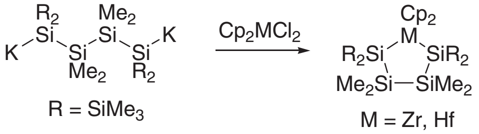
Within the remit of investigating systems linked to the chemical vapor deposition (CVD) of Ti/Si/N thin films, recent studies have targeted the mechanistic pathways of reactions of d^0 $M(NMe_2)_4$ (M = Ti, Zr, Hf) complexes with silanes. $M(NMe_2)_4$ reacts with SiH_2RPh (R = H, Me, Ph) to give H_2, aminosilanes, and black solids. Interesting intermediates of the type $\{(Me_2N)_3M(\mu\text{-}H)(\mu\text{-}NMe_2)_2\}_2M$ (M = Zr, Hf) have been isolated and structurally characterized. $\{(Me_2N)_3M(\mu\text{-}D)(\mu\text{-}NMe_2)_2\}_2M$ were prepared from $M(NMe_2)_4$ and SiD_2Ph_2. When $(Me_2N)_3ZrSi(SiMe_3)_3$ was treated with SiH_2RPh, the products were aminosilanes and $(Me_2N)_2Zr(H)Si(SiMe_3)_3$. The deuteride ligand in $(Me_2N)_2Zr(D)Si(SiMe_3)_3$ undergoes H/D exchange with SiH_2RPh (R = Me, H). Silane reacts with $Ti(NMe_2)_4$ in CVD at 450 °C to produce thin Ti/Si/N ternary films which consist of TiN and Si_3N_4.[19]

The complex $ArN{=}Hf(SiPh_3)_2(THF)_2$ has been isolated from the reaction of $ArN{=}HfCl_2(THF)_2$ ($Ar = 2,6\text{-}Pr^i_2C_6H_3$) with 2 equiv. of $LiSiPh_3(THF)_3$. Reaction of $ArN{=}HfCl_2(4\text{-}Bu^tC_5H_4N)_2$ with $KSi(SiMe_3)_3$ leads to $ArN{=}HfCl\{Si(SiMe_3)_3\}(4\text{-}Bu^tC_5H_4N)_2$. When $Cp^*HfCl_2\{Si(SiMe_3)_3\}$ is treated with LiNHAr ($Ar = 2,6\text{-}Pr^i_2C_6H_3$) followed by thermolysis, the Hf–Si bond is cleaved and the final product is **7**.[20]



7

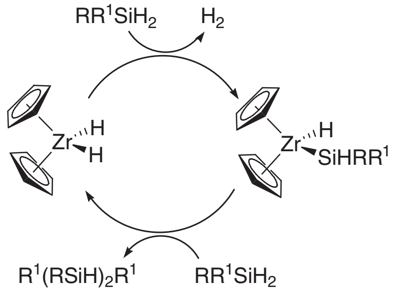
A series of Zr(IV) and Hf(IV) silyl complexes $Cp_2MClSi(SiMe_3)_2R$ has been made by reacting Cp_2MCl_2 with $KSi(SiMe_3)_2R$ (M = Zr, R = H, Me, $SiMe_3$, $SiMe_2Bu^t$, $SiMe_2(CMe_2)_2H$, $SiMe_2Si(SiMe_3)_3$; M = Hf, R = H, $SiMe_3$). With 2 equiv. of $KSi(SiMe_3)_3$, $Cp_2M\{Si(SiMe_3)_3\}_2$ (M = Zr, Hf) can be isolated.[21,22] An analogous procedure (Equation (1)) can be used to prepare metallocycles,[23] and reaction of KSi_6Me_{11} with Cp_2MCl_2 (M = Ti, Zr) leads to the formation of $Cp_2MCl(Si_6Me_{11})$. The Zr(IV) derivative forms $Cp_2ZrMe(Si_6Me_{11})$ when treated with MeLi.[24]



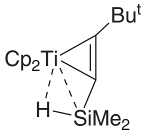
(1)

When Cp_2TiMe_2 reacts with SiH_4 in the presence of PMe_3, the product is $Cp_2Ti(PMe_3)(SiH_3)$ which is the first example of a structurally characterized, unsubstituted silyl complex of a group 4 metal.[25] The reaction between R_3SiH (SiR_3 = SiMePhCl, $SiPh_2Cl$, $SiMeCl_2$, $SiCl_3$) and $Cp_2Ti(PMe_3)_2$ generates the complexes $Cp_2Ti(PMe_3)$-$H(SiR_3)$ which contain non-classical Ti–H–Si–Cl interligand interactions. NMR spectroscopic data were used to provide evidence for a direct Si–H bond. Interestingly, the reaction of $SiH(OEt)_3$ with $Cp_2Ti(PMe_3)_2$ leads to an NMR-silent product (assumed to contain Ti(III)).[26] In the alkyne complex **8**, significant bending of the Si–H bond toward the metal center has been observed, providing evidence (supported by theoretical results) of the strong accepting ability of the σ^*(Si–H) orbital.[27,28]

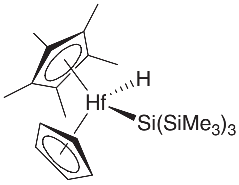
The synthesis and reactivity of complex **9** have been reported. Among reactions studied are those with $SiH_2(SiMe_3)_2$ to give $CpCp^*Hf(H)SiH(SiMe_3)_2$, and with acetone to yield $CpCp^*Hf(OCHMe_2)(SiMe_3)_3$.[29] The complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2ZrCl\{Si(SiMe_3)_3\}$ and $Cp_2MCl\{Si(SnMe_3)_3\}$ (M = Ti, Zr, Hf) result when the corresponding lithium silyl and metallocene dichloride reagents are combined. Reactions of the Zr(IV) and Hf(IV) complexes with Grignard reagents have been studied, and $(\eta^5\text{-}C_5H_4SiMe_3)_2ZrCl\{Si(SiMe_3)_3\}$ was found to catalyze the dehydropolymerization of $PhSiH_3$ and Bu_2SnH_2.[30] Silicon–silicon bond formation through dehydrocoupling of hydrosilanes catalyzed by group 4 metallocene complexes is currently an active area of research,[31] with the Tilley σ-bond metathesis mechanism (Equation (2)) being central to the process. Silane dehydropolymerization reaction mixtures that are catalyzed by $Cp'_2ZrCl_2/2BuLi/B(C_6F_5)_3$ or $[Cp'_2Zr(\mu\text{-}H)H]_2/2B(C_6F_5)_3$ (Cp′ = Cp, Cp*, C_5H_4Me) give rise to isolable complexes $[\{Cp'_2Zr(\mu\text{-}SiH_2R)\}_2{}^{2+}][BR^1{}_n(C_6F_5)_{4-n}{}^-]_2$ (R = Ph, $PhCH_2$; R^1 = H, Bu).[32] The pathway by which they are formed has been studied in detail using NMR and EPR spectroscopies, and by trapping unstable intermediates with PMe_3.[33] In addition, the kinetics of the photochemical reaction of $[\{Cp_2Zr(\mu\text{-}SiH_2Ph)\}_2{}^{2+}][BBu_n(C_6F_5)_{4-n}{}^-]_2$ with $PhCH_2SiH_3$ have been investigated; a paramagnetic Zr(III) intermediate was detected, supporting a Zr(IV)/Zr(III) redox mechanism.[34] Following from work that shows that cationic hafnocene alkyl and hydride complexes are highly reactive in σ-bond metathesis reactions,[35] Tilley and Sadow have described a reactive cationic hafnium(IV) silyl complex that possesses an agostic Si–H–Hf interaction. The Hf–Si bond in complex **10** reacts with the C–H bonds of arenes by a concerted, σ-bond metathesis process.[36] In an extension of this work, a significant development has been the preparation of the zwitterionic complex $[CpCp^*HfSi(SiMe_3)_3][MeB(C_6F_5)_3]$. This is stable for at least 12 h in solution and has been spectroscopically characterized; its reactions with primary and secondary silanes have been described.[37]



(2)



8



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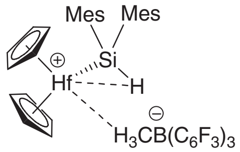
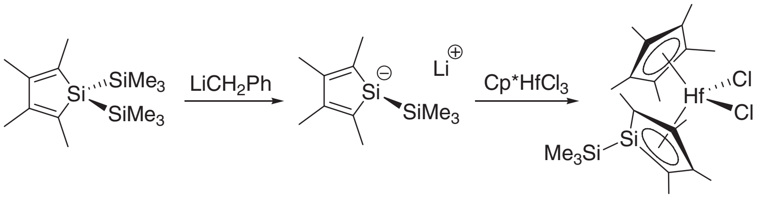


Mes = mesityl

10

Equation (3) shows the formation of an η^5-silolyl complex of Hf(IV); the analogous germolyl derivative has also been made. Both have been structurally characterized.[38] An alternative route to the silolyl complex shown in Equation (3) involves the reaction of Mg[η^1-$C_4Me_4SiSiMe_3$]$_2$ with Cp*MCl$_3$ (M = Hf), and the corresponding reaction for M = Zr is also successful.[39]



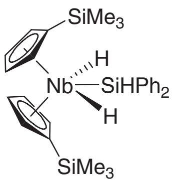
(3)

3.10.4 Group 5 Metals

Between 1993 and 2004, synthetic studies of compounds involving bonds between silicon and group 5 metals were restricted to niobium and tantalum.

3.10.4.1 Niobium

Organosilanes R_3SiH ($R_3 = Me_2Ph$, $MePh_2$, PhH_2, Ph_2H, Ph_3) react with (η^5-$C_5H_4SiMe_3$)$_2$NbH$_3$ to give (η^5-$C_5H_4SiMe_3$)$_2$NbH$_2$(SiR$_3$). Structure **11** has been confirmed crystallographically (Nb–Si = 2.616(3) Å).[40] The reactivity of (η^5-$C_5H_4SiMe_3$)$_2$NbH$_2$(SiPh$_3$) has been investigated. It reacts with CO (1 atm) at ambient temperature to yield SiPh$_3$H and (η^5-$C_5H_4SiMe_3$)$_2$NbH(CO), and with 2,6-Me$_2$C$_6$H$_3$NC or H$_2$ (3 atm), again eliminating SiPh$_3$H. With GePh$_3$H or SnPh$_3$H, (η^5-$C_5H_4SiMe_3$)$_2$NbH$_2$(SiPh$_3$) undergoes σ-bond metathesis, forming (η^5-$C_5H_4SiMe_3$)$_2$NbH$_2$(EPh$_3$) (E = Ge, Sn).[41] Cp$_2$NbH$_2$(SiMe$_3$) readily loses SiMe$_3$H, and the Cp$_2$NbH fragment can be trapped with PMe$_3$. The reaction of **12** with excess SiMe$_3$H gives Cp$_2$NbH(SiMe$_3$)$_2$ which, when treated with PMe$_3$ at 55 °C, forms Cp$_2$Nb(SiMe$_3$)(PMe$_3$).[42]



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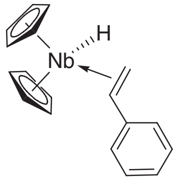
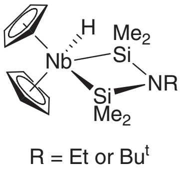


12

Compound **12** oxidatively adds $SiMe_2HX$ (X = Cl, Ph); a comparison of the structures of $Cp_2NbH(SiMe_2X)_2$ for X = Cl and Ph provides evidence for a Cl···Si···H interligand hypervalent interaction.[43] Reactions of $Cp_2NbH_2(SiMe_2X)$ (X = Cl, Ph) with organotin halides lead to stannyl-for-silyl displacement.[44] Cp_2NbBH_4 reacts with $SiHR_3$ ($R_3 = (OEt)_3$, Me_2Ph, Me_2Cl) in the presence of an amine to give $Cp_2NbH_2(SiR_3)$; for $R_3 = Me_2Cl$, the product is obtained as a mixture of two isomers, with the sterically more strained isomer being preferred. A mix of isomers is also obtained by heating Cp_2NbH_3 with $SiHMe_2Cl$ at 50 °C, but at 90 °C, H_2 is eliminated and the isolated silyl product is $Cp_2NbH(SiMe_2Cl)_2$. $LiAlH_4$ reduces the latter, yielding $Cp_2NbH(SiMe_2H)_2$, which reacts with $[Ph_3C][PF_6]$ and Br_2·dioxane to produce $Cp_2NbH(SiMe_2F)_2$ and $Cp_2NbH(SiMe_2Br)_2$, respectively.[45] A neutron diffraction study of $Cp_2NbH(SiMe_2Cl)_2$ has confirmed that the hydride ligand is positioned between the two silyl groups.[46] The addition of excess Bu^tNH_2 or $EtNH_2$ to $Cp_2NbH(SiMe_2I)_2$ results in the formation of **13**. Compound **13** with R = Bu^t has unexpected structural features: the $(SiMe_2)_2NBu^t$ unit lies such that the molecular symmetry is effectively C_{2v}, there is a short Si–Si contact (2.654(2) Å), and the Nb–Si bonds are long (2.680(2) and 2.685(1) Å).[47] A paper that pulls together a range of results covers a wide variety of derivatives and explores various methods of synthesis, as well as structural details. $Cp_2NbH(SiMe_2X)_2$ can be prepared by electrophilic or nucleophilic strategies; when X = F, Br, or I, the best approach is electrophilic substitution at the Si–H bond in $Cp_2NbH(SiMe_2H)_2$, while for X = Br, I, or triflate (OTf) an alternative route is reaction of $Cp_2NbH(SiMe_2Cl)_2$ with $SiXMe_3$. Compounds of type $Cp_2NbH(SiMe_2EPh_n)_2$ (E = S, $n = 1$; E = P, $n = 2$) and $Cp_2NbH(SiMe_3)_2$ are most efficiently prepared by nucleophilic displacement of Cl in $Cp_2NbH(SiMe_2Cl)_2$. The latter method fails for nucleophiles such as amides or alkoxides. The synthesis of $Cp_2NbH_2(SiMe_2X)$ derivatives is more difficult than that of the bis(silyl) analogs.[48]

Whereas the tantalum complex $CpTa(NAr)(PMe_3)_2$ (Ar = 2,6-diisopropylphenyl) reacts with $SiHMe_2Cl$ to produce $CpTa(NAr)(PMe_3)(H)(SiMe_2Cl)$ with an interligand hypervalent interaction, the niobium analog reacts to give **14**, which features an unprecedented stretched β-agostic Si–H–M interaction.[49] In contrast, when $CpNb(NAr)(PMe_3)_2$ is treated with $SiHPh_2Cl$, $CpNb(NAr)(PMe_3)(H)(SiPh_2Cl)$ is formed. These observations have led to a more general study of reactions of $SiHRR^1Cl$ with $CpNb(NAr)(PMe_3)_2$.[50] Selective halogenation of one Si–H bond in $Cp_2NbH(SiMe_2H)_2$ has produced the first asymmetrical complexes of type $Cp_2NbH(SiMe_2H)(SiMe_2X)$ (X = F, Cl, Br) which possess interligand hypervalent interactions.[51] Treatment of Cp_2NbH_3 with $SiCl_2R^1R^2$ (R^1, R^2 = Me, Ph) or $SiCl_3Me$ results in the formation of $Cp_2Nb(H)_2(SiCl_nR_{3-n})$ (R = R^1, R^2; $n = 1, 2$), while use of $SiCl_4$ leads to $Cp_2Nb(H)_2(SiCl_3)$ and $Cp_2NbH(SiCl_3)_2$.[52]



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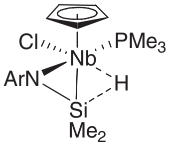

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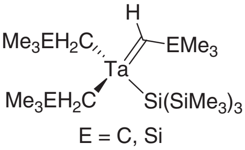
3.10.4.2 Tantalum

Complexes free of anionic π-ligands and which contain Ta–Si bonds include $(Me_3CCH_2)_2Ta({=}CHBu^t)\{Si(SiMe_3)_3\}$,[12] **15** and **16**.[53] The syntheses of complexes **15** from $(Me_3ECH_2)_3TaCl_2$ (E = C, Si) and $LiSi(SiMe_3)_3(THF)_3$ involve elimination of $SiH(SiMe_3)_3$ to form the $Ta{=}CH(EMe_3)$ unit. For E = Si, the intermediate $(Me_3SiCH_2)_3TaCl\{Si(SiMe_3)_3\}$ was observed, and data from kinetics studies are consistent with $(Me_3SiCH_2)_3TaCl\{Si(SiMe_3)_3\}$ being converted to **15** (E = Si) via the intermediate $(Me_3SiCH_2)_2Ta({=}CHSiMe_3)Cl$.[53]



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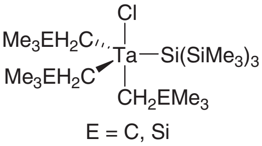
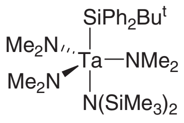


16

The reaction between $Ta(NMe_2)_3Cl_2$ and $Li(SiMe_3)(THF)_3$ leads to $Ta(NMe_2)_3\{Si(SiMe_3)_3\}Cl$ (structurally characterized) followed by $Ta(NMe_2)_3\{Si(SiMe_3)_3\}_2$.[54] $Ta\{N(SiMe_3)_2\}({=}NSiMe_3)(SiPh_2Bu^t)_2$ and $Ta\{N(SiMe_3)_2\}({=}NSiMe_3)(NMe_2)(SiPh_2Bu^t)$ were reported in 2000 and represented the first examples of Cp-free group 5 imido disilyl and silyl complexes.[55] Amido complexes free of anionic π-ligands include $Ta(NMe_2)_3(SiR_3)Cl$ and $Ta(NMe_2)_4(SiR_3)$ ($R_3 = (SiMe_3)_3$, Ph_2Bu^t); $Ta(NMe_2)_4\{Si(SiMe_3)_3\}$ reacts with O_2 to give $Ta(NMe_2)_3(\eta^2\text{-}ONMe_2)\{OSi(SiMe_3)_3\}$.[56] Complex **17** (prepared from $Ta(NMe_2)_3Cl\{N(SiMe_3)_2\}$ and $Li(SiPh_2Bu^t)(THF)_2$) undergoes γ-H abstraction, forming **18**; the conversion follows first-order kinetics. Related cyclizations for Hf(IV) and Zr(IV) species have also been described.[57]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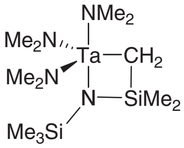
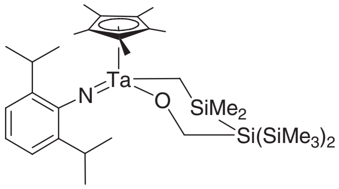

18

Complexes containing Ta–Si bonds are dominated by those with ancillary cyclopentadienyl ligands. A neutron diffraction study of $Cp_2TaH(SiMe_2H)_2$ confirms the presence of a classical hydride ligand (Ta–H = 1.785(15) Å).[58] The first, thermally stable group 5 metal dihydrogen complex was reported in 2001: $[Cp_2Ta(H_2)(CO)][BF_4]$ was formed by protonation of $Cp_2TaH(CO)$. Chaudret and co-workers reasoned that, in theory, protonation of $Cp_2Ta(H)_2(SiMe_2Ph)$ might also yield a dihydrogen complex, but reaction of $Cp_2Ta(H)_2(SiMe_2Ph)$ with $HB\{C_6H_3(CF_3)_2\}_4{\cdot}2Et_2O$ instead resulted in the formation of $[Cp_2(H)_2Ta(\mu\text{-}H)Ta(H)_2Cp_2][B\{C_6H_3(CF_3)_2\}_4]$.[59]

Imido complexes have drawn significant attention. Carbon monoxide adds to $Cp^*TaH(NAr)\{Si(SiMe_3)_3\}$ (Ar = 2,6-$Pr^i_2C_6H_3$); when a pentane solution of the carbonyl complex is left standing at room temperature, compound **19** results.[60] The reaction between $Cp^*TaH(NAr)\{Si(SiMe_3)_3\}$ (Ar = 2,6-$Pr^i_2C_6H_3$) and $SiPhH_3$ leads to $Cp^*_2Ta_2(H)_2(\mu\text{-}ArNSiHPh)_2$ as the major product, and the paramagnetic $Cp^*_2(ArN)Ta_2(H)_2(\mu\text{-}ArNSiHPh)_2$ in lower yield.[61] The complex $CpM(NAr)(PMe_3)_2$ (M = Ta, Nb; Ar = 2,6-$Pr^i_2C_6H_3$) reacts with $SiHMe_2Cl$ to produce $CpTa(NAr)(PMe_3)(H)(SiMe_2Cl)$ with an interligand hypervalent interaction, or complex **14** with a stretched agostic Si–H–M interaction (see also Section 3.10.4.1).[49,62] A detailed ^{29}Si NMR spectroscopic, structural, and theoretical study of the series of complexes $CpTa(NAr)(PMe_3)(H)(SiR_3)$ (R_3 = SiMePhH, $SiMe_2Cl$, $SiMeCl_2$, $SiCl_3$; Ar = 2,6-$Pr^i_2C_6H_3$) has been reported. For the non-classical M–H···Si–X interactions, it was found that there is a correlation between the magnitude of J(Si–H) and the identity of X which is opposite to that found for silane σ-complexes; DFT calculations on model systems illustrated that an increase in J(Si–H) does not necessarily correspond to a stronger Si–H interaction.[63] The very bulky imido ligand $[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3N]^{2-}$ ($[Ar^*N]^{2-}$) has been incorporated into a family of Ta(V) complexes; these include $Ta(NAr^*)(NHAr^*)Cl_2$, which reacts with $LiSi(SiMe_3)_3(THF)_3$, $LiSiBu^tPh_2(THF)_2$, or $LiSiHMes_2(THF)_2$ to yield $Ta(NAr^*)(NHAr^*)(SiR_3)Cl$ (Mes = mesityl).[64] Treatment of $Cp^*Ta(NAr^*)Cl_2$ with $KSi(SiMe_3)_3$ leads to $Cp^*Ta(NAr^*)Cl\{Si(SiMe_3)_3\}$, which reacts with H_2 with elimination of $SiH(SiMe_3)_3$ and formation of $Cp^*Ta(NAr^*)HCl$. $Cp^*Ta(NAr^*)Cl(SiH_2Ph)$ forms when $PhSiH_3$ reacts with $Cp^*Ta(NAr^*)Cl\{Si(SiMe_3)_3\}$, but this decomposes to $Cp^*Ta(NAr^*)HCl$; attempts to prepare stable analogs of the intermediate complex by increasing the steric demands of the silyl group were not successful.[65] The series of complexes $Cp^*Ta(NAr)Cl(SiR_3)$ (Ar = 2,6-$Pr^i_2C_6H_3$; $SiR_3 = Si(SiMe_3)_3$, $SiPh_3$, $SiHMes_2$) have been prepared; for the $SiPh_3$ and $SiHMes_2$ derivatives, difficulties were encountered in purifying the products. The silyl derivatives react with H_2 (5.4 atm) to yield **20**, which, when treated with $LiSi(SiMe_3)_3(THF)_3$, gives the $[Li(THF)_3]^+$ salt of complex **21**. Elimination of LiCl from this salt results in the formation of $Cp^*Ta(NAr)H\{Si(SiMe_3)_3\}$, the reactivity of which has been studied.[66]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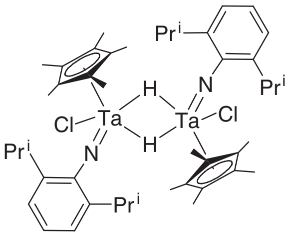

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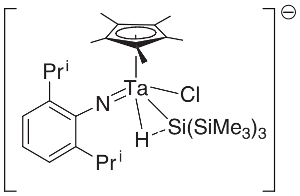


21

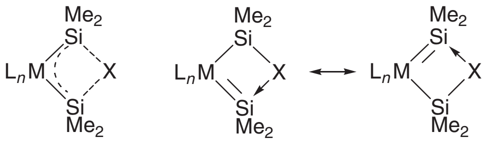
3.10.5 Group 6 Metals

Moving across the *d*-block results in an increase in number of M–Si-bonded derivatives, and group 6 is the first group for which significant numbers of compounds are known for all members of the triad. The complexes covered in Corey and Braddock-Wilking's review[3] will not be discussed again in this section.

3.10.5.1 Chromium

Base stabilization of silylene complexes is exemplified in a variety of group 6 metal complexes.[67] Complex **22**[68] reacts with organolithium reagents to give compounds **23** in high yields.[69] Complex **24** has also been reported, along with an iron analog in which the $Cr(CO)_5$ unit is replaced by $Fe(CO)_4$.[70] Base stabilization by $(Me_2N)_3PO$ is exemplified in $\{(Me_2N)_3PO\}Si\{{=}Cr(CO)_5\}Cl(CH{=}CH_2)$ and $\{(Me_2N)_3PO\}Si\{{=}Fe(CO)_4\}Ph(CH{=}CHPh)$.[70] The reactivities of the chloro derivative **25**, of its $Fe(CO)_4$ analog, and of related $(Me_2N)_3PO$-stabilized species have been explored. For example, **25** reacts with Ph_2PLi, $CH_2CHMgBr$, MeI, and PhLi to introduce the respective substituent onto the Si center.[71]

Donor-bridged bis(silylene) complexes (Equation (4)) are now known for all the group 6 metals.[72–74] For example, when $CpCr(CO)_3$ is photolyzed with $HSiMe_2SiMe_2OMe$, the product is **26** (M = Cr; X = OMe). Structural data for members of this family show that the four-membered ring is folded (internal dihedral angle for **26** with M = Cr, X = OMe is 162.4°), and this is attributed to steric repulsion between CO and silicon-bound Me groups. The fluxional behavior of bis(silylene) complexes has been investigated.



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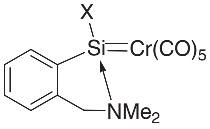
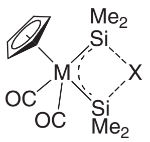


22: X = H
23: X = Me, Ph, Bu^t, PhCC, Me_3SiCC
24: X = $CH{=}CH_2$
25: X = Cl

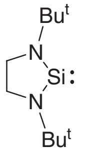


M = Cr, Mo, W; X = OMe
M = Mo, W; X = NEt_2

26

Photolysis of silylenes **27** and **28** (L) with $Cr(CO)_6$ in THF leads to *trans*-$CrL_2(CO)_4$, which has been structurally characterized. Analogous reactions occur with $Mo(CO)_6$ and $W(CO)_6$;[75] reactions of **27** with $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$[75] are described later in this chapter.

The heterometallic disilyl derivative $CpFe(CO)_2SiMe_2SiMe_2\{\eta^6\text{-}C_6H_5Cr(CO)_3\}$ and its Cp^*Fe analog are formed by heating the corresponding iron disilane with $Cr(CO)_6$. Photolysis of a benzene solution of $CpFe(CO)_2SiMe_2SiMe_2\{\eta^6\text{-}C_6H_5Cr(CO)_3\}$ resulted in the formation of the silylene-bridged complex **29**; an analogous reaction takes place with $Cp^*Fe(CO)_2SiMe_2SiMe_2\{\eta^6\text{-}C_6H_5Cr(CO)_3\}$. Mechanistic implications of these observations have been discussed.[76]



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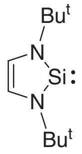

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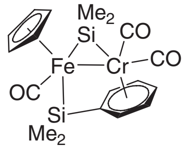


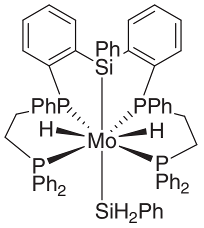
29

3.10.5.2 Molybdenum

Metallosilanes containing SiH_3 units may be prepared using SiH_3X (X = halogen) as a precursor, or by treatment of a metal-bound chlorosilyl group with $LiAlH_4$. The latter method has advantages over the former, and is exemplified in the reactions of $Cp^1(CO)_2(PMe_3)MSiHCl_2$ (Cp^1 = Cp or Cp^*, M = Mo; Cp^1 = Cp, M = W) with $LiAlH_4$.[77] These derivatives possess highly stable M–Si bonds, while the silicon-bound H atoms are hydridic. Dimethyldioxirane reacts with $Cp^1(CO)_2(PMe_3)MSiHCl_2$ (Cp^1 = Cp, M = Mo; Cp^1 = Cp^*, M = Mo, W) to yield the corresponding metallosilanetriols. Condensation of these derivatives with Me_2SiHCl leads to examples of complexes containing $M\text{–}Si(OSiMe_2H)_3$ units.[78]

A route to dimetallic oligosilane derivatives is illustrated by the reaction of $BrMe_2SiSiMe_2Br$ with $Na[(\eta^5\text{-}C_5Me_4Et)Mo(CO)_3]$; related diiron species have also been prepared.[79] Ionic *d*-block metal silyl derivatives are exemplified by $[L_2Li][Mo(CO)_5Si_6Me_{11}]$ ($L = MeOCH_2CH_2OCH_2CH_2OMe$), prepared by reacting $[L_2Li]\text{-}[Mo(CO)_5I]$ with KSi_6Me_{11}.[80] As part of a wider study of $Cp^*M(CO)_3(BH_2PMe_3)$ (M = Mo, W) complexes, the reaction of $Cp^*Mo(CO)_3(BH_2PMe_3)$ with Me_3SiCl has been shown to form $Cp^*Mo(CO)_3SiMe_3$ and Me_3PBH_2Cl.[81] Structural characterization of $(Et_2PCH_2CH_2PEt_2)_2(CO)Mo(H)SiHPh_2$ reveals an Mo–H bond distance of 2.04(2) Å, which is significantly longer than in the corresponding SiH_3Ph complex. Detailed comparisons have been made between the silyl and corresponding germyl systems.[82] Treatment of $[CpM(CO)_2(PMe_3)]^-$ (M = Mo, W) with $Cl_3SiOSiCl_3$ or $Cl_3SiOSiCl_2OSiCl_3$ leads to polychlorinated metallosiloxane complexes; analogous reactions have been carried out using $[CpFe(CO)_2]^-$, and in this case, the dinuclear complex $Cp(CO)_2\text{-}FeSiCl_2OSiCl_2OSiCl_2Fe(CO)_2Cp$ was isolated.[83]

Some intriguing Mo–Si bond-forming reactions have used $MoH_4(dppe)_2$ as a precursor (dppe = bis(diphenylphosphino)ethane). Reaction of this complex with excess $PhSiH_3$ in toluene at reflux resulted in the formation of **30**. With 1 equiv. of $PhSiH_3$, trihydrido complex **31** (R = Ph) was formed.[84] The latter reacts with O_2 to produce an Mo(IV) peroxo complex,[85] with 2,3-Hacac to give **32**,[86] and with carboxylic acids to give **33** (Hacac = pentane-2,4-dione). Complex **33** (R = H) is an effective catalyst for CO_2 fixation, and was the first molybdenum compound to effectively catalyze the hydrogenation of CO_2.[87] Compounds **31** react with a range of isocyanides, liberating H_2 and forming isocyanide complexes. Values of ν(CN) in the IR spectra of the latter are consistent with significant backbonding from Mo to the isocyanide ligands.[88] It has also been shown that **31** with R = Ph catalyzes the dehydrogenative polymerization of $ArSiH_2R$ (Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4; R = H, Me).[89]



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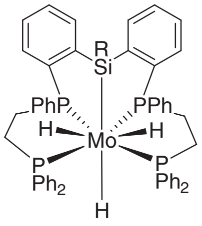
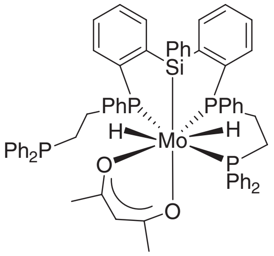


R = Ph, C_6F_5, 4-$Me_2NC_6H_4$

31



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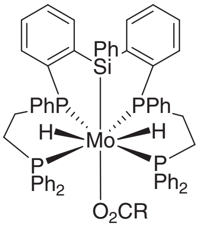
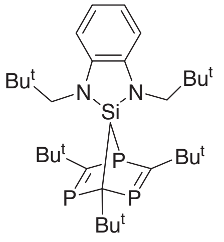


R = H, Me, Ph

33

Several silylene complexes of molybdenum were described in the previous section along with the corresponding chromium species. Other silylene derivatives of molybdenum include $Cp^*(dmpe)Mo({=}SiR_2)(H)$ ($R_2 = Me_2$, Et_2, MePh, Ph_2), formed by reacting $Cp^*(dmpe)Mo(\eta^3\text{-}CH_2Ph)$ (which is in equilibrium with $Cp^*(dmpe)Mo(\eta^1\text{-}CH_2Ph)$ in solution) with SiH_2RR^1 (dmpe = bis(dimethylphosphino)ethane). X-ray crystallographic data for $Cp^*(dmpe)Mo({=}SiMe_2)(H)$ revealed a short Mo–Si bond distance of 2.315(2) Å. From a consideration of both structural and NMR spectroscopic data, it was concluded that the hydride ligand is disordered over bridging positions on both sides of the Mo–Si bond. Neutron diffraction data for a single crystal of $Cp^*(dmpe)Mo({=}SiEt_2)(H)$ confirmed the presence of an Mo–H–Si bridge (Mo–H = 1.85(1), Si–H = 1.68(1) Å).[90] Silylene **1** and $P_3C_3Bu^t_3$ undergo a [1+4]-cycloaddition to give **34**. The cycloaddition can be reversed by treating **34** with $Mo(CO)_4(nbd)$ (nbd = norbornadiene); this gives *cis*- and *trans*-$Mo(CO)_4(\mathbf{1})_2$ and $Mo(CO)_3(\eta^6\text{-}P_3C_3Bu^t_3)$. Structural data for *trans*-$Mo(CO)_4(\mathbf{1})_2$ (Mo–Si = 2.4472(6) Å) confirm little structural change for silylene **1** upon coordination.[91] The first silylyne molybdenum cationic complex has been prepared by the reaction of $Cp^*(dmpe)Mo(\eta^3\text{-}CH_2Ph)$ with SiH_2ClMes, followed by treatment of the resulting silylene complex with $[Li(OEt_2)_3][B(C_6F_5)_4]$. The product is $[Cp^*(dmpe)(H)MoSiMes][B(C_6F_5)_4]$, and the small value of *J*(Si–H) suggests that the hydride ligand has little interaction with the Si center. X-ray crystallographic data confirm an extremely short Mo–Si bond: 2.219(2) Å.[92]

A number of silyl complexes of Mo and W containing bulky imido ligands have been reported. The reaction of $(ArN)_2MoCl_2(dme)$ ($Ar = 2,6\text{-}Pr^i_2C_6H_3$) with $LiSi(SiMe_3)_3(THF)_3$ leads to $(ArN)_2Mo\{Si(SiMe_3)_3\}Cl$ (structurally characterized) (dme = dimethoxyethane); the analogous W complex has also been isolated and characterized. $(ArN)_2Mo\{Si(SiMe_3)_3\}Cl$ undergoes an insertion reaction with $2,6\text{-}Me_2C_6H_3NC$, and reacts with AgOTf to give $(ArN)_2Mo\{Si(SiMe_3)_3\}(OTf)$. With Me_3CCH_2MgCl, $(ArN)_2M\{Si(SiMe_3)_3\}Cl$ (M = Mo, W) reacts to yield $(ArN)_2M\{Si(SiMe_3)_3\}(CH_2CMe_3)$; for M = Mo, structural data confirm the presence of an agostic interaction involving the α-H atom of the neopentyl ligand.[93] $(ArN)_2MoCl_2(dme)$ reacts with $LiNMe_2$ and $LiSi(SiMe_3)_3(THF)_3$ to give $(ArN)_2Mo(NMe_2)\{Si(SiMe_3)_3\}$.[94] The imido complex $(2,6\text{-}Me_2C_6H_3N)_2Mo(PMe_3)_3$ reacts with $SiHCl_3$ to give $(2,6\text{-}Me_2C_6H_3N)Mo(PMe_3)_3Cl_2$ and $(2,6\text{-}Me_2C_6H_3NSiHCl)_2$, while with SiHClMeR (R = Me, Cl), the reaction proceeds to complexes **35**. Significantly, the values of *J*(Si–H) for these species are 97 Hz for R = Me, and 129 Hz for R = Cl, that is, introduction of the electron-withdrawing Cl group increases the value of *J* rather than decreases it as might be expected.[95]



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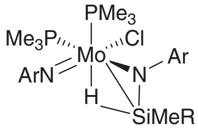


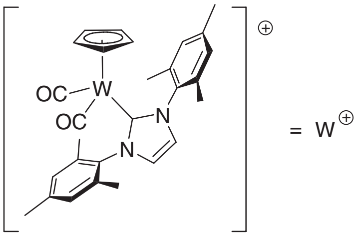
Ar = 2,6-$Me_2C_6H_3$
R = Me, Cl

35

3.10.5.3 Tungsten

Silyl complexes include $(ArN)_2W\{Si(SiMe_3)_3\}Cl$ ($Ar = 2,6\text{-}Pr^i_2C_6H_3$),[93] which was described above with its Mo analog and related complexes. Treatment of $(Bu^tCH_2)_2W({\equiv}CBu^t)Cl$ with $Li(THF)_3SiPh_2Bu^t$ produces $(Bu^tCH_2)_2W({\equiv}CBu^t)(SiPh_2Bu^t)$, which is in equilibrium with $(Bu^tCH_2)W({=}CHBu^t)_2(SiPh_2Bu^t)$. The reaction of the latter with O_2 results in the unexpected migration of the silyl group to form $(Bu^tCH_2)_2W({=}O)\{{=}C(SiPh_2Bu^t)(Bu^t)\}$.[96]

By far, the most W–Si bonds reported in the period that this review covers involve $W(CO)_n$ or $(\eta^5\text{-}C_5R_5)W$-containing compounds. A significant development has been that of a recyclable catalyst for the hydrosilylation of ketones; the system begins with a polar liquid substrate (ketone or ester) and finishes with a non-polar liquid product (alkoxysilane). The rest state of the catalyst is a mixture of the $[B(C_6F_5)_4]^-$ salts of **36** and **37**; the tungsten complex is far more active than its molybdenum analog.



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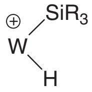

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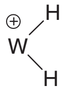
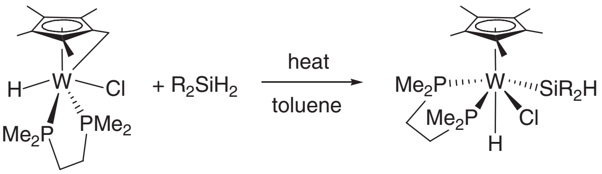


Reaction of [Li(dme)$_2$][M(CO)$_5$I] (M = Mo, W) (made from M(CO)$_6$ and LiI·Et$_2$O) with LiSiMe$_2$Ph gives [Li(dme)$_2$][M(CO)$_5$(SiMe$_2$Ph)].[98] The bis(silyl) complexes Cp$_2$W(SiMe$_3$)(SiR$_2$X) (X = Pr^i, CD$_3$, Cl, OTf) undergo thermal isomerization to Cp$_2$W(SiMe$_2$X)(SiR$_2$Me), and the rate depends on R and X, on solvent polarity, and on the presence of a strong Lewis acid catalyst. The mechanism that has been proposed involves dissociation of X$^-$, followed by methyl migration and reassociation of X$^-$.[99] Disilane derivatives are represented by (η^5-C$_5$Me$_4$Et)(CO)$_3$WSiMe$_2$SiMe$_2$X (X = Me, Cl, Br, W(CO)$_3$(η^5-C$_5$Me$_4$Et)) and (η^5-indenyl)(CO)$_3$WSiMe$_2$SiMe$_2$X (X = Cl, W(CO)$_3$(η^5-indenyl)).[100] In the previous section, a series of complexes containing M–Si(OSiMe$_2$H)$_3$ (W = Mo, W) units were described.[78] Related to this work is the synthesis of Cp*W(CO)$_2$(PMe$_3$){Si(OH)$_3$}, CpW(CO)$_2$(PMe$_3$){SiMe$_2$OH)}, and Cp*W(CO)$_2$(PMe$_3$){SiMe$_2$OH}. Condensation of the latter with R$_2$SiCl results in the formation of Cp*W(CO)$_2$(PMe$_3$)SiMe$_2$OSiR$_3$ (R = SiCl$_3$, SiMe$_2$H).[101] The formation of polychlorinated siloxane complexes of Mo, W, and Fe was described above.[83]

When *cis*-Cp*W(CO)$_2$(MeCN)Me reacts with SiHMe$_2$(CH=CR$_2$) (R = H, Me), the Si–H bond is activated and the products are silaallyl complexes Cp*W(CO)$_2$(η^3-SiMe$_2$CHCR$_2$), confirmed crystallographically for R = Me. These complexes are very reactive toward methanol, forming *trans*-Cp*W(CO)$_2$H(η^2-MeOSiMe$_2$CH=CH$_2$) and **38**.[102] Bridging SiR$_2$ groups in dimetallic compounds have been reported for both homo- and heterometallic systems of tungsten. Oxidative addition of two Si–H bonds occurs when W(CO)$_6$ reacts with Ph$_2$SiH$_2$ to yield W$_2$(CO)$_{10}$-(μ-SiPh$_2$), confirmed crystallographically. The reactivity of W$_2$(CO)$_{10}$(μ-SiPh$_2$) is interesting: with a large excess of norbornene in chloroform, NMR spectroscopic data indicate that ring-opening metathesis polymerization is initiated.[103] Cp*(CO)$_2$W(μ-SiMe$_2$)(μ-H)Re(CO)$_2$Cp* is formed from the reaction of *cis*-Cp*W(CO)$_2$(MeCN)Me with Cp*Re(CO)$_2$H(SiMe$_2$H); when photolyzed, this complex converts to Cp*(CO)$_2$(H)W(μ,η^1,η^2-SiMeCH$_2$)-Re(H)(CO)$_2$Cp*.[104] The photolysis of Cp*W(CO)$_2$Me with Cp*Fe(CO)$_2$(SiH$_2$CHPh$_2$) leads to Cp*(CO)$_2$W-(μ-CO)(μ-SiHCHPh$_2$)Fe(CO)Cp*, which represents the first example of a silanediyl-bridged Fe–W complex.[105] An intriguing reaction is that between **39** and the silylene fragment SiR$_2$ (R = Me, Ph; generated from SiR$_2$Cl$_2$ and active Mg). It leads to the introduction of a μ-SiR$_2$ unit across the W–P bond, confirmed by X-ray diffraction for the product with R = Me.[106]

The base-stabilized silylene complexes **40** (R$_2$ = Ph$_2$, Et$_2$, MePh) have been prepared by reacting Cp*W(CO)$_2$(Me)(py) with R$_2$SiH$_2$ (py = pyridine). Structural confirmation comes from **40** with R = Ph, and a mechanism for the reaction has been proposed.[107] Complex **40** (R = Ph) reacts with HCl forming Cp*(CO)$_2$H$_2$WSiPh$_2$Cl. When treated with an excess of LiAlH$_4$, Cp*(CO)$_2$H$_2$WSiPh$_2$Cl is converted to Li[Cp*(CO)$_2$HWSiPh$_2$H], which can also be produced directly from **40** (R = Ph) by reaction with LiAlH$_4$.[108] When SiMe$_2$HSiMe$_3$ reacts with Cp*W(CO)$_3$Me or (η^5-C$_5$Me$_4$Et)W(CO)$_3$Me, the products are **41** in which the silyl(silylene)tungsten unit is stabilized by an internal ligand. Photolysis of Cp*W(CO)$_3$Me with SiMe$_2$HSiMeMes$_2$ results in the donor-free complex Cp*W(CO)$_2$(=SiMes$_2$)(SiMe$_3$).[109] Base-free silylene derivatives [Cp*(dmpe)-H$_2$W(=SiR$_2$)][B(C$_6$F$_5$)$_4$] (R$_2$ = Ph$_2$, Et$_2$, MePh) have also been reported,[110] and a related work reports the reaction shown in Equation (5) as part of a wider study of these systems.[111] Recent additions to the family of tungsten silylene complexes are Cp*(CO)$_2$W(H){=SiHC(SiMe$_3$)$_3$} and its (η^5-C$_5$Me$_4$Et) analog. NMR spectroscopic and structural data confirm the presence of a strong hydrido–silylene interligand interaction.[112]



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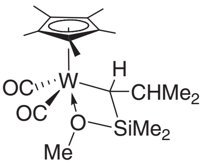

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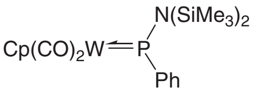

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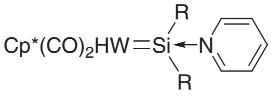

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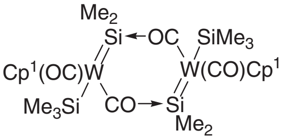


$Cp^1 = Cp^*, C_5Me_4Et$

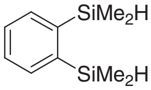
41

3.10.6 Group 7 Metals

3.10.6.1 Manganese

The review by Corey and Braddock-Wilking[3] covers a number of manganese and rhenium complexes and these are not further discussed here. Silyl derivatives have drawn the most attention among compounds with manganese–silicon bonds. Reactions between $Mn(CO)_5Si(4\text{-}MeC_6H_4)_2H$ and $LiAlH_4$, $NaBH_4$, or $NaBH_3CN$ result in release of $Si(4\text{-}MeC_6H_4)_2H_2$, while with $Na[(MeOCH_2CH_2O)_2AlH_2]$ followed by aqueous acid, alkylsilanols are formed.[113] The solid-state structure of $Mn(CO)_5SiPh_3$ has been determined ($Mn\text{–}Si = 2.504(6)$ Å),[114] and CP MAS ^{29}Si NMR spectroscopic data for this complex have been analyzed along with ^{119}Sn and ^{207}Pb NMR data for analogous Sn and Pb derivatives.[115] $Mn(CO)_5(Si_6Me_{11})Cl$ is formed when KSi_6Me_{11} reacts with $Mn(CO)_5Br$.[24] The photochemical cleavage of the Si–H bond in Et_3SiH by reaction with $CpMn(CO)_3$ has been investigated by ultrafast IR spectroscopy.[116] Interest in Si–H bond activation leads to one particular problem: the bonding in $Cp(CO)_2MnHSiCl_3$ and the information that can be gained from values of J(Si–H) in NMR spectra. This topic has been the focus of discussion from different standpoints in two thought-provoking letters.[117,118] DFT calculations (B3LYP level) have been carried out on the model complex $Cp(CO)_2MnSiH_4$, which investigate the consequences of the interactions between the Lewis acid SiH_4 and Lewis base $Cp(CO)_2Mn$.[119] Silane dissociation in $CpMn(CO)_2\{\eta^2\text{-}H(SiH_{3-n}Cl_n)\}$ ($n = 1, 2, 3$) and the dependence of the $Mn\cdots(\eta^2\text{-}H\text{–}Si)$ interaction on the number of Cl substituents have been investigated theoretically; the silane dissociation energies increase with an increasing number of Cl substituents.[120] Photolysis of $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ with $HPh_2SiSiPh_2H$ leads to $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2HSiPh_2SiPh_2H$ or $(\eta^5\text{-}C_5H_4Me)(CO)_2MnHSiPh_2SiPh_2HMn(CO)_2(\eta^5\text{-}C_5H_4Me)$ depending on the reaction stoichiometry. However, when $HMe_2SiSiMe_2H$ is used, only the dinuclear product is obtained. The products can also be accessed through ligand exchange starting from $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(THF)$, and studies have also been reported for the analogous Re complex.[121] Silanes 42, 43 or $O(SiMe_2H)_2$ react with $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2L$ ($L = CO, PMe_3$) to give double Si–H oxidative addition and dinuclear products; an exception to this pattern of reactivity is for 42 combined with $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(PMe_3)$.[122]

The coordinated solvent in 44 (structurally characterized) is displaced by silanes at low temperature, but on warming, the η^2-Si–H bond breaks. Complex 44 catalyzes the reaction of $SiHEt_3$ with PhOH to give Et_3SiOPh and H_2.[123] The THF ligands in $Mn\{Si(SiMe_3)_3\}_2(THF)_2$ are readily displaced by dmpe, Ph_2CO, and $CNC_6H_3\text{-}2,6\text{-}Me_2$. In the latter case, only one THF ligand was displaced, and a second product was $Mn(CNC_6H_3\text{-}2,6\text{-}Me_2)_5\{Si(SiMe_3)_3\}$.[124]



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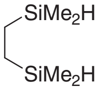

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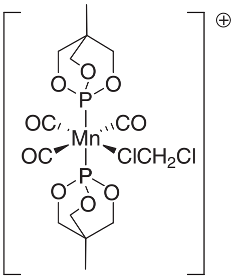

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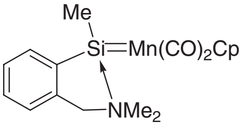
The complexes $Mn(CO)_5SiCl_3$, $Co(CO)_4SiCl_3$, and *cis*-$Fe(CO)_4(SiCl_3)_2$ have been prepared and their UPS spectra recorded.[125] For M = Mn or Re, $M(CO)_5SiCl_3$ reacts with arenes (either in the liquid arene or in a heptane solution) in a sealed tube at 230–260 °C to give (η^6-arene)$M(CO)_2SiCl_3$; in solution, the arene ring is stereochemically nonrigid.[126] The silyl derivatives $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2SiMePh_2]^-$ (R = H, Me) have been used as precursors in the synthesis of the first examples of *d*-block metal borylene complexes.[127]

Donor-stabilized silylene complexes of manganese include **45 and 46**, which have been prepared by the reaction of the corresponding R_2SiH_2 or $RSiH_3$ compound with $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, Me).[71,128]



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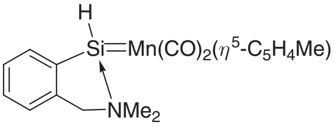

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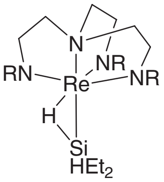
3.10.6.2 Rhenium

Crabtree has used the reactions of silanes and metal hydrides to prepare silyl complexes, and toward this end, rhenium polyhydrides such as $ReH_7(PPh_3)_2$ and $ReH_7(AsPh_3)_2$ have excellent potential. The reactions of $ReH_7(PPh_3)_2$ with **42 and 43** (H_2L) led to the first examples of chelating bis(silyl) polyhydride complexes $ReH_5L(PPh_3)_2$.[129] Although $ReH_7(AsPh_3)_2$ reacts with Ph_3SiH to give $ReH_6(SiPh_3)(AsPh_3)_2$, it does not react with chelating silanes.[130]

As part of a study involving rhenium complexes of the tripodal ligand $N(CH_2CH_2NHC_6F_5)_3(H_3L)$, the complex LReBr was treated with $SiPhH_3$ and $SiEt_2H_2$ and products with η^2-silane ligands (e.g., **47**) were proposed on the basis of the observed *J*(Si–H) values.[131] Related to the work reported above for Mn[123] is the formation of **48**.[132] The reaction of $Cp^*(CO)_2Re(H)SiMe_2H$ with *cis*-$W(CO)_2(MeCN)Me$ produces a complex featuring a μ-$SiMe_2$ unit between the Re and W centers. Photolysis of this product results in the formation of $Cp^*(CO)_2HW(\mu\text{-}\eta^1,\eta^2\text{-}SiMeCH_2)ReH(CO)_2Cp^*$.[104] Photolysis of Ph_2SiH_2 with **49** results in Si–H activation and the formation of a bridging $SiPh_2$ group between the Re centers.[133] Complexes of type (η^6-arene)$M(CO)_2SiCl_3$ (M = Mn, Re) were described above.[126]



R = C_6F_5

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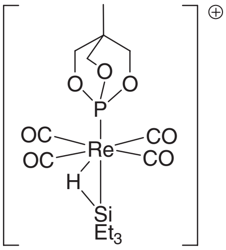

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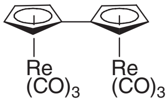

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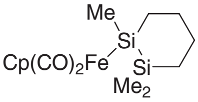
The tris(imido) complexes $(ArN)_3ReSiR_3$ ($Ar = 2,6\text{-}Pr^i{}_2C_6H_3$; $R_3 = Me_3$, Ph_2H, PhH_2) can be prepared by lithiation of $(ArN)_3ReCl$ followed by treatment with SiR_3Cl. Reactions of $(ArN)_3ReSiR_3$ with CO and $SiPhH_3$ have been described.[134]

3.10.7 Group 8 Metals

Studies of complexes with bonds between group 8 metals and silicon up to 1997 are adequately covered in the review by Corey and Braddock-Wilking,[3] and overlap with this review is avoided in the discussion below.

3.10.7.1 Iron

A wide range of silyl derivatives of iron is known. The photolysis of Ph_2CHSiH_3 with $Cp^*Fe(CO)_2Me$ leads to $Cp^*Fe(CO)_2(SiH_2CHPh_2)$ as well as *cis*- and *trans*-$Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Si(H)CHPh_2)$. The reaction of $Cp^*W(CO)_2Me$ with $Cp^*Fe(CO)_2(SiH_2CHPh_2)$ yielded the first example of a silanediyl-bridged Fe–W complex.[105] The disilyl complexes **50–52** have been reported; their photolysis results in silylene eliminations.[135] $CpFe(CO)_2CH_2$(*cyclo*-Si_5Me_9) is formed from $Na[CpFe(CO)_2]$ and (*cyclo*-Si_5Me_9)CH_2Cl. Although $CpFe(CO)_2$-CH_2(*cyclo*-Si_5Me_9) is stable at room temperature, it is very reactive upon irradiation, undergoing rearrangement.[136] In Section 3.10.5.3, the reaction of $BrMe_2SiSiMe_2Br$ with $Na[(\eta^5C_5Me_4Et)Mo(CO)_3]$ was mentioned. This work also includes the formation of $(\eta^5\text{-}C_5H_4Et)Fe(CO)_2SiMe_2SiMe_2Cl$, $(\eta^5\text{-}C_5H_4Et)Fe(CO)_2(SiMe_2)_6Br$, and $(\eta^5\text{-}C_5H_4Et)Fe(CO)_2(SiMe_2)_6Fe(CO)_2(\eta^5\text{-}C_5H_4Et)$.[79] Reactions of $CpFe(CO)_2SiR_2SiR^1{}_2X$ (R, $R^1 = Me$, Bu; $X = Cl$, OMe) include the formation of disilametallocycles and high molecular mass polymers.[137] A series of indenyl complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2Si_2Me_2Ph_3$ with isomeric disilane substituents have been synthesized and characterized, and their photochemical conversion to monosilyl derivatives has been described.[138] $CpFe(CO)_2SiMe_3$, $CpFe(CO)_2SiMe_2SiMe_3$, and $CpFe(CO)_2SiMe_2SiMe_2Ph$ have been prepared using electrochemical synthesis. The 4-bromo derivative of the latter has been converted to $CpFe(CO)_2SiMe_2SiMe_2(C_6H_4\text{-}4\text{-}CH{=}C(CN)_2)$, and UV–VIS spectroscopic and electrochemical data are consistent with there being strong intramolecular donor–acceptor interactions in this complex.[139]



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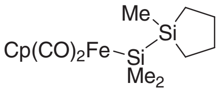

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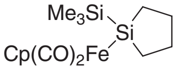

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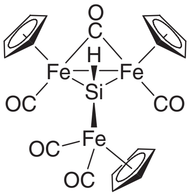
In the complexes $CpFe(CO)_2SiPh_2X$ ($X = MeO$, $4\text{-}MeC_6H_4S$) and $CpFe(CO)_2SiPh(2\text{-}MeOC_6H_4)X$ ($X = Cl$, OMe), there is no tendency for the X group to migrate from Si to Fe with elimination of silylene. In their electrospray mass spectra, however, the complexes show loss of the X group and this suggests that cationic silylene iron complexes may form; for complexes containing the Si-attached $2\text{-}MeOC_6H_4$ substituent, internal stabilization of the silylene by the MeO group is possible.[140] $CpFe(CO)_2SiMe_2Cl$ (or its Cp^* analog) hydrolyzes in the presence of Et_3N to give $CpFe(CO)_2SiMe_2OH$.[141] $Cp^*Fe(CO)_2SiMeRBr$ ($R = Me$, Ph) forms in the reaction of BBr_3 and $Cp^*Fe(CO)_2SiMe_2R$. Treatment of $Cp^*Fe(CO)_2SiMeRBr$ with another equivalent of BBr_3 results in the formation of $Cp^*Fe(CO)_2SiRBr_2$. With a longer silyl substituent, bromodemethylation occurs at the α-Si, for example, the conversion of $Cp^*Fe(CO)_2SiMe_2SiMe_3$ to $Cp^*Fe(CO)_2SiMeBrSiMe_3$ and then to $Cp^*Fe(CO)_2SiBr_2SiMe_3$.[142] Acetic acid reacts with $CpFe(CO)_2SiMe_2SiMe_2Cl$ (or with the Cp^* analog) in the presence of pyridine or Et_3N to give $CpFe(CO)_2$-$SiMe_2SiMe_2OCOMe$. With 2-pyridone, $Cp^*Fe(CO)_2SiMe_2SiMe_2Cl$ reacts to give $Cp^*Fe(CO)_2SiMe_2SiMe_2O(2\text{-}C_5H_4N)$,[143] and the photochemically initiated cyclization of this compound has been studied.[143,144] Related to this is a report of the hydrido complex $Cp^*Fe(CO)(H)\{SiMe_2O(2\text{-}C_5H_4N)\}_2$.[145]

The complex $(\eta^6\text{-}C_6H_5Me)Fe(H)_2(SiCl_3)_2$ is a very strong acid and is deprotonated by bases including py, 2,2′-bipyridine (bipy), and 2,6-lutidine. For each of these bases, the formation of M–H···H bonded species was observed before loss of H^+ occurred.[146] A series of $(\eta^6\text{-}C_6H_{6-x}R_x)Fe(CO)(SiCl_3)_2$ complexes has been prepared, and for complexes with $x = 6$, $R = Me$, and $x = 2$, $R = Pr^i$, crystallographic data have been reported. Barriers to arene rotation have been studied using ^1H NMR spectroscopy.[147] A series of papers explores *cis*-$Fe(CO)_4(SiCl_3)_2$ as a precursor for CVD formation of FeSi films.[148–150]

Diiron complexes containing bridging SiR_2 groups are well exemplified. $\{Cp(CO)_2Fe\}_2(\mu\text{-}SiH_2)$ is light sensitive and rapidly converts to $Cp(CO)Fe(\mu\text{-}SiH_2)(\mu\text{-}CO)Fe(CO)Cp$, present in both *cis*- and *trans*-forms. Upon photolysis, $\{Cp(CO)Fe\}_2(\mu\text{-}SiH_2)$ reacts with $CpFe(CO)_2Me$ to give the first trismetallated silane, **53**.[151] Halogen-for-hydrogen exchange gives a route from $\{Cp(CO)Fe\}_2(\mu\text{-}SiH_2)$ to $\{Cp(CO)Fe\}_2(\mu\text{-}SiX_2)$ (X = F, Br, I), and their structures, along with that of the previously prepared chloro derivative, have been determined.[152] The presence of three bridging silyl groups in $Fe_2(CO)_6(\mu\text{-}SiMe_2)_2(\mu\text{-}SiMeCl)$ has been confirmed crystallographically.[153] The tetrahydrido complex $\{Cp^*Fe\}_2(\mu\text{-}H)_4$ reacts with $SiPh_2H_2$ to give $\{Cp^*Fe\}_2(\mu\text{-}H)_2(\mu\text{-}SiPh_2)$,[154] but with $SiBu^t{}_2H_2$ and $SiPr^i{}_2H_2$, the products are **54** and the corresponding isopropyl derivative.[155] Photolysis of a 2 : 1 mixture of $Cp^*Fe(CO)_2Me$ and Ph_2CHSiH_3 leads to the formation of $Cp^*(CO)Fe(\mu\text{-}SiHCHPh_2)(\mu\text{-}CO)Fe(CO)Cp^*$.[105]



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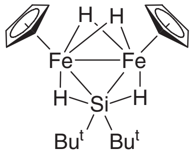

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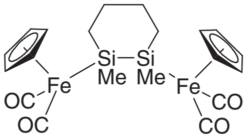
When $Cp(CO)_2FeSiMe_2SiMe_2CH_2Fe(CO)_2Cp$ is photolyzed, it rearranges to $Cp(CO)_2FeSiMe_2CH_2SiMe_2\text{-}Fe(CO)_2Cp$.[156] The photochemistry of $Cp(CO)_2FeCH_2SiMe_2SiMe_2CH_2Fe(CO)_2Cp$ and of its isomers $Cp(CO)_2FeSiMe_2CH_2CH_2SiMe_2Fe(CO)_2Cp$ and $Cp(CO)_2FeSiMe_2CH_2SiMe_2CH_2Fe(CO)_2Cp$, and of $(SiMe_2)\text{-}\{(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2R\}_2$ (R = Me, Ph) has also been studied.[157,158] Compound **55** rearranges to **56** and finally to **57** when irradiated.[159] Rearrangements that have been thoroughly investigated involve the conversion of the diiron-coordinated $(\eta^5\text{-}C_5H_4)SiMe_2SiMe_2(\eta^5\text{-}C_5H_4)$ ligand (and related derivatives) to two $(\eta^5\text{-}C_5H_4)SiMe_2$ units which are coordinated through the cyclopentadienyl unit to one Fe and σ-bonded (Si–Fe bond) to the second metal center.[160–166]



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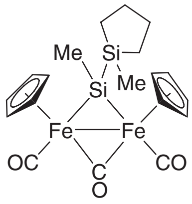

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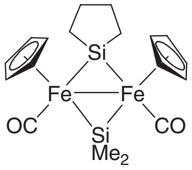


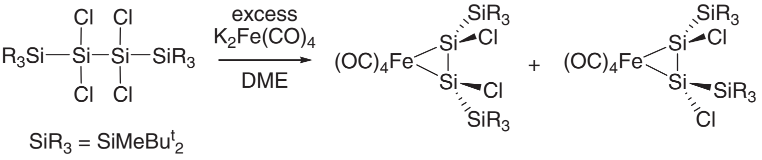
57

A number of iron silyl derivatives involve ligands with Si–N or Si–P bonds. The reaction of $K[Cp^*Fe(CO)_2]$ with $ClSiMe_2NR_2$ (R = Me, Et, Pr^i, Ph) in THF involves the solvent and leads to the formation of $Cp^*(CO)_2Fe(CH_2)_4OSiMe_2NR_2$. In contrast, when $Li[Cp^*Fe(CO)_2]$ reacts with $ClSiMe_2NR_2$ (R = Me, Et) in Et_2O or toluene in the presence of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), Fe–Si bond formation occurs. $Cp^*(CO)_2FeSiMe_2NPh_2$ proved to be more difficult to access, the best route being by reaction of $Cp^*Fe(CO)_2Me$ with $HSiMe_2NPh_2$.[167] When $Cp^*(CO)(py)FeSiMe_2NPh_2$ is heated in toluene, the pyridine ligand inserts into the Fe–Si bond.[168] Photolysis of $Cp(CO)_2FeSiMe_2PPh_2$ results in the initial formation of $Cp(CO)Fe\{\kappa^2(Si,P)\text{-}SiMe_2PPh_2\}$ followed by dimerization.[169]

Most of this section is devoted to derivatives containing CO and Cp-type ligands. An exception is a family of coordinatively unsaturated, silyl complexes $LFeSiR_2R^1$ involving the tripodal ligand $[PhB(CH_2PPr^i{}_3)_3]^-$.[170]

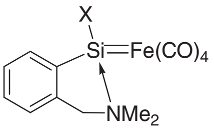
Iron-containing silanol complexes have been made by the insertion of O (from dimethyldioxirane) into α-Si–H bonds, for example, in $CpFe(CO)_2SiH_2SiH_3$.[171] Hydrolysis of $CpFe(CO)_2SiMe_2Cl$ (or its Cp* analog) in the presence of Et_3N leads to $CpFe(CO)_2SiMe_2OH$, and this can be converted into $CpFe(CO)_2SiMe_2OSiR_3$ (R = various) by treatment with R_3SiCl.[141] The silanols $\{CpFe(CO)_2\}_2Si(X)OH$ (X = H, OH, Cl) are formed when $\{CpFe(CO)_2\}_2SiHCl$ is hydrolyzed, or when $\{CpFe(CO)_2\}_2SiH(X)$ (X = Cl, H) reacts with dimethyloxirane. Condensation reactions of the silanols have been studied.[172] $CpFe(CO)_2SiRR^1OH$ (R; R^1 = Me, Pr^i, Ph) reacts with trialkylgallanes, eliminating an alkane and forming $\{CpFe(CO)_2SiRR^1(\mu\text{-}OGaR^2{}_2)\}_2$ for a wide range of R^2 groups.[173] Reactions of chlorosiloxanes with $[CpFe(CO)_2]^-$ and $[Cp^*Fe(CO)_2]^-$ lead to the corresponding iron-containing siloxanes, for example, $CpFe(CO)_2SiCl_2OSiCl_3$.[83]

Before moving on to M═Si bonded compounds, mention should be made of the disilene complexes (Equation (6)), which are formed as (*E*)- and (*Z*)-isomers in 28% and 9% yields, respectively; (*E*)-to-(*Z*)-isomerization follows first-order kinetics.[173]

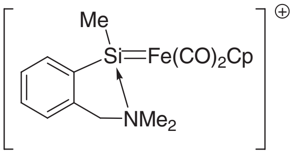


(6)

The formation of group 6 metal silylene complexes with ligands 28 and 29 was described in Section 3.10.5. Silylene 28 reacts with $Fe_2(CO)_9$ to give the trigonal-bipyramidal complex Fe(28)$(CO)_4$ with 28 coordinated in an equatorial site.[75] Chromium and manganese complexes related to 58–60 were described earlier. Complex 58 has been prepared by photochemical coupling of the appropriate hydrosilane with $Fe(CO)_5$ and is stabilized internally by the NMe_2 group.[128] External base stabilization is observed using *N*,*N*-dimethylimidazolidinone (L), and this is a strong enough base to convert $Fe_2(CO)_8(SiPh_2)_2$ to $(CO)_4Fe({=}SiPh_2)L$.[128,175] Compound 59 is one of a family of base-stabilized $ArAr^1Si{=}Fe(CO)_4$ (Ar, Ar^1 = aryl) species; 59 has been structurally characterized (Fe–Si = 2.259(1), Si–N = 1.962(2) Å). Especially strong donor stabilization is observed for Ar = 8-[(dimethylamino)-methyl]naphthyl.[175] Nucleophilic substitution of the chloro group in 60 provides a route to a number of related derivatives.[71] The salt [61][PF_6] has been prepared by hydride abstraction from the corresponding (hydrosilyl)iron derivative using [Ph_3C][PF_6]. Methanol reacts with [61][PF_6] to give the methoxysilyl derivative [$Cp(CO)_2FeSiMe(OMe)C_6H_4$-2-$CH_2NHMe_2$][$PF_6$].[176] Photolysis of $Fe(CO)_5$ with $SiHMe_2OR$ (R = alkyl, aryl) in the presence of hexamethylphosphoric triamide (HMPA) leads to the formation of $(CO)_4Fe{=}SiMe_2{\cdot}$HMPA and $SiMe_2(OR)_2$. In the absence of HMPA, and with R = py, $SiHMe_2OR$ reacts with $Fe(CO)_5$ to produce 62.[177] Stabilization of the $Fe{=}SiMe_2$ unit has also been observed with triflate as part of a study of the reactivity of iron-bonded alkoxysilyl groups.[178] Insertion by the stannylene reagent $SnNBu^tSiMe_2NBu^t$ into the N–H bond in $L(CO)_3Fe\{{=}Si(OR)_2\}NHMe_2$ (R = Me, Et; L = $(Me_2N)_2POR$) leads to base-stabilized silylene and stannylene derivatives,[179] and $L(CO)_3Fe\{{=}Si(OMe)_2\}NHMe_2$ is also the precursor to the first example of a heterometallic complex (FeCu) containing a bridging aminosilyl ligand.[180]



58: X = H
59: X = Ph
60: X = Cl



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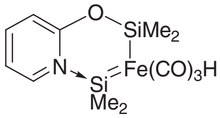

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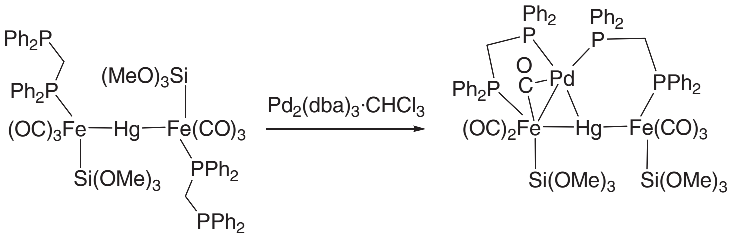
The base-stabilized bis(silylene) complex $Cp(CO)Fe(\eta^2\text{-}SiMe_2OBu^tSiMe_2)$, which is in equilibrium with $Cp(CO)_2Fe({=}SiMe_2)SiMe_2OBu^t$, reacts at 80 °C with $EH(SiMe_3)_3$ (E = Si, Ge) to form $Cp(CO)_2FeSiMe_2OBu^t$ and $E(SiMe_2H)(SiMe_3)_3$.[181] The complex $Cp^*(CO)Fe({=}SiMes_2)(SiMe_3)$ was the first example of a donor-free silyl(silylene) complex of iron.[182]

Braunstein and co-workers have produced a range of dimetallic complexes containing Fe–Si bonds, and work prior to 1994 has been reviewed.[183] The bis(diphenylphosphino)methane (dppm) ligand supports dimetal frameworks between Fe and Re,[184] Pd and Pt,[185–193] and Ni,[194] and in many examples, a second bridge is provided by an $Fe{-}SiR_2(RO{\rightarrow}M)$ unit. One system that must be singled out for attention is the product of the reaction shown in Equation (7). The bonding in this heteropolymetallic complex involves direct interactions between the Pd(0) and Hg(II) d^{10}-centers, and the fluxional behavior of the complex in solution has been interpreted in terms of the Pd atom sliding along the Fe–Hg–Fe chain.[193]

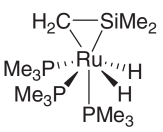


(7)

3.10.7.2 Ruthenium

Reactions between silanes and octahedral Ru(II) centers are represented in a range of examples. $RuH_2(PPh_3)_4$ reacts with R_3SiH ($R = 1\text{-}NC_4H_4$) to give $RuH_3(SiR_3)(PPh_3)_3$; related osmium complexes have also been prepared and characterized.[195] Bis(silyl) dihydride complexes $RuH_2(SiR_3)_2(PMe_3)_3$ have been made by the reactions of SiR_3H ($SiR_3 = SiH_2Ph$, $SiHPh_2$; or $(SiR_3)_2 = Me_2SiCH_2CH_2SiMe_2$) with $RuH_3(SiMe_3)(PMe_3)_3$ or $RuH(SiMe_3)(PMe_3)_4$. The products possess pentagonal-bipyramidal structures in solution and in the solid state, with hydride ligands in the equatorial plane. For $SiR_3 = SiH_2Ph$ or $SiHPh_2$, there is no evidence for agostic Si–H–Ru interactions, but the solution spectroscopic data for $RuH_2(Me_2SiCH_2CH_2SiMe_2)(PMe_3)_3$ are consistent with the presence of one classical Ru–H ligand, and one non-classical Ru–H–Si interaction. $RuH_3(PMe_3)_3SiMe_2CH_2SiMe_3$ has also been prepared and characterized, and structural and spectroscopic data are discussed in terms of possible weak non-classical Ru–H–Si interactions.[196] Reactions of hydrosilanes with $Ru(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$, *cis*-$Ru(PMe_3)_4Me_2$, and $Ru(PMe_3)_4H_2$ lead to *cis*-$Ru(PMe_3)_4H(SiR_3)$, where $SiR_3 = SiMe_3$, $SiMe_2CH_2SiMe_3$, $SiEt_3$, or $SiMe_2H$. These silyl complexes are octahedral with mutually *cis* silyl and hydrido (or silyl and methyl) ligands; for four complexes that were structurally characterized, the longest Ru–P bond is always *trans* to Si as a consequence of its strong *trans*-influence.[197] Triphenylborane abstracts PPh_3 from $Ru(PMe_3)_4H(SiMe_3)$ to give a 16-electron complex which exists in equilibrium with the 18-electron species **63**.[198]

The chlorosilane $SiHMeCl_2$ reacts with $RuHCl(CO)(PPh_3)_3$ or $RuPhCl(CO)(PPh_3)_2$ to give $Ru(SiMeCl_2)Cl(CO)(PPh_3)_2$. The latter readily reacts with OH^- or EtOH to yield $Ru\{SiMe(OH)_2\}Cl(CO)(PPh_3)_2$ or $Ru\{SiMe(OEt)_2\}Cl(CO)(PPh_3)_2$, respectively. 8-Aminoquinoline displaces a PPh_3 ligand from $Ru(SiMeCl_2)Cl(CO)(PPh_3)_2$ and forms an *N,N′*-chelate; although the NH_2 group lies adjacent to the Si–Cl bonds, no reaction between the functionalities was observed.[199] In the conversion of $RuH(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ to $Ru(SiClPh_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$, the silyl group replaces the hydride ligand with no structural rearrangement of the other ligands. Reactions of $Ru(SiClPh_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with 2-hydroxypyridine, 2-aminopyridine, and thallium acetate follow a common path with replacement of silicon-bound Cl and substitution of one PPh_3 ligand to give, for example, **64**.[200] Other chlorosilyl complexes include $[RuCO)_2Cl_3(SiPh_2Cl)]^{2-}$[201] and $Ru(CO)_3(SiCl_3)_2$,[202] both of which have been structurally characterized.



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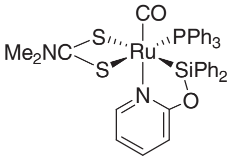

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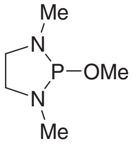
As part of a wider study of the photochemical behavior of $RuL(CO)H_2$, where $L = PhP(CH_2CH_2PPh_2)_2$, it was shown that photolysis of this complex with $SiEt_3H$ gives $RuL(CO)H(SiEt_3)$. On laser flash irradiation of $RuL(CO)H_2$, reductive elimination of H_2 occurs in less than 100 ns. The resulting transient species is rapidly quenched by a range of reagents, and the second-order rate constants decrease in the order $k_2(H_2) > k_2(C_2H_4) > k_2(CO) > k_2(Et_3SiH)$.[203] The reaction of $SiMeH(CH_2CH_2CH_2PPh_2)_2(HL^1)$ with $Ru(PPh_3)_2(CO)_3$ yields $RuH(L^1)(CO)_2$ as a mixture of *syn*- and *anti*-diastereoisomers. The pure *syn*-diastereoisomer can be accessed independently. Its slow stereomutation at 295 K to an equilibrium mixture of 4.5 *syn* : 1 *anti* has been followed; the diastereoisomerization occurs by a non-dissociative pathway.[204]

Silyl derivatives containing a $Cp^*Ru(PMe_3)_2$ unit include $Cp^*Ru(PMe_3)_2SiCl_3$, $Cp^*Ru(PMe_3)_2Si(NMe_2)_3$, $Cp^*Ru(PMe_3)_2Si(SEt)_3$, $Cp^*Ru(PMe_3)_2Si(SMes)_3$, and $Cp^*Ru(PMe_3)_2Si(SCy)_2Cl$, all prepared from the reaction between SiR_3H and $Cp^*Ru(PMe_3)_2CH_2SiMe_3$. Reactions of these derivatives with Me_3SiOTf are exemplified by that of $Cp^*Ru(PMe_3)_2Si(SEt)_3$ which gives $Cp^*Ru(PMe_3)_2Si(SEt)_2OTf$. Treatment with $NaBPh_4$ converts this into the silylene complex $[Cp^*Ru(PMe_3)_2\{{=}Si(SEt)_2\}][BPh_4]$, and this illustrates the more general formation of $[Cp^*Ru(PMe_3)_2({=}SiX_2)]^+$ where X = thiolate, Me or Ph.[205] Chlorosilanes react with $CpRuH(PR_3)_2$ to give complexes of type $CpRu(PR_3)_2SiX_3$ (e.g., $SiX_3 = SiCl_3$, $SiHCl_2$, SiH_2Cl, SiHMeCl; $PR_3 = PPhMe_2$). Treating these complexes with $LiAlH_4$ leads to $CpRu(PPhMe_2)_2SiX_3$ with $SiX_3 = SiH_3$, $SiMeH_2$, or $SiMe_3$, respectively. As the steric demands of the phosphine increase, the reactivity of $CpRuH(PR_3)_2$ toward $ClSiX_3$ decreases. Detailed NMR spectroscopic data for members of the $CpRu(PR_3)_2SiX_3$ series has allowed the effects of the silicon substituents on the spectroscopic parameters to be assessed.[206] The crystal structures of $CpRu(PR_3)_2SiX_3$ ($PR_3 = PMe_3$ and $SiX_3 = SiCl_3$, $SiMeCl_2$, $SiPhCl_2$; $PR_3 = PMe_2Ph$ and $SiX_3 = SiCl_3$) have been determined, and structural trends have been rationalized in terms of π-backbonding from Ru 4*d* to σ^*(Si–Cl) orbitals.[207] The reactions between Lewis acids and $CpRu(CO)L(SiX_3)$ where L is the phosphine donor ligand **65**, and $SiX_3 = SiMe_3$ or $SiMe_2SiMe_3$, have been compared with those involving related alkyl, germyl, and stannyl derivatives. When the Lewis acid is $BF_3{\cdot}OEt_2$, OMe abstraction occurs to give a cationic phosphenium complex; this is independent of the group 14 substituent. For the silyl and germyl derivatives, the phosphenium complex is relatively stable, but for the alkyl substituent, migratory insertion of the phosphenium ligand into the Ru–C bond takes place; for the stannyl derivatives, a stannylene complex forms as a result of migration of one of R groups on Sn to the phosphenium P center.[208]

When $Ru_3(CO)_{12}$ reacts with the bis(cyclopentadiene) $C_5H_5Me_2Si_2Me_2C_5H_5$ in boiling heptane, complex **66** is obtained in low yield, and the complex undergoes a thermal rearrangement to **67**.[209] A similar situation arises for the reaction between $Ru_3(CO)_{12}$ and $C_5Me_5Me_2Si_2Me_2C_5Me_5$ in boiling decalin.[210] This chemistry is reminiscent of iron-containing systems described earlier.[160–166] Related to **67** is the complex $Me_2Si[(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$, the structure and solution properties of which have been reported.[211]



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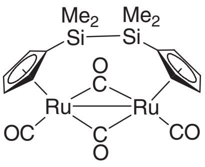

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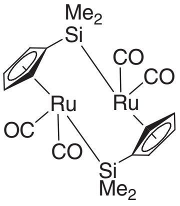

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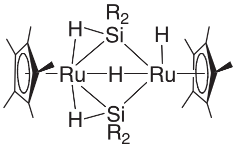
Silyl derivatives incorporating (η^6-arene)Ru units include $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiX_3)_2$ ($X_3 = Cl_3$, $MeCl_2$), prepared from $Ru(PPh_3)_3Cl_2$ with $SiHX_3$ in benzene. When the organosilane precursor is $SiHMe_2Cl$, a mixture of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)_2$, $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)(SiMeCl_2)$, and $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMeCl_2)_2$ is obtained. Methylation of any of these compounds with $AlMe_3$ results in the formation of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_3)_2$.[212] The coordinatively unsaturated $[(\eta^6\text{-}C_6H_6)Ru(\eta^3\text{-}Pr^iNCMeNPr^i)]^+$ reacts with Me_3SiCHN_2 to give an amidinato–carbene complex with terminal Ru–$SiMe_3$ group. The latter migrates to the carbene group when the complex is treated with CO.[213]

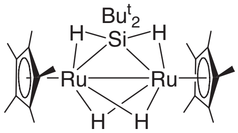
Silyl derivatives of ruthenium that exhibit η^2-Si–H interactions are now well exemplified. For $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}HSiPh_3)(PCy_3)_3$, structural and theoretical data illustrate that weak interactions between the Si atom and hydrides stabilize the complex.[214] Related to this is a series of complexes that form when disilanes $(R_2SiH)_2X$ (R = Ph, X = O; R = Me, X = O, C_6H_4, CH_2CH_2, $CH_2CH_2CH_2$, $OSiMe_2O$) react with $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$. In each product, the coordinated disilane participates in two Ru–(η^2-Si–H) interactions; their presence results in the sterically demanding PCy_3 groups being mutually *cis*. The study has been extended to mixed phosphine derivatives.[215] Hydride/(η^2-Si–H) exchange is observed in $RuH_2\{(\eta^2\text{-}HSiMe_2)_2CH_2CH_2\}(PCy_3)_2$ and $RuH_2\{(\eta^2\text{-}HSiPh_2)_2O\}(PCy_3)_2$.[216] $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ reacts with 2 equiv. of $H_2SiMePh$ to give a mixture of $Ru_2H_4(\mu\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}SiH_4)(PCy_3)_4$ (structurally characterized) and $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}HSiPh_3)(PCy_3)_2$. Elimination of SiH_4 from the former complex occurs when it reacts with, for example, CO and $CNBu^t$.[217] Warming an equilibrium mixture of $RuHSiMe_3(PMe_3)_3$ and $RuH_2(\eta^2\text{-}CH_2SiMe_2)(PMe_3)_3$ from −40 to 0 °C results in chlorination of one hydride and formation of *fac*-$Ru(CH_2SiMe_2)HCl(PMe_3)_3$, which exhibits an agostic Si···H···Ru interaction. The *mer*-isomer has also been isolated and structurally characterized. The transformations represent the first example of an M–$SiMe_3$ to β-agostic

M–CH_2SiMe_2–H conversion.[218] The reaction of $Cp^*RuCl(PPh_3)_2$ with excess $SiHMe_2Cl$ gives $Cp^*RuH_2(SiMe_2Cl)(PPh_3)$. Its structure has been compared with that of $Cp^*RuH_2(SiMesHCl)(PPr^i_3)$, allowing the presence of a non-classical silyl–hydride interaction in the latter to be confirmed.[219] Protonation of $CpRu(SiCl_3)(PMe_3)_2$ leads to $[CpRu(\eta^2\text{-}HSiCl_3)(PMe_3)_2]^+$ in which the η^2-silane coordination mode has been confirmed by structural analysis.[220] In $RuH_3(SiCl_2Me)(PPh_3)_3$, three Ru–H···Si interactions are present: Ru–Si = 2.2760(4) Å, three Ru–H ≈ 1.6 Å, and three Si···H ≈ 1.9 Å.[221] Similar interactions have been observed in $TpRuH(\eta^2\text{-}HSiR_3)(PPh_3)$ (Tp = hydridotris(pyrazolyl)borate; R = various).[222]

Dinuclear ruthenium complexes with bridging silyl ligands include $Ru_2H_4(\mu\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}SiH_4)(PCy_3)_4$ mentioned above.[217] Related to this is the reaction of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ with Et_2SiH_2, Ph_2SiH_2, or $Bu^t{}_2SiH_2$ to give **68** or **69**. When $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ reacts with $HSiMe_2(CH{=}CH_2)$, the μ-dimethylvinylsilane complex **70** is formed. When **70** is heated, the Si–C(sp^2) bond breaks, yielding a product containing μ-$SiMe_2$ and μ-CMe units.[223] Treatment of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ with Ph_3SiH leads to a mixture of $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}SiPh_2)_2RuCp^*$ and $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}SiPh_2)RuCp^*$. For the former, fluxional behavior involves rotation around the Ru–Si bonds which results in isomerization between *syn*- and *anti*-forms.[224]



R = Et, Ph
68



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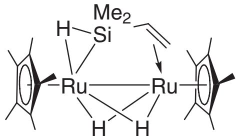
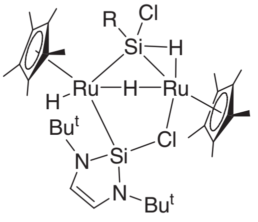


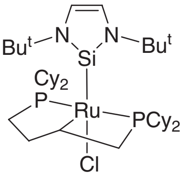
70

Photolysis of $Ru_2(CO)_6(\mu\text{-dppm})(\mu\text{-}SiTol_2)$ in the presence of excess SiH_2Tol_2 results in oxidative addition of one Si–H bond to one Ru center and the formation of a non-classical Ru–H···Si interaction to the μ-$SiTol_2$ unit (Tol = tolyl). Further reaction yields $Ru_2(CO)_4(SiHTol_2)_2(\mu\text{-dppm})(\mu{:}\eta^2{:}\eta^2\text{-}H_2SiTol_2)$.[225]

Silylene **28** has already figured in a number of metal complexes described in this review. It reacts with $Ru_3(CO)_{12}$ to give the trigonal-bipyramidal complex $Ru(\mathbf{28})_2(CO)_3$ with **28** coordinated in the axial sites.[75] Silylene **28** also reacts with $Cp^*{}_4Ru_4Cl_4$, yielding the 16-electron complex $Cp^*RuCl(\mathbf{28})$ which, when treated with SiH_3R (R = Ph, *n*-hexyl), gives **71**.[226] Four equivalents of **28** react with $LClRu(\mu\text{-}Cl)_3RuL(N_2)$ (L = $Cy_2P(CH_2)_4PCy_2$) to give the mononuclear complex **72**; the product (which has been structurally characterized) illustrates activation of the carbon backbone of the chelating $Cy_2P(CH_2)_4PCy_2$ ligand.[227]

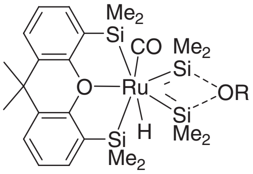


R = Ph, C_6H_{13}
71



72

The first donor-stabilized bis(silylene) ruthenium complex, $CpRu(Me_2SiOMeSiMe_2)PPh_3$, was reported in 1994. Structural data confirmed short Ru–Si bonds (av. 2.326 Å for two independent molecules).[228] When the bis(silylene) complex is heated in the presence of a two-electron donor L (L = PPh_3, PMe_3, $P(OMe)_3$, Bu^tNC), cyclometallation of one phenyl substituent of the coordinated PPh_3 ligand occurs and the product is $CpLRu(2\text{-}SiMe_2C_6H_4PPh_2\text{-}P,Si)$.[229] The reaction between $SiHMe_2NMe_2$ and $Ru(SiMe_2Cl)Cl(CO)(PPh_3)_2$ leads to a mixture of products: $Ru(Me_2SiNMe_2SiMe_2)H(CO)(PPh_3)_2$, $Ru(Me_2SiNMe_2SiMe_2)Cl(CO)(PPh_3)_2$, and $(Me_2SiNMe_2SiMe_2)(CO)Ru(\mu\text{-}Cl)(\mu\text{-}SiMe_2)_2RuH_2(CO)PPh_3$.[230] The bis(silylene) derivative **73** is catalytically active in the oligomerization–deoligomerization of $SiHMe_2SiMe_3$ to $H(SiMe_2)_nMe$.[231] Complex **73** contains the (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl) ligand, L. This also features in the coordinatively unsaturated $RuL(CO)(PCy_3)$ which reacts readily with CO to give $RuL(CO)_3(PCy_3)$.[232]



R = Me, Bu^t

73

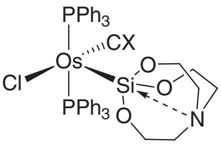
3.10.7.3 Osmium

The osmium(IV) silyl derivative $OsH_3(SiMe_3)(CO)(PPh_3)_2$ results from the reaction of $SiHMe_3$ with $OsPh(CO)(PPh_3)_2Cl$, and the $SiMe_3$ ligand can be replaced by $SiEt_3$ or $SiPh_3$ in reactions with the corresponding silane.[233] The reaction of $OsPh(CO)(PPh_3)_2Cl$ with $SiHMeCl_2$ has also been reported; the product, $Os(SiMeCl_2)(CO)(PPh_3)_2Cl$, reacts with OH^- or EtOH to give $Os\{SiMe(OH)_2\}(CO)(PPh_3)_2Cl$ or $Os\{SiMe(OEt)_2\}(CO)(PPh_3)_2Cl$, respectively. The latter adds CO, and structural data for $Os\{SiMe(OEt)_2\}(CO)(PPh_3)_2Cl$ and $Os\{SiMe(OEt)_2\}(CO)_2(PPh_3)_2Cl$ show quite different Os–Si bond distances: 2.3196(11) Å in the former, and 2.4901(8) Å in the latter.[199] Tris-*N*-pyrrolylsilane is accessible from the reaction of $SiHCl_3$ and pyrrole, and a number of osmium and ruthenium complexes of tris-*N*-pyrrolylsilane have been reported.[195,234]

Excess $SiHPr^i_2Cl$ reacts with $Cp^*Os(PMe_3)_2CH_2SiMe_3$ to give $Cp^*Os(PMe_3)_2SiPr^i_2Cl$; this contrasts with the formation of a bis(silyl) derivative when $SiHMe_2Cl$ reacts with $Cp^*Os(PMe_3)_2CH_2SiMe_3$, and the difference is attributed to the greater steric demands of the diisopropylsilyl group. $Cp^*Os(PMe_3)_2SiPr^i_2Cl$ can be converted to $Cp^*Os(PMe_3)_2SiPr^i_2OTf$, and reaction of this with $Li[B(C_6F_5)_4]\cdot 3Et_2O$ in fluorobenzene yields the silylene derivative $[Cp^*Os({=}SiPr^i_2)(PMe_3)_2][B(C_6F_5)_4]$.[235] $Cp^*OsBr(PPr^i_3)$ oxidatively adds SiH_4 or primary or secondary silanes to give 18-electron silyl complexes from which bromide abstraction leads to silylene derivatives of type $[Cp^*OsH_2({=}SiR_2)(PPr^i_3)][B(C_6F_5)_4]$.[236]

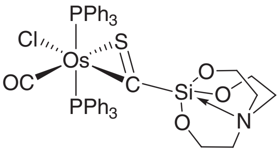
When $OsPh(CO)(PPh_3)_2Cl$ reacts with $SiH(OEt)_3$, the square-pyramidal complex $Os\{Si(OEt)_3\}(CO)(PPh_3)_2Cl$ is produced; the silyl group occupies the axial site. Reversible addition of CO is observed, and the chloro ligand in $Os\{Si(OEt)_3\}(CO)(PPh_3)_2Cl$ can be replaced by Ph or $2\text{-}MeC_6H_4$ substituents to give stable five-coordinate complexes.[237] The five-coordinate complex **74** has been structurally characterized for X = O and exhibits a very long Si···N distance (3.000(7) Å); the environment around the N atom is essentially planar and reactions take place with electrophiles (H^+, Me^+) leading to a further increase in the Si···N separation. Complex **74** with X = S reacts with CO to give **75** in which the Si–N distance is 2.086(6) Å.[238] The complex $Os\{Si(OCH_2CH_2)_3N\}H(CO)_2(PPh_3)_2$ (formed as a mixture of three isomers) has also been reported. With $OsH_4(PPh_3)_3$, $SiH(OCH_2CH_2)_3N$ forms $OsH_3\{Si(OCH_2CH_2)_3N\}(PPh_3)_3$ in which the three hydride ligands interact only weakly with the Si atom.[239]

Examples of bis(silylene) complexes of osmium are limited. The reaction between $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ and an excess of $SiHMe_2NMe_2$ leads to a mixture of $Os(Me_2SiNMe_2SiMe_2)H(CO)(PPh_3)_2$ and $Os(Me_2SiNMe_2SiMe_2)Cl(CO)(PPh_3)_2$.[230] The osmium pincer complex $OsH_2Cl\{CH(C_2H_4PBu^t_2)_2\}$ undergoes an intriguing reaction with 2 equiv. of SiH_3Ph to yield the silylene/silyl complex **76** in which the $Os{=}SiH_2$ unit is internally base stabilized.[240]



X = O, S

74



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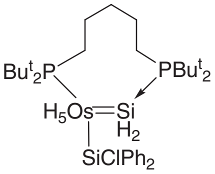
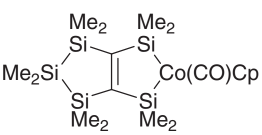


76

3.10.8 Group 9 Metals

3.10.8.1 Cobalt

The Co–Si bond is exemplified in a relatively restricted selection of compounds. Of relevance to materials chemistry is the use of $Co(SiCl_3)(CO)_4$ as a precursor for cobalt silicide thin films, deposited by low-pressure CVD. The films are metallic conductors.[241] Within the period of this review, early contributions to Co–Si bonded complexes include cyclopentasilyl derivatives (e.g., $Co(CO)_3(PPh_3)(Si_5Me_9)$),[242] and complex **77**.[243] Dicobalt octacarbonyl reacts with $Ph_2HSi–SiHPh_2$ to give $Co(SiPh_3)(CO)_4$, and analogous products are formed with other disilanes.[244] With $O(SiHPh_2)_2$, $Co_2(CO)_8$ reacts to give the dicobalt species $(OC)_4CoSiPh_2OSiPh_2Co(CO)_4$; this is stable as a solid in air, but is rather air sensitive in solution.[140] For the series of complexes $Co_2(CO)_6(\mu\text{-}RSiXSiR)$ ($X = CH_2CH_2$, C_6H_4, $CH_2CH_2CH_2$; R = Me, Ph), structural data reveal a short Si···Si interaction which depends on the identity of the spacer X.[245] The sila[1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMeH$ opens to give **78** when it reacts with $Co_2(CO)_8$; labeling studies indicate that the ring opening is an intramolecular process. If the reaction is carried out in the presence of NEt_3, **79** is obtained.[246]



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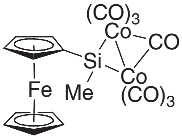
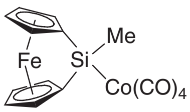


78



79

Diphenylsilane reacts with $Cp^*Co(\eta^2\text{-}C_2H_4)_2$ to give a mixture of the Co(V) complexes $Cp^*Co(H)_2(SiHPh_2)_2$ and $Cp^*Co(H)_2(SiHPh_2)(SiEtPh_2)$. The reaction can be driven toward the formation of $Cp^*Co(H)_2(SiHPh_2)_2$ by using an excess of SiH_2Ph_2.[247] In $(\eta^5\text{-}C_5H_4CH_2CH_2PBu^t{}_2)Co(\eta^2\text{-}C_2H_4)$, the cyclopentadienyl ligand acts as a chelate by virtue of the dangling phosphine donor. Reaction of this complex with $SiHR_3$ (various R) results in the formation of $(\eta^5\text{-}C_5H_4CH_2CH_2PBu^t{}_2)CoH(SiR_3)$, formed as a racemate. Variable-temperature NMR spectroscopic data are consistent with racemization in solution involving reversible dissociation of the *P*-donor.[248]

3.10.8.2 Rhodium

Rhodium(I) silyl complexes have been prepared by the reaction of $RhMe(PMe_3)_4$ with $SiHR_3$ ($R_3 = Ph_3$, $(OEt)_3$, $Me(OMe)_2$). Ratios of reagents are critical, since the formation of Rh(III) complexes *fac*-$Rh(PMe_3)_3(SiR_3)_2(H)$ ($R_3 = (OEt)_3$, $Me(OMe)_2$) becomes dominant if 2 equiv. of silane are used. Reaction of $RhPh(PMe_3)_4$ and $SiHPh_3$ also gives a route to an Rh(I) silyl complex, but with $HSi(OEt)_3$ or $HSiMe(OMe)_2$, even with a 1 : 1 stoichiometry, the only products are *fac*-$Rh(SiR_3)_2(H)(PMe_3)_3$.[249] The reaction of $RhCl(PMe_3)_3$ with $Li(THF)_3Si(SiMe_3)_3$ produces $Rh\{SiMe_2SiMe(SiMe_3)_2\}(PMe_3)_3$ via 1,2- and 1,3-migrations. In contrast, the analogous reaction with $IrCl(PMe_3)_3$ (generated *in situ*) leads to an iridacycle.[250] In $Rh\{\kappa^2\text{-}PhB(CH_2PPr^i{}_2)_3\}(PMe_3)_2$, one arm of the tripodal $[PhB(CH_2PPr^i{}_2)_3]^-$ ligand is uncoordinated. This Rh(I) complex reacts with 1 equiv. of SiH_2Ph_2 with concomitant loss of one arm of the $[PhB(CH_2PPr^i{}_2)_3]^-$ ligand to produce $Rh(H)_2(SiHPh_2)(PMe_3)\{PhB(CH_2PPr^i{}_2)_2\}$.[251] Oxidative addition of $SiHPh_3$ to $RhCl(PMe_3)_3$ occurs to give *mer*-$RhCl(H)(SiPh_3)(PMe_3)_3$. When $SiH(C_6H_4\text{-}4\text{-}CF_3)_3$ reacts with $RhCl(PMe_3)_3$, a mixture of *mer*-$RhCl(H)\{Si(C_6H_4\text{-}4\text{-}CF_3)_3\}(PMe_3)_3$, *fac*-$Rh(H)_2\{Si(C_6H_4\text{-}4\text{-}CF_3)_3\}(PMe_3)_3$, and *cis*,*mer*-$RhCl_2(H)(PMe_3)_3$ is formed.[252] Contrasting behavior of LRhX ($L = Pr^i{}_2P(CH_2)_3\ PPh(CH_2)_3PPr^i{}_2$; X = H, Cl, Me) toward $SiH(SEt)_3$ has been observed. For X = Cl, no reaction occurs, whereas for X = H, oxidative addition of the silane takes place. For X = Me, both the Si–H and Si–S bonds are activated, and the products are the Rh(I) complexes, LRhSEt and $LRhSi(SEt)_3$.[253]

When the dinuclear complex $Pr^i{}_3P(H)(Ph_3Si)Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh(SiPh_3)(H)PPr^i{}_3$ is treated with an excess of $SiH(C_6H_4\text{-}4\text{-}F)_3$, $SiHPh(C_6H_4\text{-}4\text{-}F)_2$, or $SiH_2Ph(C_6H_4\text{-}4\text{-}F)$, silyl ligand exchange occurs. Thermolysis of solutions of $Pr^i{}_3P(H)(R_3Si)Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh(SiR_3)(H)PPr^i{}_3$ (R = Ph or $4\text{-}FC_6H_4$) results in the formation of $Pr^i{}_3P(H)Rh(\mu\text{-}SiR_3)(\mu\text{-}SiR_2)(\mu\text{-}Cl)Rh(H)PPr^i{}_3$ with loss of benzene and fluorobenzene, respectively.[254,255] Secondary silanes (e.g., SiH_2Ph_2) react with $LRh(\mu\text{-}H)_2RhL$ ($L = Pr^i{}_2PCH_2CH_2PPr^i{}_2$) to give complexes containing bridging silylene ligands.[256]

Cyclopentadienyl rhodium silyl derivatives include $Cp^*Rh(H)_2(SiEt_3)_2$, which has been used as a precursor to heterometallic clusters.[257] The photolysis of $CpRh(PPh_3)(\eta^2\text{-}C_2H_4)$ with $SiHR_3$ (R = Et, Pr^i) results in oxidative addition of the Si–H bond and concomitant loss of ethene, as confirmed by a single crystal structure determination of $CpRh(H)(PPh_3)(SiPr^i_3)$ (Rh–Si = 2.386(2) Å).[258] An interesting combination of ligands is found in the complex $Cp^*Rh(H_2)(SiEt_3)(Bpin)$ where $[Bpin]^-$ is the pinacolatoboryl ligand. The complex undergoes elimination of BpinH faster than it does $SiHEt_3$ or H_2.[259] Oxidative addition of an Si–H bond occurs when $SiHR_3$ (R_3 = various) is photolyzed with $CpRh(\eta^2\text{-}CH_2CHCO_2Bu^t)_2$. Significantly, the formation of the Rh(V) species $CpRhH_2(SiEt_3)_2$ was also detected in this reaction.[260] When the Rh(III) complex $[Cp^*Rh(Me)(PMe_3)(Cl_2CH_2)]^+$ reacts with $SiHR_3$ (R = Me, Et, Ph), CH_4 is lost and the products are $[Cp^*Rh(PMe_3)(SiR_3)(\eta^2\text{-}HSiR_3)]^+$ for R = Me or Et, or $[Cp^*Rh(PMe_3)\{(C_6H_4)(\eta^2\text{-}HSiPh_2)\}]^+$ which contains an Rh–C rather than Rh–Si direct bond.[261]

The square-planar complex $LRh(PMe_3)_2$ for HL = $HMe_2SiCH_2CH_2PPh_2$ contains L^- in a chelating mode. When $LRh(PMe_3)_2$ reacts with $SiHMe_2Ph$, selective dehydrogenative coupling of $SiHMe_2Ph$ occurs to produce $(Me_2PhSi)_2$ and octahedral $LRhH_2(PMe_3)_2$. Variable-temperature NMR spectroscopic studies of $LRh(PMe_3)_2$ and of the related $LRh(PMe_3)_3$ show that the PMe_3 ligands undergoe exchange which is intramolecular for $LRh(PMe_3)_2$, but intermolecular for $LRh(PMe_3)_3$.[262,263]

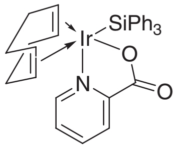
The first rhodium silanol complex to be reported was *trans*-$Rh(PEt_3)_2(H)Cl(SiPr^i_2OH)$. In solution, this is in equilibrium with the starting materials $Rh(PEt_3)_3Cl$ and $SiHPr^i_2OH$. In contrast, $\{(Pr^i_2P(CH_2)_3PPr^i_2)RhCl\}_2$ does not react with $SiHPr^i_2OH$, even when the silanol is present in a 10-fold excess; this suggests that the *trans*-phosphine configuration is important.[264] Rhodium(III) complexes $RhX(H)(SiR^1_nR^2_{3-n})(PPh_3)_2$ with alkoxy substituents in the silyl ligand have been prepared by the oxidative addition of $HSiR^1_nR^2_{3-n}$ to $RhX(PPh_3)_3$ (X = I, R^1 = $OSiMe_3$, R^2 = Me, n = 1; X = I, R^1 = OEt, n = 3; X = I, R^1 = OEt, R^2 = Me, n = 2; X = I, R^1 = OEt, R^2 = Me, n = 1; X = Cl, R^1 = $OSiMe_3$, R^2 = Me, n = 1; X = Cl, R^1 = OEt, n = 3; X = Cl, R^1 = OEt, R^2 = Me, n = 2; X = Cl, R^1 = OEt, R^2 = Me, n = 1). Structural data for representative members of this series confirm distorted square-pyramidal complexes with the silyl group occupying the apical position; Rh–Si distances are noticeably short.[265]

3.10.8.3 Iridium

Not surprisingly, there is some overlap between compounds of rhodium containing M–Si bonds and those for which M = Ir. The reactivity of LRhX (L = $Pr^i_2P(CH_2)_3PPh(CH_2)_3PPr^i_2$; X = H, Cl, Me) toward $SiH(SEt)_3$ was described above. When the precursor is LIrMe, $SiH(SEt)_3$ reacts to yield *fac*-$LIrMe(H)\{Si(SEt)_3\}$, and there is no Si–S bond activation as was observed with rhodium.[253] The square-planar complex $Ir(CO)_2(PCy_3)(C{\equiv}CPh)$ reacts with $SiHR_3$ (R = Et, Ph, or R_3 = HPh_2, H_2Ph) to give octahedral Ir(III) complexes after oxidative addition of the Si–H bond. Analogous reactions have been carried out using $Ir(\eta^4\text{-}TFB)(PCy_3)(C{\equiv}CPh)$ (TFB = tetrafluorobenzobarrelene) as the precursor, and NMR spectroscopy has been used to monitor the reaction pathways. $HSiEt_3$ reacts with $Ir(TFB)(PCy_3)(C{\equiv}CPh)$ to give $IrH_2(SiEt_3)(TFB)(PCy_3)$ and $PhC{\equiv}CSiEt_3$; in contrast, $HSiPh_3$ and H_2SiPh_2 react to give $Ir\{C(SiPh_3){=}CHPh\}(TFB)(PCy_3)$ and $IrH_2\{Si(C_2Ph)Ph_2\}(TFB)(PCy_3)$, respectively. $Ir(CO)_2(PCy_3)(C{\equiv}CPh)$ and $Ir(\eta^4\text{-}TFB)(PCy_3)(C{\equiv}CPh)$ catalyze the addition of $HSiEt_3$ to phenylethyne, and it was concluded that intermediates of the types $M(H)(C{\equiv}CR)(SiR_3)$ and $M\{C(SiR_3){=}CHR\}$ may be important in the formation of dehydrogenative silylation and *anti*-addition products.[266]

Reactions between $Ir(cod)(O_2CArN)$ ($NArCO_2^-$ = pyridine-2-carboxylate, isoquinoline-2-carboxylate, quinoline-2-carboxylate, pyrazine-2-carboxylate) and $SiHPh_3$ result in the reversible formation of **80** or analogous complexes (cod = cycloocta-1,5-diene).[267]

Secondary silanols add to $Ir(PEt_3)_2(\eta^2\text{-}C_2H_4)Cl$ to give Ir(III) derivatives of type $Ir(PEt_3)_2H(Cl)(SiR_2OH)$ (R = Pr^i, Bu^t); the solid-state structure of $Ir(PEt_3)_2H(Cl)(SiPr^i_2OH)$ reveals Si–OH···Cl hydrogen-bonded interactions. Treating $Ir(PEt_3)_2H(Cl)(SiPr^i_2OH)$ with BuLi yields **81**. The silanol $SiHPr^i_2OH$ reacts reversibly with $Ir(PPh_3)_3(CO)H$ to give $Ir(PPh_3)_2H_2(CO)(SiPr^i_2OH)$.[264] Related rhodium chemistry was described in the previous section.[264]



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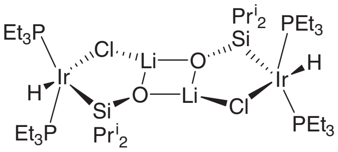
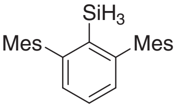


81

When $IrCl(PMe_3)_4$ reacts with $LiSiMe_2Ph$, the transient $Ir(PMe_3)_3(SiMe_2Ph)$ undergoes cyclometallation to give *fac*-$Ir(PMe_3)_3H(2\text{-}C_6H_4SiMe_2)$. This is also formed when *fac*-$Ir(PMe_3)_3Me(H)(SiMe_2Ph)$ is heated. Treatment of *fac*-$Ir(PMe_3)_3H(o\text{-}C_6H_4SiMe_2)$ with CO leads to $Ir(PMe_3)_2(CO)_2(2\text{-}C_6H_4SiMe_2)$. This study illustrates that metallation of silyl ligands may take place reversibly and under mild conditions.[268] Oxidative addition of **82** to $IrCl(PEt_3)_3$ occurs alongside H/Cl exchange at the Si center to yield $Ir(H)_2(PEt_3)_3\{SiHCl(C_6H_3\text{-}2,6\text{-}Mes_2)\}$, the solid-state structure of which has been determined. Chloride abstraction from the latter results in the silylene complex $[Ir(H)_2(PEt_3)_3\{{=}SiH(C_6H_3\text{-}2,6\text{-}Mes_2)\}]^+$.[269] Silane **82** also reacts with $IrCl(PEt_2Ph)_3$, and in this case the product is **83**.[270] Complex **84** forms when $Ir(H)R(PMe_3)_2(Ph_2CH_2CH_2SiHMes\text{-}P,Si)$ (R = Me, Et) is heated; reductive elimination of RH is followed by C–H activation. The intermediate can be trapped by oxidative addition of MeOH (present as the solvent).[271,272] After Si–H bond activation, $HSi(CH_2C_6H_4\text{-}2\text{-}PPh_2)_3$ (HL) is a source of a tetradentate ligand; it reacts with $Ir_2(cod)_2Cl_2$ to give Ir(L-*Si*,*P*,*P*′,*P*′′)(H)Cl.[273] In the reaction of $Ir_2(coe)_4Cl_2$ with bis(8-quinolyl)methylsilane (HL^1), the product is the octahedral complex Ir(L-*Si*,*N*,*N*′)(H)(coe)Cl (coe = cyclooctene). [274]



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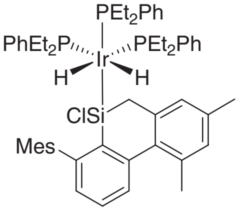

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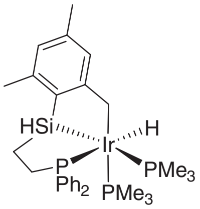


84

The tripodal ligand $[PhB(CH_2PPr^i{}_2)_3]^-$ was first reported in 1999.[275] It has been used in the formation of silylene and silyl complexes of iridium.[251,275,276] Related to $[PhB(CH_2PPr^i{}_2)_3]^-$ is the family of hydrotris(1-pyrazolyl)borate ligands, $[Tp^{Rx}]^-$. The iridium(V) polyhydride $Tp^{Me_2}IrH_3(SiEt_3)$ has been prepared from the reaction of $Tp^{Me_2}IrH_2(C_4H_4S)$ with $HSiEt_3$.[277]

The iridium(III) species $Cp^*Ir(PMe_3)(Me)OTf$ undergoes rapid Si–H activation when reacted with silanes. Work from Tilley and Bergman offers insight into the involvement of Ir(V) in the reaction pathway. A study of the reaction between $Cp^*Ir(PMe_3)(Me)OTf$ and SiH_2Mes_2 shows that the kinetic product is an Ir(V) cyclometallated species, formed as a result of oxidative addition of a C–H bond of one of the silicon-bonded mesityl Me groups. Significantly, the cyclometallated complex isomerizes to the silylene $[Cp^*Ir({=}SiMes_2)(PMe_3)H][OTf]$. A detailed kinetics study has been published.[278,279] The reaction of $Cp^*Ir(PMe_3)(Me)(SiMe_2OTf)$ with $LiB(C_6F_5)_4{\cdot}2Et_2O$ yields $[Cp^*Ir(\eta^2\text{-}CH_2SiMe_2)(PMe_3)H][B(C_6F_5)_4]$ and the base-stabilized silylene complex $[Cp^*IrMe\{{=}SiMe_2(Et_2O)\}(PMe_3)][B(C_6F_5)_4]$.[280] The reactions of iridium(III) silyl and silylene complexes with unsaturated organic substrates have been investigated, for example, that of $[Cp^*Ir({=}SiMes_2)(PMe_3)H][OTf]$ with 4-tolualdehyde. The results have been assessed in the context of silyl and silylene complexes of Ir(III) being pre-catalysts for the catalytic hydrosilylation of ketones.[281]

3.10.9 Group 10 Metals

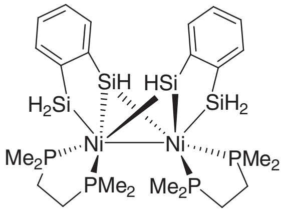
As in previous sections, use has been made of the excellent review by Corey and Braddock-Wilking[3] to cover much of M–Si bond (M = Ni, Pd, Pt) chemistry up to 1997.

3.10.9.1 Nickel

Even though nickel(II) complexes have found use as hydrosilylation catalysts, studies of reactions between such complexes and hydrosilanes remain limited, and few compounds containing Ni–Si bonds were reported between 1993 and 2004. Reactions between $Ni(PR_3)_2(NCS)_2$ (R = Ph, Bu^n) and $SiHCl_3$, $SiHMeCl_2$, and $SiHMe_2Cl$ result in the formation of $Ni(PR_3)_2(SiMe_nCl_{3-n})_2$ ($n = 0$–2). Of these, $Ni(PR_3)_2(SiMeCl_2)_2$ and $Ni(PR_3)_2(SiMe_2Cl)_2$ represent the first examples of Ni(II) complexes with both an Ni–Si bond and at least one alkyl group attached to Si.[282] $Cp^*{}_2Si$ reacts with $CpNiCl(PPh_3)$ to yield $\{Cp^*{}_2(Cl)Si\}NiCp$ in which there is a direct Ni–Si interaction; one of the silicon-bonded Cp^* substituents is π-coordinated to the nickel atom.[283]

Four equiv. of silylene **1** react with $Ni(PPh_3)_2Cl_2$ and $Ni(cod)_2$ to give $Ni(PPh_3)(\mathbf{1})_3$ (structurally characterized) and $Ni\mathbf{1}_4$, respectively. When $Ni(PPh_3)_2Cl_2$ is treated with 5 equiv. of **1**, the product is $Ni(\mathbf{1})_4$. The conversion of $Ni(cod)_2$

to Ni(**1**)$_4$ shows **1** functioning as a simple ligand. In contrast, conversion of Ni(PPh$_3$)$_2$Cl$_2$ to Ni(PPh$_3$)(**1**)$_3$ or Ni(**1**)$_4$, or NiCl$_2$ to Ni(**1**)$_4$, illustrates the ability of **1** to also function as a reducing agent.[284,285] The reaction of Ni(dmpe)$_2$ with 1,2-(SiH$_3$)$_2$C$_6$H$_4$ (H$_2$L) leads to the nickel(IV) complex Ni(dmpe-*P*,*P*′)(L-*Si*,*Si*′)$_2$. ^{31}P NMR spectroscopic studies of the reaction indicate the presence of the intermediates Ni(dmpe-*P*,*P*′)(dmpe-*P*)(L-*Si*,*Si*′) and {(dmpe)-(L-*Si*,*Si*′)Ni}$_2$(μ-dmpe), and when the latter is heated at 110 °C for 30 min, complex **85** forms. Structural data have confirmed the unusual Ni$_2$Si$_2$ core. Starting from Ni(depe)$_2$ (depe = 1,2-bis(diethylphosphino)ethane), reaction with 1,2-(SiH$_3$)$_2$C$_6$H$_4$ (H$_2$L) leads directly to the depe analog of **85**. Related studies involving 1,2-(SiMe$_2$H)$_2$C$_6$H$_4$ have also been carried out.[286,287] In the reaction of **86** (H$_3$L) with Ni(depe)(PEt$_3$)$_2$, the product is Ni(depe)(HL), in which the central SiH$_2$ group of the silyl ligand is involved in an Ni–H–Si interaction. Solution NMR spectroscopic data indicate that there is rapid exchange of five Si-bound H atoms at room temperature; the fluxional process is frozen out at −80 °C.[288]



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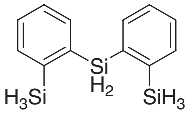
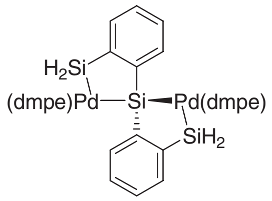


86

3.10.9.2 Palladium

The first report of a palladium(0) complex containing silylene ligands came in 2001. Silylene **28** reacts with Pd(PPh$_3$)$_4$ to give the dinuclear complex (Ph$_3$P)Pd(μ-**28**$_2$Pd(PPh$_3$), which has been structurally characterized (Pd–Si = 2.3996(3), 2.4154(4) Å). The complex catalyzes Suzuki coupling reactions of aryl boronic acids with bromoarenes in high yield.[289] A similar product, (Bu$^t_3$P)Pd(μ-**27**)$_2$Pd(PBu$^t_3$), is produced from treatment of Pd(**27**)$_4$ or Pd(**27**)$_3$ with PBu$^t_3$; the latter Pd(0) complexes are formed from reactions of silylene **27** with Pd(PBu$^t_3$)$_2$ or PdMe$_2$(cod).[290] Four equivalents of silylene **1** react with PdCl$_2$(PPh$_3$)$_2$ with both ligation of **1** to Pd(II) and insertion of Cl, the product being *trans*-Pd(**1**)$_2$(**1**Cl)$_2$ in which there are two silylene and two chlorosilyl ligands (structurally confirmed). This behaviour contrasts with that of **1** with nickel(II), but parallels that with Pt(II).[285]

Silanes SiHR$_3$ (R$_3$ = Ph$_3$, Ph$_2$Me, PhMe$_2$, Et$_3$) react with the dinuclear complex Pd$_2$(μ-dcpe)$_2$ (dcpe = 1,2-bis-(dicyclohexylphosphino)ethane) to give Pd(SiR$_3$)H(dcpe). The stability of the silyl palladium(II) hydrides depends upon the degree of phenyl substitution in the SiR$_3$ ligand. The variable-temperature solution NMR spectra of the Pd(SiR$_3$)H(dcpe) complexes are consistent with there being rapid intramolecular exchange of silyl and hydride substituents.[291] Oxidative addition of Si–H bonds in silane **86** occurs during its reaction with Pd(PEt$_3$)$_4$ in the presence of dmpe or depe, giving dipalladium(II) complexes, for example, **87** which has been crystallographically characterized. When the reaction was carried out in the presence of dcpe, the product was complex **88** in which an Si–Si bond was formed as a result of intramolecular dehydrocoupling.[292] Reaction of PdMe$_2$(dmpe) or Pd(PhCH=CH$_2$)(dmpe) with 1,1-diphenyl- and 1,1-dimethylsilacyclobutanes resulted in the formation of **89**, the reactivity (for R = Ph) of which has been discussed.[293] Related to this is the formation of square-planar **90 and 91**.[294] When allyl bromide reacts with *trans*-PdL$_2$(SiF$_2$Ph)$_2$ (L = PMe$_3$, PMe$_2$Ph, PMePh$_2$), the products are CH$_2$=CHCH$_2$SiF$_2$Ph and *trans*-PdBr(SiF$_2$Ph)L$_2$. Dry HCl (in CH$_2$Cl$_2$) reacts with *trans*-PdL$_2$ (SiF$_2$Ph)$_2$ to yield *trans*-PdCl(SiF$_2$Ph)L$_2$.[295] The palladium(II) complexes LPdCl$_2$ in which L is the ferrocenyl-based *P*,*N*-donor shown in **92** have been used as catalyst precursors in the asymmetric hydrosilyation of alkenes. These dichlorides react with SiHCl$_3$ to give complexes **92**, structural characterization of which reveals extreme distortion from an ideal square-planar geometry at Pd(II) and long Pd–P bonds. Theoretical investigations of the origins of these features reach the conclusion that they arise as a result of steric factors.[296]



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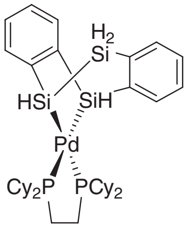

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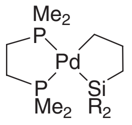
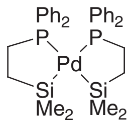


R = Me, Ph

89



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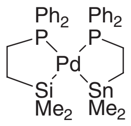

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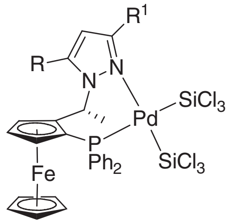
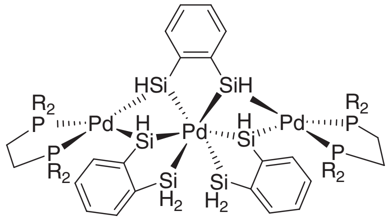


R = R^1 = Me
R = Me; R^1 = Ph
R = H; R^1 = 2,4,6-$Me_3C_6H_2$

92

Bridging silyl ligands in dipalladium or heterometallic compounds containing palladium are illustrated in a number of examples. Reactions between *trans*-$PdEt_2(PR_3)_2$ ($PR_3 = PMe_3$, PEt_3, $PMePh_2$) and SiH_2Ph_2 give a range of dinuclear complexes: $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)$,$(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Ph(PMe_3)_2$, and $(R_3P)Pd(\mu\text{-}SiHPh_2)_2$-$Pd(PR_3)$ ($PR_3 = PEt_3$,$PMePh_2$). Treating *trans*-$PdEt_2(PR_3)_2$ ($PR_3 = PMe_3$, PEt_3) with SiH_2MePh gives an analogous product. In all these species, agostic Pd–H–Si interactions are observed.[297,298] Related heteronuclear complexes $(Cy_3P)Pd(\mu\text{-}SiHPh_2)_2Pt(PCy_3)$,[299] $(Et_3P)Pt(\mu\text{-}SiHPh_2)_2Pd(PEt_3)$, and $(Et_3P)_2Pt(\mu\text{-}SiHPh_2)_2Pd\text{-}(PEt_3)$ have also been described. In the synthesis of $(Cy_3P)Pd(\mu\text{-}SiHPh_2)_2Pt(PCy_3)$ from $Pd(PCy_3)_2$ and $Pt(dmpe)(SiHPh_2)_2$, additional products are the homometallic complexes $(Cy_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PCy_3)$ and $(dmpe)Pt(\mu\text{-}SiHPh_2)_2Pt(dmpe)$. Agostic M–H–Si interactions are again observed.

The first palladium(IV) silyl complex was reported in 1996: Pd(dmpe)(L-*Si,Si′*)$_2$ where $H_2L = 1,2\text{-}(H_3Si)_2C_6H_4$ was made by reacting $PdMe_2(dmpe)$ with $1,2\text{-}(H_3Si)_2C_6H_4$.[301] When heated in toluene at 80 °C, this Pd(IV) complex and its analog Pd(depe)(L-*Si,Si′*)$_2$ undergo condensation reactions to form 93 which appears to formally contain Pd(VI) and two Pd(II) centers.[302] However, the results of an independent study of the bonding in this complex show that there is strong evidence to describe the central Pd as being in oxidation state +2, interacting with two η^2-coordinated Si–Si single bonds (2.49 and 2.59 Å). [303]



R = Me, Et

93

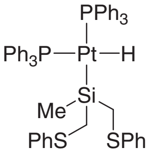
The first η^2-disilene complexes of palladium were described in 2003: structural data for $L_2Pd\{\eta^2\text{-}(Me_2Bu^tSi)_2Si{=}Si(SiMe_2Bu^t)_2\}$ ($L_2 = (PMe_3)_2$ or dmpe) indicate that a metallocyclic description with strong

π-back-donation is appropriate.[304] The related complex $(Cy_3P)Pd\{\eta^2\text{-}(Me_2Bu^tSi)_2Si{=}Si(SiMe_2Bu^t)_2\}$ (Si–Si = 2.2740(11) Å) represents the first 14-electron disilene palladium complex; it was synthesized by treating $Pd(PCy_3)_2Cl_2$ with the corresponding 1,2-dilithiodisilane in THF at room temperature.[305]

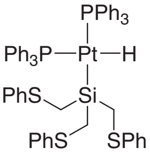
3.10.9.3 Platinum

Square-planar platinum(II) complexes containing silyl ligands are well represented. The contrasting reactivities of *cis*- and *trans*-$PtMe(SiPh_3)L_2$ ($L = PMe_2Ph$, $PMePh_2$) toward $PhC{\equiv}CH$ are worthy of note: only the *cis*-isomers undergo alkyne insertion.[306] Another comparative study is of the thermolysis of *cis*- and *trans*-isomers of $PtR(SiPh_3)(PMe_2Ph)_2$. The *trans*-isomer with R = Et is relatively thermally stable, while *trans*-$PtMe(SiPh_3)(PMe_2Ph)_2$ reductively eliminates $SiMePh_3$. In contrast, each of the *cis*-isomers with R = Me, Et, Pr, Bu eliminates $SiRPh_3$ on heating, and reaction pathways have been discussed.[307] The reactions of isocyanides CNR ($R = Bu^t$, Cy, Pr^i) with *cis*-$Pt(SiHPh_2)_2(PR^1{}_3)_2$ (R^1 = Me, Et) result in the formation of *cis*-$Pt(SiHPh_2)_2(CNR)(PR^1{}_3)$; structural data reveal that the Pt–Si bond *trans* to the PMe_3 group is longer than that *trans* to the isocyanide.[308] Thermolysis (at ≈35 °C) of *cis*-$Pt(C{\equiv}CAr)(SiAr^1{}_3)(PMe_2Ph)_2$ (Ar = Ph, $4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}NCC_6H_4$; Ar^1 = Ph, $4\text{-}MeOC_6H_4$, $4MeC_6H_4$, $4\text{-}CF_3C_6H_4$) results in reductive elimination and the formation of platinum(0) silylalkyne complexes $Pt(ArC{\equiv}CSiAr^1{}_3)(PMe_2Ph)_2$. The rates of reductive elimination have been correlated to the electron-donating abilities of the substituents on the aryl groups.[309] Mixed silyl/stannyl derivatives of type *cis*-$Pt(SiR_3)(SnMe_3)(PMe_2Ph)_2$ ($R_3 = Me_3$, Me_2Ph, $MePh_2$, Ph_3) are formed when $Pt(cod)_2$ reacts with $R_3SiSnMe_3$. The preferences for the insertion of $PhC{\equiv}CH$ into the Pt–Si or Pt–Sn bonds has been studied; under thermal conditions, insertion occurs into the Pt–Si bond, while competition (which depends on the silyl or phosphine substituents) is observed when the reaction is under kinetic control.[310,311] A solid-state structural investigation of *cis*-$Pt(SiMePh_2)_2(PMe_2Ph)_2$ and *cis*-$Pt(SiFMe_2)_2(PEt_3)_2$ shows that the complexes contains twisted, square-planar coordination geometries. In solution, the complexes are stereochemically non-rigid, and NMR spectroscopic data have been interpreted in terms of a unimolecular twist-rotation through a pseudo-tetrahedral transition state.[312]

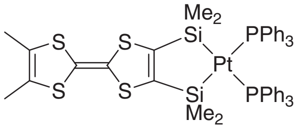
Platinum(0) precursors are commonly used in the preparation of platinum(II) silyl complexes. Oxidation addition of a range of $SiHR_2R^1$ compounds to $Pt(PCy_3)_2$ is a general route to *cis*-$Pt(PCy_3)_2(H)(SiR_2R^1)$. Spectroscopic data are consistent with each silyl group exhibiting a stronger *trans*-influence than a hydride ligand.[313] Both $(PhSCH_2)_2SiHMe$ and $(PhSCH_2)_3SiH$ react with $Pt(PPh_3)_2(\eta^2\text{-}CH_2{=}CH_2)$ to give the platinum(II) complexes **94** and **95**. While **94** is fluxional in solution on the NMR spectroscopic timescale, complex **95** is static.[314] Reactions between $Si(ER)Me_3$ (E = Se, Te) and $Pt(PEt_3)_3$ produce *trans*-$Pt(ER)(SiMe_3)(PEt_3)_2$. Although yields were high, the compounds are relatively unstable. $Si(ER)Me_3$ (E = Se, Te) react more rapidly with $Pt(PEt_3)_3$ than does $Si(SR)Me_3$.[315] The novel tetrathiafulvalene (TTF) derivative **96** has been prepared in a three-step process. Treatment of $3,4\text{-}Me_2TTF$ with lithium diisopropylamide (LDA), followed by reaction with 2 equiv. of $SiHMe_2Cl$, results in the formation of the corresponding 3′,4′-bis(silyl) derivative. This reacts with $Pt(PPh_3)_2(\eta^2\text{-}CH_2{=}CH_2)$ to generate **96**. Cyclic voltammetric data for **96** reveal two reversible or quasi-reversible, one-electron oxidation processes centered on the TTF unit. These exhibit significant cathodic shifts (0.2 V) with respect to the corresponding processes for 3,4-dimethyl–3′,4′-bis(dimethylsilyl)tetrathiafulvene.[316]



94

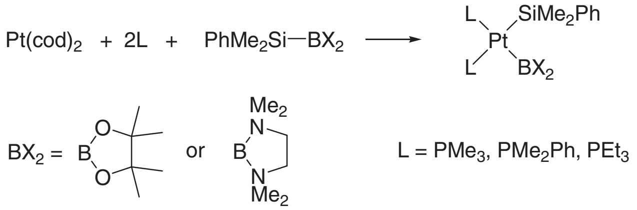


95



96

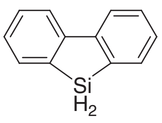
Proposed steps during the silylborylation of alkynes are the oxidative addition of silylborane to a low-valent metal species, alkyne insertion into the M–B (or possibly M–Si) bond, and Si–C reductive elimination. These processes are supported by the results of the reactions summarized in Equation (8).[317]



(8)

A series of papers deals with platinum(II) silyl complexes containing chelating *P,N*-donor ligands (in general, L) including $Ph_2PCH_2CH_2NMe_2$ (L^1), $Ph_2PCH_2CH_2CH_2NMe_2$ (L^2), 1-Me_2N–2-$Ph_2PC_6H_4$ (L^3), and 1-Me_2NCH_2–2-$Ph_2PC_6H_4$ (L^4). Reactions between $LPtMe_2$ and $SiMe_3I$ in benzene at 60 °C produce LPt(Me)I and $SiMe_4$ rather than Pt–Si bonded complexes. However, with 1,2-bis(dimethylsilyl)benzene, the square-planar LPt{1,2-$(SiMe_2)_2C_6H_4$} complexes are produced.[318] When exposed to O_2 at 60 °C, L^1Pt{1,2-$(SiMe_2)_2C_6H_4$} is quantitatively converted to the bis(silanolate), L^1Pt{1,2-$(OSiMe_2)_2C_6H_4$}.[319] Monosilyl derivatives $L^1Pt(Me)SiR_3$ are obtained when L^1PtMe_2 reacts with $SiHR_3$ ($R_3 = Et_3$, $MePh_2$).[320]

In the previous section, several dipalladium or mixed palladium/platinum species containing bridging SiR_2H and agostic M–H–Si interactions were described. These included $(Cy_3P)Pd(\mu\text{-}SiHPh_2)_2Pt(PCy_3)$,[299] $(Et_3P)Pt(\mu\text{-}SiHPh_2)_2Pd(PEt_3)$, and $(Et_3P)_2Pt(\mu\text{-}SiHPh_2)_2Pd(PEt_3)$.[300] Further examples of agostic M–H–Si interactions are seen in a number of multinuclear systems. In $(Me_3P)(Ar_2ClSi)Pt(\mu\text{-}SiHAr_2)(\mu\text{-}H)Rh(PMe_3)_3$ (Ar = Ph, 4-FC_6H_4), the agostic H interacts with the Rh center.[321] Monitoring of the reaction of silane **97** (SiH_2R_2) with $Pt(PPh_3)_2(\eta^2\text{-}CH_2{=}CH_2)$ illustrates the sequential formation of $(Ph_3P)_2Pt(H)(SiHR_2)$, $(Ph_3P)_2Pt(H)(\mu\text{-}SiR_2)(\mu\text{-}SiHR_2)Pt(PPh_3)$ containing one agostic interaction, and finally $\{(Ph_3P)Pt\}_3(\mu\text{-}SiR_2)_3$ which contains a triangular Pt_3 core.[322,323] In contrast, the reaction of $Pt(PR_3)_3$ (R = Et, Pr) with $SiH_3(Hex)$ (Hex = *n*-hexyl) produces $Pt_2(PR_3)_2\{\mu\text{-}SiH(Hex)\}_2$ (with short Si···Si contacts) and compound **98**. The ratio of these products depends on the reaction conditions.[324] Structural and spectroscopic data support the presence of one Pt–H–Si interaction in $(Ph_3P)Pt(\mu\text{-}SiH_2Ar)Pt(PPh_3)$ where Ar is the sterically demanding 2-Pr^i-6-MeC_6H_4 group.[325] This aryl group has also been incorporated into the derivatives $(Ph_nMe_{3-n}P)_2Pt(\mu\text{-}SiHAr)_2Pt(PMe_{3-n}Ph_n)_2$. Crystallographic data reveal acute Si–Pt–Si angles; detailed variable-temperature NMR spectroscopic studies have also been carried out.[326]



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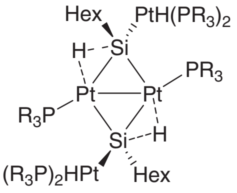
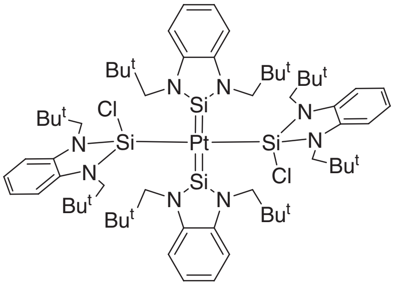


R = Et, Pr

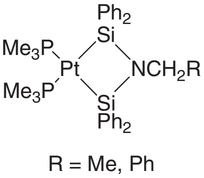
98

A number of metal complexes involving the stable silylene **1** have already been described in this review. In the reaction of 4 equiv. of **1** with $PtCl_2(PPh_3)_2$, both coordinated silylene and chlorosilyl ligands are present in the product, **99**, in which the Pt–Si bond distances are 2.269(2) and 2.437(2) Å. Similar results are observed for the reaction of **1** with $PdCl_2(PPh_3)_2$. When **1** reacts with $Pt(PPh_3)_4$, the product is $Pt(PPh_3)_3$**1**.[284,285] $Mes_2Si(SiMe_3)_2$ serves as a source of a silylene ligand when it is photolyzed with $Pt(PCy_3)_2$ in hexane solution. Structural characterization of the green product, $(Cy_3P)_2Pt({=}SiMes_2)$, confirms a short Pt–Si bond (2.210(2) Å). Photolysis of $Pt(P^iPr_3)_3$ and $Mes_2Si(SiMe_3)_2$ in benzene generated red $(Pr^i_3P)_2Pt({=}SiMes_2)$, but this could only be characterized in solution by NMR spectroscopy; once solvent was removed, conversion back to $Pt(PPr^i_3)_3$ occurred. In contrast, $(Cy_3P)_2Pt({=}SiMes_2)$ is stable in the solid state, but does decompose on standing in solution over a period of days.[327] The $SiMes_2$ ligand in $(Cy_3P)_2Pt({=}SiMes_2)$ can be displaced by, for example, phosphines, alkenes, and alkynes, and it reacts with ROH (R = H, Me, Et), eliminating $SiH(OR)Mes_2$.[328] The $SiMes_2$ ligand is also observed in the platinum(II) complex $[(Pr^i_2PCH_2CH_2PPr^i_2)Pt({=}SiMes_2)H][MeB(C_6F_5)_3]$, this being formed by treatment of $[(Pr^i_2PCH_2CH_2PPr^i_2)Pt(SiHMes_2)Me]$ with $B(C_6F_5)_3$. This reaction was the first in which facile 1,2-migration of hydrogen has led to an observed *d*-block metal silylene complex.[329]



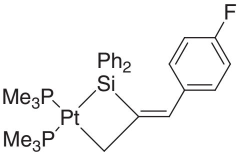
99

Several silaplatinacyclic compounds have been reported in the last few years. Double addition of Si–H bonds to the C≡N triple bond of PhCN or MeCN occurs when these nitriles react with $Pt(SiHPh_2)_2(PMe_3)_2$. The nature of the silaplatinacyclic products **100** has been confirmed by X-ray crystallography.[330] The outcome of the reaction of $Pt(SiHPh_2)_2(PMe_3)_2$ with 4-fluorophenylallene is critically dependent on the conditions. A 2 h reaction at room temperature yields **101**, while 18 h at 50 °C results in the formation of **102**. If 3 equiv. of allene are used at room temperature, Pt–C bond formation occurs.[331] Conditions are also critical in the reaction of $Pt(SiHPh_2)_2(PMe_3)_2$ with $MeO_2CC{\equiv}CCO_2Me$.[332] Addition of a C=Si bond to Pt(0) has been observed in the formation of **103**. Structural data reveal bond distances of Pt–C, Pt–Si, and Si–C in the metallocycle of 2.161(11), 2.298(3), and 1.838(12) Å, respectively, and theoretical studies suggest that the best bonding picture is one between a π-complex and σ-cyclopropane analog.[333] The η^2-disilene complex $(Me_3P)_2Pt\{\eta^2\text{-}Si_2(SiMe_2Bu^t)_4\}$ has been prepared by reacting *cis*-$PtCl_2(PMe_3)_2$ with $Li_2Si_2(SiMe_2Bu^t)_4\}$; structural data are consistent with this being classified as a metalladisilacyclopropane.[334]



R = Me, Ph

100



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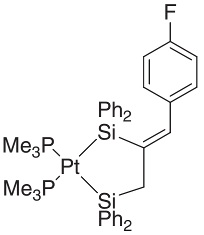
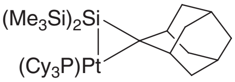
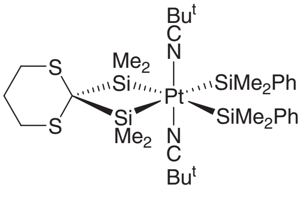


102

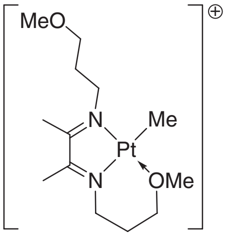


103

Platinum(IV) complexes containing Pt–Si bonds are represented by a small number of compounds. In 1996, complex **104** was reported. This was synthesized by the reaction of 2,2-bis(tetramethyl-2-phenyldisilanyl)dithiane with $Pt_3(CNBu^t)_6$. In contrast, treatment of $Pd(CNBu^t)_2$ with the same dithiane derivative gives a square-planar Pd(II) species.[335] Oxidative addition occurs when the platinum(II) complex **105** reacts with $SiHEt_3$. The result is an octahedral, cationic platinum(IV) silyl hydride.[336] Another platinum(IV) silyl hydrido complex, $(Tp^{Me})Pt(SiEt_3)H_2$ (Tp^{Me} = hydridotris(3,5-dimethylpyrazolyl)borate), is formed when $SiHEt_3$ reacts with $(Tp^{Me})PtMe_2H$. When treated with methanol, $(Tp^{Me})Pt(SiEt_3)H_2$ reacts to yield $(Tp^{Me})PtH_3$ which is an unusual example of a platinum(IV) hydrido complex containing an *N*-donor ligand.[337] Treatment of $(Tp^{Me})Pt(SiEt_3)H_2$ with $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ results in one of the pyrazolyl rings being protonated, and the formation of a five-coordinate platinum(IV) silyl dihydride.[338]



104



105

3.10.10 Group 11 Metals

Bond formation between a group 11 metal and silicon is illustrated only for Cu and Au, and examples of well-characterized complexes published between 1993 and 2004 are few, despite the importance of triorganosilylcopper reagents in organic synthesis.[339]

Metal complexes involving silylene **1** have been described in previous sections for a range of *d*-block metals. Silylene **1** also reacts with $CuI(PPh_3)_3$ and forms $CuI(PPh_3)_2$(**1**). Structural characterization of the latter confirms a distorted tetrahedral coordination environment for the Cu(I) center (Cu–Si = 2.289(4) Å).[285]

Starting from $CuAr^*$, where Ar^* is the bulky aryl substituent 2,6-$Mes_2C_6H_3$, Klinkhammer has prepared the donor–acceptor complex $(Me_3Si)_3SiCuSn\{Si(SiMe_3)_3\}Ar^*$ by treatment of $CuAr^*$ with $Sn\{Si(SiMe_3)_3\}_2$. An analogous reaction using $Pb\{Si(SiMe_3)_3\}_2$ resulted in the formation of $(Me_3Si)_3SiCu$ and $Pb\{Si(SiMe_3)_3\}Ar^*$, although it was not possible to isolate $(Me_3Si)_3SiCu$ in a pure form. Structural data for $(Me_3Si)_3SiCuSn\{Si(SiMe_3)_3\}Ar^*$ confirm the presence of a Cu–Sn bond (the first example to be reported); the Cu(I) center is in a linear environment with Cu–Si and Cu–Sn distances of 2.2727(11) and 2.4992(5) Å, respectively.[340] The cuprates $Li[Cu_2\{Si(SiMe_3)_3\}_3]$ and $[Li_7(OBu^t)_6][Cu_2\{Si(SiMe_3)_3\}_3]$ have been prepared by reactions of $Li[Si(SiMe_3)_3]$ with $CuOBu^t$. Crystallographic data confirm the presence of similar A-frame type $[Cu_2\{Si(SiMe_3)_3\}_3]^-$ ions in both cuprates, each Cu carrying a terminal $Si(SiMe_3)_3$ substituent, and a Cu···Cu unit bridged by the third $Si(SiMe_3)_3$ group.[341] When $M[Si(SiMe_3)_3]$ (M = Na, K, Cs, see Section 3.10.11) reacts with $CuOBu^t$ in toluene and −20 °C, the products are $[M(C_6H_5Me)][Bu^tOCuSi(SiMe_3)_3]$. In the solid state, dimers are present. Each is based on a central M_2O_2 ring, with *O*-bonded $CuSi(SiMe_3)_3$ units.[342] Copper(I) chloride reacts with $Bu^t{}_3SiNa(THF)_n$ to give $(Bu^t{}_3Si)_2CuNa(THF)_n$ ($n = 2$ or 4). The structures of both complexes have been determined. In $(Bu^t{}_3Si)_2CuNa(THF)_2$, the Si–Cu–Si unit deviates slightly from linearity, being affected by a Cu···Na interaction (2.7393 (18) Å). In $(Bu^t{}_3Si)_2CuNa(THF)_4$, the $[Na(THF)_4]^+$ and $[(Bu^t{}_3Si)_2Cu]^-$ ions are well separated and the Si–Cu–Si unit is linear (Cu–Si = 2.307(2) Å).[343]

Gold–silicon bond formation has been achieved in reactions of $LiSiPh_3$ with R_3PAuCl (R = Me, Ph). Whereas $Ph_3PAuSiPh_3$ undergoes ligand-redistribution reactions forming homoleptic ions, $Me_3PAuSiPh_3$ is less prone to this process and it has been possible to obtain single crystals of the Au–Si-bonded complex. Structural data confirm a mononuclear complex with linear P–Au–Si unit.[344] The reaction of $Cp^*{}_2Si$ with Ph_3PAuCl generates the Au(I) complex $(\eta^1\text{-}Cp)_2ClSiAuPPh_3$ in which the Au–Si bond length is 2.3629(16) Å. Replacing the PPh_3 group in the starting material by $CNBu^t$, pyridine, or tetrahydrothiophene allows one to access other members of this series of Au–Si bond-containing complexes.[283]

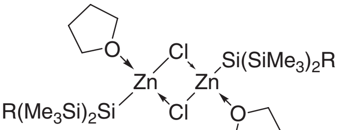
3.10.11 Group 12 Metals

In discussing the formation of bonds between silicon and group 12 metal atoms, overlap between this review and that of Corey and Braddock-Wilking[3] has been avoided.

The bis(silyl) derivative $Zn\{Si(SiMe_3)_3\}_2$ has been shown to be a useful reagent for the preparation of $Na[Si(SiMe_3)_3]$ and $K[Si(SiMe_3)_3]$.[345] The series of complexes $Zn(SiBu^t{}_3)_2$, $Cd(SiBu^t{}_3)_2$, and $Hg(SiBu^t{}_3)_2$ has been synthesized from reactions between $NaSiBu^t{}_3$ and $ZnCl_2$, $CdMI_2$ or $HgCl_2$ in THF. By adjusting the ratio of reagents, it is also possible to access $Zn(SiBu^t{}_3)Cl(THF)$, $Cd(SiBu^t{}_3)I$, and $Hg(SiBu^t{}_3)Cl$. Treating $Zn(SiBu^t{}_3)_2$ with BBr_3 leads to the formation of $Zn(SiBu^t{}_3)Br$, whereas reaction with $BiCl_3$ yields $Zn(SiBu^t{}_3)BCl$. Each of the bis(silyl) derivatives is monomeric with a linear Si–M–Si unit. Tetrameric structures are observed in the solid state for $Zn(SiBu^t{}_3)Br$ and $Hg(SiBu^t{}_3)Cl$.[346,347] Dimeric structures **106** are observed for $Zn\{SiR(SiMe_3)_2\}Cl(THF)$ (R = Ph, $SiMe_3$).[348]

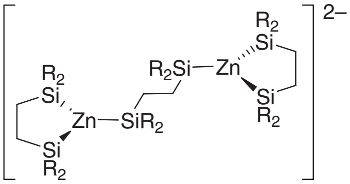
A redetermination of the structure of $Hg(SiMe_3)_2$ has shown that the solid state contains dimers in which there are weak Hg···Hg interactions.[349] The related complex $Hg\{Si(SiMe_3)_3\}_2$ has been prepared, and spectroscopic and structural data for this and the analogous Cd(II) complex have been presented.[350] The reaction between $SiH(SiMe_2SiMe_3)_3$ and $HgBu^t{}_2$ leads to the formation of $(Me_3SiSiMe_2)_3SiHgHgSi(SiMe_2SiMe_3)_3$, which contains a linear SiHgHgSi core.[351] When $HgBu^t{}_2$ is heated with $SiH_2(SiPr^i{}_3)_2$ and the product is then lithiated (Li in THF), the resulting silyl derivative is $(THF)_2Li(Pr^i{}_3Si)_2SiHgSi(SiPr^i{}_3)_2Li(THF)_2$. Structural data confirm the presence of a novel Li–Si–Hg unit, and the linearity of the Si–Hg–Si unit. Methylation and hydrolysis of $(THF)_2Li(Pr^i{}_3Si)_2SiHgSi(SiPr^i{}_3)_2Li(THF)_2$ have been studied, and the complex has also been shown to be a source of the $Li(Pr^i{}_3Si)_2Si$ radical. [352]

The reactions of $Cp^*{}_2Si$ with HgX_2 (X = Cl, Br) or Hg_2Cl_2 result in the formation of $(\eta^1\text{-}Cp^*)_2XSiHgX$ or $\{(\eta^1\text{-}Cp^*)_2XSi\}_2Hg$ (X = Cl, Br).[353] The novel complex $[K(18\text{-crown-6})]_2$[**107**] has been prepared by reacting anhydrous $ZnCl_2$ with 1.5 equiv. of $[K(18\text{-crown-6})]_2[(Me_3Si)_2SiCH_2CH_2Si(SiMe_3)_2]$.[354] The iodo-bridged complex $[(Me_3Si)_3SiCd(\mu\text{-}I)_3CdSi(SiMe_3)_3]^-$ results when CdI_2 reacts with 2 equiv. of $LiSi(SiMe_3)_3$ in THF. The germyl analog has been structurally characterized.[355]



R = $SiMe_3$, Ph

106



R = $SiMe_3$

107

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3.11
Organopolysilanes

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3.11.1 Introduction

Polysilanes are hybrid inorganic–organic polymers comprising helical chains of catenating *sp*^{3}-hybridized silicon atoms each with two side-chain (usually organic) substituents. Overlap of σ-orbitals between silicon atoms 1,2 and 1,3 to each other results in σ-electron delocalization along the silicon backbone and electronic band structure with an HOMO–LUMO bandgap of 3–4 eV. The electronically delocalized backbone is chromophoric, showing a UV absorption typically in the wavelength range of 300–400 nm, and fluorophoric, showing emission with a relatively small Stokes shift. The transition energy depends on the extent of electronic delocalization, which is sensitive to structural, electronic, and conformational effects deriving from the side chain and is affected by state, solvent, temperature, pressure, and other environmental conditions. The polymers are amenable to study by an extremely wide range of techniques, including ^{1}H, ^{13}C, and ^{29}Si NMR, IR, Raman, UV, circular dichorism (CD), FL, FL anisotropy, X-ray, atomic force microscopy (AFM), viscometry and chromatography. Polysilane structure–property relationships are therefore uniquely traceable, and their properties are limited only by the imagination of the interested investigator. As a research area, the field is relatively young, only taking off in the early 1980s when the key to making the polymers soluble was discovered: reducing repeat unit symmetry or increasing side-chain length, thus reducing the crystallizability—beautifully simple with hindsight but an epoch-marking leap at the time. Cooperation and lively global competition have resulted in the rapid growth of the field with advances being communicated at the regular international and convivial meetings by the still active founding fathers and their chemical descendants. Initial excitement at the wide range of potential applications in the technological era has been tempered by the synthetic challenges, and the field is now maturing, as theoretical and experimental research support and stimulate each other. The extensive knowledge and techniques now available enable the synthesis of polymers with defined structures designed for particular properties and functions. Progress in polysilane research can be appreciated at a glance from the plot in Figure 1, which shows a breakdown of annual publications over the last half century or so.

Over the years since the publication of COMC II (1995), different aspects of organopolysilane chemistry have been reviewed in many book chapters and review articles, and these are noted in the text below. Wide coverage of the area was also given in a book published a few years ago with chapters contributed from many experts in the field.[1]

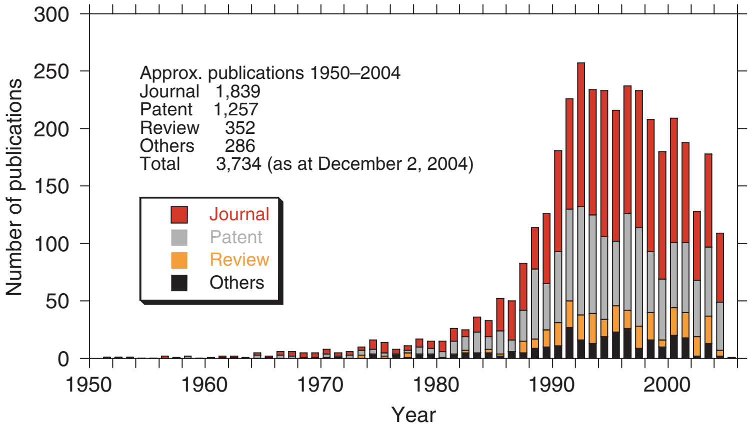


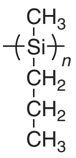
Figure 1 Annual polysilane publications since 1950.

This chapter aims to cover developments in polysilane synthesis and structure from 1993-1994 to 2004-2005. Short-chain cyclic and linear compounds are treated first, followed by long-chain polymers and finally branched systems. Given the vastness of the task apparent from Figure 1, coverage is necessarily selective, with an emphasis on the experimental, and the author regrets not being able to include many other thoroughly worthy and beautiful examples of research in the wider realms of polysilane chemistry, science, and technology.

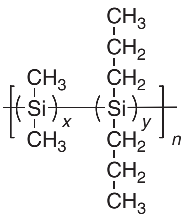
3.11.2 Nomenclature

IUPAC names are unambiguous, though it is possible for compounds to have more than one IUPAC acceptable name, and this applies to the polysilanes. As referring to the class of polymers, generally, "polysilane" is accepted.[2,3] Concerning individual polymers, since the monomers from which polysilanes are derived are usually different to the constitutional repeat unit (CRU), source-based names are not usually appropriate, and structure-based naming is preferred, for which the IUPAC rule for polymers is to give the name as poly(CRU). For the example of **1**, the name "poly(methyl-*n*-propylsilylene)" would thus be acceptable, although the rules imply that when a polysilane is considered as an organic single-strand polymer "poly(methyl-*n*-propylsilanediyl)" is preferred. The latter form is in occasional use in the literature. When considered as an inorganic single-strand polymer, the name becomes "*catena*-(methyl-*n*-propylsilicon)" or "poly(methyl-*n*-propylsilicon)," neither of which is in common use. Another commonly used variation for **1** would be "poly(methyl-*n*-propylsilane)," and though not the IUPAC recommended name, the utility of many semisystematic or trivial names is recognized and accepted.

Co-polymers are acceptably represented by either poly(CRU^A-*connective*-CRU^B) or *connective*-co-poly(CRU^A/CRU^B), where the connective is *co*, *ran*, *stat*, *alt*, *block*, *per*, *graft* (the connective *co* should not be used as a prefix in the latter co-polymer naming system), indicating respectively unspecified, random, statistical, alternating, periodic, block, or graft co-polymers. Structure **2** above would thus be named as poly(dimethylsilylene-*co*-di-*n*-propylsilylene), assuming a non-specified sequence of repeat units.



1



2

Concerning the nomenclature of higher-dimensionality silicon polymers such as networks, ladders, cages, and dendrimers, the variety of architectures possible is too great to treat concisely here, and the reader is directed to IUPAC sources.[2]

In this chapter, the general term "polysilanes" will be used, and homopolymers and co-polymers will be named according to the examples of **1** and **2** above as poly(methyl-*n*-propylsilylene) and poly(dimethylsilylene-*co*-di-*n*-propylsilylene), respectively.

3.11.3 Oligomers

Short polymer chains are often referred to as oligomers (*oligo*: Greek for "few"), and catenating chains of up to about 20 silicon atoms of relatively low molecular weight are usually termed oligosilanes. Generally, these materials are more soluble due to their lower molecular weight, and early work on polysilanes almost exclusively concerned these short-chain compounds (see chapter Organopolysilanes, COMC I (1982)). For these shorter-chain Si catenates, the experimentally recognized shift of the longest wavelength UV absorption maximum to progressively lower the energy as the chain length increases, due to the increasing degree of σ-electron delocalization, has also been systematically studied from theoretical perspectives.[4]

3.11.3.1 Synthesis of Oligosilanes

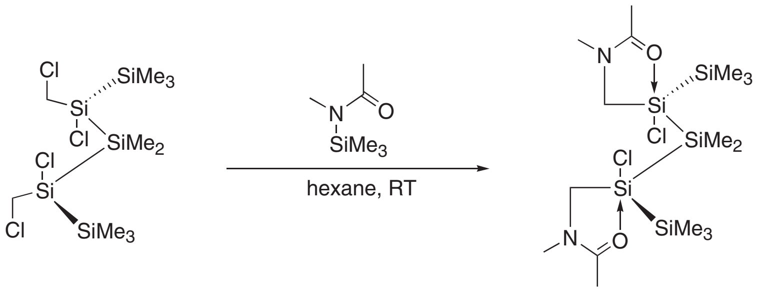
In its widest sense, the term oligosilane thus covers cyclic and linear silicon compounds, synthesized and isolable as either homomolecular species (e.g., $Me(SiMePr)_nMe$, where n has a unique value, i.e., a single molecule species of defined molecular weight and structure) or multimolecular species (e.g., $(SiMePr)_n$, where n does not have a unique value and the product is a mixture of different length molecules containing the same constitutional repeat unit). Oligosilanes were covered extensively in COMC I (1982) and COMC II (1995), and more recently in other reviews. Research covered in this section will be restricted to those topics which relate to the chemistry and photophysics of polysilane high polymers, in the context of which the oligomers are useful model compounds for the polymers, since they can often be isolated as homomolecular species, and their structures can often be determined more accurately (e.g., single crystal X-ray diffraction) and correlated more closely with their properties.

Synthesis is typically by alkali metal-mediated coupling of dichlorosilanes or 1,2-dichlorodisilanes, although electrochemical coupling of chlorosilanes and dehydrocoupling of primary and secondary silanes also often lead to oligomeric (as opposed to high polymer) fractions.

3.11.3.2 Conformational Studies: Oligosilanes as Models for High Polymers

Polysilane main-chain conformations constitute an enormous and often complex field of study. The silicon chain in polysilanes, despite the electronic delocalization, comprises Si–Si single bonds, about which rotation is possible. The approximately tetrahedral Si–Si–Si bond angle thus theoretically permits chains with any value of Si–Si–Si–Si dihedral angle, although both electronic and steric factors determine the actual conformation. The conformations are often temperature and pressure dependent, and there have been many studies, both theoretical and experimental, in solution and solid states, probing the conformation–property relationship in polysilane high polymers using the chromophoric and fluorophoric nature of the unique σ-electron delocalized main chain. X-ray studies have also provided much detailed information, although the difficulty of obtaining single crystals has precluded the most accurate single crystal diffraction studies. Oligosilanes have therefore been used as model compounds in conformational studies.

By the time of publication of COMC I (1982), little data on conformations were available, though it was reported that Si_4Me_{10} could adopt both *anti*- and *gauche*-rotameric conformations (see chapter Organopolysilanes, ref. 10, COMC I (1982)). In COMC II (1995), more emphasis was placed on the conformations of the high polymers. Experiments and calculations have moved symbiotically forward since then, stimulating each other. Interactions between substituents on silicons 1 and 4 in tetrasilanes were found to be responsible for splitting the *gauche*-state into two states with minima at $\omega \approx 55°$ and $90°$.[5] Matrix isolation IR and UV spectra of several Si_nH_{2n+2} oligosilanes were measured by Michl and co-workers and compared with the results of *ab initio* calculations to assign the spectra.[6] Calculations predicted dihedral angles ω of 180° and 57° for the n-Si_4H_{10} *anti*- and *gauche*-conformers and similar energies, though experimentally the *anti*-conformer was found to be the more stable in the matrix. The results



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Scheme 1 Preparation of conformationally constrained oligosilanes.

suggested that the conformation affects the intensity of the σ–σ^*-transition rather more than the energy. Further studies on other Si_nX_{2n+2} systems with larger substituents (where X = Cl,[7] Me,[8] SiH_3[8], or Et[9] indicated that interactions between substituents in positions 1 and 3 become important as their size increases, and that the *anti*-conformation becomes a transition state between two minima at around $\omega \approx 165°$. These findings led to the proposal to classify the conformations of linear chains into the six dihedral categories of *anti*, *A* (≈180°), *transoid*, *T* (≈165°), *deviant*, *D* (≈150°), *ortho*, *O* (≈90°), *gauche*, *G* (≈60°), and *cisoid*, *C* (≈40°).[10]

The desirability of experimental evidence concerning low-lying electronic states in conformationally fixed oligosilanes was recognized,[6] and elegant responses were provided by the groups of Tanaka[11] and Tamao.[12] Tanaka and co-workers prepared a pentasilane, **3**, containing two pentacoordinate silicon atoms in the 2 and 2′ positions by reaction of a bis(chloromethyl)-substituted pentasilane with *N*-methyl-*N*-trimethylsilylacetamide, as shown in Scheme 1.

Single crystal X-ray diffraction of **3** revealed that the backbone was in the *all-anti*-conformation. This chain-extended conformation was also reflected in the long wavelength UV absorption maximum of 257 nm in the solid (thin film) state, and was surprisingly maintained also in solution, suggesting locking of the backbone conformation. The conformational locking was corroborated by evaluation of the ^{29}Si NMR nOe η-values, which indicated essentially a dipole–dipole relaxation mechanism, and is characteristic of segmental motion-restricted chains. Calculations of potential energy as a function of dihedral angle correlated closely with the change of dipole moment as the dihedral angle was changed, as shown in Figure 2, providing strong evidence for an electronic origin of the locking effect, and it was postulated that cancellation of the strong dipole moments in the O–Si–Cl linkage when in the *all-anti* conformation is the driving force.[11]

Conversely, Tamao and co-workers constrained the Si chain in oligosilanes with 4, 6, 8, and 10 Si atoms to adopt an alternating *cisoid*- and *anti*-conformation using two tetramethylene tethers to further link the silicon atoms in each disilane unit, producing oligomers by the route shown in Scheme 2.[13]

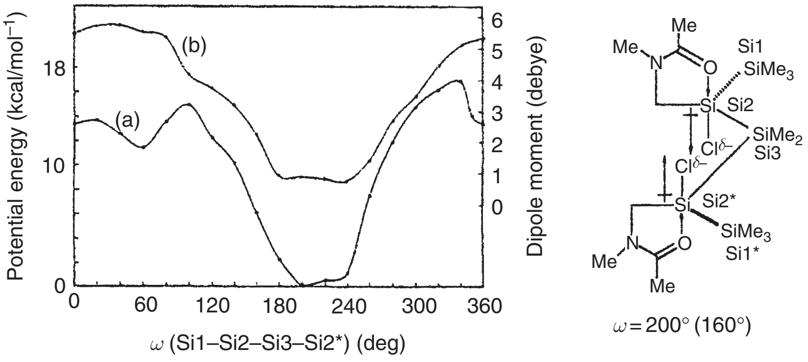
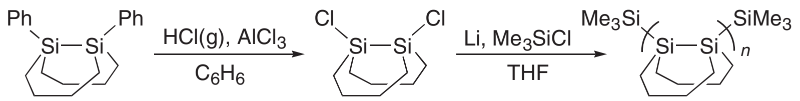


Figure 2 Correlation of potential energy and dipole moment change with dihedral angle, ω.[11] Reprinted with permission from El-Sayed, I.; Hatanaka, Y.; Onozawa, S.; Tanaka, M. *J. Am. Chem. Soc*. **2001**, *123*, 3597–3598. © 2001 American Chemical Society.



Scheme 2 Preparative route to *cisoid/anti*-constrained oligosilanes.

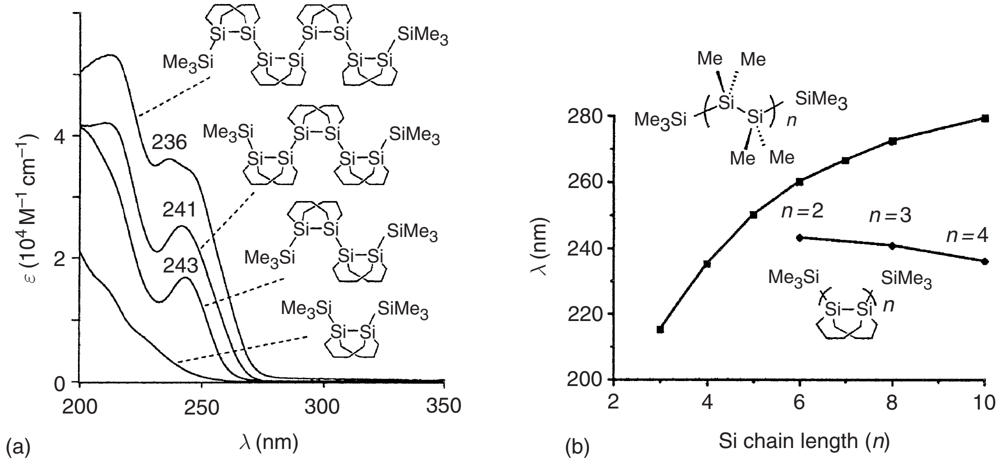
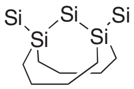


Figure 3 (a) UV absorption spectra of *cisoid/anti*-alternating oligosilanes with 4–10 Si atoms. (b) Comparison of UV absorption maxima of constrained and unconstrained oligosilanes.[13] Reprinted with permission from Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 25, 7486–7487. © 2003 American Chemical Society.

The oligomers were separated by recycling preparative gel permeation chromatography (GPC) and characterized by NMR, mass spectroscopy, and for the hexasilane by X-ray crystallography, which showed that the main chain had a *CAC* conformation, indicating preservation of the *cisoid* disilane configuration during oligomerization. The UV spectra showed an absorption maximum around 240 nm, which was almost unchanged as the chain length increased in remarkable contrast to those of similar unconstrained oligosilanes, as shown in Figure 3.

It is well recognized from numerous studies that as the degree of σ-electron delocalization increases, the HOMO–LUMO gap decreases, and the UV absorption maximum shifts to longer wavelength (see COMC II (1995), chapter Organopolysilanes, p 104, ref. 126). It was therefore concluded that the presence of the *cisoid* turn effectively suppressed the σ-conjugation in the oligosilane main chain.

Extending this methodology, Tamao and co-workers recently prepared a pentasilane, 4, containing a central trisilane unit constrained to the *all-anti* conformation by tethering with bis(tetramethylene) groups, as confirmed by single crystal X-ray diffraction.[14]



(Other substituents Me)

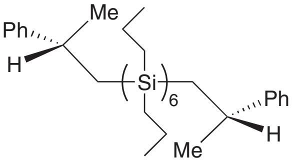
4

The UV spectrum of 4 showed a peak at 253 nm, red shifted by 3 nm compared with n-Si_5Me_{12}, indicating that the latter should not have an exactly *all-anti* conformation. This was confirmed by magnetic circular dichroism (MCD) which showed no Si–Si region absorption for the *all-anti* 4, but did show an absorption for n-Si_5Me_{12}.[14]

3.11.3.3 Oligosilane Chirality

In their study of the conformations of oligosilanes with methyl and ethyl substituents,[9] Michl and co-workers pinpointed the specific substituent–substituent interactions in tetrasilanes responsible for inducing *C*, *D*, and *A* conformations, allowing a prediction of backbone dihedral angle and direction of twist, given a specific arrangement of ethyl groups.

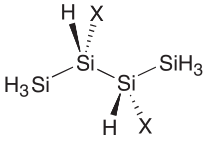
It was noted that this could also rationalize chirality transfer from side chain to main chain. Others have investigated extensively such side-chain to main-chain chirality transfer in the polysilane high polymers (see Section 3.11.6.1). Although the oligomers obtained as byproducts in the Wurtz-type coupling reactions employed do show optical activity, there have been few studies directed specifically toward chirality in oligosilanes. Main-chain chirality has also been induced in high polymers by substituting enantiopure chiral end groups, though the cooperative helical interactions are weak due to the low ratio of end groups to internal groups. In oligosilanes, where the ratio is much greater, chain end effects are stronger and helical chirality has been induced. Kira and co-workers prepared a hexasilane with *n*-propyl side chains and either (*R*)- or (*S*)-2-phenylpropyl terminal groups (**5**(*R*) denotes the (*R*)-substituted molecule; see also Section 3.11.5.3.1 on solid-state structure and Section 3.11.6.1.2 on higher-order structure below).[15]



5(*R*)

For the analogous decamer, at temperatures below 153 K, strong CD signals in the backbone σ–σ^*-transition region were observed, indicating chirality transfer. X-ray crystal structure analysis of the hexamer (see Figure 21 below) and MM2 calculations of the achiral model compound, tetradecapropylhexasilane, show loose helical structures, providing further evidence for chirality transfer.[15]

Most optically active polysilanes owe their optical activity to induced main-chain chirality, as outlined above. However, backbone silicon atoms with two different side-chain substituents are chiral. Long-chain catenates, however, are effectively internally racemized by the random stereochemistry at silicon, and inherent main-chain chirality is not observed. For oligosilanes, however, inherent main-chain chirality has been demonstrated. A series of 2,3-disubstituted tetrasilanes, $H_3Si[Si(H)X]_2SiH_3$ (where X = Ph, Cl, or Br), were obtained from octaphenylcyclotetrasilane and contain two chiral main-chain silicon atoms, **6**.[16] These give rise to four diastereoisomers: the optically active *S*,*S* and *R*,*R* forms, the activity of which is equal but opposite, resulting in a racemic (and consequently optically inactive) mixture and the two *meso*-forms, *S*,*R* and *R*,*S*, which are optically inactive by internal compensation. It is reported that the diastereoisomers could be distinguished in NMR and GC/MS experiments. For the case of 2-phenyltetrasilane, a racemic mixture of (*R*)- and (*S*)-enantiomers was obtained.

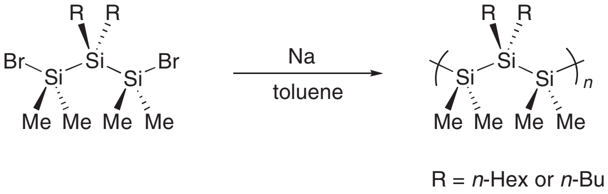


6

Since none of these forms could be isolated, optical activity was not observed. If, however, a chiral group X could be substituted, then such diasteroisomers should be separable.

3.11.3.4 Polymerization of Cyclics and Linear Species

The most common route to polysilane-high polymers is by the Wurtz-type alkali metal-mediated polycondensation of dichlorosilanes. However, α,ω-dihalooligosilanes can also be coupled in a similar manner. Wurtz-type polymerization of $BrSiMe_2SiR_2SiMe_2Br$ led to bimodal molecular weight distributions of alternating co-polymers of the type $(SiMe_2SiR_2SiMe_2)_n$ (R = hexyl or Bu),[17] as in Equation (1).



(1)

Analysis of the samples by pyrolysis-GC/MS and solution ^{29}Si NMR indicated that some randomization occurred due to cleavage of the original Si–Si bonds. The extent of randomization was significantly greater in the higher molecular weight fractions.

Disilanes and cyclic silanes can be polymerized via a number of routes, depending on their substituents, and are described in Section 3.11.4.

3.11.4 Synthesis of Polysilane High Polymers

Chains comprising more than about 20 catenating silicon atoms in the backbone are usually included within discussions on polysilane high polymers. The distinction between oligomers and polymers at about this number is fuzzy, though an approximate association of main-chain UV σ–σ^*-absorption maximum chain length dependency with these terms can be made, as indicated in Figure 4, by the superimposition of the labels and arrows on data from the literature.[18] For the compounds generally referred to as oligomers and lower molecular weight polymers, the UV λ_{max} moves to longer wavelength as the chain length is increased, due to the chain length being shorter than the conjugating segment length, whereas for the high polymers, there is only a slight dependency, as chain length is greater than conjugating segment length.

3.11.4.1 Advances in Synthesis

Kipping first discovered polysilanes in the 1920s when he condensed dichlorodiorganosilanes using sodium. This method, often referred to as the Wurtz-type (or Kipping) method, remains the most straightforward route to high molecular weight polysilanes and is typically carried out using molten sodium in boiling toluene. However, the reaction constituted a drawback in the functionalization of polysilanes, essentially limiting the choice of side-chain substituents to sodium-tolerant alkyl and aryl groups due to the very harsh reducing conditions employed, and afforded little regio- or stereocontrol. Limited to these functionalities, despite their unique optoelectronic properties and exciting potential for application, polysilanes found commercial exploitation only chemically as precursors to β-SiC, by virtue of the thermal rearrangement of side-chain carbon atoms to backbone positions to give polycarbosilanes, the pyrolysis of which affords β-SiC.[19,20] Since the publication of COMC II (1995), and seeking to expand control over polymer properties and morphology, the preparation of polymers with reactive functional groups, controlled stereochemistry, and controlled higher-order structure has thus been a major challenge.

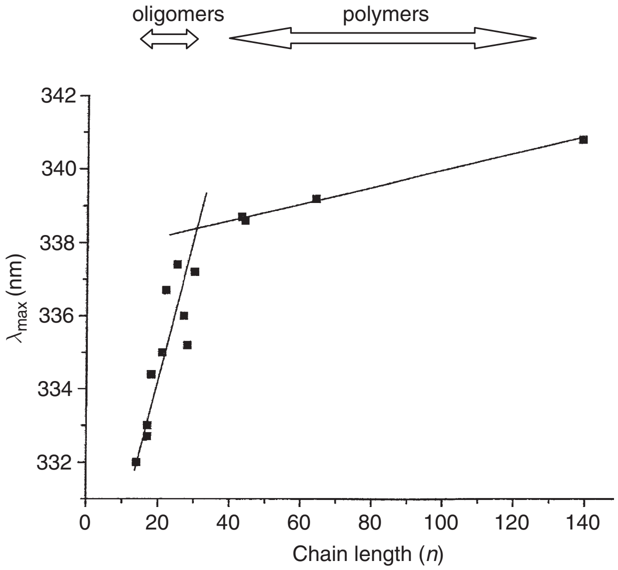


Figure 4 Dependency of main-chain UV σ–σ^* absorption maximum on chain length for poly(methylphenylsilylene) (PMPS) in toluene.[18] Adapted with permission from Jones, R. G.; Wong, W. K. C.; Holder, S. J. *Organometallics* **1998**, *17*, 59–64. © 1998 American Chemical Society.

This section covers advances in preparative methodology: evolution of the Wurtz-type (Kipping) process through a better understanding of its mechanism; syntheses with regio- and stereocontrol; polymerization of masked disilenes and ring-opening polymerization (ROP) of cyclic monomers; syntheses with functionalized monomers; syntheses allowing post-polymerization functionalization; dehydrocoupling; and other techniques. In many cases these methods are quite structure specific, so for the future, the same challenge to find a generally applicable synthetic methodology with the above requirements of functionality tolerance and control still exists.

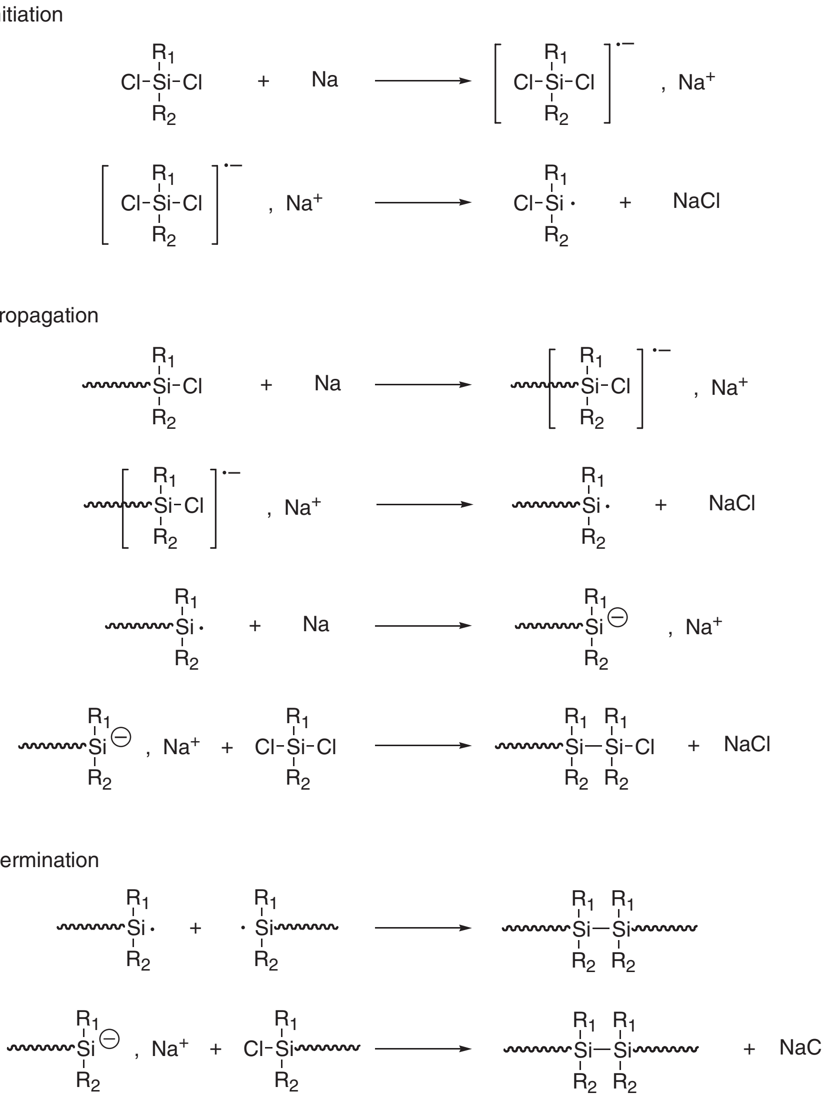
3.11.4.1.1 Wurtz-type metal-mediated reductive coupling of dihalosilanes

The Wurtz-type or Kipping coupling is still the most general route to polysilanes and operates by metal-mediated reductive dechlorination of bis-halogenated silicon monomers.[21] The reaction is widely used in polysilane synthesis and has been reviewed recently.[22] The procedure is often carried out using sodium in refluxing toluene (a good solvent for alkyl and aryl polysilanes), the boiling point of which is above the melting point of sodium (105 °C), thus ensuring continuous availability of fresh reductant surface. Alternative reductants are K, which due to its greater reactivity often leads to low molecular weight products,[23] Na–K alloy,[23] C_8K[24–29] which is useful for monomers with polar substituents, as described later in Section 3.11.4.2.1.(i), and which in the synthesis of poly(methylphenylsilylene) (PMPS) has been shown to lead to more stereoregular polymers, with a higher than usual isotactic triad content[26] (the more esoteric reducing metals, yttrium and pyrophoric lead, have been shown to give products with molecular weight of about 31,000 and 850, respectively, after 30 days,[30] but will not see widespread use). Use of 18-crown-6 with K and Na–K has also been reported.[31,32] At lower temperatures with solid sodium, the reaction in toluene essentially does not proceed for dialkyl-substituted monomers, although some success was reported using the additive 15-crown-5 in diethyl ether[33] and either ethyl acetate or 15-crown-5 in toluene at 65 °C;[34] phenyl-substituted monomers react faster and at temperatures below the melting point of sodium due to the stabilization of the silyl radical by the phenyl substituent.[23,35] Very recently, Holder, and co-workers published the results of a study of poly(dialkylsilylene)s aimed at increasing the yields in the Wurtz-type synthesis, and found that by carrying out the synthesis at room temperature in THF, crude yields in the range of 50–80% were achievable, and that after fractionation, the yield of high molecular weight fraction (M_n in the range 10,000–45,000) was typically 50–60%.[36] However, the use of THF, while promoting yield, does appear to have a deleterious effect on molecular weight as has also been noted by other workers.[23] Monomers are usually dialkyl- or diaryldichlorosilanes, since the harsh reaction conditions in the typical Wurtz coupling (molten sodium in toluene at 110 °C) limit the substituents on silicon to simple alkyl and aryl groups and the high polymers are non-polar, being insoluble in water and low alcohols. Heteroatom polysilanes with O or N attached directly to the silicon main chain usually cannot be prepared by Wurtz-type coupling of the heteroatom-substituted dichlorosilanes, as the alkoxy or amino functionalities are also good leaving groups and compete with chlorine,[37–40] although in a notable exception to this, Seki *et al.*[41] synthesized polysilanes with pyrrolyl groups directly attached through the nitrogen atom to the main chain. Functionalized side chains with remote *O*- or *N*-groups are more resistant toward the conditions in the Wurtz process, and a number of polymers with such substituents have been prepared and permit the preparation of polar polysilanes which can show hydrophilic character. These are described in the section below on functionalization. Polymerizations with two different dichlorosilane co-monomers lead to random co-polymers. Co-polymers with regularly alternating structures are best prepared using alternative synthetic strategies (see below), although creative use of the Wurtz-type coupling has been demonstrated. If two different silicon units are incorporated within the same monomer, then regularly alternating co-polymers can be prepared. West and co-workers showed that sodium-mediated coupling of α,ω-dibromotrisilanes of the type $Br–SiR_2–SiR^1{}_2–SiR_2–Br$ led to the regularly alternating co-polymers $(SiR_2–SiR^1{}_2–SiR_2)_n$.[17]

3.11.4.1.1.(i) Mechanism and polymodality

The currently accepted mechanism of the alkali metal-mediated Wurtz-type condensation of dichlorosilanes is essentially that outlined in COMC II (1995) (chapter Organopolysilanes, p 98) which derived from studies by Gautier and Worsfold,[42] and the groups of Matyjaszewski[43] and Jones,[22,44,45] a modified polymerization scheme of which is included here. The mechanism was deduced from careful observations on the progress of polymerizations in different solvents (such as those which better stabilize anions and those which do not), at different temperatures,[44] with additives, and with different alkali metal reductants. Silyl anions, silyl anion radicals,[42] and silyl radicals[28,46,47] are believed to be involved, as shown in Scheme 3.

Polymerizations often afford polymodal product molecular weight distributions,[18] with typically a low molecular weight fraction of several hundred daltons (fraction I), an intermediate fraction of about 4,000 (fraction II) and then a high molecular weight fraction of 10^5 or 10^6 (fraction III), though the relative proportions of the fractions depend



Scheme 3 Polysilane polymerization mechanism.[44] Reprinted with permission from Jones, R. G.; Budnik, U.; Holder, S. J.; Wong, W. K. C. *Macromolecules* **1996**, *29*, 8036–8046. © 1996 American Chemical Society.

greatly on many factors such as the substituents on silicon, solvent, alkali metal, and reaction temperature (see chapter Organopolysilanes, p 97, COMC II (1995)). The origin of the polymodality was previously understood to arise from (i) backbiting by a silyl anion chain end associated with the sodium surface forming the thermodynamically favorable five-and six-membered ring compounds (fraction I); (ii) the forcing of some shorter, growing, chains off the sodium surface due to the decreasing sodium surface area as reductant is consumed (fraction II); and (iii) the coupling of silyl radicals, terminating the reaction with formation of high molecular weight chains (fraction III). In the interval since COMC (1995), further studies have been carried out and a new explanation of the polymodality has been advanced. Particularly, it was required to account for the molecular weight of fraction II. A rationale based on a correlation of fraction II molecular weight (around 4,000) with maximum electronic stabilization was offered. Key to this idea is the polymer segment length: the degree of σ–σ^* conjugation in the chain increases as the chain length increases with the addition of repeat units "in a regular conformation," that is, *transoid* or *deviant*, up to about 35 or 40 backbone atoms in poly(methylphenylsilylene) (PMPS), after which there is no energetic advantage for maintaining the regular conformation, and the formation of a conformational defect (kink) becomes inevitable.[45] This length corresponds well with the molecular weight of fraction II.[18] The conjugation-suppressing kink (*gauche*-turn or helix reversal)[301] then diffuses from the free end along the chain toward the metal surface, where with maximum

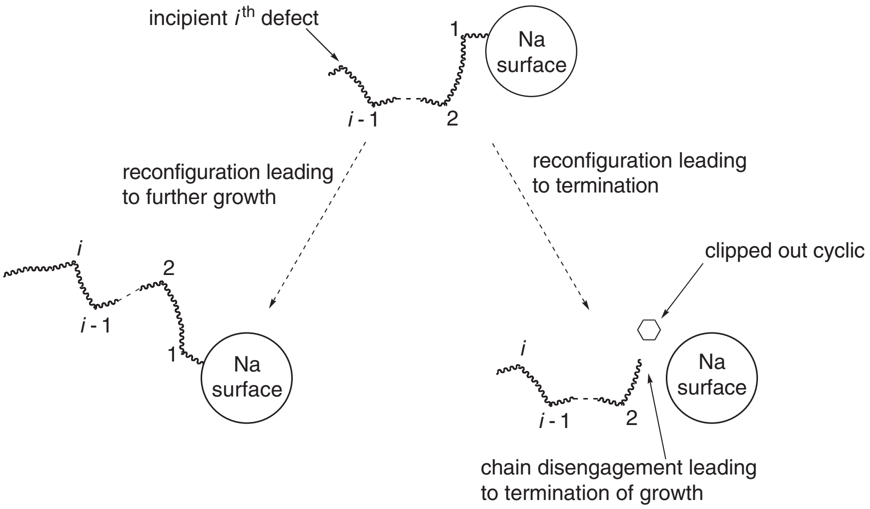


Figure 5 Schematic illustration of defect diffusion-controlled polymerization.[45] Reprinted with permission from McLeish, T. C. B.; Jones, R. G.; Holder, S. J. *Macromolecules* **2002**, *35*, 548–554. © 2002 American Chemical Society.

probability, backbiting to clip out a cyclic (due to the favorable conformation), and disengagement of the chain from the silicon surface to give a chain of about 35 silicon atoms (fraction II) may occur. This is shown schematically in Figure 5.

If backbiting does not occur, the mobile kink can diffuse away from the surface again, while the chain length continues to increase, though the probability of arrival at the sodium surface and backbiting/termination decrease. When the chain reaches double the segment length, a second kink is expected statistically, which may interact with the first so as to annihilate it, reducing even further the probability of chain disengagement. Thus, as the chain length increases, the probability of chain disengagement decreases, leading eventually to the highest molecular weight product, fraction III. Since the backbiting reaction is thermally activated, it has been suggested that lower-temperature polymerizations should result in greater predominance of fraction III, although yields would be lower,[18] and suitable anion-stabilizing solvent/additive systems must be used, as noted above.

Despite the apparent simplicity of the condensation reaction itself, the mechanism is thus quite complex, and discussions on the nature of the intermediates and also end products[48] continue. Supporting evidence for the intermediacy of silyl radicals was afforded by Si–H bands in the IR spectra of products[46,47,49] generated in solvents susceptible to hydrogen atom abstraction by radicals, and there is also IR evidence for siloxy linkages,[33] although chains were generally considered to be Cl-terminated, at least for phenyl-containing polymers.[35,44] Very recently, however, evidence for H-terminated polymers has been published for a number of symmetrically and asymmetrically substituted poly(dialkylsilylene)s. The Si–H stretch intensity decreased with increasing molecular weight, suggesting their presence as end groups; ^{1}H, ^{29}Si, and {^{1}H–^{29}Si}heteronuclear correlation spectroscopy showed only Si–H end groups, with no evidence for Si–Cl, Si–OH, or Si–OR groups. These data strongly support the supposition of silyl radicals. The use of the Si–H group in further functionalization was also recognized.[48]

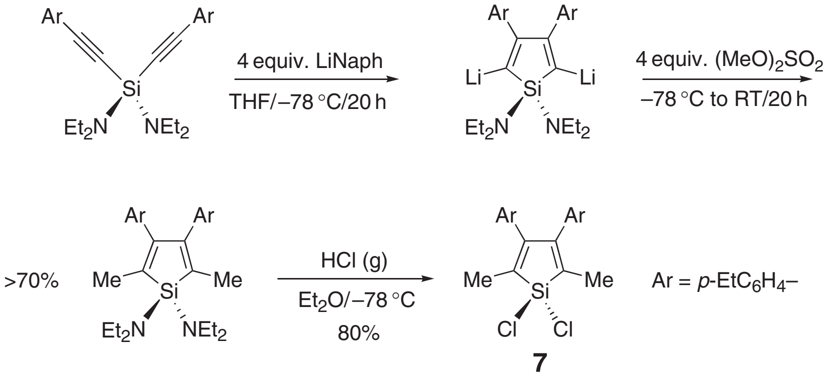
3.11.4.1.1.(ii) Ultrasonic activation

Ultrasonic activation was also reported prior to COMC II (1995). Effects on reaction times, yields, and polymodality were discussed[50–52] and briefly mentioned in COMC II (1995) (chapter on Organopolysilanes, p 97). Since then, more detailed studies on the sonochemical synthesis of polysilanes, comparing the Wurtz reaction with and without ultrasound and reporting on the effects of silicon substituents, solvents, alkali metals, and reaction temperature, have been reported[23] and summarized in a book chapter.[53] As ultrasound source, both an ultrasonic cleaning bath and an immersion probe were used, although the latter was preferred due to the greater temperature control and reproducibility afforded.[23] Ultrasound-induced cavitational erosion of the alkali metal is first used to generate an alkali metal dispersion (about 1 h for sodium, depending on source, and about one-sixth of that time for potassium) and then facilitates further reaction by regenerating fresh reductant surface. Ultrasonically assisted polymerization can be performed at lower reaction temperatures (typically around 60 °C) and results in monomodal polymeric fractions (cyclics are formed). The formation of a single polymeric fraction is the result of ultrasonically induced shear forces which selectively degrade higher molecular weight chains to a limiting value of about 50 000, concommitantly reducing the polydispersity index (PDI) (equal to M_w/M_n) to around 1.2. Interestingly, the sonochemical polymerization of di-*n*-hexyldichlorosilane cannot be performed at 60 °C and requires 80 °C. At this temperature, the vapor pressure of toluene is too high to form bubbles and cavities, thus reducing the shear forces, and resulting in higher molecular weight products and higher PDI. Use of K as reductant in the synthesis of PMPS led to low molecular weight and cyclic polysilanes and also to toluene-incorporated polymers, though for poly(dihexylsilylene) (PDHS), Na–K alloy and K gave good results. The optimum conditions for sonochemical polysilane synthesis using a probe-type sonicator, at least in the cases of PMPS and PDHS, were found to be: initial monomer concentration ca. 0.30 M; reaction temperature ca. 60 °C; polymerization solvent toluene; initial metal : monomer ratio ca. 2.3; alkali metal reductant: Na for PMPS and K for PDHS. Finally, it was noted that the high local temperatures and pressures during sonication have little, if any, effect on the polymerization reaction.[23]

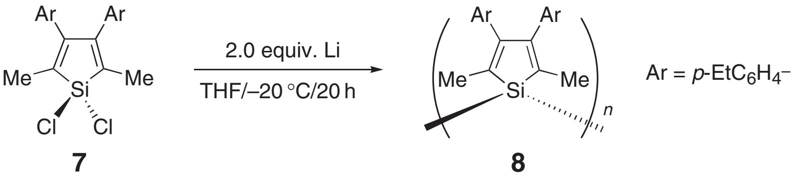
3.11.4.1.1.(iii) Poly(1,1-silole)s

These are polysilanes in which each CRU is a silole ring catenating through the silicon atom, and constitute a new class of polysilanes since COMC II (1995),[54–56] which had previously been the subject of theoretical investigations.[57] Rather unusually, these polymers were found to be accessible via Wurtz-type coupling of 1,1-dichlorosilole monomers using lithium in THF at −20 °C for 20 h (using sodium, only oligomers could be prepared, which appeared from the IR spectra to contain Si–O–Si linkages).[54,55] Another key issue for successful polymerization was monomer structure: small groups (Me) were necessary in silole positions 2 and 5 in order to reduce steric congestion, and *para*-ethyl groups were substituted on the phenyls in silole positions 3 and 4 in order to increase solubility, as shown in Scheme 4 and Scheme 5.

Complex 8 showed unique chemical reactivity, degrading completely to the dilithiosilole in the presence of excess lithium. Conventional polysilanes, in contrast, are degraded to oligomers. Rather surprisingly, however, the UV absorption spectrum of 8 (λ_{max} = 320 nm (sh); M_n = 6,300, M_w/M_n = 1.14) is not significantly different to its conventional polysilane counterparts, though the fluorescence, excited at the UV absorption maximum, shows a large Stokes shift (emission λ_{max} = 460 nm),[55] indicating significant differences between ground and excited states.



Scheme 4 Synthesis of 1,1-dichlorosilole monomer, 7.



Scheme 5 Formation of poly(1,1-silole), 8, by Li-mediated Wurtz-type coupling.

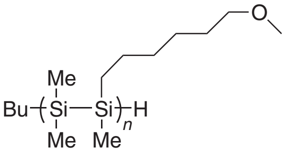
3.11.4.1.2 Polymerization of masked/*in situ* disilenes

The Wurtz-type dechlorinative reductive coupling generally restricts the products to those containing alkyl or aryl groups at silicon. Also, there is little control over co-polymer structure, molecular weight, or molecular weight distribution. As a result, other polysilane synthetic methodologies, both general and specific, were (and are) required. An elegant and versatile route from phenyldisilabicyclooctadienes, referred to as "masked disilenes,"[58–61] was developed by Sakurai and co-workers, and initial developments in this field were covered in COMC II (1995) (see chapter Organopolysilanes, pp 98–99). A typical example of the methodology is shown in Scheme 6: 2,2,3,3-tetraalkyl-1-phenyl-2,3-disila-bicyclo[2.2.2]octa-5,7-diene, **9**, is prepared and then anionically polymerized to give the co-polymer, **10**.

In this method, attack by an anionic initiator (*n*-BuLi, potassium alkoxides/cryptand[2.2.2],[62] or silyl anions in benzene)[63] occurs regioselectively on the less hindered silicon of **9**, resulting in an anionically terminated disilanyl-lithium which then attacks another monomer at the less hindered silicon atom. The process continues rapidly (the reaction is usually complete within a few minutes) in a "living" polymerization fashion to yield **10** on alcohol workup.

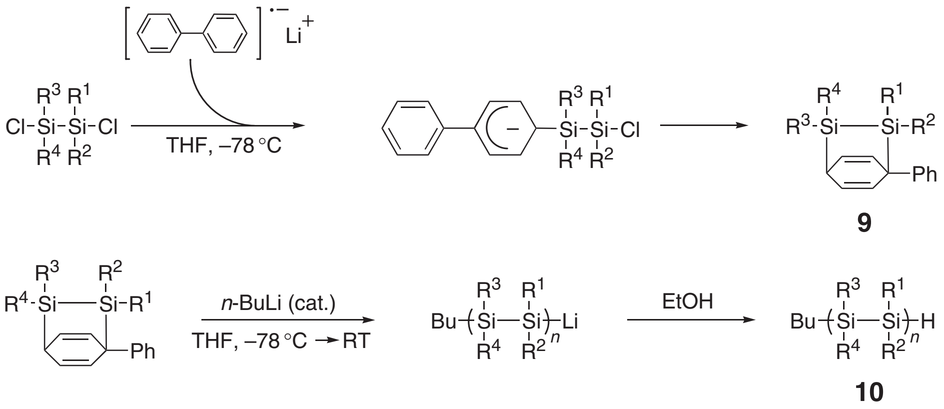
Through this method, greater control can be exercised over polymer structure and molecular weight. Where group R^1 is *n*-propyl and R^2, R^3, and R^4 are methyl, the monomer **9** is formed regioselectively, and polymerization affords the regularly alternating head-to-tail (H–T) co-polymer poly(dimethylsilylene-*alt*-methyl-*n*-propylsilylene). The greater the difference between the steric requirements of the two silicon atoms, the greater the regioselectivity, though if the groups are too bulky, polymerization may not be possible.[64,65] The high structural regularity of the polymers was confirmed by NMR and also reflected in the solubility characteristics: the polymer obtained from the monomer with $R^1 = R^2 = n\text{-Pr}$ and $R^3 = R^4 = \text{Me}$ was found to be insoluble due to the high crystallinity resulting from the high degree of H–T structural order. In contrast, the constitutionally related co-polymer with the same CRU but prepared by Wurtz-type coupling of 1,2-dichloro-1,1-dimethyl-2,2-di-*n*-propyldisilane was found to be soluble, due to the random sequence with both H–T and head-to-head (H–H) coupling.[64]

Using this approach, a series of dialkylamino heteroatom polysilanes was prepared (see Section 3.11.4.2) and also a remote *O*-functionalized polysilane, bearing a 6-methoxyhexyl ether group, **11**.[60,66]

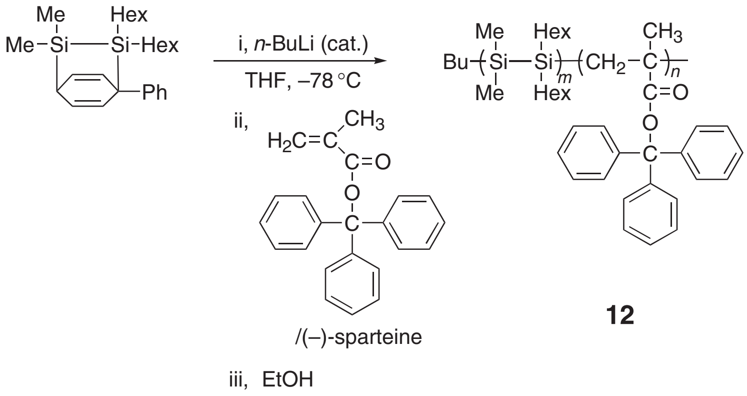


11

Complex **11** formed good Langmuir–Blodgett (LB) films, which could be transferred to hydrophilic and hydrophobic quartz surfaces. On the former, the UV $\lambda_{\max}$ was found to be 322 nm, and on the latter, 306 nm. This remarkable chromism originates in the chain extension induced by hydrogen bonding with the hydrophilic surface. In



Scheme 6 "Masked disilene" route to regularly alternating co-polymers.



12

Scheme 7 Helical sense programming from masked disilene.

the absence of this, on the hydrophobic surface, the chain forms a collapsed globule with concommitantly reduced σ-conjugation and UV spectral blue shift. Complex **11** also showed piezochromism, as described in Section 3.11.5.4.[67]

The masked disilene approach results in an anionic terminus on the initally formed polymer chain. As noted in COMC II (1995) II (chapter Organopolysilanes, p 99), this can then be applied in the synthesis of polysilane block co-polymers with other alkenes. An interesting example of this was published in 2001. An anionically terminated polysilanyllithium was used to initiate polymerization of triphenylmethyl methacrylate in the presence of the optical activity inducing chiral amine, (−)-sparteine, to form the block co-polymer, poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(triphenylmethyl methacrylate), PMHS-*b*-PTrMA, **12**, as shown in Scheme 7.[68] Under these conditions, the PTrMA part of **12** was formed with a single helical screw sense, as evidenced by positive Cotton effects at 210 nm in the CD spectrum. At temperatures above −20 °C, the polysilane chain adopts a random coil, consistent with a UV absorption at 310 nm and lack of bands in the CD spectrum. Below −20 °C, a new UV absorption is evident at 340 nm, with a coincident positive Cotton effect in the CD spectrum. The bathochromic UV shift on lowering the temperature indicates a new, more extended, conformation, while the growth of the CD band indicates that the conformation is helical. The evidence thus suggests a *transoid* helical conformation. Increasing the temperature resulted in loss of the polysilane CD signal, but on reducing the temperature again, the CD signal was restored. The experiment showed that chiral information could be stored in the PTrMA part and transfered to induce preferential screw sense (PSS) helical chirality in the attached PMHS part, a phenomenon which the authors termed “helical sense programming.”[68]

Similarly, use of the chiral anionic initiator (+) or (−) potassium menthoxide with the same masked disilene afforded a polysilane with a PSS helical conformation. Optically active polysilanes are discussed further in Section 3.11.6.

In another elegant application of the masked disilene method, the anionic polysilanyl chain ends were chemically bound to substrate surfaces to form end-graft polysilanes. These systems are discussed in Section 3.11.4.2.3.

The masked disilene approach, while offering major improvements in polymer structural control, has a few drawbacks: monomers bearing bulky groups (e.g., 1,1-di-*i*-Bu, aryl) and Si–OR substituents cannot be polymerized; the overall synthetic scheme from commonly available reagents is rather involved. Despite these, however, the route remains attractive, and further developments, such as in the control of stereochemistry, will likely be explored.

3.11.4.1.3 Dehydropolymerization

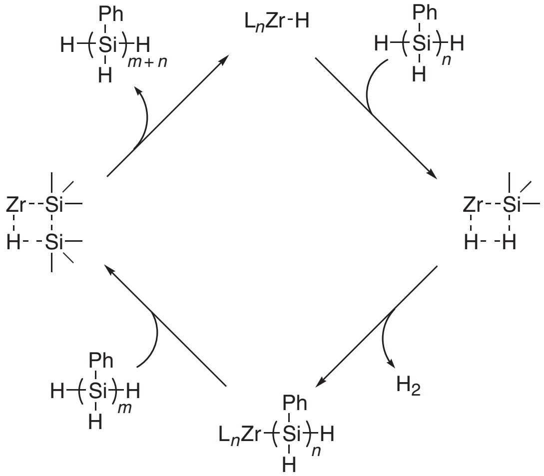
There are two approaches to dehydropolymerization: one using early transition metal catalysts and the other using late transition metal catalysts. Concerning the first, more intensively investigated and widely applicable, method, much research has been carried out in the field since the stimulating report in 1985 by Harrod and co-workers that polysilanes with moderate molecular weights could be prepared.[69] Investigations into various aspects of the method were covered in COMC II (1995) (chapter on Organopolysilanes, pp 99–100), and a number of mechanisms were proposed for the reaction, including silylene,[70,71] radical,[72,73] and oxidative addition/reductive elimination[74]-based routes. Currently, the most widely accepted mechanism[75] is an alternative σ-bond metathesis mechanism based on detailed kinetic and mechanistic investigations by Tilley and co-workers, although the lack of catalytic metal center-derived stereochemical control during chain growth has been discussed as implicating radical reactions.[76] Several reviews have also been published,[77–80] the most recent and comprehensive being a 30-year review on the area by Corey, published in 2004.[80a] Concerning the second, late transition metal, method by which generally only low molecular weight oligomeric materials are accessible, there are very few reports. In this section, a brief overview of the methods is given followed by recent developments.

3.11.4.1.3.(i) Early transition metal-catalyzed dehydrocoupling

In a typical early transition metal-catalyzed dehydrocoupling reaction,[81] a primary silane (best results appear to be achieved for $PhSiH_3$) is polymerized in the neat liquid state using a d^0-derivatized group 4 metallocene catalyst, with optimum results being found for the "mixed ring" zirconium complex, $CpCp^*Zr[Si(SiMe_3)_3]Me$, due to the good balance of steric properties, according to the mechanism of Tilley[75] expressed in Scheme 8.

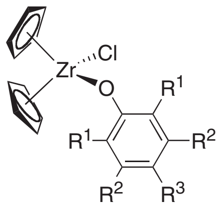
Since COMC II (1995), published work in this area has included several studies of the influence of catalyst and monomer structure on the dehydropolymerization of silanes, as this likely affect the chemistry of polymer chain growth.

The catalytically active species is considered to be a coordinatively unsaturated metal hydride which is formed from the added catalyst precursor during an induction period.[81] Ti-, Zr-, and Hf-based catalysts have been compared,[77,79,82,83] with those of Zr generally showing the highest catalytic activity and affording the highest molecular weight polymers corresponding to linear chains of up to 100 catenating Si atoms. The greatest M_w achieved to date using the dehydrocoupling approach is 13,800, for the $[CpCp^*ZrH_2]_2$-catalyzed coupling of $PhSiH_3$ (for which $M_n = 5{,}660$).[81] Although the hydride derivatives are the most effective catalysts, presumably due to the fact that the M–H bond is pre-existing, and thus no precatalyst induction period to form the M–H bond is necessary, the synthesis and handling of these compounds is more difficult.[81] Other modifications such as the use of cationic 14-electron zirconocene derivatives or complexes with chelating $Me_2Si(\eta^5\text{-}C_5H_4)_2$ ligands appear inefficacious. Two different groups reported comparisons of the use of zirconocene derivatives with chiral and achiral substituents to couple phenylsilane[76] and *p*-tolylsilane.[84] Despite affording stereocontrol in group 4 metallocene-catalyzed polymerization of olefins, it was found that chiral substitution of the metallocene Cp rings had no effect on the tacticity of the polysilane chain. Another study investigated the use of the group 4 metallocenefluorides Cp_2MF_2 (M = Ti or Zr) as catalysts,[85] since it was reported that a titanium(III) hydride was formed from Cp_2TiF_2 using $PhSiH_3$, the driving force of the conversion being the formation of the very stable Si–F bond.[86] Reaction of Cp_2TiF_2 with $PhSiH_3$ resulted initially in the vigorous evolution of hydrogen. The reaction continued slowly for about a week and was investigated using EPR, although it was unclear whether the Ti(III) compounds observed were part of the catalytic cycle (no EPR signals were observed in the case of Zr). Interestingly, a polymerization reaction carried out in the presence of diethylamine yielded a 50% diethylamino-substituted product. The molecular weights of the products were rather low, indicating a DP of about 20 (see Harrod's guideline in Ref: 81 for estimation of degree of polymerization (DP) from M_n values for polyphenylsilane). Neither catalyst was effective for preparing linear polymers from the disilane, $H_2MeSiSiMeH_2$.[85] Dehydropolymerization reactions are terminated by exposing the reaction mixture to air which



Scheme 8 σ-Bond metathesis polymerization mechanism proposed in Zr-catalyzed dehydrocoupling.

renders the catalyst inactive by oxidation. Corriu and co-workers found that Cp_2TiMe_2 and Cp_2TiCl_2/*n*-BuLi catalysts are deactivated by oxygen to a latent catalytic species, which, upon heating, regenerates an active catalyst.[87] Developing these ideas, the same group then studied aryloxy-substituted metallocene catalysts and found them to be stable, tunable dehydrocoupling catalyst precursors, which on gentle heating (50 °C, 15 min) with the monomer formed the active M–H catalyst.[88] A related study considered catalysts generated from the reaction of chloro(aryloxy)-substituted Cp_2Zr complexes **13** with 1 equiv. of *n*-BuLi.[89]



13a: R^1 = *t*-Bu; R^2 = H; R^3 = Me
13b: R^1 = *i*-Pr; R^2 = R^3 = H
13c: R^1 = R^2 = R^3 = H
13d: R^1 = R^2 = R^3 = F
13e: R^1 = OMe; R^2 = R^3 = H

The presence of sterically demanding **13a** or electron-withdrawing **13d** metal substituents resulted in higher molecular weights and shorter reaction times. Additionally, **13a** was successfully used to polymerize monomers with donor S, O, and N groups on the phenyl ring, although the product molecular weights were low. It was mentioned that coordination of the donor groups in such monomers to the metal center in conventional zirconocene-based catalysts could be responsible for the inhibition of polymerization.[89] Incorporation of other electronegative substituents on the Cp_2MY_2 metal center (where $Y = NMe_2$, OPh, and F) has also been reported together with the effect of these catalysts on primary, secondary, and tertiary silanes: for $PhSiH_3$, polymerization occurred together with H/Y exchange; for $PhMeSiH_2$, H/Y exchanged products and disilane were formed, but no polymer; for Ph_2MeSiH, only H/Y exchange occurred, with no coupling.[90]

At about the same time, another group reported studies into the effect of monomer structure on the dehydropolymerization reaction using Cp_2ZrMe_2.[91] The presence of electron-withdrawing and/or less sterically demanding substituents on the monomer was also found to result in higher molecular weight polymers. In contrast to the studies[89] above, however, the formation of polymers from the donor *O*-bearing monomers *p*-methoxyphenylsilane and *p*-isopropoxyphenylsilane was successful, albeit with low molecular weight ($M_n = 2{,}000$).

The product from the dehydrocoupling of $PhSiH_3$, poly(phenyl(H)silylene), can itself be used as a precursor polymer for further functionalization, using the susceptibility of the Si–H functionality to radical attack, as is described in Section 3.11.4.2.

3.11.4.1.3.(ii) Late transition metal-catalyzed dehydrocoupling

This topic was not covered in COMC II (1995), since at that time there had been no reports on the synthesis of even moderate molecular weight polysilanes. In 1997, a communication was published describing the preparation of polymers with molecular weight up to about 40,000 by dehydrocoupling of the secondary silanes, diethylsilane, and hexylmethylsilane, using the platinum-based catalyst, $Pt(COD)_2$.[92] The respective polymers, poly(diethylsilylene), **14**, and poly(hexylmethylsilylene), **15**, were reported to be synthesized with reasonable molecular weight and in good yield (for **14**: $M_w = 39{,}000$, $M_n = 38{,}000$; 38%; for **15**: $M_w = 25{,}000$, $M_n = 15{,}000$; 46%). The reported UV λ_{max} of these two polymers (268 nm for **14** and 290 nm for **15**), however, are at somewhat shorter than expected wavelengths, considering the molecular weights. Phenyl-substituted monomers were found to undergo redistribution reactions, though polymerization of silafluorene was reported to afford poly(silafluorene) ($M_w = 8{,}100$, $M_n = 3{,}200$; 47%; UV: 281, 290, 327 nm), which can also be considered as a poly(silole). Despite the apparent success and promise of the method, this work was not followed up. A year later, a report appeared describing the use of the indenyl Ni-based alkene polymerization catalyst: $[(1\text{-MeInd})Ni(PPh_3)Cl]$ reacts with $AgBF_4$, $AlCl_3$, methylaluminoxane, or $LiAlH_4$ to produce intermediates which catalyze the dehydropolymerization of $PhSiH_3$.[93] In a book chapter, successful dehydropolymerization of 1,2-dimethyldisilane using Wilkinson's catalyst, $[Pd(allyl)_2Cl_2]$, or $[Pd(dba)_2]$ affording polymers with M_w up to 19,000 (PDI = 1.5) was described.[94] Based on the observation of the redistribution product Ph_2SiH_2, and previous work on the reaction of $[Pt(PEt_3)_3]$ with the more sterically demanding disilane 1,1,2,2-tetramethyldisilane in which redistribution occurred,[80] a similar redistribution mechansim was assumed to be operative, although the participation of silylenes was not clarified.[94] In general, while dehydrocoupling using late transition metal catalysts is useful for preparing oligomers,[95] it is still not a viable technique for producing high molecular weight polysilanes.

3.11.4.1.4 Ring-opening polymerization (ROP)

By 1993, little work on the preparation of polysilanes by ROP had been reported, and in COMC II (1995), two examples were described (chapter Organopolysilanes, p 100): the anionic ROP of the *all-anti*-cyclotetrasilane $(MePhSi)_4$, initiated by *n*-BuLi or Me_2PhSiK[96,97] and the thermally initiated ROP of $(MePrSi)_4$ and $(MeHexSi)_4$.[98] In neither of these is the stereoselectivity high, due to the very high reactivity of the butyllithium or silylpotassium in the former case, or the radical nature in the latter case. In the former case, if the reaction is not terminated, backbiting can occur, resulting in polymer degradation within 5 min.[99] Since then, considerable research and several reviews[61,100] have been published on the area.

Successful ROP depends on the negative enthalpy changes, in particular, the release of ring strain energy, outweighing the negative entropy changes (many monomer molecules combine to form a single polymer molecule) to give an overall negative free energy change. There is thus a requirement for considerable ring strain in the silacycle monomer: sufficient strain is found in three- and four-membered rings, five-membered rings are borderline; larger rings rarely undergo ROP. There is also a requirement for low temperature (assuming a negative entropy term): ROP only occurs below a certain critical temperature called the ceiling temperature, T_c, which is also related to the monomer concentration, as shown in Equation (2). The initial monomer concentration, $[M]_0$, must be greater than the equilibrium monomer concentration, $[M]_e$:[100]

$$T_c = \frac{\Delta H_p{}^{o}}{\Delta S_p{}^{o} + R\ln[M]_0} \tag{2}$$

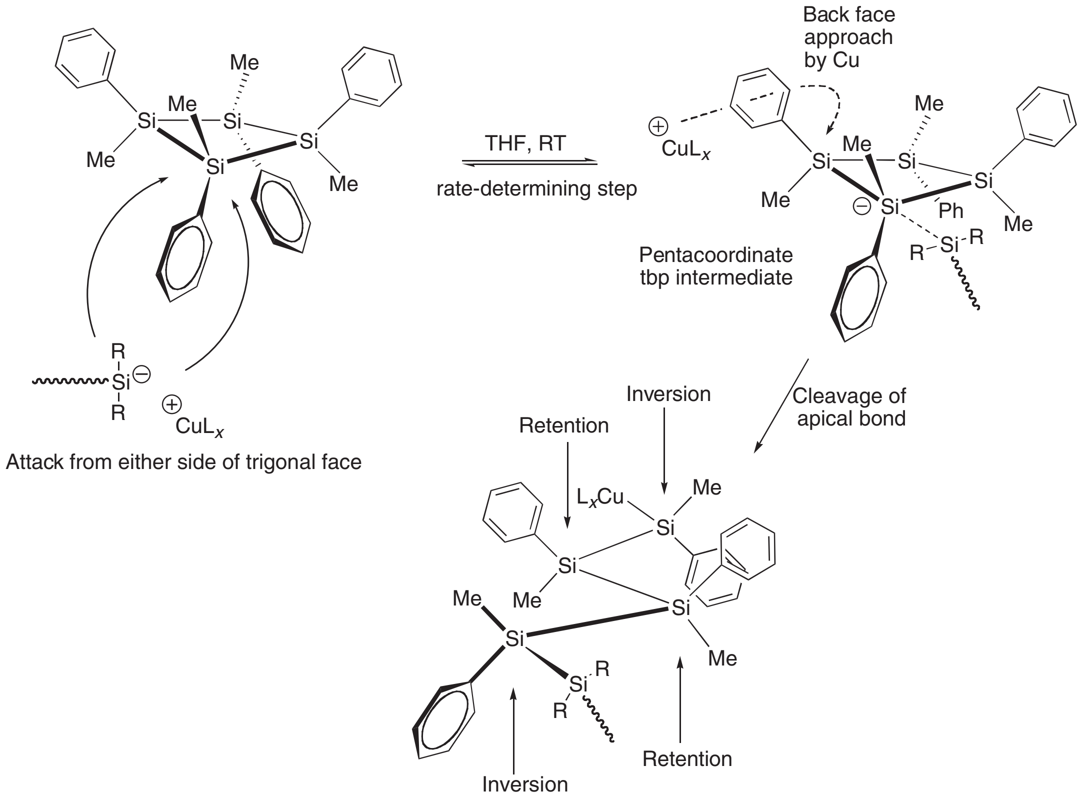
3.11.4.1.4.(i) ROP of four-membered ring monomers

Since COMC (1995), efforts have been made to better control chemo-, regio-, and stereoselectivities, and with this aim, less active, bulkier, silyl cuprate catalysts were investigated.[99,101] In contrast to the *n*-BuLi-catalyzed system, when the catalyst $(PhMe_2Si)_2Cu(CN)Li$ was used in the ROP of the *all-anti* isomer of $(MePhSi)_4$, no depolymerization by backbiting was observed, even after 2 h. ROP also occurred with greater selectivity, leading to reduced macrocycle formation, and most significantly, polymers with controlled microstructure, due to the preferential stereochemistry of the ring-opening process when the propagating anion attacks monomer rings with defined configurations. As shown in Scheme 9, the propagating reactive silyl chain end can attack a new monomer ring Si atom through either trigonal Me–Ph–Si face in a rate-determining step to form an intermediate containing a trigonal-bipyramidal pentacoordinate silicon atom, with the bulkier Si chain and adjacent ring silicon groups in apical positions.[100] Cleavage of the apical ring Si–Si bond occurs, affording a new Cu-terminated silyl end of a polymer chain, now four main-chain atoms longer. A key question was whether the ring cleavage proceeded with inversion or retention of configuration at both attacked Si and new chain end Si. ^{29}Si NMR data clearly showed peaks due to heterotactic (δ −38.5 ppm), syndiotactic (δ −39.0 ppm), and isotactic (δ −41.0 ppm) triads in the ratio expected for two inversions,[100] and also permitted a correction of the previous assignments of these triads. In contrast, *n*-BuLi/[2.1.1] cryptand-initiated ROP afforded PMPS with partially racemized chain end Si, which was considered to be due to the greater ease of pyramidal atomic inversion of the silyl end when the counterion was cryptated Li^+, as opposed to cuprate.

3.11.4.1.4.(ii) Photochemical ring-opening polymerization

A unique synthetic approach to polysilanes based on the solid-state ROP of crystalline octachlorocyclotetrasilane, $(SiCl_2)_4$, **16**, to give perchloropolysilane, $(SiCl_2)_n$, **17**, has been reported. In a single crystal X-ray crystallographic analysis[102] of **16**, it was noted that the planar, centrosymmetric $(SiCl_2)_4$ rings are held adjacent to each other within the solid crystal lattice in a step-like array, as shown in Figure 6. The unit cell was monoclinic ($P2_1/n$ with dimensions of $a = 4.0569(10)$, $b = 6.783(2)$, $c = 13.346(3)$ Å; $\beta = 104.6800(10)°$). The Si–Si bond lengths are 2.372(2) Å (slightly longer than normal; 2.34 Å is typical), consistent with a strained ring; the Si–Si–Si bond angles are 90.12(5)° and 89.88(5)°, and the Cl–Si–Cl bond angles are 112.17(7)° and 111.84(7)°.

On photolysis, the bright yellow crystals of **16** became off-white in color, but retained their crystalline nature. Single crystal X-ray diffraction[103] of the product, **17**, revealed infinite parallel-aligned *all-anti* chains of $SiCl_2$ repeat units in an orthorhombic unit cell ($P2_12_12_1$ with dimensions of $a = 7.3255(2)$, $b = 7.1815(2)$, $c = 13.2844(4)$ Å), as shown in Figure 7. The Si–Si bond length is 2.414(8) Å, even longer than in the ring monomer; the Si–Si–Si bond angles are 114.4(6)° and the Cl–Si–Cl bond angles are 111.0(4)°.



Scheme 9 Mechanism of anionically initiated ROP formation of polysilanes.

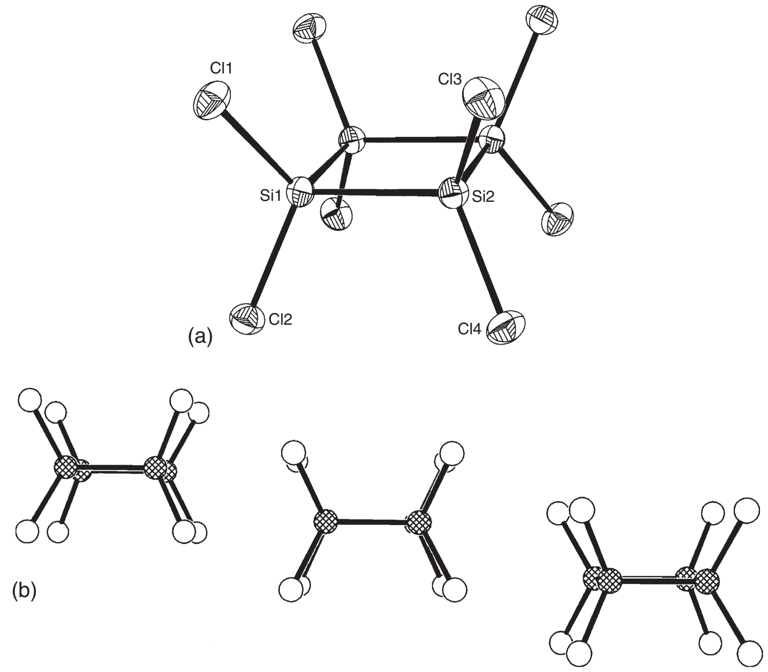


Figure 6 X-ray structure of 16, showing (a) single molecule and (b) arrangement of molecules within lattice.[102] (a) Reprinted with permission from Koe, J. R.; Powell, D. R.; Buffy, J. J.; West, R. *Polyhedron* **1998**, *17*, 1791–1793. © 1998 Elsevier.

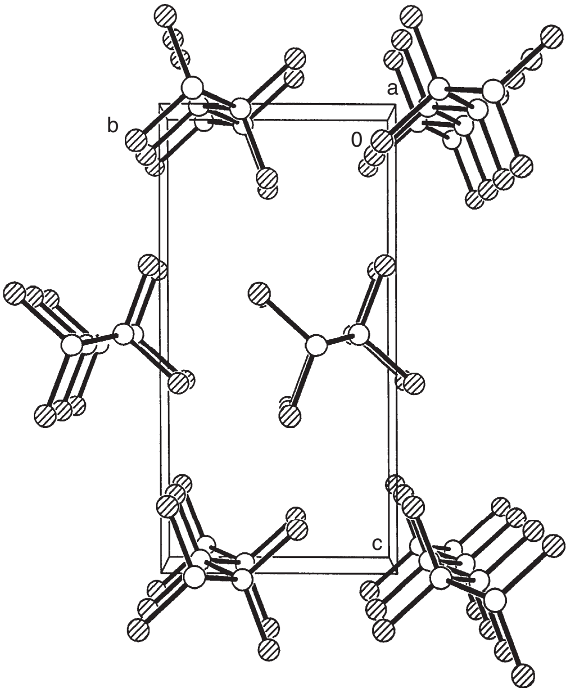


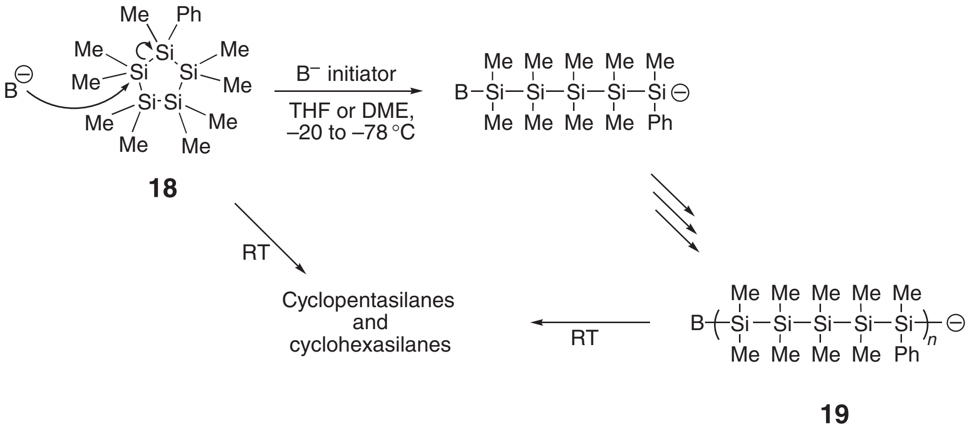
Figure 7 Single crystal X-ray structure of **17**, showing chains of linked $SiCl_2$ units.[103] Reprinted with permission from Koe, J. R.; Powell, D. R.; Hayase, S.; Buffy, J. J.; West, R. *Angew. Chem. Int. Ed.* **1998**, *37*, 1441–1442. © 1998 Wiley-VCH.

It is well known that the Si–Si bond is photochemically labile, affording radical cleavage products. Normally these react rapidly with molecules in the surrounding medium—usually solvent or air. In the current methodology, however, photolysis in the solid state *in vacuo* ensures that there are no other agents around to quench the radicals. Due to the crystal-lattice-enforced alignment of molecules, the radicals combine with each other in linear fashion with their nearest neighbors forming linear chains of catenating silicon atoms, rather than reforming the strained four-membered ring.

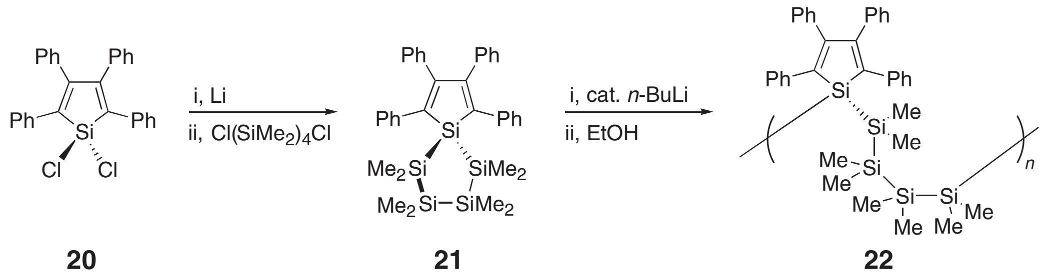
Although **17** is almost insoluble in all solvents, the Si–Cl bonds are nevertheless chemically very active and can be replaced by a variety of nucleophilic agents, such as alkoxy and amino groups. Complex **17** is thus a useful precursor polysilane for the synthesis of the heteroatom polysilanes, poly(bis-alkoxysilylene)s and poly(bis-aminosilylene)s, which are described in Section 3.11.4.2.2. The effects of attaching heteroatoms directly to the silicon backbone have been theoretically investigated for oxygen,[78,104,105] halogens,[106,107] sulfur,[105,108] and nitrogen.[105]

3.11.4.1.4.(iii) ROP of five-membered ring monomers

It was noted above that five-membered ring systems are borderline ROP candidates, due to the low ring strain. Their potential for ROP can be enhanced, however, for example, by stabilizing the silyl chain end. This was successfully demonstrated by Suzuki and co-workers, who incorporated a phenyl substituent on a cyclopentasilane silicon atom, as this moiety is known to stabilize silyl anions.[35,109] ROP initiation of phenylnonamethylcyclopentasilane, **18**, at low temperature in THF or dimethyl ether (DME) regioselectively generated an atactic, sequence-ordered polysilane, **19**, as indicated in Scheme 10 and evidenced by the clear observation of only three, well-defined, peaks in the ^{29}Si NMR spectrum and supporting ^{1}H, ^{13}C, and two-dimensional (2-D)^{1}H–^{29}Si COSY NMR spectra. Several initiators were investigated: with tetrabutylammonium fluoride (TBAF) the product polymer molecular weights were rather low (3,000–8,000), but no additive was needed, as the strength of the Si–F bond formed was sufficient to drive the reaction; best results were obtained for the slightly bulkier silyl potassium, Me_2PhSiK, for which hexamethylphosphoramide (HMPA) additive was required ($M_n = 58{,}000$; $M_w/M_n = 1.78$). Interestingly, and also indicative of the lesser ring strain compared to the cyclotetrasilanes, **18** did not undergo ROP with the less active silylcuprate initiators.[109]



Scheme 10 Formation of sequence-ordered polysilane **19** by ROP of phenyl-substituted cyclopentasilane.



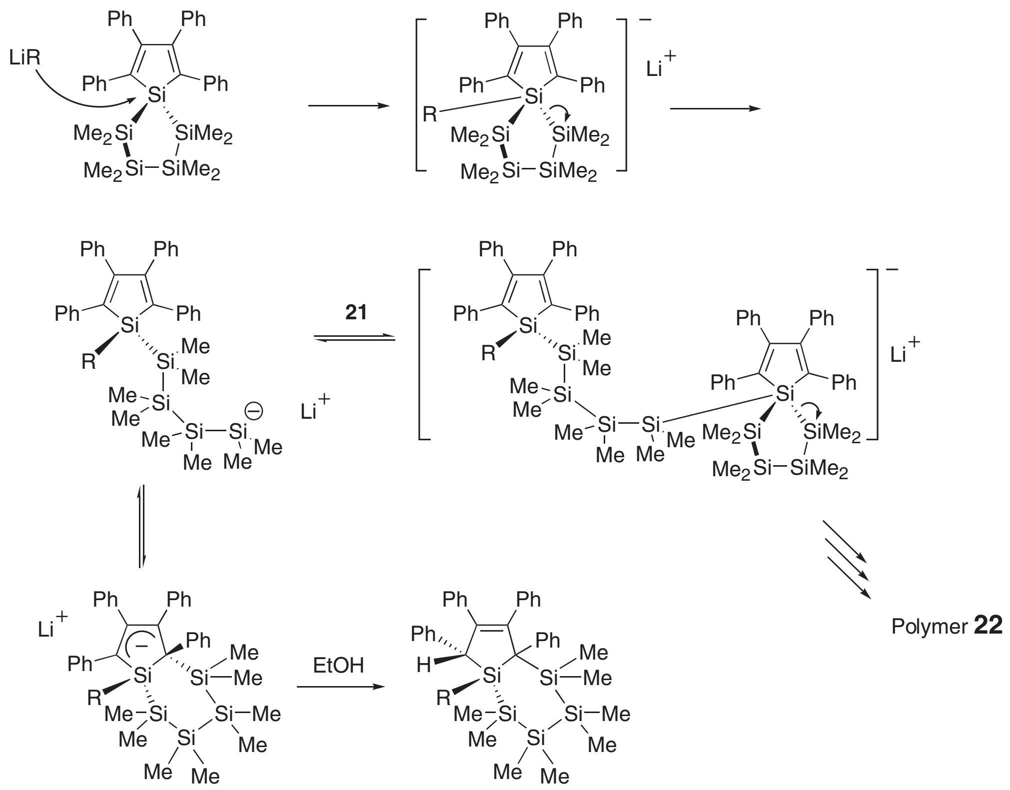
Scheme 11 ROP route to silole-incorporated polysilanes.

The ring-opening route also opened the way to the new class of silole-incorporated polysilanes,[61,110,111] though the synthesis of such polymers by Wurtz[54–56] (see Section 3.11.4.1.1) and dehydrocoupling[92] (see Section 3.11.4.1.3) routes has also been reported. These polymers are of interest due to their intimate combination of high-lying electron-donor polysilane chain HOMO, and low-lying electron-acceptor silole LUMO orbitals, and have been investigated theoretically.[57] Double lithiation of dichlorotetraphenylsilole, **20**, followed by reaction with 1,4-dichloro-octamethyltetrasilane afforded the silole-incorporated monomer, **21**. ROP of **21** initiated by a catalytic amount of *n*-BuLi proceeded regioselectively and smoothly in THF at −40 °C to yield the sequence-ordered silole-incorporated polysilane, **22**, in 41% yield ($M_n = 17{,}000$; $M_w/M_n = 1.3$). Monomer and polymer synthesis are shown in Scheme 11.

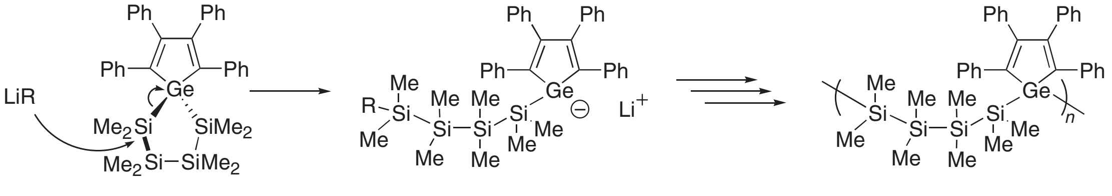
Similarly to the NMR characterization of **19** above, the high-sequence regularity of **22** was indicated by the observation of only three clear peaks in the ^{29}Si spectrum. Mechanistic studies on the ring opening of **21** using a large excess of methyllithium and X-ray analysis of the bicyclic product implied a mechanism involving anion attack on the *spiro*-silicon to form a ring pentacoordinate silicate intermediate, cleavage of which affords a dimethylsilyl-terminated anionic chain in equilibrium with a bicyclic allylic anion; chain propagation occurs from the chain form, as suggested in Scheme 12. This new class of polysilanes exhibited UV absorptions due to polysilane skeleton (320 nm) and silole ring (360 nm). The excitation spectrum monitored at 520 nm (at which wavelength any emission is due to the silole ring) reproduced the entire absorption spectrum, indicating a large degree of energy transfer between polysilane chain and silole ring. The fluorescence quantum yield (4.1×10^{-2}) was also very high (10 times greater than that of hexaphenylsilole).[110]

Interestingly, the germole analog of **21** was also prepared and subjected to ROP, forming the sequence-ordered Si/Ge co-polymer, **23** ($M_n = 11{,}000$, $M_w/M_n = 1.8$, yield 60%; UV $\lambda_{max} = 320$, 360 nm), although the mechanism was found to be completely different,[112] passing through a germole-terminated anionic intermediate, after attack by the initiator on a silicon adjacent to germanium, as shown in Scheme 13.

A carbon-substituted five-membered ring, **24**, was also successfully ring-opened via a σ^*–π-stabilized α-silyl carbanion intermediate after initiator attack on a silicon adjacent to carbon to give a sequence-ordered C/Si



Scheme 12 Proposed mechanism of silole-incorporated polysilane 22 formation by ROP.



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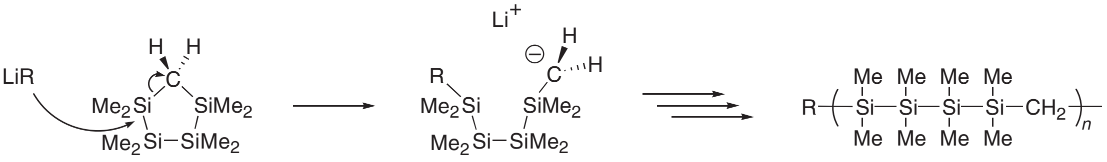
Scheme 13 ROP formation of sequence-ordered Si/Ge heterocopolymer, 23.



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25

Scheme 14 ROP formation of sequence-ordered C/Si heterocopolymer, 25.

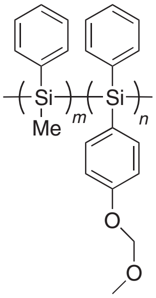
heterocopolymer, 25, as in Scheme 14. UV spectroscopic studies indicated that the tetrasilanylene units are able to conjugate through the methylene unit to a limited extent (UV $\lambda_{max} = 245$ nm; cf. 235 nm for $Me(SiMe_2)_4Me$).[110]

It is noted here that the related poly(1,1-silole)s, polysilanes, in which each CRU is a silole ring catenating through the silicon atom, have been prepared by Wurtz-type coupling of dichlorosilole monomer[54,55] and are described above in the section on Wurtz-type coupling (Section 3.11.4.1.1).

The key advantages of the anionic ROP method are that with suitable catalysts, polymers with controlled microstructure can be prepared, and also that polymers with functional groups can be formed. (Although prior to the time frame of this edition, ROPs of $[(H_3C{\equiv}C)SiPh]_4$, $[(MeO)SiPh]_4$, and $[(NC)SiPh]_4$ have also been reported, few experimental details or analytical data were given.)[97]

3.11.4.1.5 Electropolymerization

There is a brief reference to electroreductive silicon polymer formation in COMC II (1995) (chapter Organopolysilanes, p 96), but the very limited extent of the field at that time precluded further comment. Since then, the field has seen considerable progress, and the mild conditions have permitted the synthesis of functionalized polymers of moderate molecular weight (10^4), an example of which is the co-polymer poly(methyl-4-methoxymethoxyphenylsilylene)-*co*-poly(methylphenylsilylene), **26**, with a protected phenolic function, which was prepared with a molecular weight $M_w = 19{,}000$.[96] Deprotection afforded the phenolic polymer. Several reviews on the area have been published.[113–115]



26

The possibility to form Si–Si bonds by electrochemical reduction was already known around the mid-1970s, when Hengge obtained disilanes using a divided cell with platinum electrodes.[116–118] Related work was published by Corriu around 1980.[119–121] However, it was not until around 1990 that greater degrees of Si catenation were achieved. Using an undivided cell and a low oxidation potential sacrificial anode of aluminum, methyl- and phenyl-substituted oligomers[122] and insoluble poly(dimethylsilylene)[123] were synthesized from chlorosilane monomers by a group in France, while a group in Japan used a magnesium sacrificial anode in the polymerization of methylphenyldichlorosilane, giving PMPS with $M_w = 9{,}000$.[124] In addition to Al and Mg sacrificial anodes, Ni,[125] Cu,[125] and Zn[113] have also been used.

In an undivided cell, the sacrificial anode is used so that it is oxidized in preference to the silyl and chloride ions. There is thus a requirement for the reduction potential of the sacrificial anode to be more negative than the reduction potential of the silyl chlorides, $E^{\theta}_{\mathrm{SiCl}}$, that is, $E^{\theta}_{\mathrm{M}} < E^{\theta}_{\mathrm{SiCl}}$ (Equation (3) and Equation (4)):

$$E^{\theta}{}_{\mathrm{M}} \qquad \mathrm{M}^{n+} + ne^{-} \rightarrow \mathrm{M} \tag{3}$$

$$E^{\theta}{}_{\mathrm{SiCl}} \qquad n/2\ \mathrm{R_3Si{-}Cl} + ne^{-} \rightarrow \mathrm{R_3Si^{-}} + \mathrm{Cl^{-}} \tag{4}$$

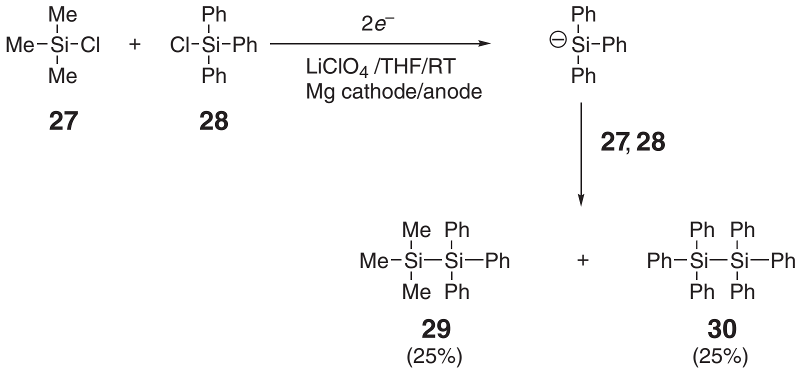
This order is always found for M = Mg, but not necessarily for M = Al, Cu, and Zn. In order to ensure that the required order is achieved, a complexing agent such as hexamethylphosphoramide (HMPA) or tris(3,6-dioxaheptyl)-amine (TDA-1) is added to render the metal reduction potential more negative.

Overall, electroreductive coupling proceeds as in Equation (5):

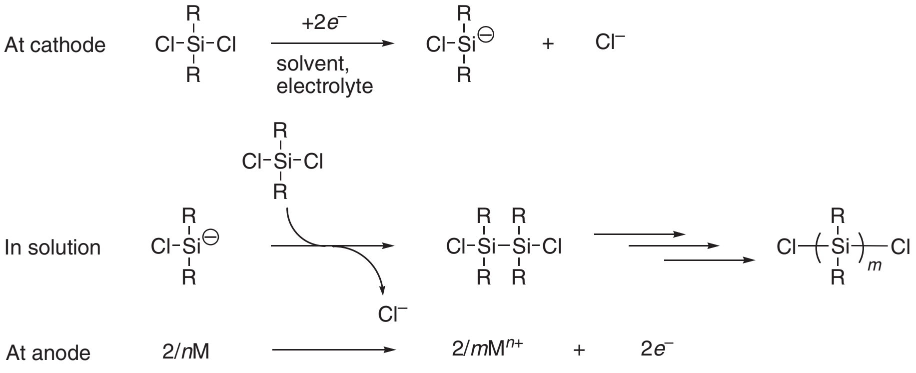
$$m\mathrm{R_2SiCl_2} + 2me^{-} \rightarrow (\mathrm{R_2Si})_m + 2m\mathrm{Cl^{-}} \tag{5}$$

The reaction is considered to proceed via a silyl anion mechanism, although the possibility of a radical-based mechanism has also been discussed.[115,125] In order to clarify the mechanism, coupling experiments on a 1 : 1 mixture of chlorotrimethylsilane, **27** (reduction potential <−3.0 V),[126] and chlorotriphenylsilane, **28** (reduction potential vs. standard calomel electrode (SCE) < −3.0 V),[120] were performed, in which the mixed coupling product 1,1,1-trimethyl-2,2,2-triphenyldisilane, **29**, and the homocoupling product hexaphenyldisilane, **30**, only, were found,[125] as indicated in Scheme 15.

This result is consistent with the anionic mechansim, outlined in Scheme 16, since the lower reduction potential of **28** should lead to the formation of the triphenylsilyl anion, which would then react with the chlorosilanes **27** and **28**



Scheme 15 Heterocoupling experiment to clarify mechanism.



Scheme 16 Silyl anion electropolymerization mechanism.

equally, as they are both similarly highly electronegative, thus affording 29 and 30 in approximately equal amounts, as is, in fact, observed. In the radical mechanism, if only 28 forms a radical, then the formation of the mixed product 29 is not reasonable; and if both 27 and 28 form radicals, then the absence of the hexamethyldisilane homocoupling product is not reasonable. Given the experimentally observed products, the anionic mechanism is thus favored.[125]

In general, an undivided cell electroreductive system usually employs a magnetically stirred glass cell, supporting electrolyte, solvent with complexing co-solvent, sacrificial anode (bar of metal) and cathode (stainless steel mesh, or same metal bar as the anode if an alternating polarity setup is used), and monomers. The system must be rigorously dried and deoxygenated, for example, by bubbling argon, in order to avoid the formation of siloxy linkages in the silicon chain; pre-electrolysis is effective here and involves addition of Me_3SiCl to the cell which reacts with any water present to form siloxanes and HCl, electrolysis of which removes H as hydrogen gas. The monomer is then added and electrolysis is carried out, often with sonication[113] to ensure fresh electrode surfaces. The product is isolated by removal of salts (and distillation for oligomers or reprecipitation/washing for polymers). In the undivided cell with sacrifical anode, the anode metal is oxidized and then complexed by the complexing co-solvent, such that the supporting electrolyte can be used at a much lower concentration (ca. 0.02 M) than in a classical divided cell, where the electrolyte concentration needs to be about 0.3 M (same as initial monomer concentration).[113]

Many modifications of this system have been investigated to increase the effectiveness of polymerization,[113–115] as is apparent from Table 1.

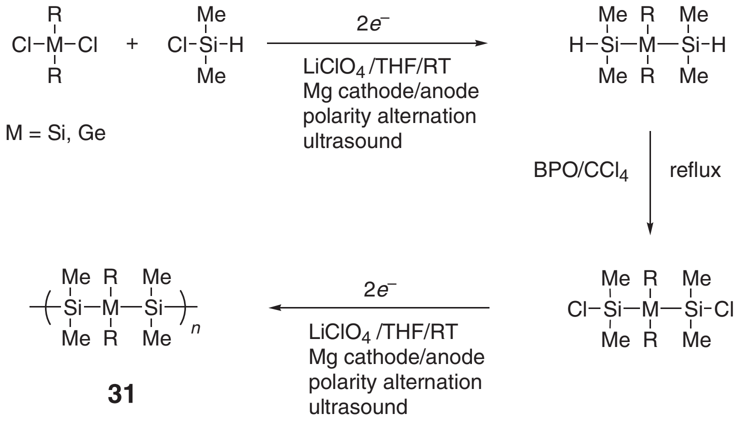
These include the variations of sacrificial anode, sonication, and alternating polarity cell mentioned above, different solvent/co-solvent and electrolyte systems, monomer concentration, total current passed, and temperature. Best results appear to be obtained with THF and dimethyl ether (DME) as solvent and a perchlorate supporting electrolyte: in some systems using fluorides, electrolyte decomposition occurred releasing fluoride anion which formed unreactive fluorosilanes.[125]

Table1 Selected electropolymerization data

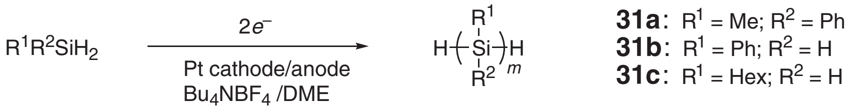
Monomer	*Solvent/ Co–solvent*	*Electrolyte*	*Anode*	*Cathode*[a]	*Polarity Alt*[b]	*Sonication*	*Product*	*Yield (%)*	M_n	*PDI*	*UV λmax* nm^{-1}	*Comment*	*References*
$Cl_2Si\ Me_2$	THF/ HMPA	Bu_4NBr	Al	SS	No	No	PDMS	30				DP > 25	122
Cl_2SiMe_2	None	Bu_4NBr	Al	SS	No	No	PDMS	72					113
Cl_2SiMe_2	small amount HMPA	Bu_4NBr	Al	SS	No	No	PDMS	76					113
Cl_2SiMe_2	TDA-1/ HMPA	Bu_4NBr	Al	SS	No	No	PDMS	90					113
$Cl_2SiMePh$	THF/ HMPA	Bu_4NBr	Al	SS	No	No	PMPS	50	5,000	1.8			113
$Cl_2SiMePh$	THF	$LiClO_4$	Mg	Mg	No	No	PMPS	0	−10 °C	1.5			125
$Cl_2SiMePh$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	PMPS	43	5,200		340		125
$Cl_2SiMePh$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	PMPS	7	31,000			High monomer conc.	125
$Cl_2SiMePh$/ $Cl_2GeBuPh$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	PMPS/G	33	20,600		335	1 : 1 Monomer ratio,but 55 : 45 incorporated	125
$Cl_2GeBuPh$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	PBPG	10	19,900		355		125
Cl_2SiBu_2	DME	Bu_4NClO_4	Ag	Pt	No	No	PDBS	62	8,400	1.9	314		127
Cl_2SiHex_2	DME	Bu_4MClO_4	Ag	Pt	No	No	PDHS	68	4,100	4.6	314		127
Cl_2SiHex_2/ Cl_2GeHex_2	DME	Bu_4NClO_4	Ag	Pt	No	No	PDBS/G	59	1,500	1.1	305	1 : 1 Monomer ratio, but 64 : 36 incorporated	128
Cl_2SiBu_2/ Cl_2SiHex_2	DME	Bu_4NClO_4	Ag	Pt	No	No	PDB/HS	74	1,800	2.2	307	1 : 1 Monomer ratio, but not determined in polymer	128
$ClMe_2SiSiMePhCl$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	P(DMS-*CO*-MPS)	2.4	3,600	2.3		Not regioselective	129
$(ClMe_2Si)_2SiPh_2$	THF	$LiClO_4$	Mg	Mg	Yes	Yes	$[(Me_2Si)_2SiPh_2]n$	35	5,500	1.54		At −10°C; sequence-ordered	129
$MePhSiH_2$	DME	Bu_4NBF_4	Pt	Pt	No	No	PMPS	60	454	1.05	240(sh)	H-terminated	130, 131
$n\text{-}HexSiH_3$	DME	Bu_4NBF_4	Pt	Pt	No	No	PDHS	70	1,120	1.09	252	H-terminated	131

[a] SS = stainless steel.

[b] Polarity Alt = Polarity Alternation.



Scheme 17 Electropolymerization route to sequence-ordered polymers.



Scheme 18 Dehydropolymerization of dihydrosilanes.

Disilane and germasilane monomers have also been successfully coupled, and using trisilane monomers with different substituents on central and terminal silicons, the interesting, more structurally regular, sequence-ordered co-polymers have been prepared, as shown in Scheme 17 and in analogy to the report by West on the Wurtz-type preparation of sequence-ordered co-polymers.[17]

More recently, electrochemical oligomerization of hydrosilanes has been demonstrated.[130,131] A DME/TBAF solvent/electrolyte system with platinum electrodes was found to lead successfully to products **31**, according to the reaction in Scheme 18, after use of a THF/LP system had led to deposition of lithium.

The route has the advantage that the anode does not need to be sacrificial, thus avoiding the generation of metal salts. However, the molecular weights of products obtained using this method are as yet very low, and mass spectral data for the oligomeric PMPS indicate a maximum DP of 5.

3.11.4.1.6 Others: Chemical vapor deposition (CVD) polymerization, redistribution, and disproportionation

Kira and co-workers have described a new and unique approach to the synthesis of polysilanes: starting from octapropylcyclotetrasilane, $(SiPr_2)_4$, **32**, poly(dipropylsilylene), **33**, was prepared by photo-CVD (CVD = chemical vapor deposition).[132] It is known that silylenes are extruded upon photolysis of cyclosilanes, and also that silylenes can insert into Si–H bonds (see COMC II (1995)). It was considered that if these two features of silylenes could be combined, polysilanes might be generated. In the experiment, the setup for which is shown schematically in Figure 8, **32** was vaporized by heating at 270 °C *in vacuo*, and then photolyzed using UV light ($\lambda = 254$ nm).

The product **33** ($\lambda_{max} = 345$ nm) was formed as a film (estimated by the optical density of the UV spectrum to be several tens of nanometres thick) on a target quartz plate, the surface of which had been treated with 10 wt.% NaOH solution, followed by dichlorodimethylsilane and finally $LiAlH_4$ to afford a surface terminated with $-OSiMe_2H$ groups. On the basis of trapping experiments (to confirm the formation of silylenes) and photo-CVD in the presence of styrene (to confirm the absence of radical species), a mechanism based on silylene formation and insertion into the surface Si–H bond was shown to be likely, as outlined in Scheme 19.

By comparison of the UV, excitation, and PL spectral data with those of other poly(dialkylsilylene)s, a linear Si chain was inferred. Since poly(dipropylsilylene) is insoluble, the molecular weight could not be measured, but the UV absorption maximum at 345 nm is indicative of a DP of greater than at least 20 repeat units. The photo-CVD

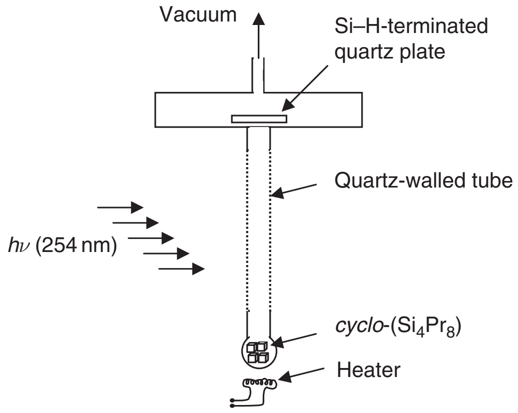
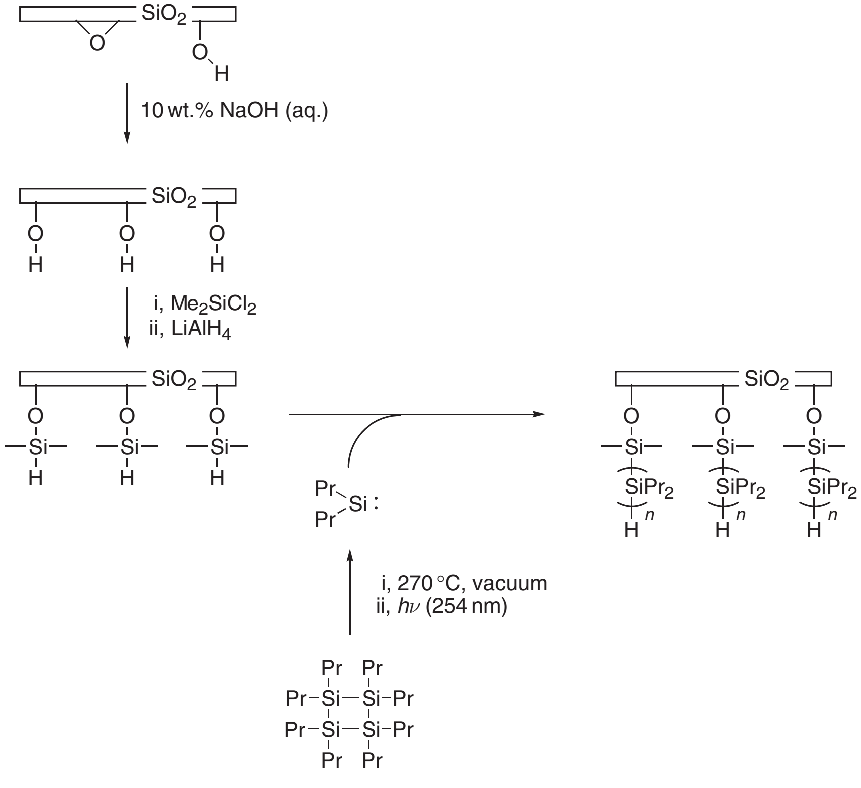


Figure 8 Schematic diagram of experimental setup for photo-CVD polysilane synthesis.



Scheme 19 Photo-CVD mechanism: silylene extrusion and insertion into surface Si–H.

approach thus permits the formation of less soluble and/or crystalline polysilanes, and may be useful where only small amounts of polymer (as in thin films) are required.

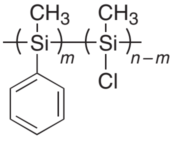
Several other synthetic techniques have also been described. Redistribution polymerization was outlined in COMC II (1995) (chapter Organopolysilanes, p 99) and proceeds by phosphonium salt-catalyzed redistribution of chlorodisilanes.[133] Disproportionation polymerization, which is a similar process, has been described for the formation of polymers by ethoxide-catalyzed disproportionation of alkoxydisilanes via silyl anion intermediates.[134] These procedures give rise to network polymeric products of rather low molecular weight (see below, Section 3.11.7.1).

3.11.4.2 Advances in Functionalization

With the aim of expanding the range of properties and thus also applications of polysilanes, functionalization with chemically interactive or physically responsive groups is an area of intense research. In a 1994 review of the area, Matyjaszewski loosely defined a functional group in this context to be either one that is potentially functionalizable (i.e., can undergo subsequent chemical transformation), or one that affects the polysilane properties in a unique way.[135] In this chapter, polysilanes with potentially functionalizable groups are termed "precursor polysilanes." Although this definition has gray areas, it is nonetheless a useful tool of classification, and will be used here. Functionalization can be either post-polymerization, in which case polymers preformed by any synthetic method are then further reacted, or pre-polymerization, in which case functionalization is carried out at the monomer stage.[135] Generally the latter affords polymers with a greater degree of structural control, although the functionalities which can be incorporated are rather limited. Co-polymerization of conventional (alkyl or aryl) monomers with functionalized monomers is often possible, even if homopolymerization of the functionalized monomer does not yield polymers. Functionalization of polysilanes was reviewed in 2000 in chapters 13 and chapter 15 of the book *Silicon-containing Polymers*.[60,61]

Functionalization of polysilanes by chemical modification (post-polymerization) was covered in COMC II (1995) (chapter Organopolysilanes, p 101), where the formation of precursor polysilanes with potentially functionalizable side groups such as chloride, type **34** (via HCl/$AlCl_3$ chlorodephenylation of PMPS),[136] triflate, type **35** (via triflate replacement of phenyl groups)[135,137] or alkyl halide (via chloromethylation of phenyl groups,[138,139] type **36**, or addition of HCl or HBr to double bonds[140]) was discussed. Four other precursor polysilanes, which utilize the reactivity of the Si–Cl or Si–H bond, have been successfully applied in functionalization since COMC (1995): perchloropolysilane, **17** (see Section 3.11.4.2.2.(i) for synthesis),[103] poly[methyl(H)silylene-*co*-methylphenylsilylene], **37**, prepared by Wurtz-type coupling of the respective dichlorosilane comonomers,[141] and poly[phenyl(H)silylene], **38**, prepared by metal-catalyzed dehydrocoupling of $PhSiH_3$.[69,75]

Under the HCl/$AlCl_3$ conditions described in COMC II (1995), **34** was prepared with up to 70% chlorodephenylation. A new route has now been published to **34** and its alkyl analogs in which halodephenylation was carried out using AlX_3 (X = Cl, Br) and the appropriate acetyl halide. The reaction essentially goes to completion, with about 1% Ph groups remaining, although some chain cleavage occurs resulting in precursor polymers of type **39** with a DP of about 25.[35]



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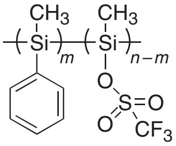

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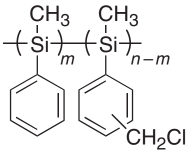

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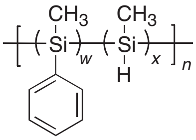

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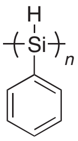

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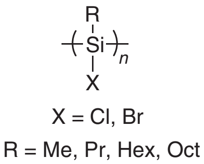

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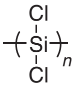


17

In this review, advances in the preparation of functionalized polysilanes by both pre- and post-polymerization functionalization and their properties will be reviewed. First, polymers with remote side-chain functionalities are covered, then those with the functionality directly attached to the main chain and finally those which are end group-functionalized. Chiral functionalization will be treated separately (see Section 3.11.6).

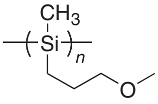
3.11.4.2.1 Remote functionalization

If the functional group is remote from the main chain, due to the presence of an intervening alkyl or aryl spacer, pre-polymerization functionalization may be possible, although if the functional group is sensitive to the conditions of the polymerization reaction, post-polymerization functionalization will be necessary.

3.11.4.2.1.(i) Remote *O*-functionalization

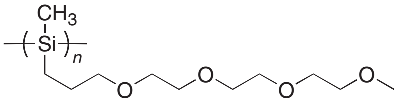
For side chains with one oxygen substituent, sodium-mediated Wurtz coupling is still possible, though as the number of oxygen atoms (e.g., in oligoether groups) and thus also the monomer polarity increases, sodium becomes much less effective and C_8K has been found to give reasonable results. Polysilanes with such polar side chains are often soluble in alcohols and may even be soluble in water. Phenyl-containing polysilanes with one oxygen atom substituted on the phenyl ring were reported in COMC II (1995) (chapter Organopolysilanes, p 101) and shown to enable the preparation of LB films on water.[142,143] Since COMC II (1995), a wide range of *O*-functionalized polysilanes has been prepared.

The first alkyl side-chain ether-substituted polysilane to be prepared was **40**, with a single oxygen atom in one of the side chains. The polymer is soluble in alcohols, including methanol, in addition to common non-polar organic solvents.[144,145]



40

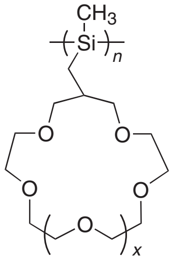
Complex **40** can be further modified to new alkyl triflate precursor polysilanes by reaction with methyl triflate, since this reagent is inert toward Si–Si bonds.[135] The potential of these polar polysilanes was rapidly appreciated and further ether units were added into the side chains to increase the polarity, resulting in **41**, the first water-soluble polysilane, synthesized independently by two groups using sodium-mediated Wurtz coupling, though in low yield.[146,147] The high polarity was reflected in the very high surface tension found for the polymer, suggesting enhanced adhesibility and wettability.[146] The same polymer was later shown to exhibit remarkable iono-[148] solvato- and thermochromism[149] (see Section 3.11.5.2).



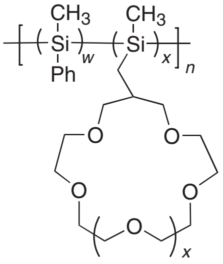
41

The low yield for Wurtz-type polymerization of monomers containing multiple ether functions has been found to be quite general.[146,147] In detailed investigations of a wide range of oligoether-substituted polysilanes,[150] Jenneskens and co-workers have greatly improved the preparative yields of such polymers through use of graphite potassium, C_8K,[147,150] mentioned above as an alternative reductant. Under quite specific conditions (ratio of C_8K : monomer of exactly 2; reaction temperature of 0 °C in THF for 2–2.5 h), high molecular weight (as evidenced by ^{29}Si NMR analysis) **41** was obtained in yields of up to 35%. Later work on co-polymer systems comprising polar and apolar repeat units showed that C_8K is appropriate for the reductive coupling of polar monomers, but that as the feed ratio of the apolar monomer increases, co-polymer yield markedly decreases. In co-polymerizations using Na, yields are not strongly correlated with feed ratio, thus indicating the greater utility of sodium in such co-polymerizations.[29] It was also considered in this chapter that the better results in the synthesis of oligoether-substituted polysilanes afforded using C_8K stem from the ability of the polar monomers to intercalate into the graphite layers.

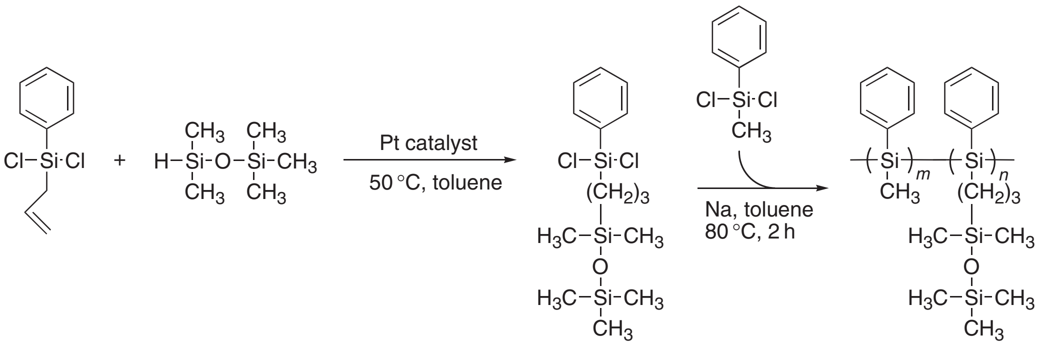
With the success of C_8K in the syntheses of **41** and related co-polymers, the same methodology was applied to the synthesis of polysilanes bearing pendant crown ether substituents, viz. **42–44**,[150,151] which were synthesized in yields from 6% to 28%, with molecular weights of the order of 10^4. The polymers were found to be water soluble and thermochromic in accordance with the Schweizer thermochromism theory (see Section 3.11.5.2.4).[152]



42: $x = 0$
43: $x = 1$
44: $x = 2$



45: $x = 2$



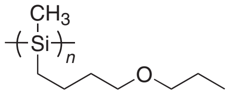
Scheme 20 Synthesis of siloxane-pendant polysilanes.

Related crown ether-pendant polysilanes **45** were recently prepared by hydrosilylation post-polymerization functionalization of poly[methyl(H)silylene-*co*-methylphenylsilylene], **37**, although due to the low molecular weight of **37**, the product **45** is also of low molecular weight.[153]

Polysilane co-polymers with pendant siloxane groups were also synthesized, aiming at air oxidation-resistant polysilanes, utilizing the partial tendency for phase separation of polar side chain and apolar main chain, resulting in surface accumulation of siloxane groups,[154,155] as shown in Scheme 20.

The oxygen atom not only imparts polarity, but also flexibility, as was discussed[156] for two early ether-substituted polysilanes, poly(5-oxaoctyl-*n*-propylsilylene) and poly(5-oxaoctyl-*n*-hexylsilylene). To investigate this further, Yuan and West, using the same standard Wurtz procedure, prepared a series of poly(oxaoctylmethylsilylene) isomers and their symmetrical counterparts, in which the position of the oxygen atom was varied in side-chain positions 5, 6, and 7.[157]

Complexes **46–48** are fully amorphous due to their side-chain imbalance, whereas complexes **49–51** are more ordered due to the side-chain balance, existing as hexagonal columnar mesophases above their transition temperatures, and a crystalline phase below, at the transition between which an abrupt thermochromic transition was observed. Temperature-dependent X-ray diffraction and UV spectroscopic studies indicated greater conformational flexibility as the oxygen is moved closer to the backbone, reflecting the increasing effect of the flexible oxygen linkage on the side-chain and main-chain mobility.[157]



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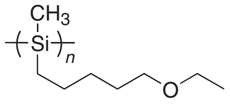

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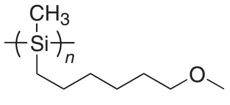

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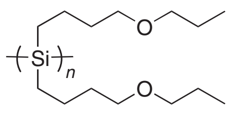

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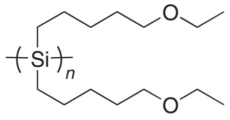

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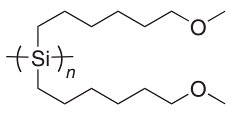
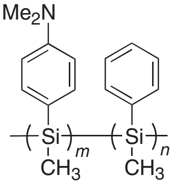


51

Polymers with single oxygen atom alkoxy groups substituted on phenyl rings are less well known, though there were several reports in the mid to late 1980s.[21] At around the turn of the millenium, a group at NTT Basic Research Laboratories interested in chirality in polymers synthesized a number of poly(alkylalkoxyphenylsilylene)s, both with and without enantiopure chiral alkoxy groups (see Section 3.11.6 below for chirality in polysilanes), and a Dutch group reported related (non-chiral) polymers.[158] The synthesis of these polymers using the Wurtz-type route is straightforward. However, for two or more oxygens in the alkyl substituent on the phenyl ring,[158] both monomer and polymer preparation are more complicated: oligoethoxy groups in the former can coordinate strongly to the magnesium salts from the Grignard coupling, preventing distillation. To reduce this, a poorer solvent can be added to precipitate the salts.[159,160] For polymer synthesis, it was found that using sodium, the yields were very low, whereas with C_8K, reasonable yields were obtained, although the molecular weights were not so high.

3.11.4.2.1.(ii) Remote *N*-functionalization

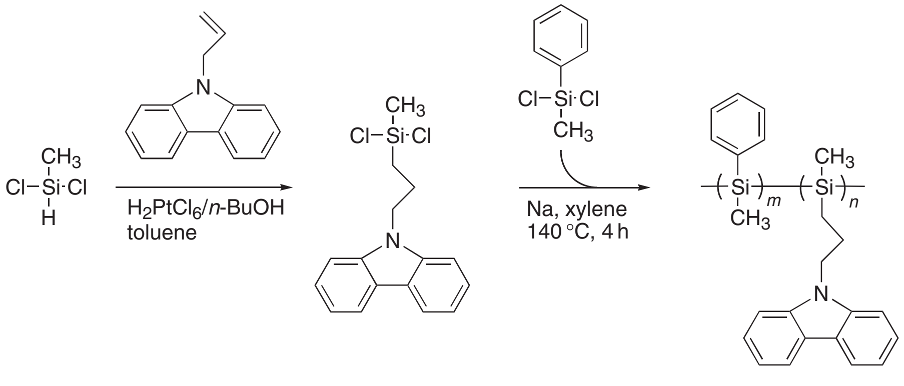
The Wurtz coupling technique has also been successfully applied to nitrogen-containing dichlorosilane monomers. These polymers are of interest due to the electronic effects of N incorporation on the σ–σ^*-transition of the electronically delocalized silicon backbone,[161] their relatively high electrical conductivity on doping with iodine,[162] charge-photogeneration ability,[163] charge carrier trapping ability,[164] thermoluminescence properties,[165] and photoelectric properties.[166] Amongst the first such polymers to be synthesized were a series of co-polymers incorporating the electron-donating *N*,*N*-dimethylaminophenyl group of type **52**.[161] In the $m = 100\%$ homopolymer, the UV absorption maximum occurs at 350 nm, the nitrogen substituent causing a red shift of about 5 nm compared to the case of the $n = 100\%$ homopolymer (PMPS). This was considered to be due to a direct electronic (as opposed to conformational) effect, due to the possibility of the nitrogen atom being able to conjugate with the silicon atom.



52

A year or so later, *N*-carbazolyl-substituted polysilanes were reported by a group at Shin-Etsu (see Scheme 21).[162] In these, the alkyl spacer between the nitrogen atom and the silicon chain electronically insulates the carbazolyl group from conjugation with the main chain. Although homopolymerization of the *N*-carbazolyl-substituted dichlorosilane resulted in low molecular weight materials, high molecular weight products were obtained in co-polymerizations with dichloromethylphenylsilane. The polymers **53** were obtained in yields between 202% and 75%. UV data were not reported for the $n = 100\%$ homopolymer, though a short while later, a closely related series of polymers was synthesized by another group,[163] including the $n = 100\%$ *N*-carbazolyl-substituted homopolymer ($M_n = 3{,}200$), for which the UV absorption maximum was reported at 294 nm (Si σ–σ^*-transition masked by carbazolyl group absorption).

The low homopolymer molecular weights presumably originate in the steric congestion arising from the bulky 3-(*N*-carbazolyl)propyl group. Less sterically hindered homo- and co-polysilanes containing the *N*,*N*-dimethylaminophenyl and *N*-pyrrolylalkyl groups were later also obtained by the same Shin-Etsu group, with variable (though generally higher) molecular weight and yields.[167] For the *N*,*N*-dimethylaminophenyl-substituted polymers of types **54 and 55**, the DP increased as the fraction of methylphenylsilylene repeat unit increased. For the *N*-pyrrolylalkyl-substituted homopolymers, the DP increased as the alkyl spacer length increased.



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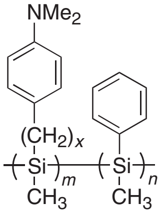
Scheme 21 Route to *N*-carbazolyl-functionalized polysilanes **53** via Wurtz coupling.



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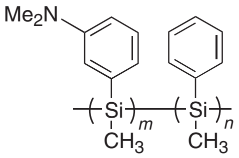

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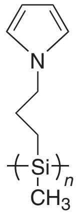

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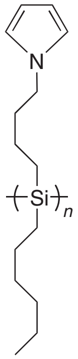

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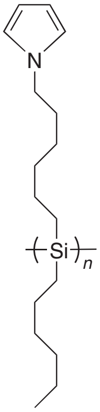
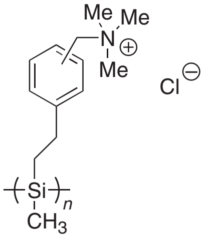


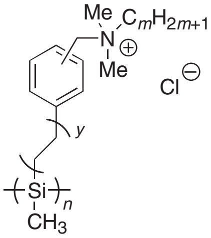
58

Further work on the ionic, quaternary ammonium halide polysilanes with *N*-octadecyl substituents mentioned[139] in COMC II (1995) (chapter Organopolysilanes, p 101) investigating the spectroscopic properties of their LB films has also been reported.[168,169] These polymers with C_n ($n = 18, 12, 8$) *N*-alkyl substituents, formed by amine quaternization of fully chloromethylated poly{methyl[(phenyl)ethyl]silylene}, were not soluble in water due to the long C_{18} chains, but showed good LB film-forming properties. Polarized UV spectroscopy of the deposited LB molecular films revealed that the Si backbone is preferentially oriented along the dipping direction possibly due to flow orientation on the water surface. It was considered that the LB films were composed of periodic double layers having a homogeneous and amorphous character.[169] When quaternization was performed using trimethylamine, however, the first fully water-soluble polysilane, **59**, was obtained.[170,171]



59

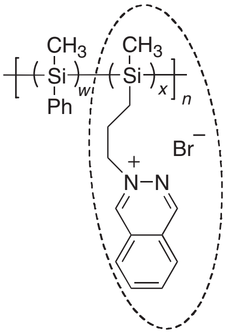
Complex **59** was found to show remarkable solvatochromism: UV emission and absorption spectra were measured for various water/ethanol solvent ratios, and maxima were found for approximately 1 : 1 mixtures.[170] Since $\lambda_{\max}$ red-shifts with increasing σ-electron conjugation, which increases, as chain extension increases, to a maximum when the chain is in the fully extended *all-anti* conformation, it seems likely that at this solvent ratio, the greatest solvation of polymer main chain and side chains are achieved. Addition of the surfactant sodium dodecyl sulfate (SDS) to aqueous solutions of **59** induced stoichiometric red-shifts and intensity increases in the UV σ–σ^*-absorption and σ^*–σ-emission $\lambda_{\max}$ up to a maximum, after which there were no further changes in ε or $\lambda_{\max}$. Charge neutralization would normally be expected to lead to a more coiled global polymer conformation in the polar solvent and hence a spectral blue shift. The observed spectral red shift was rationalized as resulting from surfactant-binding-induced rigidity, resulting in a coil-to-rod transition. In addition to the σ^*–σ-transition band, a low intensity emission is evident in the spectra at long wavelength. This could originate in defects introduced during chloromethylation. Based on the results of another group[172] concerning related polymers, another possible origin for this could be intramolecular exciplex formation. This group[172] found two kinds of emission bands in the **59** analogs, **60–65**. In solution, the band in the region 400–500 nm was considered to arise due to formation of an intramolecular exciplex between a σ-conjugated main-chain silicon atom and the attached ammonium center; little solvatochromism of the exciplex was evident. This band was only observed for the $y = 0$ polymers **60–63**, which was rationalized as a distance effect, the distance between the interacting excited states being too great to allow orbital interaction when methylene spacers were present. In (random) cast films, a further emission at around 560 nm was considered to be due to “intermolecular” Si···N exciplex formation, possible in the random films but precluded by molecular ordering in the LB films.



60: $y = 0$; $m = 8$
61: $y = 0$; $m = 10$
62: $y = 0$; $m = 14$
63: $y = 0$; $m = 18$
64: $y = 1$; $m = 14$
65: $y = 2$; $m = 14$

Chiral amines have also been used to prepare the quaternary ammonium salts, forming optically active polysilanes (see Section 3.11.6.1.3).[173]

Finally, ionic aminopolysilanes were synthesized by hydrosilylation of *N*-(allyl)cycloimmonium bromide using precursor polysilane **37** affording **66**, which showed properties consistent with the formation of molecular dipoles.[174]

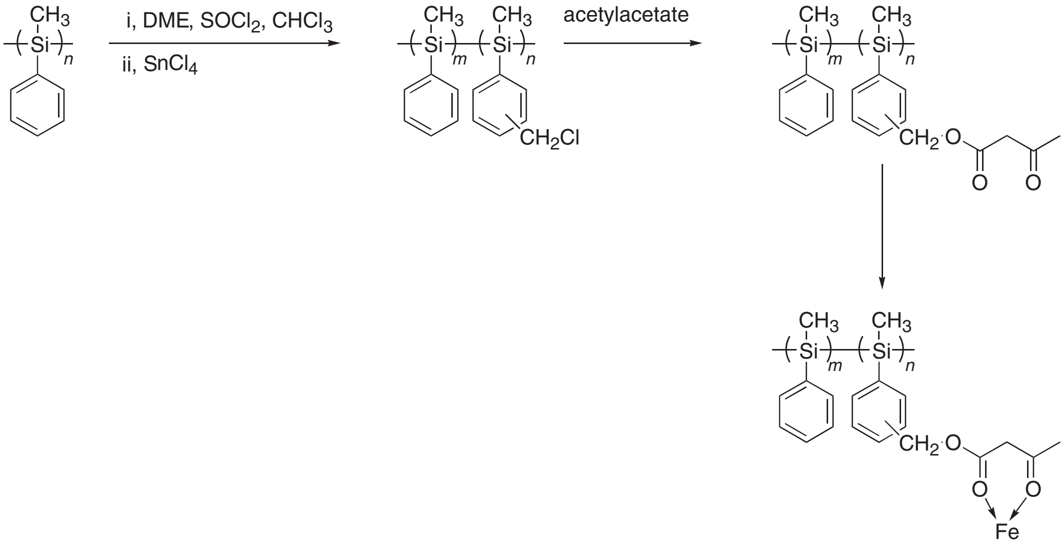


66

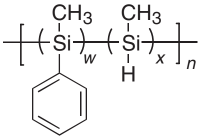
3.11.4.2.1.(iii) Metal functionalization

Prior to the publication of COMC II (1995), there were very few metal-functionalized polysilanes: Pannell *et al.* prepared a co-polymer incorporating the chemically robust ferrocenyl group in side-chain positions from dichloromethylphenylsilane and dichloroferrocenylmethylsilane, and although some photostabilization of the usually light sensitive silicon main chain was observed, other properties were little different from PMPS;[175] and Manners and co-workers prepared co-polymers incorporating metal and silylene moieties in the main chain via ROP of strained silyl ferrocenophanes,[176] although these latter polymers essentially do not display polysilane character (extended σ-electron delocalization and near UV σ–σ^*-transition), and as such are beyond the scope of this chapter. Since the publication of COMC II (1995), there have been relatively few reports of metal functionalization of polysilanes, and those published have reported post-polymerization functionalization, as metallation does not usually survive the utilized polymerization method (Wurtz-type coupling), utilizing the coordination of a side-chain group to a Lewis acid metal center.[177,178] Jones and co-workers used a modified phenyl chloromethylation reaction (starting from dimethyl ether, DME) on PMPS, and using this, introduced an acetylacetonate group which readily coordinated Fe(III),[179] as shown in Scheme 22. The product was intractable, however, and the structure did not permit any direct interaction between metal and main-chain σ-electron system.

Other than this system, metallated polysilanes contain the metal in low-valent oxidation states. Such systems have been reported by two groups. In 1995, an alternative functionalization route starting from poly[methyl(H)silylene] or poly[methyl(H)silylene-*co*-methylphenylsilylene], **37**, was reported, in which the polysilane Si–H moiety was hydrosilated using 1,3,5-hexatriene, affording the diene-modified polymer **67**, which was metal functionalized using triiron dodecacarbonyl to give the iron tricarbonyl–polysilane coordination complex, **68**.[177]



Scheme 22 Metal functionalization of poly(methylphenylsilylene) via chloromethylation.



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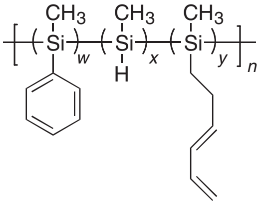

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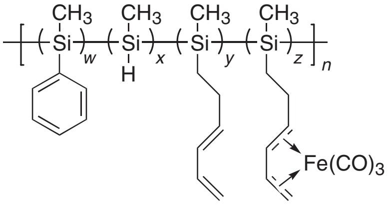
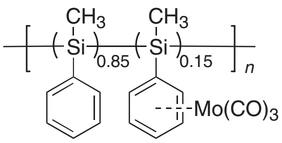


68

The highest molecular weight polymer of type 67 ($M_w = 12{,}530$) was obtained for $w = 0.48$, $x = 0.52$, and in its synthesis from the corresponding type 37 polymer and subsequent metallation to give 68, there appears to be little or no degradation. Since the difunctional 1,3,5-hexatriene has two potential hydrosilylation sites, cross-linking of polymer chains can occur, and was held responsible for the low hydrosilylation yield of 13%. Use of 1,3,5-heptatriene obviates this problem and the yields were concommitantly higher—over 80%. These polymers gave α-Fe–SiC magnetic ceramic composites on pyrolysis, as evidenced by XRD analysis.

In further work on metal-containing polysilanes, the group at Kent University used the η^6-coordinating ability of the phenyl ring to prepare PMPS complexes of Mo[180] 69, Mn[181] 70, and Cr[178] 71, and model compound phenyl-bearing silane complexes of the same metals and also Ru.[181]



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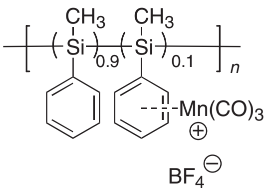

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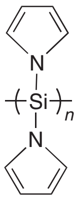
Complex 69 was prepared in about 60% yield with about 15% metallation and a small drop in molecular weight (from 73,000 for PMPS to 68,000 for 69), which, allowing for the increase in statistical repeat unit, indicates some degradation. Related model compounds based on the coordination of phenyl rings in phenyltrimethylsilane and 1,2-diphenyltetramethyldisilane were compared with 69. The UV absorption maxima (224 and 337 nm) were almost unchanged from those of the precursor PMPS (223 and 338 nm), which possibly reflects the low metal loading as suggested by the authors, but is nevertheless somewhat surprising, given the considerable steric and electronic effects expected. The polymers are unstable toward air in THF solution, forming an intractable material, presumably by cross-linking.[180] Complex **70**, with a 10% loading of Mn(CO)$_3^+$ as determined by atomic absorption spectroscopy (AAS) was prepared in moderate yield by refluxing PMPS with [(naphthalene)Mn(CO)$_3$][BF$_4$] in dichloromethane for 1 h. No UV or molecular weight data were given, so the effects of the different metal are not clear. For chromium, a tricarbonylchromium-coordinated dichloromethylphenylsilane monomer was prepared. In THF, when co-polymerized with dichloromethylphenylsilane in a Wurtz-type coupling, a very small amount of phenyl ring metallation was observed in the product (2–3%), but none was observed at all in toluene or for homopolymerization of the metallated monomer.[178] The most interesting result from the chromium experiments was that the tacticity of the product PMPS was affected significantly by incorporation of the metal moiety, although the underlying reasons were not clear.

3.11.4.2.2 Direct functionalization

Polysilanes with functionalities Z directly attached to the silicon main chain are generally more difficult to synthesize and less stable, due to the reactivity of both the Si–Z and Si–Si linkages. Such polymers are usually not accessible via the Wurtz-type coupling reaction, and alternative synthetic strategies (see Sections 3.11.4.1 and subsequent) or post-polymerization techniques have to be employed.

3.11.4.2.2.(i) Heteroatom functionalization

Heteroatom polysilanes, polymers with a heteroatom (non-carbon atom) attached directly to the silicon main chain, usually cannot be prepared by the Wurtz-type technique and necessitate alternative preparative techniques. As an exception to this, polysilanes with pyrrolyl groups directly attached through the nitrogen atom to the main chain have been synthesized using this route by Seki *et al.*,[41] although with lower molecular weights than conventional alkyl- and aryl-substituted polsilanes. Pyrrole was reacted with *n*-butyllithium to give pyrrolyllithium, addition of which to tetra- or trichlorosilanes in ether gave the *N*-pyrrolyl-substituted monomers. Wurtz-type coupling of the monomers using sodium in toluene at 75 °C afforded the series of *N*-pyrrolyl-substituted homopolysilanes **71–74**, with M_w of 15,000, 8,000, 17,000, and 29,000, respectively. Complex **71** was found to be rather unstable and degraded within a couple of hours. Based on the photoluminescence spectra[41] and on prior theoretical predictions,[105] σ-n mixing (dependent on the degree of rotation of the pyrrole group) as well as σ-π mixing were presumed to occur.



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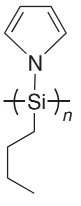

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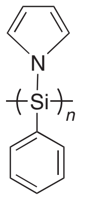

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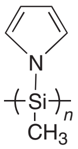

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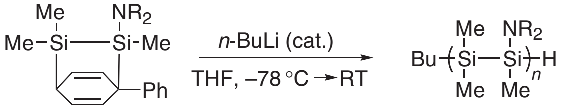
The masked disilene strategy was also successfully applied to the synthesis of dialkylamino-substituted polysilanes,[60,61,63] by the *n*-butyllithium-initiated polymerization of dialkylamino-substituted phenyldisilabicyclooctadienes, as shown in Scheme 23.

Complex **75a** and **75b** were reported to be insoluble[63] and no data were given for **75d**.[182] The di-*n*-butylamino derivative **75c** was, however, soluble. M_n was reported as 27,000 and UV spectroscopy indicated a strongly red-shifted σ–σ^*-transition at 363.4 nm (ε_{Si-Si} = 5,800 Si-unit^{-1}dm^{3}cm^{-1}), which underwent a continuous small thermochromic blue shift as the temperature was reduced. The strong spectral red shift is in agreement with theoretical predictions[104,105,107] of bathochromic shifts based on a σ-n mixing interaction for polysilanes containing Si-bound heteroatoms with available non-bonding electrons, and also with experimental observations on alkoxy-substituted



75a: NR$_2$ = NEt$_2$
75b: NR$_2$ = NPri$_2$
75c: NR$_2$ = NBun$_2$
75d: NR$_2$ = N(Me)Hex

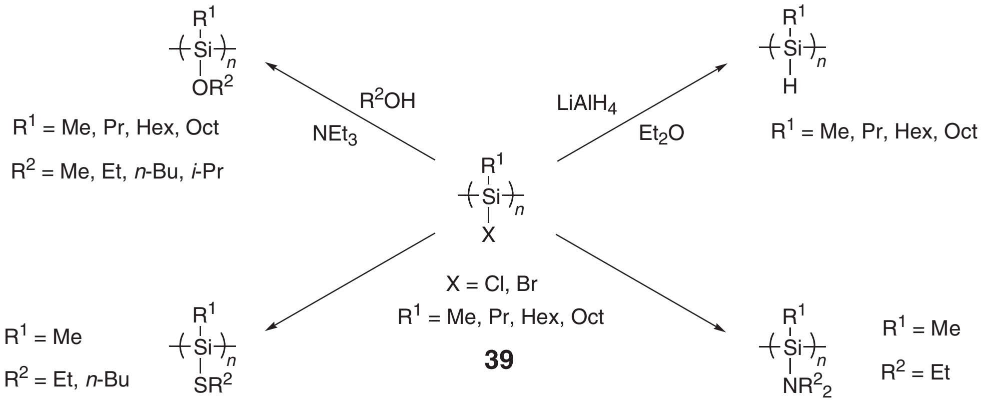
Scheme 23 Preparation of dialkylamino-substituted heteroatom polysilanes by masked disilene method.

polysilanes (see below). One of the key features of the masked disilene route is that alternating co-polymers can be synthesized with high regioselectivity, due to the preferential disilabicyclooctadiene ring cleavage attack by the anion at the less hindered $SiMe_2$ site (8-position) of the monomer. Usually, however, a small amount of minor regioisomer is formed. In the synthesis of **75**, however, regioselectivity was complete. An electronic effect due to the amino group was considered to augment the steric effect. Utilizing the lability of the Si–amine bond, it was recently shown that the di-*n*-butylamino group in **75c** could be replaced by Cl using acetyl chloride to afford the strictly alternating Cl-substituted precursor polymer.[183] Reaction of this with various nucleophiles led to a new class of functionalized strictly alternating co-polysilanes. Use of PhLi afforded a true polysilastyrene, poly(dimethylsilylene-*alt*-methylphenylsilylene).

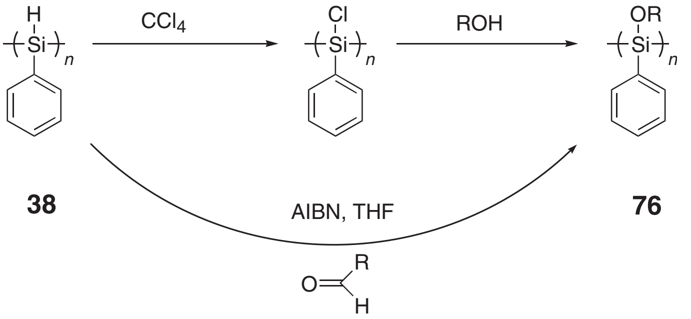
Oxygen-substituted heteroatom polysilanes are not accessible by Wurtz coupling due to the good leaving character of the OR group.[37,38,39] Other direct synthetic routes, including the masked disilene approach, are also precluded, so these –OR side-chain polymers have been prepared by post-polymerization functionalization of the precursor polymers **17**, **34**, **35**, **37**, and **38**, shown above. The first oxygen-attached side-chain polysilanes were prepared from **34** and **35**, and were covered in COMC (1995) (chapter Organopolysilanes, p 101). Up to 80% of phenyl groups could be replaced by alkoxy groups. In a new variation on these methods, Herzog and West developed new Cl- or Br-containing precursor polysilanes **39** using an AlX_3/RCOX system and showed that a wide range of heteroatom-substituted polysilanes is accessible from these, as shown in Scheme 24.[35] Reactions of **39** with the bulky $HNEt_2$ and *t*-BuOH led to partially substituted products. Most of the products showed UV absorption maxima in the region 300–304 nm. This is rather a short wavelength for a heteroatom-substituted polysilane, since theoretical investigations[105,184] showed that for Si-bound heteroatoms, with available non-bonding electrons, a σ-n mixing interaction should occur resulting in a spectral red shift; presumably, the short λ_{max} thus reflects the low molecular weight of the samples. Interestingly, the thio-substituted polymers showed the longest wavelength absorption maxima at 316 nm.

Recently, a detailed study on alkoxy-substituted homo- and co-polymers synthesized using the method of Herzog and West was reported, combining spectroscopic and computational data.[78] Molecular dynamics calculations showed that the conformation of the polysilanes was determined by the Coulomb interaction between the alkoxy side chains, and the conformations of the polyalkoxysilanes are similar to those of dialkylpolysilanes. MO calculations indicated that the interaction between the orbitals of the oxygen atom in the side chain and those of the silicon atom in the σ-conjugated main chain was larger in the LUMO than in the HOMO. The resulting stabilization of the LUMO was responsible for shifting the absorption maximum to longer wavelength. Polymers with increasing proportions of alkoxy side chains showed progressively smaller thermochromism in non-polar solvents, which was explained on the basis of Schweizer's thermochromism theory[152] as resulting from the larger energy difference between extended and disordered conformations. This energy difference was considered to increase with alkoxy group ratio due to the increasing electrostatic interactions between vicinal alkoxy groups. The opposite trend was found in polar solvents. The small solvatochromic effects were considered to be due to the steric shielding of the oxygen atom from the solvent by the alkyl side chain.[78]

A different methodology using the reactivity of the Si–H bond in **38** was reported in two communications, as COMC (1995) was being completed. Precursor poly[phenyl(H)silylene] **38** is conveniently prepared by the



Scheme 24 Assymmetrically functionalized monoheteroatom polysilanes via chlorodephenylation.



Scheme 25 Radical-based routes to assymmetrically functionalized monoheteroatom polysilanes.

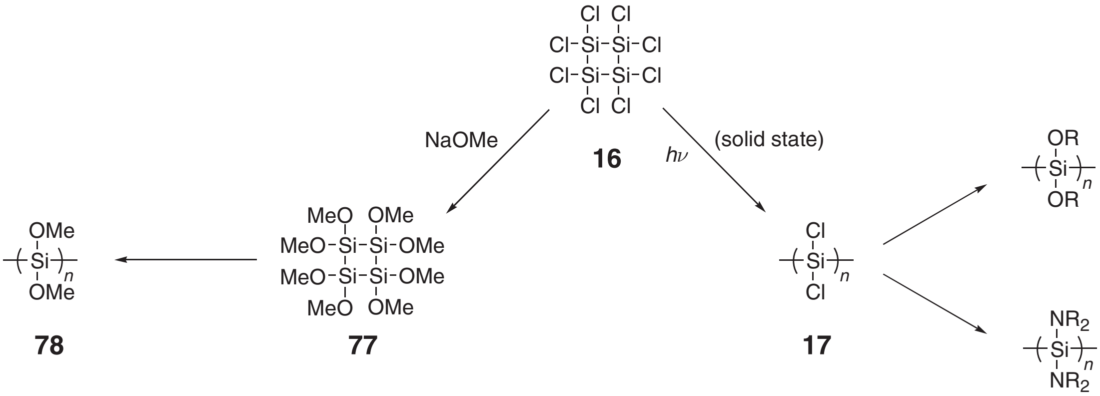
Harrod-type catalytic dehydrocoupling method using early transition metal catalysts (see COMC II (1995), chapter Organopolysilanes, p 99, and earlier in this review, Section 3.11.4.1.3.(i)).[69,75] Si–H bonds are susceptible to free radical attack, and use of this was made in the free radical substitution of **38** to prepare a number of oxy-functionalized polysilanes, as shown in Scheme 25.[185,186]

In this study, $[PhSi(CH_2C_nH_{2n+1})]_m$ alkyl analogs of **76** with the same number of atoms in the side chain were also synthesized. The UV spectra showed that the Si main-chain absorption in **76** was red-shifted 26 nm compared to the alkyl analogs. The reason for this was discussed in terms of σ-n mixing; that is, an electronic, rather than conformational, effect. Theoretical studies had predicted this effect, suggesting its origin in a destabilization of the HOMO due to the mixing interaction and consequent decrease in HOMO–LUMO gap.[187]

Recently published experimental and theoretical studies by another group on poly(methylpentoxysilylene) and poly(methylpentoxysilylene-*co*-hexylmethylsilylene) synthesized by the $AlCl_3$/RCOCl route found similar UV spectral red shifts for oxygen-attached side-chain polysilanes.[78,79] In contrast to the above, *ab initio* MO calculations on model silicon tetramers suggested that the oxygen orbital largely affects the excited state of the silicon backbone and that as a result, the reduced HOMO–LUMO gap derives from stabilization of the LUMO.

Currently, the only routes to symmetrically substituted bis-heteroatom polysilanes, aside from the Wurtz-coupled **72**, start from octachlorocyclotetrasilane, $(SiCl_2)_4$ (see Scheme 26). In one route, octamethoxycyclotetrasilane, **77** (prepared from $(SiCl_2)_4$), was subjected to ROP affording $[Si(OMe)_2]_n$, **78**, with molecular weight 45,000 and σ–σ^*-transition at 332 nm in the UV spectrum, although few details are reported.[97] In the other route (as described in Section 3.11.4.1.4.(ii)), octachlorocyclotetrasilane, **16**, was crystallized[102] and subjected to topotactic photolytic ROP to give the crystalline[103] linear precursor polymer $(SiCl_2)_n$, **17**. Reaction of the insoluble **17** in toluene with alcohols or amines afforded soluble bis(alkoxy)- and bis(amino)-substituted polysilanes with DP of ca. 25 in high yield.

Short alkoxy side-chain polymers are water sensitive, but polymers with long alkyl chains are stable in water, presumably due to the ability of the long alkyl chains to wrap around the core and protect the sensitive Si–O functionality.[188,189] These polymers also showed UV absorption maxima red-shifted about 22 nm relative to their



Scheme 26 Routes to bis(heteroatom)-substituted polysilanes from **16**, Si_4Cl_8.

dialkyl analogs, for example, UV λ_{max} for $[Si(O\text{-}n\text{-}Oct)_2]_n = 344$ nm versus λ_{max} for $[Si(n\text{-}Oct_2)]_n = 321$ nm. Incorporation of the (*S*)-2-methyloctoxy group afforded optically active polymers with preferential helical screw sense (see Section 3.11.6.1). The observed helicity was corroborated by force field calculations, which indicated similar helical conformations for both dialkoxy- and dialkyl-substituted polymers. Based on their similar conformational properties, it was suggested that the origin of the spectral red shift was electronic, due to a σ-n mixing interaction, as for polymers **76** above, rather than conformational.

3.11.4.2.2.(ii) Direct attachment of carbon functional groups

There have been very few reports of polysilanes containing a carbon functional group such as unsaturated groups directly attached to the silicon main chain. This appears to be due to the difficulties in synthesis and characterization due to instability of these compounds. These polymers are expected to show significant differences to conventional polysilanes in their properties due to the interaction of main-chain σ-electron and side-chain π-electron systems.

Silole incorporation was noted above in Section 3.11.4.1.1.(iii) where poly(1,1-silole)s synthesized by Tamao and co-workers via Wurtz-type coupling were described. The related silole-incorporated polysilanes bearing silole units on every fifth silicon in a regular sequence prepared by Sakurai and co-workers using anionic ROP were described in Section 3.11.4.1.4.

Cyano incorporation was briefly reported (though with few details) by ROP of a mixture of dicyanohexaphenylcyclotetrasilane isomers prepared by passing the precursor mixture of ditriflatohexaphenylcyclotetrasilane isomers through an ion-exchange resin containing cyano groups. The resulting polymer had $M_n = 6{,}800$ and a UV λ_{max} at 342 nm.[97]

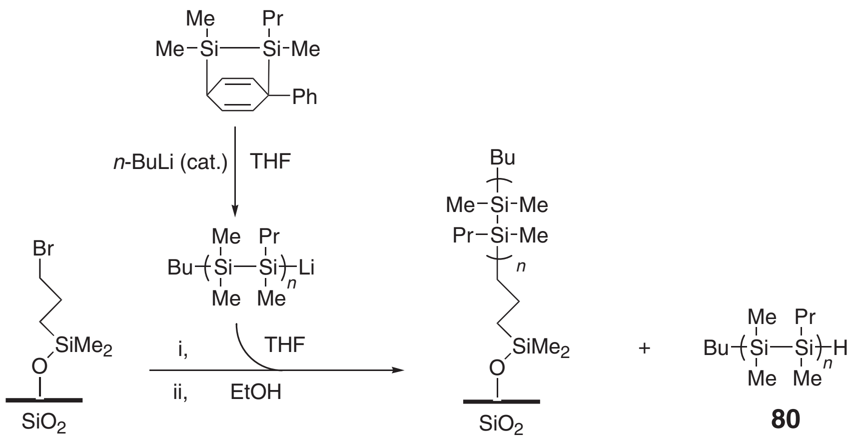
Ethynyl group incorporation was likewise noted in one communication, effected by reaction of triflate precursor polysilane **35** with lithium phenylacetylide, though the product was not explicitly characterized.[137] One other report of ethynyl-substituted polysilanes was published, describing the synthesis of a series of co-polymers prepared from the co-monomers, dichloro(phenylethynyl)methylsilane and dichloromethylphenylsilane, at different co-monomer ratios.[96] The usual Wurtz-type procedure was employed, except that due to the higher reactivity of the ethynyl-substituted monomer, the latter was added to the reaction mixture 10 min after the other co-monomer. Even with this modification, the major reaction products were cyclic and cross-linked materials. FTIR spectroscopy of the soluble co-polymer fractions showed a C≡C absorption at 2,160 cm^{-1}, confirming incorporation of ethynyl moieties, though at lower ratios than the monomer feed ratio. Based on the shape of the IR signals, it was acknowledged that even the soluble products could be branched. It had been expected that extension of the electronic delocalization through the additional π-system of the side chain would lead to a bathochromic shift in the UV spectra; however, no shift was observed, although the UV profile tailed into the visible, causing coloration in the products. In a further unexpected phenomenon, the intensity of the lowest energy transition (σ–σ^*, modified by mixing with phenyl π-orbitals in the co-polymers with Si–Ph moieties) was found to decrease as the ratio of ethynyl-bearing monomer increased. The emission spectra showed a strong, broad, fluorescence band at 480 nm upon excitation at 345 nm (peak of the σ–σ^*-UV absorption transition), but no emission upon excitation at 280 nm (π–π^*-UV absorption transition), indicating no energy transfer between the polysilane-delocalized σ-electron system and the side-chain π-system. The intensity of the 480 nm emission band increased with increasing ethynyl content. It was suggested that this band could be due to intramolecular excimer formation, as was proposed for naphthyl-substituted co-polysilanes,[190] and also discussed for ionic quaternary ammonium-substituted polysilanes.[172] However, emission bands in this region have also been shown to arise from main-chain defects such as branching points. Given that the existence of branching in these ethynyl-substituted polymers was considered possible, the contribution of defect-based emission should also be explored. Clearly, further experimental and theoretical investigation of these systems is required.

3.11.4.2.3 End-group functionalization

In a very interesting development, increasing the potential of polysilanes for application yet further, polysilanes have been end-grafted onto substrate surfaces using a variety of approaches. This surface-tethering of polysilanes requires the functionalization of one end (terminus) of the polymer main chain with a group which can be attached to a reactive surface or derivatized surface.

The first examples employed a lithium-terminated polymer chain, utilizing the primary product of the *n*-butyllithium-catalyzed polymerization of a masked disilene (see Section 3.11.4.1.2) and a reactive siloxy alkylbromide anchor-derivatized quartz surface, affording the end-grafted polysilane **79**, as shown in Scheme 27.[191]

The functionalized substrates showed UV absorption maxima at 330 nm, with absorbance directly proportional to the reactive anchor density. The UV absorbance did not decrease on leaving in toluene solution overnight in the dark,



79

80

Scheme 27 End-graft polysilanes via anionic polymerization of masked disilene.

confirming the covalent linking of surface and polysilane chain. By comparison with excess unattached hydrolysis product 80, M_n for the silicon chain was shown to be ca. 17,000. Commensurate with their monodisperse yet solid nature, the end-graft polysilanes showed thermochromic properties intermediate between those of dilute solution and bulk film samples, as evident in the UV spectra reproduced in Figure 9.[65] The spectrum of 80 in dilute solution shows an abrupt thermochromic transition at 260 K on warming due to the change from ordered to random conformation. In films of 80, the tight intermolecular crystalline packing inhibits any conformational change, so the UV spectra are temperature invariant. The variable-temperature UV spectra of 79, however, show a continuous disordering as temperature increases, attributed to partially restricted molecular motion due to the tethering and also lower levels of intermolecular interaction.

In a different approach, lithium end-functionalization of a polymer chain was also achieved by a "cut and graft" technique,[65] involving scission of Wurtz-coupled high molecular weight poly[*n*-decyl-(*S*)-2-methylbutylsilylene] (PDMBS), using a small amount of lithium 4,4′-di-*t*-butylbiphenylide. This technique (albeit with concommitant molecular weight reduction) allows the lithium end-functionalization of polymers such as those with long alkyl side chains which are inaccessible by the masked disilene route. It was found that a long alkyl spacer in the reactive anchor was required. In contrast to 79, PDMBS in the end-graft state showed the same thermochromic properties as the solution-state analog, indicating that both forms of PDMBS show behavior characteristic of isolated molecules with low intermolecular interaction.[65] This was confirmed by AFM, by which individual polymer molecules were observed as isolated dots on a flat quartz surface,[65] and later on sapphire and Si(1 1 1) surfaces.[192] The same "cut and graft" methodology was also applied to PMPS and poly(bis-*p*-*n*-butylphenylsilylene) (PBPS). AFM indicated dot and "worm" images, respectively, the latter due to the chain rigidity and extension resulting from incorporation of two phenyl rings.[193] More recently, the same group reacted polysilanyllithiums with a long alkyl chain linker bearing a bromine at one end and a tris(thioether)silyl group at the other, as shown in Scheme 28, affording polysilanes 81 and 82 with a sulfide tripod terminus which could be chemisorbed onto a gold surface.[194] The products were characterized by UV spectroscopy and AFM.

Most recently, a simple, mild, one-pot immobilization method was developed to attach the rigid rod-like helical polysilane, poly(*n*-decyl-*i*-butylsilylene), via a siloxy linkage to hydrophilic quartz or mica substrate surfaces.[28,195] Triethylamine was used as a catalyst to couple the Si–H and/or Si–OR termini of the dialkylpolysilane chains (which are generated during the course of Wurtz-type synthesis and workup)[51,195] with the surface –OH groups. AFM, UV, and IR data were used to analyze the reactions.

3.11.5 Electronic and Molecular Structure, Conformations, and Properties

The unique optoelectronic properties of polysilanes are perhaps the most important and interesting feature of these materials. Understanding the interrelation between these properties and the polymer structure, morphology,

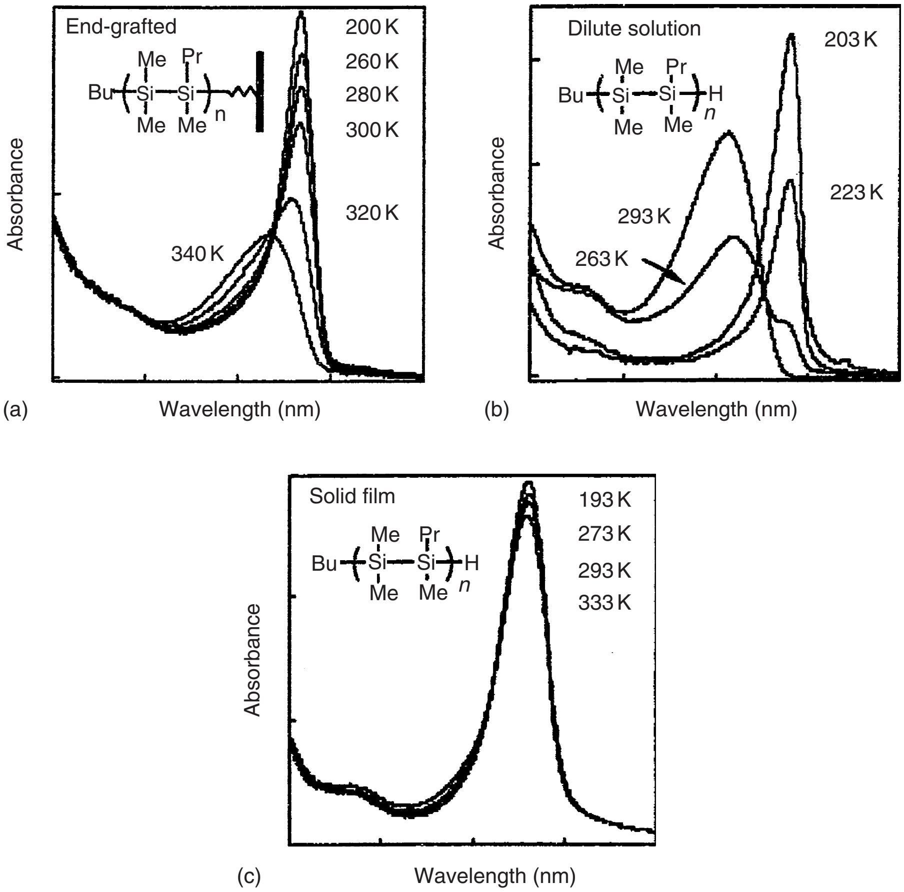
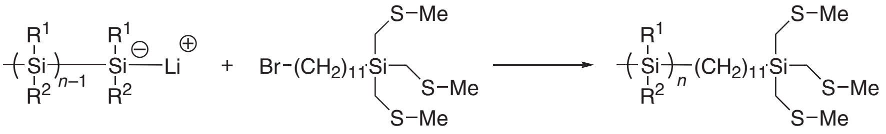


Figure 9 Thermochromic UV properties of (a) end-graft polysilane 79, (b) dilute solution, and (c) film analogs 80.[65] Reprinted with permission from Ebata, K.; Furukawa, K.; Matsumoto, N.; Fujiki, M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1999**, *40*, 157–158, © 1999 American Chemical Society.



81: R^1 = Me; R^2 = *n*-Pr
82: R^1 = *n*-octadecyl; R^2 = *i*-Bu

Scheme 28 Synthesis of sulfide tripod-terminated polysilanes.

environment, and state is thus critical for the further development and application of the field. The subject has been reviewed in depth several times.[21,196,197]

3.11.5.1 Electronic Structure

As the number of silicon atoms in the delocalized backbone σ-electron system increases, the number of HOMO and LUMO states increases, resulting in a band structure for high molecular weight polymers. Electronic absorptions from the HOMO (σ) to LUMO (essentially σ^*) are responsible for the characteristic UV absorption of polysilanes observed between 300 and 400 nm, the transition moment for which is in the direction of the Si chain.[198] Polysilanes are extremely attractive candidates in various optoelectronic applications[21] due to the tunability of the absorption maximum in this range. This optoelectronic tunability results from the possibility to modify the σ–σ^* (i.e., HOMO–LUMO) transition energy, which has been shown by many theoretical and experimental studies to be sensitive to main-chain and side-chain steric and electronic factors, which are interdependent. The effects of these factors can, however, be considered independently, by holding one or other constant. The longest wavelength absorption maximum occurs for a backbone Si–Si–Si–Si dihedral angle of 180° (i.e., the fully extended *all-anti*-conformation), which is that in which σ-conjugation is maximized. Additional UV spectral red shift occurs when unsaturated π-system side chains are connected directly to the main chain, due to the mixing of σ- and π-orbitals which results in a smaller HOMO–LUMO gap. In the following sections, an overview of the developments in understanding of electronic and steric factors will be given.

3.11.5.1.1 Conformations

Calculations on gas-phase oligosilane molecules afford an understanding of the interactions in, and conformational structure of, a single, isolated, polysilane molecule. In some cases, these have been correlated with the results from gas-phase or matrix-isolation studies on small model compounds.[8,199,200] In the solution phase, additional interactions occur between polymer molecule and solvent (van der Waals, in the absence of any polar substituents on polymer and solvent) to solvate the polymer molecules. The solvation affects the global conformation of the molecule, which can be globule-, coil-, or rod-like.[201–206] The conformations in solution are dynamic, with mobile helical reversals[207] and kinks or defects[45] separating segments within which conformations are considered to be dominated by a single dihedral angle. In the solid state, polymer–polymer intermolecular interactions and crystal-packing forces increase the conformational complexity, and compound conformations (such as AD_+AD_-) are postulated. Solid polymers can exist in crystalline, liquid crystalline, or amorphous phases, depending on chain length,[208] substituents, repeat unit symmetry, and temperature. For those with the most regular structures which can exist in a crystalline form, an increase in temperature may result in partial disordering at a phase-transition temperature to a hexagonal columnar liquid crystalline mesophase (hcm). Further increase in temperature can result in transitions to more disordered phases, such as nematic liquid crystalline or amorphous.

At the time of publication of COMC (1995), three distinct polysilane conformational types were known in the solid state (see chapter Organopolysilanes, p 102). These were: (i) *all-anti* (*all-trans*, as it was formerly termed), with a Si–Si–Si–Si dihedral angle of 180° and UV $\lambda_{\max}$ in the range 330–370 nm, reported for the symmetrical polysilanes $(SiR_2)_n$ with linear alkyl C-x chains: C-1 (i.e., $(SiMe_2)_n$),[209] C-2,[210] C-3,[210,211] C-4 at high pressure,[212,213] C-6 and C-7,[214] and the non-symmetrically substituted (MeSi-n-Pr)$_n$ (now considered to exist in a monoclinic unit cell)[215,216] and (EtSi-n-Pr)$_n$;[211] (ii) 7_3 helix, with a dihedral angle of ca. 154° and UV $\lambda_{\max}$ in the range 310–320 nm, reported for C-4 and C-5;[217] (iii) AG_+AG_- (or TGTG′, as it was formerly termed) with alternating *anti*- and *gauche*-angles, proposed for C-8, C-9, C-10, C-12, and C-14[218] on the basis of molecular mechanics calculations and X-ray studies. However, it has been suggested[196,197] that a more reasonable conformation would be AD_+AD_-, since the UV absorption for these polymers occurs at ca. 350 nm, around that of *transoid* polymers. More recent correlations of DSC, X-ray and UV data suggest that a combination of D and T is possible (see below). In COMC (1995), the molecular packing of unsymmetrically substituted polymers was noted to be less efficient. For small differences, the *all-anti* to hcm transition temperature decreased (e.g., C-5/C-6 and C6-/C-7); for slightly greater differences, crystallization may not occur, for example, C-2/C-4, C-3/C-5, and C-4/C-6 showed liquid crystalline phases (hcm and/or nematic); for large differences, the polymers, including PMPS, were fully amorphous (glassy below, and elastomeric above, T_g).

Since the publication of COMC II (1995), a huge number of polysilane structural types have been investigated experimentally and theoretically, with small and large substituents, both symmetrically and non-symmetrically substituted on the main chain. Spectroscopic data, in particular, from thermochromic studies in the solid state, have now shown the existence of more phases than the above three, as evidenced by their separate absorption bands. While such UV absorption spectra can show the number of phases, and can give a qualitative indication of conformation, the exact structures and dihedral angles are difficult to determine. The challenge has been to correlate the data, both experimental (such as ionization potential, DSC, X-ray, and UV) and theoretical. Infrared and Raman spectroscopy have also been applied in the analysis of structure and bonding: *all-anti*-conformations should be pre-resonance enhanced (see later),[219] have no IR–Raman coincidences, and the enhanced intensity Raman lines of bonds to side-chain atoms indicate hyperconjugation of side chain with the electronically delocalized backbone.[218,220–222]

3.11.5.1.2 Calculation and spectroscopy of small molecules and oligomers

Conformational study on small model compounds is one way of probing the conformations of the polysilanes, and avoids difficulties arising from the sheer size of the polymer molecules. As discussed in the section above on oligomers (Section 3.11.3), the results of matrix-isolation experiments were correlated with the results of *ab initio* calculations for tetrasilanes, allowing the assignment of five experimentally observed conformations, *anti*, *A* (dihedral angle $\omega \approx 180°$), *transoid*, *T* ($\omega \approx 165°$), *deviant*, *D* ($\omega \approx 150°$), *ortho*, *O* ($\omega \approx 90°$), *gauche*, *G* ($\omega \approx 60°$) and one as yet unobserved conformation, *cisoid*, *C* ($\omega \approx 40°$).[10] These conformations are considered to be possible for the high polysilanes, although as the size of substituents on silicons in positions 1 and 3 increases, interactions between them disfavor the *A* conformation.[197] Also, high-polymer main chains can show combinations of these conformations, as in the AD_+AD_- noted above, although in solution the *all-transoid* pair of enantiomers (helicity reversals raise the energy)[223] is predicted to have the lowest enthalpy for all chain lengths.[196] Thus among all experimentally determined polymer conformations, the *A* conformation is only found in special circumstances, such as where side-chain crystallization forces an *all-anti*-chain, as in poly(dihexylsilylene),[214] or where small substituent size permits it, as in poly(dimethylsilylene)[224] or perchloropolysilane[103] (see Section 3.11.4.1.4.(ii)).

3.11.5.1.3 Calculation of polysilane electronic structure

A number of groups have been active in addressing polysilanes computationally. As mentioned in Section 3.11.1, this area is beyond the scope of this chapter, and so coverage will be restricted to brief notes on a few of the major developments.

One of the main aims of such computations is the prediction and rationalization of the optoelectronic spectra in various steric and electronic environments by either semiempirical or *ab initio* methods or a combination of these, considering equilibrium structures, rotation barriers, vibrational frequencies, and polarizabilities. The accuracy of the results from these calculations can be evaluated by comparison of the predicted ionization potentials (which are related to the orbital energies by Koopman's theorem) with experimental values.

Calculations investigating conformational energies have been performed for the parent oligosilane, $H(SiH_2)_nH$,[225] and more complex permethyl Si_n oligomers including Si_4,[6,226] Si_5,[199] Si_6,[227] Si_7, and Si_8,[228] the Si_4 perethyl oligomer,[9,200] and oligosilanes with chloro[7] and phenyl[229] substituents, and are comprehensively treated in a recent review.[196] A range of possible helical conformations was found, with the *all-anti*-conformation only being favored for the smallest substituents. For anion and cation radicals, in contrast to the neutral Si_4 oligomers, only a stable *all-anti*-conformation was found.[230]

Calculations of the HOMO–LUMO gap energy as a function of alkyl substituent size are in agreement with the experimentally observed increase in lowest energy UV λ_{max},[231] and the effects of changing from alkyl to aryl side chains have also been reported.[232,233,234] Similarly, the UV λ_{max} red-shifts when heteroatom substituents with lone pairs are directly attached to the main chain, due to σ-n mixing:[104,105] these effects have been theoretically investigated for oxygen[78,104,105] halogens,[106,107] sulfur,[105,108] and nitrogen.[105]

Concerning electronic delocalization in polysilanes and its dependence on conformation and side chain, initially, the Sandorfy C model (which was developed for hydrocarbons) was applied; only the strongest interactions, that is, primary (β_P) and geminal (β_G), were considered in this model (the ratio β_P/β_G is a measure of main-chain electron delocalization).[21] The model was extended to the PPP level, but conformational dependence was not included. Ground-state properties are adequately approximated using this model.[196] However, in the LUMO, the side-chain σ^*-orbitals interact with the Si 3*s*-orbitals, which is of importance in the excited state when these orbitals are occupied, although in the ground state, these orbitals are unoccupied and thus not critical. To include the conformational terms which were evidently important from the experimental data, the "ladder C" and "ladder H" models were developed which included the vicinal interaction, β_V, the only term with a dihedral angle dependence.[225,235] These consider a basic set of orbitals together with resonance integrals, the former including only silicon main-chain orbitals and the latter including main-chain and side-chain silicon orbitals and the orbital bonding with the silicon side-chain orbital, as shown in Figure 10. The ground-state (HOMO) is almost purely $3p_z$ in character (assuming the long axis is z, as indicated below), and thus is very sensitive to dihedral angle, whereas the LUMO, which has considerable 3*s*-character, is much less sensitive.[21]

Recently, the relationship between electronic structure and conformation was examined for chains up to Si_{40}.[228] The parameters of the Huckel-type ladder C and H models of Si_nMe_{2n+2} oligosilanes were optimized to reproduce orbital energies from *ab initio* HF calculations of 84 conformers of geometry-optimized Si_2 to Si_8 permethylated model compounds. The HOMO destabilizes as the dihedral angle increases up to *all-anti*, with greater destabilization being found for greater chain lengths, as shown in Figure 11. It is seen that above ca. 30 silicon atoms, the HOMO

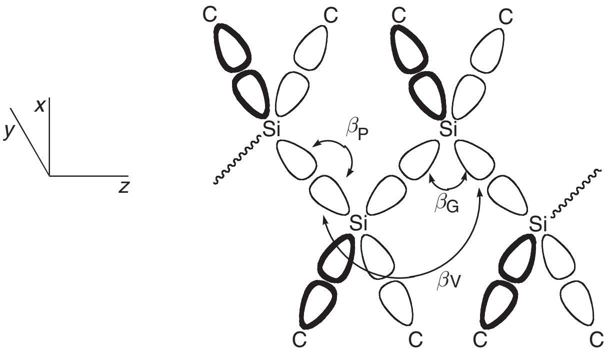


Figure 10 Orbitals and resonance integrals in ladder H model (bold Si–C orbitals out of paper, normal Si–C orbitals into paper; Si–Si in plane).

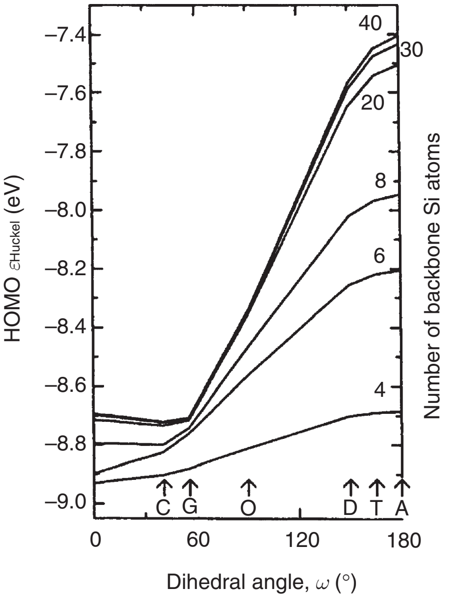


Figure 11 Ladder H-calculated HOMO energy for oligosilanes with uniform dihedral angle, ω.[228] Adapted with permission from Schepers, T.; Michl, J. *J. Phys. Org. Chem.* **2002**, *15*, 490–498, © 2002 John Wiley and Sons Ltd.

energy does not change significantly with further increase in chain length. This computational result mirrors the experimental observation of UV λ_{max} variation with degree of polymerization (see Figure 4). A sharp change in slope is evident for Si_8 and above at $\omega \approx 55°$, whereas for the shorter chains, the slope change is gradual. This was interpreted in terms of an orbital crossing between the HOMO and HOMO-1, and also found in ladder H calculations for these orbitals. This result is in agreement with *ab initio* calculations.[236]

The effect of chain segmentation on main-chain electronic delocalization by introduction of *cisoid* twists (also termed "kinks") into an *all-transoid* chain was also considered. Similar results were found to those previously recorded,[21] where the effect of introducing *gauche*-turns into an *all-anti* chain was discussed, that is, delocalization is interrupted by the kinks, and concentrated in the longer segment, the interruption being greater for two or more consecutive kinks. In apparent contrast, *ab initio* calculations on an *anti*-chain with periodic *gauche*-kinks by different authors had found that the introduction of such kinks did not result in localization of holes and electrons.[237] These differences were reconciled by the key new finding in a calculation of the effects of incorporation of multiple *gauche*-twists in a *transoid* chain (repeating GT_3GT sequence) that the HOMO remained delocalized (see Figure 12).[228]

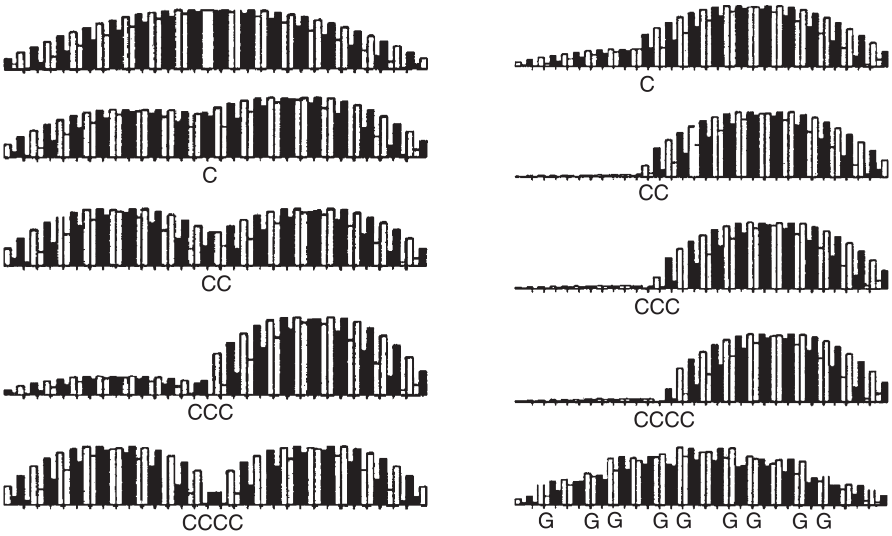


Figure 12 Ladder H HOMO coefficients for conformers of $Si_{31}Me_{64}$ with *cisoid* (C) or *gauche* (G) kinks in an *all-transoid* chain (amplitude shown by bar length and sign by fill).[228] Adapted with permission from Schepers, T.; Michl, J. *J. Phys. Org. Chem.* **2002**, *15*, 490–498. © 2002 John Wiley and Sons Ltd.

3.11.5.2 Solution Studies: Global Conformation, Solvato- and Thermochromism

In solution, polymer molecules are dispersed in the solvent so that the complicated issues of interchain polymer–polymer interactions (molecular packing arrangements) and temperature-dependent phase transitions which occur additionally in solid phases and their relationship with conformation do not arise (these are treated in the next section). In solution, the interactions are polymer–solvent and intrachain polymer–polymer. In a good solvent, the former predominate to maximize solvent–polymer contact and chains are generally extended. In a poorer solvent, intrachain interactions predominate, resulting in chain coiling and spectroscopically evidenced conformational change. Such solvent-dependent UV spectroscopic changes are termed “solvatochromism.” Solvatochromic effects are generally small for polysilanes with non-heteroatom alkyl and aryl substituents, though they become noticeable in heteroatom-functionalized polymers. With further decrease in the ability of the solvent to solvate the polymer, polymer–polymer attractions begin to predominate, and aggregation and then precipitation result. For a given solvent system, the reversible shift of UV absorption maximum on changing sample temperature is termed “thermochromism” and indicates a reversible change in the HOMO–LUMO gap, which is sensitive to substituent type, chain length, segment length, and conformation. Since no chemical transformation occurs, the origin of the phenomenon is thermally induced segment and conformational change. Regarding polysilanes in solution, as has been explained above, (i) the electronic and conformational properties are strongly coupled, and (ii) several well-defined conformations are known and predicted. Additionally, the energy barriers between the different conformations are often small. It is therefore to be expected that polysilanes exhibit thermochromism.

3.11.5.2.1 Solvation

The structural variations shown among polysilanes depend, as noted above, on the phase of the sample, and interaction of the polymer molecules with the surrounding medium has significant effects on the molecular properties. Experimental studies which probe the single molecule in its unperturbed state are thus particularly important for linking theoretical studies on isolated molecules with conventional solution and also solid-state studies. The experimental unperturbed state is called the θ state and is a solution in which polymer–solvent interactions are exactly equal to solvent–solvent interactions, that is, the θ solvent is neither a good solvent (in which solvation causes extension of the polymer to maximize favorable polymer–solvent interactions), nor a poor solvent (in which the polymer molecule contracts due to the greater strength of intramolecular interactions and then aggregates due to intermolecular polymer–polymer interactions). In the unperturbed θ state, the polymer conformation should correlate to the conformation predicted from molecular dynamics (MD)/rotational isomeric state (RIS) calculations. From such studies, structure–property relationships of polymers and correlations between primary and higher-order structures

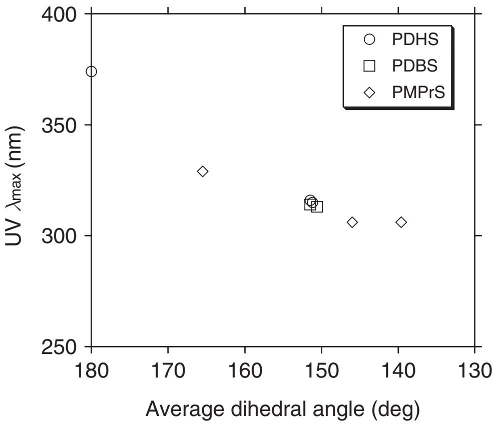


Figure 13 Correlation of UV absorption (λ_{max} (nm)) with average dihedral angle (replotted from data in Ref: 222).

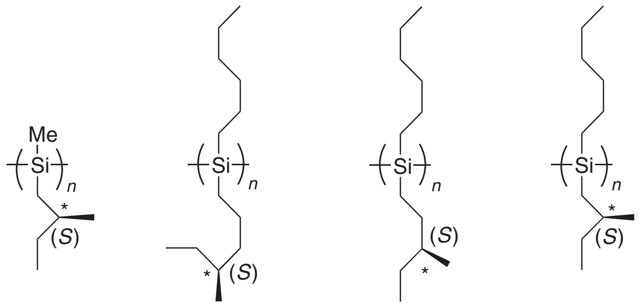
can be established.[223] Using the techniques of static light scattering (SLS), size-exclusion chromatography (SEC), and SEC-multiangle laser light scattering, the θ solvents and characteristic ratios (C_∞) of several polysilanes have been evaluated: for poly(dihexylsilylene), in the θ solvent comprising hexane (58.2 wt.%) and 2-propanol (41.8 wt.%) at 25 °C, $C_\infty = 42.5$; for poly(dibutylsilylene), in the θ solvent hexane at 19.1 °C, $C_\infty = 42.3$; for poly(methylpropylsilylene), in the θ solvent comprising hexane (62.6 wt.%) and 2-propanol (37.4 wt.%) at 25 °C, $C_\infty = 19.9$.[202,223,238] Independent investigations by a different group on the characteristic ratio of poly(dihexylsilylene) using a variety of techniques afforded values of 19 (from intrinsic viscosity),[239] 26 (from SLS in the θ solvent comprising 58.7 wt.% hexane and 41.3 wt.% 2-propanol at 25 °C),[201] and 31 (from SEC-light scattering).[202] Comparing these values with that for polyethylene, ca. 6.7,[240] a typical carbon backbone polymer, it is evident that the polysilanes are stiffer and more extended. RIS calculations for the polysilanes above afforded calculated C_∞ values of 54.0, 42.0, and 12.3, respectively, comparable with the experimental values.[223] Calculated average Si–Si–Si–Si dihedral angles in the calculated θ state were correlated with the experimental UV absorption maxima of the experimental θ state, and together with known UV/structure correlations, the master curve of UV λ_{max} versus average dihedral angle, shown in Figure 13, was constructed.

The plot was then used to estimate the average dihedral angle for the 355 nm peak which becomes apparent in the spectra of PDBS and PDHS at their respective −36 and −31 °C thermochromic transitions.[223] A value of ca. 175° was predicted, which is in the range also shown by a decameric di-*n*-propylsilylene,[15] although somewhat larger than the value of 165° suggested in other discussions.[197]

3.11.5.2.2 Global conformation and optical characteristics of polysilanes

The electronic structure of a chromophoric main-chain polymer is usually connected to its conformational mobility, changes in which are observable as solvato-, thermo-, electro-, and piezochromisms in the optoelectronic spectra. In 1996, Fujiki published a study correlating the global conformation of 21 different polysilanes (i.e., globule, coil, stiff, or rod-like) with their optoelectronic properties.[203] Typical UV absorption spectra of four poly(dialkylsilylene)s bearing different chiral side groups in THF at 30 °C are shown in Figure 14: poly[methyl-(*S*)-2-methylhexylsilylene] (**83**, $\alpha = 0.59$), poly[*n*-hexyl-(*S*)-4-methylpentylsilylene] (**84**, $\alpha = 0.75$), poly[*n*-hexyl-(*S*)-3-methylpentylsilylene] (**85**, $\alpha = 0.92$), and poly[*n*-hexyl-(*S*)-2-methyl-butylsilylene] (**86**, $\alpha = 1.25$).[204] The position of the branch determines the side-chain–side-chain interaction and hence main-chain stiffness/conformational mobility[204,241] (see Section 3.11.6 for aspects relating to optical activity in polysilanes).

As the value of α increases from 0.59 to 1.25, the UV peak absorptivity increases, whereas the full width at half maximum(FWHM) decreases. The polymers in the study included seven optically active poly(dialkylsilylene)s with four different types of chiral β,γ or δ-branched alkyl substituent, 11 optically inactive poly(dialkylsilylene)s with six different types of achiral β,γ or δ-branched substituent, an optically inactive poly(dialkylsilylene) with racemic chiral side groups, and two optically inactive poly(alkylphenylsilylene)s, with λ_{max} in the range of 290–352 nm. A semi-empirical relationship between the main-chain absorption characteristics and the global conformation in solution was found, such that the main-chain peak intensity per silicon repeat unit, ε (Si-repeat-unit)$^{-1}$ dm^{-3} cm^{-1}, increased exponentially as the viscosity index, α, increased, as shown in Figure 15 (the FWHM decrease is also exponential).[204]



83 **84** **85** **86**

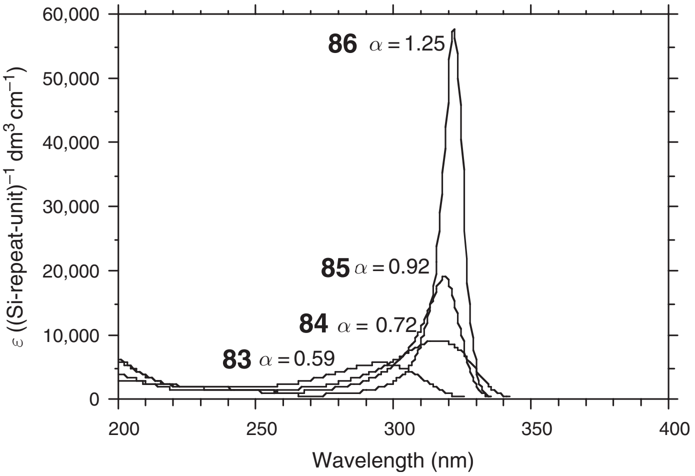


Figure 14 UV absorption spectra of polysilanes 83–86 in THF at 30 °C.[204] Reprinted with permission from Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563, © 2001 Wiley-VCH.

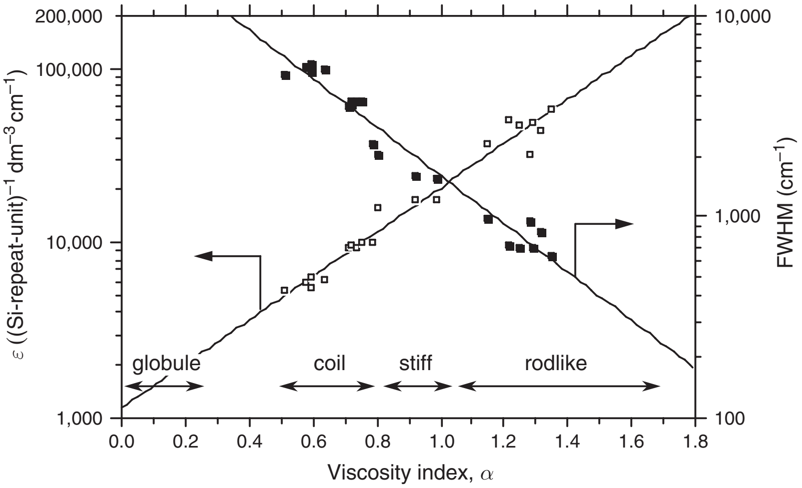


Figure 15 Correlation between UV peak intensity (ε), FWHM, and α of various polysilanes in THF at 30 °C.[203,204] Reprinted with permission from Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7424–7425, © 1996 American Chemical Society.

These changes were also reflected in the ^{29}Si NMR band shape, which was broader for more conformationally restricted polymers (see Section 3.11.6.2).[204,242]

Thus, the degree of σ-conjugation, global conformation, and UV absorption characteristics in polysilanes are controllable by the choice of side groups. For example, poly[methyl-(*S*)-2-methylhexylsilylene] **83** has the most shrunken shape with $\alpha = 0.59$, whereas its longer *n*-alkyl derivative, poly[*n*-hexyl-(*S*)-2-methylbutylsilylene] **86**, takes a rigid rod-like conformation with $\alpha = 1.25$. Poly[*n*-hexyl-(*S*)-4-methylpentylsilylene] **84** with $\alpha = 0.75$ has a random coiled conformation similar to ordinary optically inactive polysilanes. Poly[*n*-hexyl-(*S*)-3-methylpentylsilylene] **85** with $\alpha = 0.92$ is stiff (semirigid or semiflexible) and shows intermediate properties between **84** and **86**.

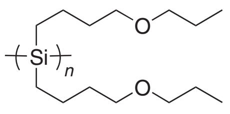
The semi-empirical ε–α–FWHM relationship is useful in discussion of the global conformational properties of polysilanes and prediction of the upper limit of ε for an ideal rigid rod polysilane, and either value of ε or FWHM gives information on the degree of chain coiling in solution under those conditions. Extrapolating the ε–α trend and given that the maximum α value for an ideal rigid rod polymer is 1.7–1.8,[203] ε values around 150,000 (Si-repeat-unit)$^{-1}$ dm^{-3} cm^{-1} can be predicted. Experimentally, this was tested by reducing the temperature of the UV measurement, and indeed ε for optically inactive poly[*n*-hexyl-(2-methylpropyl)silylene] in isooctane progressively increases from 45,000 with an FWHM of 800 cm^{-1} (8 nm) at 321 nm to 110,000 with an fwhm of 400 cm^{-1} (4 nm) at 317 nm when the temperature was cooled from 25 to -75 °C. This ε value, one of the highest among all polysilanes, was considered to correspond to an almost perfect rigid rod structure.[203,204]

Also important to the correlation between global conformation and optoelectronic properties are the investigations of single molecules of polysilanes by AFM, by which molecules could be directly imaged, and their contour lengths, diameters, and general shapes studied. These studies are dealt with in Section 3.11.5.3.

3.11.5.2.3 Solvatochromism

As noted above, solvatochromic effects in polysilanes are generally small, unless interactive functional side-chain groups are present, which can interact with solvents in different ways. Oxygen-substituted side chains can interact strongly with –OH group-containing solvents and solvatochromism is thus expected, particularly where hydrogen bonding is strong.

For example, addition of the strongly hydrogen-bonding alcohol, hexafluoroisopropanol (HFIP), to a chloroform or benzene solutions of $\{[n\text{-PrO(CH}_2)_4]_2\text{Si}\}_n$ (poly[bis(4-propoxybutyl)silylene]: **49**)[243] resulted in an abrupt solvatochromic transition when the HFIP concentration exceeded 4% or 2.5% (v/v), respectively, as shown in Figure 16 for $CHCl_3$. The absorption band at 325 nm in the UV spectrum of **49** is replaced by an absorption at 348 nm. The reason for the abruptness of the solvatochromism is not well understood. In THF, the transition was not abrupt, since THF can quench the polymer–HFIP solvatochromic effect due to the greater strength of the THF–HFIP interaction[244] (see below for the thermochromism of this polymer).



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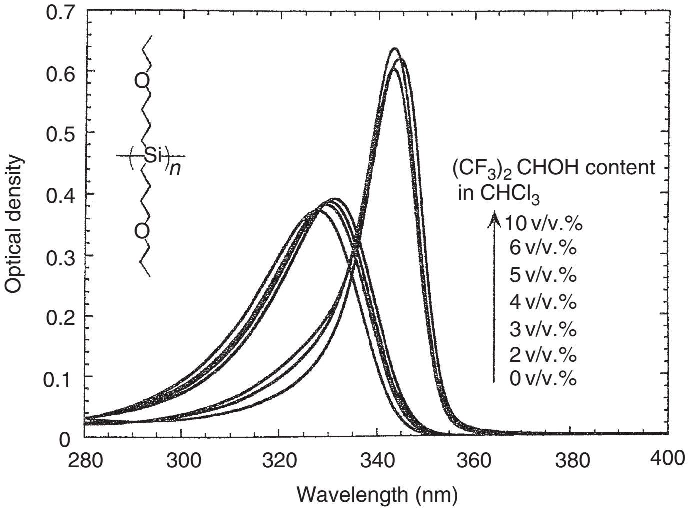
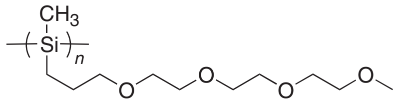


Figure 16 Abrupt solvatochromism of **49** on addition of HFIP.[243] Reprinted with permission from Oka, K.; Fujiue, N.; Dohmaru, T.; Yuan, C.-H.; West, R. *J. Am. Chem. Soc.* **1997**, *119*, 4074–4075, © 1997 American Chemical Society.



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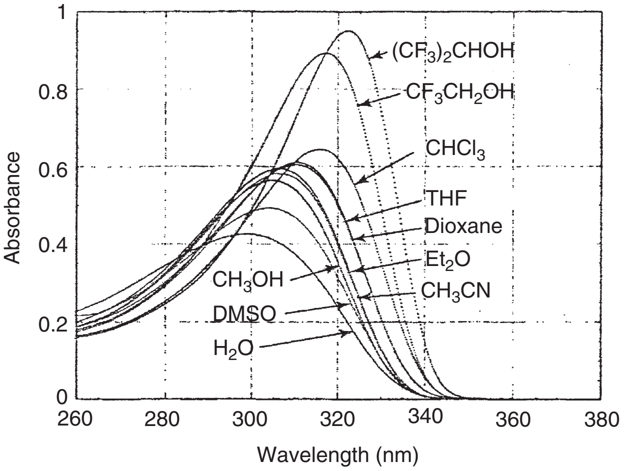


Figure 17 Selected UV spectra for **41** in various solvents showing solvatochromism.[197] Reprinted from West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y. Eds.; Wiley: 2001; pp 541–563, © 2001 John Wiley and Sons Ltd.

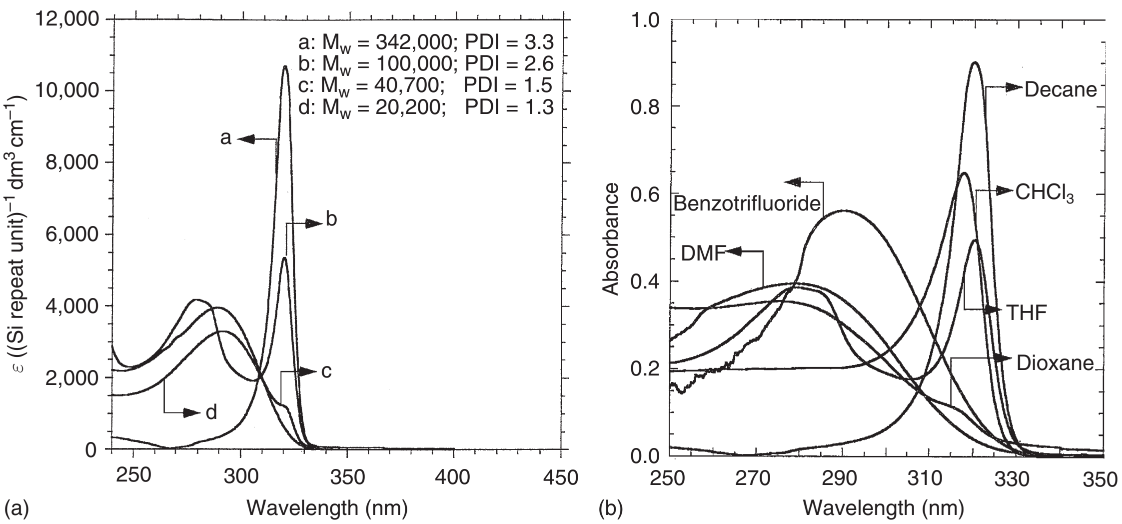
UV data for the non-ionic water-soluble polysilane **41** (see Section 3.11.4.2.1.(i)) were recorded in 20 different solvents.[149] Selected spectra are shown in Figure 17.

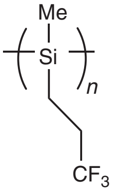
The shortest wavelength λ_{max} for **41** was 299.6 nm in water; in THF, an intermediate value of 310.4 nm was found; and the longest was 322.4 nm in HFIP. The effects were considered to originate owing to the different solubilities of non-polar main chain and polar side chains in the various solvents, and the possibility for hydrogen bonding: in water, the oligoethoxy side chain is well solvated, but the main chain and methyl side chain are not, resulting in strongly asymmetric forces acting on the backbone and consequent chain coiling, affording a strongly blue shifted absorption maximum; in THF, the main chain and side chain are both well solvated, resulting in a more extended chain and spectral red shift; and in HFIP, a strong hydrogen bonding interaction between side-chain ether oxygen and the strongly $\delta+$ polarized fluoroalcohol hydroxyl proton is considered to effectively increase the steric bulk of the side chains, causing main-chain extension. Addition of THF again quenched the latter polymer–HFIP solvatochromic effect. No simple correlation between solvatochromic shift and solvent parameters, such as dielectric constant, ionization potential, refractive index, and Schweitzer's solvent constant, was found.[149]

Other workers also investigated **41** and the related polymers poly(4,7,10-trioxaundecylmethylsilylene), poly(4,7,10-trioxahexadecylmethylsilylene), and poly(4,7,10,13-tetraoxanonadecylmethylsilylene), the latter two of which contain instead of a CH_3, a C_6H_{13} moiety as the side-chain end group.[205] Similarly to the above, UV absorption and fluorescence emission spectroscopy of aqueous solutions revealed highly folded random coils for **41** and poly(4,7,10-trioxaundecylmethylsilylene). The coiling is likely due to the poor balance of side-chain solvation: the oligoethoxy side chain is well solvated in water, but the main chain and methyl side chain are not, resulting in strongly asymmetric forces acting on the backbone and consequent chain coiling. In contrast, in organic solvents the backbone adopts a more extended conformation, since the solute–solvent interactions, which in H_2O prevent the silicon backbone from adopting a more extended conformation, are reduced. These changes in backbone conformation were found to be accompanied by an increase in the average backbone silicon segment length from 15 to 21–24 atoms and consequential doubling of the exciton coherence length. This is supported by the increase in the quantum yield in going from polar aqueous to apolar organic solvents.[205]

Recently, a very interesting example of solvatochromism was reported by Fujiki and co-workers.[206] Poly(methyl-3,3,3-trifluoropropylsilylene), **87**, synthesized via Wurtz coupling, showed solvatochromism as a result of weak, non-covalent intramolecular Si···F–C interactions which rendered the conformation of the polysilane uniquely controllable by solvent choice and molecular weight. UV, shown in Figure 18, photoluminescence, NMR, and viscosity studies on the polymer indicated a 7_3 helical rod-like conformation at room temperature in non-coordinating solvents (e.g., toluene and decane), since the intramolecular interaction resulted in constraining the chain in a rigid helix.

In coordinating solvents (with N, O, or F as donor), a globule-like conformation was adopted, as indicated in Figure 19, since coordination by the solvent destroys the weak Si…F coordination, resulting in the spectrum expected for a poly(methyl-*n*-propylsilylene) analog.





87

Figure 18 UV chromisms of 87 dependent on (a) molecular weight and (b) solvent.[206] Reprinted with permission from Saxena, A.; Fujiki, M.; Naito, M.; Okoshi, K.; Kwak, G. *Macromolecules* **2004**, *37*, 5873–5879, © 2004 American Chemical Society.

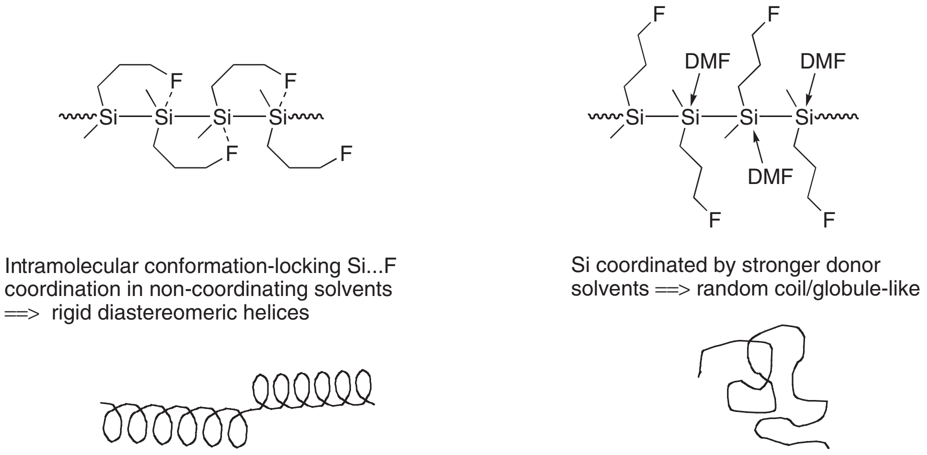


Figure 19 Conformations of poly(methyl-3,3,3-trifluoropropylsilylene), 87, in coordinating and non-coordinating solvents.

The Lewis basicity of the solvents was found to be more important for the solvatochromism than the solvent polarity, since such Si…solvent and Si…F interactions are competitive in the presence of solvents with donor atoms. In contrast, the analogous non-fluorinated polysilane, poly(methyl-*n*-propylsilylene), revealed a disordered conformation in both coordinating and non-coordinating solvents. Additionally, the UV spectra of various molecular weight fractions of 87 showed an unusual molecular weight dependency: an isosbestic point is apparent, suggesting an equilibrium between globule- and rod-like conformations at room temperature, which was also evident from the viscosity measurements.[206] Related work on C–F…Si interactions in optically active polysilanes is described in Section 3.11.6.1.1. Finally, concerning fluoro-substituted polysilanes, very recently, the photoluminescence intensity of **87** in solution and film states has been shown to be sensitive to the presence of nitroaromatic compounds, leading to the suggestion for the application of fluoroalkylated polysilane films as chemosensors for explosives.[245]

The molecular weight dependency of thermochromic transitions was also investigated by Sakurai and co-workers, who found that the transition temperature for PDHS and PDBS was proportional to the inverse of the number average molecular weight at low molecular weights.[208]

3.11.5.2.4 Thermochromism

When COMC II (1995) was published, two general types of thermochromism (reversible) had been recognized for polysilanes on lowering the temperature: a gradual bathochromic transition, and an abrupt transition to longer wavelength absorption. From the vast amount of experimental data now accumulated, five different types of thermochromic behavior on cooling can be characterized:

(i) Abrupt transition to longer wavelength. This is observed for polysilanes substituted with identical or very similar long alkyl side chains, for example, $(\mathrm{Si}^n\mathrm{Hex}_2)_n$, as shown in Figure 20(a). The range of the transition temperature is typically very narrow.[246]
(ii) Smooth transition to longer wavelength. An example of this type is shown in Figure 20(b) and occurs for polysilanes somewhat different side chains, such as $[\mathrm{Si}(^n\mathrm{Pr})(^n\mathrm{Hex})]_n$.[246]
(iii) Bathochromic drift to longer wavelength. Polymers in this category have very different side chains and are exemplified by $[\mathrm{SiMe}(^n\mathrm{Hex})]_n$ (Figure 20(c)).[246]
(iv) Hypsochromic drift or no thermochromism. These polymers have bulky side chains; an example is $[\mathrm{Si}(4\text{-}t\text{-}\mathrm{BuPh})_{0.5}(4\text{-}n\text{-}\mathrm{BuPh})_{0.5}]_n$ (Figure 20(d)).[247]
(v) Abrupt transition to shorter wavelength. This is observed for certain diarylpolysilanes, particularly those with alkoxy-substituted phenyl rings, for example, $[\mathrm{Si}(4\text{-PrOPh})_2]_n$ (Figure 20(e)).[247]

The origins and driving force of solution-state thermochromism have been the subject of many theoretical and experimental investigations. From the calculation of the structures of oligomers[228] and polymers,[204] investigations of enantiopure chiral-substituted polymers (see Section 3.11.6.1), and experiments on the structures of θ state polymers,[223] it is clear that in the absence of solvent or crystallization effects, the silicon backbones of most polysilanes are helical. Under certain conditions, the UV absorption of the backbone shifts bathochromically as in Figures 20(a)–20(c), indicating a decrease in the HOMO–LUMO gap due to an increase in σ-conjugation, usually induced by a change to a more extended structure with dihedral angles close to 180°. In Figures 20(d) and 20(e), however, for polymers with bulky phenyl groups, the UV absorption maximum is already at very long wavelength at high temperature, due to the extended conformation and electronic effects of the aryl groups,[248] and as the temperature is lowered, gradual or abrupt blue shifts of the absorption are apparent. For polymers such as $[\mathrm{Si}(4\text{-}t\text{-}\mathrm{BuPh})_{0.5}(4\text{-}n\text{-}\mathrm{BuPh})_{0.5}]_n$, a slight thermal shortening of Si–Si bond length with lower temperature, accompanied by main-chain twisting to alleviate the increased steric side-chain interactions, has been considered to be the origin of the effect.[248] For $[\mathrm{Si}(4\text{-PrOPh})_2]_n$, the abrupt shift could indicate a transformation to a highly twisted conformation to alleviate unfavorable dipole alignment due to the polar side-chain arrangement, although an alternative explanation on electronic grounds is that the phenyl rings could be forced out of maximum conjugation, eliminating the red-shifting effect of the σ–π-mixing which is usually responsible for the long wavelength absorption in aryl-substituted polysilanes.[248] The question then for the polymers with non-bulky groups, viz. $(\mathrm{Si}^n\mathrm{Hex}_2)_n$, $[\mathrm{Si}(^n\mathrm{Pr})(^n\mathrm{Hex})]_n$, and $[\mathrm{SiMe}(^n\mathrm{Hex})]_n$, is then what is the driving force which stabilizes the extended state? In answer to this, three mechanisms have been suggested. First, Schweizer's "single chain" model,[152] in which the driving force for the extension is the greater polarizability of the molecule due to the increased σ-conjugation. Second, the "aggregation" model (does not apply to solution-state thermochromism),[218,249] in which it was considered that, due to inter- or intramolecular substituent interactions, the side chains in PDHS could pack more efficiently in the *all-anti*-conformation, thereby promoting chain extension, and that this is the driving force for the adoption of the *all-anti*-conformation, despite the lower calculated energy of the helical conformation. On increase of the temperature above the transition temperature (42 °C), the intermolecular interactions are broken, allowing adoption of the lower-energy helical form. Third and most recently, the cooperative transition model,[208,246] in which the conformation depends on the temperature dependence of the conformational stabilization energies of extended and helical sequences. This has been very successfully applied to the solution-state thermochromism of PDHS.

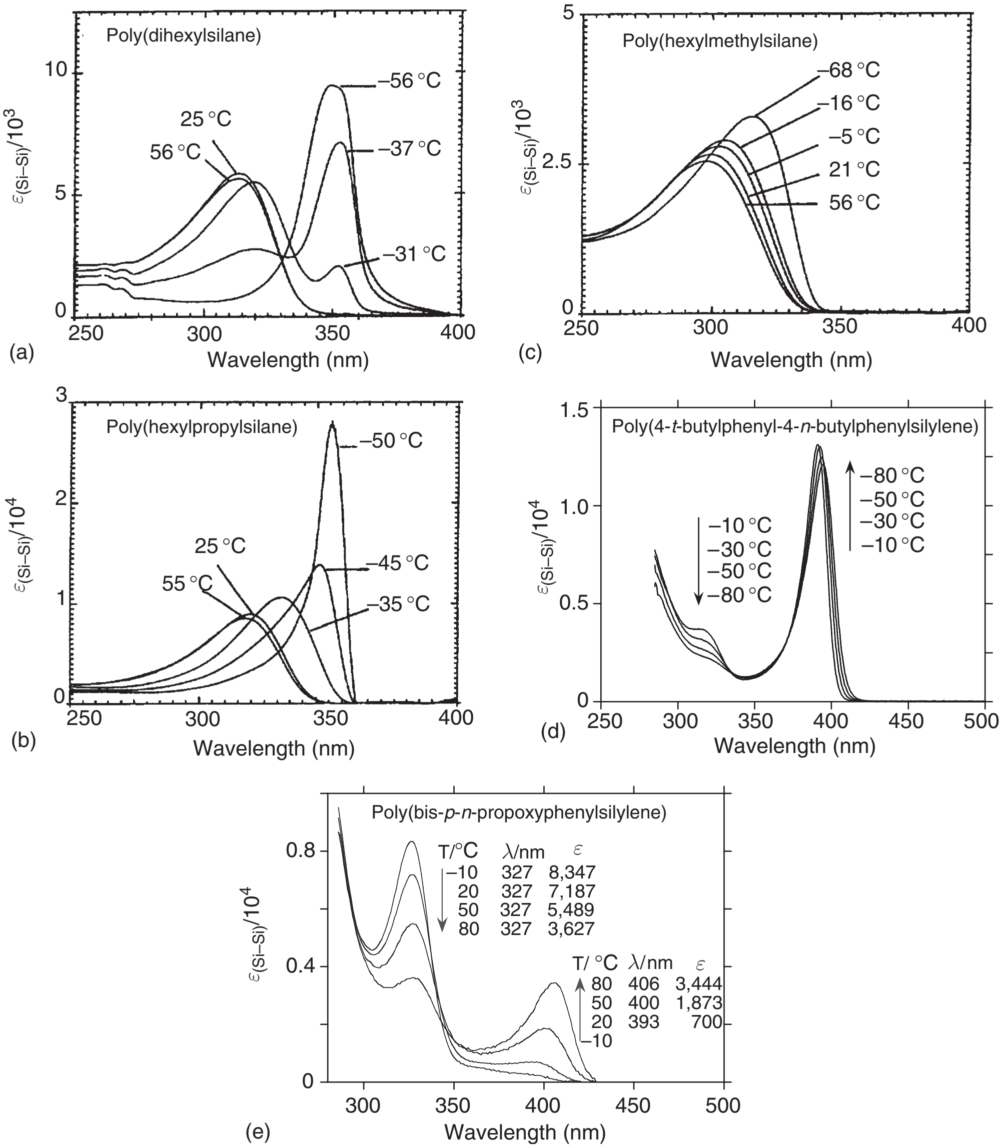


Figure 20 Temperature-dependent UV spectra of polysilanes illustrating five different types of thermochromism (in hexane for (a)–(c)[246] and in toluene for (d) and (e)[247]). Figures 20(a)–20(c) reprinted with permission from Sanji, T.; Sakamoto, K.; Sakurai, H.; Ono, K. *Macromolecules* **1999**, *32*, 3788–3794. © 1999 American Chemical Society.

Many studies on polysilane thermochromism appear to support the Schweizer theory for conjugated polymers,[151,248,250,251] for which a conformation-dependent dispersion interaction between the polymer and the local medium (solvent, the polymer's own side chains, or those of an adjacent polymer molecule) is the key. The theory is expressed in terms of the ratio V_D/ε, where V_D is the conformation-dependent dispersion energy per backbone bond, and ε is the mean free energy of defect formation (i.e., the energy required to rotate a particular bond from the *all-anti* to the "defect" conformation). The defects are kinks (strong helical turns) in the chain which interrupt the delocalization and hence reduce the polarizability and dispersion interactions. Schweizer identified a critical value of the ratio, $(V_D/\varepsilon)_c = 0.37$. For values of V_D/ε greater than this, abrupt thermochromism is predicted. An estimate of $V_D \approx 0.97\ \mathrm{kcal\,mol^{-1}}$ was obtained by Gahimer *et al.*,[250] close to the estimate by Schweizer of ca. $1.1\ \mathrm{kcal\,mol^{-1}}$; ε was taken to be ca. $1\ \mathrm{kcal\,mol^{-1}}$.[152] Polysilanes are thus candidates for abrupt thermochromism, especially where V_D is large and ε is small, as is the case for conformationally mobile polysilanes, such as PDHS. In contrast, where the energy of defect formation is large due to the steric hindrance of bulky side chain, especially where the bulk is close to the backbone, then ε is large and $V_D/\varepsilon < (V_D/\varepsilon)_c$, such that no abrupt thermochromism is observed.

The origin and mechanism of thermochromism in the polysilanes is an area of ongoing discussion, and it is likely that under different conditions, different mechanisms are operative, which could be usefully clarified by further study.

3.11.5.3 Solid-State Studies: Phase Transitions and Thermochromism

3.11.5.3.1 Single crystal X-ray crystallography

Single crystal analysis of polysilanes is rare, since the structural variations in polymer samples usually preclude the formation of crystals of sufficient quality and size, although there are a few reports. The structure of 1,6-bis[(*R*)-2-phenylpropyl]dodecapropylhexasilane, **5**(*R*), with terminal chiral groups has been reported;[15] the conformation is *M*-screw sense *all-transoid* with backbone dihedral angles in the range −172° to −177°, and was described as a 15_7 helix; the structure is shown in Figure 21.

Perchloropolysilane (see Section 3.11.4.1.4.(ii)) was also successfully analyzed by single crystal X-ray diffraction and has an *all-A* conformation. The single crystal X-ray structure of the model oligomer 1,7-dichlorotetradecaphenylheptasilane has been reported, which revealed a helical conformation with SiSiSiSi torsion angles in the range of 154–162°.[252]

3.11.5.3.2 Atomic force microscopy

The technique of atomic force microscopy (AFM) has permitted the direct observation of single polysilane molecules. Poly[*n*-decyl-(*S*)-2-methylbutylsilylene] (PDMBS), 88, hydrophobic, of high molecular weight ($M_w = 5{,}330{,}000$ and $M_n = 4{,}110{,}000$), PSS, helicity, and rigid rod-like structure due to the aliphatic chiral side chains, was deposited from a very dilute (10^{-10} Si-unit) dm^{-3}] toluene solution onto a (hydrophobic) atomically flat (atomic layer steps only present) sapphire (1012) surface. After drying the surface for a few minutes in a vacuum, AFM images were taken at room temperature in air in the non-contact mode.[204,253] An example is shown in Figure 22, in which the polymer chain is evident as a yellow trace.

The faint vertical lines are the sapphire single atomic steps. The total contour length of the PDMBS chain is 2,000 nm and the average molecular height is 1.0 ± 0.2 nm, consistent with the molecular diameter estimate of 0.9 nm from a space-filling model of the polymer. Segments of 150–800 nm length, corresponding to chains of ca. 800 to 4,000 catenating silicon atoms, separated by kinks, are apparent in the image and are consistent with the extremely narrow and intense UV and CD profiles at 318 nm.[254]

Following these investigations, AFM has also been successfully employed to image PDMBS, one terminus of which had been chemically anchored to a silicon substrate, as well as of other flexible polysilanes bonded to solid substrates.[255–259]

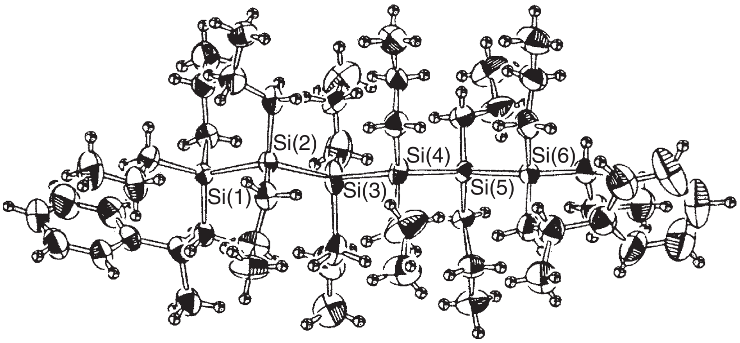
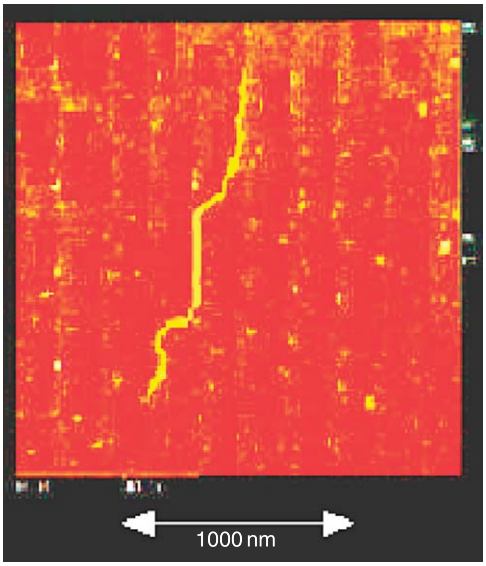


Figure 21 Single crystal X-ray structure of 1,6-bis[(*R*)-2-phenylpropyl]dodecapropylhexasilane.[15] Reprinted with permission from Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345–11346. © 1997 American Chemical Society.



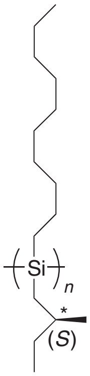


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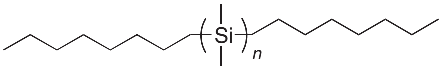
Figure 22 AFM image of PDMBS 88 (yellow trace) on sapphire surface.[204] Reprinted with permission from Fujiki, M. *Macromol. Rap. Commun.* **2001**, *22*, 539–563. © 2001 Wiley-VCH.

3.11.5.3.3 Dialkylpolysilanes

Most polymers do not form crystals suitable for single crystal X-ray diffraction, so powder or film methods are usually employed. X-ray and UV data recorded at various temperatures provide the detailed information required to correlate conformational and electronic properties, since the former is sensitive to the inter- and intrachain packing, and the latter is sensitive to the conformation. DSC provides further evidence for any phase transitions. Detailed studies have been performed by Winokur and West,[260,261] who reported a comparison of the polymorphism, structure, and chromism in poly(di-*n*-octylsilylene), $(\mathrm{Si}\text{-}n\text{-}\mathrm{Oct}_2)_n$, 89, and poly(di-*n*-decylsilylene)$(\mathrm{Si}\text{-}n\text{-}\mathrm{Dec}_2)_n$, 90. These investigations will be described in detail for the useful insights into polysilane structures that they afford.



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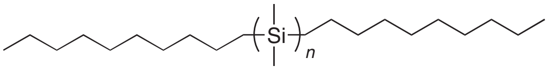

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The polymers form semicrystalline films and powders which were investigated using DSC, *in situ* quenching studies by X-ray scattering and UV-VIS absorption, in combination with detailed model calculations. These polymers showed a range of monotropic and enantiotropic structures during thermal cycling. At 70 °C, the polymers are in the partially disordered hcm phase, M. Rapid quenching of M (<2 s) to −30 °C afforded quenched mesophase (QM), which on warming led sequentially to forms III, I, and II in irreversible steps (cooling of a once-formed ordered phase does not result in reversion to the previous form). The DSC trace for quenching $(\mathrm{Si}\text{-}n\text{-}\mathrm{Dec}_2)_n$ from 70 °C and then heating to 75 °C shows four different phase changes at temperatures indicated by arrows and the five phases noted above, as is evident in Figure 23. The structures of these phases were probed by X-ray diffraction, the profiles for which at suitable corresponding temperatures are shown in Figure 24. Only two of these (I and II) were previously reported.[218,262] The phase denoted II^* is metastable and was found in toluene-precipitated or cast films of 90.

Earlier reports had suggested a hexagonal lattice and AG_+AG_- conformation for the type I phase.[218] However, modeling of the X-ray data, an example of which is shown for the type I phase of $(\mathrm{Si}\text{-}n\text{-}\mathrm{Dec}_2)_n$ in Figure 25, found that a triclinic unit cell, with $a = 27.9$, $b = 16.9$, and $c = 7.9$ Å, is more reasonable for the data obtained. The AG_+AG_- conformation was effectively precluded, since no AG_+AG_- arrangement can span the 27.9 Å repeat distance of the *a*-axis. A backbone comprising contributions from *T (transoid)* and *D (deviant)* turns was proposed, which would give rise to three different Si environments (*T*Si*T*, *T*Si*D*, and *D*Si*D*, where these represent a silicon connected to neighbors by either *T* or *D* turns). This result is qualitatively consistent with solid-state $^{29}\mathrm{Si}$ NMR studies.[262] It is

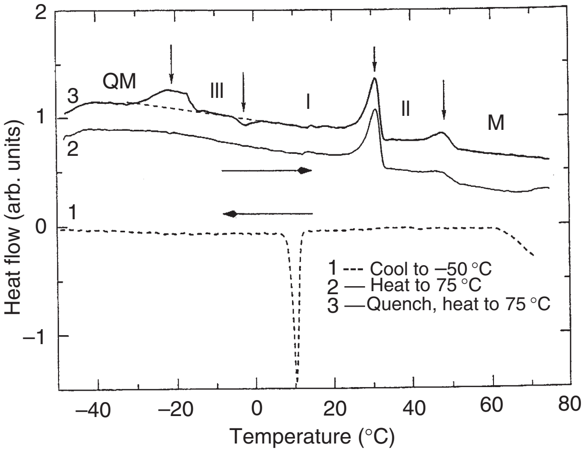


Figure 23 DSC traces for (Si-n-Dec$_2$)$_n$, **90**, showing four different phase changes at temperatures indicated by arrows.[260] Reprinted with permission from Chunwachirasiri, W.; West, R.; Winokur, M. J. *Macromolecules* **2000**, *33*, 9720–9731. © 2000 American Chemical Society.

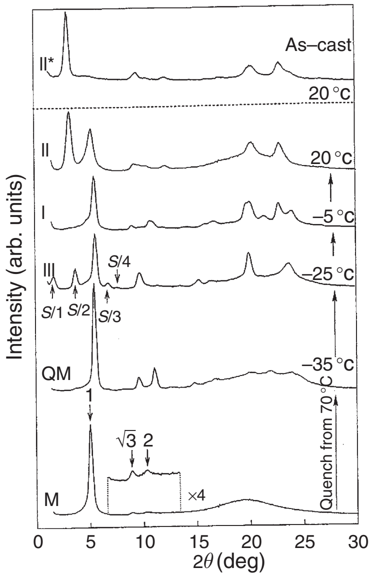


Figure 24 Powder X-ray diffraction profiles for (Si-n-Dec$_2$)$_n$, **90**, at different temperatures.[260] Reprinted with permission from Chunwachirasiri, W.; West, R.; Winokur, M. J. *Macromolecules* **2000**, *33*, 9720–9731. © 2000 American Chemical Society.

acknowledged, however, that the X-ray data, while unequivocal in distinguishing between phases, are not sufficiently resolved to afford even a qualitative determination of backbone conformation.

The phase transitions for 90 were also evident in the UV-VIS spectra, as seen in Figure 26: M has an absorption maximum at 315 nm, QM at 350 nm, and multiple absorptions with peaks at ca. 315, 350, 365, and 378 nm are evident for phase I and the other phases. Isosbestic points observed between the phases indicate coexistence of two states during structural evolution, and the existence of multiple UV peaks for a phase is considered to indicate the existence of several conformations for that phase. In this report,[260] all structures were modeled with conformations between *all-T* and *all-D*; thus, the conformational nature of the different phases of (Si-n-Dec$_2$)$_n$ is not clear. Similar UV absorptions observed for structurally related polymers, such as PDHS (see below), are suggestive of comparable backbone conformations.

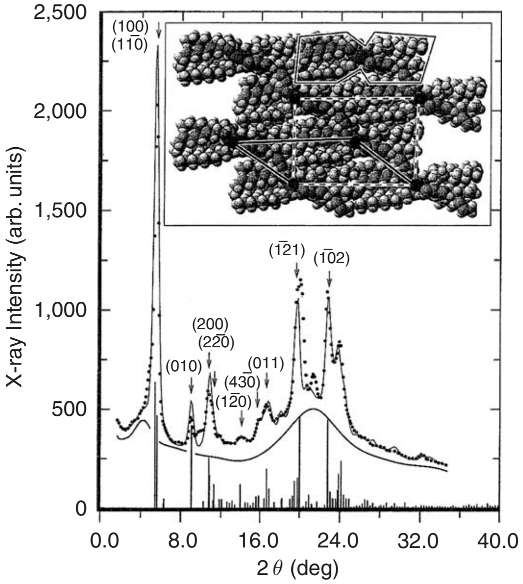


Figure 25 Comparison of calculated powder profile (upper line) and experimental data (dots) for (Si-n-Dec$_2$)$_n$, **90** (arbitrary background: lower line; Bragg contributions: bars).[260] Reprinted with permission from Chunwachirasiri, W.; West, R.; Winokur, M. J. *Macromolecules* **2000**, *33*, 9720–9731, © 2000 American Chemical Society.

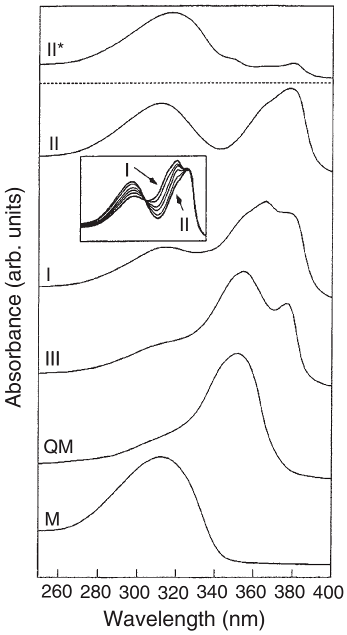


Figure 26 UV spectra of different phases of (Si-n-Dec$_2$)$_n$, **90**.[260] Reprinted with permission from Chunwachirasiri, W.; West, R.; Winokur, M. J. *Macromolecules* **2000**, *33*, 9720–9731, © 2000 American Chemical Society.

The studies reveal a hierarchical sequence of molecular ordering processes in (Si-n-Dec$_2$)$_n$: the lowest energy is the intrachain ordering of Si main chain and side chains. Next are alkyl interchain rearrangements which enhance 3-D order, but do not change the fundamental main-chain packing arrangement. The highest-energy processes are those requiring lateral translations of the polymer chains, resulting in alteration of the main-chain lattice. Complex 89 was found to be even more complex.

3.11.5.3.4 Poly(di-*n*-hexylsilylene)

UV peaks at similar wavelengths have also been found for solid-state samples of the most intensively studied polysilane, poly(di-*n*-hexylsilylene) (PDHS) for which an orthorhombic unit cell has been assigned[249] and confirmed.[263,264] For this polymer, the recent work of Leites and West has shown temperature-dependent forms with maxima at 350, 365, or 377 nm,[265] and Kyotani *et al.*[266] have found that cast films prepared under different conditions of temperature and drying speed have absorption maxima at 357, 370, or 375 nm. Also for PDHS, Winokur *et al.* published a correlation of UV and X-ray data,[264] in particular, confirming that the structure refinements at room temperature (i.e., below the crystalline to hcm transition temperature of 45 °C) are consistent with an *all-anti* backbone and correlate to the longest wavelength absorption maximum.[264] More recently, the influence of alkyl side-chain structure on the conformation of PDHS, and also the di-*n*-butyl analog, PDBS, was also analyzed by X-ray and MM3 calculations, and for both polymers, the alkyl side-chain construction was identified as an asymmetric *cisoid–transoid* conformational arrangement.[267] Further, Bukalov *et al.*[219] found pre-resonance Raman enhancement only of samples of PDHS absorbing at 375 nm (which, based on the work of Shorygin,[268] should be evident for normal modes corresponding to stretching vibrations of bonds involved in the chromophore, which in this case is the σ-conjugating delocalized backbone, for which conjugation is maximized in the *all-A* conformation).[218]

The evidence available thus strongly suggests that PDHS and other dialkylpolysilanes absorbing in the UV at 375 nm have *all-anti* backbone conformations. The other correlation of UV absorption and conformation which is reasonably certain is the crystalline X-ray-characterized 7_3 helix of poly(*n*-butylsilylene).[217,269] This polymer has a dihedral angle of ca. 154° and corresponds to the Michl and West designation of an *all-D* conformation. The UV absorption for this form is at around 320 nm. Also absorbing at this wavelength are the partially disordered hcm and fully disordered amorphous modifications. The utility of Raman spectroscopy was evident again in the ability of the technique to distinguish between *all-A*, *all-D* and AD_+AD_-, as shown in Figure 27, though the distinction between *all-D* and disordered forms is not so clear. (It is cautioned in Ref: 218 that the implication from the Raman spectra below of conjugation only in the *all-anti* form is contrary to other experimental and theoretical data; further study is clearly warranted).

The similarity of the UV and Raman data for these forms suggests that the disordered phases may comprise chains with essentially *deviant* backbone dihedral angles, even if the chains are not regularly aligned.

However, the unambiguous conformational assignment of the UV bands of $(\text{Si-}n\text{-Oct}_2)_n$, $(\text{Si-}n\text{-Dec}_2)_n$, and PDHS at 350 and 365 nm is still lacking. Based on the Michl-West conformer classification,[10] since these bands fall between the 375 nm *all-A* and 320 nm *all-D*, it is reasonable that they could be due to intermediate conformations such as *all-T* or a

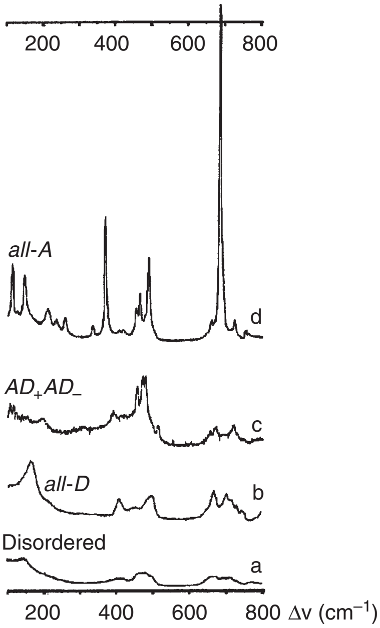
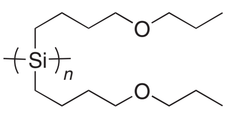


Figure 27 Typical Raman patterns for various main-chain PSi conformations; room temperature; excitation at 514.5 nm.[219] Reprinted with permission from Bukalov, S. S.; Leites, L. A.; Magdanurov, G. I.; West, R. *J. Organomet. Chem.* **2003**, *685*, 51–59, © 2003 Elsevier.

combination such as AD_+AD_-, TD_+TD_- or even AT_+AT_-. Some other possibilities have also been suggested:[196] (i) the bands could be due to disrupted *all-A* conformations, in which *all-A* segments of different length (and thus different degrees of conjugation) exist; or (ii) side-chain crystallization in the 375 nm form could force a slight opening of the Si–Si–Si bond angles, whereas in the higher energy form(s), despite an *all-A* backbone, the side chains could be disordered and thus not force opening of the Si–Si–Si angle. As regards (i), however, the question arises as to why different segment length *all-A* regions should form, and then be limited to one or two such segment lengths only. Other polymers, which on the basis of X-ray results are considered to have *all-A* conformations, that is, $(\mathrm{SiMe}_2)_n$, $(\mathrm{SiEt}_2)_n$, $(\mathrm{Si}^n\mathrm{Pr}_2)_n$, $(\mathrm{SiMe}^n\mathrm{Pr})_n$,[215,216,270] and low-temperature or high-pressure forms of $(\mathrm{Si}^n\mathrm{Bu}_2)_n$ and $(\mathrm{Si}^n\mathrm{Pent}_2)_n$, also show preresonance Raman enhancement in support of this,[219] although they show quite different UV $\lambda_{\max}$ to the 375 nm band observed for $(\mathrm{Si}\text{-}n\text{-}\mathrm{Oct}_2)_n$, $(\mathrm{Si}\text{-}n\text{-}\mathrm{Dec}_2)_n$, and PDHS, above, viz. 342, 352, 355, 341, 350, and 362 nm, respectively. Assuming that these polymers do indeed have *all-A* conformations, it is reasonable that the origins of these differences could indeed be due to kink-disrupted *all-A* conformations, where the *all-A* segments have a statistically preferred length, dependent upon, for example, solubility, which decreases as side chain length decreases.

Very recently, the thermochromism of PDHS in the solid state was correlated with changes in the material′s refractive index.[271] A large reversible change in refractive index (Δn) of about 0.07 was found on thermal treatment, which was coincident with the material's thermochromism, suggesting that, in part, the origin of the effect derives from a change in molecular polarizability, that is, the extent of σ-conjugation, and arises from a switching of the Si backbone between *all-anti* and helical conformations. By incorporating a pigment film for optothermal energy conversion, possible application in reversible information recording using near-IR light irradiation was demonstrated. Related to the thermochromic properties of PDHS in the bulk state, Seki found that monolayers of PDHS deposited on a hydrophobic surface were constrained to the helical/disordered form with UV $\lambda_{\max}$ at 320 nm, with almost no absorption evident at 370 nm for the extended *all-anti* state,[272] that is a surface-mediated chromism, similar to that observed for certain alkoxy-substituted polysilanes.[67,273,274] However, on deposition of the sixth layer, a dramatic increase of the 370 nm peak was observed, indicating that with sufficient depth, the polymer chains can aggregate and crystallize to give the *all-anti* form.[272] These results are consistent with those of Despotopoulou *et al.* who found suppression of crystallinity in PDHS at thicknesses below 50 nm and absence of the *all-anti* form below 10 nm thickness.[275–277] The molecular chain and lamellar crystal orientation in ultrathin films of PDHS on silicon wafer substrates was also found to be film thickness dependent, being perpendicular to the surface for a monolayer and parallel to the surface when thicker than 13 nm.[278]

Finally, concerning dialkylpolysilanes, it is interesting to note that the solid-state (film) UV spectral profile of the thermochromism exhibited by **49**,[157] shown in Figure 28, almost exactly matches that of the solvatochromism (see Figure 16 above). This indicates that the "before" and "after" conformations are essentially the same and that the reduction of temperature or addition of HFIP are responsible for similar conformational changes in the polymer: an abrupt straightening of the polysilane backbone.



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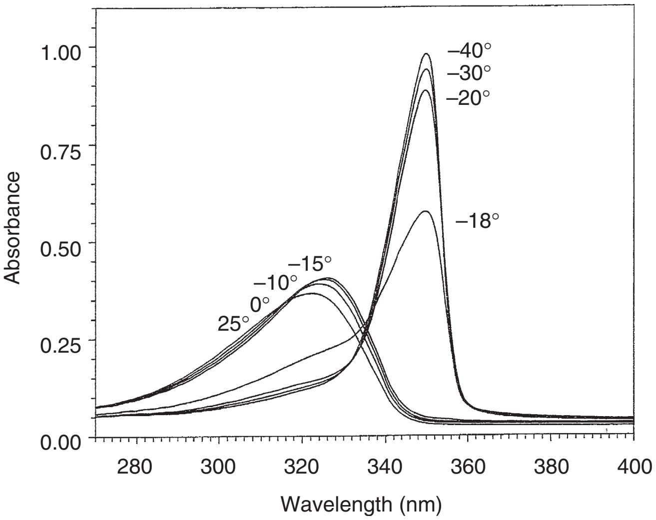


Figure 28 Abrupt thermochromism of **49**.[157] Reprinted with permission from Yuan, C.-H.; West, R. *Macromolecules* **1998**, *31*, 1087–1092, © 1998 American Chemical Society.

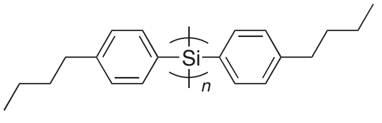
3.11.5.3.5 Polyalkylarylsilanes

Polyalkylarylsilanes such as PMPS have an absorption band around 345 nm due to the mixing of aryl π-orbitals with the σ-delocalized Si backbone (see Ref: 279 for a detailed assignment and discussion of UV bands to electronic transitions in PMPS). Although previously considered to be amorphous and not to exhibit thermochromic transitions, Demoustier-Champagne *et al.* investigated the structure of PMPS using wide-angle X-ray scattering at various temperatures and optical polarizing microscopy.[215,279a] The results clearly show the existence of an ordered phase in PMPS, with approximately 10% crystallinity at room temperature. Below 190 °C, assuming an *all-anti* conformation, the experimental diffraction pattern can be fitted to a monoclinic crystal lattice. The atactic chains pack in near-hexagonal symmetry, with two types of disorder existing in the packing. At about 190 °C, a transition to an hcm phase occurs, as the chains rotate about their long axis, while maintaining the *all-anti* conformation. This is taken to indicate conformational locking due to the presence of the phenyl groups. On further increasing the temperature, the sample finally melts at around 260 °C into an isotropic amorphous phase. The existence of PMPS in different forms is reflected in the solid-state ^{29}Si NMR spectrum of PMPS in which a broad signal with a downfield shoulder is evident.[280] Studies on PMPS doped with chiral groups (see Section 3.11.6.1.1.(iii)) also indicate that PMPS adopts a helical conformation rather more ordered than previously supposed.

3.11.5.3.6 Diarylpolysilanes

These polymers show the longest wavelength UV absorptions among the polysilanes: ca. 395 nm.[281] Electronic and steric factors are considered responsible. Electronically, the presence of a second phenyl group compared to the alkylarylpolysilanes above and the concomitantly increased σ–π mixing results in a further decrease in the HOMO–LUMO gap and hence further red-shifted absorption maximum.[21] X-ray investigations of diarylpolysilanes are problematic due to the disorder of the phenyl rings, but the chains are considered to be rigid and extended.[282] The single crystal X-ray structure of the model oligomer 1,7-dichlorotetradecaphenylheptasilane has been reported, which revealed a helical conformation with SiSiSiSi torsion angles in the range of 154°–162°.[252] This is consistent with force field calculations.[248] Similar to the unusual behavior of these polymers in solution, they can show the opposite thermochromic trend to the dialkylpolysilanes: a UV absorption shift from 325 to near 400 nm at higher temperature was recorded for poly(bis-4-butoxyphenylsilylene).[283] The surprisingly short wavelength absorption for a diarylpolysilane was rationalized by supposing a conformation strongly distorted to avoid unfavorable dipole alignment which would arise in a highly extended conformation. The absence of any DSC peaks was taken to indicate that no phase change occurred. However, a group at NTT Basic Research Labs observed similar thermochromism for a film of poly[bis(4-*n*-butylphenyl)silylene] (PBPS, **91**),[284] a diarylpolysilane which does not have an oxygen in the alkyl group on the phenyl rings. Interestingly and in contrast to the above, spectroscopic and calorimetric techniques indicated a structural phase transition at about 355 K. This was considered to accompany a conformational change in the Si-backbone from the extended, higher-temperature form ($\lambda_{max} = 390$ nm) to a disordered, lower-temperature form ($\lambda_{max} = 315$ nm).[284] The variable-temperature UV spectra are shown in Figure 29.

It was suggested that the bulky 4-*n*-butylphenyl substituents render the extended conformation more stable due to the intramolecular steric interactions, which predominate at higher temperatures, while at lower temperatures,



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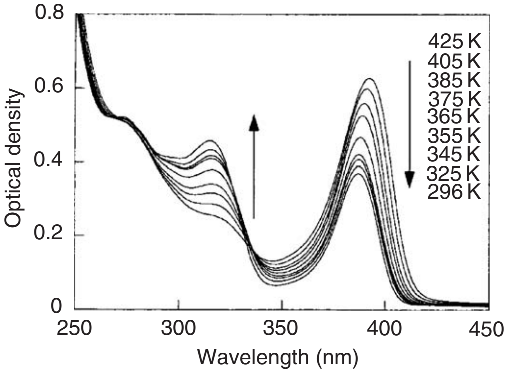


Figure 29 Variable-temperature UV spectra of solid film of PBPS, **91**.[284] Reprinted with permission from Bleyl, I.; Ebata, K.; Hoshino, S.; Furukawa, K.; Suzuki, H. *Synth. Met.* **1999**, *105*, 17–22, © 1999 Elsevier.

packing forces predominate to favor the disordered form.[284] However, the invocation of packing forces in the low-temperature form is suggestive of a regular, rather than disordered, structure, and a possible alternative to a disordered form would be a *deviant*-conformation. A similar difference of phases was observed for poly{[4-*n*-butylphenyl][3-(*S*)-2-methylbutylphenyl]silylene}: UV samples prepared as films showed a narrow (FWHM = 11 nm) absorption at 321 nm, while a pressed bulk (precipitated from toluene/isopropyl alcohol) sample showed a broader (FWHM = 25 nm) absorption at 397 nm.[247] The extremely narrow film state UV absorption indicates a high degree of structural regularity supporting the suggestion of an ordered helical phase. It is interesting to note that the UV absorption maxima of these diarylpolysilanes with peaks near 320 nm are very similar to those for the high temperature hcm phases of dialkylpolysilanes, such as that for PDHS shown in Figure 20(a), except that the absorptions for the dialkyl-substituted polymers are considerably broader. These observations are consistent with the idea that the hcm form in the latter is essentially a disordered *deviant*-helical form, while in the diarylpolysilanes, the narrower absorption at 320 nm appears to indicate a regular *deviant*-helical form, with little or no red shifting due to the σ–π-mixing which is usually observed in aryl-substituted polysilanes. Presumably in adopting the helical conformation, the phenyl rings also rotate out of conjugation with the backbone.

3.11.5.3.7 NMR spectroscopy

Variable-temperature solid-state ^{2}D and ^{29}Si NMR studies have been performed by Frey and co-workers on deuterated PDHS (PDHS-d) which shed light on the backbone conformation and mobility.[285] The ^{29}Si chemical shift is very sensitive to the conformation of the Si backbone. The polymer (and its non-deuterated analog for comparison) was synthesized by Wurtz-type coupling of the deuterated monomer. Surprisingly, DSC showed greater crystallinity and a higher phase-transition temperature for the PDHS-d sample compared with the non-deuterated form. In the ^{29}Si magic angle spinning NMR spectra, as shown in Figure 30(a), a discontinuous upfield shift was considered to indicate an increasing fraction of *gauche*-conformations, in keeping with previous observations.[286] However, on the basis of the recent X-ray results above, it seems more likely that these fractions are *deviant* and CNDO/MO calculations by Takayama on the dihedral angle dependence of chemical shift for $Si_{11}H_{24}$ (see below)

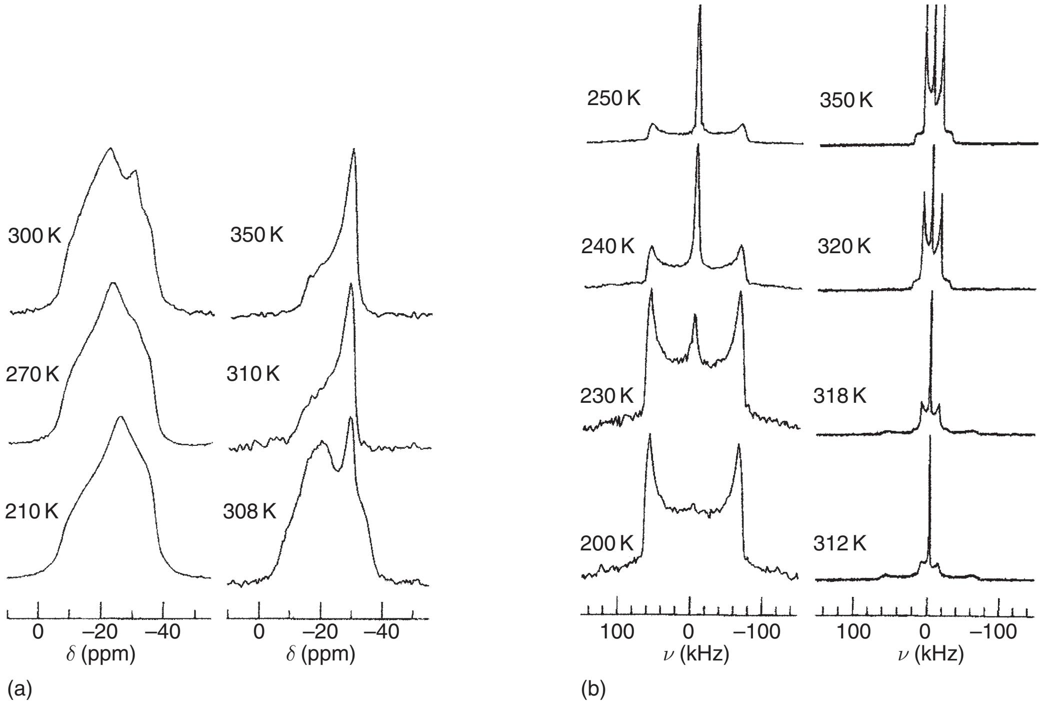


Figure 30 Variable-temperature solid-state NMR spectra (relative intensities distorted due to different relaxation rates): (a) ^{29}Si (referenced to Q_8M_8 (Bruker); (b) ^{2}H (isotropic peak truncated to show hcm and crystalline fractions).[285] Reprinted with permission from Mueller, C.; Schmidt, C.; Frey, H. *Macromolecules* **1996**, *29*, 3320–3322. © 1996 American Chemical Society.

appear to support this.[287] Variable-temperature ^{2}H-NMR spectra for the PDHS-d indicate that the polymer is rigid and immobile at 200 K. Then at 230 K, an isotropic peak becomes evident which grows with increasing temperature (this correlates with the T_g observed by DSC at 233 K). The isotropic peak is considered to be due to a small amorphous fraction which becomes mobile above T_g, while the major fraction is still crystalline. The amorphous phase does not convert to the hcm phase. The spectrum changes dramatically at the transition to hcm in the temperature range 310–320 K, in which three components can be distinguished, as evident in Figure 30(b). The small splitting values above the transition temperature indicate that the Si–C bonds undergo large bond angle changes, and thus that the backbone is flexible and highly mobile in the hcm phase.[285]

The utility of solid-state NMR in conformational analysis of polysilanes was further demonstrated by Takayama, who investigated $(\mathrm{SiMe_2})_n$, $(\mathrm{SiEt_2})_n$, $(\mathrm{SiMe_2}\text{-}co\text{-}\mathrm{SiEt_2})_n$, and $(\mathrm{SiMeEt})_n$ by ^{29}Si and ^{13}C NMR spectroscopy, comparing the data with CNDO/MO-calculated ^{29}Si shielding constants.[287] As noted above, X-ray diffraction data indicated *all-A*-conformations for the dimethyl and diethyl derivatives, although small deviations were considered possible in $(\mathrm{SiEt_2})n$;[208,209] mutual exclusion of IR and Raman bands, indicating a centrosymmetric unit cell, was consistent with this.[210] A plot of the calculated ^{29}Si NMR chemical shift dependence on dihedral angle for the model compound $\mathrm{Si_{11}H_{24}}$ is shown in Figure 31. For dihedral angles in the range 180° to about 140°, that is, small deviations from planarity, the chemical shift is calculated to move upfield from that of the *all-A*-conformation. An upfield chemical shift in the solid-state ^{29}Si NMR spectrum is therefore expected for a *transoid*-conformation (dihedral angle $\approx$ 165°) and should be a maximum at about 150°, corresponding to an *all-D* (7_3 helix) -conformation. For deviations larger than these, the shift moves rapidly in the opposite direction, so that beyond about 140°, the shift is downfield from the

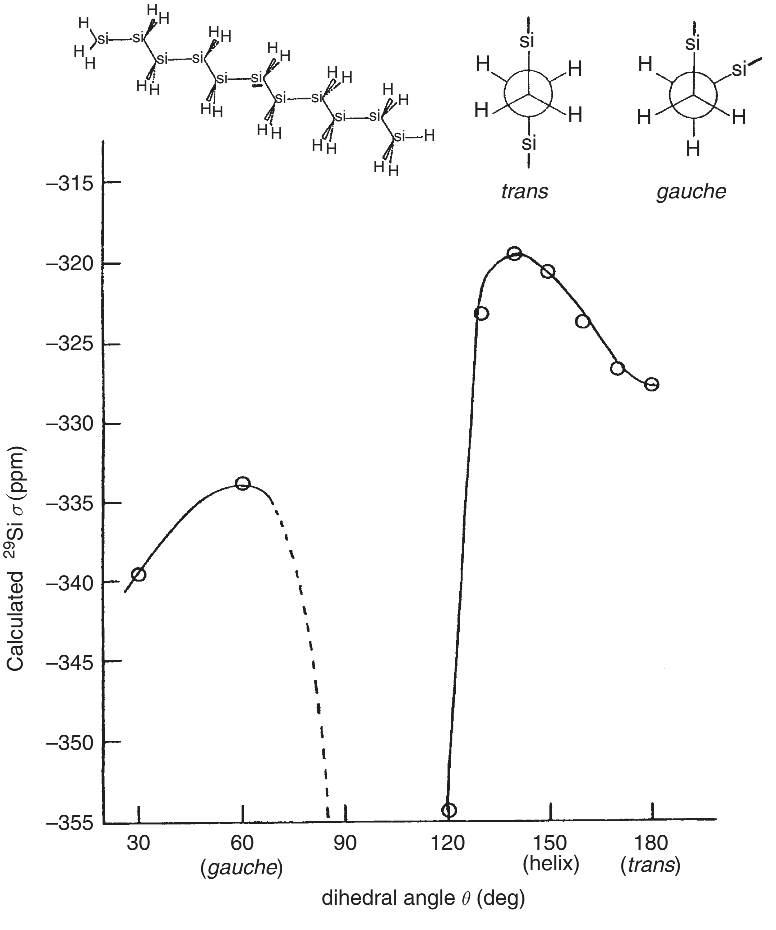


Figure 31 CNDO/MO-calculated ^{29}Si nuclear shielding for the central Si in $\mathrm{Si_{11}H_{24}}$ as a function of dihedral angle.[287] Reprinted with permission from Takayama, T. *J. Mol. Struct.* **1998**, *441*, 101–117, © 1998 Elsevier.

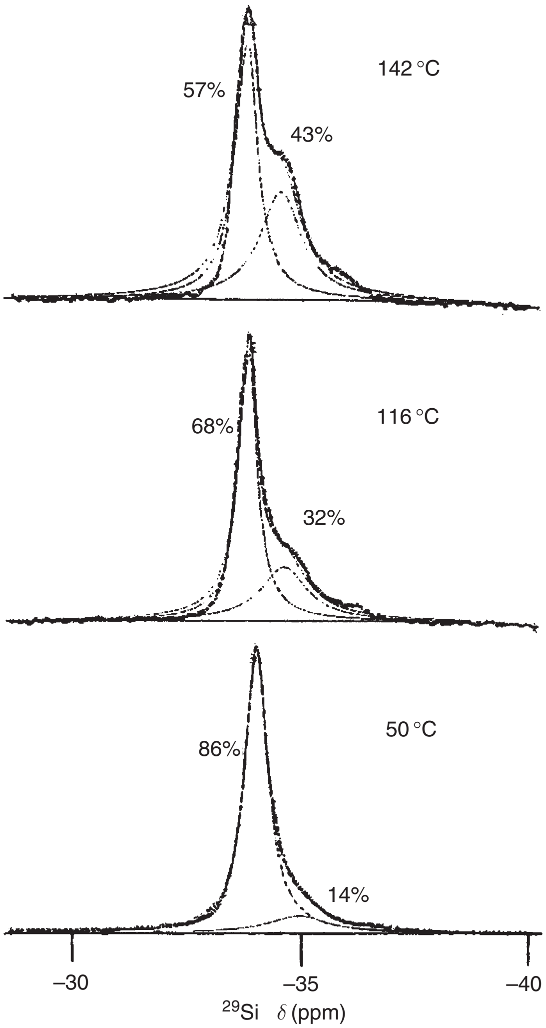


Figure 32 Solid-state ^{29}Si NMR spectra of $(SiMe_2)_n$ at selected temperatures and deconvolution constituents.[287] Reprinted with permission from Takayama, T. *J. Mol. Struct.* **1998**, *441*, 101–117, © 1998 Elsevier.

all-*A*-value. Downfield shifts would therefore be expected for *cisoid*-, *gauche*-, and *ortho*-conformations. The solid-state ^{29}Si NMR spectrum of PMPS has also been reported, as mentioned above.[280]

The experimental spectra for $(SiMe_2)_n$ at selected temperatures are shown in Figure 32. The growth with temperature of a feature slightly upfield from the low-temperature crystalline peak is thus evidence for existence of *deviant*-turns within a predominantly *anti*-conformation.

For $(SiEt_2)_n$, at low temperature, a single peak is observed. As the temperature increases, this drifts downfield and a second peak begins to grow in, downfield from the first. Further increase in temperature results in a gradual downfield drift of both peaks, until at 25 °C the peak due to the low-temperature form disappears (not apparent in the DSC). The transition resulting in the new downfield peak is considered to indicate a phase transition from the ordered crystalline form to a disordered form.[287] Since the new peak is shifted downfield from the original, the dihedral angle of the new form should be less than around 130°, that is, *ortho* or *gauche*. The gradual downfield drifts are considered to indicate the formation of another, "*gauche*-rich," conformation. For $(SiMe_2\text{-}co\text{-}SiEt_2)_n$, as the temperature increases, there is a slow drift downfield for the $SiEt_2$ peaks, but almost no change for the $SiMe_2$ units, consistent with greater flexibility in the former. For $(SiMeEt)_n$, the data were interpreted as indicating almost no change in main-chain conformation over the temperature range −70 to 120 °C, although the side chains converted to a more disordered phase at 80 °C.

Due to the extensive investigations of PDHS, it is worth considering again the ^{29}Si NMR data[285] in Fig. 30(a) in the light of the dependence of chemical shift on dihedral angle calculated by Takayama.[287] The spectra show a discontinuous transition and growth of a new peak to the upfield side of the peak due to the low-temperature crystalline form, which was considered to indicate an increasing fraction of *gauche*-turns.[285,286] However, from the discussion of chemical shift dependence on dihedral angle above, it seems more likely that the new form has *deviant*-, rather than *gauche*-turns. As mentioned above, this is also supported by X-ray and UV data.[196]

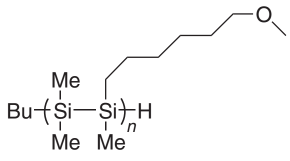
3.11.5.4 Other Chromisms: Iono-, Piezo-, Electro-, and Magnetochromism

3.11.5.4.1 Ionochromism

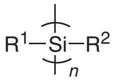
Films of poly(methyl-4,7,10,13-tetraoxatetradecylsilylene), **41**, incorporating $LiClO_4$ in Li:Si ratios of 0–4 were prepared from THF solution and showed an increasing blue shift in the UV absorption maximum as Li content increased.[148] This indicates restriction of the backbone to a less extended conformation. These films showed different thermochromic responses: as the temperature is reduced, a smooth bathochromic shift of $\lambda_{\max}$ is observed until a certain temperature, below which a gradual hypsochromic shift occurs, resulting in a kink in the $\lambda_{\max}$ versus temperature curves. The kink temperature correlates well with the polymer glass transition temperature, T_g, the increase of which with Li content is rationalized by the restriction of side-chain mobility, and presumably thus also main-chain mobility, through increasing coordination of side chain oligoether units to lithium ions. Most efficient coordination was considered to be achieved when the Li:Si ratio was 1, and four oxygens could intramolecularly coordinate a single Li cation, as shown in Scheme 29, although it was noted that intermolecular coordination was also possible.[148] It was noted by other researchers[288] regarding a related polymer, poly(4-ethoxyethoxybutylmethylsilylene),[289] that only two oxygen atoms per side chain do not permit efficient Li^+ complexation. In aqueous solution, **41** exhibits no ionochromism with Li^+, although a 5 nm blue shift was observed on addition of Eu^{3+}.[149]

3.11.5.4.2 Piezochromism

Piezochromism refers to the pressure dependence of the UV absorption wavelength and for polysilanes occurs due to a pressure-induced conformational change, as in the change from helical to *all-anti* conformations of $(\mathrm{Si}^n\mathrm{Bu}_2)_n$ and $(\mathrm{Si}^n\mathrm{Pent}_2)_n$ bulk films at high pressure[213] and noted also in COMC (1995) (chapter Organopolysilanes, p. 105). In these cases, 3-D packing effects may also affect the conformational changes. Piezochromism of polysilane monolayers, in which 3-D packing does not occur, has now also been studied. Polysilanes with purely alkyl or aryl substituents are hydrophobic and do not form monolayers on water. However, as noted above, with ether or ammonium side-chain substituents, alcohol- or water- solubility may be possible, and if the correct balance between hydrophobicity and hydrophilicity is achieved, stable monolayers can be formed, as was found for **11**[67] (synthesized by masked disilene polymerization and described in Section 3.11.4.1.2)[60,66] and for **92–97** synthesized by Wurtz-type coupling.[273]

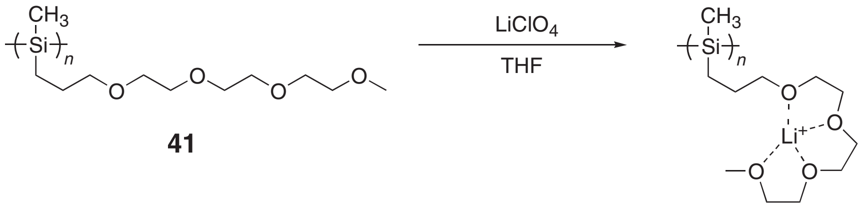


11



92: $R^1 = (CH_2)_6OCH_3$; $R^2 = CH_3$
93: $R^1 = (CH_2)_{10}OCH_3$; $R^2 = CH_3$
94: $R^1 = R^2 = (CH_2)_6OCH_3$
95: $R^1 = R^2 = (CH_2)_{10}OCH_3$
96: $R^1 = (CH_2)_6OCH_3$; $R^2 = i\text{-}C_4H_9$
97: $R^1 = (CH_2)_{10}OCH_3$; $R^2 = i\text{-}C_4H_9$

Yoshida *et al.* reported that LB films of **48 and 92–97** showed piezochromism, observing a reversible UV spectroscopic change during monolayer compression on a water surface using the setup shown in Figure 33 which permitted both compression-induced and flow-induced orientation of the molecules.[66,67,273]



Scheme 29 Intramolecular coordination of Li^+ by oligoether side chain of **41**.

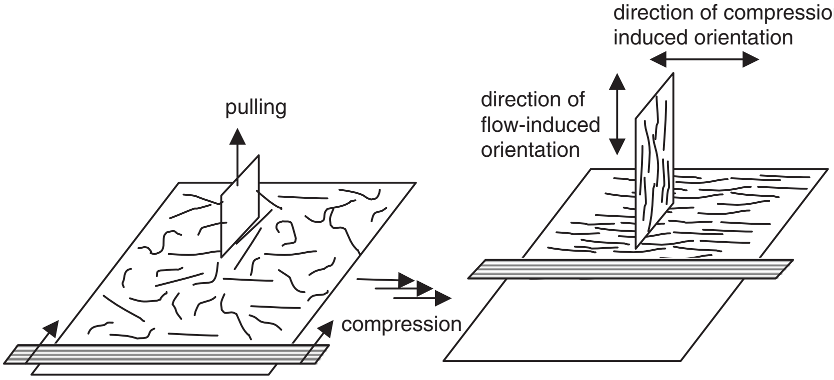


Figure 33 Setup to obtain compression- and flow-oriented polysilane monolayers.

At surface pressures below 17 mN m^{-1}, λ_{max} was 334 nm, characteristic of a 7_3 helical conformation; at 17 mN m^{-1}, an inflection point of the surface pressure-area isotherm was observed, above which the λ_{max} shifted abruptly to 347 nm, considered to indicate an *all-anti* conformation. A significant change in the in-plane orientation of the **11** monolayer was also described. The dichroic ratio of a monolayer film prepared at the lower surface pressure of 13 mN m^{-1} was 1.11, interpreted as indicating that the polysilane backbone was aligned parallel to the substrate-drawing direction. In contrast, at the higher surface pressure of 18 mN m^{-1}, the dichroic ratio was 0.84, and taken to indicate that at the higher pressure, the backbone became aligned perpendicular to the drawing direction.[67] The nature of the surface-mediated chromism in **92–97** was found to be dependent on the main-chain rigidity, which was greater for the polymers with shorter alkyl side chains.[273] Other surface/pressure-mediated chromisms have also been reported.[169,272,290]

3.11.5.4.3 Electrochromism

Reversible solid-state electrochromism was observed in poly[(3,3,3-trifluoropropyl)methylsilylene$_{0.45}$-*co*-methylpropylsilylene$_{0.55}$]. With a response time of less than 100 ms, the UV absorption increased by ca. 50% at an electric field strength of 3.1×10^8 V m^{-1} accompanied by a 5 nm red shift of the λ_{max} from 294 to 299 nm. The difference spectra showed growth of a band at 314 nm as the electric field strength increased. This electrochromic behavior was rationalized in terms of side-chain orientation-dependent structural changes in the silicon chain, and constitutes the first known example of electrochromism not involving an electrochemical reaction.[198]

3.11.5.4.4 Magnetic field effects on UV properties

Movement of the main chains of polysilane **41** (see above) and PMPS in THF solution under varying magnetic fields has also been investigated by UV absorption spectroscopy.[291] The polar oligoethoxy side chains were forced to align in the direction perpendicular to the magnetic field, and the Si main chains followed this. Since the UV absorption due to the σ–σ^*-transition is greater in the direction of the Si chain,[198] application of a magnetic field orthogonal to the incident light beam should cause the chain segments to become aligned so as to have the greatest UV absorption. It was indeed found that the absorption intensity increased by about 5% in a 5 T field, although λ_{max} was unchanged. Carrier transport properties of the polysilane samples prepared under high magnetic fields were obviously different from those prepared under no magnetic field.[291]

3.11.5.5 Chemical and Photochemical Properties: Degradation; Chemical Reactions

3.11.5.5.1 Degradation

Polysilane reactivity has been discussed mainly with reference to functionalization or substitution. Where the reactivity concerns reaction of the main chain, that is, scission of the catenating Si backbone, the process is commonly referred to as degradation (or depolymerization), particularly if the process is undesired or uncontrolled. Both physical and chemical processes, involving light, heat, ionizing radiation, ultrasound, and chemical reagents, can result in depolymerization, which can be followed by GPC and UV spectroscopy, since as molecular weight decreases, the σ–σ^*-absorption shifts to shorter wavelength. Matyjaszewski published a detailed study on the degradation of both alkyl- and aryl-substituted polysilanes.[292]

Light. The sensitivity of polysilanes to light has been well studied and was covered in COMC II (1995) (chapter Organopolysilanes, p. 105). It is the basis of the proposed application of polysilanes as chemical resists in the manufacture of microchips.[293] The silicon chain is cleaved with formation of radicals which usually scavenge O (resulting in the formation of siloxanes)[294] or H from the surrounding medium. The technique is also useful in the lab where reduction of polymer molecular weight is required (e.g., for purposes of comparison of properties of polymers with defined molecular weights). Longer chains are cleaved first, resulting in a narrowing of polydispersity as photolysis proceeds. The solvent can also affect the degradation process: while photoinduced degradation of poly(methylphenylsilylene-*co*-diphenylsilylene) was found in dichloromethane, none was observed in chlorobenzene.[295] The effect of photodegradation on UV,[296] fluorescence,[294] and far IR[297] properties has been described. Spectral bleaching with concomitant blue shift (resulting from the molecular weight dependence of both σ–σ^*-transition energy and molar extinction coefficient) and siloxane formation is apparent in the former, and in the latter, the characteristic linear chain Si–Si asymmetric ($463\,\mathrm{cm}^{-1}$) and symmetric ($383\,\mathrm{cm}^{-1}$) stretches are supplemented by a new band at $480\,\mathrm{cm}^{-1}$ attributed to branching structure resulting from incorporation of a silyne unit. UV flash photolysis has revealed the formation of silyl radicals, silylenes, and also radical cations and anions.[298] More highly branched polysilanes were found to be more resistant to the photo-oxidation process.[299] UV laser ablation of PMPS has been shown to lead to a polycarbosilane-type structure by rearrangement and probable insertion of side-chain methyl carbon atoms into Si–Si bonds.[300] The photoscission of Si–Si bonds has been observed to be reduced in fullerene-doped[301] and other electron-acceptor-containing[302] polysilanes. Very recently, some theoretical aspects of the effects of structure on photostability were reported.[303]

Heat. In the solid state, thermal degradation starts as a slow process at around 150 °C.[292] Cyclics and siloxanes (Si–O–Si characteristic IR stretch at $1{,}100\,\mathrm{cm}^{-1}$) are formed and the polydispersity increases.[292] In solution, thermally induced degradation is slower (23 h, 190 °C for complete degradation). The rate of degradation increases with increase in temperature.

Ionizing radiation. Further studies on the effects of ionizing radiation such as ^{60}Co γ-ray radiation and ion beams on polysilanes have been reported.[295,304–306] Both positive and negative resist properties can be shown, depending on the side-chain type, branch density, and the presence or absence of radical initiators.

Ultrasound. Mechanical degradation due to shear forces during ultrasound cavitational processes result in homolytic cleavage of high molecular weight polysilanes, although the degradation has a lower molecular weight limit of typically around 50,000.[292] Concomitant with the chain cleavage is a decrease in polydispersity: it is considered that longer, more entangled chains are more susceptible to cleavage by the shear forces. Consistent with this, polysilanes in dilute solution are less susceptible to cleavage. The fate of the radicals is unknown, though in toluene solution, silyl radicals have been shown to react with the solvent.[292] No cyclics are found in the degradation products.

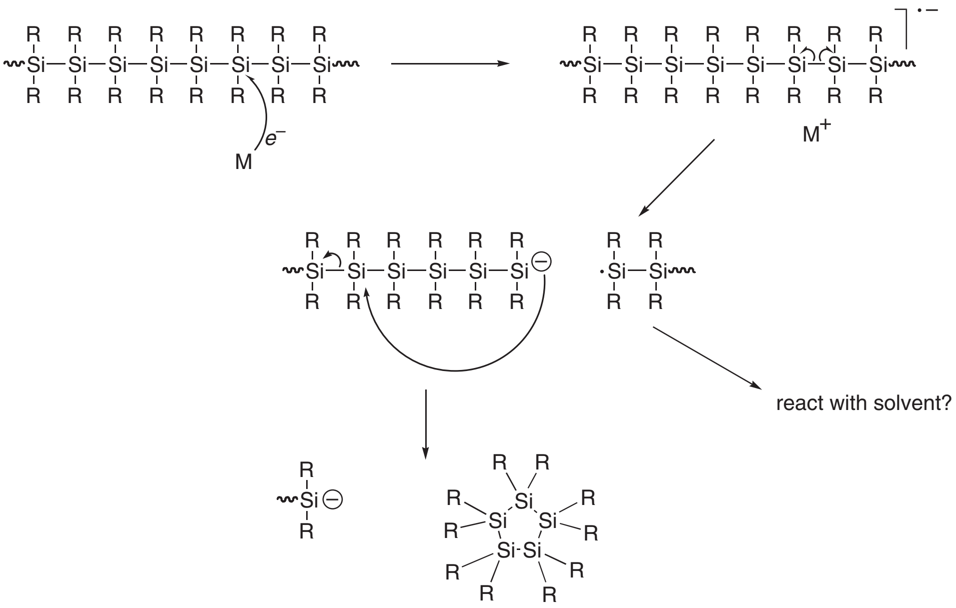
Degradation by chemical reagents. The rate of degradation by reducing metals depends on solvent, polysilane substituents, the alkali metal, and temperature.[292] Degradation is promoted in solvents which are able to solvate the alkali metal cations, such as THF, diglyme, ether, or HMPA. In non-coordinating solvents such as heptane, octane, or toluene, the rate is much slower, though addition of coordinating additives, such as the above solvents, or cryptand-[2.2.2] results in an increase in the degradation rate. Polysilanes bearing phenyl groups are much more rapidly degraded, since the phenyl ring can stabilize radical anions. The activity of the metal toward polysilane degradation increases in the order Li < Na < K. Initially, electron transfer occurs from the metal to the polysilane chain forming an intermediate radical anion which cleaves to form a radical and a silyl anion. The silyl ion then attacks Si–Si bonds by backbiting, either intra- or intermolecularly, the latter being faster and favored entropically, clipping out five- and six-membered rings. The mechanism proposed by Matyjaszewski[292] is given in Scheme 30. Backbiting (which can occur during both degradation and reductive coupling) is distinguished from end-biting (which occurs only during reductive coupling), since different cyclics are formed.

Strong electrophiles, including halogens and strong protic acids, can cleave Si–Si bonds, affording α–ω difunctional oligosilanes; HCl reacts the most slowly. With strong nucleophiles, cyclic oligomers are formed.

3.11.5.5.2 Chemical reactions of polysilane Si–Si bonds

Functionalized polysilanes, such as those bearing reactive alkenyl, halo-, amino-, or alkoxy substituents, are chemically reactive, permitting cross-linking, or further functionalization reactions, as already described in Section 3.11.4.2. However, the Si–Si bond can itself react chemcially under a variety of conditions.

Polysilanes as reducing agents. In a paper on the formation of conductive circuits by UV patterning of polysilane films, the inherent reducing ability of polysilanes to effect the reduction of a silver salt to silver metal was described.[307] PMPS, PPHS [$(\mathrm{PhSiH})_n$], and PDHS were separately spin-coated on glass or silicon wafer substrates, and after drying



Scheme 30 Metal-induced chemical degradation of polysilanes.

were treated with a 5 wt.% solution of $AgBF_4$ in ethanol and then dried. The spectroscopic properties of the resulting films were analyzed by UV and IR and their conductivities were measured. For the PMPS sample, the 333 nm UV absorption disappeared, indicating scission of the Si–Si bond. For PPHS, IR spectroscopy showed resonances for new Si–O–Si–H and Si–O–Si linkages, indicating that PPHS had been oxidized by contact with $AgBF_4$.[307]

Reaction with m-chloroperbenzoic acid (m-CPBA). The Si–Si bonds of polysilanes will undergo stoichiometric insertion of an oxygen atom in the presence of *m*-CPBA, forming siloxane linkages.[308] Exhaustive insertion (requiring long reaction times and excess *m*-CPBA) results in the formation of polysiloxanes, although the latter are not generally synthesized via this route. The reaction has however been applied to the synthesis of ladder polysiloxanes by insertion into the Si–Si bonds of ladder polysilanes (see Section 3.11.7.3).

3.11.6 Higher-order Structure

The properties of compounds depend integrally on the structural identity of their constituent molecules or ions. Other properties depend on levels of structural order beyond that of molecular identity and concern how the molecules or ions are arranged, that is, their higher-order structure. Some properties, such as magnetism, crystal and liquid crystal phases, and melting point, are only evident in the bulk state as a result of “intermolecular” higher-order structure. Other properties, such as optical activity resulting from rotational isomerism, can result from control of “intramolecular” higher order. In this section, higher-order structure in the polysilanes is covered, in particular, that resulting in optical activity, a field which is covered for the first time in the the COMC series, but which has been reviewed several times recently in other publications.[204,309–312]

The experimentally observable phenomenon of optical activity is usually considered in the context of variation of molecular chirality arising from a particular stereochemical configuration at a particular atom such that the molecule has no improper rotation S_n axis. Molecules with opposite chirality configurations are enantiomers and show oppositely signed optical activity. Molecules differing only in conformation are called conformers or rotational isomers. In most cases, the difference in energy between rotational isomeric states is very small, such that at ambient temperature all are populated and no optical activity results. However, if one particular conformer is stabilized, for example, by restriction of rotation about a bond, the molecule can become chiral, and thus optically active.

Most polysilanes are synthesized by the Wurtz-type coupling reaction, which is non-stereospecific, and hence the configuration is usually undefined, although in a few cases, stereochemically defined polysilanes have been synthesized (ROP of *all-anti* 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane[99,101] and masked disilene polymerization).[61]

As has been discussed (see Section 3.11.5.2.2), polysilanes are essentially helical,[197,309,311] with typically *transoid* (15_7) or *deviant* (7_3) conformations.[10] Since a helix with a single screw sense, either *P* (plus; right-handed) or *M* (minus; left-handed), is a chiral motif, the polysilanes might be expected to be optically active. However, the polysilane molecules are conformationally mobile and thus internally racemized by the presence of equal numbers of opposite screw sense twists and mobile helix reversals, resulting in optical inactivity. Where, however, the higher-order structure can be controlled by the application of a chiral field so as to produce polymer chains with a unique single screw sense, or at least a PSS, that is by restricting main-chain single bond rotation, optical activity does indeed result. A key advantage of the electronically delocalized σ-conjugating polysilanes over non-conjugating carbon-based polymers is that the silicon main chain is itself a chromophore and fluorophore, such that the helical chirality of the main chain can be directly probed using the optoelectronic spectroscopies of CD or circularly polarized luminescence (CPL). This section details the development of the field of optically active polysilanes, which was initiated just at the beginning of the period of overage of this chapter (that is, the early/mid-1990s).

3.11.6.1 Polysilane Single Molecule Chirality and PSS Helicity

Preferential helical screw sense polysilanes with main-chain chirality are essentially of two types: those in which PSS chirality is induced by an internal chiral field, for example, incorporation of enantiopure chiral (unichiral) side chains or end groups, and those which are inherently achiral, in which PSS chirality is induced by an external chiral field, such as a unichiral additive or solvent.

3.11.6.1.1 PSS induction by enantiopure chiral side chains

3.11.6.1.1.(i) Poly(dialkylsilylene)s

The first optically active polysilanes were reported independently by two groups in 1994: Möller and co-workers prepared optically active co-polymers by Wurtz-type co-polymerization of unichiral and achiral dichlorosilane co-monomers (described below),[313] and Fujiki prepared optically active homopolymers by Wurtz-type polymerization of unichiral monomers.[254] The nature of the side-chain branch is critical for two reasons: (i) forming a chiral center and (ii) increasing the steric bulk of the side chain such that main-chain conformational mobility is restricted and conformational locking, due to the interaction between chiral centers in a PSS helix, occurs. The position of the chiral branching point is also critical:[241] too far from the main chain and no PSS is observed, since the conformational locking effect decreases with distance from nearest-neighbor side chains and the main chain;[204] too close and the steric congestion is too great to permit synthesis. The restricted backbone mobility resulting from substitution with branched groups is also evident in the ^{29}Si NMR spectra, which become progressively broader as the conformational locking effect increases.[204,242,314] Since it is the main chain itself which is helical and thus chiral, CD shows a band (Cotton effect) with the same profile as the UV absorption. A good example of the spectral characteristics of such polysilanes is provided by poly(*n*-decyl-(*S*)-2-methylbutylsilylene), 88, as shown in Figure 34.[204,254]

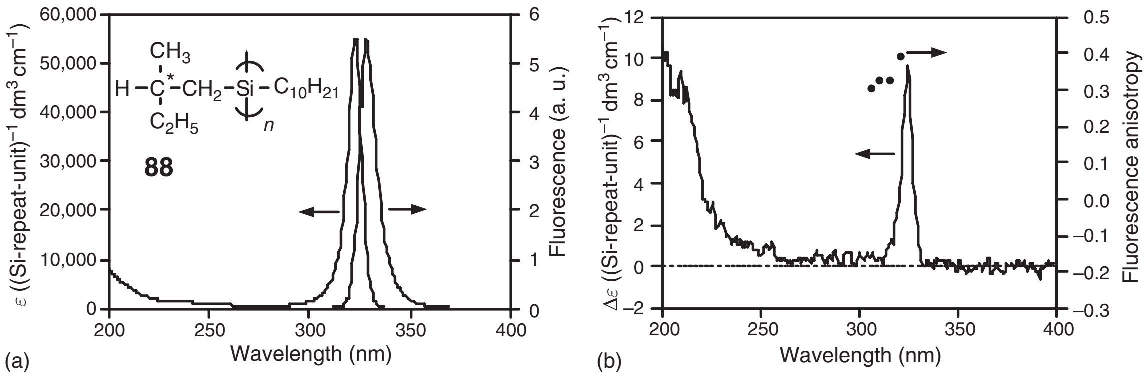


Figure 34 (a) UV and CD spectra and (b) FL spectrum and FL anisotropy of poly(*n*-decyl-(*S*)-2-methylbutylsilylene), **88**, in isooctane at 20 °C.[204] Reproduced with permission from Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563, © 2001 Wiley-VCH.

In dilute isooctane at 20 °C, polymer 88, isolated with $M_w = 5{,}330{,}000$ and $M_n = 4{,}110{,}000$, showed UV, CD, and FL spectral features typical of a rod-like chromophore and fluorophore (see Section 3.11.5.2.2 for a correlation of global conformation with optoelectronic characteristics). These arise due to the conformational control induced by preferential chiral side group interactions and result in a single screw sense helical structure. First, as is evident in Figure 34, 88 exhibits a very intense, narrow UV absorption at 323 nm, with $\varepsilon = 55{,}000$ (Si-repeat-unit)$^{-1}$ dm^3 cm^{-1} and FWHM = 8 nm; these are considerably greater and less, respectively, than the values of ε and FWHM for conventional random coil poly(dialkylsilylene)s. Second, the CD band at 323 nm fits completely within the UV band at the same wavelength. Third, the FL spectral profile at 328 nm is the mirror image of the UV and CD band profiles. Fourth, the FL anisotropy value around the 323 nm UV and CD bands reaches the theoretical limit of 0.4 expected for a random distribution of a rigid rod chromophore collinear with the fluorophore in a rigid medium; the high viscosity index (α) of 1.35 is in agreement with this. The helicity of the molecules (screw pitch and sense, and diastereomeric and/or enantiomeric purity) can be characterized by the dimensionless parameter, the Kuhn disymmetry ratio g_{abs}, defined as the ratio of the strength of CD (polarized) to UV (unpolarized) absorption, that is, $g_{\text{abs}} = 2\Delta\varepsilon/(\varepsilon_L + \varepsilon_R) = \Delta\varepsilon/\varepsilon$, where ε is the molar absorptivity per repeat unit. In this example, $g_{\text{abs}} \approx 1.85 \times 10^{-4}$. The dissymmetry ratio is also a function of the magnetic and electric dipole moments (m and μ, respectively) and the angle θ between them, such that $g_{\text{abs}} = 4 \cdot R/D = 4|m||\mu|\cos\theta/(m^2 + \mu^2)$, where R is the rotatory strength, D is the dipole strength, and both R and D are normalized to one repeat unit. The Kuhn disymmetry ratio, g_{abs}, was also found to be almost independent of both alkyl side group length and silicon main-chain length.[315] Care should be exercised, however, in discussing the Kuhn disymmetry ratio, since helix reversals and segments of opposite screw sense, if absorbing at the same wavelength, will reduce the value of the g_{abs} ratio. For an optically active polysilane, it is thus very often difficult to ascertain whether opposite screw senses both exist and absorb at the same wavelength resulting in a low g_{abs}, or whether the low g_{abs} is due to the smaller dihedral angles. In these cases, knowledge of the approximate conformation and expected UV $\lambda_{\max}$ can assist in the assessment of helical purity.

In some cases, opposite screw senses do coexist in a molecule, but due to their side-chain packing requirements, the dihedral angle and thus helical pitch differ considerably. For these polymers, positive and negative Cotton effects due to the opposing screw sense segments are apparent in the CD spectrum.[316,317] An important experiment in chemical molecular manipulation, dubbed "cut and paste," was also carried out by Fujiki on one such polymer.[316] It was found that the CD spectrum of poly[methyl-(*S*)-2-methylbutylsilylene] exhibited a negative extremum at 305 nm and a positive extremum at 277 nm, as is evident in Figure 35, suggesting the possibility of two opposite screw senses of differing screw pitch (the different side-chain packings would result in different helical or dihedral angles which would give rise to different absorption maxima).

Irradiation of a CCl_4 solution sample of the polymer at the wavelength of the higher energy, positive, CD extremum resulted in the spectral bleaching of all CD and UV bands. On the other hand, irradiation at the longer

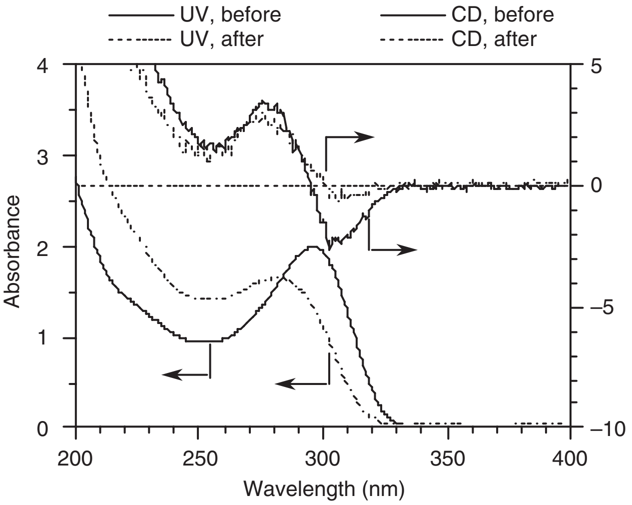
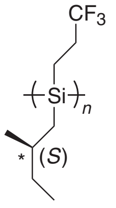


Figure 35 UV and CD spectra of poly[methyl-(*S*)-2-methylbutylsilylene] in isooctane at 25 °C before and after "cut-and-paste" experiment.[204] Reprinted with permission from Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563, © 2001 Wiley-VCH.

wavelength, negative, extremum, resulted in the almost complete disappearance of the band at this wavelength, and the resulting blue-shifted UV band almost matched the profile of the remaining CD extremum.[254] This indicated selective photolytic degradation of the greater pitch helix upon irradiation at 305 nm. After removal of the low molecular weight material resulting from the degradation, the remaining Cl-terminated telomers were succesfully recombined in hot toluene using sodium to generate a nearly single screw sense helical polymer, the spectra of which are shown by the dotted lines in Figure 35.

As already noted in Section 3.11.5.2 and also earlier in this section, in considering the stability of a particular conformation, the position of the chiral branching point is critical.[241] This was clearly demonstrated in a recent communication in which the chiroptical characteristics of six polysilanes were compared.[318]

Comparing the fluorinated and non-fluorinated pairs, it was found that **103** with a γ-branch showed virtually no optical activity, even at $-40\,^{\circ}\mathrm{C}$, due to the remoteness of the branching point and concomitantly extremely weak conformational locking. In contrast, its fluorinated analog, **102**, showed a positive Cotton effect due to a PSS conformation. Other investigations by the same group on achiral polysilanes[206] showed that side-chain-bound CF_3 could coordinate to the silicon backbone via intramolecular C–F…Si interactions, which, although weak, were sufficient to induce backbone stiffening resulting in conformational changes (see Section 3.11.5.2 on solvatochromism). In this chapter, the polymers contain unichiral groups so that on intramolecular C–F…Si coordination, the stiffening effect is sufficient to permit induction of a PSS helical conformation, resulting in the observed CD signal. Polymers **100 and 101**, also bearing γ-branched unichiral groups, displayed analogous effects in their CD spectra, as shown in Figure 36.



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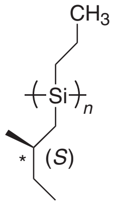

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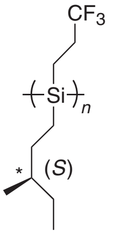

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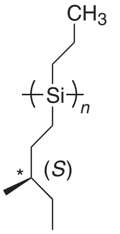

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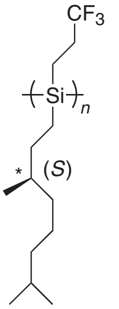

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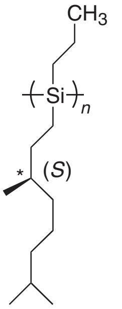

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Contrasting with these, the CH_3-terminated **99** did show a Cotton effect. This is because the chiral side chain is β-branched, so that the chiral locking effect is sufficient to afford a stable PSS conformation. CF_3-terminated **98** also showed a Cotton effect, though the CD and also UV intensity were about half those of **99**, presumably due to some competition between the C–F···Si interaction and chiral side-chain packing effects.

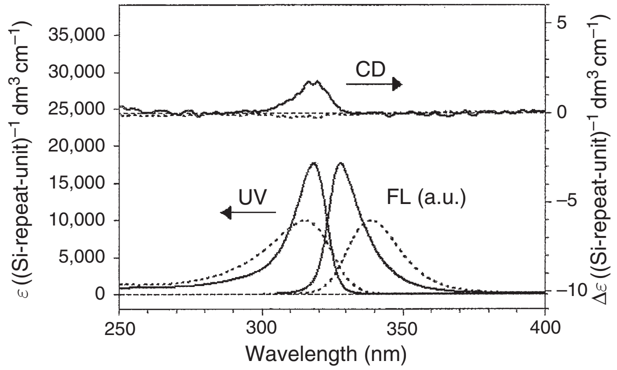
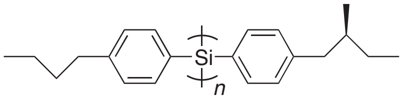


Figure 36 UV, CD, and FL spectra of **100** (solid line) and **101** (dashed line).[318] Kim, S.-Y.; Saxena, A.; Kwak, G.; Fujiki, M.; Kawakami, Y. *Chem. Commun.* **2004**, 538–539. Reproduced by permission of The Royal Society of Chemistry.

3.11.6.1.1.(ii) Poly(diarylsilylene)s

Among the polysilanes, those with phenyl rings directly attached to the silicon main chain have the lowest energy HOMO–LUMO gap, and it is well known that this arises due to effects which are both conformational (the bulky Ph rings enforce a very stiff, extended-backbone conformation) and electronic (σ–π mixing of orbitals occurs to reduce the HOMO–LUMO gap).[21,283] In order to probe the backbone conformation further and determine whether it was *all-anti*, diarylpolysilanes substituted with unichiral groups on the phenyl rings, such as **104–107**, were investigated.[248,282,310,317,319]

It was found that these showed UV absorption maxima at the same wavelength (ca. 395 nm) as their non-chiral-substituted analog, poly(bis-*n*-butylphenylsilylene), as shown in Figure 37, from which it was concluded that the dihedral angles of these polymers were the same.[282] The CD spectra showed Cotton effects, thus indicating that the polymers adopted PSS helical conformations and that they do not take *all-anti* conformations.



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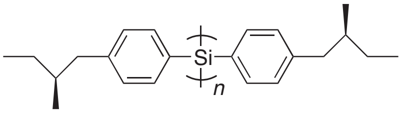

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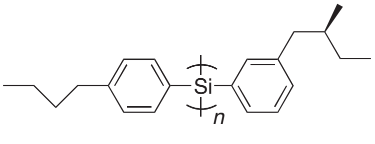

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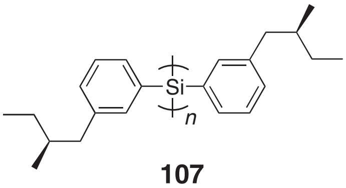

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Force field calculations[248] on H-terminated 30-mer **91** and **104** homologs, plots of which are shown in Figure 38, and also X-ray crystallography on a heptameric poly(diphenylsilylene),[252] corroborated the evidence for helicity and suggested *transoid*-conformations.

3.11.6.1.1.(iii) Poly[(alkyl)(aryl)silylene]s

Due to their greater asymmetry, steric locking effects may not be as strong as in the symmetrically dialkyl- and diaryl-substituted polysilanes. Depending on the structure of the side chains, main-chain-derived optical activity due to an induced PSS may or may not be observed. An interesting example is decribed in the literature: the *meta*-substituted polymer, poly[methyl-*m*-(*S*)-2-methylbutoxyphenyl]silylene, did show a CD band (negative sign), whereas the *para*-substituted polymer did not.[320] It was considered that steric locking of the side chains was less effective in the *para*-case such that, despite the presence of unichiral side-chain substituents, no optical activity was evident.[320,321] Nevertheless, chiral substituent effects played a major role in clarifying the structure of PMPS. Co-polymers based on the PMPS structure were synthesized and their cooperative helical induction effects investigated[322] with the

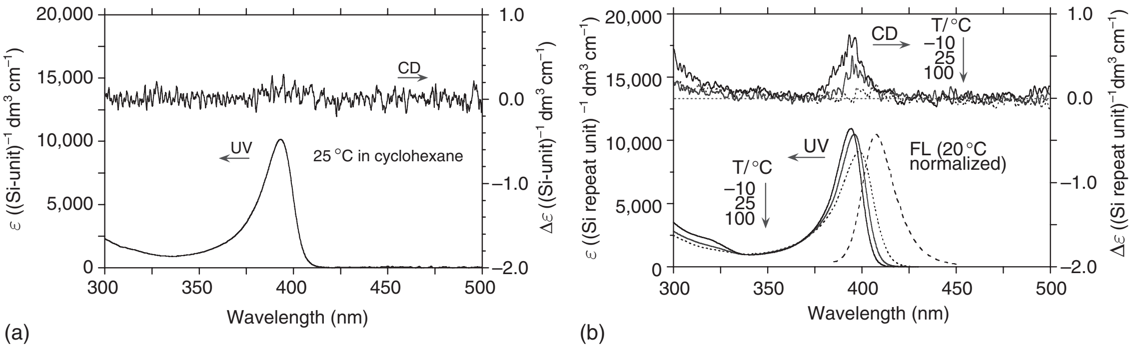


Figure 37 UV and CD spectra for (a) $(Ar_2Si)_n$, **91** and (b) $(ArAr^*Si)_n$, **104** (where Ar = 4-*n*-butylphenyl, and Ar* = 4-*(S)*-2-methylbutylphenyl).[282] Reprinted with permission from Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734–9735, © 1999 American Chemical Society.

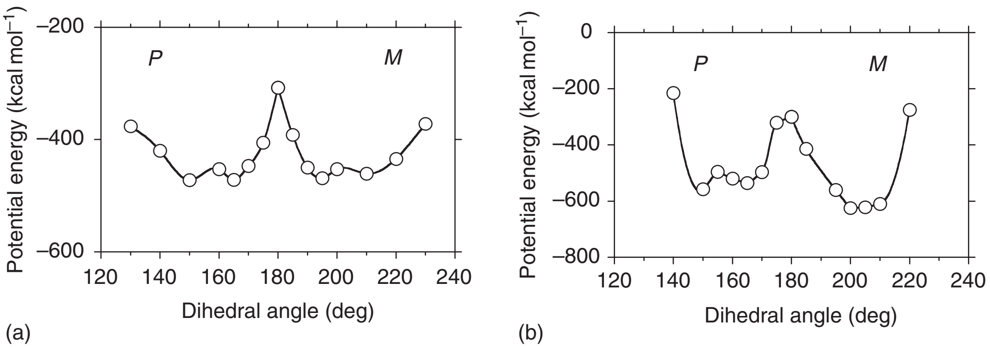
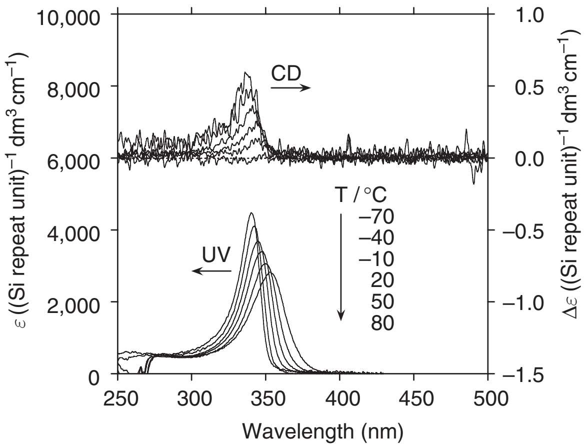


Figure 38 Force field-calculated potential energy as a function of backbone dihedral angle for (a) H–$(Ar_2Si)_{30}$–H and (b) syndiotactic H–$(ArAr^*Si)_{30}$–H (where Ar = 4-*n*-butylphenyl, and Ar* = 4-*(S)*-2-methylbutylphenyl).[248] Reprinted with permission from Koe, J. R.; Fujiki, M.; Motonaga, M.; Nakashima, H. *Macromolecules* **2001**, *34*, 1082–1089, © 2001 American Chemical Society.

object of elucidating the conformation of PMPS, which for many years was uncertain, with both random and helical conformations being suggested. The similarity between the UV, FL, and FLA spectra of optically inactive PMPS and the optically active co-polymer, PMPS*, derived from the co-monomers dichloromethylphenylsilane and dichloro-(*S*)-2-methylbutyl(phenyl)silane in the ratio of 20 : 1 indicated that both polymers should adopt similarly helical conformations, except that in the latter a PSS conformation is observed, while in the former, turns of both screw senses are present in equal proportions. PMPS* co-polymers showed a marked positive helical cooperativity effect[322] (see Section 3.11.6.1.1.(v) for a discussion on cooperativity effects). It thus appears now that PMPS adopts a more ordered helical conformation than previously supposed.

3.11.6.1.1.(iv) Poly(bis-alkoxysilylene)s

These constitute a new class of polysilanes, as already described in Section 3.11.4.2.2, exhibiting red-shifted optoelectronic spectra due to electronic σ–n mixing.[188,189] Reaction of the precursor polysilane, $(SiCl_2)_n$, with optically active alcohols in the presence an amine resulted in the formation of optically active poly(bis-alkoxysilylene)s. The variable-temperature CD and UV spectra for poly(bis-(*S*)-2-methyloctoxysilylene), **108**, are shown in Figure 39, indicating adoption of a PSS helical conformation on substitution with the chiral alkoxy group, despite the greater flexibility[157] of the oxygen side chain to backbone linkage.



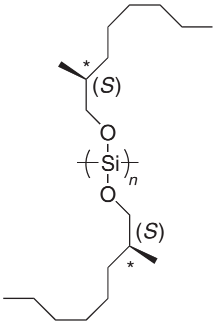


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Figure 39 Variable-temperature CD and UV spectra and structure of optically active poly(bis-alkoxysilylene), **108**.[188] Reprinted with permission from Koe, J. R.; Motonaga, M.; Fujiki, M.; West, R. *Macromolecules* **2001**, *34*, 706–712, © 2001 American Chemical Society.

3.11.6.1.1.(v) Co-polymers and cooperativity

Möller and co-workers co-polymerized dichlorodi-*n*-pentylsilane with either dichloro-bis-(*S*)-2-methylbutylsilane or dichloro-(*S*)-2-methylbutyl-*n*-pentylsilane in various ratios and found a linear dependence of optical activity on mole fraction of chiral co-monomer.[313] On the other hand, studies by Fujiki on co-polymers **109** formed by the co-polymerization of achiral (racemic) dichlorohexyl-2-methylbutylsilane and chiral dichlorohexyl-(*S*)-2-methylbutylsilane or dichlorohexyl-(*R*)-2-methylbutylsilane have shown that a preferential helical screw sense can be induced by even as little as 0.6 mol% of chiral co-monomer, and that at 5 mol%, the helicity, as gauged by the g_{abs} value, is essentially the same as that of the chiral homopolymer, as shown in Figure 40.[323,324] This indicates a positive non-linear cooperative "sergeants and soldiers" effect (positive cooperativity),[325] such that the direction of twist initiated by chiral repeat units is propagated through achiral repeat units. This type of cooperativity is also shown by the aryl(alkyl) co-polymers **110**.[322]

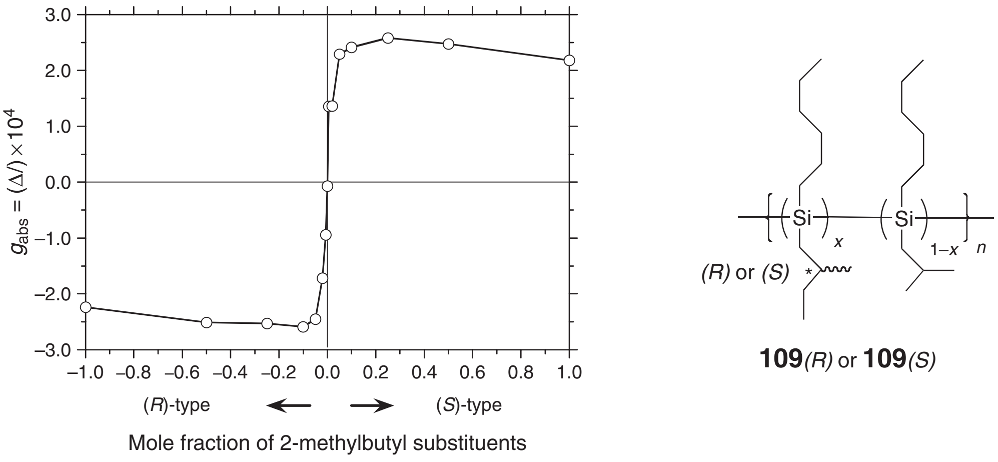
Interestingly, bis-aryl-substituted co-polymers showed unusual substitution position-dependent and chiral mole fraction-dependent cooperativity:[248,310] positive cooperativity for the *para*-substituted poly(bis-*p*-*n*-butylphenylsilylene)-*co*-(bis-*p*-(*S*)-2-methylbutylphenylsilylene), **111**, at lower chiral content, but reversing above a chiral content of 50% such that the g_{abs} decreased again, becoming negative for the 100% chiral polymer. Negative cooperativity is shown by the *meta*-polymer poly(bis-*p*-*n*-butylphenylsilylene)-*co*-(bis-*m*-(*S*)-2-methylbutylphenylsilylene).[248] These cooperative effects were successfully reproduced by Sato *et al.* in theoretical studies using an Ising model modified to include interactions between bonded chiral and achiral repeat units. Experimental and calculated plots are shown in Figure 41.[326]

Another cooperativity effect, dubbed "majority rule" has also been noted. Where opposite enantiomer chiral groups are both present in side chains, such as (*S*) and (*R*)2-methylbutyl groups, the overall helicity is determined in a non-linear manner by the ee only, as is evident in Figure 42.

3.11.6.1.1.(vi) Solid-state studies

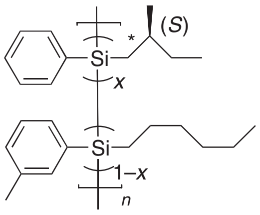
The control of optical activity, chirality, and conformation in polysilanes has opened up a new dimension in potential applications. However, in any practical device, the polymer would have to be in the solid state, as a film, and as yet there have been few reports of investigations into solid-state polysilane chiroptics. Partly this is because solid-state CD studies can be complicated by artifacts such as polymer molecule alignment along micrometer-scale and smaller grooves cut in the substrate surface during polishing. Care must be taken to ensure that film samples are indeed isotropic, showing the same CD signals upon rotation of the sample in the plane orthogonal to the incident light beam.

Very recently, however, two papers were published by the group of Fujiki which report successful solid-state CD studies of chiral polysilanes. In the first, a helix–coil transition was described for film samples of poly[(*S*)-3,7-dimethyloctyl-*n*-propylsilylene)], **113**.[327] This polymer has a relatively low glass transition temperature, T_g, which was considered critical for the observation of a helix–helix transition in the solid state, since helical inversion would be precluded if the inversion temperature, T_c, were below T_g, as the segmental motion of the chain,



109(*R*) or **109**(*S*)

Figure 40 Kuhn disymmetry ratio (g_{abs}) of **109** as function of (*S*)- or (*R*)- chiral center mole fraction.[323] Reprinted with permission from the author Fujiki, M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1996**, *37*, 454–455.



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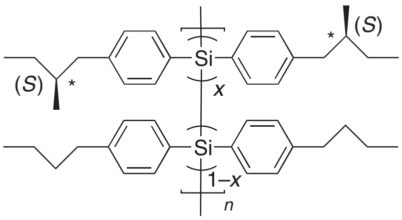

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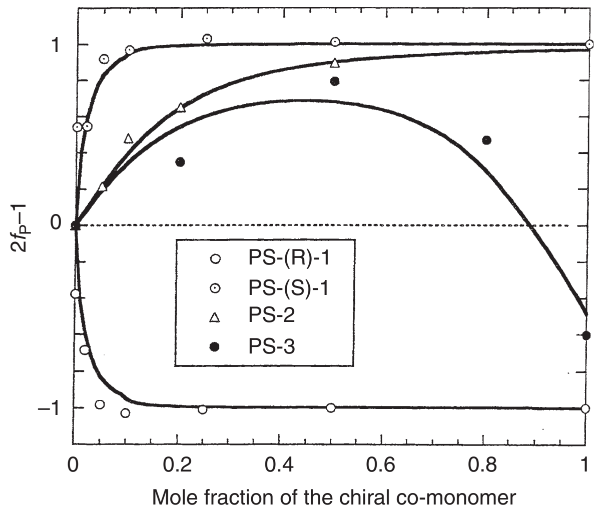
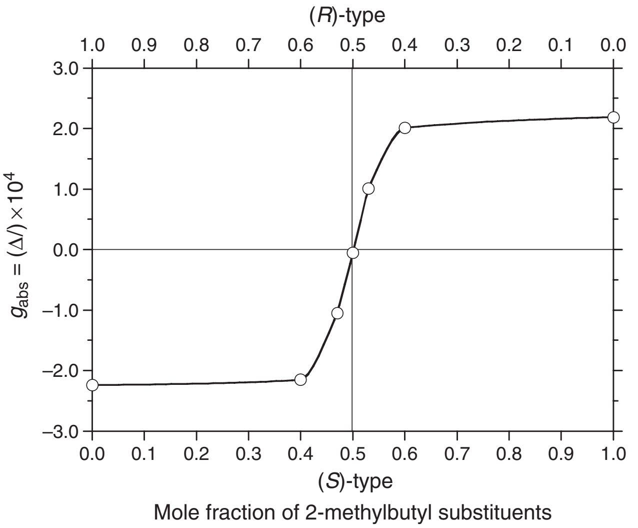


Figure 41 Composition dependence of the enantiomer excess $2f_P - 1$ of the *P* helical state of polysilanes **109**(*R*): ○ **109**(*S*): ⊙, **110**: Δ and **111**: • (calculated: solid curves; experimental: symbols).[326] Reprinted with permission from Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Macromolecules* **2002**, *35*, 5355–5357, © 2002 American Chemical Society.



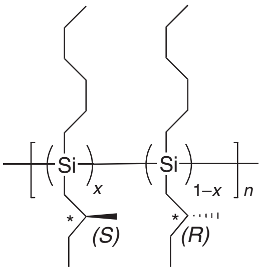


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Figure 42 Kuhn dissymmetry ratio for the series of co-polymers **112** as function of (*R*)- or (*S*)-enantiomer mole fraction.[323] Reprinted with permission of the author from Fujiki, M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1996**, *37*, 454–455.

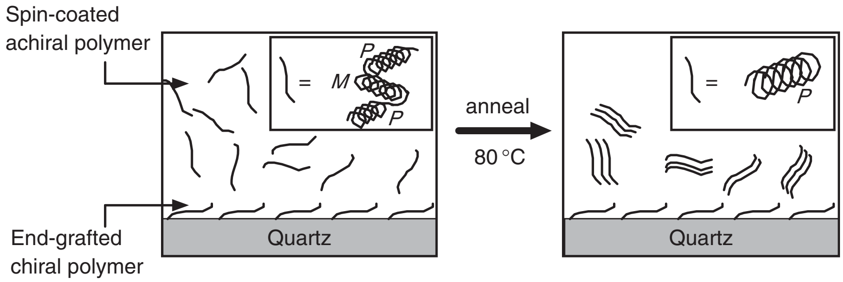


Figure 43 Cartoon representation of solid-state thermodriven chiral transfer and amplification.[328]Adapted with permission from Saxena, A.; Guo, G.; Fujiki, M.; Yang, Y.; Ohira, A.; Okoshi, K.; Naito, M. *Macromolecules* **2004**, *37*, 3081–3083, © 2004 American Chemical Society.

necessary for inversion, would be frozen out. DSC showed a second-order transition corresponding to a T_g for polymer **113** of −47 °C and a first-order transition at around −8 °C which was considered to correspond to a helix–coil transition.

In the second, a chiral polysilane thin film was shown to act as a helical command surface in a novel example of chiral induction.[328] Poly(*n*-decyl-(*S*)-2-methylbutylsilylene), **88**, was chemically end-grafted to a quartz surface as noted in Section 3.11.4.2.3 above.[195] An achiral γ-branched polysilane, poly(*n*-decyl-3-methylbutylsilylene), PD3MBS, was spin-coated onto the **88** film. After annealing, a strong bisigned Cotton effect[329] was apparent in the CD spectrum with extrema at 324 (negative) and 309 (positive) nm, which indicated a van der Waals interaction-mediated chirality transfer from **88** to PD3MBS. The phenomenon was described as another example of “sergeants and soldiers"-type cooperativity, as depicted in the cartoon illustration in Figure 43.

Interestingly, no chiral induction was apparent when a β-branched polymer, poly(*n*-decyl-2-methylpropylsilylene), PD2MPS, was spin-coated onto a film of **88**. It is likely that the β-branching position results in a very stiff, locked conformation for PD2MPS, which, due to the relative weakness of the van der Waals interaction, is not obedient to the command from the PSS helical surface-tethered chains.

3.11.6.1.2 PSS induction by enantiopure chiral end groups

As noted in the sections above on oligosilanes and also solid-state structure, a di-*n*-propylsilane hexamer with enantiopure (*R*)-2-phenylpropyl termini, **5**(*R*), was synthesized by Kira and co-workers and the single crystal X-ray structure reported (the (*S*)-2-phenylpropyl analog was also synthesized).[15] From the crystallography, the molecule showed *M* screw sense helicity, with main-chain dihedral angles of ca. −175°. The (*R*) chiral decameric homolog of this molecule, 1,10-bis[(*R*)-2-phenylpropyl]eicosapropyldecasilane, **113**(*R*), and its (*S*) chiral analog, were also prepared, and the CD and UV spectra at 85 K in an isopentane/methylcyclohexane matrix were reported.[15] For the (*R*)-chiral decamer **113**(*R*) below 153 K, a strong positive Cotton effect was observed, indicating a PSS induced by cooperativity between the chiral termini and achiral side groups. A broader weaker negative Cotton effect was also apparent at slightly shorter wavelength, the origin of which was unclear. One possibility is that it could be a less regular helix of opposite screw sense. This work was followed by extension to high molecular weight poly(di-*n*-hexylsilylene) with the same chiral termini (PDHS*),[330] and constitutes strong experimental evidence for the adoption of a 15_7 helical conformation in solution at lower temperatures for PDHS, which was long believed to adopt an *all-anti*-conformation in solution (see Section 3.11.5.2 on conformations). Bisignate Cotton effects were observed for PDHS* below 233 K and are considered to originate from an exciton couplet for two spatially interacting polysilane chromophores.[15,207,330]

Fujiki also reported end-chain chiral functionalization in (*S*)-2-methylbutyl-terminated poly(*n*-hexyl-2-methylpropylsilylene), **114**, and found a weak, though definite, induced PSS ($g_{abs} \approx -1 \times 10^{-5}$) of the “opposite sign” to the PSS induced when the unichiral groups were incorporated in the side chains.[204,323]

A convenient synthetic approach to polysilanes with functional end groups is via the anionic polymerization of masked disilenes, as noted in Sections 3.11.4.1.2 and 3.11.4.2.3, and in Section 3.11.6.1.5. Recently, Sanji, and co-workers used a chiral potassium (+)- or (−)-menthoxide as the anionic initiator and prepared chirally terminated poly(1,1-dimethyl-2,2-di-*n*-hexylsilylene), **115**, with molecular weights between 6,800 and 20,000.[331] A negative bisigned Cotton effect was observed in solution at −40 °C (the sign of a bisigned Cotton effect is given as that of the longer wavelength side), as shown in Figure 44.

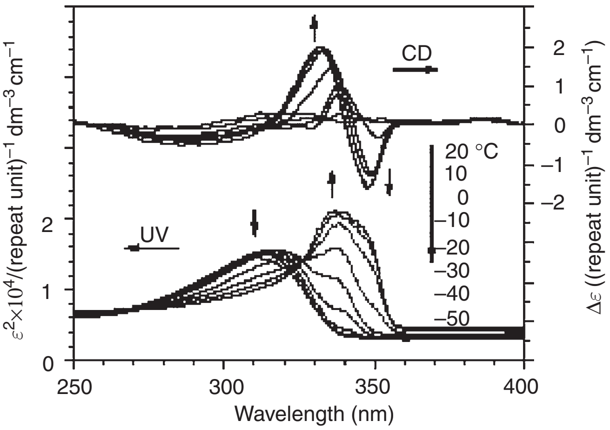
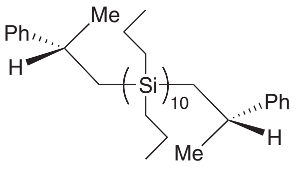
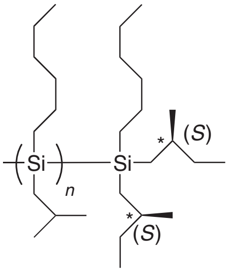


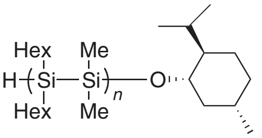
Figure 44 Temperature-dependent UV and CD spectra of (+)-menthoxy-terminated polysilane **115** in isooctane ($M_n = 6{,}800$).[331] Reprinted with permission from Sanji, T.; Takase, K.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1607–1611, © 2004 Chemical Society of Japan.



113(*R*)



114

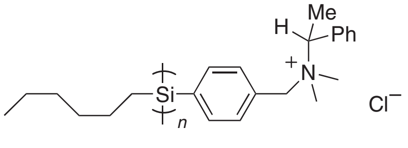


(1*S*,2*R*,5*S*)-(+)-menthoxy-terminated **115**

The origin of the bisignate nature was considered to be excitonic,[331] due to the interaction between chromophores on different segments. Although this is a possibility, the UV profile at lower temperatures indicates two different conformations, and it may be that these are of opposite screw sense helicity, thus accounting for the bisignate CD profile. The occurrence of opposing screw senses at different wavelengths and resulting bisignate CD signals has been shown to occur in several cases[204,207,317] (see Figure 35 for an example). In the solid state at room temperature, a positive Cotton effect is observed. This is also understandable if the opposing screw senses origin of the bisignate solution CD is accepted, since packing forces would favor one conformation over the other.

3.11.6.1.3 PSS induction by post-polymerization functionalization

As already described in Section 3.11.4.2.1 on functionalization, amphiphilic polysilanes containing chiral ammonium pendant groups have been described.[173] Chloromethylation of poly(hexylphenylsilylene) (PHPS) using $SnCl_4$ in CH_3COCH_2Cl (the polymer molecular weight decreased from 1.5×10^5 to 1.0×10^4 followed by treatment with optically active (+)-*N*,*N*-dimethyl-α-methylbenzylamine to give the amphiphilic polysilane (+)-**116**, soluble in water, ethanol, and acetonitrile, in 88% yield.



116

The (−) and racemo forms were also prepared. The CD spectrum of the (+) and (−) polymers in ethanol showed negative and positive bisigned profiles respectively, indicating main-chain helical screw sense chirality. The origin of the bisignate nature of the CD signals was not discussed, and particularly where there is an additional chromophore (the phenyl ring), it is unclear.

3.11.6.1.4 PSS induction by chiral solvation

Recently, the first example of chiral solvation of a polysilane was demonstrated: dissolution of the inherently optically inactive poly(methylphenylsilyene), PMPS, and poly(hexylmethylsilylene), PHMS, in the optically active solvents (*S*)-2-methyl-1-propoxybutane and (*S*)-(2-methylbutoxymethyl)benzene induced the polymer chains to adopt PSS helical conformations as evidenced by (positive-signed) Cotton effects almost coincident with the UV σ–σ^* transition at 340 and 305 nm, respectively.[332]

3.11.6.1.5 PSS induction by helicity transfer and complexation

Another interesting chiral chain end effect is exhibited by the helical polymer block co-polymer, poly(1,1-dimethyl-2,2-di-*n*-hexylsilylene)-*b*-poly(triphenylmethyl methacrylate), reported by Sanji and Sakurai (see Scheme 7) and prepared by the anionic polymerization of a masked disilene.[333] The helical poly(triphenylmethyl methacrylate) block (PTrMA) is reported to induce a PSS of the same sign in the poly(di-*n*-propylsilylene) block in THF below −20 °C, and also in the solid state, by helicity transfer, as evidenced by the positive Cotton effect at 340 nm, coincident with a fairly narrow polysilane backbone UV absorption characteristic of an *all-transoid*-conformation. This phenomenon was termed "helical programming." Above 20 °C, the polysilane block loses its optical activity and the UV absorption shifts to 310 nm in a reversible, temperature-dependent effect, due to the disordering of the chain, as shown in Figure 45.

A concomitant shift in the UV absorption wavelength to 310 nm characteristic of a random coil conformation is apparent.[333] The report is not explicit concerning the screw sense of the PTrMA block, and thus the screw sense of the silicon helix is not certain.

Sanji *et al.* have very recently described another strategy for induction of PSS chirality in polysilanes, based on threading oligosilanes through the helical cavities afforded by organic macromolecules. Mixing a naphthylacetoxypropyldecasilane with γ-cyclodextrin in water produced the inclusion compound indicated in Scheme 31.[334,335]

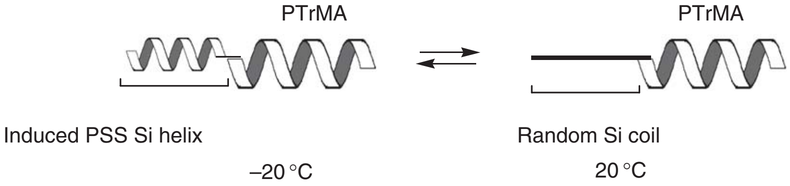
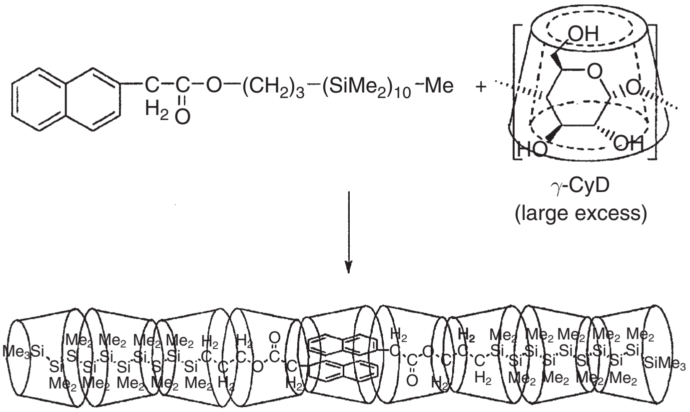


Figure 45 Cartoon showing temperature-dependent Si chain helical induction by PTrMA block.[333] Adapted with permission from Sanji, T.; Takase, K.; Sakurai, H. *J. Am. Chem. Soc.* **2001**, *123*, 12690–12691, © 2001 American Chemical Society.



Scheme 31 Induction of PSS helicity in oligosilane by wrapping in γ-cyclodextrin.[335] Reprinted with permission from Sanji, T.; Kato, M.; Tanaka, M. *Macromolecules* **2005**, *38*, 4034–4037, © 2005 American Chemical Society.

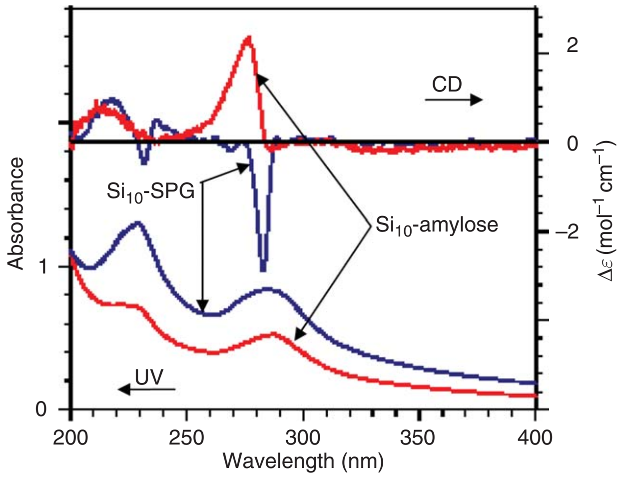


Figure 46 CD and UV spectra for amylose- and schizophyllan-wrapped decasilane.[337]Reprinted with permission from Sanji, T.; Kato, N.; Kato, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2005**, (in press), © 2005 Wiley-VCH.

Upon threading the oligosilane molecules into the asymmetric γ-cyclodextrin cavity to form a pseudorotaxane-type aggregate,[335] a bisignate Cotton effect became apparent at about 290 nm, indicating induced PSS helicity. The reason for the bisignate nature of the signal was not clear.

Similarly, inclusion complexes were formed between the decasilane and the polysaccharides schizophyllan[336,337] and amylose.[337] Amylose adopts a "left"-handed helical conformation, and forms inclusion complexes as a result of hydrophobic interactions with guest molecules confined within the helical cavity. Schizophyllan (SPG) comprises β-1,3-linkages between glucose units (β-1,3-glucan) and adopts a "right"-handed triple helix in nature. A molecular mechanics study of the minimum energy structure of the simple model complex formed by the interaction between permethyldodecasilane and an amylose fragment containing 16 repeating α-1,4-D-glucopyranose units indicated that the amylose fragment adopts a left-handed helical conformation by wrapping around the oligosilane axle. In the helical cavity created by the amylose wrapping, the oligosilane main chain also assumes a left-handed helical conformation with an Si–Si torsion angle of about 165°. The experimental UV and CD spectra of the SPG and amylose inclusion compounds are shown in Figure 46.

From the positive Cotton effect observed in the amylose case and the negative Cotton effect in the SPG case, it is clear that the oligosilane adopts opposite screw sense helical conformations in the two cases.[337] It now appears possible to associate an *M*-screw sense helix with a positive sign Cotton effect (and vice versa), although other experimental confirmations of this are desirable.

3.11.6.2 Temperature Dependence of Screw Sense and PSS Selectivity

From Figures 37(b) and 39, it is evident that the magnitudes of Cotton effect $\Delta\varepsilon$ values in the CD spectra are greatest at the lowest temperatures, and that as the temperature is raised, $\Delta\varepsilon$ magnitudes decrease, in some cases eventually to zero and in other cases only slightly. This indicates greater helical screw sense selectivity at lower temperature, and at higher temperatures, a decrease in selectivity due to thermal population of the less stable rotameric state. A change in relative population of the two helical states requires that the barrier height to the opposite screw sense is not too great (see Figure 38(b)[204,207,282] above for an example of an asymmetric plot of force field-calculated potential energy dependence on screw sense and helical angle for an optically active polysilane). In experimental terms, this means that the polymer main chain must not be too stiff and must show some flexibility, which is evidenced both by shorter persistence lengths, q, and narrower ^{29}Si NMR resonances.[242,314,338]

Although the trend on raising the temperature is toward less screw sense selectivity, depending on the side-chain structure, a dramatic reversal of Cotton effect sign may occur at a critical temperature, T_c, indicating a helix–helix transition, that is, an abrupt switch from one helical screw sense to the other. Such helical inversions have generated considerable interest as a possible basis for molecular switching or memory devices and have been found for certain dialkylsilylene[314,338,339] and diarylsilylene[317,340] homo- and co-polymers.

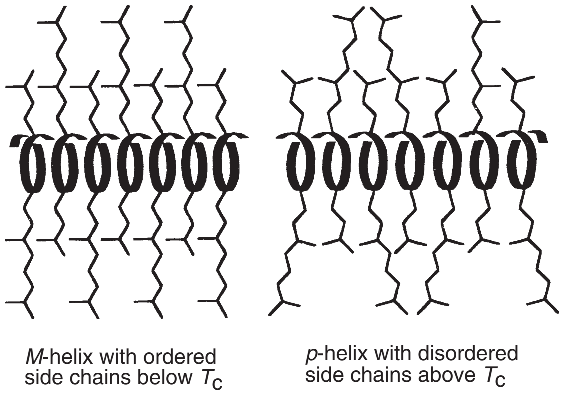
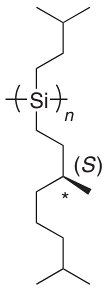


Figure 47 Structural models of *P* and *M* helical **117** above and below T_c.[314] Reprinted with permission from Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343, © 2000 American Chemical Society.

Homopolymers such as poly[(*S*)-3,7-dimethyloctyl-2-methylpropylsilylene], **117**, were initially studied, and the helix–helix transition was discussed in terms of an entropically driven phenomenon in which at temperatures below T_c the side chains of the helical polymer are in a very ordered state and enforce a particular screw sense, whereas above T_c, the side chains become disordered such that the main chain can relax into the opposite screw sense.[314] This concept is expressed in Figure 47.



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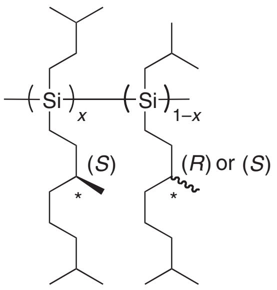
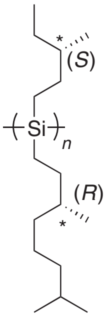


118(*R*) or **118**(*S*)



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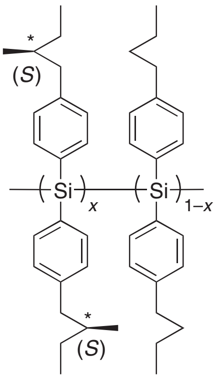

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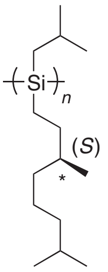
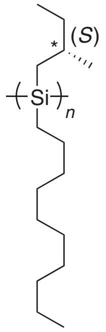


121(*S*)



88

The UV and CD spectra of **117** and **121** (*S*) are shown in Figure 48. Considering **117**, at −40 °C a negative Cotton effect, coincident with the UV absorption, is evident, and at −5 °C a positive Cotton effect, coincident with the UV absorption (both of which are slightly red-shifted with respect to the −40 °C profiles), is observed. It is thus apparent that **117** underwent a helix–helix transition at some temperature between −5 and −40 °C. In contrast, the Cotton effects of **121**(*S*) were positive at all temperatures, indicating that no helix–helix transition occurred. Similarly to **121**, **88** did not undergo a helix–helix transition. These results are due to the different stiffness of the molecules, which is quantified by the viscosity index, α.

The viscosity index, α, for γ-branched **117** (for a molecular weight fraction of ca. 5×10^4) was found to be 1.11, while for **121**(*S*)), with both β- and γ-branching points, α was 1.29, and for **88**, with a single β-branching point, 1.35 (for comparison, α for poly(methyl-*n*-propylsilyene) was 0.64, for poly(di-*n*-butylsilylene) 0.71, for poly(di-*n*-hexylsilylene) 0.74, and for poly(methylphenylsilylene) 0.79),[203,315] indicating that while **117**, **121**(*S*), and **88** have very stiff backbones, among these, that of **117** is the most flexible. It appears fairly general that β-branched polymers are the stiffest and conformationally locked, while γ-branched polymers are stiffer than non-branched polymers and stiff enough to support a preferential screw sense, their increased flexibility compared to β-branched polymers renders them capable of undergoing helix–helix transitions. This was also reflected in the ^{29}Si NMR line widths which are

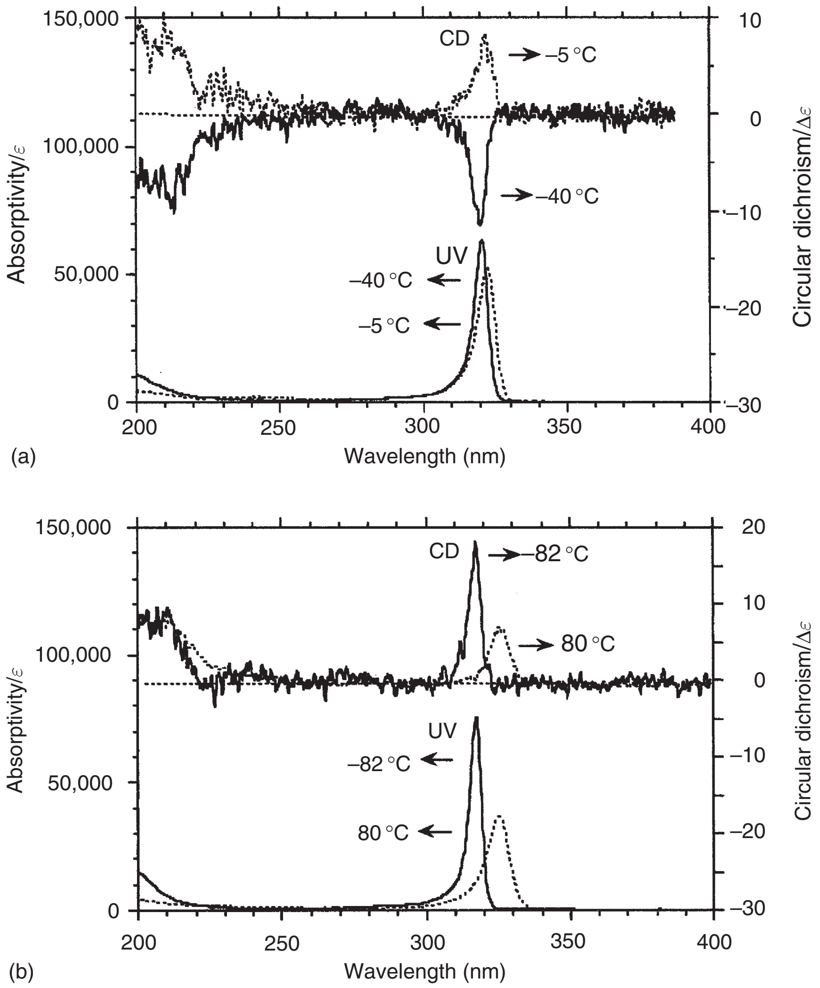


Figure 48 (a) CD and UV absorption spectra in isooctane of (a) **117** ($M_w = 1.6 \times 10^6$) and (b) **121**(*S*) ($M_w = 4.2 \times 10^4$).[314] Reprinted with permission from Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343, © 2000 American Chemical Society.

compared in Figure 49, in which it is clear that the narrowest line width, indicating greatest flexibility/conformational mobility, was observed for **117**.[314]

In order to gain more control over T_c, co-polymer systems were then designed, such as **118**(*R*) or **118**(*S*), comprising in addition to the repeat unit in **117** either an (*R*)- or (*S*)-chiral repeat unit of slightly different structure, which results in different side-chain packing preferences and hence different values of T_c at different temperatures.[314] In this way, it was possible to fine-tune T_c in the temperature range from −64 to 79 °C. Extending this concept, homopolymers with two different chiral centers, such as **119**, were prepared, the latter with T_c at about 0 °C.[338] Potential applications of **119** in quantum computing were discussed, though in any practical device, the polymer would have to be in the solid state, as a film. Although a few chiroptical studies of solid-state polysilanes have been reported (see above), helix–helix transitions in the solid state are still a challenging target.

3.11.6.3 Chirality in Polysilane Aggregates

Aggregates are microprecipitates of tens to thousands of polymer molecules which can be invisible to the naked eye or appear as a faint cloudiness in the solution. They form when a poor solvent such as methanol is added to a molecularly dispersed solution of the polymer in a good solvent, such as toluene or THF, or vice versa. Since aggregates are the first stage of a solid precipitate, they are also useful as model materials of the solid bulk state polymers and are amenable to study by many solution techniques such as solution-state UV and CD spectroscopy. Chiral molecules

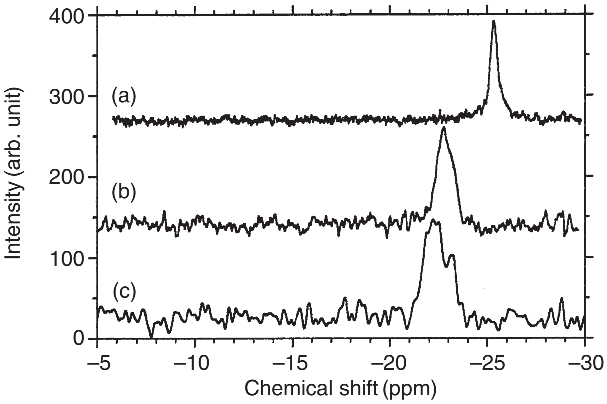


Figure 49 ^{29}Si NMR backbone resonances for (a) **117**, (b) **121**(*S*), and (c) **88** in CDCl$_3$ at 30 °C[314] Reprinted with permission from Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343, © 2000 American Chemical Society.

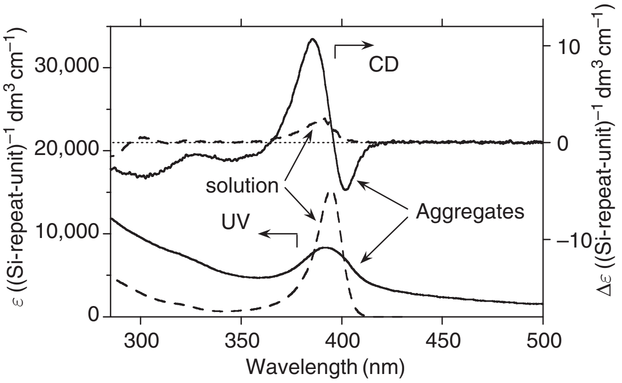


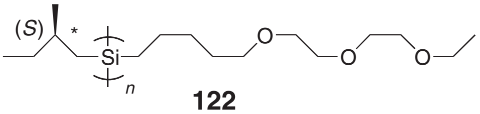
Figure 50 Comparison of aggregate (in toluene/MeOH 40/60) and solution- (in toluene) state UV and CD spectra of **111** (1×10^{-4} M; $M_w = 102{,}000$).

may aggregate in a chiral arrangement, in which case, instead of a single Cotton effect of positive or negative sign coincident with the UV spectrum, a bisigned Cotton effect is produced as a result of coupled excitonic interactions (Davidov coupling). By convention, a bisigned Cotton effect takes the sign of the longer wavelength extremum.

The UV and CD spectra of aggregates of **111**, poly[bis-*p*-*n*-butylphenylsilylene$_{0.5}$-*co*-bis-*p*-(*S*)-2-methylbutylphenylsilylene$_{0.5}$] (see above), in a toluene/methanol 40/60 solution are shown in Figure 50, compared with the solution spectra, and are typical of the spectra obtained for poly(diarylsilane)s under such conditions.[340]

Often the UV absorption tails into the visible due to light scattering by the microparticles, although the λ_{max} is usually very close to that in solution. The aggregate CD spectrum, however, is markedly different from the solution-state spectrum, showing an intense bisigned Cotton effect coincident with the UV due the Davidov coupling.

Aggregate CD spectra are very sensitive to many factors including side-chain type, solvent, chiral additives, and temperature. Bisigned CD spectra of dialkylsilylene co-polymers in THF solution were described in the early studies of optically active polysilanes by Möller and co-workers who considered aggregation to be the cause of the bisigned signals.[341] Another report concerning aggregates of optically active polysilanes was published in 1998. Poly[(*S*)-2-methylbutyl-6,9,12-trioxatetradecylsilylene), **122**, bearing an oligoethoxy side chain was found to be soluble in alcohols, affording sharp UV and CD signals indicative of a rigid rod-like PSS structure.[207] On addition of greater than 50% water, a non-solvent, to an ethanol solution, bisigned CD signals appeared due to the formation of chiral aggregates.



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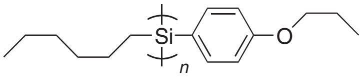
Then, around 2000, a series of investigations on the switchable chiroptical characteristics of poly[(alkyl)alkoxyphenylsilylene]s by Nakashima *et al.* was published concerning chiral aggregates, their formation, and solvent dependence.[321,342] On addition of mixtures of either (*R*) or (*S*) chiral alcohols with MeOH to THF solutions of the achiral polymer **123**, bisigned Cotton effects became evident in the silicon backbone region of the CD spectrum, indicating chiral aggregates.[342] This was rationalized as resulting from transfer of chirality from the chiral alcohol (through hydrogen bonding between the alcohol and the side-chain alkoxy group) and amplification by induction of a PSS and aggregate formation.

Concerning the unichiral-substituted poly[(alkyl)alkoxyphenylsilylene]s, it was found that the formation of stable chiral aggregates depends critically on the polysilane structure and stereochemistry. Poly[*n*-hexyl-(*p*-(*S*)-2-methylbutoxyphenyl)silylene], **124**, was found to be optically inactive when molecularly dispersed in dilute THF solution (5×10^{-5} M), even at −80 °C, due to the existence of dynamically equivalent amounts of right (*P*)- and left (*M*)-handed screw sense helical main-chain domains. However, in good/poor co-solvent systems, **124** showed a marked bisignate CD signal due to the formation of chiral aggregates, the sign and magnitude of which were dependent on solvent polarity, solvent addition order, and thermal effects.[321] Figure 51(a) shows the dependence of aggregate chirality on solvent addition order. Opposite chirality aggregates were obtained depending on whether the poor solvent (MeOH) was added to the good solvent (THF)/polymer solution (method I) or the reverse (method II). In Figure 51(b), the dependence of CD sign on good/poor solvent ratio is apparent.



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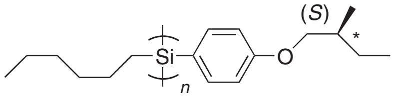

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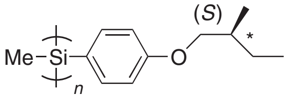

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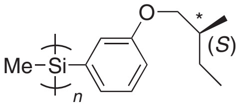

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These effects were rationalized on the basis of a hard-core model, shown in Figure 52, in analogy to cholesteric systems. If the ratio $p/d < \pi$, then right-handed screws generate a right-handed superhelix, whereas if $p/d > \pi$, then right-handed screws generate a left-handed superhelix.[329] Thus, the chirality of the aggregates could depend on the helicity of the single molecules and the solvent polarity.[321] An alternative model to explain the solvent dependence of the aggregate chirality is the chiral dispersion model, in which sign inversion of the chiral intermolecular interaction can be induced by a change of the solvent dielectric constant.[329]

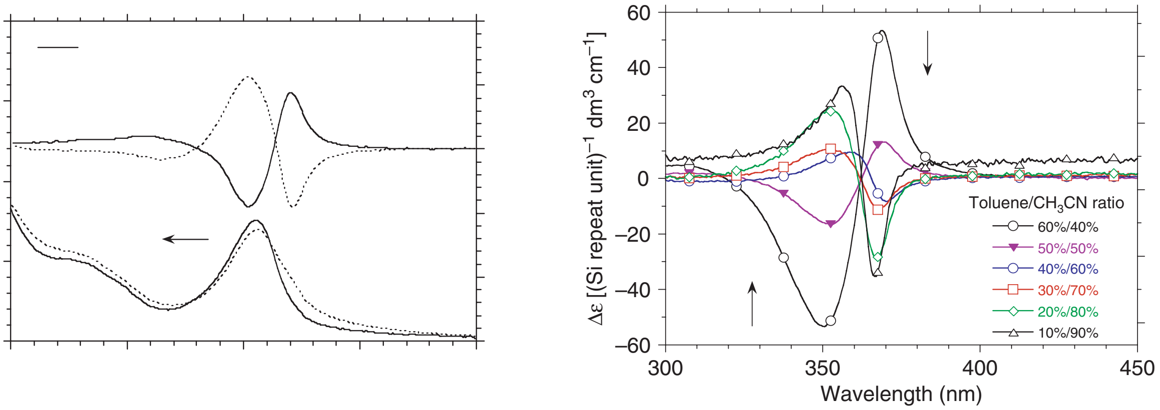


Figure 51 (a) UV–VIS and CD spectra of **124** aggregates prepared by methods I and II at 55%/45% THF/methanol volume ratio at 20 °C; (b) CD spectra of **124** aggregates in toluene/acetonitrile prepared by method I.[321] Reprinted with permission from Nakashima, H.; Fujiki, M.; Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, *123*, 1963–1969, © 2001 American Chemical Society.

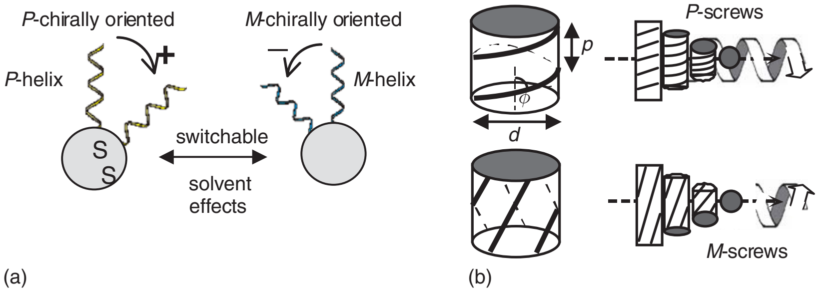
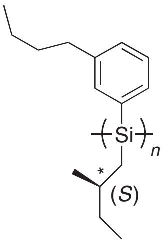


Figure 52 (a) Chiral aggregation cartoon and (b) hard-core model to explain chirality of aggregates.[321] Adapted with permission from Nakashima, H.; Fujiki, M. Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, *123*, 1963–1969, © 2001 American Chemical Society.

The less sterically hindered poly[methyl-(*p*-(*S*)-2-methylbutoxyphenyl)silylene], **125**, exhibited a weak, bisignate, non-switchable CD signal in a mixed toluene/acetonitrile system only, and no CD signals were evident in pure toluene or THF due to masking of the helicity. In contrast, although the even less sterically hindered, less polar poly[methyl-*m*-(*S*)-2-methylbutoxyphenyl)silylene], **126**, did show optical activity in pure THF or toluene (negative Cotton effect at 310 nm), the CD signal disappeared on formation of aggregates in good/poor co-solvent systems. The more coiled nature of **126**, arising from the imbalance of side chains, and also the *meta*-ring substitution position, which may result in less efficient side-chain packing, were considered responsible.

In order to further experimentally probe the hard-core model of polysilane aggregate chirality, a series of poly-[(alkyl)alkylphenylsilylene]s, differing in phenyl ring-substituent position and chain length were synthesized, designed such that the polymer chain diameter, *d*, and helical pitch, *p*, in the hard-core model were varied.[343]

With the same (*S*)-2-methylbutyl side chain in each case, the solution CD was, as expected, almost identical, with positive Cotton effects. However, on addition of MeOH to form aggregates, while **127** showed a negative bisigned Cotton effect, **128** showed a positive bisigned Cotton effect, as shown in Figure 53.



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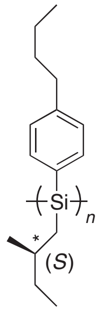

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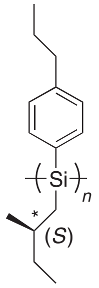

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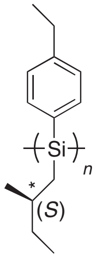

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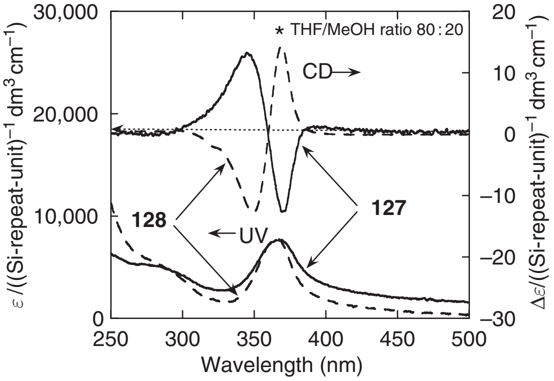


Figure 53 CD and UV spectra of **127** and **128** aggregates in THF/MeOH (80 : 20) (**128** CD intensity scaled down by factor of 10).

This indicated that while the single molecules were of the same PSS helicity, the aggregates were of opposite chirality. This was consistent with the hard-core model, since the *para*-substituted polymer, **128**, should have greater *d*, and the *meta*-substituted polymer should have smaller *d* and also greater *p*, due to the *meta*-phenyl substituent extending less outward and more toward neighboring repeat units. To further test the hypothesis, **129** and **130** were prepared, with shorter *para*-substituents. Again, in agreement with the model, **130** showed negative bisigned CD, due to the decrease in *d*. Polymer **129** showed spectra similar to **128**. These experimental results were also supported by calculations using *p* and *d* values evaluated by computer modeling.

A novel approach to aggregate control was described by Terao *et al.*, who confined optically active polysilanes inside poly(ureaurethane) microcapsules and then induced aggregation at 20 and −78 °C by addition of the polysilane-containing microcapsules to THF or ethanol.[344]

3.11.6.4 Circularly Polarized Photoluminescence (CPPL) from Polysilanes

The emissive counterpart to CD is circularly polarized photoluminescence (CPPL). Where the fluorophore is chiral, then the photo-excited state can return to the ground state with emission of circularly polarized light, the direction of polarization of which depends on the relative intensities of the right-handed and left-handed emissions (I_R and I_L, respectively), which in turn depends on the chirality of the material, or more accurately, the chirality of the photo-excited state of the material. CPPL studies on polysilanes are extremely rare, however, due to the low CPPL intensity and rapid sample degradation in solution, and problems due to artifacts in the solid state.

The first successful observation of CPPL from a polysilane[312,324] employed an enantiopure chiral-substituted poly(diarylsilylene) co-polymer, poly[bis-*p*-*n*-butylphenylsilylene-*co*-bis-*p*-(*S*)-2-methyl butylphenylsilylene], **111** (1 : 1 repeat unit ratio), in order to circumvent the above photodegradation problem, since among the polysilanes, these are the most photorobust. Additionally, the sample was prepared in an aggregated phase, since these are also more durable. The CPPL emission spectrum was measured while irradiating at 385 nm, on the higher-frequency side of the positive extremum at 392 nm. The CPPL λ_{max} occurred at 409 nm, matching the emission peak, and was negative in sign. The luminescence dissymmetric ratio, g_{lum}, was approximately -1.8×10^{-3}, which is similar in magnitude to the g_{abs} value (1.4×10^{-3}) at 390 nm, indicating similar helical characteristics of the polymer in excited and ground states. This observation of CPPL for a polysilane is a promising indicator of the possibility of circularly polarized electroluminescent (CPEL) emission from these polymers.

The solution CPPL spectrum of the polymer was also successfully obtained, using a home-constructed dynamic flow-through cell, so that multiple scans could be obtained to increase the signal/noise ratio. Ten scans were recorded and afforded a very similar, though noisier, CPPL profile to the aggregate case.

3.11.6.5 Cholesteric Liquid Crystallinity of Helical Rod Polysilane

Under certain conditions, stiff rod-like helical polymers can spontaneously form lyotropic or thermotropic cholesteric liquid crystal (TChLC) phases.

The persistence length, *q*, in isooctane of poly(*n*-decyl-(*S*)-2-methylbutylsilylene) (PDMBS), **88**, which adopts an almost 7_3 helical structure, was determined to be 70 nm.[345] This is similar to that of its hexyl homolog, poly(*n*-hexyl-(*S*)-2-methylbutylsilylene) ($q = 85$ nm), and very much greater than that of poly(*n*-hexyl-(*S*)-3-methylpentylsilylene) ($q = 6.2$ nm), confirming conclusions that polysilanes with β-branched alkyl side chains are much stiffer than those with more remote branching or no branching at all (see also Section 3.11.5.2).[241] This polymer was found to exhibit both TChLC[346] and lyotropic liquid crystallinity.[345]

In the temperature range 70–140 °C, a relatively low molecular weight PDMBS fraction ($M_w = 1.11 \times 10^4$, $DP_w = 46$, and $M_w/M_n = 1.19$, average contour length 9 nm, diameter 1.5 nm) formed a thermotropic liquid crystalline phase as shown by the iridescent colors observed due to the reflection of light from many helicoidal periods in randomly aligned textures, and further evidenced by the observation using an optical microscope of a Grandjean monodomain optical image, including partly oily streaks between 70 and 140 °C, which are characteristic of the TChLC phase.[346,347] The variable-temperature CD reflection spectra, shown in Figure 54, were also indicative of a cholesteric Grandjean domain.

The CD reflection spectra are quite sharp at all temperatures, and the reflection wavelength, corresponding to the optical pitch of the TChLC phase, increased progressively with temperature from 500 nm at 70 °C to 1,000 nm at 140 °C. It was considered that the positive sign of the CD reflection band indicated *M* screw sense helicity of the cholesteric phase. Very recently, a smectic A-cholesteric phase transition was also observed for PDMBS.[348]

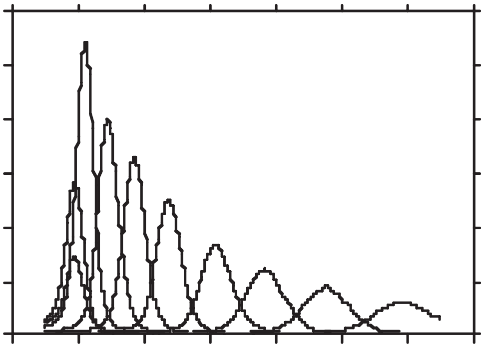


Figure 54 (a) CD reflection bands of PDMBS cholesteric phases at various temperatures (cooling run) and (b) UV and CD absorption spectra at 80 °C.[346] Reprinted with permission from Watanabe, J.; Kamee, H.; Fujiki, M. *Polymer J.* **2001**, *33*, 495–497, © 2001 Society of Polymer Science Japan.

3.11.6.6 Others

In a unique investigation, chiral polysilanes have been used to probe one of the most fundamental issues of the universe.[349] With respect to the origin of chirality, a long-standing issue is whether mirror image molecules are energetically identical. It has been debated whether the very tiny, parity-violating weak neutral current at the atomic level might distinguish between mirror image molecules; several amplification and detection mechanisms have been proposed. Since high polymers are composed of many thousands of repeat units, it was considered that, tiny though the differences between an enantiomeric pair might be, the differences may be cumulative in a PSS polymer and hence detectable using chiroptical techniques in combination with achiral Si NMR and viscometric data. Data were presented which appeared consistent with a difference between right- and left-handed molecules,[349] though other experiments are needed to support the ideas.

3.11.7 Higher Dimensionality Silicon Polymers

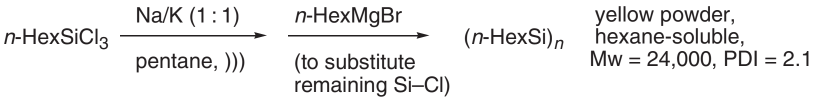
Since this field is relatively new and coverage was brief in COMC II (1995), a summary of the development of the field is given, followed by recent results.

Polymerization of trifunctional monomers such as $RSiCl_3$ leads to polymers such as $(RSi)_n$, termed "polysilynes," with higher dimensionality than the 1-D linear rod polymers $(R_2Si)_n$ discussed above, prepared from difunctional monomers R_2SiCl_2. Co-polymerization of tri- and tetrafunctional monomers with di- and trifunctional monomers also yields higher-dimensional materials. Depending on the synthetic strategy, a broad range of silicon architectures can be generated, including network (irregular/random), ladder, cage, and dendrimer structures. Many among the latter three types form crystals suitable for single crystal X-ray analysis, and provide information valuable in structure–property correlations. As expected, σ-electron delocalization is considerable.

3.11.7.1 Network Polymers: Polysilynes, $(RSi)_n$

The first thorough investigations into silicon–silicon-bonded network polymers were by Bianconi *et al.* around 1988,[350,351] although West and co-workers had reported in 1972 that the reaction of $MeSiCl_3$ with sodium naphthalenide led to an intractable solid,[352] and Baney *et al.* described in 1983 the phosphonium ion-catalyzed disproportionation polymerization of disilane fractions from direct process residues to give a soluble, yellow material considered to comprise a branched chain structure incorporating silicon rings.[133] Similar to the breakthrough in polysilane chemistry, the switch of substituent group from methyl to hexyl or other longer alkyl chains and coupling under Wurtz-type conditions resulted in the generation of the first soluble polysilynes in yields of around 30%, according to the reaction in Scheme 32, using ultrasonic activation and just under the stoichiometric 3 equiv. of a sodium–potassium amalgam. Polysilyne formation has also been investigated theoretically.[353]

DSC and X-ray indicated a lack of crystallinity and structural regularity. ^{29}Si NMR showed a major, broad peak at δ −57 ppm in solution and δ −60 ppm in the solid state (cf. δ −24.8 ppm for poly(dihexylsilylene)),[286] with minor

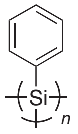


Scheme 32 Synthesis of soluble polysilyne.

resonances between δ −10 and δ −30 ppm, attributable to silicon–dialkyl edge groups, ruling out the unlikely but empirically possible silicon analog of poly(acetylene) with silicon–silicon double bonds (Si═Si resonances commonly occur in the range $\delta + 60$ to $\delta + 90$ ppm).[354,355] Peaks in the ^{13}C NMR spectrum showed increasing broadness on going from the outermost carbon inward toward the silicon main chain. These data were taken to indicate considerable rigidity of the silicon framework and diversity of Si environments. However, based on the good solubility of the materials, it was concluded that the materials were not fully cross-linked into rigid 3-D amorphous architectures, but rather consisted of a rigid network of sp^3-hybridized Si atoms bonded in sheets or open cages of fused rings.[350] Photolysis in the presence of oxygen resulted in a material with an IR absorption at 1,100 cm^{-1} due to the formation of Si–O–Si linkages, but showed little evidence of molecular weight decrease, which was taken to indicate either greater σ-delocalization of the excited state or enforced recombination of radicals. In the UV spectrum, the tailing into the visible and high molar absorptivity, ε, was considered indicative of the extension of σ-electron delocalization into three dimensions. Other investigations of related materials were carried out, but evidence regarding the structures of the polysilynes remained inconclusive.[356]

During the last decade or so, further work has begun to shed light on the morphology and properties of these so-called “network” polysilanes. Matyjaszewski put forward the view that due to their good solubility, the polysilynes could reasonably have dendritic structures,[357] that is, they are hyperbranched but not cross-linked. Such dendritic polymers form upon chain extension from a trifunctional monomer AB$_2$, where A is less reactive than B, can only react with B, and where the first A is sterically protected inside the growing molecule. Despite the fact that the RSiCl$_3$ monomer appears structurally incompatible with the concept, it was reasoned that in accordance with the heterogeneous chain-growth process of the Wurtz-type coupling, the formation of a silyl anion from a growing polymer chain end Si–Cl bond is more facile than that from a monomer Si–Cl bond, due to the delocalization of the charge along the chain which is possible in the former. Also, the monomer Si will be more electrophilic toward the silyl anion than a chain end Si, due to the presence of the three attached Cl atoms. Thus, Si–Cl reactivity is differentiated and monomer adds at a greater rate than cross-linking.[357] Matyjaszewski also prepared branched polysilanes by incorporation of the tetrafunctional monomers Si(SiMe$_2$X)$_4$ (X = Cl, Br) and SiCl$_4$, postulating the presence of cyclic structures and at higher proportions of SiCl$_4$, silicon clusters (easily oxidized), and noting the effects of structural variation on the optoelectronic spectra.[358]

Structural effects on properties were also studied in detail by a group from Tohoku University, who prepared poly(methylphenylsilylene) (PMPS; $M_w = 3{,}120$, $M_w/M_n = 1.76$) and poly(phenylsilyne) (**131**; poly(penfafluorophenylrilyne)(PPS); $M_w = 1{,}090$, $M_w/M_n = 1.30$) by Wurtz-type coupling using sodium and 18-crown-6 in hot toluene and compared their optical and electrical properties.[359,360]



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PPS was discussed in terms of a network structure, and showed a broad UV–VIS absorption band extending to 420 nm, while PMPS with a linear Si skeleton showed by comparison, a relatively sharp σ–σ^* absorption band at 334 nm, as shown in Figure 55(a). The emission spectra were also very different, as is evident in Figure 55(b).

The broad emission and low-fluorescence quantum yield of PPS suggested a distribution of trapping sites in the Si skeleton, which were also considered responsible for the lower-than-expected conductivity. The far-IR spectrum of PPS suggested the existence of cyclohexasilane rings connected by linear chains.[361,362] Subsequent investigations by Irie *et al.* on the electronic absorption spectra of radical ions of poly(alkylsilyne)s were taken to indicate the presence of various cyclic silicon species, in corroboration of this conclusion.[363] The large Stokes shift and broadness of the fluorescence emission indicate a range of fluorophore structures, different from the chromophore structures. This is

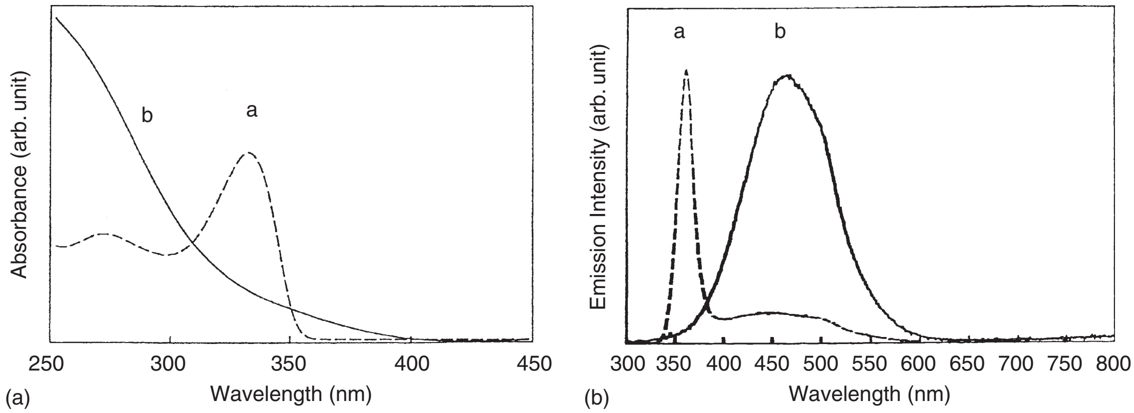


Figure 55 (a) Absorption and (b) emission spectra of PMPS (- - - -) and PPS **131** films.[359] Reprinted with permission from Watanabe, A.; Tsutsumi, Y.; Matsuda, M. *Synth. Met.* **1995**, *74*, 191–196. © 1995 Elsevier.

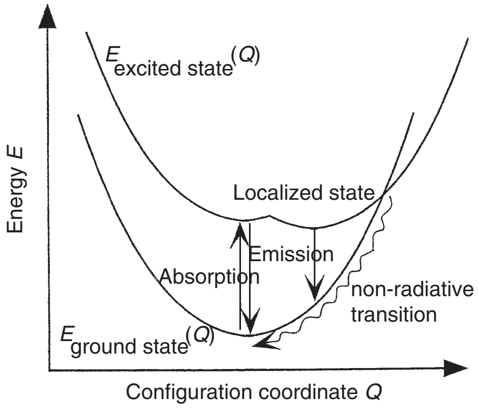


Figure 56 Configuration coordinate model for higher-dimensionality polysilanes.[360] Reprinted with permission from Watanabe, A. *J. Organomet. Chem.* **2003**, *685*, 122–133, © 2003 Elsevier.

consistent with a random arrangement of branching sites and migration of the excited state to a lower energy branching point trap. Time-resolved emission spectroscopy on dendrimers which have a regular branched structure, in contrast to the random branching of the network polysilanes corroborate this nicely.[360,364] At 77 K in 3-methylpentane, the 1G dendrimer (see below for further discussion on dendrimers) $[(SiMe_3)_2SiMeSiMe_2]_3SiMe$ showed dual emission at 350 and 460 nm between 0 and 2 ns after excitation at 279 nm, attributed to linear and branched fluorophores, respectively. As the time delay was increased, the 350 nm absorption decreased, indicating intramolecular energy transfer from the linear to the branched part. A configuration coordinate model was employed in the rationalization of this observation, as depicted in Figure 56, in which distortion of the molecules in the excited state is responsible for localization of the excited state at a different minimum energy point to the absorption, accounting for the large Stokes shift. Semi-empirical MO calculations (PM3) on the ground and excited states[360] of the 0G dendrimer $(SiMe_3SiMe_2)_3SiMe$ suggested a conformational deformation at the central silicon atom, resulting in the close approach of a β-Si atom and increased bond order between these two atoms, affording a pseudo-cyclic trisilane, which was considered to be the emitting state. Calculations on the linear chain did not show such distortion. The structural and spectroscopic similarity of dendrimer and network polysilanes thus indicates the presence of linear Si chains connecting branching Si points.[360]

WAXD, DSC, and vibrational studies on *n*-hexyl-substituted polysilanes with 5%, 33%, or 67% *n*-hexylsilyne branching points showed that the introduction of branching partially reduced the high-crystallinity characteristic of PDHS.[365] It was also found that the charge carrier mobilities decreased with increasing branching points, and

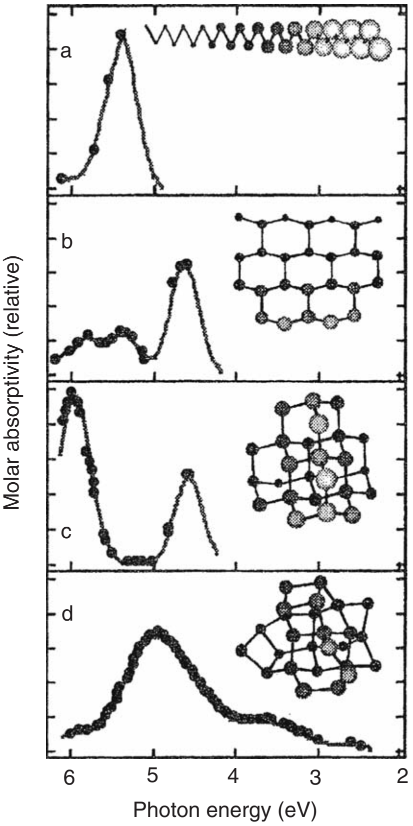


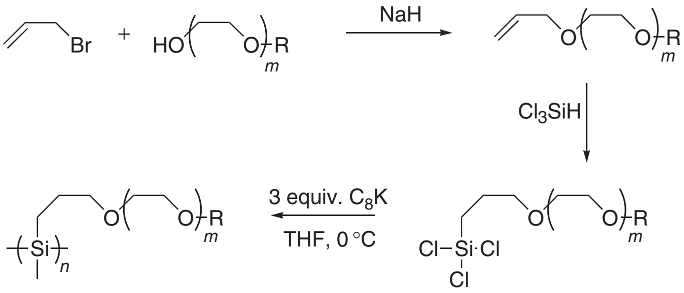
Figure 57 Absorption spectra calculated for architectures with 26 Si atoms.[362] Reprinted with permission from Watanabe, A.; Fujitsuka, M.; Ito, O.; Miwa, T. *Mol. Cryst. Liq. Cryst.* **1998**, *316*, 363–366, © 1998 Gordon and Breach Ltd.

considered that the latter act as scattering points for both charge and exciton carrier migration, consistent with the findings of the Tohoku University group described above.[359]

The experimental observations of red shifts of the UV absorptions tails with increase in silicon dimensionality were corroborated by ZINDO-calculated spectra comparing linear polysilane, network polysilyne, crystalline cluster, and amorphous cluster structures, which showed respectively lowest absorption transition energies of 5.38 eV (230.4 nm), 4.60 eV (269.5 nm), 4.57 eV (271.2 nm), and 2.46 eV (503.9 nm), as shown in Figure 57.[362]

The perfluorophenyl analog of PPS,[366] of interest as a new route into fluorinated inorganic silicon materials, has also been synthesized. Although fluoroalkylated polysilanes have been prepared by Wurtz-type coupling using sodium in hot toluene, the yields were very low due to side-reactions of the sodium with the fluoro substituents.[49] In keeping with their successful electrochemical preparation of polysilynes,[367,368] the group devised a high yield (51.3%) one-pot electrochemical synthesis of poly(pentafluorophenylsilyne) ($M_w = 14{,}240$, $M_w/M_n = 6.69$) from bromopentafluorobenzene and tetrachlorosilane using a magnesium electrode in THF.[367] For comparison purposes, PPS was also synthesized by the same route ($M_w = 2{,}157$, $M_w/M_n = 1.59$). The effect of perfluorination of the phenyl ring is to blue-shift the emission maximum from 455 to 445 nm, though otherwise the polymers were structurally similar. The electrochemical route was also found to afford access to poly(methylsilyne) ($M_w = 3{,}299$, $M_w/M_n = 1.70$), which was inaccessible via the Wurtz route,[352] and co-polymers thereof.[369] Electrochemical polymerization has also been found to give higher molecular weight polysilynes than Wurtz-type polymerization, and using the method, nework polygermanes were also successfully prepared, although at lower molecular weight.[370]

In addition to the disproportionation polymerization of methylchlorodisilanes by Baney *et al.* noted above,[133] the disproportionation route has also been applied to disilanes bearing alkoxy moieties, as the latter also make good leaving groups.[371] Using sodium ethoxide as catalyst, 1,1,2,2-tetraethoxy-1,2-dimethyldisilane was reacted with an alkyl or aryl triethoxysilane, and polymers with molecular weights up to 20,000 were prepared. The ^{29}Si NMR spectra



Scheme 33 Synthesis of oligo(ethoxyethylene)-substituted polysilynes **132**: R = Me, $m = 2$; **133**: R = Me, $m = 3$; **134**: R = Hex, $m = 2$.[373]

showed strong, broad resonances at around δ −60 ppm, which is in the range typical for polysilynes. Synthesis by this route results in the presence of alkoxy functionalities in the polymers.

Other functionalized network polysilanes have also been prepared by Wurtz-type homo- or co-polymerization using *N*,*N*-dialkylamino-functionalized aryltrichlorosilanes, or by the substitution of OMe groups in $[\mathrm{MeSi(OMe)}_x(\mathrm{R})_y]_n$[372] using aryl Grignard reagents, and their conductivity upon doping with iodine investigated.[372a] The undoped p-$\mathrm{R_2NC_6H_4}$ (R = Me, Et)-substituted network polymers exhibited conductivites of 10^{-9}–10^{-7} S cm^{-1}, but on doping, this increased to ca. 10^{-3} S cm^{-1} due to the stabilization of the positive charge carriers by the electron-donating p-$\mathrm{R_2NC_6H_4}$ groups. The conductivities were stable for over 15 h.

Functionalization of network polysilanes with oligo(oxyethylene) groups affords non-ionic water-soluble polysilynes,[373] in analogy to the linear polysilanes investigated by the same group.[205] Similar to the linear polysilane synthesis, polymerization was effected by the Wurtz-type coupling using $\mathrm{C_8K}$ as the reductant (sodium-mediated polymerizations of oligoether-substituted monomers give very low yields; with $\mathrm{C_8K}$, the oligoether goups can intercalate between the layers in $\mathrm{C_8K}$ and the yields are very good, although molecular weights are lower). The synthesis is shown in Scheme 33.

Structures 132 and 133 were water soluble and exhibited lower critical solution temperatures (LCST) of 49 °C, but were not soluble in hexane, while the hexyl-terminated analog was not water soluble but did dissolve in hexane. ^{1}H, ^{13}C, and ^{29}Si (ca. δ −60 ppm) NMR all showed broad resonances for backbone or near-to-backbone atoms, which indicate restricted mobility and are characteristic of polysilynes. DSC analysis showed only glass transitions (T_g values: −80.7 °C for **132**, −79.5 °C for **133**, and −91.3 °C for **134**), indicating that all the polymers are amorphous. The hexyl group has an internal plasticizing effect to lower the T_g of **134**, in addition to its effect on solvent compatibility. The T_g values are similar to those of linear polysilanes with the same substituents[147] suggesting that T_g is more dependent on side-chain than main-chain architecture. The optoelectronic spectra are typical of other polysilynes, with a broad semiconductor-like UV absorption tailing into the visible. The spectra do not appear to show significant solvatochromism, indicating that polymer–solvent interactions do not affect the chromophore or fluorophore conformations. The observation of an LCST for 132 and 133 is particularly significant, since for the analogous polysilanes, the LCST was considered to correspond to a folding/unfolding process.[205] The similarity of the thermoresponsive behavior of the polysilanes and the polysilynes thus suggests that the polysilyne structure should also be similar. This result is difficult to reconcile with either extended sheet-like or hyperbranched/dendritic architectures suggested above, since folding and unfolding of these structures is unlikely.[373] PM3 calculations on Si–Cl reactivity were in agreement with the $\mathrm{AB_2}$ mechanism of Matyjaszewski,[357] that is, that the Si–Cl functionality in oligomers forms radical anions more readily than that in monomers. Further calculations showed that within an oligomer, terminal silyl radical formation is preferential, suggesting that chain extension is more favorable than branching, and the authors suggest an ABC system to be more appropriate than $\mathrm{AB_2}$. The calculations also indicated that in pentasilanes, the formation of cyclic structures (due to end-biting by a terminal silyl radical of a chlorine on the other Si terminus) is favorable, supporting the observations discussed above of other groups that cyclosilanes are constituent moieties in polysilynes.

Concerning polysilyne architecture, it thus appears most likely to be a hybrid semi-linear chain incorporating small branches and cyclics (which may also be branched), as represented in Figure 58.

Such a structure would be more rigid than a polysilane and contain a range of structural elements, accounting for the observed spectroscopic properties, but would still be soluble due to its semi-linear nature.

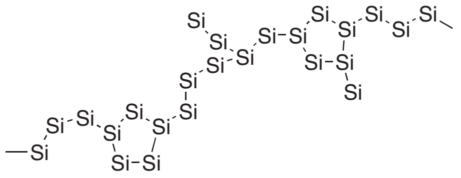


Figure 58 Representation of polysilyne structure incorporating branches and cycles.

3.11.7.2 Dendrimers

Dendrimers are structurally defined branched polymeric molecules and can form good X-ray quality crystals. This is particularly useful in the correlation of structure and properties. Two main synthetic approaches have been used: divergent, which is appropriate for smaller dendrimers, and convergent, which is better for larger dendrimers. Branched polysilanes with a structurally defined branched core were described in 1994, but the growth from the core was not controlled and non-uniform structures were obtained.[357]

The first true, structurally uniform, polysilane dendrimers were reported in 1995 by two groups, with total Si atom counts of 16[374] and 31.[375] Figure 59 shows the single crystal X-ray structure of the 31 Si atom dendrimer, which was prepared according to the divergent synthetic strategy shown in Scheme 34. 1,3-Diphenyl-2-lithiopentamethyltrisilane, **135**, was reacted with $PhMe_2SiCl$ to generate the triply branched dendrimer core with phenyl chain ends, **136**. The phenyl group was removed using trifluoromethanesulfonic acid and reaction with **135** again yielded the first-generation dendrimer, **137**, with 13 Si atoms and a longest chain of seven Si atoms. Similar dephenylation and substitution with 2-lithioheptamethyltrisilane (to facilitate NMR analysis) yielded the second-generation dendrimer, **138**, with 31 Si atoms and a longest chain of 11 Si atoms, which was purified by recycling SEC.

The ^{29}Si NMR spectrum of **138** showed seven signals, the substitution pattern being readily distinguished by chemical shift difference. Starting at the core and moving out along a branch, these occurred at the following chemical shifts: core Si δ −62.3 ppm, next to core $SiMe_2$ δ −26.7 ppm, branching SiMe δ −64.3 ppm, next $SiMe_2$ δ −30.0 ppm, outermost SiMe δ −80.1 ppm, and peripheral diastereotopic $SiMe_3$ at δ −11.3 and δ −11.4 ppm. The shifts of the

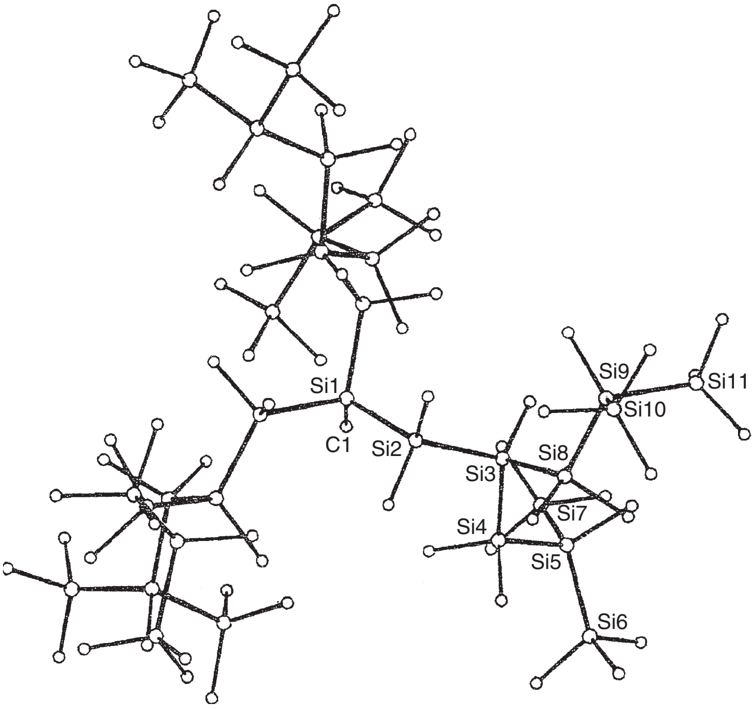
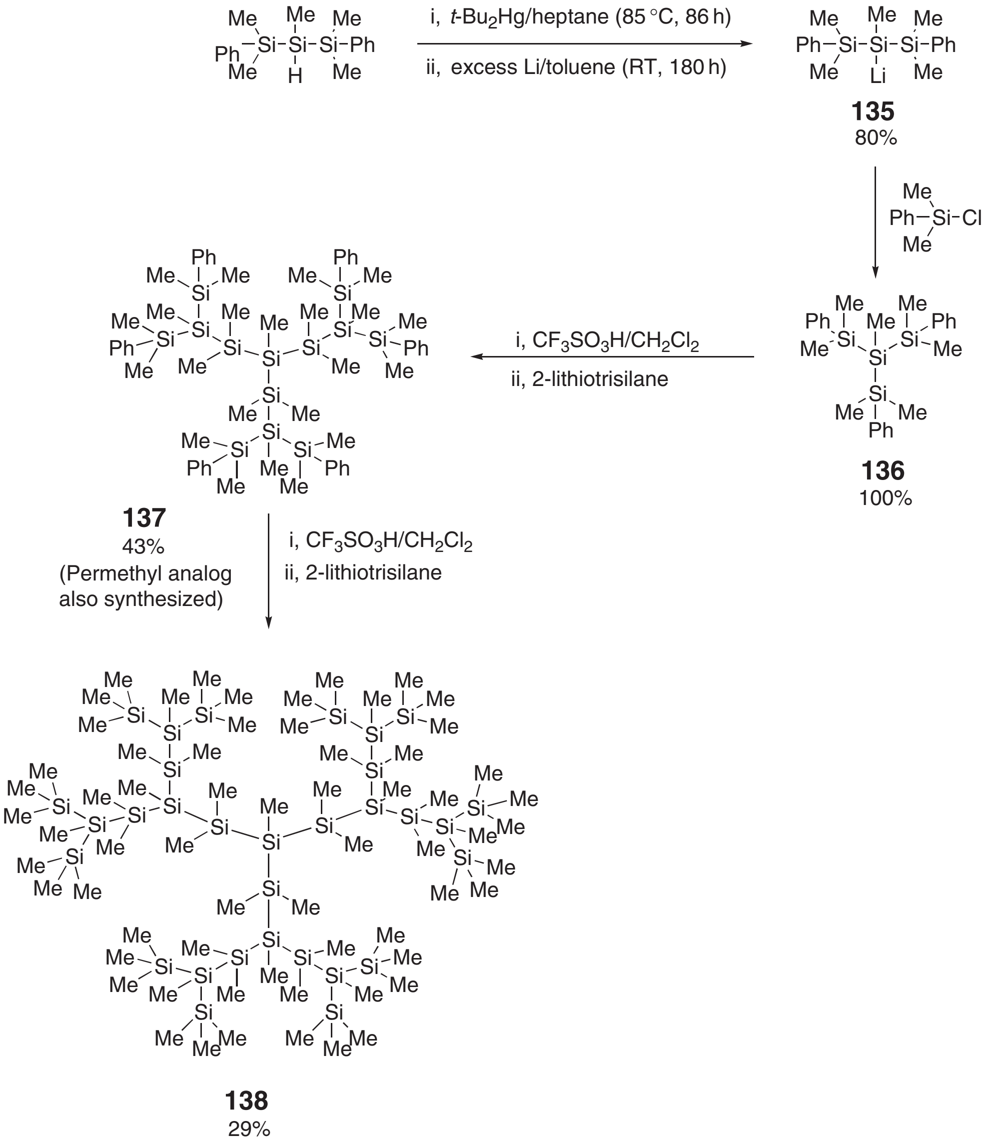


Figure 59 X-ray structure of 31 Si dendrimer.[375] Reprinted with permission from Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, 117, 4195-4196, © 1995 American Chemical Society.



Scheme 34 Divergent route to dendrimer polysilanes.[375]

triply Si–Si-bonding silicons is around δ −63 ppm, which is the same as the shift observed in polysilynes, corroborating the evidence for branching in the latter.[375]

A different group also prepared the permethyl analog of **137**, $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$, and pioneered the use of the double quantum coherence filtering 2-D ^{29}Si–^{29}Si INADEQUATE NMR with beautiful results to demonstrate the connectivity in the molecule and confirm its structure.[376] Figure 60 shows the 1-D and 2-D ^{29}Si NMR spectra. The very much more-than-adequate technique is applicable to monodispersed branched and dendritic polysilanes, but requires high machine sensitivity (600 MHz was used) and rather lengthy accumulation time (4 days). The technique was also applied to an even larger polysilane dendrimer.[377]

Employing a convergent approach a few years later, **139**, a dendrimer with a different structure and longest chain of 13 Si atoms, though same total Si count of 31, was prepared.[378] In the convergent route, long branched chain arms are constructed first (in the current example, by coupling of chlorosilanes with branched lithiosilanes[379]) and then attached to the core in the final step, as indicated in Scheme 35.

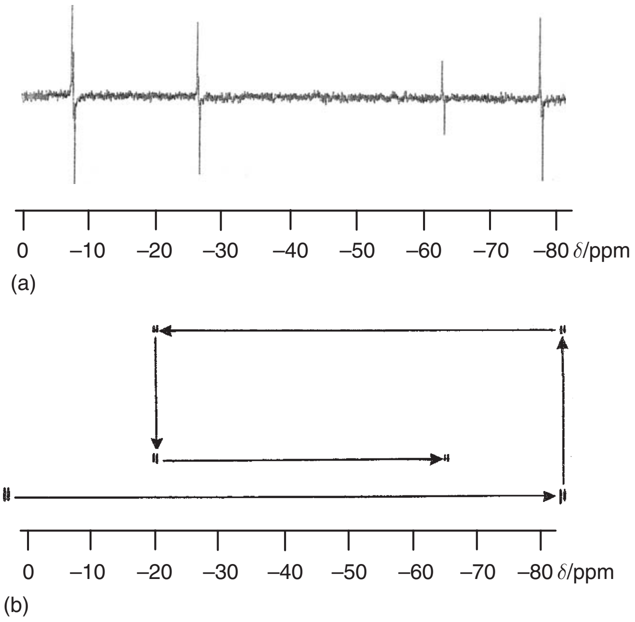


Figure 60 (a) 1-D and (b) 2-D ^{29}Si-^{29}Si INADEQUATE NMR spectra for **137**, $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$.[376] Reprinted with permission from Lambert, J. B.; Basso, E.; Qing, N.; Lim, S. H.; Pflug, J. L. *J. Organomet. Chem.* **1998**, *554*, 113–116, © 1998 Elsevier.

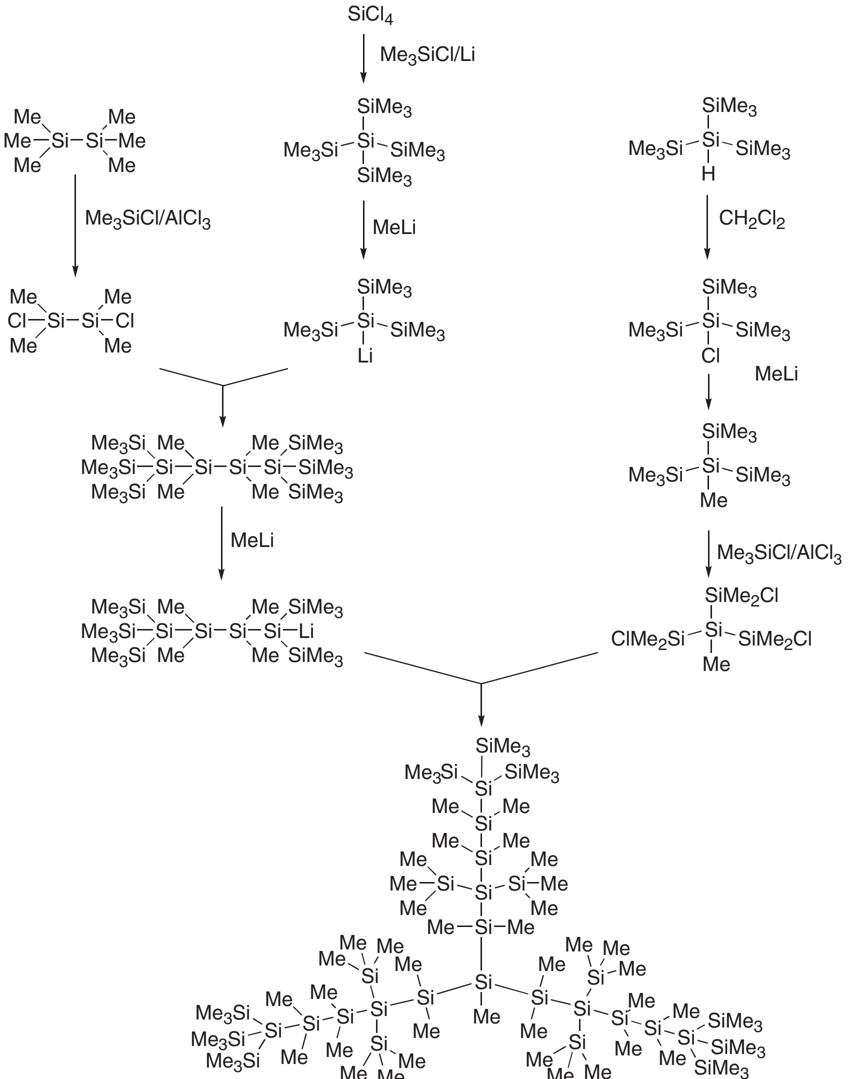
The connectivity in **139** was also successfully analyzed using 2-D ^{29}Si–^{29}Si INADEQUATE NMR spectroscopy.[377]

Despite the apparently close structural similarity between network and dendrimer polysilanes, the UV spectrum of **139** is not at all like the UV spectra of typical polysilynes, much more like that of a linear polysilane, as is clear from Figure 61, with absorption peaks at 260 and 283 nm, although the molar absorptivity, ε, is much greater (1.8×10^5 and 1.16×10^5 Si-unit^{-1} dm^3 cm^{-1}, respectively).[378] These spectral characteristics are due to the structural regularity and lack of cyclic components, and the high ε is due to the multiplicity of electronically delocalized paths between peripheral silicon atoms on different branches. For comparison, a 12-silicon linear polysilane has UV absorption maxima at 264 and 285 nm, and ε of 4.3×10^4 and 4.35×10^4 Si-unit^{-1} dm^3 cm^{-1}, respectively.[380] The structurally related dendrimer with a seven-Si longest chain reported by the group showed a single UV peak at 272 nm ($\varepsilon = 3.4 \times 10^5$ Si-unit^{-1} dm^3 cm^{-1}).[374] Thus, as with linear polysilanes, the UV absorption maximum shifts to longer wavelength with longer chain length.

The dynamics of polysilane dendrimer excited states were also studied by Watanabe as mentioned above in a comparison with polysilynes,[360,364] and suggested that a configuration coordinate model is applicable to the photophysics of branched silicon chains. Calculations showed a distorted geometry of the excited state localized at a branching point.

Single crystal X-ray analysis of **139** revealed an approximately spherical nanoscale molecule, shaped like a fish bowl, as shown in Figure 62.[378] Bond lengths and angles are normal, though there was considerable variation in the silicon chain dihedral angles; in the new terminology,[10] these are *transoid*, *ortho*, and *gauche*.

Despite the numerous strongly helical turns, the UV absorption maximum is close to that for the linear dodecasilane. The reasons for this were not clear, and possibilities included that the dodecasilane is not predominantly *all-anti*, or that σ-conjugation is not a maximum for completely *all-anti* conformations. These possibilities do not seem likely, as studies on oligomers show highly extended conformations, and theory indicates maximum σ-conjugation for *all-anti* conformations. A further possibility which should be considered is that the structure in solution is in fact quite different from that in the solid state. Whereas in the solid state, intra- and intermolecular interactions may promote the approximately spherical shape, in solution, solvation could result in the dendrimer arms adopting much more extended conformations, and hence a longer UV λ_{max} (assuming that the UV was recorded in solution—the report does not explicitly state the measurement conditions, although since values are quoted for the molar absorptivity, ε, it seems very probable). Further discussion on the structures of these and other dendrimers is given in a recent survey by Lambert.[381]



139

Scheme 35 Convergent route to polysilane dendrimer **139**.[378]

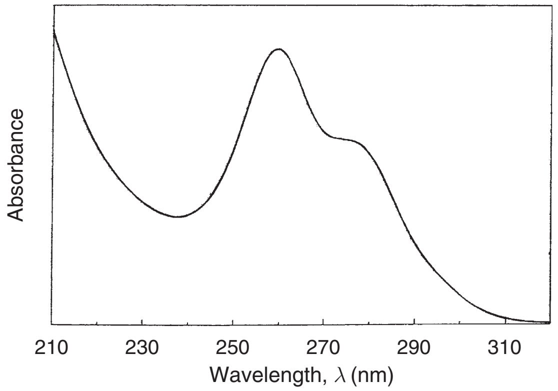


Figure 61 UV spectrum of 31-Si polysilane dendrimer **139** with 13-Si longest chain.[378] Reprinted with permission from Lambert, J. B.; Wu, H. *Organometallics* **1998**, *17*, 4904–4909, © 1998 American Chemical Society.

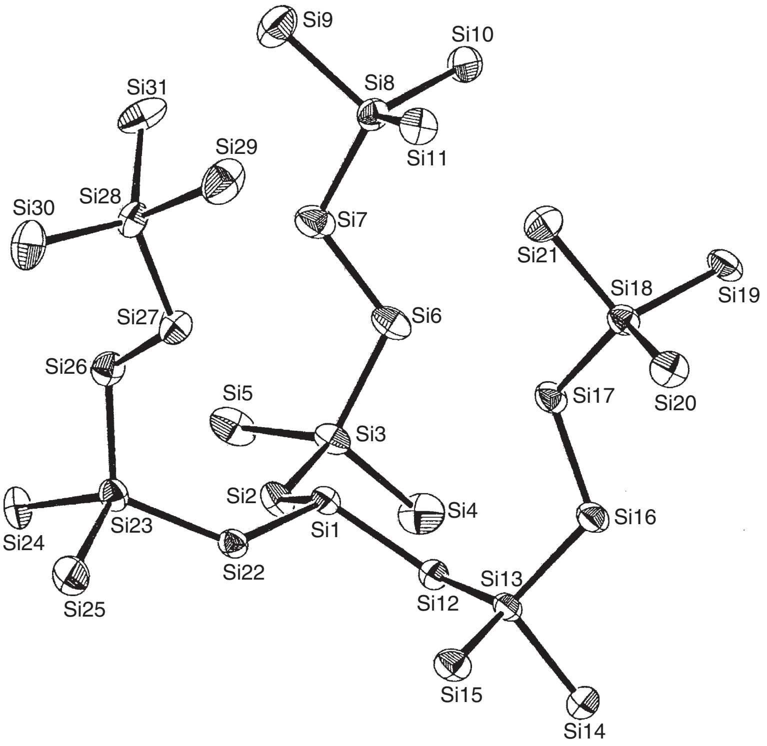


Figure 62 X-ray structure of polysilane dendrimer **139** showing fish bowl shape.[378] Reprinted with permission from Lambert, J. B.; Wu, H. *Organometallics* **1998**, *17*, 4904–4909, © 1998 American Chemical Society.

Among the polysilanes, as described in Section 3.11.6.1, chirality usually refers to a preferential helical screw sense of the linear silicon backbone, induced by substitution with enantiopure chiral side or end groups or other chiral field, that is, the chirality is a higher-order supramolecular phenomenon. In one case, the stereochemistry of the silicon atoms in an oligomer was controlled to afford asymmetric silicon atoms, as noted in the section on oligosilanes above.[16] However, little work has been carried out on chirality in polysilane dendrimers. Similar to the above oligomer example, Kawakami and co-workers reported the synthesis of an optically active polysilane dendrimer.[382] Substitution of the chlorines in the first-generation dendrimer $(ClMe_2Si)_3SiMe$ with the optically active (*R*,*R*)-bis[methyl(1-naphthyl)]phenylsilyllithium afforded a dendrimer with an optically active periphery.

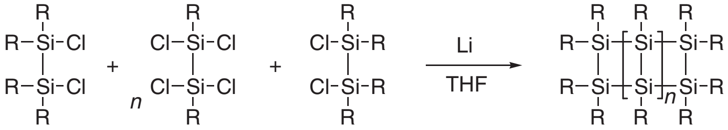
3.11.7.3 Ladders and Cages

Cyclopolysilanes have been known since the early days of organosilicon chemistry. Four-, five-, and six-membered rings are often stable, in particular the cyclopentasilanes, which are the thermodynamic products of the alkali metal-mediated Wurtz-type coupling of dichlorosilanes,[292] while the ring-strain energy in the smallest cycles renders them much more reactive. The cyclopolysilanes exhibit fascinating chemical and photophysical properties too diverse to include here; they are covered elsewhere in this encyclopedia. In this section, multiply fused silicon ring systems are covered: the ladder and cage polysilanes.

3.11.7.3.1 Ladder polysilanes

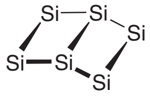
Ladder polysilanes constitute a special case of fused polycyclic silicon macromolecules, in which cyclotetrasilane rings systematically catenate to form a silicon double helix, comprising two multi-linked silicon chains. Work in this area was initiated in this area by Matsumoto in 1987, and now comprises an integral part of the literature on higher-dimensionality polysilanes.

The ladder polysilanes can be prepared by a general route by co-condensation of $Cl(i\text{-}Pr)_2SiSi(i\text{-}Pr)_2Cl$ and $Cl_2(i\text{-}Pr)SiSi(i\text{-}Pr)Cl_2$ with lithium, as shown in Scheme 36.[383]

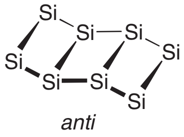


Scheme 36 General synthesis of ladder polysilanes (substituents *i*-Pr).

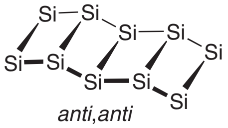
This Wurtz-type coupling affords a mixture of air stable crystallizable products with two, three, four, and five fused rings (**140**, **141**-*a*, **141**-*s*, **142**-*a*,*a*, **142**-*a*,*s*, and **143** respectively; substituents *i*-Pr), separable by recycling HPLC.



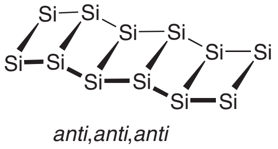
140



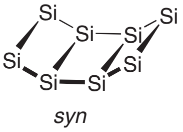
141-*a*



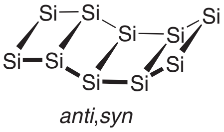
142-*a*,*a*



143



141-*s*



142-*a*,*s*

Selective routes to specific structures have also been developed.[308] Complex **140** was also synthesized quantitatively by the intramolecular sodium-mediated transannular coupling of *cis*- or *trans*-1,4-dichlorocyclohexasilanes.[384] However, when R = Me, only intermolecular coupling was observed.[385] An analog of **141** with *i*-Pr groups on the terminal silicons and *t*-Bu groups on the central silicons was synthesized in 40% yield by coupling of *all-trans*-$(\mathrm{Bu}^t\mathrm{ClSi})_4$ with 2 equiv. of $\mathrm{Cl}(i\text{-Pr})_2\mathrm{SiSi}(i\text{-Pr})_2\mathrm{Cl}$; no *syn*-isomer was formed, indicating that inversion of configuration at silcon occurred during the reaction. Very recently, ladder polysilanes with six, seven, and eight ring chains have been described.[386]

The structural constraints imposed by the fused cyclic structure of the catenates and the ability to cleanly separate product mixtures greatly facilitates crystallization, and single crystal X-ray structures have been obtained for a number of ladder polysilanes.[308] For the *all-anti* molecules, the non-planarity of the Si_4 rings induces a unidirectional helical twist to the ladder structure, as is evident in Figure 63.

The twist angles between the terminal rungs of **141**, **142** and **143** are 44.0, 63.0, and 80.3°, respectively. The double helix structures crystallize with equal amounts of left- and right-handed screw sense forms, as expected in the absence of any chiral field. Some ladder polysilanes crystallize with both helical forms in the same centrosymmetric unit cell; for others, the two forms can crystallize separately. It will be interesting to carry out the crystallization in a chiral field.

The optoelectronic properties of the compounds have also been investigated.[386–388] The lowest energy UV absorption maximum of the *all-anti* forms shifted bathochromically with increasing number of rings in the chain, indicating increased electronic delocalization, as for the linear polysilanes. Expressed as "number of rings"/λ_{max} (nm), the values were: two/310, three/345, four/380, five/414, six/440, seven/464, and eight/483 nm. Interestingly, the absorptions of forms incorporating *syn*-junctions extend to longer wavelength than their *all-anti* isomers. The reason was considered to be due to the greater strain in the *syn*-ladders, resulting in destabilization of the HOMO.

Oxidation using *m*-CPBA proceeds with insertion of an oxygen atom into the Si–Si bonds in a domino-like fashion, firstly down side, then down the other and in the bridging bonds.[389,390] This sequential insertion arises due to the strain resulting in a ring by insertion of oxygen into the ring adjacent to it. The degree of *O*-insertion can be controlled by controlling the reaction conditions, and interesting polysilane/polysiloxane hybrids can be formed, as indicated in Scheme 37. The crystal structure of the product of three-oxygen insertion into **141** is shown in Figure 64. Eventually, insertion of oxygen into every Si–Si bond occurs, affording the corresponding ladder polysiloxanes.

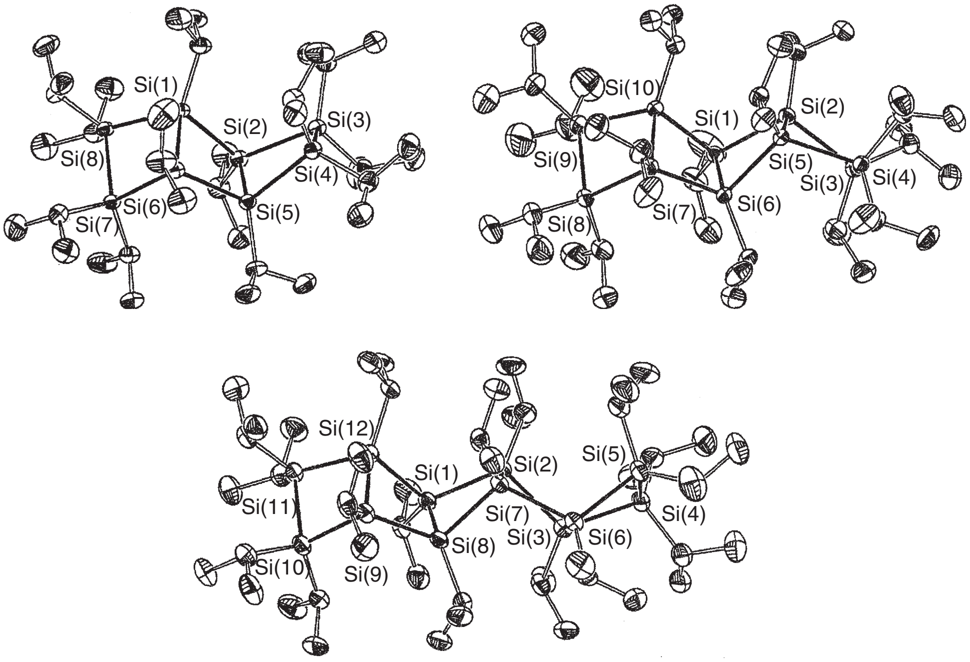
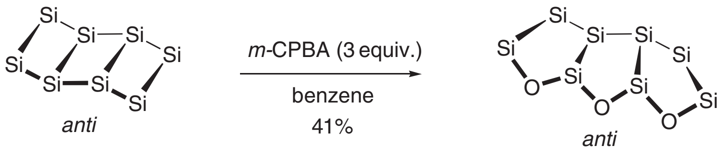


Figure 63 Single crystal X-ray structures of *all-anti* ladder polysilanes **141**, **142**, and **143**.[308] Reprinted with permission from Kyushin, S.; Matsumoto, H. *Adv. Organomet. Chem.* **2003**, *49*, 133–166, © 2003 Elsevier.



Scheme 37 *m*-CPBA oxidation of ladder polysilanes to hybrid silane/siloxane polymers (substituents *i*-Pr).

The optoelectronic properties of the oxygen-inserted materials have also been measured.[308] Compared to the parent ladder polysilanes, the absorption bands are blue shifted, as would be expected on insertion of a conjugation-inhibiting moiety.

With electrophiles such as aqueous HCl, HBr, PCl_5, and $[PdCl_2(PhCN)_2]$, ring opening of the bicyclic ladder occurs to cleave the bridgehead Si–Si bond (no reaction occured with HF), affording halo-substituted cyclohexasilanes. Under similar conditions, the tricyclic ladder cleaved only one bridgehead Si–Si bond to afford fused two-ring systems, the products, including fused hexasilane and tetrasilane rings, or two pentasilane rings, depending on the nature of the electrophile.[391]

The ladder polysilanes also show interesting photochemistry: on irradiation with a high-pressure mercury lamp, the tricyclic ladder extruded the transient intermediate four-membered cyclic disilene which could be trapped using methanol, 1,3-butadiene, and anthracene, as shown in Scheme 38.

3.11.7.3.2 Cage polysilanes

A number of cage polysilanes with silicon architectures in the shapes of a cube, trigonal prism, and tetrahedron have also been prepared and crystallographically analyzed. These were synthesized prior to the years covered in this chapter, but as they were not mentioned in the previous organopolysilane chapter, their structures will be briefly noted here.

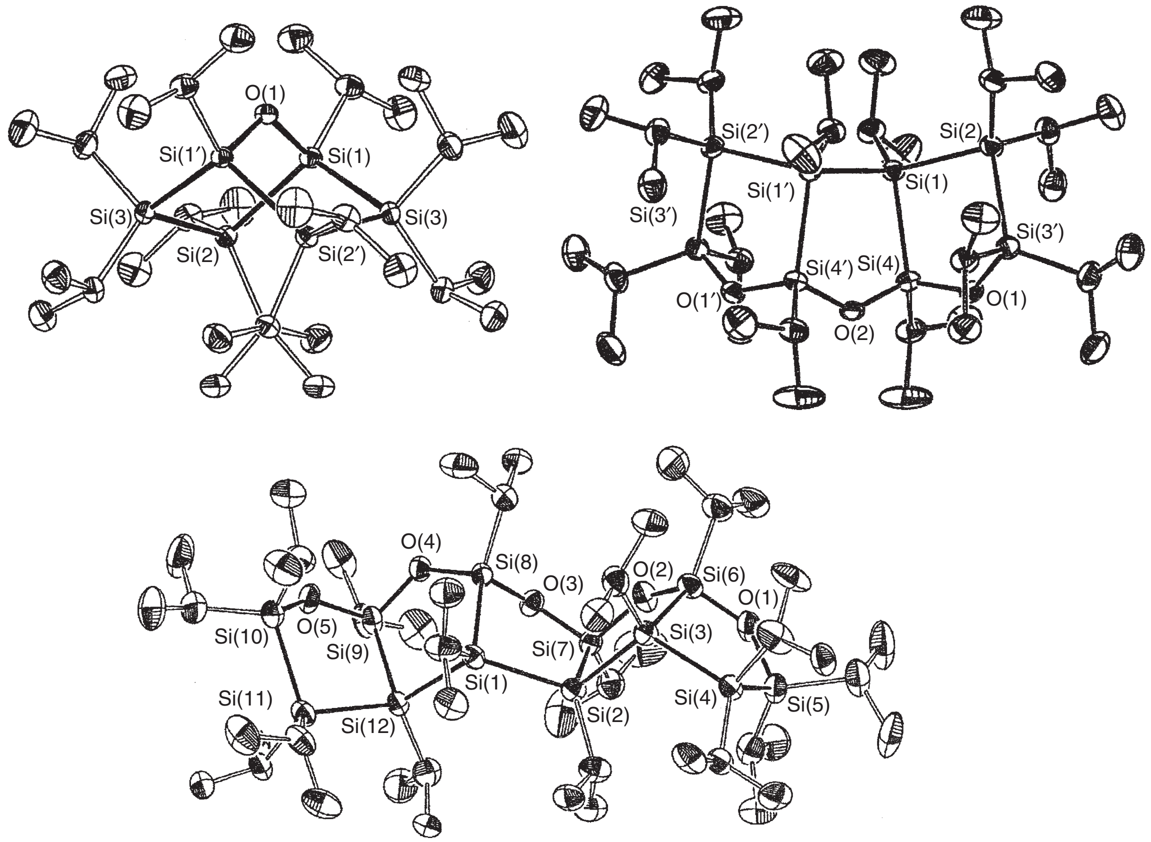
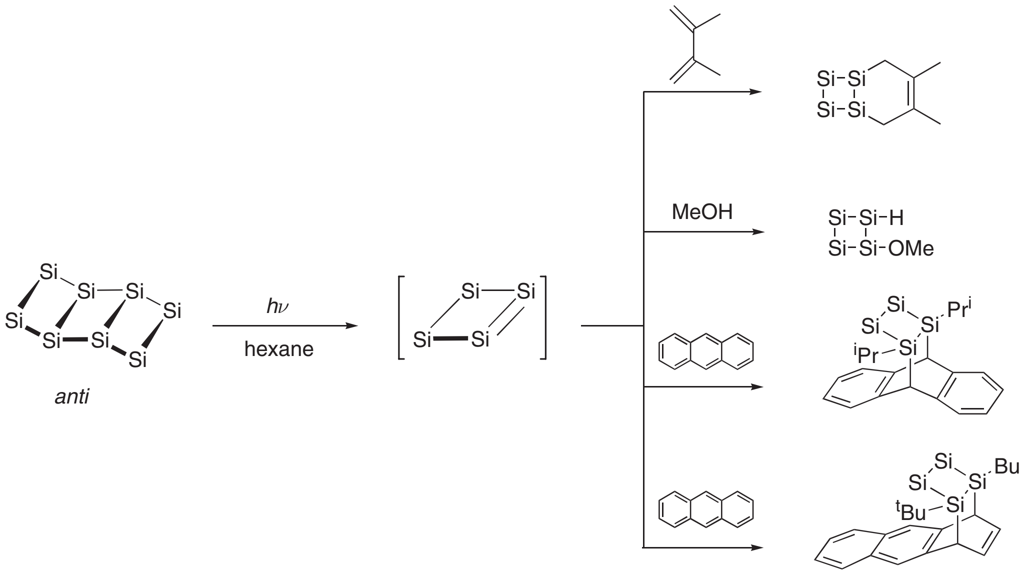
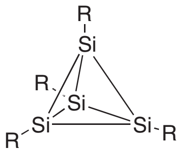


Figure 64 X-ray structure of hybrid silane/siloxane ladder.[308] Reprinted with permission from Kyushin, S.; Matsumoto, H. *Adv. Organomet. Chem.* **2003**, *49*, 133–166, © 2003 Elsevier.

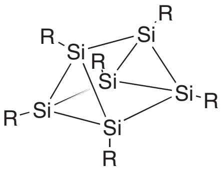


Scheme 38 Photolysis of ladder polysilane and trapping products of extruded cyclic disilene (substituents *i*-Pr, except as noted).[308]

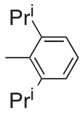
In each of the structures, each core silicon atom is attached to three other core silicon atoms, affording the 3-D 149 cages.[392–397]

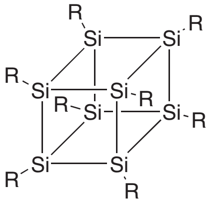


144:[392] R = $\mathrm{SiBu^t_3}$



145:[393] R =



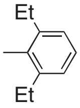


146:[394] R = Bu

147:[395] R = $\mathrm{SiMe_2Bu^t}$

148:[396] R = $\mathrm{CMe_2CMe_2H}$

149:[397] R =



3.11.8 Future Perspectives

The organopolysilanes constitute a maturing and broadening field at the crossroads of many research avenues: organic and inorganic, molecular and macromolecular, experimental and theoretical, synthetic and analytical, chemical and physical, and advances in research will occur in each of these branches. The relationship between structure and properties is extremely complex and work remains to be done in this area in terms of understanding the σ-electron delocalization and conformation in both ground and excited states. Inroads are now being made into conformational control, which, at a supramolecular level, should lead to organopolysilanes with novel properties. Further application-oriented research to exploit the unique σ-electron delocalization, which is responsible for so many of their most interesting properties, provides a challenge worthy of the best chemical ingenuity and creativity.

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3.12
Silicones

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3.12.1 Introduction

Considering the growing popularity of silicones as materials in everyday life, it is clearly challenging to review the recent literature in a meaningful chapter. The unusual properties of this class of polymers continue to reveal new secrets and new potentials, and this adds to the growing interest in studies of fundamentals of silicones: the mechanisms of the reactions of their synthesis, and their uses in model studies of ideal networks. As a result, in the last couple of decades, many hundreds of reviews of various aspects of this class of polymers have been published. In the last decade alone, several major symposia have been dedicated to silicone chemistry, technology, and applications, including American Chemical Society meetings, International Symposia on Organosilicon Chemistry, and a series of regional workshops. It is always easy to miss some pertinent sources of information because it is not easy to define what silicones are. If one sticks to the rules of the official nomenclature, then silicones would be "polymeric or oligomeric 'siloxanes,' usually considered unbranched, of general formula $[–OSiR_2–]_n$." Such a definition would make the subject fairly narrow to cover. For the sake of this chapter, a liberal definition of silicones as "polyorganosiloxanes" has been adopted. Thus, where appropriate, polymers which have repeating siloxane bonds in macromolecules, and the monomers from which they are made, have been included. Intended as an update of the field for the last decade, this chapter on silicones could either deal in a systematic manner with a few aspects of silicones, or provide an overview of the field, emphasizing the interrelations between various areas, and embracing emerging ones. The latter option was chosen with the hope that it would help to provide a coherent view of this extremely broad field, without falling into the trap of being superficial. However, in an era of remarkably efficient literature-search engines, it is believed that what is really required is a source of background information with pertinent references, so that an interested reader can acquire up-to-date information on any relevant chemical subject. Wherever possible in this chapter, references will be given to recent comprehensive treatises on the subject and to specialized reviews. This information is complemented by numerous examples of representative original papers. With a few exceptions where no open literature references could be identified, this review does not cover patent literature, because within its broad scope, the task would simply be impossible.

The outline of this chapter to some extent follows the outlines of chapters on silicones in COMC(1982) and COMC(1995)[1,2] in discussing precursors, polymers, their properties, and applications. The emphasis, however, is put on new materials (e.g., new macromolecular architectures, nanocomposites, inorganic/organic hybrids, liquid crystals) and applications (e.g., biomaterials). A quick perusal of the outline shows that between the direct process (DP) of synthesis of chlorosilanes on the one hand, and biomaterials and the materials built of silsesquioxanes or dendrimers on the other, there is a huge field of organosilicon chemistry, which deals systematically with the synthetic and mechanistic studies of small molecules, macromolecules, and their assemblies. The mechanistic studies of the component reactions, including sol–gel processes, are not only important in increasing an understanding of the reactions themselves, but they are critical in maintaining new developments of more ideal (model) silicone macromolecules and their assemblies. Material science researchers participating in this endeavor should be mindful of the limitations of chemistry when drawing their dream structures of the "tailor-made" super-molecules. On the other hand, by following the mechanistic studies of novel polymerization reactions, they obtain a constant supply of new tools for the synthesis of those elaborate architectures. The role of a few major research groups involved in both the mechanistic studies of Si–O–Si bond formation and cleavage, and in the exploration of novel materials, cannot be overestimated.

3.12.2 Monomers and Precursors to Silicones

All silicones are composed of, or contain some, or all, of the four basic units:

M (monofunctional) $\equiv R_3Si(O)_{1/2}$
D (difunctional) $\equiv R_2Si(O_2)_{1/2}$
T (trifunctional) $\equiv RSi(O_3)_{1/2}$
Q (tetrafunctional) $\equiv Si(O_4)_{1/2}$

For the most common siloxanes, polydimethylsiloxanes (PDMS), R = Me. Thus, most common cyclic siloxanes would be referred to as D_n, for example, D_3, D_4, D_5, ...; linear oligomers are often called MD_nM, for example, MM, MDM, MD_2M, ...; and, T and Q units constitute parts of many highly branched oligomers and polymers, or cross-linked networks.

3.12.2.1 Functional Silanes

This is where all polyorganosiloxanes (silicones) start. The methods of the preparation of silicone monomers and their precursors have not changed significantly since the beginning of silicone technology. Functional silanes are synthesized by one of the following methods:[3]

(i) by the reaction of organic compounds with silicon at elevated temperatures;
(ii) through chlorination of silicon and subsequent substitution of some chlorine atoms by organic groups with organometallic reagents, such as organolithium compounds, Grignard reagents, organic zinc compounds, and other similar compounds; and
(iii) by the transformation of silicon into silyl hydrides and the subsequent addition to multiple bonds in hydrosilylation processes.

The example of the first category is the formation of alkyl- and arylchlorosilanes in the so-called direct process (DP). The process was discovered over 60 years ago by Rochow in the United States, and, independently, by Müller in Germany, and it is still the most important reaction in organosilicon chemistry. In fact, it is at the very basis of the silicone industry, being the primary source of organochlorosilane precursors (mostly methylchlorosilanes, comprising over 90% of the total) in the production of silicone oligomers and polymers.

The direct process, described in detail in numerous books, chapters, and research papers,[1,4–7] involves high temperature carbo–electroreduction of silica (sand) to chemical grade silicon, which, in the presence of catalysts, is reacted in a fluidized bed reactor with methyl chloride to form a mixture of dimethyldichloro- (the most desirable component), methyltrichloro-, and trimethylchlorosilanes. Methyldichloro- and dimethylchlorosilanes are also formed in addition to a few percent of a "residue," which is primarily composed of disilanes. Recent advances in DP have been reviewed by Lewis with an emphasis on the effect of promoters (trace impurities) on the process (in fact, he attributes a key role to the promoters in the so-called "quasi-revolution" in the area of DP), and on the effect of the morphology of silicon, catalyst, and a promoter on the selectivity and yield of the synthesis of methylchlorosilanes. He emphasizes the role of the mechanistic studies aimed at understanding the fundamental chemical and physical parameters in the DP. In his review, he covers the use of substrates other than MeCl (ethyl chloride, vinyl chloride, chlorobenzene, allyl chloride). Recent literature regarding reactions of silicon with alcohols leading to trimethoxy- and tetramethoxysilanes is also discussed. These efforts are in the spirit of Rochow's challenge: a non-halogen based direct process. For Lewis himself, an even greater challenge is a direct process based on SiO_2.[8] Apparently, with his own challenge in mind, Lewis has reviewed the essentials of the DP in another recent paper, entitled *From Sand to Silicones*.[9]

Efforts continue to improve the overall yields of the desired products of the DP through an understanding of the mechanisms of component reactions. Direct synthesis of organochlorosilanes by the reaction of elemental silicon with hydrogen chloride and alkene/alkyne leading to high yields of $EtHSiCl_2$ (47% selectivity), and $CH_2{=}CHSiHCl_2$ and $EtHSiCl_2$ with 39% and 23% selectivity, respectively, have been reported.[10] The intermediacy of surface silylene formation in the direct synthesis of methylchlorosilanes has been demonstrated.[11]

The chemistry of organofunctional halogenosilanes has been discussed in a systematic manner by Herzog in a chapter dealing with organosilicon halides, along with perhalogenosilanes and halogenohydrogen silanes. Physical data for the most important chlorosilanes is given.[12] Halosilanes undergo substitution reactions with alkali metal organics, Grignard reagents, and alkylaluminums.[7]

The chemistry of silicone halides was recently reviewed by Collins.[13] The primary use for $SiCl_4$ is in the manufacturing of fumed silica, but it is also used in the manufacture of polycrystalline silicon for the semiconductor industry. It is also commonly used in the synthesis of silicate esters. Trichlorosilane (another important product of the reaction of silicon or silicon alloys with chlorine) is primarily used in the manufacture of semiconductor-grade silicon, and in the synthesis of organotrichlorosilane by the hydrosilylation reactions. The silicon halohydrides are particularly useful intermediate chemicals because of their ability to add to alkenes, allowing the production of a broad range of alkyl- and functional alkyltrihalosilanes. These alkylsilanes have important commercial value as monomers, and are also used in the production of silicon fluids and resins. On the other hand, trichlorosilane is a basic precursor to the synthesis of functional silsesquioxanes and other highly branched siloxane structures.

The properties and applications of five commercially important groups of silanes: those containing Si–H (hydride functional silanes), Si–X (halosilanes), Si–C (organosilanes), Si–OSi (siloxanes), and Si–OR (silicon esters) are thoroughly discussed by Arkles.[14] As the role of functional siloxanes grows, so does the importance of the hydrosilylation reactions in this field. A broad introduction to hydrosilylation processes as applied to the synthesis of silicone precursors and to the functionalization of siloxanes is provided in the earlier editions of COMC,[1,2] and, therefore, there is no need to duplicate this background information here. Recent advances in hydrosilylation reactions have been described by Ojima *et al.*,[15] with numerous references to the earlier monograph by Marciniec.[15a] In a broad review, they cover the hydrosilylation of alkenes, alkynes, and also ketones, with the use of different catalytic systems. The mechanistic aspects of the reactions, critical to the synthesis of functional silanes (e.g., the use of Pt(0) complexes with different vinylsiloxane ligands as catalysts), continue to draw attention.[16] Other important groups of silanes include alkoxy- and aryloxysilanes.[1] In a recent chapter, Arkles discusses silicon esters, that is, silicon compounds that contain an oxygen bridge from silicon to an organic group (Si–OR).[17] The chemistry and properties of alkoxysilanes and of the related group of acyloxysilanes, and the technological aspects of their production, are reviewed. Key applications, which include, among others, the use of this class of materials as cross-linking agents in the condensation-curable systems, in manufacture of resins, and in sol–gel processes, are described. The methods of synthesis of alkoxysilanes and acyloxysilanes are also discussed in a recent chapter by Butts *et al.*[5] The most common method of synthesis of alkoxysilanes is the alcoholysis of Si–Cl bond, but, alternatively, alkyl orthoformates can be reacted with halosilanes to form alkoxy-substituted silanes.[18] The synthesis of alkoxysilanes from hydrosilanes under mild conditions, and exchange reactions between different alkoxysilanes, have also been described with recent literature citations.

3.12.2.2 Cyclic Siloxanes

The most common cyclic siloxanes, which are used in ring-opening polymerization are D_4 (octamethylcyclotetrasiloxane) and D_5 (decamethylcyclopentasiloxane). D_3 (hexamethylcyclotrisiloxane), which belongs to the same family is less common, but it is still very important for kinetically controlled polymerization. The properties of cyclic polydimethylsiloxanes, including large ring structures, have recently been reviewed.[19] The primary method of formation of cyclic siloxanes is the hydrolysis of dimethyldichlorosilane. Depending on the process conditions, various mixtures of the low molecular weight linear silanol-terminated oligomers and cyclic siloxanes can be obtained. Among the latter, D_4 and D_5 are the major components of mixtures; they may be subsequently separated by distillation, or may be used as monomers in the ring-opening polymerization. The process itself and the properties of the resulting materials have been described in numerous sources. Some of the newer references include the above-cited chapters in major encyclopedias.[2,5] It is worth commenting on the continuing research on silicones in Russia (and the former Soviet Union), which is not always appreciated because of the language barriers—many papers were published only in Russian.[20] Interest in cyclic siloxanes extends to macrocyclics, primarily driven by a need for models to compare linear polymers with their cyclic counterparts.[19] A new method of purification of macrocylic siloxanes, formed by the ring closure of silanol-terminated linear polymers (MW 2,470 g mol^{-1}), has been described.[21]

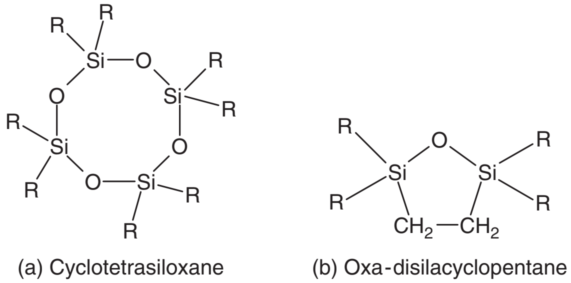
The modification of the process of hydrolysis of dimethylchlorosilane, which has recently received more attention, involves methanolysis of dimethyldichlorosilane, and proceeds according to the following scheme:[22]

$$\mathrm{Me_2SiCl_2 + MeOH \rightarrow H[O\text{-}SiMe_2]}_n\mathrm{OH + [Me_2SiO]}_n\mathrm{ + MeCl + H_2O}$$

The possibility of recycling chloromethane to the DP makes methanolysis an attractive process, as, at least formally, dimethylsiloxanes may be considered as being made of silicon and methanol, with water being the only byproduct. There must be, though, some inherent limitations of this method, considering that the hydrolysis, and not methanolysis, is still a primary industrial method of synthesis of polydimethylsiloxanes.

In a recent review of the polymerization of cyclic siloxanes, Chojnowski and Cypryk[23] use a broadened definition of cyclic siloxanes, which includes many different types of species besides the most common dimethyl-, methylphenyl-, diphenyl-, hydrogen-, or fluoroalkyl-substituted pure silacetal structures. In their discussion, they include many other cyclic compounds containing the SiOSi group which are able to participate in the polymerization or co-polymerization reactions with the cleavage and reformation of the siloxane bond, pointing to the multi-cyclic siloxanes (spirosiloxanes, silsesquioxanes), cyclic monomers containing heteroatoms, and to a large group of cyclic silaethers, for example, oxa-disilacyclopentane (Scheme 1, (b)). The ring-opening polymerization of the latter was recently reviewed along with the polymerization of other oligosilanes interrupted by heteroatoms.[24] This all-embracing classification is also adopted in this review, as it allows one to equate silicones with polymeric materials comprising siloxane bonds, that is, polyorganosiloxanes.

The discussion continues regarding the role of "silanone" and cyclodisiloxanes as reactive intermediates in the formation of Si–O–Si bond.[25] In studies of the reaction of dimethyldichlorosilane, phenylmethyldichlorosilane, or diphenyldichlorosilane with dimethyl sulfoxide in the presence of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, Weber and co-workers obtained products of the insertion of diorganosiloxy unit into the cyclic siloxane, accompanied



Scheme 1 For R = Me: (a) D_4, (b) 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane.

by the formation of cyclic siloxanes composed of the corresponding diorganosiloxy units. They presented the interpretation of these results as evidence for the silanone and cyclodisiloxane intermediates.[26] The formation of silanone in the reaction of chlorosilanes carried out in the presence of dimethyl sulfoxide was contested by Brook and co-workers,[27] who studied the "anhydrous" hydrolysis favoring the formation of hexamethylcyclotrisiloxane from dimethyldichlorosilane via linear α,ω-dichlorosiloxanes. The mechanism they proposed invoked the conversion of a chlorosilane group into a sulfonium ion intermediate. Other methods of synthesis of cyclic siloxanes have been studied. The use of the Diels–Alder reaction in the synthesis of organosilicon monomers and polymers with polyphenyl groups and condensed rings has been reviewed.[28] Addition of perfluorooctyl iodide to the double bonds of vinyltrimethylsilane and 1,3-divinyltetramethyldisiloxane, followed by a reduction of the carbon iodide bond, gives the corresponding $C_8F_{17}CH_2CH_2Si$- moiety. Following this approach, a cyclic tetramer precursor of highly fluorinated silicones was prepared without the use of hydrosilylation or Grignard reactions.[29]

A new method of the rational synthesis of cyclic and bicyclic siloxanes was described that exerts the control of reactions by exploiting the differences in reactivity of various functional groups of bifunctional silanes. New, asymmetric bicyclo[7.5.3] octasiloxane and other bicyclosiloxanes were synthesized by this method.[30] Paulasaari and Weber[31] reported the first example of trisiloxane, 1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethylcyclotrisiloxane, that had been orthogonally polymerized. Acid- or base-catalyzed ring-opening polymerization of the cyclotrisiloxane ring of this monomer by triflic acid or dilithium diphenylsilanediolate yields poly[1-hydrido-1-vinyldimethylsiloxy-3,3,5,5-tetramethyl-1,3,5-trisiloxanylene]. To the category of orthogonally polymerizable siloxanes, one can enlist other cyclic monomers participating in the reactions which do not involve the opening of the siloxane ring. Kennedy and co-workers reported the synthesis of 1,3,5,7,9-pentamethylcyclopentasiloxane and its oxidation/condensation reaction with water, in the presence of the Karstedt catalyst. The reaction led to the formation of complex aggregates of the cyclic moieties with extraordinary properties (stiff, brittle polymer with $T_g = -152\,°C$ (the lowest ever recorded), $T_m = -137\,°C$, thermally stable up to 700 °C). The authors justifiably described it as a "simple monomer which polymerizes in a complicated manner."[32]

A number of papers have been published describing OH-substituted cyclic siloxanes, which are important intermediates in the synthesis of ladder and cage structures. Thus, *cis,cis,cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane was synthesized starting from isopropyldiphenylchlorosilane as a precursor to octa(isopropyl silsesquioxane).[33] The first synthesis of all four stereoisomers of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane, $(Pr^iSiO(OH))_4$ (*all-trans-*, *cis-cis-trans-*, *cis-trans-cis-*, and *all-cis-*1), has recently been reported.[34] A combination of dephenylchlorination of tetraarylcyclotetrasiloxanes and the following hydrolysis proved to be an efficient method for the stereospecific transformation of aryl-substituted cyclotetrasiloxanes into $(Pr^iSiO(OH))_4$. The structures were established unequivocally by X-ray crystallography. *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane was prepared by a similar procedure, and was the first example of a cyclotrisiloxanetriol stabilized by relatively small substituents.[35] Earlier, a "ship-in-a-bottle" method of synthesis was described as a means of obtaining labile cyclic trimers of siloxanes. Molecular capsules provide the isolated microspace within the molecules where labile species are protected and can be considerably stabilized.[36] Several possible mechanisms for the synthesis of small ring systems $(H(OH)SiO)_n$, ($n = 3$ and 4) were investigated by *ab initio* molecular orbital methods, including electron correlation effects.[37]

From such silanol-functional cyclics, the polycyclic (ladder) siloxanes are made in a controlled manner. Thus, the reaction of $(i\text{-PrSi(OH)O})_4$ with $(i\text{-PrPhClSiO})_2$ in pyridine was described, leading to the formation of tetraphenyl tricyclic ladder siloxane. Dephenylchlorination with $AlCl_3$/HCl, and the hydrolysis allowed isolation of tetrahydroxyl tricyclic ladder siloxane in good yield. Using a similar reaction starting from tetrahydroxyl ladder siloxane, the first pentacyclic ladder siloxane was obtained.[38] Abe *et al.* describe the synthesis of

1,1,3,3-tetra-isocyanato-1,3-disubstituted disiloxane as a precursor to other oligosiloxanes.[39,40] In an excellent review, Abe also discusses (among many other aspects of oligo- and polysiloxanes) a convenient route for the synthesis of the two- and three-ring systems with all-methyl or -vinyl pendant groups via the heterofunctional condensation of disiloxane diols with tetraisocyanatodisiloxanes or tetraisocyanatocyclotetrasiloxane with disiloxanediols.[41] Oligocyclic ladder polysiloxanes can also be synthesized by the oxidation of the corresponding ladder polysilanes with *m*-chloroperbenzoic acid.[42]

Examples of organooxasilacycloalkanes have been presented by Makarova and co-workers.[43] 2,8-Dichloro-2,4,4,6,6,8,10,10,12,12-decamethyl-5-carbacyclohexasiloxane, 4,7-dichloro-2,2,4,7-tetramethyl-1,3-dioxa-2,4,7-trisilacycloheptane, and 4,8-dichloro-2,2,4,8-tetramethyl-1,3-dioxa-2,4,8-trisilacyclooctane were prepared for the first time by the heterofunctional condensation of 1,1,7,7-tetrachloro-1,3,3,5,5,7-hexamethyl-4-carbatetrasiloxane with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane, of 2,2,5,5-tetrachloro-2,5-disilahexane with dihydroxydimethylsilane, and of 2,2,6,6-tetrachloro-2,6-disilaheptane with dihydroxydimethylsilane, respectively. The synthesis of 1,3,5,7-tetramethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane, 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane, and 1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane, and their ring-opening polymerization leading to alternating carbosilane/siloxane co-polymers have recently been described.[44,45]

3.12.2.3 End-blockers and Functional Oligomers

A trivial term "end-blocker" usually refers to linear siloxane oligomers, for example, hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), etc., used to control molecular weight of polyorganosiloxanes in siloxane ring-chain equilibration processes. The end-blocker, carrying two monofunctional groups, participates in the equilibration process and terminates the polymer chains. The use of oligomeric linear organosiloxanes in the thermodynamically controlled anionic and cationic polymerization of cyclic siloxanes, and the dependence of their reactivity on the size of the molecule in those processes (e.g., MM is the most reactive component in the cationic polymerization and the least reactive in the anionic polymerization) are well known, and have been described in all major general references.[1] When the end-blocker carries non-reactive groups, the resulting polysiloxanes are the most stable. There are, however, many end-blockers known, primarily disiloxanes, which carry different functional groups including halo, hydroxy, alkoxy, and aryloxy groups, and primary amines. Their use in the synthesis of α,ω-difunctional polyorganosiloxanes has also been thoroughly studied and discussed.[1] The most important reaction used in the synthesis of these functional oligomers is the hydrosilylation reaction which has been extensively studied and reviewed over the last few decades, and there are no signs of any decrease in its potential. A novel, high-yield method of synthesis of unsymmetrical siloxanes from silanols and hydrosilanes has been reported.[46] In an excellent recent review of the chemistry of siloxane polymers and co-polymers, Drake *et al.*[47] refer to the work of Crivello and co-workers,[48,48a–48c,49] who, in a series of recent papers, described the regioselectivity of the hydrosilylation reaction, and illustrated the specificity of hydrosilylation reaction of α,ω-hydrogen functional siloxanes with unsaturated epoxides, catalyzed by $(Ph_3P)_3RhCl$ (and also by some platinum catalysts). The first Si–H group reacts considerably faster than the other, not only in disiloxane, but also in higher oligomers, thus making possible the synthesis of unsymmetrical siloxanes carrying different epoxy groups at each end of the chain. A one-pot two-step procedure in the synthesis of amphiphilic α,ω-difunctional oligomers carrying one epoxy and one alkoxy functional group was also demonstrated. The work on the novel cationically polymerizable siloxane monomers containing various functional groups by the regioselective hydrosilylation has been extended to the synthesis of a series of monomers based on the synthesis of monoadducts, followed by the oxidative dehydrodimerization of the resulting Si–H functional intermediate. By this method, the monomer-bound photosensitizers were also synthesized.[50,51] Drake *et al.*[47] further discuss the synthesis and use of various functional siloxanes in UV-curable systems. Such polymeric precursors are made either by the equilibration polymerization in the presence of α,ω-difunctional end-blockers, and/or by the functionalization (e.g., hydrosilylation) of the preformed polymers. Several different approaches are discussed, including already-mentioned photopolymerization of epoxy-functional siloxanes, novel vinyl ether-functional siloxanes, thiol–ene polymerization. The most thoroughly studied systems are those based on (meth)acrylate siloxanes in spite of their limitations due to the oxygen inhibition. UV-curable silicones obtained by the reaction of acryloxymethyldimethylacryloxysilane with silanol-terminated PDMS have been discussed by Chu,[52] with some selective references to the alternative (e.g., acrylamide), free-radically polymerizable precursors. Telechelic siloxanes with acetylenic groups were prepared by Boileau and co-workers[53] via hydrosilylation of allyl alcohol or ethylene glycol monoallyl ether, followed by the phase-transfer modification reaction with propargyl bromide. Telechelic, primary amine-terminated dimethylsiloxanes constitute another important group of the oligomeric and polymeric precursors. They are currently made by the anionic equilibration reaction involving cyclic siloxanes and

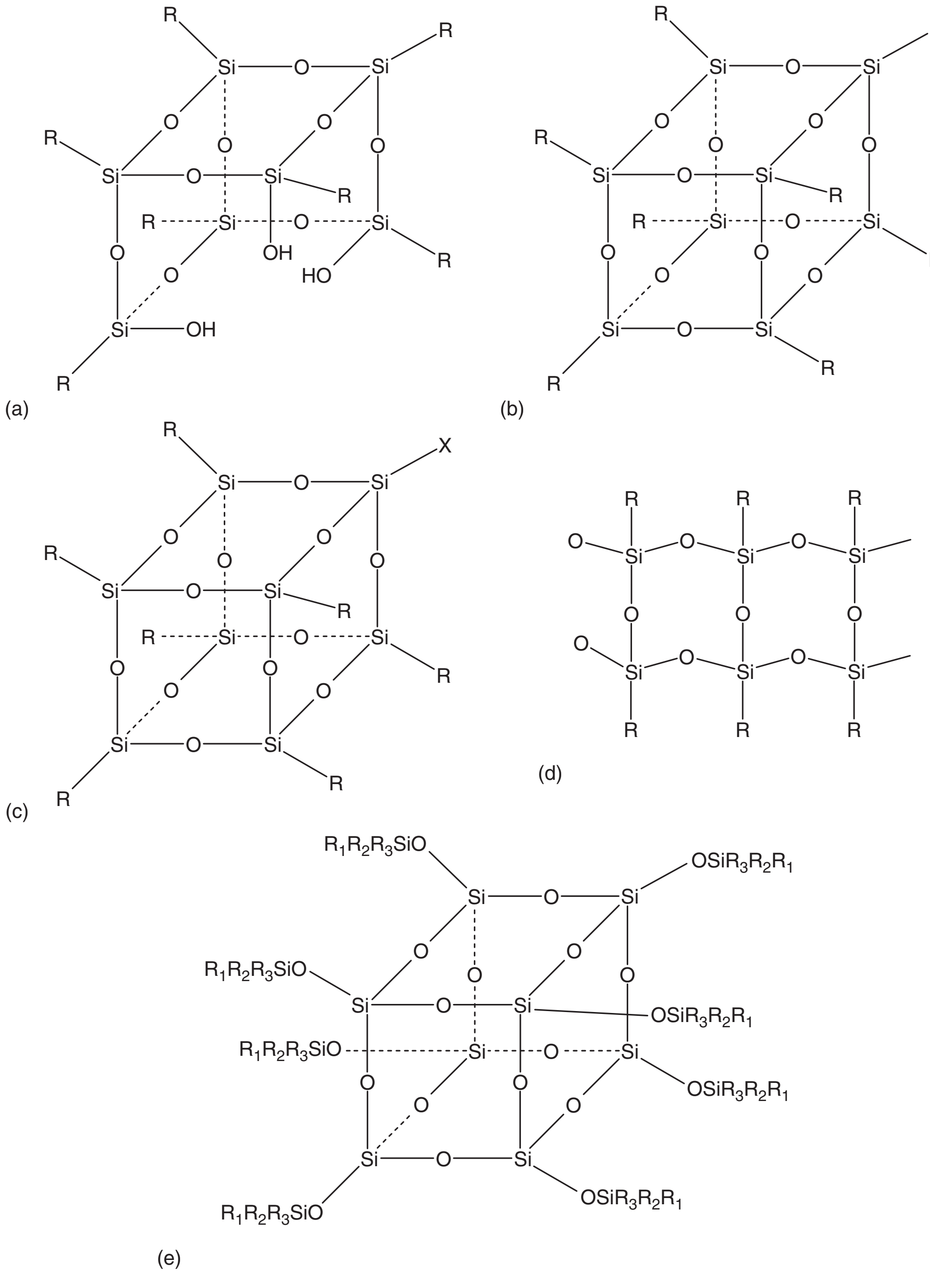
1,3-bis-aminopropyltetramethyldisiloxane (obtained via hydrosilylation of allylamine with tetramethyldisiloxane) and/or its oligomeric derivatitives, as starting materials.[1] The end-blocker itself also finds the application as a precursor in the synthesis of metal-chelating ligands.[54] Recently, the synthesis of a new capping agent, *N*-{(3-aminopropyl)dimethylsilyl}-2,2-dimethyl-1-aza-2-silacyclopentane, has been developed, which can be used to convert the silanol-functional siloxanes into the aminopropyl derivatives. In reaction with water, it forms bis-aminopropyltetramethyldisiloxane.[55] Recently, Yilgör,[56] in a short review, described the two main groups of telechelic siloxane oligomers and polymers: in the first category, a functional group is directly linked to the silicon atoms, Si–X; the second category has the functional groups attached to the terminal silicon atoms through a short hydrocarbon bridge, Si–R–X. Several different reactive groups are discussed in conjunction with the effect of the hydrocarbon-bridging groups and the siloxane backbone substituents. The methods of the preparation of telechelic siloxanes by the ring-opening polymerization of cyclic siloxanes, in the presence of different end-blockers, and the synthesis of block co-polymers based on the resulting telechelic polymers are briefly discussed. A long, but selective, list of new references is provided.[56]

"Macromonomers" (macromers) is the term often used to describe monofunctional macromolecular monomers, and was introduced to silicones by the pioneering work of Yamashita and co-workers in the early 1980s. Since then, siloxane macromers, primarily carrying free-radically polymerizable (e.g., methacryloxypropyl-) end groups, have been utilized in numerous studies. A number of monofunctional siloxanes are available today from commercial sources, carrying acryloxy, epoxy, carbinol, and other functional groups. More recent examples of the applications of macromonomers will be discussed in the following sections. Polydimethylsiloxane macromers are still primarily made by the kinetically controlled anionic polymerization of hexamethylcyclotrisiloxane with the termination of the living polymer end with an appropriate capping agent. A generalized method of synthesis, in which chlorosilanes with various protected functional groups could be used to terminate anionic polymerization, has been reported.[57] By using similar synthetic procedures, one can make siloxane macroinitiators, and these are discussed in the following sections. Methods of directly introducing two different functional groups at opposite ends in the process of kinetically controlled polymerization are useful for both classes of reactive siloxanes (macromonomers and macroinitiators). A novel functional lithium initiator, *N*-3-lithiopropyl-2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane, has been made available.[58] The use of vinyl-[59] and methacryloxy propyl-substituted[60] lithium silanolates as initiators in the synthesis of telechelic siloxanes with two different functional groups has been reported.

A new area of functional oligomers aimed at the development of siloxanes having complex structures (hyper-branched polymers, dendrimers, ladder and cage silsesquioxanes, and hybrid systems) has exploded. With those novel applications in mind, the synthesis of multifunctional siloxane oligomers of designated lengths has been studied; this involves the reaction of tris(*tert*-butoxy)silanol alternately with dichlorosilane and silanediol.[61] A good illustration of the extent of work dedicated to various functional siloxane precursors in a single laboratory is provided in the recent article by Abe and Gunji,[41] which also includes over 100 references to the most recent publications in the field. The paper provides an excellent point from which to venture into the world of the new generations of functional siloxanes. It covers such areas as the formation of oligosiloxanes, polysilicic acid esters and their polymerization reactions, linear and cyclic sila-functional oligosiloxanes (including the experimental details of the vapor-phase hydrolysis of isocyanato-functional oligomers), oxidative condensation of chlorosilanes with dimethyl sulfoxide, the synthesis of linear siloxanes of defined chain length by the ring-opening polymerization, and the synthesis of disiloxanols and cyclotetrasiloxane tetrols. It also includes a price list, current as of 2003, of the commercially available oligosiloxanes.

3.12.2.4 Functional Silsesquioxanes and Silicates

Compounds covered in this section could also be discussed in one of the preceding sections, but functional silsesquioxanes and organosilicates deserve special treatment because of the explosive growth of interest in various aspects of nanocomposites and organic–inorganic hybrids, for which silsesquioxanes and functional silicates are the primary building blocks. As is often the case in any rapidly growing field of science, the rules regarding nomenclature are either vague or are not followed. The term "silsesquioxane," writes Feher in a recent popular review of polyhedral oligosilsesquioxanes,[62] describes a very large family of substances, and it often refers to substances derived from the condensation of organosubstituted silanotriols. They have the empirical formula $RSiO_{3/2}$ ("T"), where R is a hydrogen or a carbon moiety. Various possible structures can include the random, three-dimensional arrangements expected in the so-called T-resins, the ladder-shape polymers, and various cage structures designated T8, T10, T12, depending on the number of silicon corners in the polygon; various partial cages, in which some silicon atoms form



Scheme 2 Incompletely condensed silsesquioxane (a), completely condensed silsesquioxane non-functional (b), completely condensed silsesquioxane functional (c), ladder-type silsesquioxane (d), and functional silicate (e).

silanol groups, also need to be considered.[63,64] The latter are commonly referred to as the incompletely condensed silsesquioxanes (Scheme 2).

In this chapter, in agreement with some referenced work, but not with the others, three classes of silsesquioxanes will be included: the incompletely condensed silsesquioxanes (carrying silanol groups), and two types of fully condensed silsesquioxanes, (i) non-reactive silsesquioxanes having silicon atoms substituted with the non-reactive organic groups, and (ii) reactive silsesquioxanes having one or more groups on the silicon atoms which are capable of a facile reaction with other chemicals. It may add to the confusion when one realizes that the completely condensed, non-reactive silsesquioxanes can react via the cleavage of their frameworks resulting in the incompletely condensed (functional) oligosilsesquioxanes.[65] The vast majority of new frameworks are made from a relatively small number of the readily available starting materials, but the varieties of species made so far and reported in literature run into the hundreds.[41,62] How is it possible to review a field, which, by the late 1990s, was already growing exponentially, and is continuing to grow? It is only possible to provide some background information regarding these classes of materials, illustrate some groups of applications, and refer the reader to the most pertinent reviews for a more in-depth discussion.

The incompletely condensed silsesquioxanes can be considered as intermediates in the synthesis of the whole family of silsesquioxanes, but at the same time they are the building blocks (e.g., initiators) for the new polymeric architectures.[66,67] The importance of this class of materials in model studies of silica surfaces and silicate defects,[68] and in creating various oligosilanols with novel frameworks,[69,70] makes them the subject of extensive research.[71] The use of the incompletely condensed silsesquioxanes in forming dimeric silsesquioxanes and metallasilsesquioxanes in attempts to design new routes to the well-defined Si–O assemblies has recently been reviewed in a well-illustrated research report.[72]

A general synthetic procedure for silsesquioxanes involves the acid or base hydrolysis of a trialkoxy-, or trichloro-organosilane. The resulting structure depends on the concentration of the reactive organosilane, the nature of solvent, the character of the reactive group, the organic substituent, the catalyst, temperature of the process, the mode of water addition, and the solubility of the resulting silsesquioxane in the reaction medium.[73] The optimization of the synthetic procedure for a particular class of oligo- and polysilsesquioxanes remains a major challenge.[74] A cage structure involves several rings connected together in a finite three-dimensional molecular skeleton (Scheme 2). These compounds are known as polyhedral oligosesquioxanes (POSSs).[73] Ladder-type silsesquioxanes were arbitrarily assigned to the multicyclics, and discussed in the previous section. POSSs, with all the silicon vertices carrying the same organic group or hydrogen, are prepared by the hydrolysis of the corresponding trialkoxysilanes or trichlorosilanes. Using this method, numerous multifunctional POSSs were synthesized.[75] A synthetic path to the monofunctional POSS leads through the heptameric siloxanes having partially formed cages, which are further reacted with trialkoxysilanes carrying specific functional organic group. Using this method, a broad family of monofunctional POSSs has been synthesized.[76] This method is often called the corner-capping reaction. Two other commonly practiced methods of synthesis include co-hydrolysis of trifunctional organo- or hydrosilanes, and substitution reaction with the retention of the siloxane cage.[77] Both monofunctional and multifunctional POSSs are of interest in material science as unique macromonomers, branching/cross-linking agents, etc. They consist of large molecules with molecular weights of the order of $1000\,\mathrm{g\,mol^{-1}}$ and with diameters of approximately 15 Å,[78,79] making them attractive components for hybrid systems and nanocomposites.[80] Methacrylate-functionalized mono-[81] and octafunctional ("rigid nanoplatforms"),[82] α-olefin-functionalized,[78] cationically polymerizable epoxy, octafunctional,[82] and monofunctional,[83] and 1-propenoxy-functional,[83] hydrogen-substituted for hydrosilylation reaction, or chlorosilane-functional for condensation reactions,[84] 3-chloroammoniumpropyl,[85] and dozens of others have been described. A fairly recent review with many references describes the synthesis and properties of these monomers (both mono- and multifunctional) and provides a good introduction to the field of precursor to nanocomposite materials.[76] In the introduction to the special issue of *Applied Organometallic Chemistry* in 1999 dedicated to POSSs, Laine remarks, "Polyhedral silsesquioxanes, $(\mathrm{RSiO_{1.5}})_n$ where $n = 6, 8, 10\ldots$, but especially where $n = 8$, are exemplary nanocomposite materials because all of the organic–inorganic interfaces consist exclusively of covalent bonds and the degree of bonding and the types of bonds can be extremely well defined by synthetic methods. Hence their study offers the potential to clearly identify the fundamental principles that govern interfacial properties as well as global properties in organic/inorganic nanocomposite materials."[86]

Functional silicates, often referred to as functional spherosilicates, are related to POSSs. They are prepared via base-catalyzed hydrolysis of silicic acid or orthosilicates, which result in the formation of species with the general formula $[\mathrm{Si_8O_{20}}]^{8-}$ with substituents connected to the silicon vertices via siloxane bonds. Functional spherosilicates offer a wealth of opportunities in creating reactive oligomers, useful as macromonomers,[87,88] macroinitiators for thermal and photoinduced free-radical and controlled-radical polymerizations.[89] Considering the abundance of starting materials (nearly all common minerals are silicates, e.g., T8 and T10 are present as subunits in zeolites[72]), we have witnessed an explosive growth in the field of silicate-based molecular nanotechnology. As noted in two recent extensive reports,[90] cyclic and polyhedral silicate oligomers seem to be the obvious building blocks in molecular nanotechnology, because of their reactivity in the formation of Si–O–Si bond in nanocomposites, and their practical (and potential) availability in a wide variety of functionalities. The new methods of synthesis and modification of functional silicates are subject of continued studies in a number of laboratories.[91–96] Silicates as a source of polyorganosiloxane materials have been reviewed.[97] The preparation of QM polymer systems from the naturally occurring mineral silicates (e.g., olivine, with the simplest structural feature), competitive reactions of silicic acid, cation removal, condensation, and silylation reactions have been described.[98] The experimental efforts in this prolific field of research are complemented by theoretical studies.[99]

3.12.3 Polymerization and Co-Polymerization Reactions

3.12.3.1 Synthesis of Linear Polymers and Co-polymers

The synthesis of linear siloxane polymers and co-polymers has been described with various level of details in so many textbooks, encyclopedias, and review articles that there is no real need to include any background information here. From the brief overviews[100,101] to the broad coverage of the subject, including the basics of the thermodynamically controlled (equilibrium) polymerization and kinetically controlled processes of polymerization—all can be found in the already cited references.[1,2,5,47] In the ensuing discussion of the recent advances in the field of linear polymers and co-polymers, a general outline will be followed, with some modifications, as applied by Chojnowski and Cypryk in their recent review.[3] This is because this review provides a systematic and concise account of the state-of-the-art in the synthesis of linear polysiloxanes through the late 1990s. This is also intended as an anniversary tribute to Professor Julian Chojnowski, this author's teacher, mentor, and friend. Personal bias notwithstanding, the contributions of Chojnowski and his group to the understanding of the mechanisms of polymerization reactions of siloxanes have been outstanding in recent decades.

3.12.3.1.1 Polysiloxanes by polycondensation methods

The complete hydrolysis of dichlorosilanes leads to the formation of silanol group-terminated linear polyorganosilanoxanes and a homologous series of cyclic siloxanes. The composition of such a mixture depends on the nature of organic substituents (prevalence of cyclics for higher alkyl and aryl substituents), conditions of the hydrolysis, and solvents. The hydrolysis of oligochlorosiloxanes is catalyzed by HCl. The concentration of the acid in the medium favors either homofunctional condensation of silanols (in the presence of large excess of water), or heterofunctional condensation ($\equiv$SiCl + HOSi$\equiv$). The mechanism of the hydrolytic polycondensation of organochlorosilanes has been a subject of numerous studies, as evidenced by the sheer number of references in some recent reviews.[102,102a,103] The mechanism of the formation of polydiorganosiloxanes by the methanolysis of dichlorosilanes, where MeCl, and not HCl, is formed in the reaction, is not that well understood in spite of growing practical interest in the technological processes of methanolysis, as noted earlier.[22]

Chojnowski and Cypryk[3] stress the importance of the mechanistic and theoretical studies[104] of the condensation reaction of silanols—the key reaction in silanol homocondensation processes. Silanols are not only the important intermediates in the formation of linear and cyclic siloxanes, they are at least equally important in the formation of co-polymers and polymer networks. The behavior of silanol groups in various polycondensation systems has been reviewed by Chojnowski.[105] The condensation of silanols has recently been discussed by Lickiss,[106] who also reviewed the literature on polysilanols (carrying more than one silanol group),[107] the group of compounds of a very strong interest in the synthesis of silsesquioxanes, sol–gel processes, and inorganic–organic hybrid materials. The reactivity of silanols strongly depends on the size of the molecule, the number of SiOH groups, and on the substituents on the silicon atom. The role of various catalytic systems in affecting the molecular weight distribution of the polymers obtained by the polycondensation method is discussed, including the effect of the catalysts on the competition between cyclization and linear polycondensation and disproportionation of polysiloxanols. A comparison between acid- and base-catalyzed systems is also provided.[107] The mechanism of the catalysis of silanol condensation by the new class of highly reactive catalysts, which belong to the family of phosphonitrile chlorides, has been postulated.[108] The synthesis of polydiethylsiloxane in the process of base-catalyzed condensation of silanols has been reported.[109] A very recent account of the studies of condensation and disproportionation reactions in some model silanol systems, conducted in the presence of a superacid, has been published.[110]

Chojnowski and Cypryk[3] also discuss the formation of the siloxane bond in the reactions of heterofunctional condensation involving silanol groups, pointing out the importance of those reactions in the formation of siloxane networks and co-polymers. They review in some detail the catalysis of $\equiv$SiCl + $\equiv$SiOH condensation, and the reaction of silanols with alkoxysilanes, which is the basis of the sol–gel processes. Reactions of silanols with acetoxysilanes and with silylamines have also been reviewed briefly. A very recent example of the reaction of silanols with cyclic silazene[55] falls in this category. Of practical importance is the dehydrogenation reaction of silanols with hydrogen siloxanes, often used in the formation of silicone coatings and foams.

In addition to the unconventional methods of the formation of siloxane bonds such as those discussed earlier, the non-hydrolytic reactions of chlorosilanes in the presence of dimethyl sulfoxide,[26,27] and the reaction of dichlorosilanes with metal oxides,[111] a new method has recently been discovered which involves the condensation of alkoxysilanes with organohydrosilanes with the release of hydrocarbon.[112]

The formation of polysiloxanes via ring-opening polymerization of cyclic siloxanes is also broadly covered in the same review.[3] The thermodynamics of polymerization, kinetically controlled processes, the mechanistic aspects of both anionic and cationic polymerization, and the applications are discussed with references to the earlier, most comprehensive accounts of these important processes, and with illustration of the main points in the new literature. The subject has also been reviewed recently by Chojnowski,[113] providing additional new examples. Most of the new literature cited in those reviews will be recounted here. His own group's efforts in the use of controlled ring-opening polymerization, both anionic, and, to a lesser extent, cationic, in the controlled synthesis of all-siloxane architectures has recently been described.[114] As far as anionic ring-opening polymerization is concerned, it is not surprising that most recent work is directed toward kinetically controlled polymerization systems, which are capable of forming polymers having well-defined structures. A prerequisite for such a kinetically controlled process is the elimination or at least a very significant reduction in any specific interactions between siloxanes (monomers and polymers alike) and the active species. Such interactions facilitate secondary reactions such as chain scission, backbiting, etc. The feasibility of such interactions, known in practice for a long time, has recently been confirmed by *ab initio* calculations, which showed very different results for D_3 and D_4 in the reaction with KOH-initiated polymerization.[115,116] For an efficient kinetically controlled polymerization, the monomer should be much more reactive with the active species than the polymer that is formed. Thus, highly energetic (strained) cyclic monomers are required. Cyclic trimers (e.g., D_3) are commonly used as monomers. On the other hand, initiators incapable of multidentate interactions with siloxane chains or rings should be selected. This is why the most common initiators (lithium silanolates, formed in the reaction of organolithium compounds with siloxanes)[117] are usually prepared solvated with nucleophiles or the lithium cations are kept isolated in the crown ethers or cryptands.[118,119] Under such conditions, siloxane macromers with a narrow molecular weight distribution and high functional purity can be obtained; this is very important when macromonomers are intended as building blocks for higher-order structures.[120,121] Alternatively, silanolates having weakly interacting counterions, such as tetraalkylammonium or phosphonium ions, can be used. Three initiating systems (lithium silanolate in THF, potassium silanolate complexed with 18-crown-6 in toluene, and tetramethylammonium silanolate in toluene) have been compared in the anionic ring-opening polymerization of 2,2,4,4-tetramethyl-6,6-diphenylcyclotrisiloxane. The sequencing analysis of siloxane units in the co-polymer chain was used as a good diagnostic tool for the studies of the polymerization chemoselectivity.[122] A new class of powerful initiators, polyiminophosphazene bases, described by Schwesinger, has recently gained significant interest in the studies of anionic polymerization of siloxanes.[123–125] The iminooligophosphazane uncharged bases need to be activated with the proton donors to form true initiators of anionic polymerization of siloxanes. They could also function as strong promoters in the combination with alkali metal-based initiators. Being soluble in silicones and utilized at extremely low concentrations, these compounds offer a very attractive alternative to standard catalysts. Hupfield and Taylor studied another class of initiators, amino-substituted oligophosphazenium hydroxides, which, when properly substituted, constitute proper initiators combining high efficiency with selectivity.[126] The kinetics and mechanisms of anionic polymerization of D_3 and D_4 initiated with those "superbases" have been studied.[127] Significant differences in reactivity between the two monomers (two to three orders) qualify superbases as yet another class of selective initiators which are useful in the kinetically controlled polymerization processes. However, Cai and Weber[128] reported that the anionic polymerization of vinyl-functional cyclotrisiloxanes proceeded much more selectively when initiated with diphenylsilanediolate when compared with the initiation with a phosphazane superbase. Baceiredo and co-workers have revisited a class of thermally labile phosphonium alcoholates (phosphorus ylides) as efficient initiators for the anionic polymerization of siloxanes.[129]

Stereoregularity in polyorganosiloxanes draws considerable attention because, on the one hand, it offers a way to affect the crystallinity and stress-induced crystallinity in polymers, while, on the other hand, it is a prerequisite to the synthesis of optically active siloxanes. Thus, Saam and co-workers have studied the anionic polymerization of *cis*- and *trans*-isomers of 1,3,5-trimethyl-1,3,5-tris(3,3′,3′-trifluoropropyl)cyclotrisiloxanes.[130] The polymers derived from the *cis*-isomer were solid and crystalline at room temperature, while the more typical polymers obtained from the mixtures of isomers, containing more than 50% *trans*-isomer, were liquid and amorphous. Strain-induced crystallinity in the elastomeric networks formed from polymers having certain minimum level of stereoregularity was studied.[131,132] The Monte Carlo simulations of the stereoregularity and crystallinity of poly[methyl(3,3,3-trifluoropropyl)siloxane] have been reported.[133] Stereoregular polysiloxanes obtained by the ring-opening polymerization of monomers with pseudo-chiral repeating units (poly(hydromethylsiloxane), poly(methylphenylsiloxane), and poly(methyl(3,3,3-trifluoropropyl)siloxane)) were recently reviewed by Saam.[134] Saam also provides the reference to the only example of an optically active monomer, (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane at that time, which was synthesized and polymerized by Li and Kawakami[135] in a very highly regioselective process using an organolithium initiator to form optically active and highly isotactic poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene]. The physical properties of these polymers were investigated.[136] Möller and co-workers have compared the optical properties of polydipentylsilylene and siloxane co-polymers containing bis[(*S*)-(+)-2-methylbutyl]silane units. They found out that, unlike the corresponding polysilylenes, siloxanes do not form chiral supramolecular structures in solutions.[137] Optically active polysiloxane co-polymers bearing chiral sulfur centers connected to the siloxane chain by a dimethylene bridge, or substituted in the thiol–ene reaction to the vinyl functionality bound to the silicon atoms of the monomer, or of the preformed polymer of similar structure, have been studied by Chojnowski and co-workers.[138,139]

Ahn and Clarson have studied the anionic polymerization of *cis*-2,4,6-trimethyl-2,4,6-triphenyl cyclotrisiloxane under conditions in which both propagation and backbiting reactions could take place. They have proposed a mechanism for the intramolecular reactions taking into account possible phenyl–phenyl interactions, which might facilitate the propagation reaction.[140] Controlled synthesis of vinylmethylsiloxane–dimethylsiloxane alternating, gradient, and block co-polymers in the reaction of homopolymerization of 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (highly regioselective) and its simultaneous, and sequential, co-polymerization with D_3 was recently reported.[141] Weber and co-workers synthesized the first regular polysiloxanes that contain both Si–H and trimethylsiloxy substituents using both mono- and difunctional lithium silanolates. The reactive Si–H groups were subsequently functionalized in hydrosilylation reactions.[142] They also reported the synthesis of linear, soluble co-polysiloxanes containing T and Q units.[143]

Cationic polymerization of siloxanes is of significant practical interest since it is often used in the equilibration processes of siloxanes, particularly those carrying substituents sensitive to the basic medium.[5] The reaction is usually carried out in the presence of strong protic acids, such as perfluoroalkanesulfonic acids or sulfuric acid, or acid-activated silicates.[22] However, a long list of catalysts studied over the years includes other strong protic acids, Lewis acids which are believed to require protic acids as co-initiators, and also some onium salts and other non-protic systems.[3,5] There are many component reactions which need to be considered in any attempts to understand the mechanism of the cationic polymerization, which include initiation, chain growth by both ring-opening and the end-group condensation processes, and the end-groups interconversion. The process is additionally complicated by the formation of cyclics in the early stages of polymerization. For an in-depth discussion of this complex processes, the reader is referred to recent reviews and textbooks.[1–3,5,47] Considering the complexity of the mechanism of polymerization, it is not surprising that research continues in this area, as do controversies regarding the interpretation of the experimental data.[5] The group of Sigwalt has studied the cationic polymerization of cyclic siloxanes for decades. Sigwalt and co-workers attributed the formation of D_6 in the early stages of D_3-polymerization, initiated with triflic acid, to a special type of the backbiting reaction involving transitory tertiary siloxonium ions, and they have concluded that the other homologous series of D_{3x}-cycles and macrocycles mainly result from the cyclization reactions involving participation of the end groups.[144] They also elucidated the role of silanol groups in the polymerization mechanism by studying the polymerization of D_4[145] and D_3[146] in the presence of siloxanediols and water. Olah and co-workers have studied the cationic ring-opening polymerization of D_4 initiated by the electron-deficient reagents, $R_3SiH–Ph_3C^+B(C_6F_5)_4^-$, in the absence of protic acids.[147] They postulated that the polymerization proceeds by a single "long-lived" oxonium ion end, and this is a mechanism distinct from the one postulated for systems initiated with protic acids. This catalytic system was also effective in the polymerization of vinyl- and trifluoropropyl-substituted cyclic trimers, but did not initiate polymerization of trimethyltriphenylcyclotrisiloxane. Trisilyloxonium ions were observed by NMR spectroscopy; their spectral characteristics were confirmed by *ab initio* calculations.[148] In a recent paper, Sigwalt and co-workers questioned the mechanism of the formation of persistent tertiary oxonium ions.[149] They studied the polymerization of D_3 initiated by HCl and $SbCl_5$, and discovered that such a catalytic system may result from the formation of high, controlled molecular weight polymers, containing a small concentration of cyclics (which is unusual for cationic polymerization of siloxanes). The formation of D_6 is attributed to the reaction involving transitory oxonium ions, while macrocyclics are believed to be formed by the cyclization of silanol esters. From the analysis of the concentrations of the cylics formed in both systems, the authors consider that the mechanism of propagation involving primarily silyloxonium ions postulated by Olah and co-workers is unlikely, although they allow for its participation at low temperatures.

Chojnowski and co-workers have studied the polymerization of octamethyltetrasila-1,4-dioxane, a monomer more basic than cyclosiloxanes, which is capable of forming more stable oxonium ions, and thus being a useful model to study the role of silyloxonium ions.[150–152] In recent work, these authors used Olah's initiating system and observed the formation of oxonium ion and its transformation to the corresponding tertiary silyloxonium ion at the chain ends.[153] The ^{29}Si NMR spectroscopic data and theoretical calculations were consistent with the postulated mechanism.[154] Stannett and co-workers studied an unconventional process of radiation-initiated polymerization of cyclic siloxanes and proposed a mechanism involving the intermediate formation of silicenium ions solvated by the siloxane chain in the backbiting process, and unsolvated in the propagation reactions.[155] An *ab initio* study of silyloxonium ions was recently conducted by Cypryk and Apeloig.[156]

Tetrakis(pentafluorophenyl)borate protic complexes were recently used as initiators in the polymerization studies of permethylated cyclic siloxanes.[157] Interrante and co-workers studied the polymerization of 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane initiated by triflic acid to form polycarbosiloxane co-polymer, having a regular –Si–O–Si–C– main polymer chain. They reported the successful synthesis of such an alternating co-polymer of poly(dimethylsiloxane) and poly(dimethylsilylenemethylene), and also their unsuccessful attempts aimed at the synthesis of ethyl-substituted derivatives.[158] Following earlier work concerning the isomerization of cyclic siloxanes, Basindale and co-workers discovered that triflic acid in polar aprotic solvents (nitroalkanes) initiates the interconversion of siloxanes without giving the products of their redistribution reactions.[159] Notwithstanding all the complications of the process, the cationic polymerization of cyclic siloxanes offers a potential for the synthesis of some model polymers. Möller and co-workers polymerized a series of hexa-*n*-alkylcyclotrisiloxanes using both anionic and cationic initiators, and discovered that when trifluoromethanesulfonic acid was used as the initiator, higher molecular weight polymers could be obtained even in the case of cyclotrisiloxanes substituted with the long *n*-alkyl groups.[160] The triflic acid-initiated polymerization of 1,1-diphenyl-3,3,5,5-tetramethylcyclotrisiloxane was studied as a model for the cationic polymerization of cyclotrisiloxanes having mixed siloxane units in an attempt to study the chemo- and regioselectivity of this process.[161,162] No cleavage of the polymer chain was observed, but the regioselectivity of the ring opening was poor.

Cyclic siloxanes can be polymerized in aqueous emulsions in the presence of surfactants such as dodecylbenzenesulfonic acid, and these can also function as catalysts of polymerization.[5] Both anionic and cationic polymerization are feasible under mild conditions. The latter leads to the formation of higher molecular weight polymers.[3] Emulsion polymerization of siloxanes has been investigated by Hemery and co-workers.[163] The anionic polymerization of D_4 in the presence of benzyldimethyldodecylammonium hydroxide, acting both as an emulsifier and an initiator, leads to the formation of the polymer with low polydispersity and with a lower content of cyclics, as the polymerization can be carried out under non-equilibrium conditions. The kinetics of the condensation reactions involving silanol-terminated PDMS was also studied in aqueous media.[164] The polymerization of 1,3,5-tris(trifluoropropylmethyl)-cyclotrisiloxane in mini-emulsion, initiated with NaOH, proceeds in two stages, allowing for the synthesis of linear polymer with high yield before the redistribution reactions start.[165] The cationic polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane in an aqueous emulsion is very complicated, and the process requires a neutral co-emulsifier in addition to the dodecylbenzene sulfonic acid emulsifier/initiator.[166] Stable emulsions of the silanol-terminated poly(methylphenyl)siloxanes with a surprisingly low polydispersity, attributed to the limited backbiting, were used in the preparation of interpenetrating networks with methacrylates.[167] The preparation and applications of silicone-rubber emulsions have been reviewed briefly.[168]

Solid-state polymerization of D_3, initiated by γ-irradiation, has been known for a long time. The reaction proceeds according to the cationic polymerization mechanism.[3,5] Solid-state anionic polymerization of hexaphenylcyclotrisiloxane in the presence of KOH or potassium oligosiloxanolate was recently reported. The crystalline structure of the polymers obtained in high yield in the heterogenous reaction was determined.[169]

3.12.3.1.2 Co-polymers

Silicone co-polymers are a very important class of materials, as they combine the properties of their components, and offer the possibility of designing materials with unique characteristics. Some examples of silicone co-polymers made by the homopolymerization of cyclic siloxane monomers having heterogeneous structure, and their co-polymerization with cyclic dimethysiloxanes, and also by condensation methods, have been mentioned in earlier sections. The all-silicone co-polymers with more complex topologies will be discussed in the next section. The formation of block and graft siloxane organic co-polymers dates back to the early 1960s.[1,2,5] Recent advances in this field are mostly based on the application of well-defined polysiloxane intermediates, macroinitiators and macromonomers, and well-controlled processes of polymerization. A short introduction to the subject is provided by Simionescu,[170] who describes some of the methods used to make block and graft co-polymers, and also provides a list of siloxane co-polymers made via the step-growth polymerization, such as poly(siloxane–ethers), poly(siloxane–polyesters), poly(siloxane–urea/urethanes), poly(siloxane–imides), etc. Two other recent reviews offer excellent introductions to the field of block and graft siloxane co-polymers. Burger and Kreuzer[171]discuss the fundamental principles of siloxane co-polymers and broadly illustrate the subject with the examples covering all the major classes of co-polymers in respectable details. Another recently published outstanding review of this subject is by Belorgey and Sauvet.[172] They discuss the methods of synthesis of siloxane intermediates: α,ω-difunctional siloxanes with various functional groups, and monofunctional siloxanes, with different functional groups, useful for the synthesis of diblock and graft co-polymers. With many examples (although not a comprehensive list, it includes almost 200 references), they illustrate the methods of synthesis of multi-block co-polymers (obtained by polymer–monomer and polymer–polymer condensation, by the use of PDMS-macroinitiators and "macroiniferters," by chain-extender techniques), segmented co-polymers, diblocks and triblocks, and, finally, siloxane graft co-polymers with polysiloxane trunks or polysiloxane branches. The discussion of the properties of siloxane co-polymers includes phase-separation phenomena, and mechanical and surface characteristics. In another recent review, published in Russian, polyorgano–polysiloxane block co-polymers (i.e., polyester–siloxanes, polyimide–siloxanes, polyoxyarylene (or alkylene)–siloxanes, polycarbonate–siloxanes, polysulfone–siloxanes, and siloxane–siloxane block co-polymers) have been discussed and the paper contains many references.[173] The first A–B siloxane block co-polymers were synthesized in 1960 by the anionic polymerization of D_3 on polystyryl- or polyisoprenyllithium "living" polymers. This technique continues to be applicable, with some modifications, to the synthesis of poly(α-methylstyrene)-*b*-poly(dimethylsiloxane),[174] polystyrene-PDMS,[175] and poly(vinylpyridine)-poly(dimethylsiloxane)[176] block co-polymers. "Living" polymers with carbanionic active centers are reactive, often too reactive,[174] toward siloxane bonds; they function as *in situ*-made macroinitiators, which are capable of ring-opening polymerization of cyclic siloxanes. The organic–siloxane A–B block co-polymers formed are, however, incapable of further reacting with vinyl monomers to form A–B–A′ block co-polymers, as the terminal silanolate ions are not nucleophilic enough to initiate polymerization of vinyl monomers. In a recent work, Teyssié and co-workers demonstrated, partially based on previously reported data, that alkali metal silanolates and alcoholates could be effectively converted into much more nucleophilic silyl anions in reactions with cyclic disilanes, thus forming active species capable of anionically polymerizing styrene or methyl methacrylate.[177] The concept of macroinitiators and macromonomers gained new impetus with the advent of controlled radical polymerization, in particular with atom-transfer polymerization (ATP). In the late 1990s, Matyjaszewski and co-workers studied siloxanes as a class of interesting macromolecular initiators.[178] In a review dealing with inorganic macroinitiators, they refer to the synthesis of PDMS macroinitiator with pendant or terminal ATP initiator groups containing the benzyl chloride species attached to the PDMS chain via hydrosilylation of vinyl or SiH groups.[179] In a series of papers from Matyjaszewski's group, the polymerization of methacrylates from polydimethylsiloxane macroinitiators, and co-polymerization of (meth)acrylates with siloxane macromers, have been described.[180,181] In an excellent review discussing the inorganic/organic hybrid polymers, Matyjaszewski and co-workers described how polysiloxanes, randomly functionalized with the initiator groups, were used to form "graft-from" branched co-polymers with vinyl polymers, and how a monofunctional, methacrylate group-terminated PDMS was used in the synthesis of the "graft-through" co-polymers with vinyl monomers.[182] They also discussed the use of functional polysilsesquioxanes and multifunctional cyclic siloxanes in the preparation of hybrid systems with various topologies. As an additional token, they provided a concise tutorial regarding various methods of controlled radical polymerization, including the nitroxide-mediated processes, the atom-transfer radical polymerization (ATRP), and the degenerative transfer (reversible addition–fragmentation chain-transfer) reactions. The use of POSSs in the inorganic/organic hybrid materials made by the controlled radical polymerization has been subsequently discussed in another review.[183] Haddleton and co-workers applied the copper-mediated living radical polymerization to the synthesis of amphiphilic PDMS-containing block co-polymers.[184,185] Also Chojnowski, Holder and co-workers used PDMS macroinitiators of ATRP to synthesize the amphiphilic comb-like block co-polymers of poly(oligo[ethylene glycol] methyl ether methacrylate) and polydimethylsiloxane.[186] Harwood and co-workers used the aldehyde group-terminated PDMS as an intermediate in the redox initiation system to synthesize block co-polymers with styrene, methylmethacrylate, and their mixtures.[187] The use of some conventional α,ω-dihydroxyalkyl siloxanes in the synthesis of A–B–A co-polymers by ring-opening polymerization of lactones has been recounted in a short review by Yilgör, which describes telechelic siloxanes and their use as precursors for novel materials.[56] Although, as discussed earlier, telechelic siloxanes can be used as effective macroinitiators for various polymerization reactions, many telechelic siloxanes can also be considered as ready-to-use building blocks for block co-polymers made by various step-growth polymerization methods, for example, condensation or addition reactions. When reacted with other difunctional organic components, they form alternating co-polymers (or multi-component block co-polymers, if more than one siloxane and/or organic component is used). For alternating, and also for multi-block, co-polymers, one can consider two sub-categories, one made by combining two difunctional polymers, the other made via the chain-extension reaction of a difunctional siloxane with low molecular weight organic components, for example, diisocyanates.[172] The example of the former is the block co-polymers made of poly(methylphenylsiloxane) and poly(dimethylsiloxane), prepared by the interfacial polymerization by Matisons and co-workers.[188] Amphiphilic polymers can be obtained by reacting the monofunctional siloxanes (hydrophobic) with the mono- or difunctional organic (hydrophilic) polymers. Thus, an AB block co-polymer was synthesized from PDMS carrying an Si–H terminal group and allyl-terminated polyethylene oxide. When α,ω-heterotelechelic siloxane is used, the other functional group, for example, methacryloxy, can be used for further reactions.[60] Perfectly alternating co-polymers of poly(ether ether ketone)–polydimethylsiloxane were obtained by reacting norbornene anhydride-terminated PDMS with aryl amine-terminated poly(ether ether ketimine). Ketone groups were easily deprotected on hydrolysis.[189]

Co-polymers with regular structure can also be made by reacting difunctional oligomers. Thus, Kawakami and Li described the synthesis of stereoregular and optically active polycarbosiloxanes via platinum-catalyzed polyaddition of 1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane.[190] Heterocondensation of (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol with various bis(dimethylamino)dialkylsilanes[191] and also Rh-catalyzed stereoselective cross-dehydrocoupling polymerization of oligomeric siloxanes have been explored as methods of synthesis of stereoregular, optically active co-polymers.[192,193] Co-polymers formed via hydrosilylation reactions in the presence of Karstedt catalysts have been investigated,[194–196] and the use of ruthenium complexes as catalysts has been reviewed.[197] Polysiloxanes having polyacetylene linkages regularly spaced in the main chain were synthesized by the oxidative coupling of telechelic [2-(propyn-1)oxyethyl]oxypropyl-terminated polydimethylsiloxanes.[198] Some other examples of functional groups regularly spaced within polysiloxane chain would include not only bisphenol A[199] but also silsesquioxanes.[200] Research in segmented co-polymers, for example, siloxane–urea/urethanes, has primarily been driven by the attractive physical properties of these materials. Reactive extrusion of silicone polyureas has been demonstrated.[201] With the advent of the novel method of synthesis of reactive siloxane intermediates such as primary amine-terminated siloxanes,[55] more work on this important class of thermoplastic silicone elastomers has been reported.[202–206] The structure–property correlations in a series of polysiloxane–polyurethane dispersions have recently been studied.[207] Properties and applications of the moisture-curable siloxane–urethane co-polymers are broadly covered in a recent review.[208] An interesting example of polyurethanes containing polyhedral oligomeric silsesquioxanes as hard segments has been reported.[209]

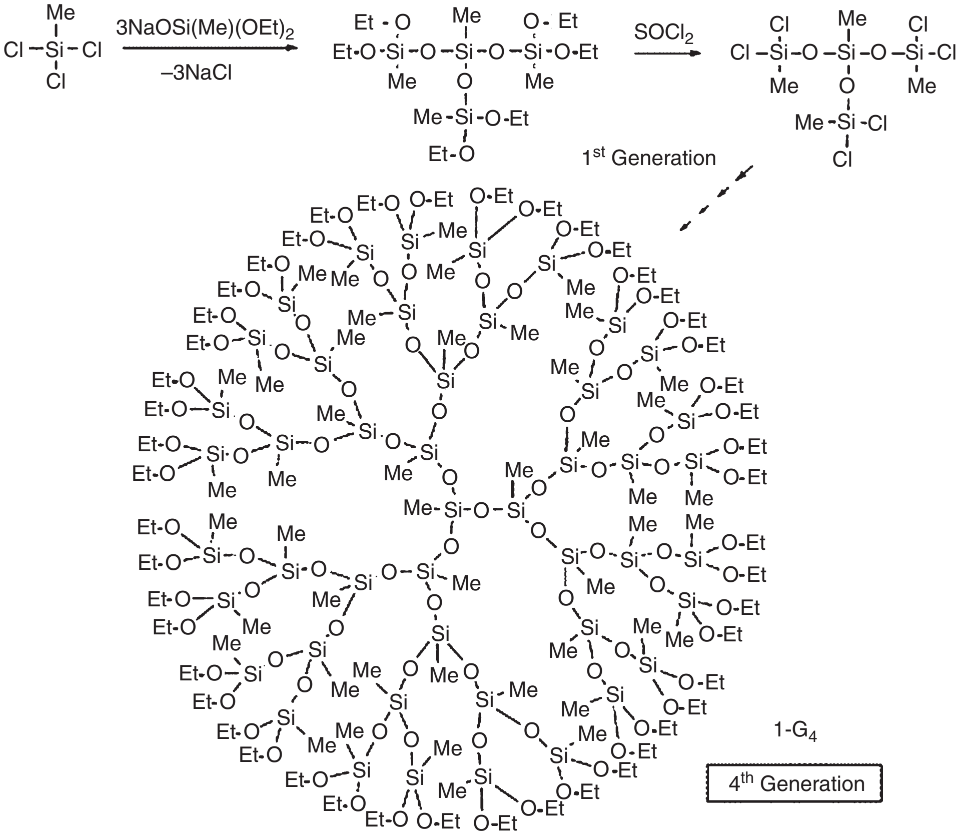
As important as standard alkyl- and aryl-substituted polyorganosilicones are, the ever-growing interest in the modification of siloxanes is easily understood, as siloxanes offer endless possibilities for introducing functional groups into polymers. Siloxanes having functional groups directly attached to the silicon atoms are often classified as silicon functional; when the functional groups are attached via Si–C alkylene or arylene group, organofunctional polymers are obtained. In a recent and superb review, Boutevin and co-workers[210] discuss the side group modified polysiloxanes, and almost 200 references are cited. Most importantly, this review provides a systematic introduction to the field of functional siloxanes by discussing three major ways by which functional polysiloxanes can be made: (i) via the polycondensation of bisilafunctional monomers, oligomers, and polymers, (ii) via the ring-opening polymerization of functionalized cyclics, and (iii) via the modification of preformed polymers. The applications of the first two methods, broadly covered in this review, have already been exemplied in the preceding sections. The modification of the preformed siloxane polymers and co-polymers is the most frequently used route to functional siloxanes. Of the chemistries employed in the modification reactions, hydrosilylation of vinyl- or hydrido-functional siloxanes is by far the most commonly used, both in the synthesis of the intermediates and in the modification of polymers and co-polymers, including those commercially available. The cited references[210] provide numerous recent examples of the synthesis of functional siloxanes ranging from the long-chain pendant fluorosilicone groups, through hydrophilic moieties, photo-cross-linkable groups, to liquid crystalline siloxanes bearing mesogenic groups attached to silicon atoms via terminally unsaturated spacers. Thiol–ene addition of organic moieties to vinyl-substituted siloxanes, which offers another facile route of modification, is illustrated with several recent examples, including the introduction of various cross-linkable groups, amino acids, optically active moieties, etc. Of the other methods of modification, the addition of alkyl halide to vinyl-substituted silicon atoms, and nucleophilic substitution of terminal halogen in the haloalkyl side-groups are discussed, as are some other transformation reactions of the functional groups.[210] A few other recent reviews and publications should be mentioned. The synthesis and applications of photo-cross-linkable polysiloxanes were surveyed by the same group.[211] Novel methods of synthesis of functional siloxanes containing grafted and/or end-capped functional groups for surface modification of textiles have been discussed.[212] Some recent examples of the use of hydrosilylation in the modification of polysiloxanes range from the synthesis of polysiloxanes with bulky tris(trimethylsilyl)methyl groups,[213] through to the attachment of benzophenone and pentafluorostyrene groups,[214] and epoxide and cyanide moieties,[215] to the amino acid-functional siloxanes,[216] phosphazanes,[217] and POSS-substituted co-polymers.[218] Dehydrogenative coupling was used to introduce fluorescent groups to polysiloxanes.[219] The synthesis of siloxane-based polyamines was reported.[220] Several other functional linear polysiloxanes, including ferrocene-substituted systems,[221] were prepared by the dehydrogenative alcoholysis of poly(methylhydro)siloxane in the presence of $[RhCl(PPh_3)_3]$.[222] The thiol–ene addition reaction was used in the synthesis of amphiphilic siloxane–siloxane block co-polymers with carboxyl functionalities,[223] and pyridyl-substituents.[224] Graft co-polymers were obtained by reacting thiol-substituted siloxane co-polymers with various vinyl monomers.[225] In a recent paper, the synthesis of polymethylhydrosiloxane, densely grafted with short propylsilane branches to form the so-called worm-like dendrimers, has been described.[226]

3.12.3.2 Synthesis of Branched Polymers and Co-polymers

Linear polysiloxane polymers and co-polymers, functionalized with large organic groups, or grafted with organic polymers, are arbitrarily discussed along with other linear polysiloxanes. When a polysiloxane forms a branch on another polymer tree (organic or siloxane), such a structure falls into the category of siloxane-branched co-polymers.

Graft co-polymers have been reviewed along with other siloxane co-polymers in a number of the papers and chapters already cited.[5,22,210] Another earlier review of polysiloxane-containing graft co-polymers with siloxane backbones or branches should be mentioned.[227] The well-defined siloxane-grafted vinyl polymers are made when polydimethylsiloxane,[228] or co-polymeric siloxane macromonomers,[229] are co-reacted with vinyl monomers in radical polymerization. Siloxane star co-polymers can be synthesized by the reaction of a monofunctional siloxane capable of reacting with a multifunctional core. Examples of such structures may be found in the early work on capping "living" siloxanes with oligomeric multifunctional siloxanes. When co-reacted with organic polymers, living polysiloxanes can form miktoarm stars (combining different elements at the same core) and terpolymers.[230] The synthesis of telechelic four- and six-branch star siloxanes have also been reported.[231,232] Functional siloxane star-branched co-polymers have been made as the precursors for the more complex, all-siloxane co-polymers.[114] Examples of electrostatically self-assembled star-branched structures, or networks, have recently been reported; these are made from the semi-telechelic or telechelic siloxanes, respectively, having cyclic onium salt groups.[233]

The field of dendrimers, hyperbranched and star polymers exploded some 20 years ago. For a general background, the reader is referred to a recent review with over 400 references by Inoue.[234] For a short review and a discussion of various types of dendrimers and dendritic polymers, the reader can also be referred to another important paper by Tomalia and Fréchet.[235] Dendrimers and hyperbranched polymers are characterized by a highly branched structure, in which all bonds converge to a focal point or core, and have a multiplicity of reactive chain ends. The synthesis of dendrimers proceeds in step-by-step sequences, by one of the two strategies: the divergent approach (from the inside out, illustrated on Scheme 3) and the convergent approach (from the outside in), in both cases giving polymers with a high degree of



Scheme 3 Siloxane dendrimer. Reprinted with permission from Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845–880. Copyright 1999 American Chemical Society.

regularity and controlled molecular weights. Hyperbranched co-polymers, although synthesized from similar building blocks, should not be confused with dendrimers, as they do not have a regular structure, and are therefore distinct from dendrimers. Thus, they have properties intermediate between the branched or star polymers and the regular dendrimers. However, unlike dendrimers, which require tedious synthetic procedures, the hyperbranched polymers are relatively easy to make in a one-pot process.

It did not take long for silicon polymers in general, and specifically siloxanes, with their diverse chemistries of functional groups, to become important members of the family of the highly branched polymers. Several reviews and recent papers discuss polysiloxanes with various architectures. Son has recently reviewed silicon-based dendrimers and hyperbranched polymers.[236] In the discussion of carbosiloxane dendrimers, he refers to the recently developed,[237] so-called "universal scheme" for the synthesis of organosilicon dendrimers, in which divergent and convergent approaches are combined. Some early examples of the siloxane dendrimers are also discussed. The examples of the hyperbranched carbosiloxanes[238,239] discussed in this comprehensive review are, with one exception, made via hydrosilylation of the appropriate di- and trifunctional silanes or siloxane oligomers. One of the examples of the hyperbranched polysiloxanes includes polyethoxysiloxanes made by the condensation of triethoxysilanol,[240] used by the group of Muzafarov as a model in their studies of molecular silica.[241] The synthesis of a hyperbranched polysiloxane via the ring-opening polymerization of 1-hydroxypentamethyl cyclotrisiloxane, regarded as the base-catalyzed proton-transfer polymerization, is also described.[242] Siloxane dendrimers are also discussed in the broader context of dendrimers containing heteroatoms, illustrated with some early examples.[243] A highly recommended review of siloxane and carbosiloxane-based dendrimers covering both chemistry and potential applications (with over 100 references) has recently been published.[244]

The overall strategy for the synthesis of "poor man dendrimers"—hyperbranched silicon-containing polymers—has been discussed.[245] Miravet and Fréchet[239] studied the synthesis of hyperbranched polysiloxysilanes via polyhydrosilylation of various AB_2, AB_4, and AB_6 monomers, for example, monovinyl, two-, four-, or six-hydrido-functional oligomeric siloxanes. They also studied the end functionalization of such hyperbranched molecules with the aim of introducing other reactive end groups, or attaching preformed organic polymers to build hyperbranched–linear star block co-polymers.[246] The hyperbranched polymers made of siloxane macromonomers A–PDMS–B_2 have also been reported.[247] Functionalized branched polysiloxanes with star-branched, comb-branched, and dendritic-branched topologies were described in a series of papers by Chojnowski and co-workers.[114,248–250] The branched macromolecules were generated by coupling reactive blocks, made via anionic polymerization of vinyl-substituted cyclotrisiloxanes and their co-polymerization with D_3, using a grafting technique. Gradient co-polymers were also used to vary the density of the branches. Dendritic polysiloxanes of the first and second generation were obtained using starlike polysiloxane, functionalized with SiCl groups, as the core.[248] Functionalized branched polysiloxanes of various structures were also synthesized on functionalized silica for the immobilization of catalysts.[249]

In a very recent article, the synthesis of two UV-curable hyperbranched polysiloxanes containing vinyl and allyl groups by polyhydrosilylation reaction of methyl-bis(methylethylvinylsiloxy)silane and methyl-bis(dimethylallylsiloxy)silane, correspondingly, was described.[251] Hyperbranched polymers so obtained were subsequently functionalized via hydrosilylation reactions to introduce epoxy or glycidyl methacrylate UV-curable groups. Functional silanes and siloxanes, for example, tris(methyldichlorosilyloxy)methylsilane and 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane, are used as "cores" in the "divergent" methods of synthesis of carbosilane dendrimers.[252] Linear and cyclic siloxanes and silsesquioxanes were also used as cores and frameworks for the construction of ferrocenyl dendrimers.[253] In a broad sense, polysilsesquioxanes, especially those made under the carefully controlled conditions of synthesis to maintain their solubility,[254] are nothing short of irregular hyperbranched polysiloxanes. In fact, both classes are studied as models for silica.[241] But it is not clear how one can classify poly(pentamethylcyclopentasiloxane), a polymer with the lowest known T_g and recently studied by Kennedy and co-workers,[32] which is apparently made of randomly connected siloxane rings.

3.12.3.3 Liquid Crystalline Silicones

Liquid crystalline (LC) compounds are characterized by small molecules, but also include polymers, which are capable of producing a thermodynamically stable phase state characterized by anisotropic properties, associated with a certain molecular orientation.[255] Three types of molecular entities, referred to as mesogens, provide the development of orientational order: rod-like, plate-like, and disc-like. Polymers containing mesogenic groups in their main chain or as side groups also show LC properties. Certain polymers, notably polyorganosiloxanes substituted with higher alkyl groups (ethyl through to hexyl) are capable of forming columnar mesophases with nearly hexagonal unit cells.[255] Beginners in the field of liquid crystals could benefit from obtaining the basic terms from an excellent web-based tutorial.[255a] Thus equipped, the reader can fully appreciate the beauty of polymeric liquid crystals, and LC silicones in particular, which is a rapidly expanding field. Since the beginning of LC silicones in the late 1970s, the subject has been described and reviewed in a great many papers, review articles, and textbooks. A few of the recent reviews and chapters are recounted here, and a few selected new references to the original research articles are given. Between an excellent early chapter by Burger and Kreuzer[171] and the latest review article by Saez and Goodby,[256] which outlines the work directed toward the self-organizing supermolecular and supramolecular materials in which dendritic liquid crystals and functional silsesquioxanes play a prominent role, there have been a number of good reviews summarizing work in all major areas. Godovsky, Makarova, and co-workers have concentrated on cyclolinear LC polyorganosiloxanes.[255,257–259] Mőller and co-workers[260] have reviewed the main-chain LC siloxanes, discussing the classification of the mesophase behavior, polymorphism of poly(di-*n*-alkylsiloxane)s, and the stability of the columnar mesophase with an emphasis on polydiethylsiloxane. Teyssié and Boileau[261] have reviewed structure–property relationships in LC polydialkysiloxanes, cyclic siloxanes, silsesquioxanes, and elastomeric network-based liquid crystals, focusing on ferroelectric LC polysiloxanes. Ferroelectric LC silicone elastomers have also recently been reviewed by Zentel *et al.*,[262] and discussed, among other classes of the side-chain LC polymers, by Hsu.[263] In a recent review, Ganicz and Stańczyk present LC siloxanes in the context of various organosilicon mesomorphic polymeric systems.[264] The importance of LC polymers with intermediate molecular weights (i.e., oligomers) has been emphasized, as such systems warrant faster response to external stimuli than LC compounds based on high molecular weight polymers.[265] LC elastomeric polysiloxane networks with ferroelectric properties, polysiloxane networks formed from cholesteric phases, and the role of hydrogen bonding in the formation of such networks have been reviewed briefly.[266] LC silicones are also discussed in a recent handbook.[267] Published just in time for the incorporation into this review is an article by Coqueret.[268] It commemorates the seminal work of Finkelmann and co-workers, entitled *Investigation on Liquid Crystalline Polysiloxanes: Liquid Crystalline Elastomers – A New type of Liquid Crystalline Material* and published in 1980. Coqueret points out the relevance of the choice of silicones to LC elastomers—organosilicon chemistry offers such a unique breadth of synthetic possibilities in polymers. It is possible to study the influence of polymer chain length, of the nature and concentration of mesogenic units, and of the character, nature, and the length of spacers on structure and properties of LC polymers. The relevance of Finkelmann's work to the development of LC elastomer-based materials with unique mechanical or electro-optical properties has been emphasized, with references given to the papers describing novel, light- or electric field-stimulated, materials.

Burger and Kreutzer[171] walk the reader through the intricacies of polysiloxanes capable of forming mesophases. Although the extreme flexibility of the siloxane chain is counter to the requirements of the LC state where rigid elongated or cyclic structures are favored, it does, on the other hand, favor arrangements of the substituents on the silicon atoms in hexagonal columns or stacks. Packing is another important factor responsible for the formation of mesophases. Thus, polydialkylsiloxanes (other than PDMS) form mesomorphic phases by themselves. The other group of LC silicones is formed when siloxanes are substituted with the mesogenic groups dominating the structures. Polysiloxane chains grafted with mesogenic groups, being attached to one or more of the reactive groups of the mesogen, having two mesogens attached to the ends of the polymer chain, or linking the mesogens in the (elastomeric) network—these are a few basic combinations of the two components. The mesomorphic siloxanes with alkyl or aryl substituents (without mesogen groups attached) are discussed first. The mesophases they form are classified as conformationally disordered (condis) crystals. Cyclic and cyclolinear siloxanes are then discussed, the latter ones having enhanced tendency to form liquid crystals because they form elongated segments;[255,259] the ladder-type polysiloxanes are also discussed. In the ensuing discussion of the mesogen group-containing silicones, the authors describe the methods of linking mesogens with siloxanes and the possible subsequent modifications of these groups. Following a list of the best known main-chain LC silicones at that time, the authors introduce linear siloxanes with mesogenic side groups. This section is filled with data concerning reactions between various mesogens and siloxane homo- and co-polymers. The last part of the review covers the early work on silsesquioxanes with mesogenic side groups, and as such, together with nearly 200 references to the earlier studies, the review represents a general opening into the field of siloxane liquid crystals and to the most complex LC structures discussed in a very recent review by Saez and Goody.[256] A great many advances have been made in the field of LC silicones over the last decade separating those two reviews, and just a few examples are presented here to illustrate this point. The literature cited in these papers covers a large portion of the pertinent body of references. One of the significant developments in the studies of LC polymers has been the application of novel analytical tools. For example, temperature-dependent atomic-force microscopy (AFM) has been used to elucidate phase transitions and order in ferroelectric liquid crystals and LC networks.[269] AFM was also successfully used to visualize morphology changes and nanostructures of polydiethylsiloxanes with different molecular weights.[270]

A significant development observed in the field of ferroelectric and cholesteric side-chain LC siloxanes[263] is related to their applications as non-linear optical materials[271] and gas chromatography stationary phases.[272] Novel synthetic methods are sought for the preparation of the side-chain LC polysiloxanes with a specified distribution of mesogen groups.[273] A comparison of linear and dendribranched LC polysiloxanes has recently been reported.[274] The role of polydialkylsiloxanes columnar mesophases in block co-polymers[275] and in random co-poly(di-*n*-alkylsiloxane/-di-*n*-hexylsiloxane)s[276] has been investigated. New mesogens continue to be researched. A new class of chiral LC polysiloxanes has been synthesized.[277] LC polysiloxanes with novel topologies are actively pursued.[278,279] Research in this field initiated with the use of dendritic cores[253] and silsesquioxanes[280–284] has continued through studies of soluble hybrid LC co-polymers[285] to nanocomposites formed from LC POSSs co-reacted within the LC polymer matrix.[286] Binary mixtures of a nematic side-chain LC co-polysiloxane and a nematic solvent have also been studied.[287] Work on the design of the "Janus-like" supermolecular liquid crystals[288] leads directly to the latest, previously mentioned review[256] where Saez and Goodby take LC polymers on the route "toward self-organization and complex matter," as expressed by J. M. Lehn.[289] The authors define the differences between a supermolecule (a giant molecule) and a supramolecular system (a self-assembled, non-covalently bonded entity), and describe the process by which mesogenic supermolecules can self-assemble. They illustrate LC polypedes (dendrimers with POSS cores), LC multipedes, and giant molecules, which somewhat resemble complex super- and supramolecular materials found in living organisms. This is followed by a discussion of Janus-like liquid crystals (i.e., materials with two faces) containing two different types of mesogenic groups grafted onto the same scaffold and capable of self-assembling. When this review is combined with a quick perusal of dozens of the most recent references cited within, it leaves no doubt that the "new field lies open for the development of materials for which their design is only limited by human imagination."[256]

3.12.3.4 Networks Formation

3.12.3.4.1 Silicone networks

Silicone networks are formed via cross-linking of polyorganosiloxane chains by a few reactions, primarily by peroxide-initiated proton abstraction, via condensation reactions of silanol end groups with multifunctional silanes (e.g., alkoxy, acetoxy), or with hydrosilanes (dehydrogenation), by photoinitiated radiation cure of functional siloxanes (mercaptans, acrylates, oxiranes), and by hydrosilylation reactions.[100,290,291] Many other, less common reactions leading to the formation of Si–O–Si or carbosilane linkages between siloxane chains discussed in previous sections can also be used in the formation of silicone networks. The formation of silicone networks has been discussed in many reviews[1,2,5] and monographs.[7] This section focuses on polydimethylsiloxane model networks, that is, those having well-controlled distribution of cross-linking sites. Stein reviewed monodispersed siloxane networks in 1996,[292] and "model silicone networks" have been reviewed separately.[293] A large number of original papers and reviews have been published since then, as silicone networks continue to be extensively studied as models for the elucidation of rubber elasticity theories. An understanding of the molecular mechanisms of rubber elasticity remains one of the most important unsolved problems of polymer physics.[294,295] The school of J. E. Mark leads the way in the studies of silicone networks. In a prolific series of publications, aided by frequent summaries and reviews, Mark and his co-workers studied and reviewed various aspects of the formation of silicone networks and their properties. The study of elastomers with improved properties through the control of network chain-length distributions, with the emphasis on the role of bimodality, has been summarized.[296,297] The effect of chain length on trimodal networks has also been calculated,[298] and the role of multimodality in affecting the physical properties of silicone networks, for example, stress-induced crystallization, has been reviewed.[299,300] The effect of the distance between the cross-linking sites on the properties of networks has been studied using AFM,[301] Brillouin scattering,[302] and pulse propagation.[303] New developments and directions in the area of elastomers, exemplified primarily by silicones, have recently been reviewed in several papers. Among the more important developments listed are networks with controlled stiffness, model elastomers for corroboration of the rubber elasticity theories, networks cross-linked in dilution (less entanglement), and novel composites and unusual elastomers, some of them with bio-inspired designs.[304,305] Hundreds of pertinent references are included in these reviews. In his recent publication entitled, *Some Interesting Things about Polysiloxanes*,[306] Mark eloquently illustrates the beauty of silicones. He starts with the introduction of polysiloxane chains, and proceeds with the discussion of the nature of the siloxane bond, and organic substituents on silicon and their effect on the physical properties of siloxanes. Chain conformations and spatial configurations are discussed in relation to the formation of cyclics and the possibility of stereoselective polymerization. The discussion of the crystallinity of siloxanes is followed by a short introduction of silicone-based liquid crystals. From a discussion of the equilibrium and dynamic flexibility of siloxane chains, which is critical, for example, to their unusually high permeability, Mark proceeds to a description of the surface characteristics of siloxanes. A short discussion of elastomeric networks follows, illustrated with examples of model (perfect) elastomers, as well as imperfect-by-design networks (e.g., with dangling ends and trapped cyclics), multimodal networks, networks made in solution, and interpenetrating polymer networks (IPNs). There are also sections on silicone-based nanocomposites and on new analytical techniques useful for investigations of siloxanes. This article is recommended reading for those who seek an introductory paper on silicones, and for those who need access to references regarding various aspects of silicone elastomers. Recently, Mark has discussed the status of and trends in the area of elastomers and rubberlike elasticity.[307] He has even tailored the discussion of silicone rubberlike elasticity in a manner that is useful for teaching basic concepts in physical chemistry.[308] The seminal work of Stepto and co-workers regarding theoretical aspects of network formation, with a special interest in silicone networks, continues. They have recently reported the results of gelation studies, involving the end-linking of PDMS chains of various lengths, at various reactive group concentrations carried out in a linear PDMS as diluent. Loop defects resulting from intramolecular reactions were detected, and these should lower the moduli of the resulting networks.[309] These findings were supported by a Monte Carlo simulation for the networks formed by end-linking reactions. However, a comparison with the experimental moduli data shows that the reductions in modulus due to loop formation are outweighed by moduli increases due to chain entanglements.[310] In another study, a universal gel-point prediction in end-linking polymerization was sought. The results for PDMS indicated the reduced accessibility of reactive groups of the long chains for intermolecular reactions.[311] Other aspects of model siloxane networks have been studied, such as the effect of pendant chains on the mechanical properties of model networks;[312] pendant chains were found to negatively affect the elastic properties of networks. Deformation studies of the "super-coiled" elastomeric networks (cross-linked at high dilution) have been reported.[313]

The synthesis and phase behavior of the model polydiethylsiloxane networks have also been studied. The networks were made by hydrosilylation of well-defined vinyl and allyl telechelic siloxanes obtained by kinetically controlled polymerization of cyclic trisiloxane.[314] The effects of molecular weight between the cross-linkings on segment orientation in polydiethylsiloxane elastomers were studied.[315]

Polydimethylsiloxane networks formed via end-linking of hydroxy-terminated polydimethylsiloxane of different molecular masses and methyltriethoxysilane were studied to elucidate the effect of siliceous domains formed *in situ* in homo- and co-condensation reactions.[316] A novel method of thermal cross-linking of siloxanes has been reported with the participation of benzophenone groups attached to the vinyl group-containing polydimethylsiloxane co-polymers.[317] Rhodium-catalyzed modification of polymethylhydrosiloxane into a highly cross-linked polysiloxane via a dehydrogenative coupling reaction followed by *in situ* oxidation has also been reported.[318] Kennedy and co-workers studied what they called "cyclosiloxane-based networks" formed by the cross-linking of SiOH-terminated PDMS chains with pentamethylcyclopentasiloxane.[319] A novel class of fluorosilicone elastomers containing perfluorocyclobutane aromatic ether linkages has been described, which forms chain-extended or cross-linked structures upon heating.[320]

3.12.3.4.2 IPNs and co-polymer networks

Silicone co-polymer networks and IPNs have recently been reviewed.[321] The development of IPNs is briefly described, and the definitions of the main (non-exclusive) classes of the IPNs are cited. Examples of latex IPNs, simultaneous and sequential IPNs, semi-IPNs, and thermoplastic IPNs are provided. The use of silicone–silicone IPNs in studies of model silicone networks is also illustrated. Networks in which siloxane and non-siloxane components are connected via chemical bonds are considered co-polymer networks, although some other names have been applied to such networks. Today, some of the examples in this category should, perhaps, be discussed as organic–inorganic hybrids, or nanocomposites. Silicone IPNs are discussed in almost all of the major references dealing with IPNs.[322–324] Silicone IPNs are also briefly discussed in some other, previously cited, reviews.[291,306]

As interest in combining distinct components to obtain novel materials expands rapidly, there is a need for a more rigorous usage of basic terminology in this field, since it is often difficult to categorize new materials, which are co-reacted, and yet are discussed as IPNs.[325] The same term is even used in discussing organic–inorganic hybrids formed by the sol–gel process.[326]

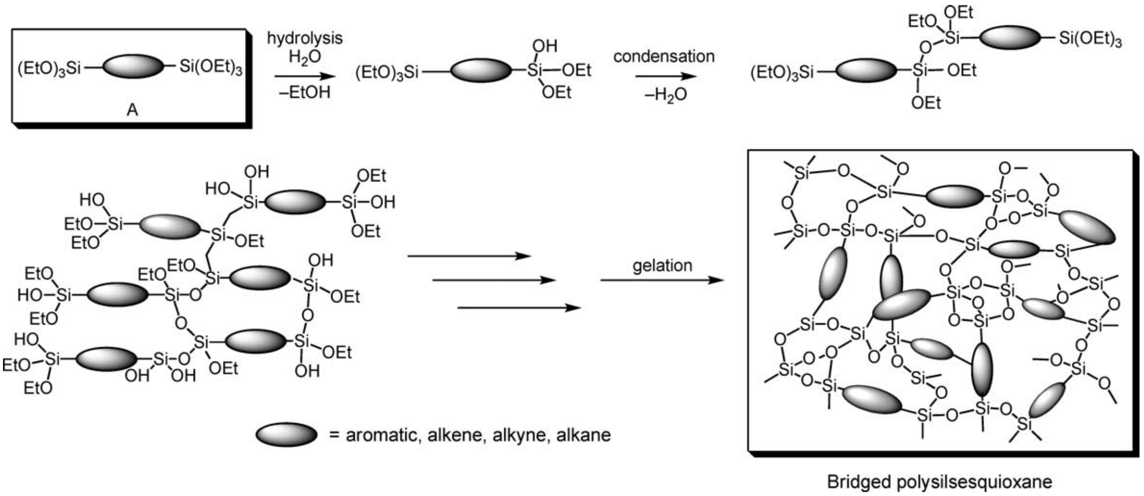
Semi-IPN was formed via *in situ* ring-opening polymerization of benzoxazine in the presence of soluble poly(imide–siloxane)s. When poly(imide–siloxane) with pendant OH functionalities was used, the two polymers were co-reacted to form an AB cross-linked polymer (co-polymer network).[327] Silicone IPNs have been extensively studied in the laboratories of Boileau and co-workers. Polycarbonate–polysiloxane-based IPNs were prepared by the sequential *in situ* polymerization method. A silicone network was formed by the condensation of functional siloxanes carrying triethoxy and hydrolyzable phenylcarbonate moieties in solutions of diethyleneglycol bis-allylcarbonate monomer, which was subsequently polymerized at elevated temperature.[328] Ring-opening polymerization in an aqueous emulsion of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane resulted in α,ω-silanol-terminated siloxane oligomers, which were used in the preparation of IPNs with polybenzyl and polymethacrylates.[329] Domain distribution in poly(methylmethacrylate)–poly(methylphenylsiloxane)-based interpenetrating networks was studied with the use of solid-state ^{13}C NMR spectroscopy.[330] The synthesis of the novel fluorinated polysiloxane networks and the formation of IPN with PDMS,[331] and an attempt to combine PDMS with cellulose acetate butyrate,[332] have been recently reported. Semi-IPNs composed of poly(methylmethacrylate) and aromatic/aliphatic siloxanes have been made by Gilmer *et al.*[333] via sequential and simultaneous polymerizations; cross-linking and grafting were detected.

Silicone-based IPNs continue to be investigated for medical applications. PDMS/poly(2-hydroxyethylmethacrylate) sequential IPNs were studied and compared with physical blends of homopolymers.[334–336] PDMS/poly(*N*-isopropyl acrylamide) IPNs have been evaluated as ophthalmic biomaterials.[337] A series of novel silanol-containing polymers was obtained by a selective oxidation of Si–H-containing precursor polymers with a dimethyldioxirane. The silanol–hydrogen bonding interactions in polymer blends, as well as the silanol self-condensation to form siloxane semi-IPN in miscible polymer blends and organic–inorganic polymeric hybrids, were reported.[338] Grafted IPNs based on the cross-linked siloxaneurethanes were reported by Makarova *et al.*[339]

A blend of MQ resin with PDMS is called semi-IPN in the interpretation of dynamic mechanical properties of such (pressure-sensitive adhesive (PSA)) systems,[340] which seems to be at least controversial, considering the solubility of MQ resin in polydimethylsiloxanes.The synthesis and properties of acrylic/silicone co-polymer networks obtained via hydrosilylation of the acrylic polymers containing alkenyl with silicones containing SiH groups have been reported.[341] Also, polysiloxane–polyacrylate composite lattices obtained via γ-ray-induced seeded emulsion–polymerization of methyl methacrylate and butyl acrylate carried out in the presence of a polymerizable polysiloxane seed latex can be considered as silicone–acrylate co-polymer networks. The graft polymerization reactions between the polymerizable polysiloxane and the acrylates were confirmed by FTIR.[342] A broad family of silicone–acrylate co-polymer networks has recently been studied.[343] They are made via photoinitiated co-polymerization of the high molecular weight telechelic siloxanes having free-radically polymerizable moieties attached to the terminal silicon atoms via polar (urea or amide) spacers and (meth)acrylic monomers. A broad family of materials with well-controlled morphology and interesting mechanical properties was obtained.

3.12.3.4.3 Organic–inorganic hybrids and nanocomposites

The field of nanocomposites and nanostructured organic/inorganic hybrids has become so broad that it has been reviewed recently in dozens of articles. A quick perusal of the references cited in just a few of many review publications coming from the group of Corriu proves the point.[344–346] For the sake of clarity, it is helpful to start with the definitions of basic terms. Nanocomposites are obtained by inclusion of nanotools (e.g., silsesquiloxanes, metal oxides) into a matrix, which can be an organic polymer or an inorganic matrix, the most popular in the latter case being silica. Nanostructured materials, on the other hand, are obtained by assembling the nanotools (e.g., bridged silsesquioxane precursors, which by themselves are organic–inorganic hybrid materials) by using chemical bonding. In such a case, the solids obtained are monophasic, since the nanotool cannot be separated from the organic (polymer) or inorganic matrix, as it is co-reacted within the matrix. "Two ways can be used for assembling such materials: organic or inorganic polymerization. In both cases the nanotool must be chemically designed in order to permit the formation of a matrix around it by chemical bonding. These possible general ways involve organic or supramolecular polymerization or inorganic polycondensation (sol–gel type chemistry)."[345] The latter method of solid synthesis, for example, sol–gel, can be described as a process in which a solution of, for example, silicon alkoxide in ethanol, becomes a sol upon partial hydrolysis, which then undergoes further hydrolysis reaching a sol–gel transition and becomes a solid. The sol–gel processes are the best known examples of "*chimie douce*," that is, "soft chemistry," a term introduced in the late 1980s to describe the controlled synthesis of solids in non-reversible reactions. In a recent chapter, Boury and Corriu discuss in detail the methodology of the preparation of nanostructured hybrid organic–inorganic solids.[345] They illustrate the differences between nanocomposites and nanostructured hybrids, and discuss the synthesis of nanostructured organopolysilsesquioxanes, and the effect of the activity of organic groups on the structure of the resulting hybrid material; 227 references are cited. In a short, recently published chapter, Corriu and Douglas[346] also discuss the organic–inorganic hybrid materials and recall the definition of the component materials for such systems: "ormosils"—organically modified silicates. An excellent early introduction to the nanostructured hybrids formed of organic blocks carrying multiple trialkoxysilyl groups as precursors was presented by Loy and Shea.[347] They explain how an interest in nanocomposites led to the development of nanostructured hybrids by incorporating the polymerizable inorganic groups and an organic moiety in the same molecule. Such inorganic/organic precursors can polymerize by the sol–gel processes (principles of which they present in the simple schematics) to form bridged polysilsesquioxanes, as illustrated in Scheme 4.



Scheme 4 Bridged silsesquioxanes. Reprinted with permission from Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306–3319. Copyright 2001 American Chemical Society.

The authors discuss bridged polysilsesquioxanes as molecular-engineered hybrid organic–inorganic materials. The significant recent interest in this field of material science is driven by opportunities to create materials with controlled porosity that are capable of selective adsorption or catalysis.[348] For a broad introduction to the methods of controlling the synthesis of organic–inorganic hybrids through soft chemistry, the reader is referred to a number of short reviews, starting with introductory notes by Eckert and Ward[349] in one of the dedicated volumes of *Chemistry of Materials*. Organosilica sol–gel materials are discussed in an excellent review.[350] A large variety of systems are discussed, including nano-scale IPNs formed by performing the sol–gel polymerization of alkoxy-functional organic moieties in the presence of organic monomers. The monomers can be subsequently polymerized within the gel matrix (IPN) or co-polymerized with the functional groups of the bridged silsesquioxanes. Crivello and Mao reported the synthesis of the novel multifunctional siloxane oligomers using the sol–gel methodology to polymerize trialkoxysilanes bearing either epoxy or 1-propenyl ether functional groups to obtain a series of soluble multifunctional siloxane oligomers,[351] which could be further reacted with additional monomers via photoinitiated cationic polymerization to form organic–inorganic hybrid matrices.[352]

The sol–gel methodology can also be applied to non-hydrolytic processes. The preparation of methylsilsesquioxane–titanium oxide hybrid by the etherolysis–condensation of a mixture of methyltrichlorosilane and metal chloride,[353,354] and by the condensation of preformed poly(methylsilsesquioxane) carrying Si–OH and Si–OCH_3 groups with titanium(IV) *n*-butoxide,[355] has been reported.

Other important building blocks for organic–inorganic hybrids are functional silicates. The formation of the three-dimensional hybrid networks in the reaction of $[Si_8O_{20}]^{8-}$ silicate species and dimethyldichlorosilane has been reported.[356] The structure of the hybrids so formed has been found to comprise the $[Si_8O_{20}]^{8-}$ building blocks, linked by $(CH_3)_2Si$ units. Homogeneous polymer hybrids were made in the ternary system by reacting octa(3-hydroxypropyldimethylsiloxy)octasilsesquioxane with phenyltrimethoxysilane by the sol–gel process carried out in the presence of hydrogen-bonded co-polymers of styrene/*N*,*N*-dimethylacrylamide.[357]

On the other hand, all the POSSs carrying multiple polymerizable groups, for example, methacrylate,[76] epoxy,[83] and many others discussed earlier as functional silsesquioxanes, would, upon homopolymerization or co-polymerization with the corresponding monomers, form what should qualify as organic–inorganic nanostructured hybrids, since the interaction between the phases are at the molecular level. In fact, Laine *et al.* have reported the catalytic co-polymerization of an octavinyldimethylsiloxy-functionalized cube with an octahydridodimethylsiloxy-functionalized cube to produce a material with well-defined microporosity.[358] In another paper, they described a new class of epoxy nanocomposites with completely defined organic/inorganic phases prepared by reacting octakis(glycidyldimethylsiloxy)octasilsesquioxane with diaminodiphenylmethane.[359] The synthesis has been reported of the organic–inorganic hybrid composites via the *in situ* polymerization of epoxy monomers in the presence of POSS-triol,[360] and also by reacting monofunctional POSS carrying aromatic diamine with stoichiometric amount of an aromatic diepoxide to generate an organic–inorganic hybrid material containing over 50 wt.% POSS.[361]

Such systems, if not formed by the sol–gel processes, are most often described as nanocomposites, as they are referred to in a short review by Joshi.[362] This review can be recommended as a source of many recent references regarding POSS as a hybrid nanofiller. The most important single feature of nanocomposites is that their properties are not only determined by the weighted sum of the properties of the components (as to the large extent is the case in composites), but they are also to a large degree determined by the nature and contribution of interfacial regions. Organic–inorganic nanocomposites with completely defined interfacial interactions have been reported.[363,364]

Mark *et al.*[365] reviewed inorganic–organic composites, which are, as they remarked, frequently synthesized using techniques very similar to those used in the new sol–gel approach to ceramics. The hydrolysis of silicates, titanates, and aluminates in the presence of polymer chains containing reactive groups for bonding onto silica, titania, or alumina leads to the formation of inorganic–organic composites.[365] Also, the formation of mixed oxide phases of silica–titania, silica–zirconia, and silica–alumina in PDMS was reported.[366] The formation of catalysts by the sol–gel precipitation of zirconia and titania particles in PDMS was recently reported.[367] Functional POSS was co-polymerized with *N*,*N*-dimethylacrylamide and bipyridine monomer to form hybrid terpolymer, which upon coordination with some metal ions to the 2,2′-bipyridine segments formed, what were called, "hybrid gels."[368] Chauhan *et al.* reported the synthesis and characterization of polysiloxane-encapsulated metal nanoparticles by sequestering metal ions with hydropolysiloxanes followed by the chemical reduction to yield the corresponding zerovalent metal nanoparticles.[369] The "palladium nanoparticle" thus formed was used as a catalyst for selective alcoholysis of polyhydrogensiloxane.[370] The inorganic/organic hybrid nanoreactors based on cyclic and cubic siloxane scaffolds have been investigated, and their utility for the synthesis of silver and palladium nanoparticles has been demonstrated.[371] Thermodynamic and transport properties of polyhedral oligomeric silsesquioxanes in PDMS were determined by molecular simulation. It was reported that the solubility of POSS in PDMS increases for the methyl-substituted POSS in comparison with the hydrogen-substituted POSS.[372] In their recent papers, Matyjaszewski *et al.*[183,373] call the co-polymers, composed of organic components and PDMS or silsesquioxanes, organic–inorganic hybrids. Both linear and cyclic siloxanes and functional POSS can be used as initiators and macromonomers in the ATRP.

PDMS nanocomposites with layered mica-type silicates were also reported.[374] A two-step sol–gel process of the *in situ* precipitation of silica led to the development of siloxane-based nanocomposites with particularly high transparencies.[375] Some unusual nanocomposites prepared by threading polymer chains through zeolites, mesoporous silica, or silica nanotubes were reviewed.[376] Poly(4-vinylpyridine) nanocross-linked by octa(propylglycidyl ether) polyhedral oligomeric silsesquioxane was reported.[377]

3.12.4 Materials and Applications

A unique set of physical properties of polyorganosiloxanes, and the versatility of chemistries available in the preparation of macromolecules and their assemblies with growing complexity, result in a huge range of novel applications. However, this does not mean that the more traditional silicone materials have become less common.[5]

3.12.4.1 Fluids

Silicone fluids can be discussed in two categories: inert fluids and functional fluids, the latter including silicon-functional and organo-functional[210] (modified) polymers. The methods of synthesis of functional siloxanes have recently been reviewed.[378]

Polydialkyl-, arylalkyl- and fluoroalkylsiloxane polymers and co-polymers, carrying no reactive (under-the-use conditions) groups, belong to the first category. There are many features of polyorganosiloxanes which make the silicone fluids unique for many applications. A number of recent chapters and review articles on silicones discuss the properties and applications of silicone fluids, which include lubricants (poor frictional lubrication), hydraulic fluids, heat-transfer media, cosmetics, refrigerants, water-proofing agents, protective coatings for building materials, anti-foams, dielectric coolants, power transmission fluids, paint additives, and many others. This subject is also briefly discussed in COMC(1995).[2] Silicone fluids carrying dimethyl, phenylmethyl, diphenyl, fluoroalkyl, or chloroalkyl substituents are the most common, but this list is by no means complete, and each class lends itself to substantially different features. Thus, fluorosilicone oils provide unusual low-temperature lubricating properties, while phenyl-substituted oils are characterized with enhanced temperature stability. The most important are PDMS fluids and polymethylphenylsiloxane fluids.[5,22] Silicone fluids are broadly discussed in a recent article.[379] PDMS fluids are usually made by the equilibration of cyclic or linear siloxanes in the presence of non-functional end-blockers, for example, MM, or other permethylated linear oligomers. The properties of the homologous series of the low molecular siloxane fluids, dimethylcyclosiloxane cyclics (D_3 to D_8) and MD_nM series (MM to MD_7M), are readily available.[5] In the same article, the physical properties of PDMS fluids with low ($<10^5$ cSt) and high ($>10^6$ cSt) viscosities, and the role of co-polymeric (phenyl) units in suppressing the melting point of crystalline PDMS, are discussed. A very low temperature dependence of the viscosity of silicone fluids is illustrated by several examples. Other properties, such as gas and moisture permeability, good dielectric characteristics, as well as thermal conductivity and compressibility, and optical properties have been discussed, with numerical data included. The mechanism of thermal decomposition of silicone fluids is also discussed.[5] Different types of inert silicone fluids are broadly discussed in another reference.[22] A very recent account of the use of silicones as antifoams has been published.[380]

A quick perusal of any of the catalogs of major suppliers of organometallic polymers reveals an abundance of functional siloxanes that are readily available. Of the functional fluids, silicon-functional (Si–OH, Si–Cl, Si–OR, etc.) polysiloxanes are primarily used as components of silicone rubbers (LIM, RTV), coatings (e.g., release coatings, PSAs), and intermediates in the synthesis of co-polymers.[1,2] Some examples of their uses are discussed in the following sections. On the other hand, many of the organomodified polysiloxanes are used as finished products in various areas. The use of organomodified silicones in personal-care products has recently been reviewed.[381] Based on the literature published through to the early 1990s, the authors describe the use of silicone fluids in general in the context of their own work. The application of water-soluble polyether–polysiloxanes in hair-care products is primarily discussed. The effect of the co-polymer composition on solution properties and surface characteristics is illustrated. Both non-ionic, for example, polyether–polysiloxane co-polymers, and polysiloxanes containing pendant ionic groups (betains or salts derived, e.g., from epoxy-substituted polysiloxanes), are discussed along with other methods of modification of polysiloxanes.

3.12.4.2 Rubbers

Silicone rubbers can be classified according to the method of curing (vulcanization) as (i) high-temperature cured, and (ii) room-temperature cured (vulcanized) (RTV). One should also mention an emerging family of thermoplastic silicone elastomers,[201–206] which may require no cure. However, only curable silicone rubbers will be discussed here. Silicone rubbers—one of the oldest and the most important silicone products—have been described in a large number of papers and reviews, including COMC (1985) and COMC (1995).[1,2] A standard method of manufacturing heat-curable silicone rubbers involves blending the high molecular weight polydimethysiloxanes (“gums”), usually containing some vinyl substituents, with the active fillers (poor mechanical properties of unfilled rubbers), other additives, which may include non-active fillers, stabilizers, and peroxide curing agents, shaping the object (e.g. compression molding, extrusion of tubes, profiles, etc.), and curing the compositions at high temperature by a free-radical proton abstraction from the alkyl moieties. Of the recent references, the most comprehensive account of the state-of-the-art in silicone rubbers can be found in the chapter already cited.[5] The methods of synthesis of the basic polymer, the requirements for the active and non-active fillers, and other additives, processing and cure conditions are discussed there. The properties of different generic classes of silicone rubbers are listed, including some for the fluorosilicone and nitrilesilicone rubbers.

Silicone rubbers made by liquid-injection molding (LIM), sometimes referred to as LSR (liquid silicone rubbers),[2] are two-component systems made from low-viscosity functional fluids, usually vinyl-functional polysiloxane and hydrogen-functional siloxanes formulated with fillers and other additives.[5] The inhibited hydrosilylation catalyst is mixed with the vinyl-functional part. Once injected into the mold, the composition is cured at high temperature. Physical characteristics of the polymers so formed are given, and some recent literature regarding LIM silicones is cited. The formation of foamed silicone rubbers from similar components is also discussed. Water or alcohol is typically added, which react with hydrosilane in the presence of the catalyst to form hydrogen. This causes foaming of the rubber during the cure cycle.[5] Silicone foams are also discussed in a recently published handbook.[382] RTV silicones also have a long history. They were discussed in detail in both COMC (1982) and COMC (1995).[1,2] They are extensively described in another important, recently published chapter,[22] where silicone rubbers in general are discussed along with silicone fluids and resins. The fillers, process aids, and stabilizers for silicone rubbers, as well as the rheology of the compositions, are discussed. Different curing chemistries utilized in silicone-rubber industry are reviewed, including, in addition to hydrosilylation and peroxide cure, condensation curing (examples of cross-linking agents listed), radiation, and oxidative coupling of mercaptoalkyl-substituted silicones. Following the discussion of the high-temperature curable rubbers (peroxide and LSR), two types of the two-component RTV systems are briefly described: based on the hydrosilylation reaction with uninhibited catalyst, and based on the condensation reaction of the silanol-terminated silicone fluid with the moisture sensitive cross-linkers, for example, alkoxysilanes, in the presence of the catalyst.

One-component RTV systems are also described, which are primarily used as sealants, adhesives, and coatings. The properties of silicone elastomers are discussed in several paragraphs; applications of silicone rubbers are also discussed.[22] Silicone rubbers can be also made in emulsions. Elastomers are formed upon removal of water. They are used as coatings, sealants, and coating additives. Such systems have recently been studied by Liles and Joffre[383] and reviewed by Liles.[168] The studies of the mechanism of condensation cure, most commonly used in silicone rubber lattices,[384,385] and of the properties of the rubbers so formed,[386] have been reported. Emulsion–polymerization and cure of the silicone elastomeric powders, used for the modification of polymeric surfaces, have been studied and reviewed.[387] For a comprehensive account of the advances in silicone-rubber technology, the reader is also referred to the second edition of the *Handbook of Elastomers*. In one of the chapters, Polmanteer covers the period from the early beginnings in 1944 to 1986, selectively citing the most pertinent references.[388] In another chapter, Klosowski gives his perspective of the developments from 1987 through to the late 1990s (with no references), with the focus being on silicone sealants.[389] Silicone sealants have also been reviewed elsewhere.[390,391]

Many other reviews have been published within the last several years concerning various aspects of silicone rubbers. The major methods of the preparation of silicone rubbers (one- and two-component RTVs, LIM, and peroxide-curable systems) have been discussed by Pohmer and Steinberger.[392] Crawford has discussed cross-linking methods, including radiation curing.[393] A highly recommended early review discussing the synthesis and applications of the photo-cross-linkable polysiloxanes was published by Boutevin *et al.*[211] Addition cure, including processing methods used for injection molding, is discussed in a couple of review articles.[394–397] The material aspects of liquid silicone rubbers and their novel applications are also reviewed.[398,399,399a,399b] Condensation-cure chemistries have been discussed by Pujol *et al.*,[400] and briefly reviewed in a recent publication (in Russian).[401] For background to any of these systems, one can always turn back to the classic account of Noll.[402]

To finish this section on a high tech note, one should mention that silicone rubbers with their ability for precise replication are the primary tools in nanoprinting. A short review of the use of silicone rubber stamps in this field has recently been published.[403]

3.12.4.3 Resins

Silicone resins, along with silicone fluids and elastomers, are discussed in most of the major publications regarding silicones, including earlier editions of COMC, where basic information regarding the types of the resins and their applications can be found.[1] The most characteristic feature of the resins is their highly branched structure (whether they are composed of M and Q units alone (MQ resins), of trifunctional T, or the combination of M, D, T, and Q), and their solubility in many common solvents. Some of the resins contain functional groups. Of the newer references, a few chapters could be recommended for an in-depth discussion.[5,7,22] Brook[7] provides an introduction to the silicone resins looking at their molecules as a precursor to silicas. Basic methods of synthesis are discussed, which involve the co-hydrolysis of chlorosilanes. However, some of the resins, most notably MQ resins, are made from ethyl silicates, or from sodium silicate, as the raw materials.[5] Silicates are reacted with trimethylchlorosilane (with the addition of functional chlorosilanes, if needed) in two different processes to obtain resins with the controlled ratio of M/Q, and it is a primary parameter controlling the properties of MQ resins. The other important factor is the concentration of the remaining silanol groups. MQ resins with a relatively narrow molecular weight distribution can also be obtained in the acid-catalyzed reaction of ethyl silicate with hexamethyl disiloxane.[404] The applications of MQ resins in PSAs and release coatings will be discussed in Section 3.12.4.4. The MQ resins also find application as surfactants, reinforcing additives for silicone rubbers, and water repellents.[5] These, and some other applications, for example, in composites, have been briefly reviewed (in Russian).[405]

TD resins and T resins have also been described.[5] TD resins are made by co-hydrolysis of dichlorosilane with trichlorosilane. Again, the ratio of the two components determines the characteristics of the resin. TD resins find applications in protective coatings, as saturants, and as paint additives. Some aspects of T resins have been discussed before: silsesquioxanes and their precursors belong to this category. Novel methods of synthesis of silsesquioxane particles with controlled composition of functional substituents, for example, aminopropyl, are being actively researched.[406] Historically, they were called silsesquioxanes even when their structures were not easy to determine. Today's applications of silsesquioxanes as building blocks for nanocomposites and organic–inorganic hybrids notwithstanding T resins are continually used in high-performance powder coatings, and in various electronic applications. Tospearl is also discussed as an example of T resin, condensed to form uniform particles with controlled size.[407] The possibility of combining various silicone resins carrying alkoxy or hydroxyl groups with organic resins, for example, polyesters, alkyl, acrylic, or epoxy, has been mentioned.[22]

3.12.4.4 Coatings

Silicones play a very important role in the coating industry because of the versatility of polymeric silicone precursors and the unique combination of properties silicones can offer. One can discuss silicone coatings within a couple of loosely defined categories:

(i) Elastomer-based coatings: They require elastomeric network made by the curing of functional fluids, or gums coated from solutions, and may contain property modifiers; thermoplastic elastomers would also belong to this category, although they do not require cure.
(ii) Resin-based coatings: Cross-linked resins form networks: hard coats, electronic coatings; they can be combined with linear polymers to modify properties (e.g., flexibility).
(iii) Surface-modifiying coatings: They may not require the formation of silicone-polymer matrix; siloxane molecules might be chemically or physically attached to the surface to modify the characteristics of the substrate, for example, fibers.

Some of the elastomer-based coatings, namely release coatings, PSAs, and paints, will be described in separate sections. Of the other applications, one should mention the use of silicone elastomeric coatings in medical products, for example, in drug delivery,[408] which require a special selection of cure chemistry (e.g., no Pt or Sn), as reviewed recently.[409] Another important use of silicone elastomeric coatings is in air bags. The subject has been reviewed from the European market perspective.[410] Silicone rubber emulsions are also used as water-repellent primer coatings, and sealers for exterior insulation.[411] The area of growing interest is the use of radiation-polymerizable silicone fluids, applicable to various types of silicone coatings (e.g., release, PSA, hard-coats, etc.). For a very broad coverage of the earlier literature of radiation-curable silicones, a review by Boutevin has already been recommended.[211] This gives detailed information regarding UV and electron beam radiation-initiated polymerization of acrylated siloxane, epoxy siloxanes, and also describes radiation-initiated hydrosilylation systems. Also, a converter's perspective of the radiation-curable silicone coatings was recently provided.[412] Silicone co-polymers, notably silicone polyureas and polyurethanes, are used widely in industry. They may be solvent coated, or delivered as emulsions. Many of such co-polymers require no cure, but they can also be developed as curable coating systems, for example, with moisture. The latter have recently been reviewed.[413] The formation of highly cross-linked films by plasma polymerization of low molecular weight siloxanes, for example, hexamethyldisiloxane, needs to be mentioned as an example of specialty coatings.[414]

Resin-based coatings require special attention as we witness a transition in this field from the more traditional resins, having random structures, as discussed previously, to the precursors with tailored structures, designed for coatings with an increasingly demanding set of requirements. The use of traditional silicone resins continues to grow.[415,416] Only a few examples of the use of functional silsesquioxanes for high-performance coatings—the area of exponential growth—would be given, as they can serve as an entry point to the literature. The use of curable polysilsesquioxanes in low dielectric coatings, needed for interlayer film in electronic devices, has been studied,[417–419] and reviewed recently.[41] Coatings made by the sol–gel processing of inorganic phase within the UV-cured organic phase have recently been reported.[420]

In the category of silicone coatings used for surface modification of the specific substrates, functional silicone fluids are often used, which can selectively interact with the chemical groups of the substrate, thus modifying its surface properties. The use of functional silicones in the textile industry has been discussed in a number of recent publications.[5,421,422] The use of different types of high-performace silicone-coated textiles, which include elastomers and resins, has recently been reviewed.[423] The use of functional silicones in personal-care products, for example, in shampoos and hair conditioners, mentioned before,[381] provides another well-known example.

3.12.4.4.1 Release coatings

Release liners serve to prevent sticky materials, for example, PSAs, from accidentally sticking together and to provide a means of delivering sticky materials (e.g., labels) from the manufacturers to the end users. They are made from various types of paper, often coated with polyolefins or polymer films, for instance polyesters or polyolefins, which are most often coated with silicone materials capable of forming a very thin (submicron) layer of elastomer with abhesive (anti-adhesive) characteristics. Other materials, such as fluoropolymers or fluorosilicones can be used, but most common release coatings are composed of cross-linked PDMS. Silicone release coatings have become an industry standard because of their desirable surface characteristics, and also because silicon chemistry offers a broad range of formulations for different coating and curing methods. Material aspects of silicones used for release coatings were discussed in COMC(1982) and COMC(1995),[1,2] as well as in many other major encyclopedias and polymer handbooks.[4,22] Curable silicone compositions for solvent-based (including emulsion) and solventless coatings are described in a large number of recent and older textbooks and monographs dealing with PSAs. A broad background information regarding this important field, and the selection rules for silicone release chemistry for a particular substrate and coating can be found in many sources.[424,425] In a recently published chapter, Kinning and Schneider[426] discuss the mechanism of abhesion of release coatings for PSAs. The pre-eminent role of silicones, among other release materials, is emphasized. Various means of deposition and curing of silicone release coatings are described. The basic chemistries of the condensation, hydrosilylation, free-radical, and cationic (e.g., epoxy) cross-linking are briefly discussed. The authors also address the key factors affecting release mechanism and the role of the controlled release additives (i.e., MQ resin). The chapter also includes the discussion of silicone organic co-polymers and co-polymer networks used to impart controlled, tight release, useful as backsize coatings for PSA tapes.[426] The key factors affecting the selection and performance of silicone release coatings were addressed in the recent report by Jones.[427] Solventless coatings, based on the addition cure, cationic polymerization of epoxy-substituted silicone fluids, and free-radically polymerizable (e.g., acrylate-functional siloxanes) systems, become increasingly popular with a primary driving force being the speed of coating and the environmental considerations.[428] The use of epoxy-functional siloxanes in the UV-initiated cationically polymerized systems has recently been discussed.[429–431] UV and electron beam-curable acrylate-functional siloxanes used in release coating applications are discussed in a number of reviews.[5,432] The information on radiation polymerization is also available from the proceedings of RadTech Conferences, and, for instance, from the internet pages of the Adhesives and Sealants Industry (ASI). The use of MQ resins to control the level of release, critical for some applications, has been discussed.[433,434]

3.12.4.4.2 Adhesives

Silicone adhesives are a generic class of materials encompassing sealants, encapsulants, and PSAs. Sealants and encapsulants were briefly discussed along with other silicone rubbers. Fundamental aspects of adhesion technology in silicones are discussed in a recent chapter by Parbhoo *et al.*[435] Silicone sealants and adhesives are also discussed in a couple of recent publications.[436–438]

Silicone PSAs are typical coating products, used in specialty tapes for the applications where unique characteristics of silicones (e.g., adhesion to low-energy surfaces, broad temperature range, bioinertness) are of interest. The mechanisms of pressure-sensitive adhesion, including the discussion of special features of silicone PSAs, have been reviewed.[439] Silicone PSAs are composed of polydiorganosiloxane network (most often PDMS) having dynamic mechanical characteristics adjusted by the use of MQ resin, as a tackifier, to satisfy the "Dahlquist criterion," as discussed in the recent chapter by Everaerts and Clemens.[440] The authors provide a critical account of the state-of-the-art in silicone PSAs, while discussing this class of materials within a broad scope of PSAs. Importantly, they point out the controversial nature of the interpretation of the role of MQ in the gum/resin blends, which was recently promulgated in at least a couple of references.[5,340]

Silicone PSAs find the application when a wide range of the temperatures at which they can be used is required.[441] Their chemical- and bioinertness makes them broadly applicable in healthcare,[442] including specially demanding soft-tissue applications.[443] The other hallmark of silicone PSAs is their good adhesion to moist surfaces and to the low surface-energy substrates, including silicone coatings. Thus, silicone PSA tapes are commonly used as splicing tapes by the film and release liner manufacturers. The most common are PSA formulations composed of the high molecular weight silanol-terminated linear polysiloxanes, blended and partially reacted ("bodied") with the silanol groups of the MQ resins in solution. The coatings of such blends are then peroxide cured at high temperatures. New generations of silicone PSAs have become available. Hydrosilylation-curable systems[444] and moisture-curable hot-melt PSAs have been recently reviewed.[445,445a]

3.12.4.4.3 Paints and antifouling coatings

Silicones may be used in paints either as the film-forming polymers, as surface-modifying components of organic co-polymers, or as additives. In high performance paints, silicones are used to impart weather and humidity resistance and to enhance high-temperature stability. Correspondingly, such paints are used for facade coatings.[446] Exterior coatings are often applied from emulsions, as discussed in recent reviews.[447–449] Zhang and Yang[449] discuss the preparation of siloxane–acrylic dispersions by the simultaneous free-radical and condensation reactions in the system composed of SiOH-functional PDMS, methacryloxypropyl trimethoxy silane, and acrylate monomers. The use of heat-resistant silicone paints has recently been reviewed.[450]

A relatively new class of applications consists of antifouling coatings. Biofouling is a serious problem in marine industry. Although traditional antifouling paints, containing heavy metals or biocides, are very effective at preventing biofouling, they are also toxic. As such, they are being systematically eliminated and replaced by the new generation of antifouling coatings, which provide the surface of a marine vehicle with the difficult-to-adhere/easy-to-release coatings. Silicone top coatings are often sprayed on the surface of the painted ship to form strongly adhering, tough, abrasion-resistant films. Some of those properties are difficult to balance. Silicone antifouling coatings have been reviewed in a number of recent papers.[451–455] The dependence of settlement and release of bioorganisms on PDMS elastomer surface energy has been studied.[456] In some antifouling systems, silicone oils are added as sacrificial additives into the silicone elastomeric networks. Test methods to control release characteristics of such coatings have been developed.[457]

3.12.4.5 Membranes

The use of silicones in membrane applications is relatively new. It is, however, a rapidly growing area as evidenced by a number of original papers and reviews published recently. Pervaporation with the use of polymer membranes has been recognized as a versatile separation process in the chemical industry.[458] A study of PDMS as an active layer in the composite pervaporation membranes for separation of alcohols and esters has been reported.[459] Two-dimensional cross-linked polysiloxane Langmuir–Blodgett films were applied to selective permeable membranes for nitric oxide sensors.[460,461]

The use of dense, organic catalytic polymer membranes for fine chemical synthesis is another area of tremendous growth. Silicones are considered by far the most studied polymer system for membrane reactors, as commented upon in a recent paper.[462] Such membrane reactors can be used for biotransformation, biodegradation, and fermentation in the production of ethanol,[463,463a] in the oxidation of cyclic alcohols to ketones by manganese porphyrins embedded in a PDMS membrane,[464] and in the oxidation of cyclohexane, using a catalyst consisting of iron phthalocyanine in zeolite Y occluded in a polydimethylsiloxane membrane.[465] The authors consider the resulting composite membrane as a model of the enzyme cytochrome P450, being embedded in a hydrophobic phospholipid layer.

In a series of papers, Kennedy and co-workers studied the amphiphilic networks and their membrane characteristics. The use of poly(pentamethyl)cyclopentasiloxane)[32] as an oxyphilic cross-linker in the novel tricontinuous membranes, consisting of hydrophilic and lipophilic polymers, was reported.[466] The presence of polysiloxane brought about high oxygen permeability, which was studied in the water-swollen membranes.[467] The use of polysiloxanes as sorbents,[468] and as carriers for the receptor molecules in the ion-exchange membranes,[469,470] was reviewed.

The use of POSSs as a support for the extractant for selective extraction of heavy metals was studied.[471] Sulfonated polysiloxanes were surveyed as solid acids and as supports for precious metal catalysts.[472]

Bridged polysilsesquioxanes having covalently bound acidic groups, introduced via modification of the disulfide linkages within the network, were studied as solid-state electrolytes for proton-exchange fuel cell applications.[473] Also, short-chain polysiloxanes with oligoethylene glycol side chains, doped with lithium salts, were studied as polymer electrolytes for lithium batteries.[474]

3.12.4.6 Additives

Siloxane polymers, having characteristics very different from any other polymers, have been commonly used as additives to produce or enhance a number of desirable physical properties in organic polymers ranging from water repellency, water vapor transmission, and oxygen permeability, to thermal stability. While silanes are commonly used as efficient coupling agents to improve interfacial adhesion between the dissimilar materials, silane-modified siloxane polymers and co-polymers used as coupling agents can introduce additional features, such as hydrophobicity.[475]

The unique surface characteristics of polysiloxanes mean that they are extensively used as surfactants. Silicone surfactants have been thoroughly studied and described in numerous articles. For an extensive, in-depth discussion of this subject, a recent chapter by Hill,[476] and his introductory chapter in the monograph he later edited,[477] are excellent references. In the latter monograph, many aspects of silicone surfactants are described in 12 chapters. In the introduction, Hill discusses the chemistry of silicone surfactants, surface activity, aggregation behavior of silicone surfactants in various media, and their key applications in polyurethane foam manufacture, in textile and fiber industry, in personal care, and in paint and coating industries. All this information (with 200 cited references) provides a broad background for the discussion of more specific issues covered in other chapters. Thus, surfactants based on silicone polyether co-polymers are surveyed.[478] Novel siloxane surfactant structures,[479] surface activity and aggregation phenomena,[480] silicone surfactants application in the formation of polyurethane foam,[481] foam control and demulsification,[482] applications in personal-care products,[483] and emulsification[484] are discussed. Other chapters survey the use of silicone surfactants as agricultural adjuvants,[485] and as surface modifiers.[486] Surfactant-enhanced spreading[487] and the ternary phase behavior of mixtures of siloxane surfactants, silicone oils, and water[488] are also covered. The chemistry, properties, and applications of organosilicone surfactant were reviewed in another article,[489] with the emphasis on the phenomena of defoaming, deaerating, and improved wetting of coatings.

Although silicone oils by themselves or hydrophobic particles (e.g., specially treated silica) are effective antifoams, combinations of silicone oils with hydrophobic silica particles are most effective and commonly used. The mechanism of film destruction has been studied with the use of surface and interfacial tensions, measurements, contact angles, oil-spreading rates, and globule-entering characteristics for PDMS-based antifoams in a variety of surfactant solutions.[490] A very recent study of the effect of surfactant composition and structure on foam-control performance has been reported.[380] The science and technology of silicone antifoams have recently been reviewed.[491]

In a series of early publications, Yilgör *et al.* evaluated siloxane co-polymers as surface-modifying additives for organic polymers.[492] The use of silicone acrylate additives to improve flow behavior of the UV-curable coating compositions and the effect of silicone on surface characteristics of the coatings has recently been reviewed.[493,494] The use of functional siloxanes in the modification of bulk characteristics of epoxy novolac resins has also been reported.[215] In this case, the elastomeric characteristics introduced with the incorporation of functional siloxanes were sought. Routes to silicone-toughened epoxy resins have also been discussed in another paper with the emphasis on structure–property relationship.[495] Tetraethoxysilane-modified polyols, called “siloxane-containing modifiers,” were used to alter the properties of photocurable epoxy resins.[496] The use of silicone resin particles of uniform size as fillers for silicone rubbers adds to the list of applications of such particles as processing aids and surface modifiers.[497]

3.12.4.7 Composites

The difference between nanocomposites, discussed in Section 3.12.3.4.3, and traditional polymer composites is the scale of the interface, as noted before. In composites, one can expect that the properties would be the weighed sum of the properties of the components of the composite. An excellent introduction to silicone composites is provided in the chapter on silicones in COMC (1982)[1] where it is noted that most of the commercial silicone elastomers should be considered composites, since they have to be, in most cases, reinforced with fillers and compounded with other modifiers. There is a large body of literature dealing with the modification of silicone elastomers with fillers. Many of them have been discussed in Section 3.12.4.2. Some of the resulting materials are difficult to qualify, as they may fall between silicone composites and nanocomposites. The use of special silicas and other novel fillers for the reinforcement of silicone rubbers has been reported. Mark and co-workers studied the reinforcing effect of bioinspired silicas,[498] the *in situ*- (sol–gel methodology) generated silicas,[499] and the *in situ*-made zirconia and titania.[500] Also, clay nanolayers have been studied as reinforcing fillers in silicones.[501] The use of Mn–Zn ferrite powder as nanofiller for PDMS was also reported.[502] Silylated silicates have been shown to reduce the modulus of silicone elastomers without affecting their ultimate strength.[503] Organic polymers, especially thermoplastics, can be used to reinforce silicone composites, for example, made of LSR, as discussed in recent papers.[504,504a,505]

On the other hand, silicones are used in organic composites. The application of alloys composed of the fully cured silicone rubber particles in a continuous thermoplastic phase, called thermoplastic silicone vulcanizate, which offers high-performance materials, has been reported.[506,507] Functionalized POSS was not only co-polymerized, but also blended with poly(methylmethacrylate) to study the effect of silsesquioxanes on the thermal stability of thermoplastics.[508]

The use of silicone elastomers for high-voltage applications (insulators and cable accessories) requires special formulations. Unusually, stringent requirements for these materials must be met.[509,510] Fluorosilicone rubbers, which offer some unique combinations of properties (e.g., chemical resistance and higher temperature stability), have attracted considerable attention and have been reviewed in recent publications.[511,512] It was noted that a modification of perfluoroether elastomers with silicone elastomer via hydrosilylation reaction opens the possibility of novel applications.[513]

Processing requirements for thermoset composites, with specific examples of silicones, were recently reported.[514] Composites based on the low molecular weight polysiloxanes for medical applications have been reviewed (in Russian).[515] Silicone rubber/hydrogel composites have been evaluated for medical applications.[516]

3.12.4.8 Ceramics

Silicon-containing ceramic precursors constitute a broad family of materials discussed thoroughly in a number of recent publications, where broad introduction into the field of modern ceramics is easy to find. Thus, Laine and

Sellinger[517] discuss Si-containing ceramic precursors, defined as "any chemical compound that transforms, when decomposed [. . .] to a glass or ceramic material," in three distinct classes: as precursors to ceramics composed of Si and N, Si and C, and Si and O. Here, precursors carrying only the organosiloxane linkages will be discussed. Among them, cyclic hydridomethyl cyclosiloxanes are mentioned, which, in the reaction with NH_3, form liquid-ceramic precursors, composed of cyclosiloxane and silazane linkages, which can be processed to silicon oxynitride (Si_2ON_2) ceramics. The work related to the generation of Si–O–C ceramics from silsesquioxanes is broadly discussed. Also, the synthesis of SiO_2 coatings with very low dielectric constants required for electronic circuitry are described. The preparation of silicon oxycarbide ceramic films by the pyrolysis of polysilsesquioxanes has been extensively studied.[518] An excellent, concise review by Zank of the pre-ceramic, polymer-derived oxycarbides has recently been published.[519] It contains a good selection of references (in 1997–1998). Zank discusses the advantages and the shortcomings of the use of different materials as ceramic precursors. Silsesquioxanes are compared with the organically modified silicates and modified (DT and MT resins) silsesquioxanes. Some possibilities of using silicones as the low-cost alternative to the highly branched resins and silsesquioxanes are also discussed. An earlier review compares different routes to ceramic matrix composites and points out the advantages of using pre-ceramic polymer precursors, such as polysilazanes and polysiloxanes[520] The manufacturing of ceramic components from materials in the system Si–Me–C–N–O (Me = Ti, Cr, V, Mo, Si, B, $CrSi_2$, $MoSi_2$, etc.) from pre-ceramic organosilicon polymers such as polycarbosilanes, silazanes, or siloxanes has also been recently described.[521] The ceramics–silicone processing (CSP) method is described as an inexpensive technology for continuous manufacturing of high-temperature superconductor wires.[522]

3.12.4.9 Biomaterials

It would be difficult to find a better opening statement to this paragraph than the one from a recent review on silicone biomaterials by Van Dyke: "Silicones are arguably the preeminent biomaterial, having been the most thorougly studied polymer over the last half-century, and particularly over the past decade."[523] The difference between "biocompatibility" (acceptance by the human body) and "bioinertness" (not readily being broken down by the body's systems) is clearly defined. Silicones are discussed in terms of their bioinertness, which is attributed to their hydrophobicity and chemical inertness. Medical applications of silicones are concisely surveyed. It is noted that the controversy over the medical effects of silicone breast implants triggered unprecedented research of silicones as biomaterials. Van Dyke provides references to the pertinent reports on this subject. In the aftermath of this controversy, the use of silicones in traditional applications expanded considerably, while the new applications (e.g., tissue engineering) were discovered. The applications of silicones in wound healing, in ophthalmic devices, and in drug delivery are briefly discussed and referenced. New developments in drug-delivery devices (silicone composites with hydrogel encapsulants), in medical coatings, and in tissue engineering (e.g., scaffolding for the growing nerves) have been pointed out. Silicones for medical and pharmaceutical applications have been a subject of a number of conferences and recent reviews.[524–526] There is a large body of literature regarding silicone materials designed for any of the major areas of medical applications. In orthopedic surgeries, the three most commonly used polymeric materials are poly(methylmethacrylate), ultrahigh molecular weight polyethylene, and silicone rubber. Their properties were compared in a recent review.[527] The use of silicone coatings on porous collagen–glycosaminoglycan (PCG) membranes as scaffolds for dermal replacement in burn victims has been studied and reviewed.[528] Silicones were also studied in the new applications as scaffolds for nerve regeneration.[529] Porous silicone rubbers find applications in the growing area of biotechnology, for example, for cells immobilization in bioreactors.[530]

From the large number of papers dealing with silicone-based breast implants, a well-referenced review on the scientific considerations regarding a "silicone syndrome,"[531] supplemented with a few other recent papers,[532–535] can serve as the entry point for further research. Silicone degradation reactions via hydrolysis and oxidation in relation to biomaterials have been reviewed.[536]

Silicones are frequently used in transdermal drug delivery. Recently, the use of loosely cross-linked silicone elastomer blends for this application was surveyed.[537] The mechanisms of controlled drug release in the silicone-based systems have been studied,[538] as silicones are evaluated for relatively new protein drug-delivery systems.[539]

Examples of silicones in ophthalmic application have been described.[540,541] However, some problems have been reported with the use of silicones in retinal tamponade.[542] Silicones are widely used in contact lenses because of their unusually good oxygen permeability and bioinertness, but the need for novel materials continues. Low-modulus fluorosiloxane-based hydrogel lenses with a wide range of water content and high-oxygen permeability have been described in a number of papers.[543–545]

In dentistry, silicones are primarily used as dental-impression materials where chemical- and bioinertness are critical, and, thus, thoroughly evaluated.[546] The development of a method for the detection of "antibodies" to silicones has been reviewed,[547] as the search for novel silicone biomaterials continues. Thus, aromatic polyamide–silicone resins have been reviewed as a new class of biomaterials.[548] In a short review, the comparison of silicones with their major competitor in biomaterials, polyurethanes, has been conducted.[549] But silicones are also used in the modification of polyurethanes and other polymers via co-polymerization, formation of IPNs, blending, or functionalization by grafting, affecting both bulk and surface characteristics of the materials, as discussed in the recent reviews.[550–552] A number of papers deal specifically with surface modification of silicones for medical applications, as described in a recent reference.[553] The role of silicones in biodegradable polyurethane co-polymers,[554] and in other hydrolytically degradable co-polymers,[555] was recently studied.

Research of biologically active silicone materials continues. The synthesis and characterization of polysiloxanes having bioactive pendant groups,[556,557] and the preparation of bioactive porous organic–inorganic hybrids for medical applications,[558] have been reported.

Bioadhesion is an area of research important in the selection of biomaterials (e.g., for implants). It is also critical in the development of the new biofouling coatings. A system for bioadhesion studies was developed, in which silicones with chemically and topologically (microengineered) modified surfaces were evaluated in the studies of the response to such surfaces of a diverse set of organisms.[559–561] A new study of micropatterning and surface modification of PDMS to control bioadhesion has been reported.[562]

Interfacial interaction between silicone and protein/starch microparticle,[563] and the use of polysiloxanes having hydrophilic groups for the stabilization of proteins against denaturation,[564] were studied.

3.12.5 Physical Properties

3.12.5.1 Surface Characteristics

As Mark remarked in his recent paper,[306] unusual surface properties of siloxane polymers permit them to serve in a variety of seemingly contradictory roles, and some of them have already been discussed in the preceding sections: release coatings and PSAs, antifoaming agents and foam stabilizers, just to name a few. Surface characteristics of siloxanes have been discussed on all levels of technical sophistication in almost all the literature sources regarding silicones, and in most polymer handbooks. In this review, many of the features have already been mentioned while discussing particular group of materials or applications. For an in-depth introduction, a chapter by Owen published in 1993 is recommended.[565] In a short recent chapter, Owen lists some exceptional properties of PDMS, such as low surface tension, low surface shear viscosity, hydrophobicity, spreading tendency, soft feel, etc., and discusses them in the context of the fundamental characteristics of polysiloxanes, such as weak intermolecular forces, chain flexibility, high bond energy, and the ionic nature of the siloxane bond.[566] A summary of the quantitative data for PDMS surface characteristics is provided, and the applications related to the unique surface properties of silicones are briefly discussed. Fearon and Owen surveyed silicone surface science opportunities discussing the fundamentals, in view of the recent polymer-dynamics theories, new analytical techniques, novel materials (nanocomposites, block co-polymers, novel surfactants, biomaterials surfaces), and came up with some interesting forward-looking statements.[567] Among many papers of Owen and co-workers regarding surface charactertics of siloxanes, a few recent reviews and papers need to be mentioned. Fluorosilicones, which are characterized with even lower critical surface tension than PDMS, have been reviewed.[568] Surface modification of fluorosilicones with plasma/corona treatment and the mechanisms of surface reorientation upon aging have been discussed.[569] The authors developed a model system for the studies of surface properties of silicones, which involves the deposition of the thin, self-assembled films of PDMS on a silicon wafer.[570] A number of other studies of the silicone surface properties have been reported. Thus, it was demonstrated that surface topology can be affected by the use of fluorinated cross-linkers in PDMS rubbers due to the phase separation, which leads to the fluoroalkyl enrichment on the surface of the coating.[571] It was determined that surface properties of silicones can be tailored by the use of fluorinated aromatic substituents.[572] The effect of surface deformation of soft materials (e.g., silicone rubbers, among other polymers) on the mechanism of wetting–dewetting has been studied.[573] Dynamic contact-angle analysis of the medical-grade PDMS networks was reported.[574]

In a recent review by Drake *et al.*,[47] the surface activity of linear polymers and co-polymers is discussed, based on many recent references. They refer to the research correlating surface characteristics of siloxanes to the nature of end groups[575] and to their concentration[576] in linear polymers. A few examples of the recent work on siloxane migration to the interfaces, with the emphasis on the behavior of block[577] and graft co-polymers,[578] and their blends with respective homopolymers are given. The role of co-polymers in the modification of the interfacial tension of polymer blends is also illustrated with the examples of preformed co-polymers,[579] and in the reactive blending processes.[580]

Hydrophobicity loss and recovery in silicone rubbers has been extensively studied and reviewed in a few recent publications with numerous references.[581,582] The ability to recover hydrophobicity after oxidation or contamination is considered as one of the important features determining the applicability of silicones in electrical and other outdoor insulation. The methods of studying of what is known as "aging and recovery" mechanisms are discussed.[583]

Interfacial behavior of different silicones was extensively studied, as indicated in Section 3.12.4.6. To add a few more examples, solution behavior of water-soluble polysiloxanes carrying different pendant hydrophilic groups, thus differing in hydrophobicity, was reported.[584] A study of the aggregation phenomena of POSS in the presence of amphiphilic PDMS at the air/water interface was conducted in an attempt to elucidate nanofiller-aggregation mechanisms.[585] An interesting phenomenon of the spontaneous formation of stable microtopographical surface domains, composed primarily of PDMS surrounded by polyurethane matrix, was observed in the synthesis of a cross-linked PDMS–polyurethane films.[586]

3.12.5.2 Bulk Characteristics

Bulk properties of polyorganosiloxanes are also unique among polymers. Many of the interesting characteristics of silicone fluids, rubbers, and resins have already been discussed. The subject was also extensively covered in COMC (1982) and COMC (1995).[1,2] The low-temperature elasticity, low crystalline melting point, fast crystallization, and mesophase properties of the higher alkyl-substituted polysiloxanes, unusually weak-temperature dependence of viscosity, and high-temperature stability would not make the list complete. All these material characteristics can be related to the structure of polyorganosiloxane molecules. This correlation is discussed in a concise, systematic manner by Dvornic in his recent survey of one of the most important of these unique features—high thermal stability of polysiloxanes.[587] He discusses the role of the siloxane bond structure, the conformational flexibility of polysiloxane chains and segments, intermolecular interactions, and how they are related to the very low activation energy of viscous flow, and points out the compensating effect of the increasing conformational disorder in reducing the temperature effect on the viscosity of silicone fluids. By referring to the recent paper by Interante and co-workers,[44] he discusses the anomaly of the increase in T_g of polydialkylsiloxanes with the increase in the size of substituents. He then proceeds with the discussion of the mechanisms of thermal and oxidative degradation and stability of siloxanes. In another, recently published, short account of the high-temperature stability of polysiloxanes, with citations from the well-established literature, Dvornic refers to the inherent strength of the siloxane bond, flexibility of the siloxane segments, and entropically higher stability of cyclic siloxane oligomers than that of the linear high molecular weight polymers at the degradation temperature as the key factors determining high-temperature behavior of polysiloxanes.[588] The mechanism of thermal degradation of polysiloxanes is a subject of continued studies,[589–591] including the use of reactive-force field simulations.[592] Photoaging of siloxanes has been surveyed, and discussed with the suggestions regarding photooxidation mechanisms.[593] Possible degradation mechanisms of silicone elastomers in high-voltage insulation applications have also been discussed, where factors such as electrical stress, corona, arcing, moisture, UV, and chemical attack have to be considered.[594] Various degradative reactions of silicones, including hydrolytic bond cleavage, metathesis reactions, oxidative degradation, and photodecomposition are discussed in the monographs by Brook[7] and Clarson.[595] A couple of the short recent surveys of silicone properties are mentioned.[596,597]

Investigation of the thermal decomposition of the novel architectures of POSS macromonomers and POSS siloxane co-polymers was reported.[598] Novel, thermally stable polysiloxanes with bulky side-chain tris(trimethylsilyl)hexyl, and reactive glycidoxypropyl substituents, were recently described.[599]

The importance of oxygen and moisture permeability of siloxanes has been discussed in Section 3.12.4.9. Among many new siloxane polymers and co-polymers, novel polyamide PDMS multiblock co-polymers were evaluated for gas permeability and thermomechanical properties.[600]

The characterization of what can be considered as material properties is part of any routine in the studies of new polymers. Thus, any major research paper on new silicone materials should be accounted for in this section. And that is, unfortunately, impossible.

3.12.5.3 Environmental Aspects

With the rapidly growing applications of silicones, it follows that there are concerns to be addressed regarding environmental aspects of the use of these materials. The stability of silicones has been and continues to be thoroughly surveyed, driven by their use in medicine and in a harsh environment. The question regarding their long-term environmental impact has also been intensively investigated. In the *Handbook of Environmental Chemistry*, a large part (over 300 pages) of the volume on *Antropogenic Compounds* is dedicated to organosilicon materials with the intention to give a comprehensive overview of the environmental impact of commercially significant silicones. Several contributions to the volume, edited by Chandra, cover various aspects of the issue, including the question of how silicones enter the environment.[601] Detection of the presence of silicones,[602] eco-relevant properties of silicones,[603] eco-toxicity testing,[604] environmental behavior of alkoxysilanes, silanols, and siloxanols,[605] volatile methylsiloxanes,[606] PDMS,[607] and polyethermethylsiloxanes[608] are thoroughly surveyed. The regulatory status of silicones in the US,[609] in Europe,[610] and in Japan[611] is discussed. The last chapter covers the silicon industry and its general environmental impact.[612] The environmental occurrence of polydimethylsiloxane has been discussed in many publications.[613,614] The fate of polydimethylsiloxane coatings[615] and PDMS in other forms in biosolids-amended landfields[616] has been studied. Also, the modeling of polydimethylsiloxane degradation in soil has been reported.[617] The devulcanization of silicone rubbers to facilitate recycling has been described in a number of publications.[618–621] A couple of very interesting paragraphs regarding the fate of polysiloxanes in the environment can be found in a recent chapter by Graiver and Fearon.[622] While discussing general environmental issues, they point out that following extensive studies of the effect of siloxanes on the environment, volatile siloxanes became the preferred non-aqueous cleaning agents in optics, surgical instruments, and aerospace components, because they do not contribute to the "greenhouse" effect, and because they degrade relatively easily instead of accumulating in the atmosphere.[622] They refer to the recent article by Xu *et al*.[623] for a recent account of the fate of other silicones in the environment. Waste minimization in the synthesis of methylchlorosilanes is another important issue. The residue cleavage might serve to obtain desirable volatile chlorosilanes. DP has been evaluated from an environmental perspective in a recent review.[624]

3.12.6 Analytical Methods

A pre-1991 monograph on the analysis of silicones is still a valuable resource.[625] Over the last decade, progress in the analytical techniques greatly facilitated an explosive growth in material science. Silicones were no exceptions. Silsesquioxanes have been known for decades, but only recently can one, with confidence, deal with them as well-defined molecular entities. This is perhaps as much because of the improved methods of their synthesis, as because of the novel methods of their characterization. Dendrimers, and hyperbranched polymers, polymer networks and polymer surfaces, and porous membranes can all be analyzed at a level of sophistication unimaginable only a decade ago. Vastly refined traditional analytical methods of NMR and IR spectroscopies, chromatography, and surface analysis—all of them routinely applied in the studies of novel silicone molecules and high polymers—are now available. In their chapter, Fearon and Owen[567] briefly introduce various modern analytical techniques in microscopy, surface analysis, in measuring surface forces, and polymer microstructure. A few examples of the use of novel analytical methods in the elucidation of silicone network structures are given first to illustrate the breadth of available techniques for bulk properties characterization. The use of Brillouin scattering,[302] pulse-propagation technique,[303] and small-angle scattering,[300] was already mentioned. Molecular orientation in uniaxially stretched silica-filled networks of PDMS was investigated using FTIR dichroism and birefringence methods.[626] The use of solid-state NMR spectroscopy to study molecular motion of PDMS and silica-filled network structure was reviewed, and the results were compared with other methods.[627] The new test method (multiple-cycle recovery) for the characterization of mechanical properties of silicone elastomers and hydrogels intended for the use in medical devices has been described.[628]

Linear and cyclic PDMS, including high molecular weight fluids, were demonstrated to be distinguishable by Raman spectroscopy when combined with the multivariate data processing algorithms.[629] Small-angle neutron scattering was also used to study the conformations of cyclic and linear PDMS in the melt.[630] Photoluminescence of cyclosiloxanes, variously substituted with methyl and phenyl groups, with chromophore behavior was studied.[631] Temperature dependence of the free volume in pure and silica-filled polydimethylsiloxane was studied using positron-annihilation lifetime spectroscopy.[632]

The use of neutron reflectivity at liquid interfaces, which is a method sensitive to both surface roughness and surfactant layer thickness, was reviewed with the examples of polydimethylsiloxane-surfactant layers.[633] Sum-frequency generation (SFG) vibrational spectroscopy was applied to study surface restructuring behavior of PDMS in water in an attempt to understand antifouling properties of silicones.[634,635]

The analysis of gas plasma-modified polydimethylsiloxane elastomer surfaces using attenuated total-reflectance FTIR spectroscopy was discussed.[636]

AFM has become a standard technnique in the analysis of surface topology. A couple of recent papers are relevant.[571,586] The methods of determination of silicones in biological matrices have been developed as the situation demanded, and have been reviewed.[637]

Silicone materials play an active role in enabling some of the analytical techniques. Thus, surface-modified silicone was described as a substrate in plastic microarray devices for DNA analysis.[638] Thermally stable aryl-substituted siloxanes are often used as stationary phases in capillary-gas chromatography.[639] The use of silicone membranes in various separation techniques was already mentioned.

3.12.7 Future Trends

The recently published chapter by Graiver and Fearon under the title *Polysiloxanes: Direction of Applications and Perspectives*[622] addresses many questions concerning the future of silicones. As with everything else in silicones, their discussion also starts with DP. They stress the need to find less energy-wasteful processes for the synthesis of basic precursors, which would not require the complete reduction of silica to elemental silicon. Structural elements in polysiloxanes, which, in their opinion, would/should be further exploited, include the use of vacant *d*-orbitals of the silicon atoms. This might affect thermal, electrical, and radiative energy of novel, silicone-based materials. The authors predict growth of the applications of polysiloxanes in harsh environment, where the abrupt changes in conditions have to be tolerated. Novel, one-component RTV systems need to be developed, and the elastomers with improved physical properties (e.g., containing phenyl groups) will be developed. Practical aspects of hyperbranched and dendritic polymers are mentioned primarily in relation to the modification of standard silicone products. The role of spatially oriented polysiloxanes is expected to grow, as they can offer improvements in mechanical properties. Silicone organic compositions are given a lukewarm assessment, as if they were not yet making strong enough inroads. Surprisingly, high expectations are placed on IPNs, as though the co-polymer networks and nanocomposites were only laboratory curiosities, which they are not. A whole field of silicone biomaterials is essentially neglected, which is, perhaps, not surprising, considering the contentious nature of some of the medical applications of silicones at the time, when the predictions were made. As previously mentioned, in the aftermath of this controversy, applications of silicones as biomaterials grow, and there is little doubt that they will continue to find new niches. In another already-cited paper,[567] while discussing new opportunities of silicone surface science, Fearon and Owen predict no competition for silicones in the area of very flexible, low surface energy materials, but they envision a growing role of highly fluorinated silicones, for example, polymethylnanofluorohexylsiloxanes, with surface energies considerably lower than that of PDMS. Their short, insightful remarks regarding many aspects of silicones are well worth reading.

The future of organosilicon chemistry as viewed from the academic vintage point seems to be even brighter. Corriu,[640] in his introductory comments to the special issue of the *Journal of Organometallic Chemistry*, hinted on some possible answers to the question: “Where organosilicon chemistry is going?” He pointed out that research in organosilicon chemistry ranges from biochemistry to the electronics, covering all aspects of chemistry (molecular and biomolecular, coordination and inorganic, macromolecular, solid state and physical), physics, and material science. He considers the introduction of organosilicon chemistry into material science as one of the most exciting fields of investigation, with an increasing use of polysilsesquioxanes, inorganic/organic hybrids, and nanoporous materials. He is convinced that organosilicon chemistry will be involved, at least in part, in a new chapter of chemistry.

If we extend this vision to the biocatalysis at silicon, as reported in some of the recent papers,[641,642] and continue learning from nature how to be “bioinspired” in making nanoporous silicas and other membranes, then, what seemed to be true in Goody’s remark about liquid crystals, might also apply to the whole field of silicones: “new field lies open for the development of materials for which their design is only limited by human imagination.”[256]

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3.13
Germanium Organometallics

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3.13.1 Introduction

A substantial amount of research has been conducted in the area of organogermanium chemistry since the time of the last comprehensive review.[1] In the interim, some detailed reviews have appeared.[2,3] Significant developments in the chemistry of both germanium(IV)- and germanium(II)-containing compounds, as well as in the area of catenated organogermanium compounds containing single and multiple Ge–Ge bonds, have occurred. Other aspects of the chemistry of this element have also been intensely investigated. The purpose of this chapter is a systematic and in-depth survey of organogermanium chemistry, focused mainly on the synthesis, structures, and reactivity of species containing at least one germanium–carbon bond.

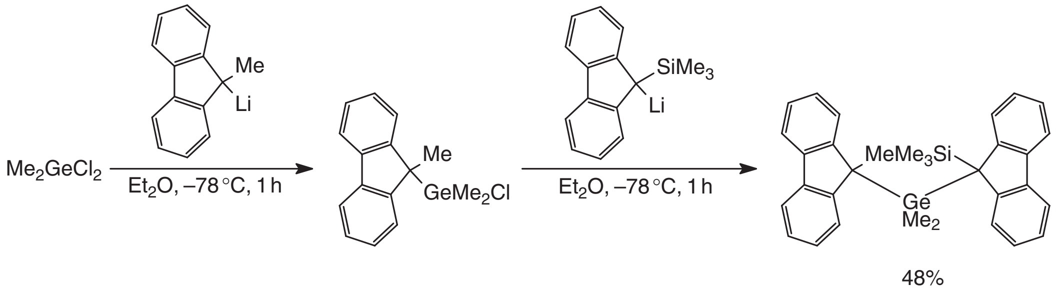
3.13.2 Compounds with Germanium–Carbon Bonds

Common methods for the formation of germanium–carbon bonds, including reactions of germanium halides with organolithium or Grignard reagents, are still used and have yielded some interesting new compounds. In addition, several novel methods for Ge–C bond formation have also been developed since the field was last reviewed.[1]

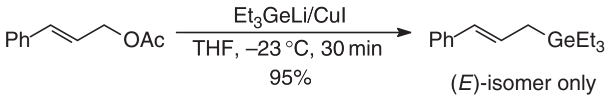
3.13.2.1 Preparation

3.13.2.1.1 Preparation from organometallic reagents

Germanium complexes containing a fluorene moiety exhibit interesting electronic properties, and species containing two such substituents oriented in a parallel fashion have been prepared from lithium salts of the corresponding fluorene (Equation (1)).[4] Allylgermanes have a number of synthetic applications and can be prepared with high regioselectivity by implementing a germylcuprate reagent (Equation (2)).[5] Germanium metallocenes bearing one (Equation (3)) or two (Equation (4)) ferrocenyl substituents were prepared and structurally characterized.[6]



(1)



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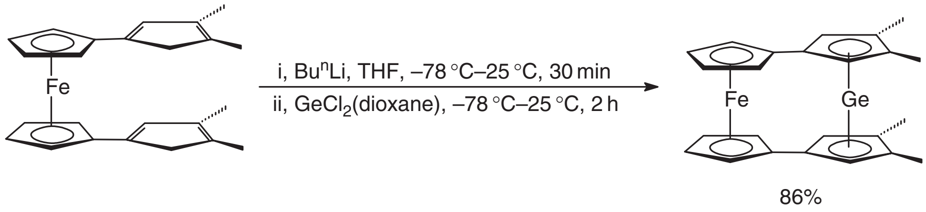

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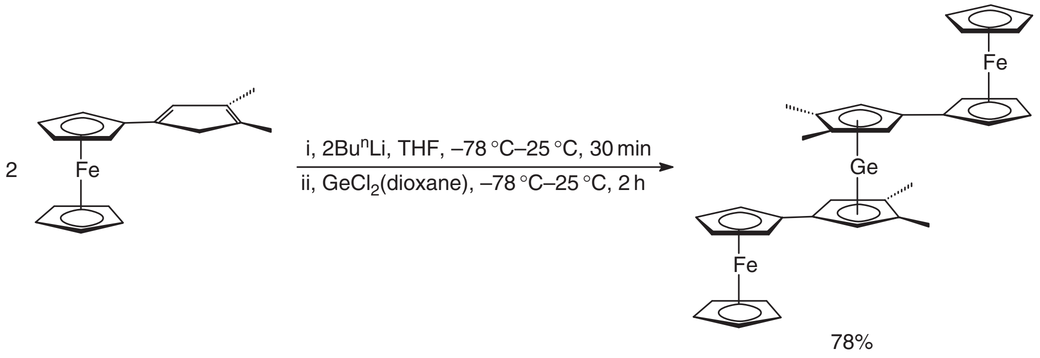
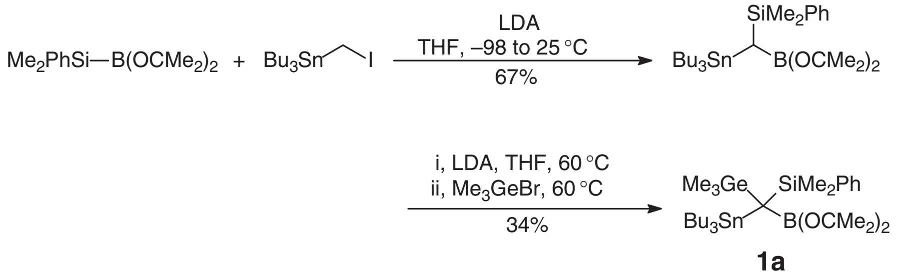
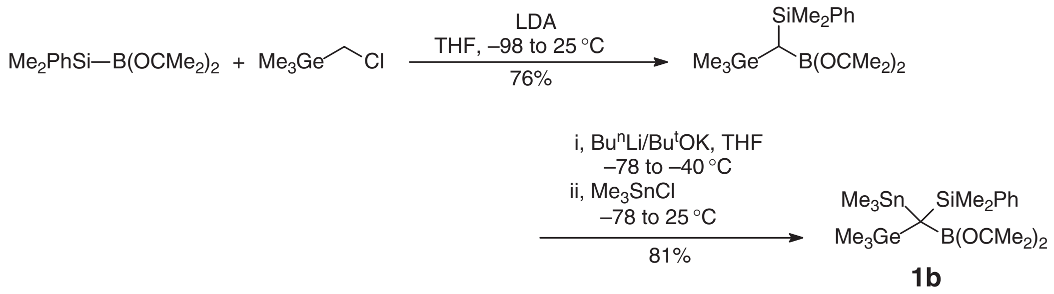


(4)

The tetrametalmethane species **1a,b** which contains carbon bonded to germanium, silicon, tin, and boron have been obtained (Equations (5) and (6)),[7] and the overall yield of **1a,b** varies with the order of attachment of the different metals.



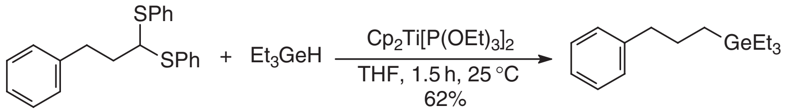
(5)



(6)

3.13.2.1.2 Other syntheses

In addition to the common methods of synthesis, it has been shown that the desulfurization of thioacetals yields organogermanes (Equations (7) and (8)) with excellent selectivity in some cases (Equation (9)).[8] Ring-opening reactions of strained [1]ferrocenophanes furnish germanium-substituted ferrocenes[9,10] (Equation (10)).[9]



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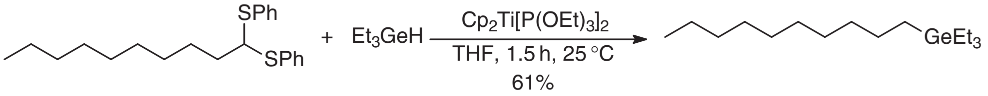

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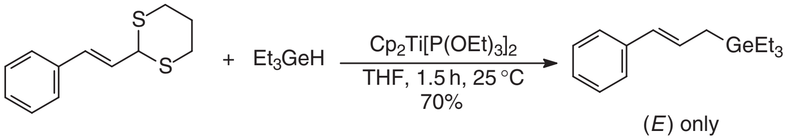

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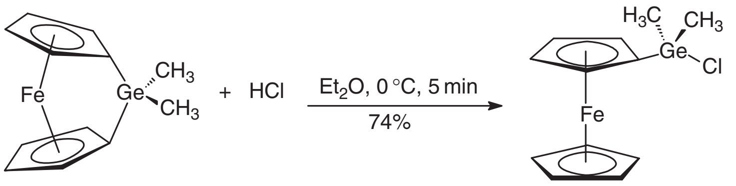


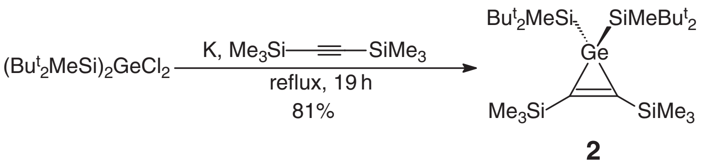
(10)

3.13.2.2 Intracyclic Germanium–Carbon Bonds

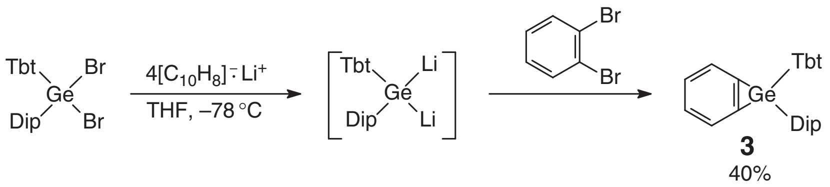
3.13.2.2.1 Small rings

3.13.2.2.1.(i) Three-membered rings

In addition to the well-known germanorbornadienes several three-membered cyclic germanium-containing compounds have been reported,[11–13] including the germacyclopropenes **2** (Equation (11))[12] and **3** (Equation (12)).[13]



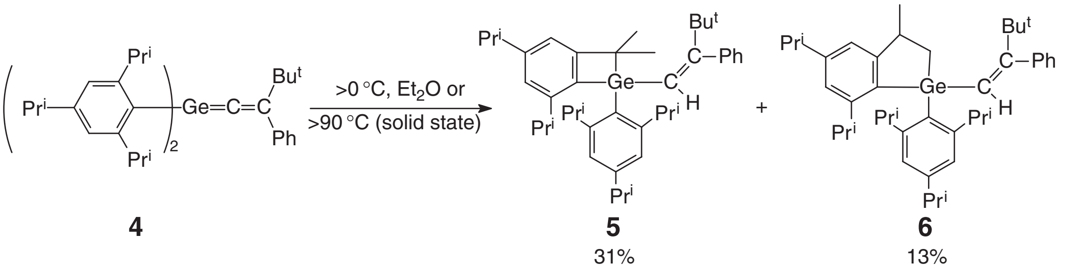
(11)



(12)

3.13.2.2.1.(ii) Four-membered rings

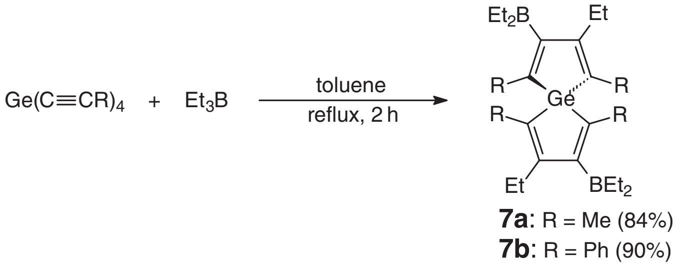
A number of four-membered cyclic germanium compounds have been prepared and characterized.[14–16] Mild thermolysis of the germapropadiene[15] **4** yielded the four- and five-membered heterocycles **5 and 6** (Equation (13)).[16]



(13)

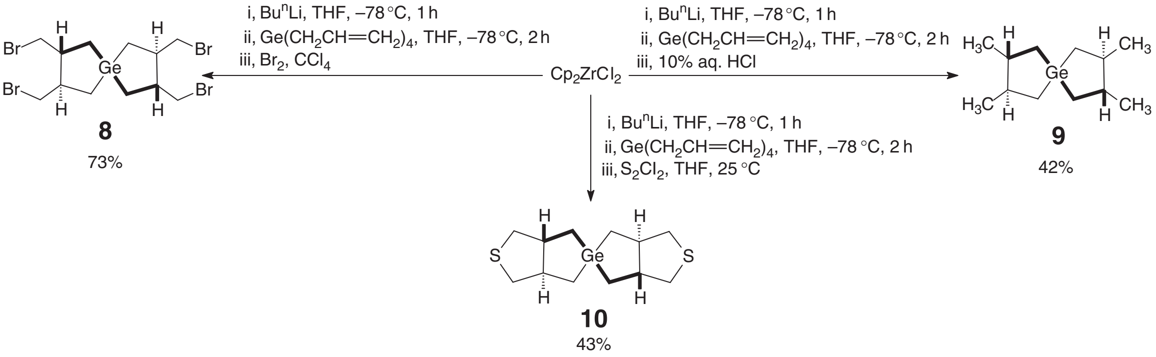
3.13.2.2.1.(iii) Five-membered rings

The synthesis and reactivities of germoles have been well documented and new aspects of their chemistry have been developed.[17–25] Several spirocyclic species have been prepared including the 1,1′-spirogermole **7**, as shown in Equation (14),[21] and the compounds **8–10**, as shown in Scheme 1.[20]

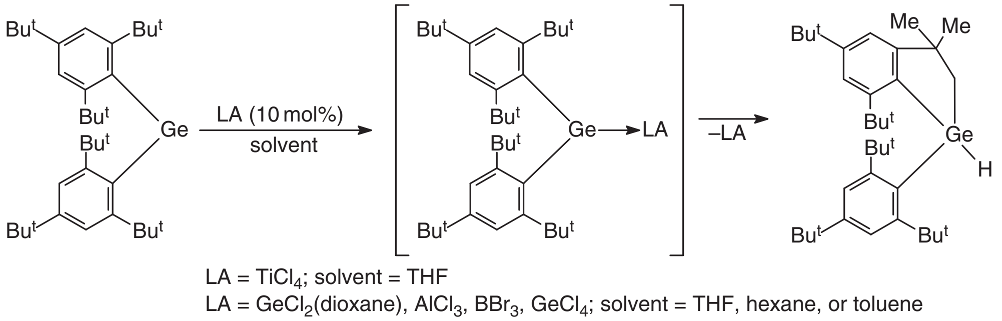


(14)

Other five-membered germanium heterocycles were prepared by the Lewis acid-catalyzed C–H insertion of a germylene (Equation (15)),[26] thermal dissociation of a germaketenethioacetal and trapping of the resulting germylene **11** (Equation (16)),[27] and from the zircona-bicyclic complexes **12** and **13** (Scheme 2 and Equation (17)).[28]



Scheme 1



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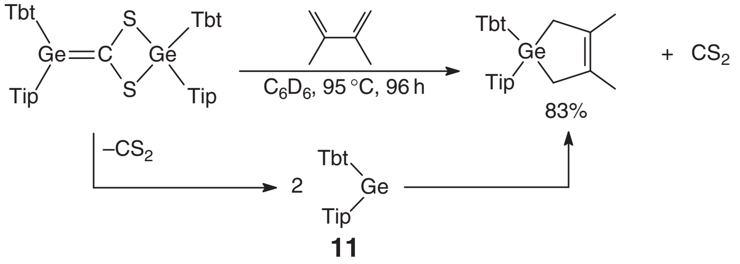

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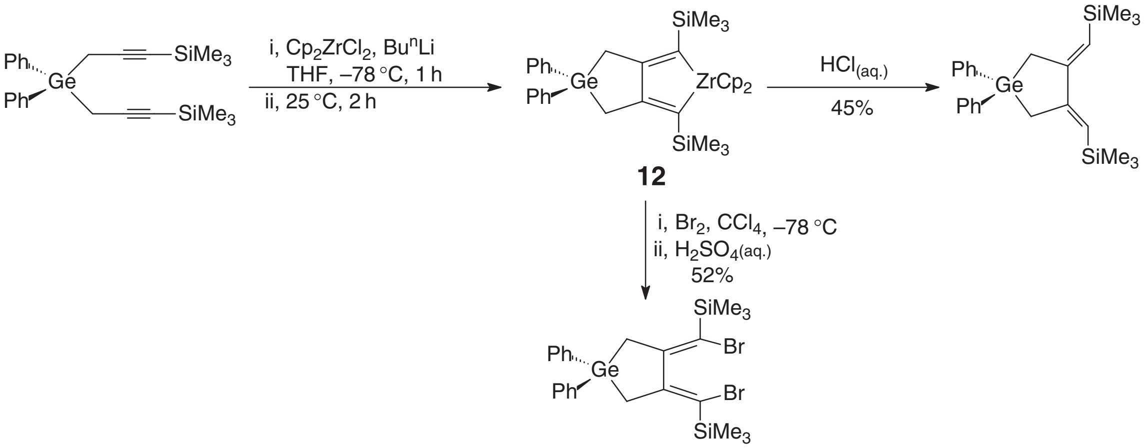
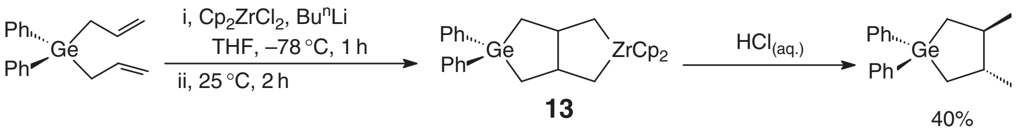
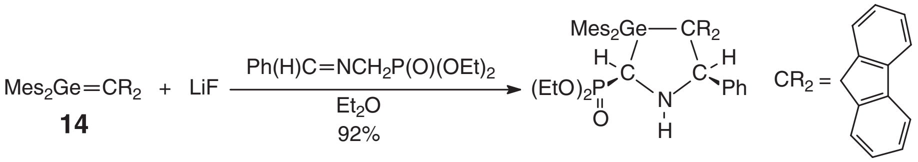


Scheme 2



(17)

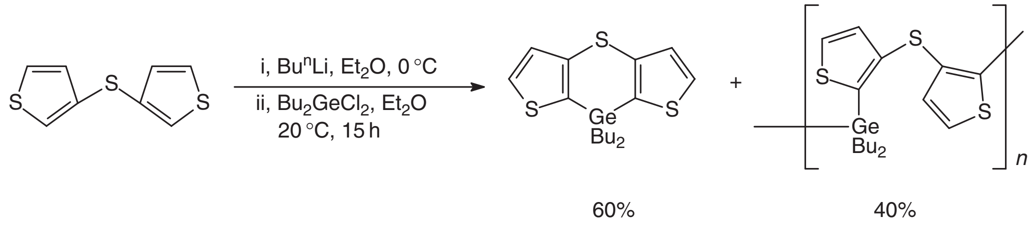
Reaction of the germene **14** with LiF in the presence of iminoesters or iminophosphonates (Equation (18)) leads to 3-germapyrrolidines.[29]



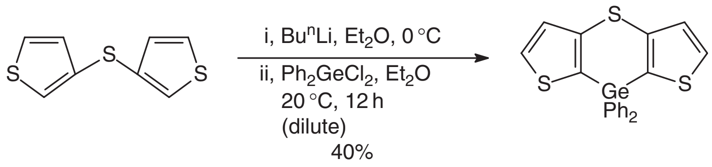
(18)

3.13.2.2.1.(iv) Six-membered rings

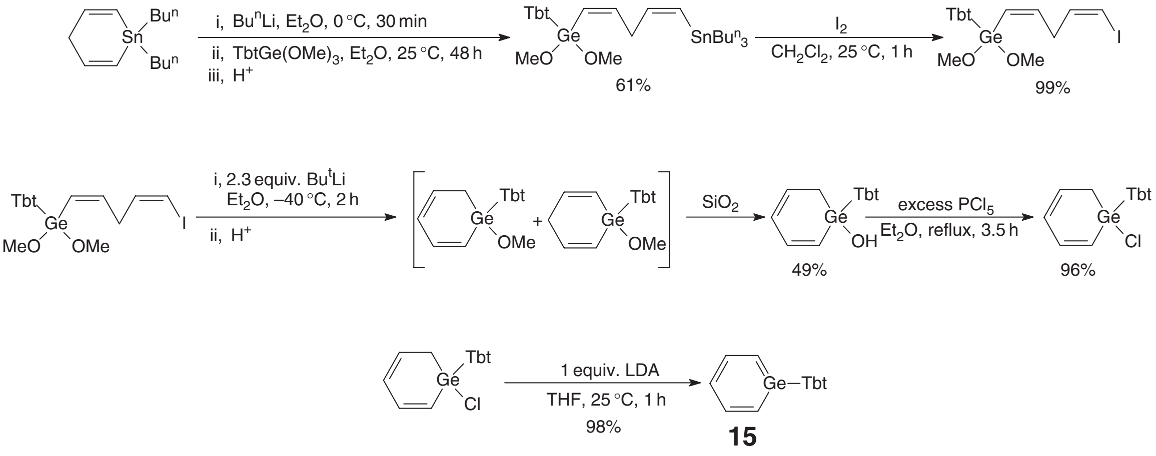
A stable germabenzene **15** has been prepared in several steps (Scheme 3) and its structure was determined (Figure 1, Table 1).[30] The germabenzene ring is planar suggesting that the π-electrons are delocalized. A fused tricyclic compound containing a six-membered germanium heterocycle and peripheral thiophene rings was isolated along with a germanium/thiophene polymer (Equation (19)).[31] When the germanium precursor employed is Ph_2GeCl_2 rather than Bu_2GeCl_2, selectivity of the products can be achieved depending on the concentration of Ph_2GeCl_2 used (Equations (20) and (21)).[31]



(19)



(20)



Scheme 3

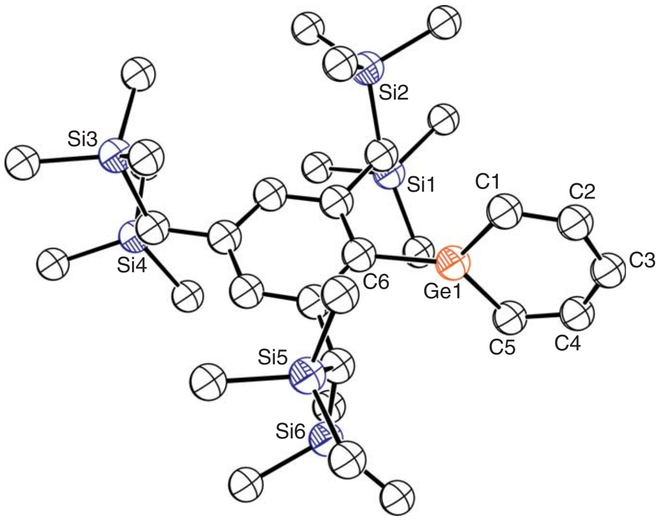
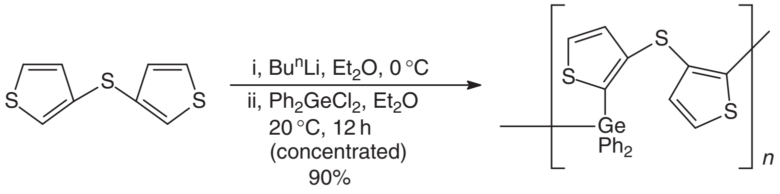


Figure 1 ORTEP diagram of the germabenzene species **15**. Reproduced from Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc*. **2002**, *124*, 6914–6920.

Table 1 Selected bond lengths (Å) and angles (°) for **15**

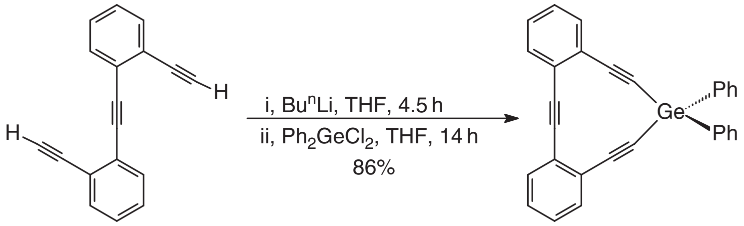
Ge(1)–C(1)	1.829(2)	C(1)–Ge(1)–C(5)	105.81(9)
Ge(1)–C(5)	1.827(2)	C(1)–Ge(1)–C(6)	125.61(8)
Ge(1)–C(6)	1.932(2)	C(5)–Ge(1)–C(6)	128.56(8)
C(1)–C(2)	1.389(3)	Ge(1)–C(1)–C(2)	117.9(2)
C(2)–C(3)	1.389(3)	C(1)–C(2)–C(3)	126.6(2)
C(3)–C(4)	1.385(3)	C(2)–C(3)–C(4)	125.5(2)
C(4)–C(5)	1.396(3)	C(3)–C(4)–C(5)	126.6(2)
		Ge(1)–C(5)–C(4)	117.8(2)



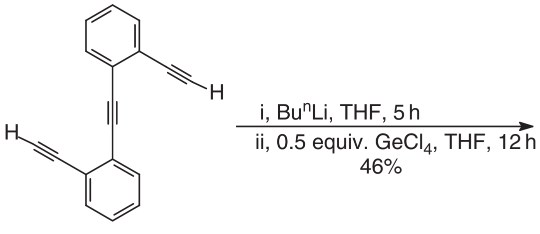
(21)

3.13.2.2.2 Larger rings

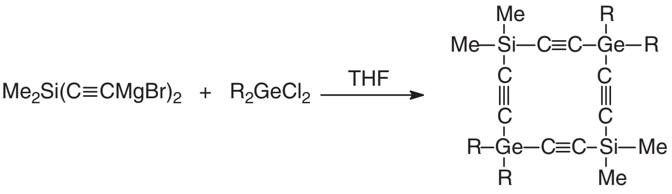
An 11-membered ring system (Equation (22))[32] and a spirocyclic derivative containing two 11-membered rings (Equation (23))[33] have been prepared and structurally characterized. The acetylenic functionalities of both of these species can complex nickel[32] or cobalt metal centers.[33] Twelve-membered rings containing acetylenic groups were obtained using Grignard precursors (Equations (24) and (25)) and an 18-membered ring was also obtained via this process (Equation (26)).[34]



(22)

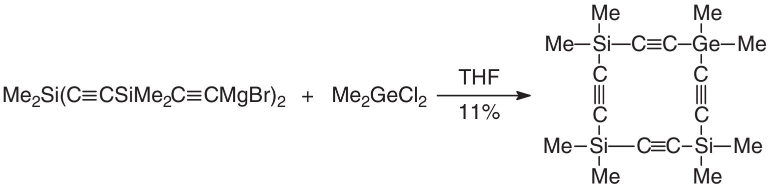


(23)



R = Me (13%)
R = Pr^i (11%)

(24)



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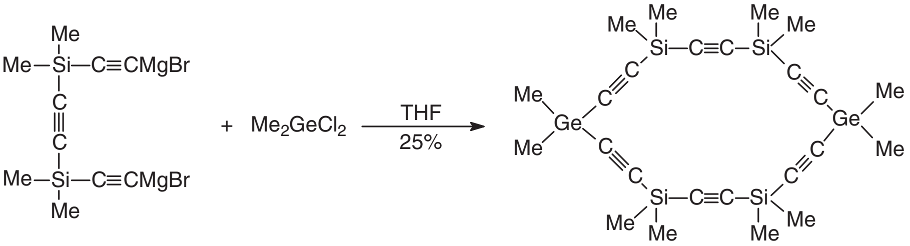


(26)

3.13.2.3 Organofunctional Germanium Compounds

A variety of transformations for the preparation of organogermanes bearing one or more functionalized organic ligands have appeared.[21,35–43] Tetraalkynyl-functionalized germanes have been prepared from alkali salts of the corresponding alkynes and halogermanes[21,36] (Equations (27) and (28)).[21] A trifluoromethyl group can be transferred to germanium via transmetallation (Equation (29))[37] and perfluoronated organogermanes were obtained by direct fluorination (Equations (30) and (31)).[38]

$$\mathrm{GeCl_4} + 4\mathrm{NaC{\equiv}CMe} \xrightarrow[\text{reflux, 20 h}\ 59\%]{\text{toluene}} \mathrm{Ge(C{\equiv}CMe)_4} \tag{27}$$

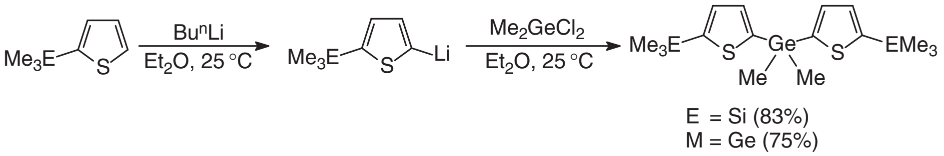
$$\mathrm{GeCl_4} + 4\mathrm{KC{\equiv}CPh} \xrightarrow[\text{reflux, 20 h}\ 54\%]{\mathrm{Et_2O}} \mathrm{Ge(C{\equiv}CPh)_4} \tag{28}$$

$$\mathrm{Ph_3GeCl} + \mathrm{Cd(CF_3)_2{\cdot}glyme} \xrightarrow[\mathrm{CHCl_3}\ 72\%]{} \mathrm{Ph_3GeCF_3} \tag{29}$$

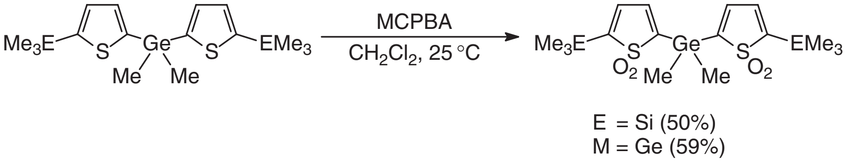
$$(H_9C_4)_4Ge \xrightarrow[\substack{-25\text{ to }0\,°C\\ \text{1,1,2-trichlorotrifluoroethane/NaF}\\ 72\%}]{He/F_2} (F_9C_4)_4Ge \qquad (30)$$

$$(H_7C_3)_4Ge \xrightarrow[\substack{-25\text{ to }0\,°C\\ \text{1,1,2-trichlorotrifluoroethane/NaF}\\ 76\%}]{He/F_2} (F_7C_3)_4Ge \qquad (31)$$

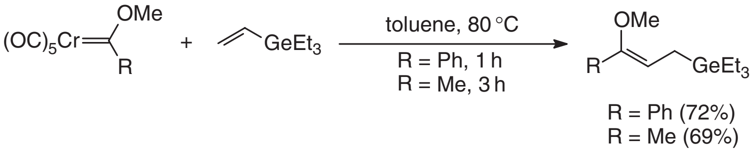
Various other types of compounds bearing functionalized ligands have been reported. Compounds containing germanium-substituted thiophenes were synthesized (Equation (32)) and their oxides were also prepared (Equation (33)).[41] Germanium-substituted enol ethers can be obtained by reaction of vinylgermanes with Fischer carbene complexes (Equation (34)) and alkenyl-functionalized chromium carbenes can be employed for the preparation of germanium-substituted 2-alkoxy-1,3-butadienes (Equation (35)).[42] The synthesis of the synthetically useful *β*-hydroxygermane **16** can be carried out in four steps starting with a vinylgermane (Equation (36)).[43]



(32)



(33)



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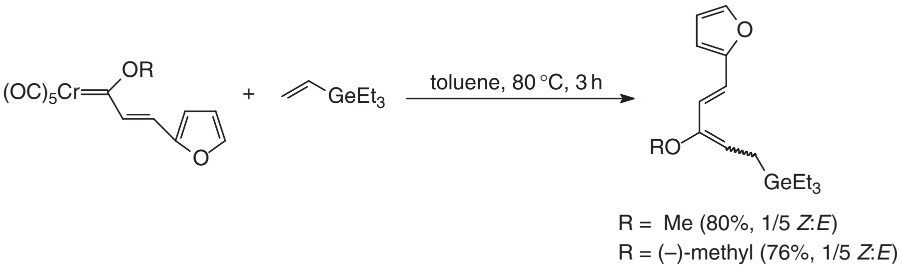
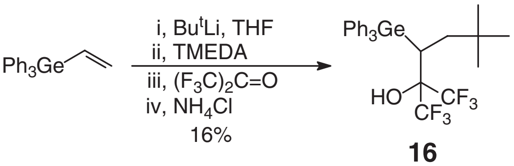


(35)



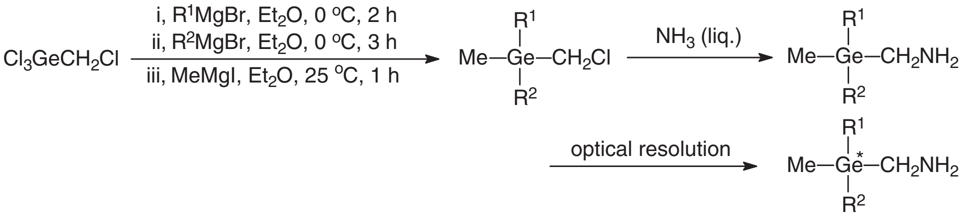
16

(36)

The preparation of resolved species which are chiral at the germanium metal center have been reported (Equation (37), Table 2)[44–47] as have species containing biologically important ligands[48–52] including derivatives of *α*-amino-phosphonic acid.[48–50]

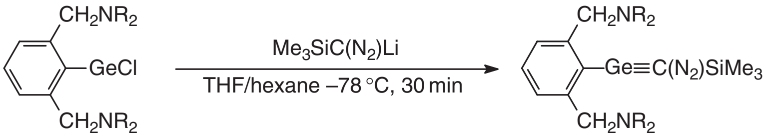
Table 2 Experimental data for compounds prepared in Equation (37)

R^1	R^2	*Yield (%)*	*Specific rotation (CH_2Cl_2) (°)*	*Optical purity (% ee)*
Ph	o-$CH_3C_6H_4$	14	−7.1	99
Ph	$C_6H_5CH_2$	14	+10.0	99
o-$CH_3C_6H_4$	$C_6H_5CH_2$	30	+6.0	98
o-$MeOC_6H_4$	$C_6H_5CH_2$	17	+21.1	97



(37)

A few examples of the species containing germanium–carbon multiple bonds have been reported, and a review[53] has appeared. The germanium–carbon triply bonded species **17** can be prepared from the germylenes **18** (Equation (38))[54] and the bis(germaethene) **19** has been reported which contains conjugated Ge═C double bonds and a C–C triple bond (Scheme 4).[55] In addition, the germaphosphaallene $Mes_2Ge{=}C{=}P(C_6H_2Bu^t_3\text{-}2,4,6)$ has been isolated.[56]



18a: R = Et
18b: R = Pr^i

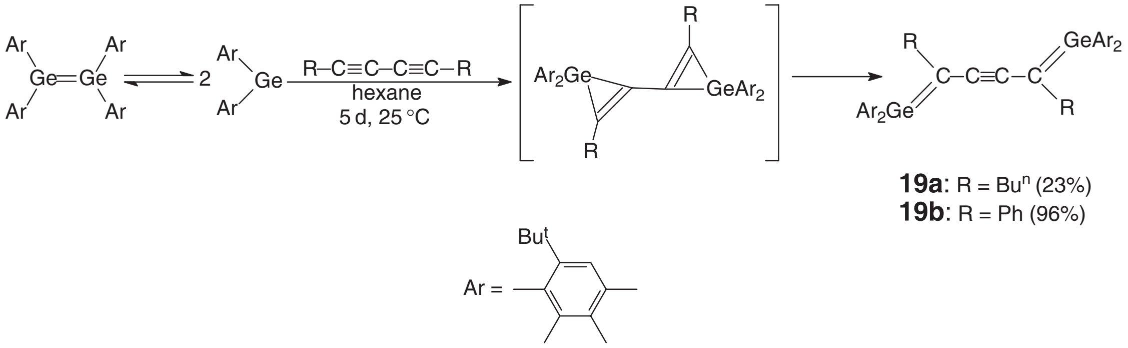
17a: R = Et (75%)
17b: R = Pr^i (40%)

(38)

3.13.2.4 Chemical Properties

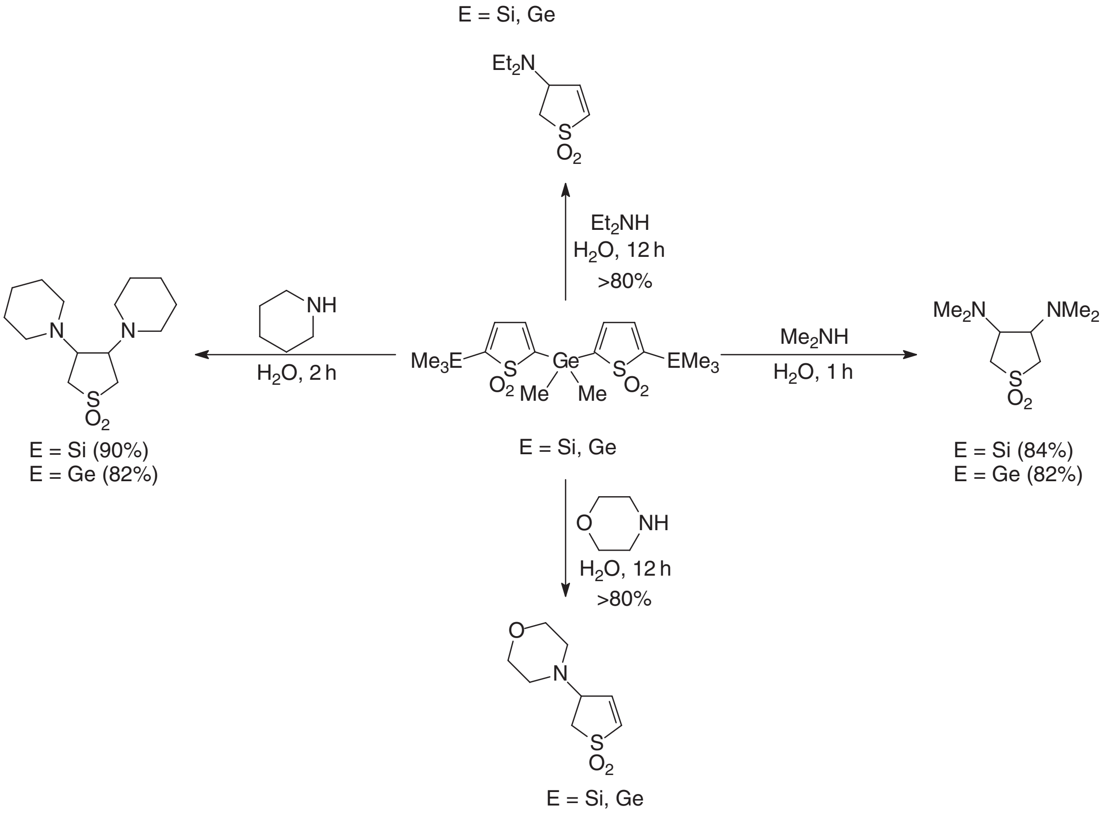
3.13.2.4.1 Cleavage of the Ge–C bond

Several new types of Ge–C cleavage reactions have been reported where the departing organic group is a functionalized species. Secondary amines undergo nucleophilic addition to germanium-substituted sulfones to yield sulfolanes



19a: R = Bu^n (23%)
19b: R = Ph (96%)

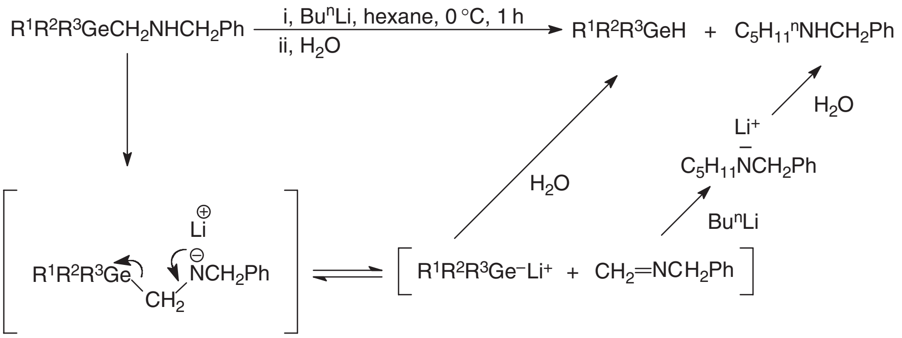
Scheme 4



Scheme 5

(Scheme 5).[41] Germyl-substituted methylamine compounds undergo germanium–carbon bond cleavage in reactions with Bu^{n}Li and the mechanism of the process has been elucidated (Scheme 6, Table 3).[57] Acylorganogermanes and related derivatives undergo several radical cyclization processes involving Ge–C bond cleavage.[58–60]

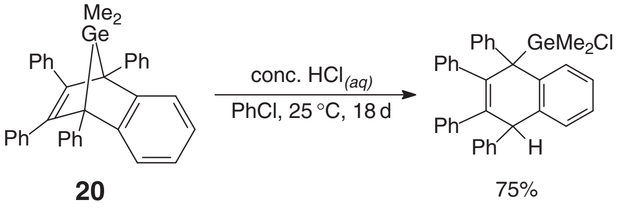
Germanium bond cleavage in strained cyclic species is a common mode of reactivity, although selectivity over which bond is broken is not often observed. However, germanorbornadienes such as **20** have been reported to undergo cleavage reactions of only one of the strained bridging bonds in the presence of HCl to furnish bicyclic products with chlorogermyl substituents (Equations (39) and (40)).[61]



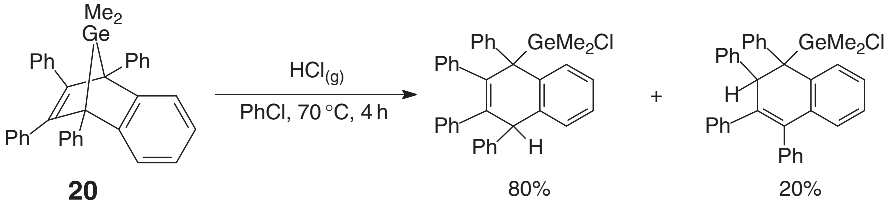
Scheme 6

Table 3 Experimental data for compounds prepared in Scheme 6

R^1	R^2	R^3	*Germyl amine* (mmol)	*Bu^nLi* (mmol)	*Hydride yield* (%)	*Amine yield* (%)
Et	Ph	Ph	1.3	1.5	63	33
Et	Ph	Ph	1.3	2.9	91	84
Et	Ph	Ph	1.3	4.0	68	0
Et	Et	Ph	1.3	2.9	68	83
Et	Et	Et	1.3	2.9	13	15
Et	Et	$PhCH_2$	1.3	2.9	83	67



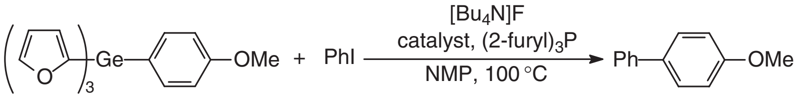
(39)



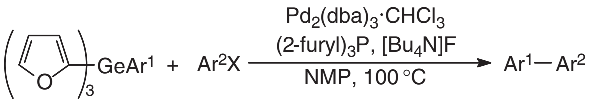
(40)

3.13.2.4.2 Coupling reactions

The use of germanium-containing reagents in coupling reactions has received considerable recent attention. Tri(2-furyl)germane derivatives have been employed in numerous palladium-catalyzed coupling reactions involving cleavage of the Ge–C bond (Equations (41) and (42), Tables 4 and 5).[62,63] Related species also have been used for a variety of other transformations including the radical reduction of organic halides,[64,65] and an example is shown in Equation (43).[65]



(41)



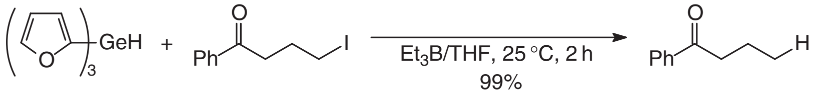
(42)

Table 4 Experimental data for compounds prepared in Equation (41)

Catalyst	*Time* (h)	*$[Bu_4N]F$* (equiv.)	*Yield* (%)
$Pd(OAc)_2$	5	1.2	0
$Pd(OAc)_2$	10	2.4	23
$Pd(OAc)_2$	5	3	52
$Pd(OAc)_2$	5	4	77
$Pd(OAc)_2$	5	5	81
$Pd(OAc)_2$	10	5	0
$Pd_2(dba)_3 \cdot CHCl_3$	5	4	90

Table 5 Experimental data for compounds prepared in Equation (42)

Ar^1	*Ar*^{2}*X*	*Time* (h)	*Yield* (%)
4-$MeOC_6H_4$	PhI	5	90
4-$MeOC_6H_4$	PhBr	6.5	100
4-$MeOC_6H_4$	3-$CF_3C_6H_4Br$	1	80
4-$MeOC_6H_4$	1-Iodonaphthalene	4	70
4-$MeOC_6H_4$	3-$MeOC_6H_4I$	2	59
4-$MeOC_6H_4$	4-MeC_6H_4I	1	56
Ph	PhI	5	61
Ph	3-$CF_3C_6H_4Br$	9	64
Ph	1-Iodonaphthalene	6	52
3-$MeOC_6H_4$	PhI	5	59
3-$MeOC_6H_4$	3-$CF_3C_6H_4Br$	10	64
3-$MeOC_6H_4$	1-Iodonaphthalene	10	65
(*E*)-1-octenyl	PhI	8	60



(43)

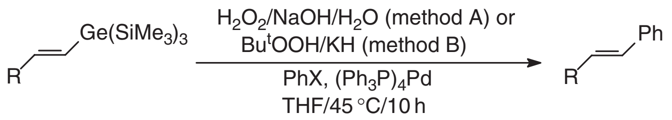
Other palladium-catalyzed interconversions involve germyl-substituted olefins[66,67] (Equations (44) and (45), Tables 6 and 7)[67] and germyl-substituted alkynes (Equations (46) and (47)).[68] A review concerning group 14 cross-coupling reactions have appeared.[69] The cleavage of the Ge–C bond in allylic germanes can be promoted photolytically[70] and in the presence of Lewis acids,[71–74] and some aspects of this reactivity have also been reviewed.[75]

Table 6 Experimental data for compounds prepared in Equation (44)

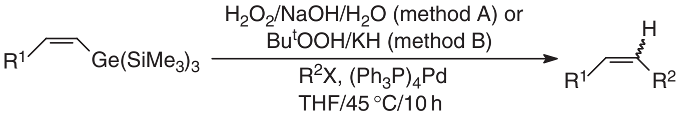
R	*X*	*Yield* (%) (*Method A*)	*Yield* (%) (*Method B*)
Ph	I	50	80
Ph	Br	88	50
Ph	Cl	37	10
Ph	OTf	15	20
$PhCH_2CH_2$	I	51	80
$PhCH_2CH_2$	Br	73	<5

Table 7 Experimental data for compounds prepared in Equation (45)

R^1	*R*^{2}	*X*	*Yield* (%) (*Method A*) (*E:Z*)	*Yield* (%) (*Method B*) (*E:Z*)
Ph	Ph	I	60 (33/67)	83 (3/97)
Ph	Ph	Br	53 (50/50)	78 (8/92)
Ph	Ph	Cl	44 (67/33)	<5
Ph	Ph	OTf	33 (98/2)	<5
4-$CH_3OC_6H_4$	Ph	I	90 (13/87)	96 (3/97)
4-$CH_3OC_6H_4$	Ph	Br	50 (64/36)	10 (2/98)
2-$CF_3C_6H_4$	Ph	I	41 (21/79)	77 (1/99)
2-$CF_3C_6H_4$	Ph	Br	30 (76/24)	15 (3/97)
4-$CF_3C_6H_4$	Ph	I	80 (55/45)	71 (5/95)
4-$CF_3C_6H_4$	Ph	Br	68 (99/1)	68 (1/99)
4-$CF_3C_6H_4$	Ph	Cl	15 (56/44)	<5
C_6H_{13}	Ph	I	36 (45/55)	60 (25/75)
C_6H_{13}	Ph	Br	64 (33/67)	60 (20/80)



(44)



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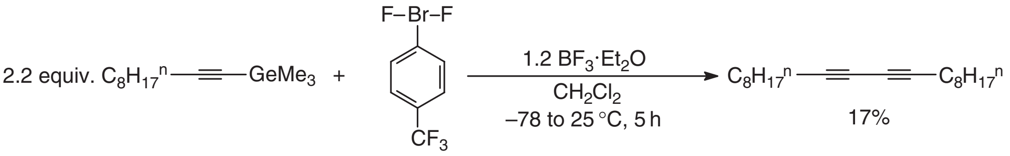
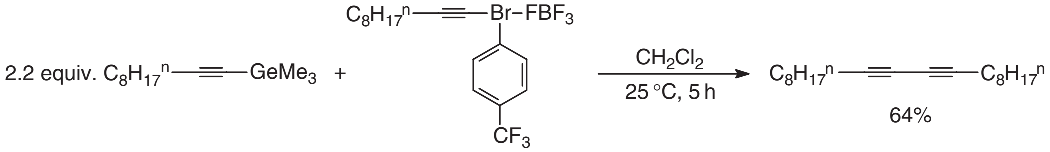


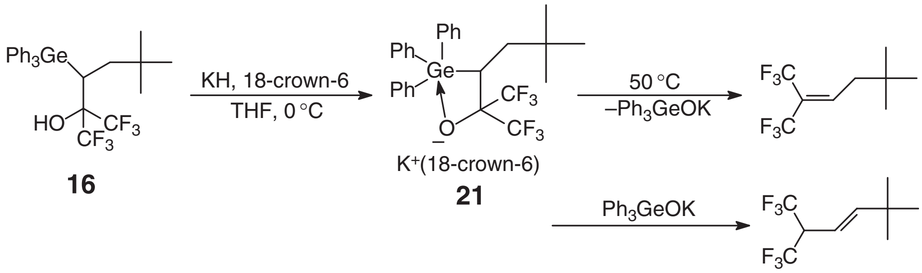
(46)



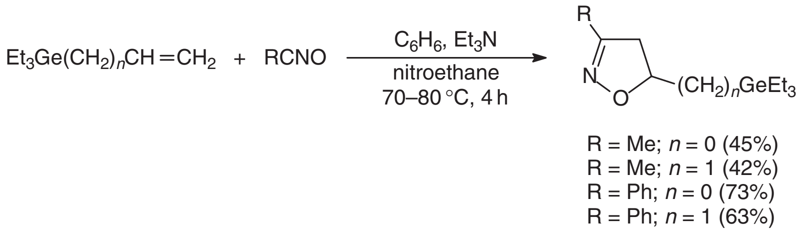
(47)

3.13.2.4.3 Other reactions

Deprotonation of the β-hydroxygermanes **16** yields an isolable intermediate in the Peterson-type reaction **21**, which can subsequently be thermally converted into the corresponding olefinic products (Equation (48)).[43] Triethylvinylgermane undergoes reactions with isocyanates[76,77] to yield isoxazolines (Equation (49)) and a similar reaction with a mixture of germyl-substituted ethylenes selectively generates similar products (Equations (50) and (51)).[77] Vinylgermanes **22** undergo exchange reactions with molybdenum alkylidene compounds to give germanium-substituted carbene complexes (Equation (52)).[78] The conversion of acylgermanes into alkenylgermanes was shown to occur with relatively high stereoselectivity (Equation (53)).[79]

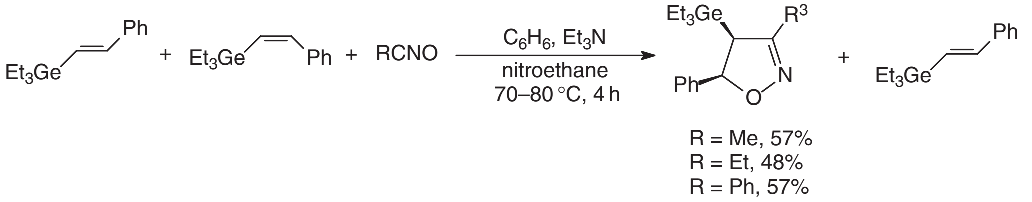


(48)



R = Me; $n = 0$ (45%)
R = Me; $n = 1$ (42%)
R = Ph; $n = 0$ (73%)
R = Ph; $n = 1$ (63%)

(49)



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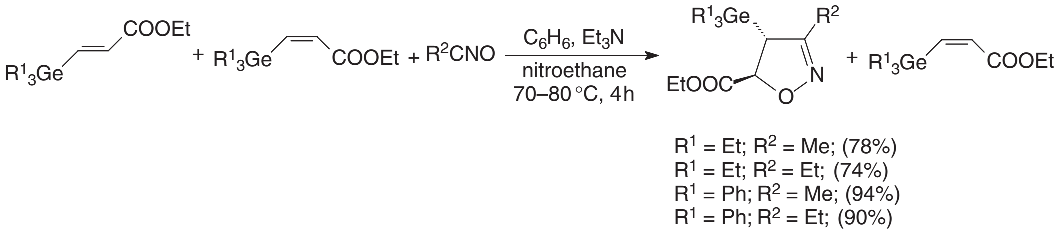
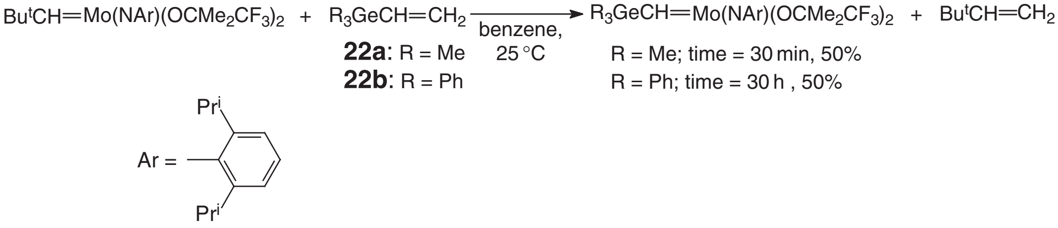


(51)



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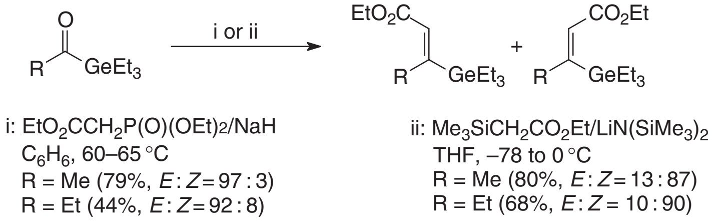


(53)

The germabenzene species **15** reacts in two different fashions with a variety of substrates to give cylcoaddition products (Scheme 7).[30] With MesCNO and 2,3-dimethylbutadiene, **15** behaves similarly to a compound with a single Ge–C double bond, whereas in reactions with styrene and phenylacetylene, **15** behaves as a 1-germabuta-1,3-diene to give Diels–Alder-type adducts. The germanium–carbon doubly bonded species **23** reacts with nitriles in several different ways, including as a 1,2-dipolar species with Bu^{t}CN, as a 1,4-dipolar species with PhCN, and as a base with various β-functionalized nitriles (Scheme 8).[80]

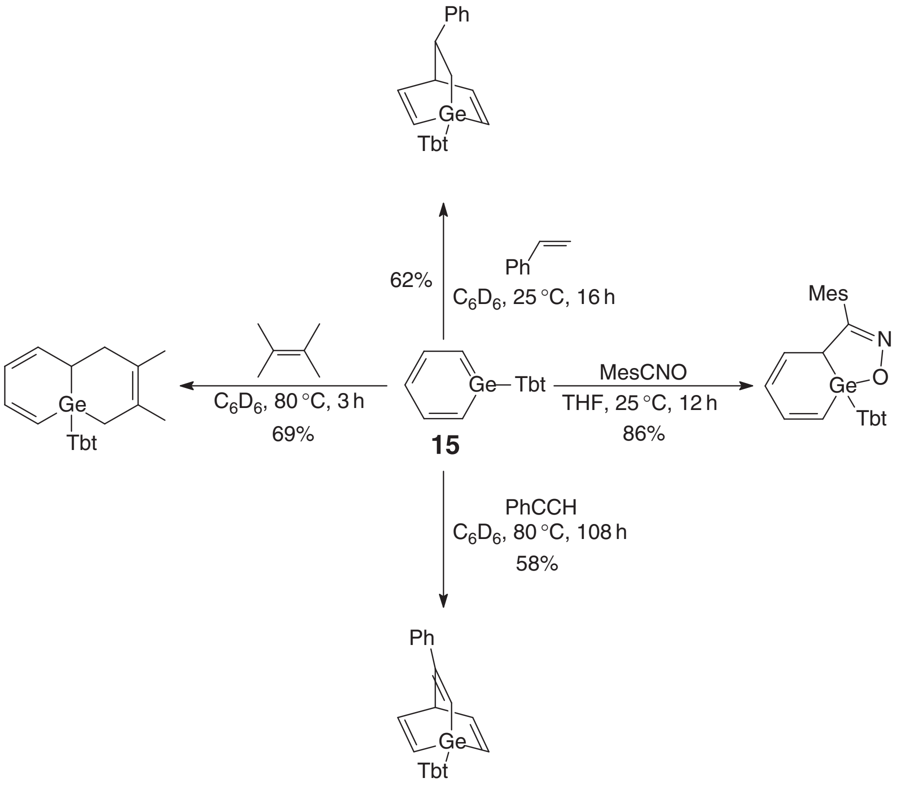
3.13.3 Compounds with Germanium–Halogen Bonds

3.13.3.1 Preparation

Various methods for the preparation of halogermanes exist and have been reviewed.[1]

3.13.3.1.1 Synthesis by direct methods

The synthesis of halogermanes by various direct methods starting with germanium metal have been reported.[81–85] A mixture of phenylchlorogermanes can be obtained by direct reaction of germanium metal with chlorobenzene in the presence of CuCl or $CuCl_2$ as a catalyst (Equations (54) and (55)).[82] The use of an activated form of germanium metal prepared according to Equation (56) or (57) allows the direct synthesis of dihalogermanes bearing functionalized organic groups (Equation (58), Table 8).[83] The selectivity of the process is dependent on the reaction time. Similar direct methods can be used for the preparation of alkylchlorogermanes[84] or arylchlorogermanes.[85]



Scheme 7

$$\mathrm{Ge} + \mathrm{C_6H_5Cl} \xrightarrow[350\,^\circ\mathrm{C},\ 60\,\mathrm{h}]{\mathrm{CuCl}\ (20\ \mathrm{wt.\%})} \underset{\substack{(n = 1\text{–}3)\\ 76\%\ (\text{total})}}{(\mathrm{C_6H_5})_n\mathrm{GeCl}_{4-n}} \tag{54}$$

$$\mathrm{Ge} + \mathrm{C_6H_5Cl} \xrightarrow[350\,^\circ\mathrm{C},\ 2\,\mathrm{h}]{\mathrm{CuCl_2} (20\ \mathrm{wt.\%})} \underset{65\%}{(\mathrm{C_6H_5})\mathrm{GeCl_3}} + \underset{35\%}{(\mathrm{C_6H_5})_2\mathrm{GeCl_2}} \tag{55}$$

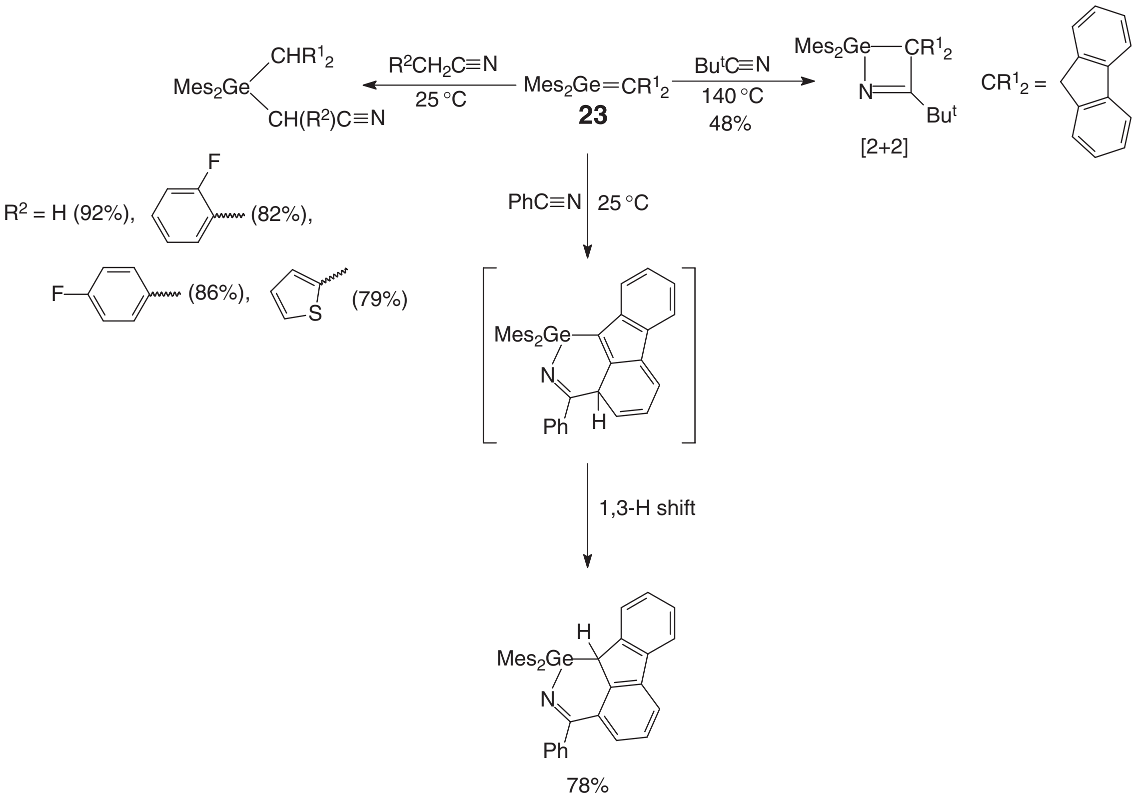
Total conversion = 62%
(based on Ge)

$$\mathrm{GeCl_2{\cdot}dioxane} + 2\mathrm{Li[Et_3BH]} \xrightarrow[25\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Ge}^* + 2\mathrm{LiCl} + 2\mathrm{Et_3B} + \mathrm{H_2} + \text{dioxane} \tag{56}$$

$$\mathrm{GeI_2} + 2\mathrm{Li\,[Et_3BH]} \xrightarrow[25\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Ge}^* + 2\mathrm{LiI} + 2\mathrm{Et_3B} + \mathrm{H_2} \tag{57}$$

Table 8 Experimental data for compounds prepared in Equation (58)

Substrate	*Product*	*Time* (h)	*Temp.* (°C)	*Yield* (%)
$H_3COOCC_2H_4Br$	$(H_3COOCC_2H_4)_2GeBr_2$	2	130	82
$H_3COOCC_4H_8Br$	$(H_3COOCC_4H_8)_2GeBr_2$	2	150	84
NCC_2H_4Br	$(NCC_2H_4)_2GeBr_2$	2	130	94
NCC_3H_6Br	$(NCC_3H_6)_2GeBr_2$	2	130	85
ClC_4H_8Br	$(ClC_4H_8)_2GeBr_2$	5	150	84

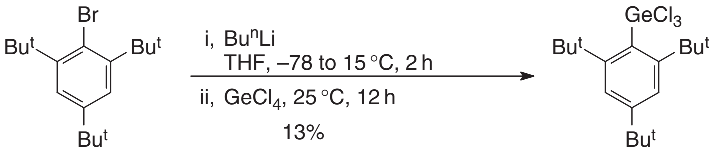


Scheme 8

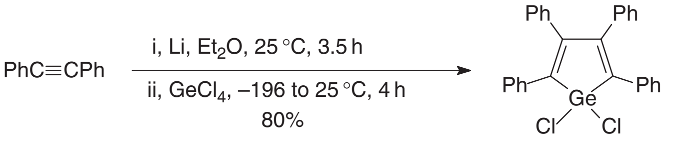
$$\mathrm{Ge}^{*} + 2\mathrm{X(CH_2)}_n\mathrm{Br} \xrightarrow[\text{130–150 °C}]{\text{THF}} 2(\mathrm{X(CH_2)}_n)_2\mathrm{GeBr_2} \qquad (58)$$

3.13.3.1.2 Synthesis via lithium salts

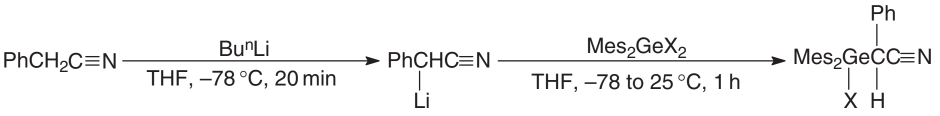
Supermesitylgermanium trichloride was prepared in modest yield from $GeCl_4$ (Equation (59)), and a dichlorogermole can be prepared from diphenylacetylene and $GeCl_4$ (Equation (60)).[19] The germylated cyano compounds **24** can be prepared via monosubstitution of Mes_2GeX_2 (Equation (61)).[86] The bulky germylated acetylene compound **25** was also prepared by a monosubstitution reaction (Equation (62)).[15]



(59)

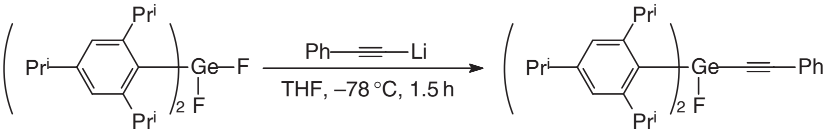


(60)



24a: X = F (69%)
24b: X = Cl (65%)

(61)



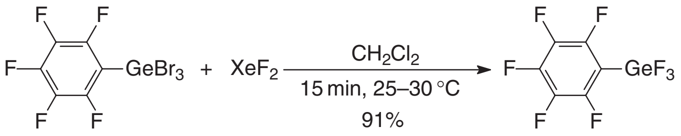
25
84%

(62)

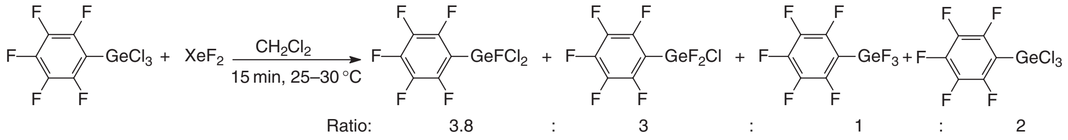
3.13.3.1.3 Synthesis by halogen-exchange reactions

Organogermanium fluorides can be prepared by reaction of germanium bromides with [Me$_4$N]F (Equation (63))[87] or XeF$_2$ (Equation (64)).[88] When a chloride precursor is used in the reaction with XeF$_2$, a mixture of products results (Equation (65)).[88]

$$Ph_3GeBr \; + \; [Me_4N]F \xrightarrow[\text{reflux, 2 h}]{CH_2Cl_2} \underset{92\%}{Ph_3GeF} \; + \; [Me_4N]Br \qquad (63)$$



(64)



(65)

3.13.3.1.4 Synthesis by transmetallation reactions

Organogermanium compounds can be prepared by transmetallation reactions with tin reagents. Examples include Me$_2$PhGeCl (Equation (66)),[89] the alkene-functionalized species **26–28**, (Equations (67) and (68)),[90] and the allenic (Equation (69)) and propargylic (Equation (70)) species **29** and **30**.[91] A series of aryltrichlorogermanes was prepared from the corresponding tin reagents (Equation (71), Table 9).[92] Transmetallation with zirconium species can also be used (Equation (72), Table 10).[93]

Table 9 Experimental data for compounds prepared in Equation (71)

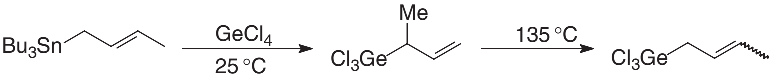
Ar	*AIBN* (mol%)	*Time* (h)	*Yield* (%)
Ph	0	12	76
Ph	2.1	22	76
C_6F_5	1.3	33	73
2,3,5,6-F_4C_5N	2.1	5	72
2,3,5,6-F_4C_5N	0	13	69
2-FC_6H_4	0	12	60
3,5-$(CF_3)_2C_6H_3$	2.0	15	59
3,5-$(CF_3)_2C_6H_3$	0	15	57
3,5-$(CF_3)_2C_6H_3$	0	12	70

AIBN = Azoisobutyronitrile.

Table 10 Experimental data for compounds prepared in Equation (72)

R^1	*R*^{2}	*Temp.* (°C)	*Time* (h)	*Yield* (%)
Me	Me	25	24	90
Et	Et	25	24	95
Pr^n	Pr^n	35	24	96
SiMe$_3$	SiMe$_3$	25	24	94
Me	SiMe$_3$	50	48	85

$$Me_2GePh_2 + SnCl_4 \xrightarrow[\text{neat, reflux, 3 h}]{AlCl_3} \underset{69\%}{Me_2PhGeCl} + PhSnCl_3 \qquad (66)$$

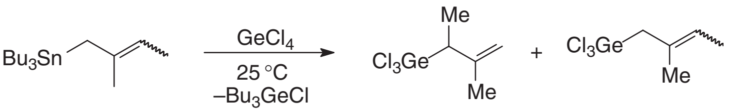


51%

26

E:*Z* = 65 : 35

(67)



38 : 62 *E*:*Z*

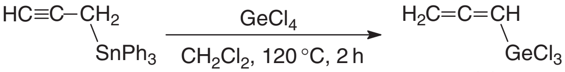
27

28

65 : 35 *E*:*Z*

Yield = 80%, 92 : 8 **28** : **27**

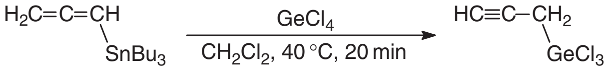
(68)



$$HC{\equiv}C{-}CH_2(SnPh_3) \xrightarrow[\text{CH}_2\text{Cl}_2\text{, 120 °C, 2 h}]{GeCl_4} H_2C{=}C{=}CH(GeCl_3) \qquad (69)$$

13%

29

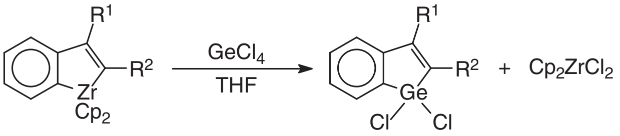


$$H_2C{=}C{=}CH(SnBu_3) \xrightarrow[\text{CH}_2\text{Cl}_2\text{, 40 °C, 20 min}]{GeCl_4} HC{\equiv}C{-}CH_2(GeCl_3) \qquad (70)$$

30

Yield = 48%

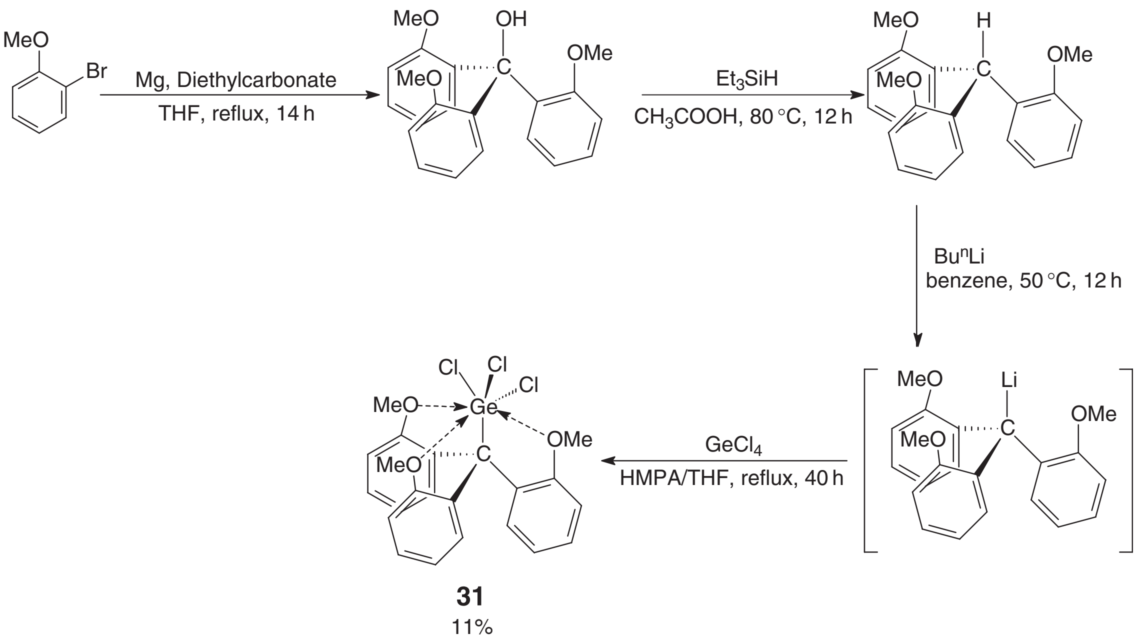
$$1\text{ equiv. }Bu^n{}_3SnAr + 1\text{ equiv. }GeCl_4 \xrightarrow[\text{150 °C, neat}]{AIBN} ArGeCl_3 + Bu^n{}_3SnCl \qquad (71)$$



(72)

3.13.3.1.5 Hypervalent organohalogermanes

The triphenylmethyl-substituted germanium halide **31** can be prepared in modest yield using GeCl$_4$ and contains a formally seven-coordinate germanium metal center (Scheme 9).[94] The structure of **31** (Figure 2, Table 11) is a tricapped tetrahedral structure where all the three Ge–O distances are shorter than the sum of the van der Waals radii (3.62 Å). A series of hypervalent germanium halides **32**–**34** can be prepared, as shown in Scheme 10.[95] The fluoride **32** is hexacoordinate, whereas the chloride **33** and bromide **34** are pentacoordinate.



31
11%

Scheme 9

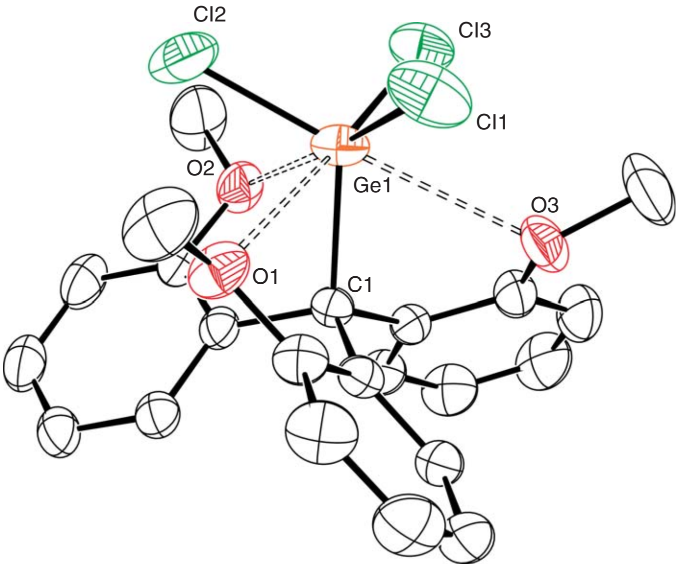
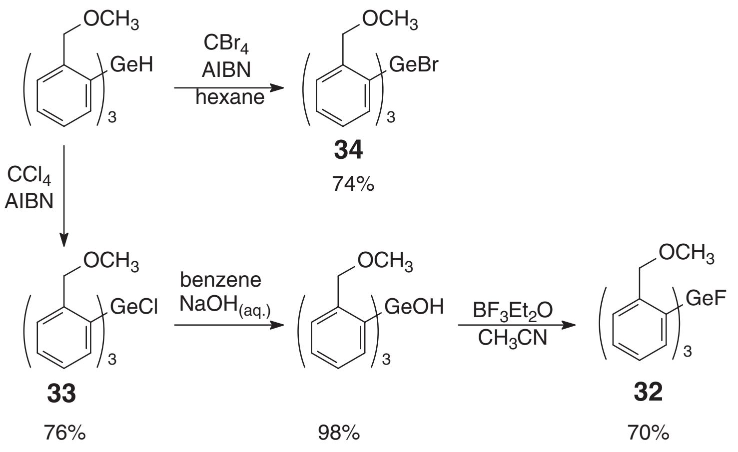


Figure 2 ORTEP diagram of the hypervalent organogermanium halide **31**. Reproduced from Takeuchi, Y.; Takase, Y. *J. Organomet. Chem*. **2004**, *689*, 3275–3277.

Table 11 Selected bond lengths (Å) and angles (°) for **31**

Ge(1)–O(1)	2.736(2)	Cl(1)–Ge(1)–Cl(2)	102.11(3)
Ge(1)–O(2)	2.806(2)	Cl(1)–Ge(1)–Cl(3)	100.19(3)
Ge(1)–O(3)	2.808(2)	Cl(2)–Ge(1)–Cl(3)	101.10(3)
Ge(1)–Cl(1)	2.1589(8)	Cl(1)–Ge(1)–C(1)	117.37(6)
Ge(1)–Cl(2)	2.1684(6)	Cl(2)–Ge(1)–C(1)	116.83(6)
Ge(1)–Cl(3)	2.1651(6)	Cl(3)–Ge(1)–C(1)	116.45(6)
Ge(1)–C(1)	2.052(2)		

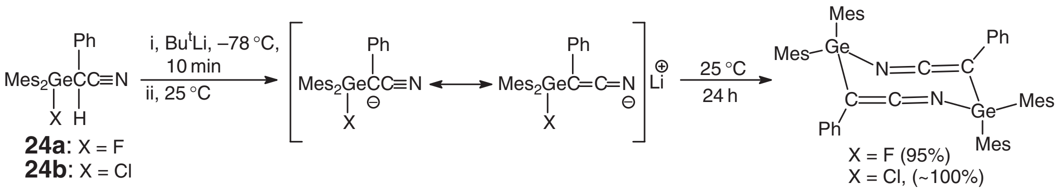


Scheme 10

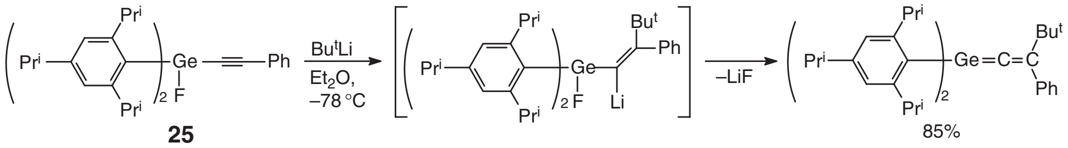
3.13.3.2 Chemical Properties

3.13.3.2.1 Reaction with organometallic compounds

The reaction of organohalogermanes with organolithium or Grignard reagents is still a synthetically important process. Several interesting species have been prepared by these procedures. Reaction of the germylphenylacetonitrile derivatives **24** with Bu^{t}Li results in the dimerization of the resulting anion to furnish an eight-membered ring containing two germylketenimine moieties (Equation (73)).[86] Lithiation of the acetylenic fluoride compound **25** yields a germapropadiene via loss of LiF (Equation (74)).[15] A complete series of ethynylisopropylgermanes was prepared using the corresponding Grignard reagents (Equation (75)).[96]



(73)

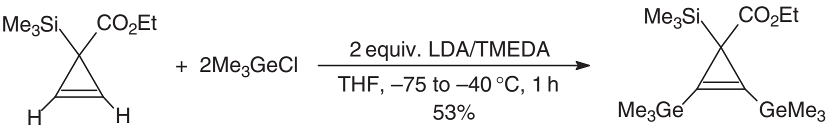


(74)

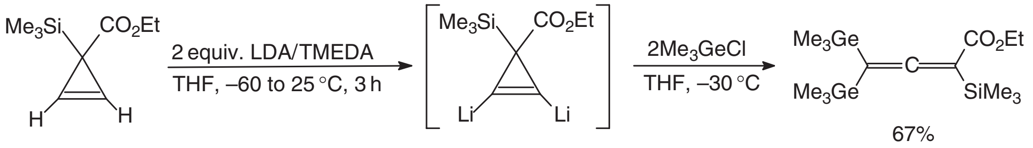
$$\mathrm{Pr^i_{4-\mathit{n}}GeCl_{\mathit{n}}} + n\mathrm{BrMgC{\equiv}CH} \xrightarrow[\mathrm{Et_2O/THF,\ 1\,h}]{} \mathrm{Pr^i_{4-n}Ge(C{\equiv}CH)_{\mathit{n}}} \quad (75)$$

$n = 1$ (85%)
$n = 2$ (90%)
$n = 3$ (77%)

Reaction of Me_3GeCl with a substituted cyclopropene in the presence of lithium diisopropylamide (LDA) yields different products depending on the order of addition of the reagents.[97] Addition of LDA to a mixture of the reactants gives the dimetallated cyclopropene (Equation (76)). Dilithiation of the cyclopropane followed by addition of Me_3GeCl gives the allene (Equation (77)).



(76)



(77)

3.13.3.2.2 Other reactions

A versatile one-pot procedure for the synthesis of organogermanium compounds from haloorganogermanium compounds has been described which gives the products in good to excellent yields (Equation (78),[40] Table 12).[39,40]

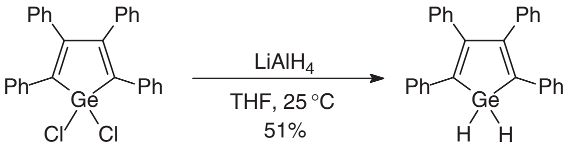
$$R_{4-n}GeX_n + R^1X \xrightarrow[\text{THF, sonication}]{\text{2–4 equiv. Mg}} R_{4-n}GeR^1{}_n \qquad (78)$$

3.13.4 Compounds with Germanium–Hydrogen Bonds

3.13.4.1 Preparation

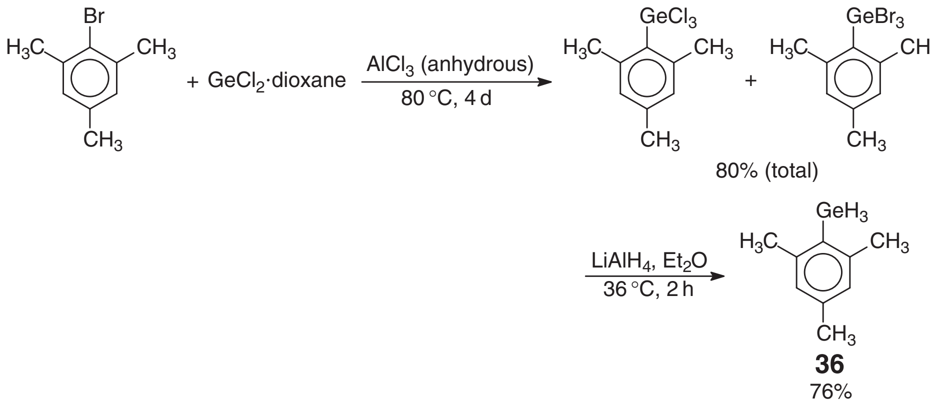
3.13.4.1.1 Organohydrogermanes

The direct reduction of organogermanium halides using $LiAlH_4$ is well known.[95,98–112] Several species of interest have been prepared by this method including the germole **35** (Equation (79)),[100] the mesityl derivative **36** (Equation (80)),[101] the supermesityl derivative **37** (Equation (81)),[102] and the optically active species **38** (Scheme 11),[103] **39** (Equation (82)),[104] **40** (Equation (83)),[105] and **41** (Scheme 12).[106]



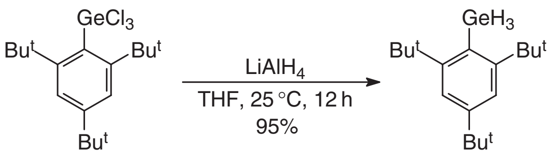
35

(79)



36

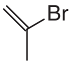
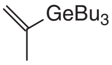
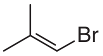
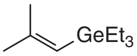
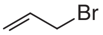
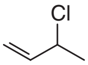
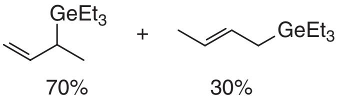
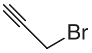
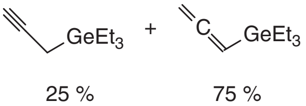
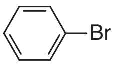
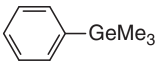
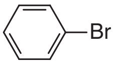
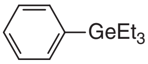
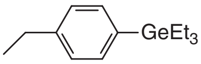
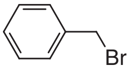
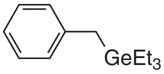
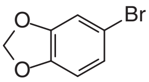
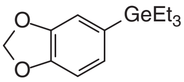
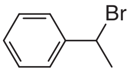
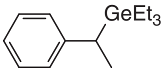
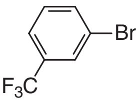
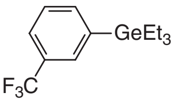
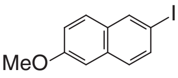
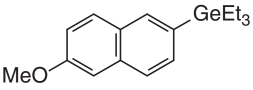
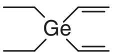
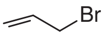
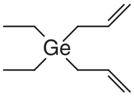
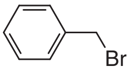
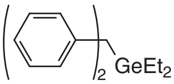
(80)

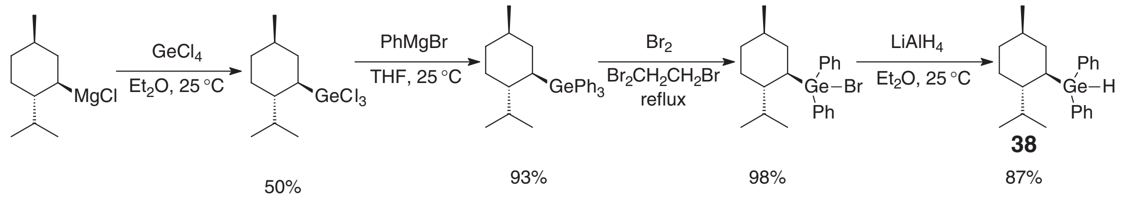


37

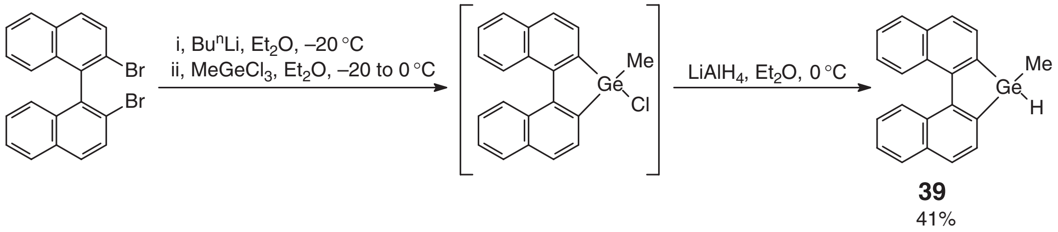
(81)

Table 12 Experimental data for compounds prepared in Equation (78)

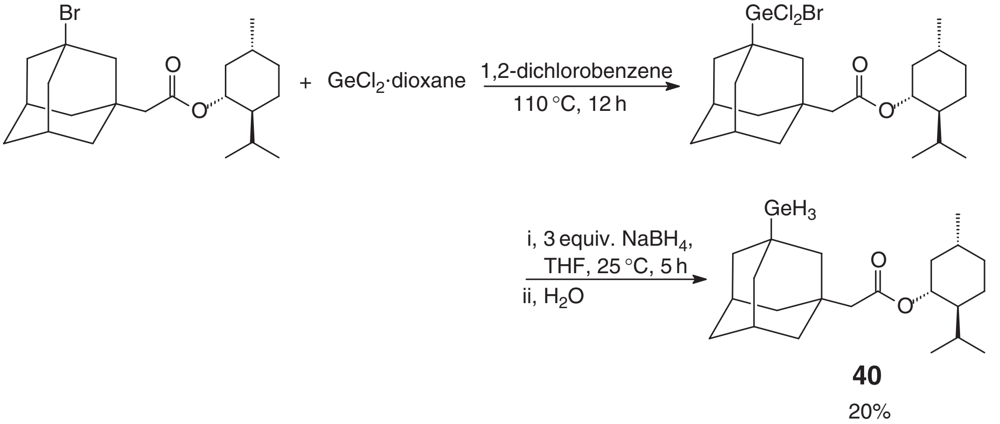
$R_{4-n}GeX_n$	R^1X	$R_{4-n}GeR^1{}_n$	*Yield* (%)
Bu_3GeCl			83
Et_3GeBr			82
Bu_3GeCl			95
Et_3GeBr			74
Et_3GeBr			90
Me_3GeBr			85
Et_3GeBr			78
Et_3GeBr			79
Et_3GeBr			80
Et_3GeBr			76
Et_3GeBr			81
Et_3GeBr			56
Et_3GeBr			68
Et_2GeCl_2	$CH_2{=}CH_2MgBr$		80
Et_2GeCl_2			85
Et_2GeCl_2			82



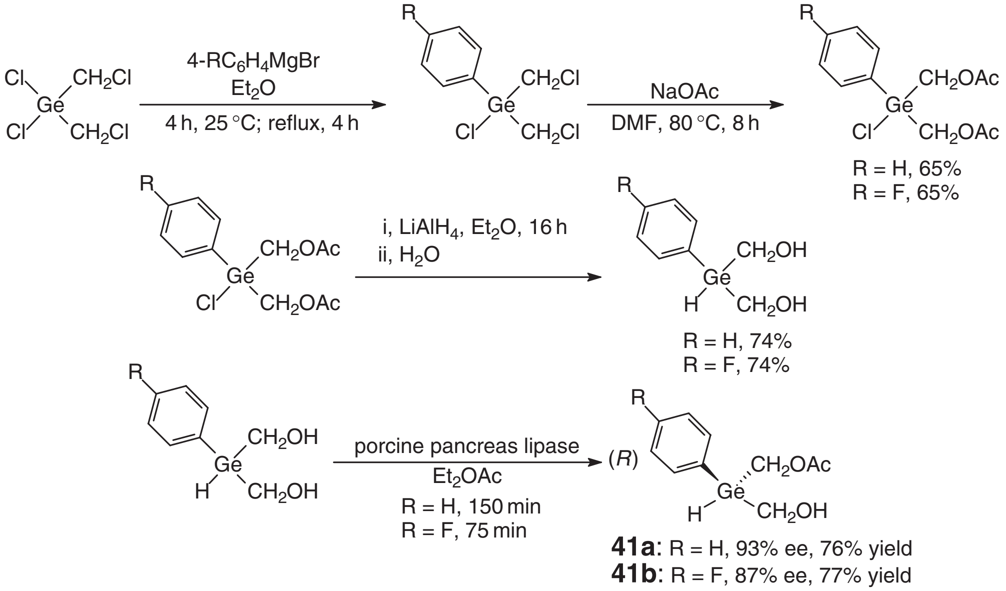
Scheme 11



(82)

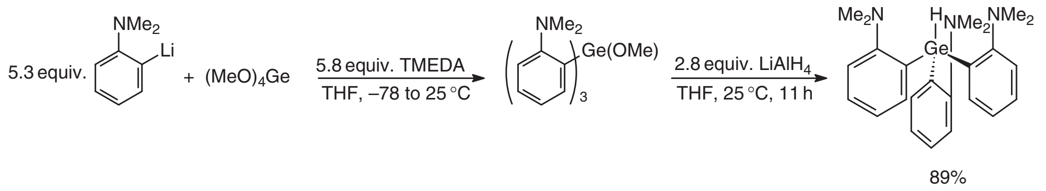


(83)

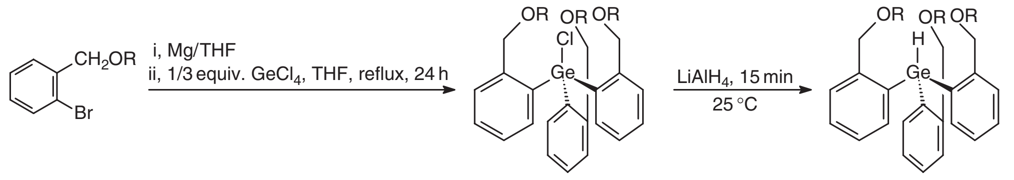


Scheme 12

Several triphenylgermanium hydrides have been prepared where the hydride atom is encapsulated by substituents on the phenyl ligands,[95,108–111] as illustrated in Equations (84)–(86).[110,111] The germanium atom of **42a–c** are formally hexacoordinate and that of **43** is heptacoordinate. A tribenzobarellenegermane compound with a trihydrogermane moiety attached to the bridgehead carbon was prepared and characterized (Equation (87)), and this species was found to be exceptionally air stable.[112]

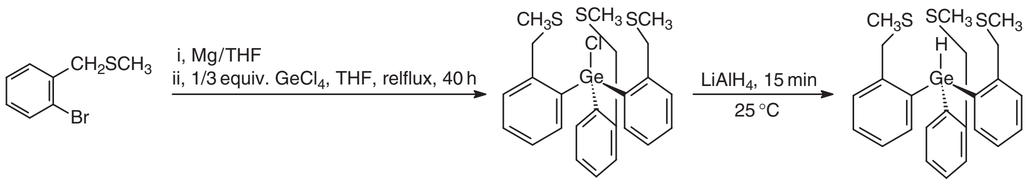


(84)



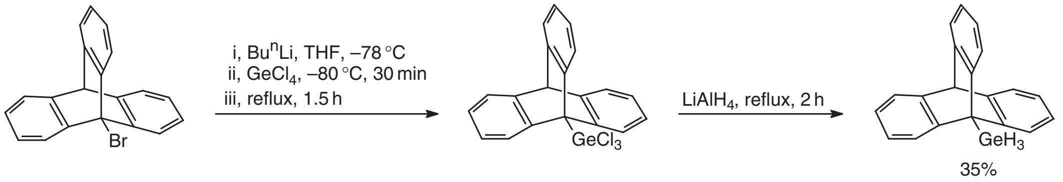
(85)

42a: R = Me (25%)
42b: R = Et (47%)
42c: R = Bu^t (14%)



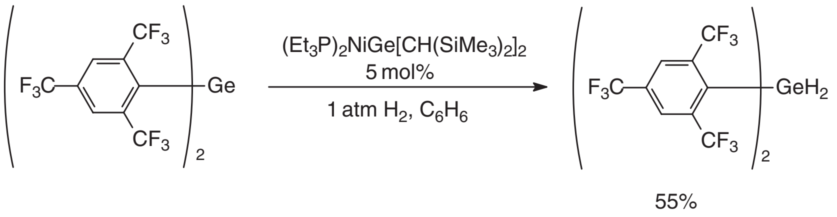
(86)

43
25%



(87)

A useful method for the preparation of diorganogermanium dihydrides employs a nickel–germylene complex[113] for the catalytic hydrogenation of germylenes (Equations (88)[114,115] and (89)).[113]



(88)

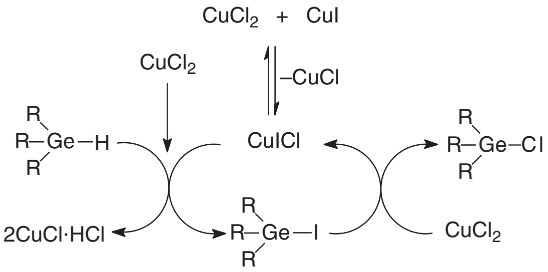
$$\mathrm{Ge[CH(SiMe_3)_2]_2} + \mathrm{H_2} \xrightarrow[\text{benzene, 25 °C, 72 h}]{\text{2 mol\% }(\mathrm{Et_3P})_2\mathrm{NiGe[CH(SiMe_3)_2]_2}} \underset{68\%}{\mathrm{H_2Ge[CH(SiMe_3)_2]_2}} \qquad (89)$$

3.13.4.1.2 Organohalohydrogermanes

Halogenation of hydrogermanes using organic or inorganic halides is the primary method for the synthesis of these species, although selectivity is usually lacking.[1,116,117] A versatile method for the preparation of various mixed

Table 13 Experimental data for compounds prepared in Equations (90) and (91)

Germane	*CuCl$_2$* (equiv.)	*CuI* (equiv.)	*Conditions*	*Product (yield)* (%)
Et_3GeH	2	0.03	Et_2O, 25 °C, 3 h	Et_3GeCl (76)
$(C_6H_{13})_3GeH$	2	0.03	Et_2O, 25 °C, 5 h	$(C_6H_{13})_3GeCl$ (88)
Et_2GeH_2	2	0.02	Et_2O, 25 °C, 1 h	Et_2GeHCl (73)
Et_2GeH_2	4	0.02	Et_2O, 25 °C, 8 h	Et_2GeCl_2 (85)
$(C_6H_{13})_2GeH_2$	2	0.03	Et_2O, 25 °C, 3 h	$(C_6H_{13})_2GeHCl$ (65)
$(C_6H_{13})_2GeH_2$	2	0.03	Toluene, reflux, 5 h	$(C_6H_{13})_2GeHCl$ (91)
$(C_6H_{13})_2GeH_2$	2	None	Toluene, reflux, 19 h	$(C_6H_{13})_2GeHCl$ (90)
$(C_6H_{13})_2GeH_2$	4	0.11	Toluene, reflux, 4 d	$(C_6H_{13})_2GeCl_2$ (87)
Ph_2GeH_2	2	None	Toluene, reflux, 31 h	Ph_2GeHCl (87)
Ph_2GeH_2	4	0.14	Toluene, reflux, 6 d	Ph_2GeCl_2 (86)
$PhGeH_3$	2	None	Toluene, reflux, 19 h	$PhGeH_2Cl$ (84)
$PhGeH_3$	4	0.17	Toluene, reflux, 9 d	$PhGeHCl_2$ (88)



Scheme 13

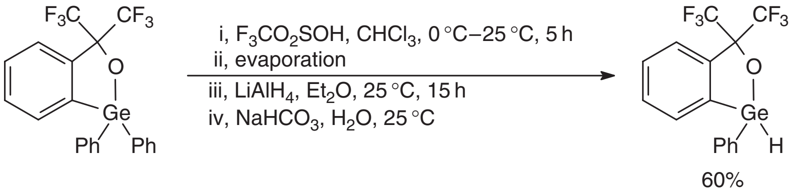
organochlorohydrogermanes has been reported which allows complete selectivity (Equations (90) and (91), Table 13).[118,119] The proposed reaction pathway for this conversion is shown in Scheme 13.[118]

$$R_{4-n}GeH_n \xrightarrow[Et_2O\text{ or toluene}]{2CuCl_2,\ CuI} R_{4-n}GeH_{n-1}Cl \qquad (90)$$

$$R_{4-n}GeH_n \xrightarrow[Et_2O\text{ or toluene}]{4CuCl_2,\ CuI} R_{4-n}GeH_{n-2}Cl_2 \qquad (91)$$

3.13.4.1.3 Other organohydrogermanes

Germanium hydrides with germanium bonded to oxygen and hydrogen have been reported. One such compound was prepared by exploiting the reactivity of the Ge–Ph bond with triflic acid (Equation (92)).[120] Germanium hydrides containing functionalized organic groups have been obtained via insertion of dihalocarbenes into the Ge–H bond of trialkylgermanes.[121] The immobilization of germanium hydrides onto resins has also been investigated.[122]



(92)

3.13.4.2 Reactivity of the Germanium–Hydrogen Bond

The hydrogen-donor ability of germanium hydrides has been studied[123] and reviewed.[124]

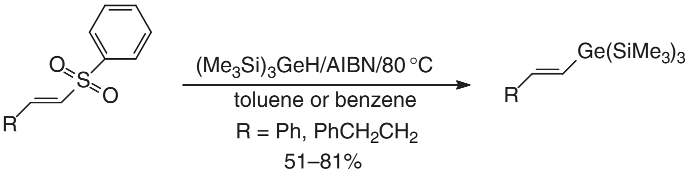
3.13.4.2.1 Halogenation of the Ge–H bond

Traditional methods for the halogenation of Ge–H bonds are still widely used.[1,116] A versatile palladium-metal-catalyzed method has been reported (Equation (93), Table 14).[125]

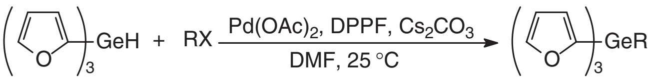
$$\mathrm{R^1}_{4-n}\mathrm{GeH}_n \xrightarrow[\substack{1\text{–}3\ \mathrm{mol\%\ PdCl_2} \\ n = 1\text{–}3}]{\mathrm{R^2X}} \mathrm{R^1}_{4-n}\mathrm{GeX}_n \qquad (93)$$

3.13.4.2.2 Alkylation or alkenylation of the Ge–H bond

Alkylation of the Ge–H bond can be achieved via free-radical-mediated desulfonylation of vinyl sulfones (Equation (94)),[67,126] or via the Pd-catalyzed coupling of aryl iodides (Equation (95), Table 15).[62] Reaction with the organolithium reagent $LiCH_2(Me)N(Me_2N)_2P{=}O$ yields the interesting heterocyclic compound **44** (Equation (96)).[120] The structure of **44** is shown in Figure 3 and selected bond lengths and angles are summarized in Table 16. The germanium atom in this species is pentacoordinate and the donor ligand arises from the deprotonation of hexamethylphosphoramide (HMPA).



(94)

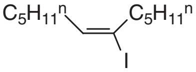
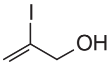
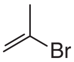
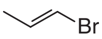


(95)

Table 14 Experimental data for Equation (93)

Germane	R^2X (equiv.)	*Time* (h)	*Product* (*yield* %)
Et_3GeH	allylBr (1.7)	3	Et_3GeBr (84)
$(C_6H_{13})_3GeH$	allylBr (2.3)	3	$(C_6H_{13})_3GeBr$ (80)
$(C_6H_{13})_3GeH$	$PhCH_2Br$ (1.5)	6	$(C_6H_{13})_3GeBr$ (88)
Ph_3GeH	allylBr (1.5)	3	Ph_3GeBr (72)
$(C_6H_{13})_2GeH_2$	allylBr (3.0)	6	$(C_6H_{13})_2GeBr_2$ (92)
Ph_2GeH_2	allylBr (3.0)	4	Ph_2GeBr_2 (81)
$(C_6H_{13})GeH_3$	allylBr (3.6)	53	$(C_6H_{13})GeBr_3$ (58)
Et_3GeH	allylI (1.5)	6	Et_3GeI (83)
$(C_6H_{13})_3GeH$	allylI (1.5)	12	$(C_6H_{13})_3GeI$ (84)
Ph_3GeH	allylI (1.5)	12	Ph_3GeI (98)
$(C_6H_{13})_2GeH_2$	allylI (3.0)	3	$(C_6H_{13})_2GeI_2$ (80)
Ph_2GeH_2	allylI (3.0)	5	Ph_2GeI_2 (75)
$(C_6H_{13})GeH_3$	allylI (4.1)	12	$(C_6H_{13})GeI_3$ (87)

Table 15 Experimental data for Equation (95)

RX	*Time* (h)	*Yield* (%)
PhI	1.5	83
4-$MeOC_6H_4I$	1	80
3-$MeOC_6H_4I$	1	88
4-MeC_6H_4I	0.5	85
2-MeC_6H_4I	2	43
4-$Me_2NC_6H_4I$	1	56
	0.5	83
	3	59
4-$MeOC_6H_4Br$	12	0
	1.5	70
	1	54
α-Bromostyrene	1	49
(*E*)-β-bromostyrene	1.5	74
2-Bromopyridine	2	73

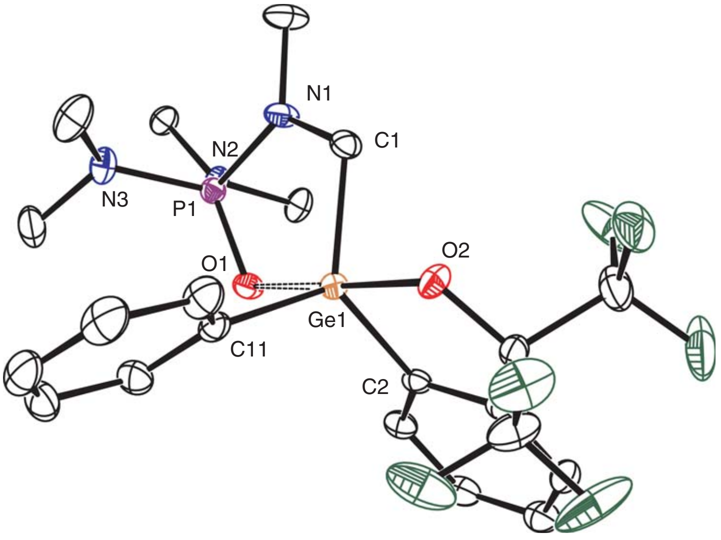
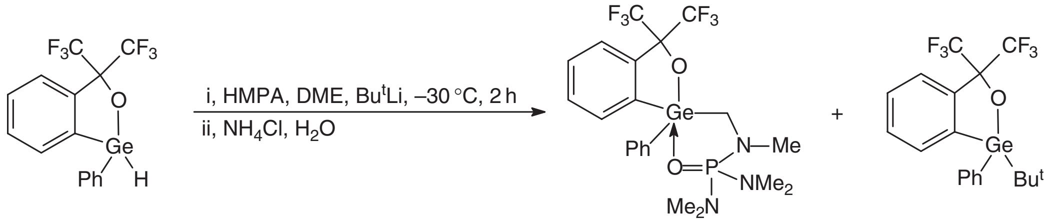


Figure 3 ORTEP diagram of the hypervalent species 44. Reproduced from Kano, N.; Goto, S.; Kawashima, T. *Organometallics* **2003**, *22*, 1152–1155.

Table 16 Selected bond lengths (Å) and angles (°) for 44

Ge(1)–O(1)	2.175(1)	O(1)–Ge(1)–O(2)	171.52(5)
Ge(1)–O(2)	1.911(1)	C(1)–Ge(1)–C(2)	123.34(8)
Ge(1)–C(1)	1.964(2)	C(1)–Ge(1)–C(3)	114.92(8)
Ge(1)–C(2)	1.942(2)	C(2)–Ge(1)–C(3)	121.30(7)
Ge(1)–C(3)	1.953(2)	C(1)–Ge(1)–O(1)	84.85(6)



44

57%

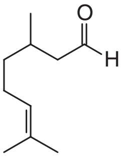
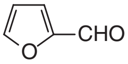
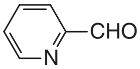
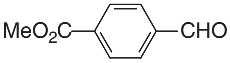
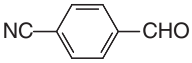
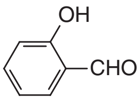
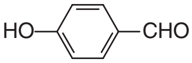
35%

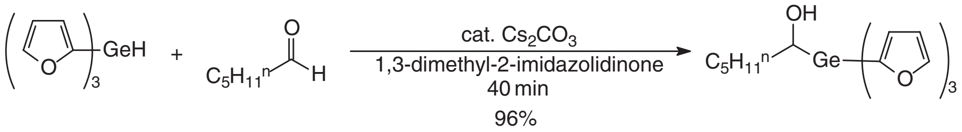
(96)

3.13.4.2.3 Hydrogermylation reactions

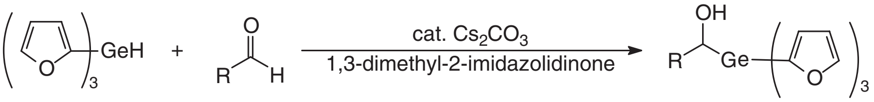
Tri(2-furyl)germane[63,127–130] has been shown to be a useful hydrogermylation reagent for alkenes,[127,128] dienes,[129] alkynes,[129,130] and carbonyl species (Equations (97) and (98), Table 17).[127] It has been employed to selectively hydrogermylate the double bond of α,β-unsaturated carbonyl compounds (Equation (99)).[127] This species can also be used to affect the hydrogermylcarbonylation of alkynes in the presence of CO (Equation (100)).[130]

Table 17 Experimental data for Equation (98)

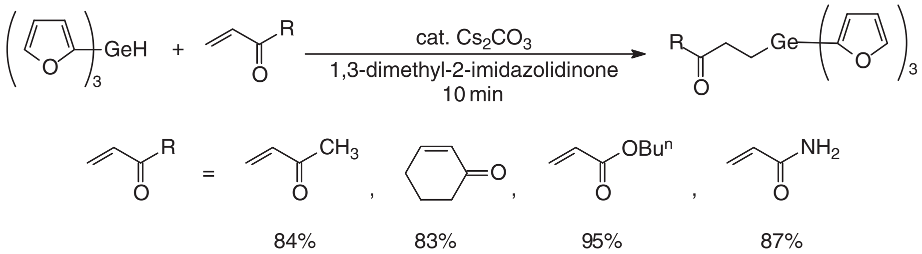
Aldehyde	*Time* (min)	*Yield* (%)
Pr^iCHO	10	99
Bu^tCHO	10	73
	10	93
$C_5H_{11}{}^n$—≡—CHO	120	92
PhCHO	5	92
	15	84
	15	91
	10	74
	5	81
	30	74
	300	0
$HCHO/H_2O$	5	91



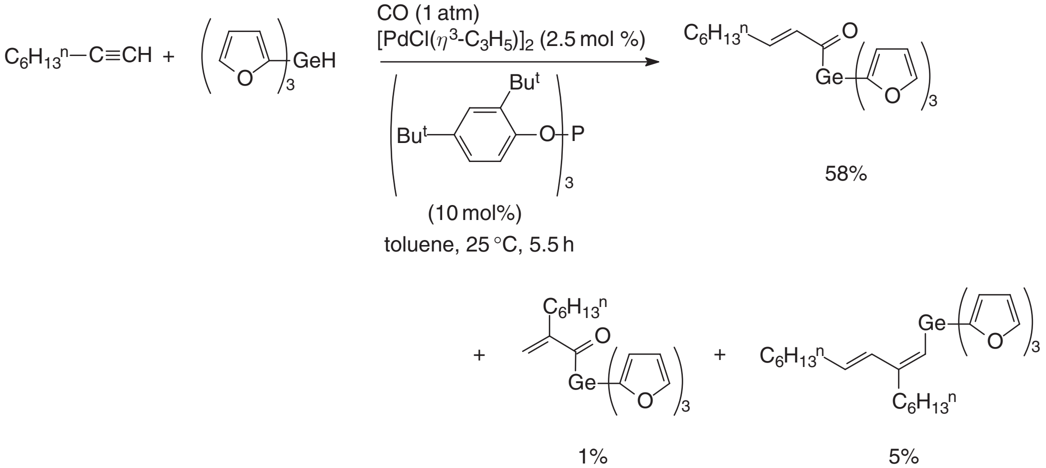
(97)



(98)

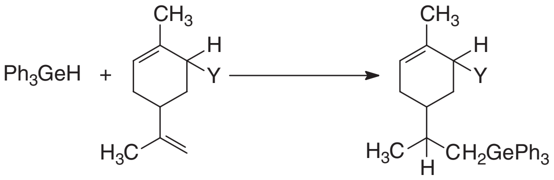


(99)



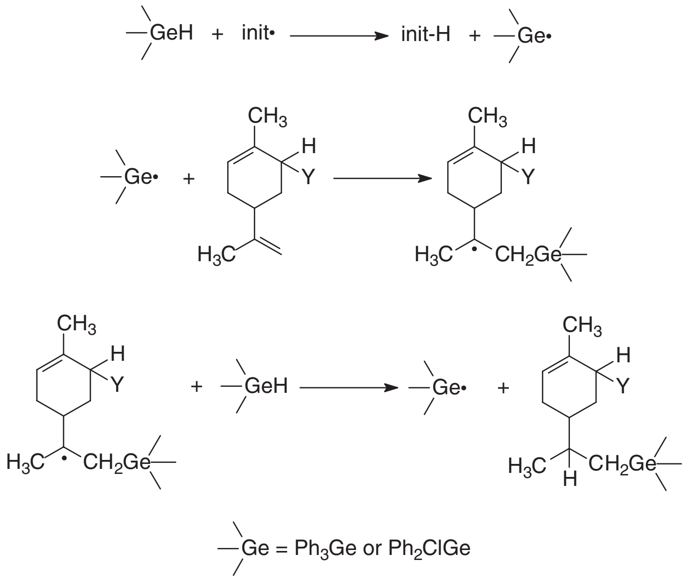
(100)

The hydrogermylation of functional ethylenic compounds by Ph_3GeH and Ph_2ClGeH was investigated (Equations (101) and (102)).[131] The Ph_2ClGeH species was found to be more reactive than Ph_3GeH, since the halogen substituent results in a harder and more electronegative Ge radical (Equation (102)). The mechanism for the hydrogermylation of limonene and carveol is shown in Scheme 14. This reaction was found to be auto-inhibited by the presence of the α,β-unsaturated carbonyl groups, such that metallation at the oxygen atom via a 1,4-addition of the Ge–H bond requires forcing radical initiation sequence (RIS) conditions (Equation (103)), since the radical **45** formed is highly delocalized (Scheme 15).[131] In non-conjugated systems, hydrogermylation of the C═C double bond is observed (Equation (104)).



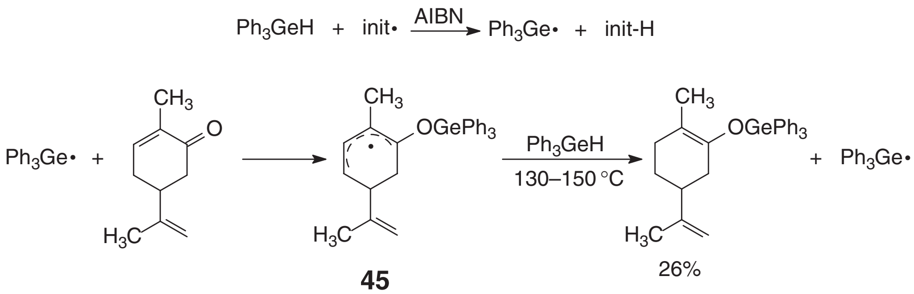
(101)

Y = H; conditions: AIBN, $PhCO_2OBu^t$, $Bu^t_2O_2$, 20 °C–130 °C 24 h, ~100%
Y = OH; conditions: AIBN, 100 °C, 24 h, 95%

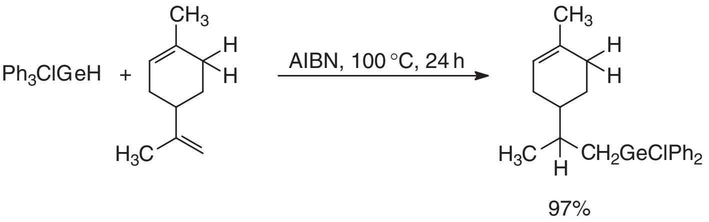


Y = H, OH

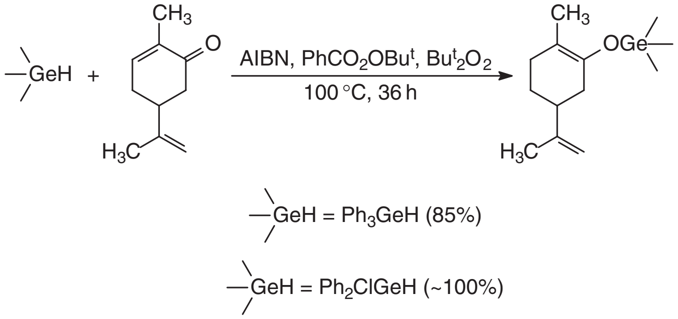
Scheme 14



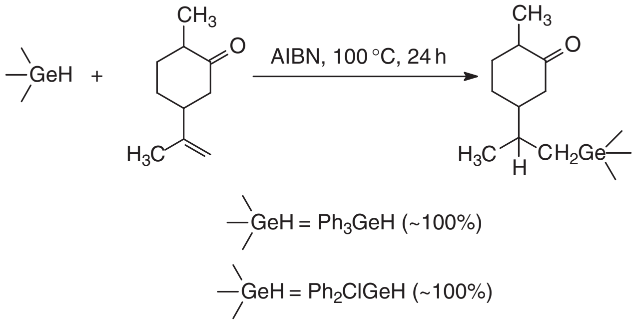
Scheme 15



(102)

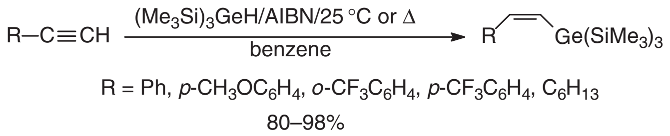


(103)

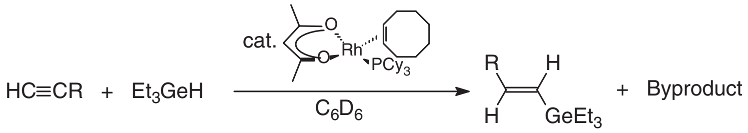


(104)

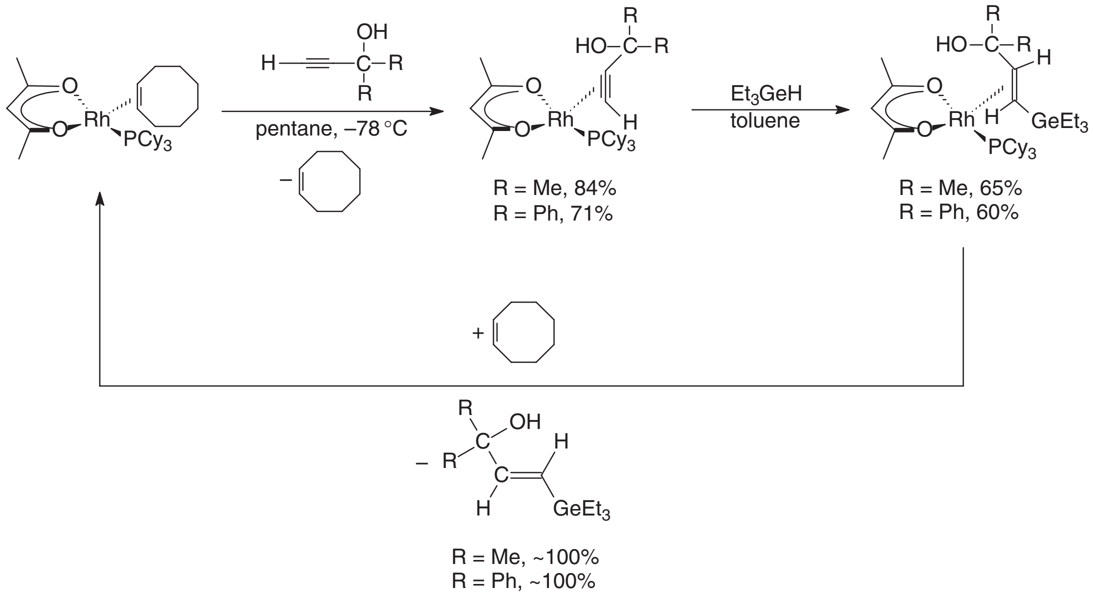
Alkynes react with the bulky germanium hydride $(Me_3Si)_3GeH$ to selectively yield (*Z*)-alkenes (Equation (105)).[67] The hydrogermylation of alkynols or alkynes can be catalyzed by a rhodium complex (Equation (106), Table 18) and some of the intermediates were identified (Scheme 16).[132] Similar rhodium species react with alkynes to yield alkenyl complexes,[133] and other transition metal complexes have been employed as hydrogermylation catalysts including those containing palladium.[134,135]



(105)



(106)



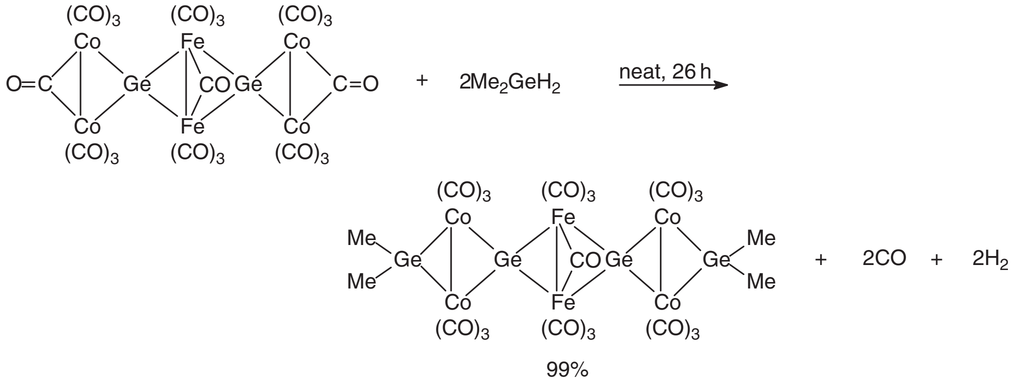
Scheme 16

Table 18 Experimental data for Equation (106)

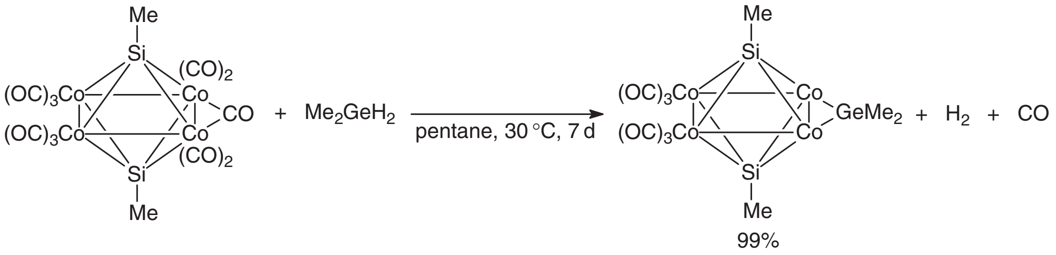
Alkyne	*Product*	*Byproduct* (yield)	*Yield* (%)
$HC{\equiv}CC(OH)Ph_2$	(E)-$Et_3GeCH{=}CHC(OH)Ph_2$	None	100
$HC{\equiv}CC(OH)Me_2$	(E)-$Et_3GeCH{=}CHC(OH)Me_2$	None	100
$HC{\equiv}CPh$	(E)-$Et_3GeCH{=}CHPh$	$H_2C{=}C(GeEt_3)Ph$ (10%)	87
$HC{\equiv}CCy$	(E)-$Et_3GeCH{=}CHCy$	$H_2C{=}C(GeEt_3)Cy$ (17%)	81
$HC{\equiv}CSiMe_3$	(E)-$Et_3GeCH{=}CHSiMe_3$	None	97

3.13.4.2.4 Reactions with transition metal complexes

A few clusters of interest containing germanium and transition metals have been reported.[136–138] Dimethylgermane was found to replace only the bridging carbonyls between cobalt in a mixed germanium/cobalt/iron cluster complex (Equation (107)), and replacement of the carbonyl bridging the iron metal centers was not observed.[137] A similar reaction leads to replacement of a bridging carbonyl in a mixed cobalt/silicon cluster (Equation (108)).[136]



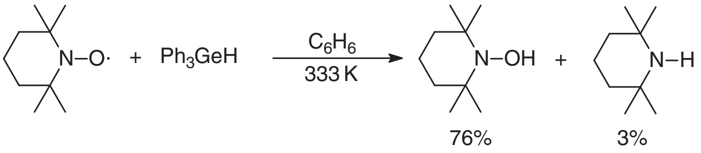
(107)



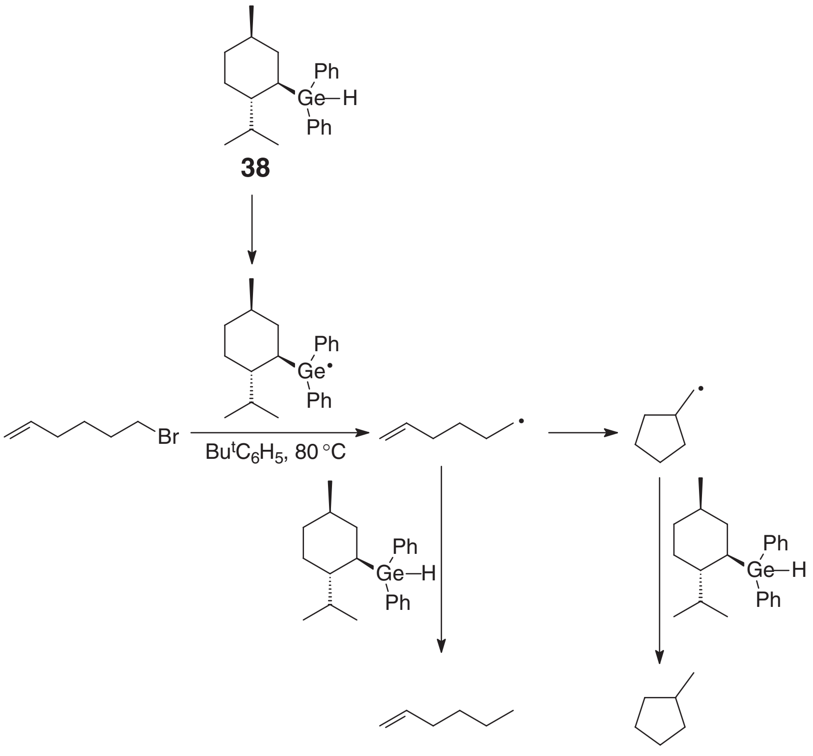
(108)

3.13.4.2.5 Reactions with radicals

The menthylgermanium hydride **38** reacts with primary alkyl radicals to yield a mixture of 1-hexene **46** and methylcyclopropane **47**, the ratio of which changes with increasing concentration (Scheme 17, Table 19).[103] The rate constant for this process is $1.02 \times 10^6\,M^{-1}\,s^{-1}$. Triphenylgermanium hydride reacts with 2,2,6,6-tetramethyl-1-piperidine-*N*-oxide (TEMPO) to yield a mixture of the corresponding hydroxylamine and amine (Equation (109)).[139] Reaction of Bu_3SnH under similar conditions gave an increased yield of the hydroxylamine and produced the amine in only 3% yield while the silicon species $(Me_3Si)_3SiH$ yields the two products in nearly a 1 : 1 ratio.[139]



(109)



46 **47**

Scheme 17

Table 19 Experimental data for Scheme 17

38 *Concentration* (M)	*Yield* **46** (%)	*Yield* **47** (%)
0.05	95.6	4.4
0.10	91.5	8.5
0.15	87.4	12.6

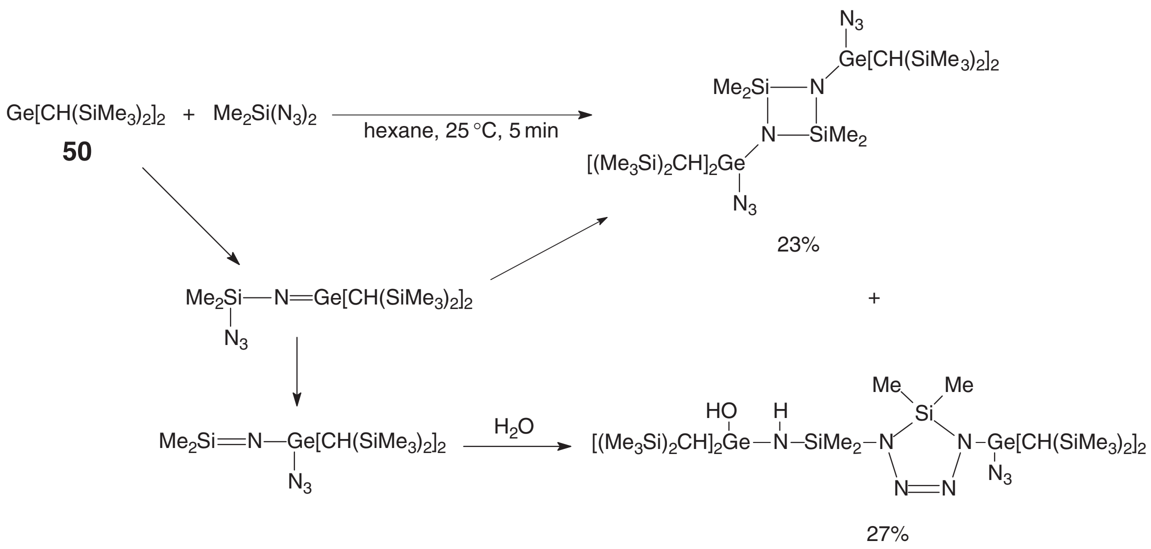
3.13.5 Compounds with Germanium–Group 15 Element Bonds

3.13.5.1 Preparation

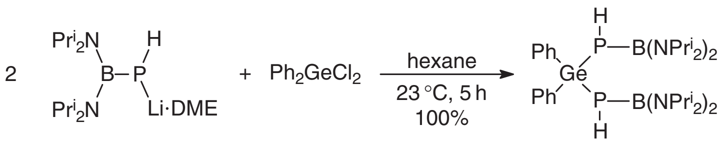
The methods for the preparation of compounds containing germanium–nitrogen bonds have been the subject of a recent review.[140]

3.13.5.1.1 Preparation from alkali metal salts

Common methods of preparation include reaction of the lithium salt of a group 15 complex with a germanium halide. This has yielded several interesting species including bis(borylphosphino)germanes **48** (Equation (110))[141] and *P*-germylated diphosphadiboretanes **49** (Equation (111)).[142] The formation of *N*-(azidosilyl)germanimines which contain a Ge═N double bond can be achieved by the reaction of the germylene **50** with bulky organodiazidosilanes (Equation (112)).[143] If less bulky substituents are present on the organodiazidosilane, dimerization occurs giving a cyclodisilazane and a siladihydrotetrazole resulting from hydrolysis (Scheme 18).[144] The chlorogermylamine **51** can be prepared from Mes_2GeCl_2 (Equation (113)) and was subsequently converted to the stable germanium–nitrogen doubly bonded species **52** (Equation (114)).[145] A compound containing germanium attached to C_{60} has also been prepared via this method.[146]

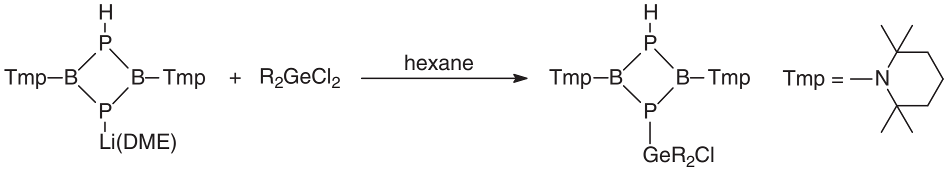


Scheme 18



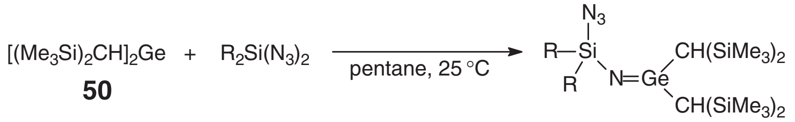
48

(110)



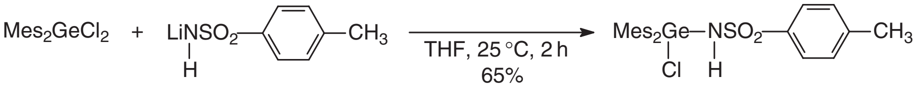
49a: R = Me (81%)
49b: R = Ph (85%)

(111)



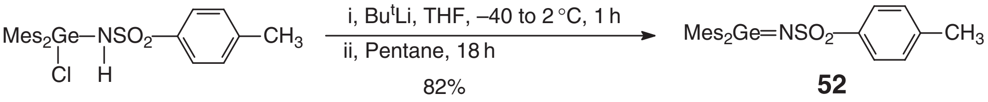
R = Mes, Bu^t

(112)



51

(113)

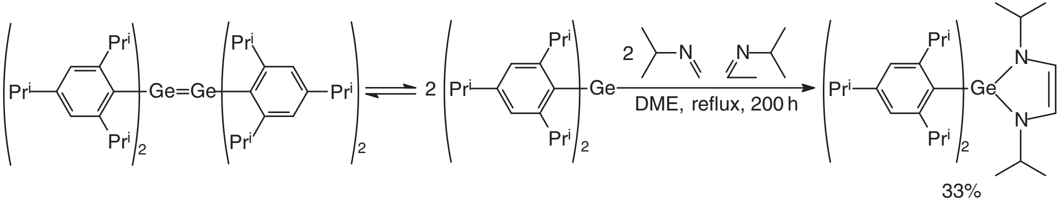


52

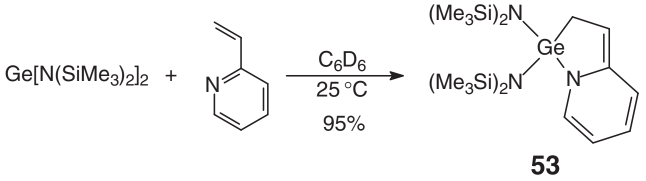
(114)

3.13.5.1.2 Preparation from germylenes

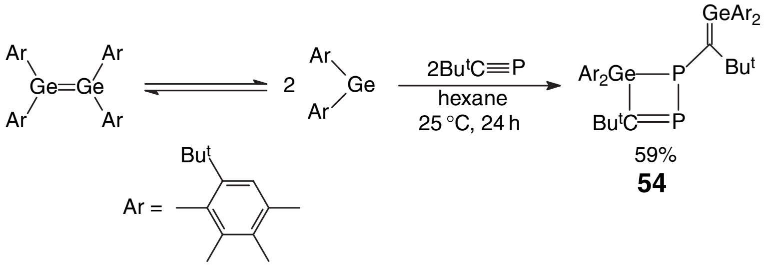
Oxadative addition reactions of germylenes are a versatile method for the formation of germanium–pnictogen bonds.[147–156] Reaction of germylenes with diazabutadienes yields [4 + 1]-cycloaddition products (Equation (115)),[148] reaction of Ge[N(SiMe$_3$)$_2$]$_2$[149–151] with 2-vinylpyridine yields a germanium enamine **53** (Equation (116)),[152] and reaction with a phosphaalkyne yields a germadiphosphacyclobutene **54** (Equation (117)).[153] The germylene **50** reacts with adiponitrile to yield the cyclized product **55** which thermally tautomerizes to the imine **56** (Equation (118)).[154]



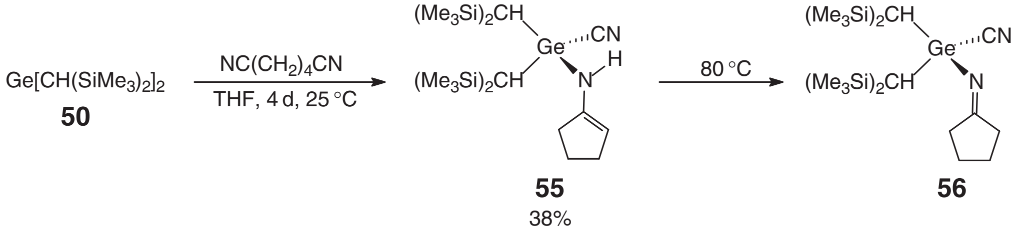
(115)



(116)

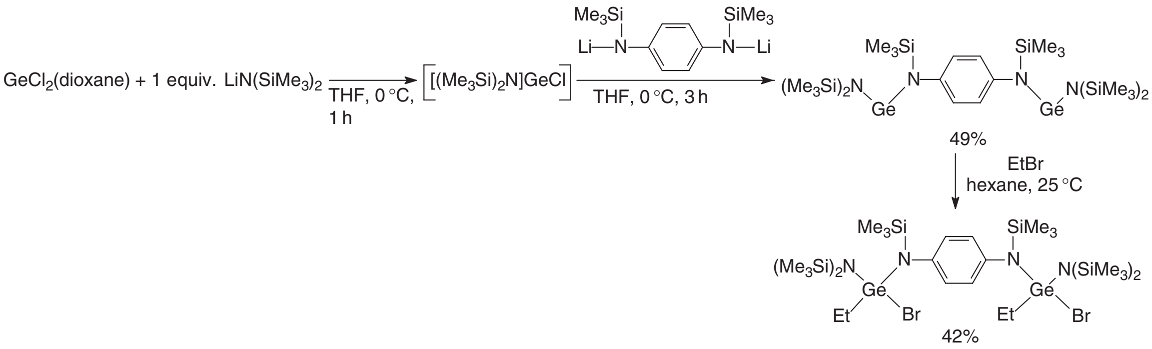


(117)



(118)

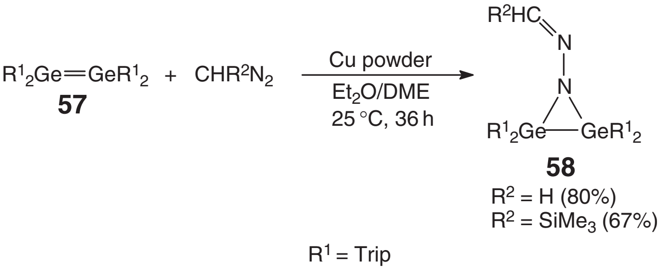
A germanium–nitrogen complex containing two Ge atoms disposed in an acyclic array was obtained via the formation of the intermediate germylene [(Me$_3$Si)$_2$N]GeCl, which was converted into a germanium(IV) adduct via an insertion reaction (Scheme 19).[157]



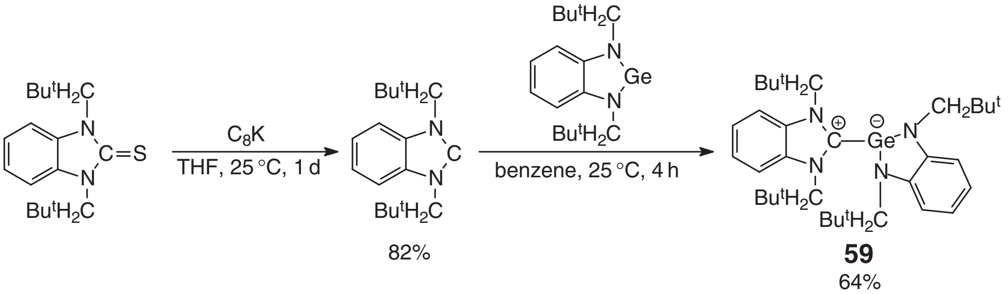
Scheme 19

3.13.5.1.3 Other methods of preparation

Reaction of the digermene **57** with diazomethane or trimethylsilyldiazomethane yields the azadigermiranes **58** via a [2+1]-cycloaddition (Equation (119)).[158] Coupling of a cyclic carbene and a cyclic germylene furnishes the zwitterionic species **59** (Equation (120)).[159]



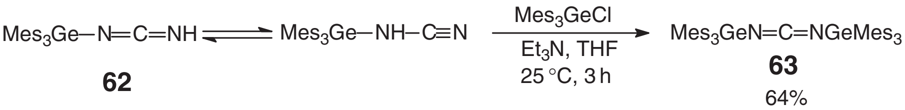
(119)



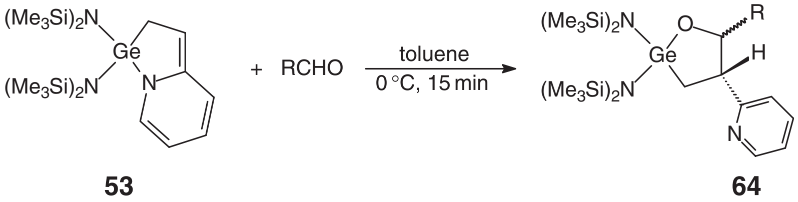
(120)

3.13.5.2 Reactions of the Germanium–Group 15 Bond

Compounds containing a germanium–nitrogen and germanium–phosphorus bond undergo a number of interesting conversions. The germanimines **60** yield bis(germanimines) upon treatment with $Ge[CH(SiMe_3)_2]_2$ **50**, which subsequently can be photolytically converted into the cyclic species **61** (Scheme 20).[143] The germylated cyanamide **62** can be converted into the bis(germylcarbodiimido)germane **63** in the presence of Et_3N (Equation (121)).[160] The bicyclic compound **63** undergoes an aldol reaction with a number of aldehydes to furnish the condensation products **64** (Equation (122), Table 20).[152]

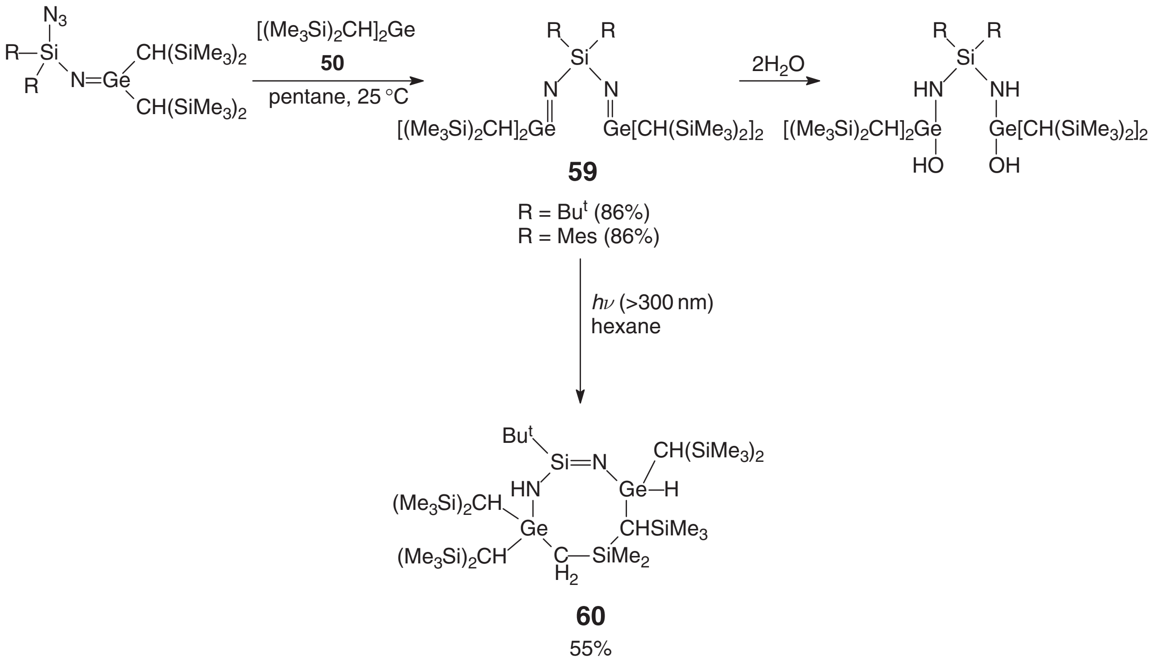


$$\underset{\mathbf{62}}{Mes_3Ge{-}N{=}C{=}NH} \rightleftharpoons Mes_3Ge{-}NH{-}C{\equiv}N \xrightarrow[\substack{Et_3N,\ THF \\ 25\,^\circ C,\ 3\,h}]{Mes_3GeCl} \underset{\substack{\mathbf{63} \\ 64\%}}{Mes_3GeN{=}C{=}NGeMes_3} \qquad (121)$$



(122)

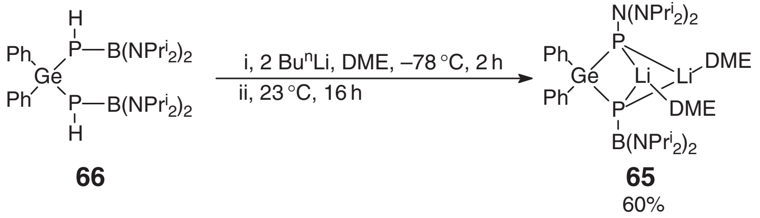
The bis(phosphides) **65** can be prepared from the lithiation of the corresponding bis(borylphosphino)germanes **66** (Equation (123)) and these species can be quantitatively converted into phosphorus-bridged complexes containing two different group 14 metals (Equation (124)).[141] Compound **67** can be converted into cage complexes containing germanium, boron, and phosphorus upon lithiation (Equation (125)).[142] Photolysis of the phosphirenes **68** results in an isomerization to provide the phosphagermetes **69** in low yield (Equation (126)).[161]



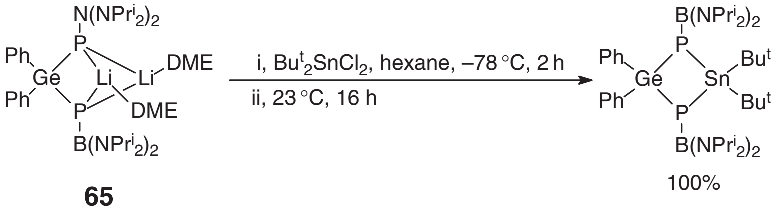
Scheme 20

Table 20 Experimental data for Equation (122)

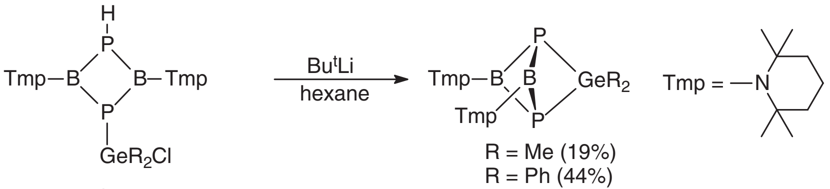
R	*Yield* (%)	*Ratio cis* : *trans*
Cl_3C	87	4 : 96
Me	82	26 : 74
Et	79	35 : 65
$PhCH_2$	78	28 : 72
Ph	90	75 : 25
m-ClPh	90	75 : 25



(123)

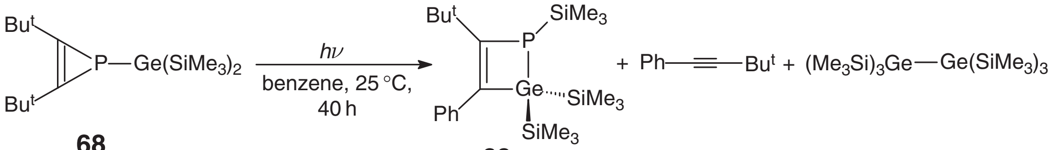


(124)



67

(125)



68 **69** 5%

(126)

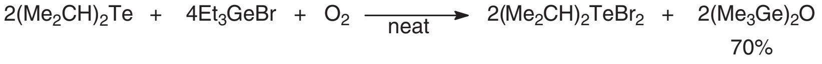
3.13.6 Compounds with Germanium–Group 16 Element Bonds

The synthesis and chemistry of compounds where germanium is linked to a group 16 element has undergone a number of developments since the field was last surveyed,[1] and a review on the subject has been published.[162] New developments include the formation of new heterocyclic compounds and formation of multiple bonds to the heavier group 16 elements. A review has also appeared on this subject.[163]

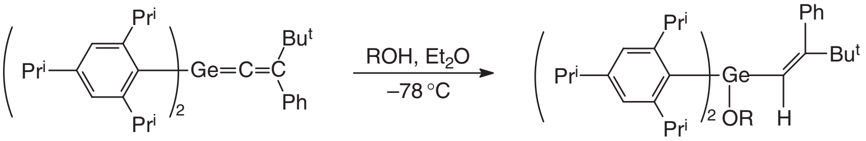
3.13.6.1 Preparation

3.13.6.1.1 Compounds with germanium–oxygen bonds

Several new types of Ge–O-bonded species have appeared and some new methods for the formation of such bonds have been described. Germoxanes can be obtained via reaction of triorganobromogermanes with oxygen in the presence of organotellurium compounds (Equation (127)).[164] The germapropadiene **4** reacts with alcohols to provide alkoxides **70** (Equation (128)) or benzaldehyde to yield a 1,2-oxagermetane **71** via a [2 + 2]-addition (Equation (129)), which exhibits unusual thermal stability for an unencumbered oxagermetane.[16]



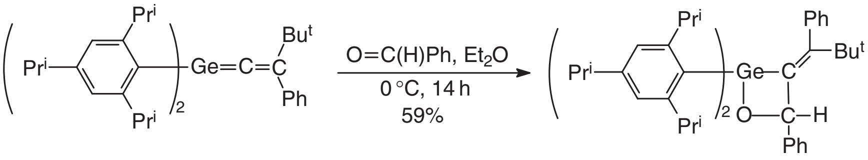
$$2(Me_2CH)_2Te + 4Et_3GeBr + O_2 \xrightarrow[\text{neat}]{} 2(Me_2CH)_2TeBr_2 + \underset{70\%}{2(Me_3Ge)_2O} \qquad (127)$$



4

70a: R = H (71%)
70b: R = Me (22%)
70c: R = Et (51%)

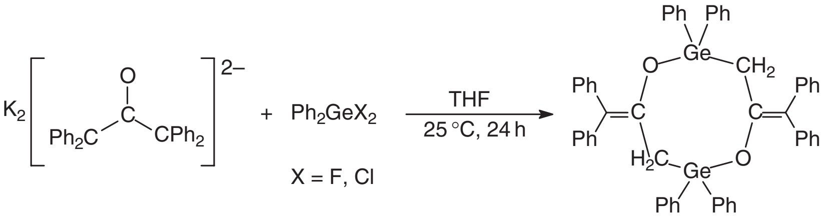
(128)



4 **71**

(129)

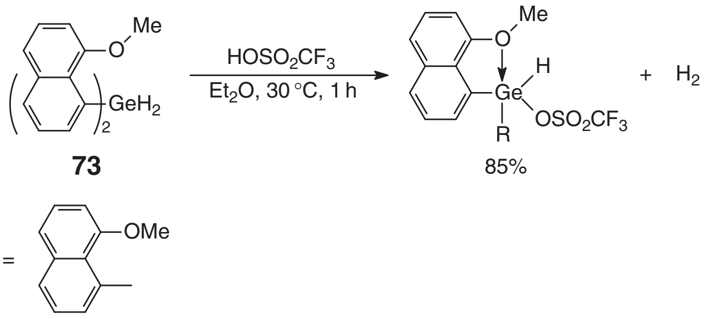
Large rings containing Ge–O bonds have been prepared.[165,166] Reaction of the dianion of 1,1-diphenylacetone with Ph_2GeX_2 yields a crown-shaped eight-membered ring (Equation (130)) and the reactivity of the germanium halides with these salts was shown to be distinctly different than that of the silicon analogs.[166]



(130)

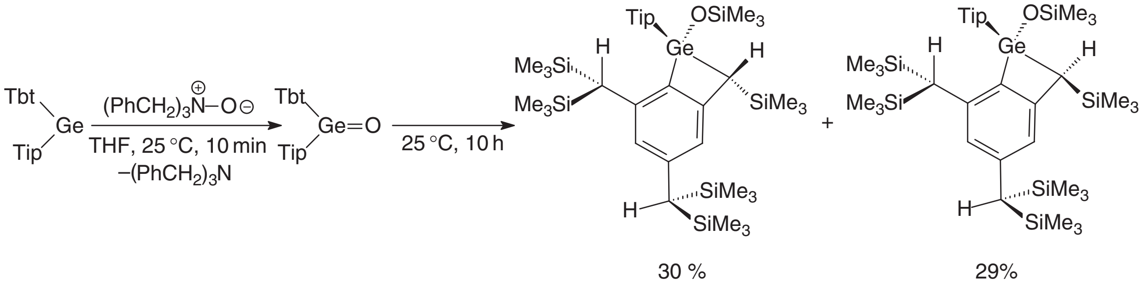
Compounds containing germanium–oxygen double bonds which are transiently stable have emerged.[167,168] A germanone which is temporarily stable in solution was prepared which undergoes intramolecular cyclization (Scheme 21),[167] and this species was also obtained from the cycloreversion of **72** (Scheme 22), as identified by its cyclization products.[168]

A number of hypervalent species containing germanium–oxygen bonds have been reported.[169–175] The reaction of the methoxynaphthylgermanium dihydride **73** with triflic acid yields a formally five-coordinate triflate complex where the germanium is weakly attached to the triflate anion (Equation (131)).[170,171] The synthesis of other functional germanium(II) and germanium(IV) triflates with typical coordination numbers has been described and their reactivities have been investigated.[176]

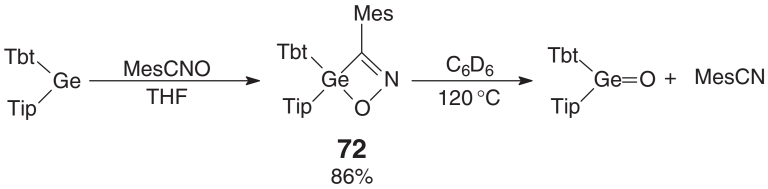


(131)

The spirocyclic pentacoordinate germanium zwitterion **74** was prepared from 2,3-naphthalenediol in three steps starting with a trichlorogermane (Equation (132)).[172] The bicyclic species **75** can be prepared in modest yield

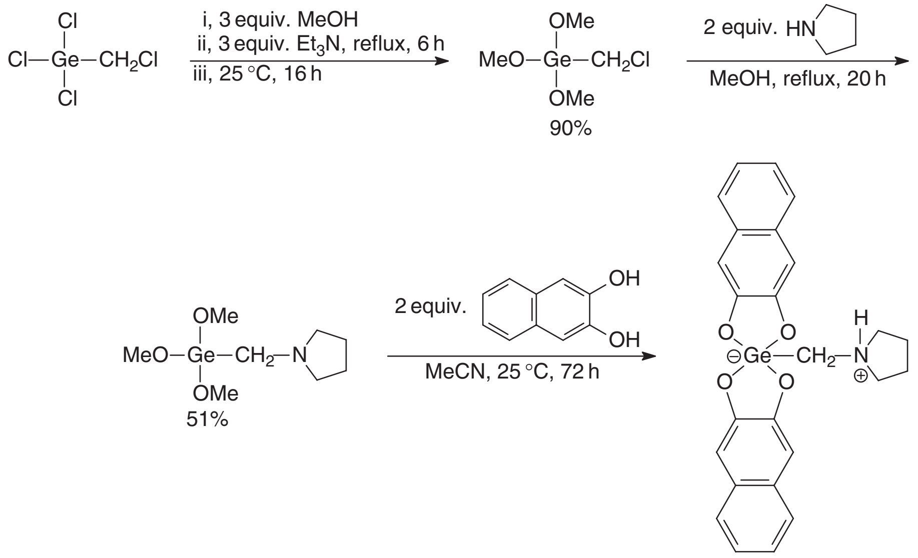


Scheme 21



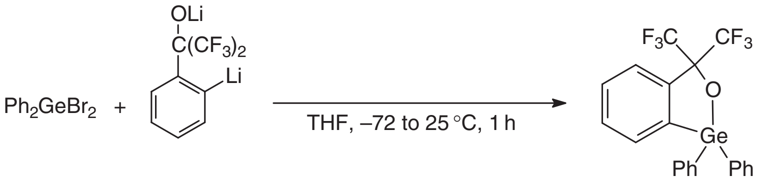
Scheme 22

(Equation (133)) and subsequently can be converted into a pentacoordinate 1,2-oxagermetanide (Scheme 23).[173] Reaction of trichlorogermanes with mercaptoacetic acid or 2-mercaptoethanol also yields pentacoordinate organogermanium compounds (Equations (134)[174] and (135)).[175]



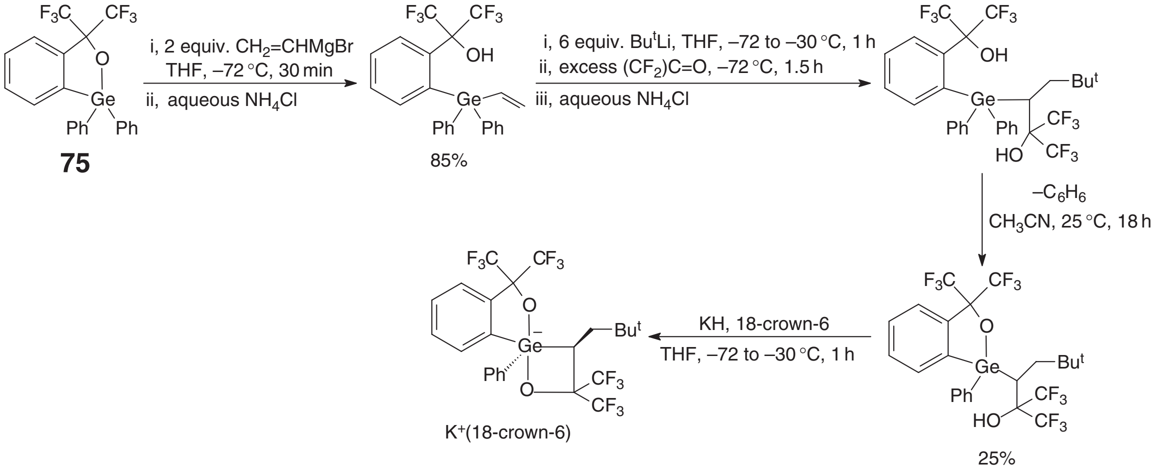
74
92%

(132)

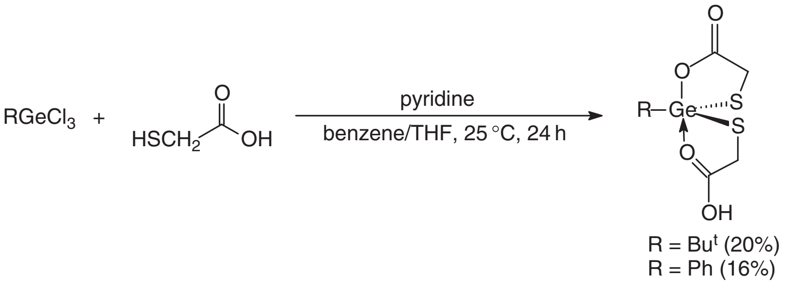


75
37%

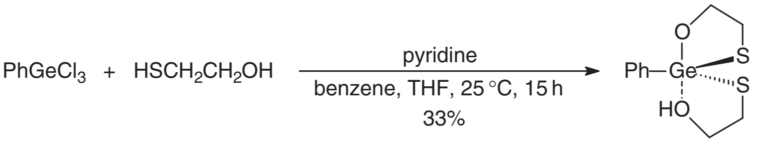
(133)



Scheme 23

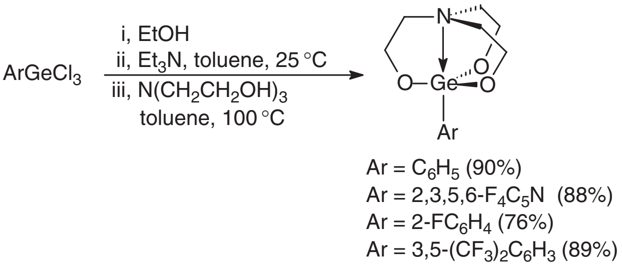


(134)

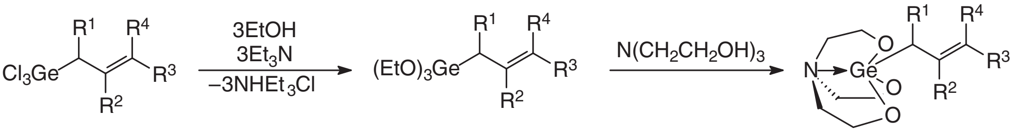


(135)

Germatranes have a number of useful synthetic applications, and a number of new species have been prepared and characterized.[90,92,177,178] Alkyl- or arylgermanium trichlorides have proved to be useful for the synthesis of germatranes (Equations (136)[92] and (137), Table 21).[90]



(136)



76

(137)

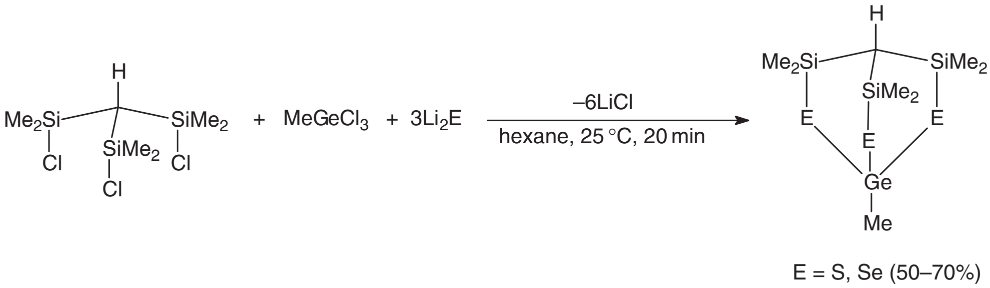
3.13.6.1.2 Compounds with germanium bonded to sulfur, selenium, or tellurium

Germanium compounds containing dithiocarbonate[179] and dithiophosphate[180,181] ligands which have Ge–S bonds have been prepared and structurally characterized. Compounds containing germanium and other group 14 elements held together by chalcogenide bridges have been synthesized such as the heavy bicyclo[2.2.2]octane derivatives which contain germanium and silicon in the skeleton[182,183] (Equation (138)).[183] Reaction of the Ge═Sn doubly bonded species **77** with propylene sulfide leads to the formation of a dithiagermastannacyclobutane, presumably occurring via two sequential insertions of sulfur (Equation (139)).[184]

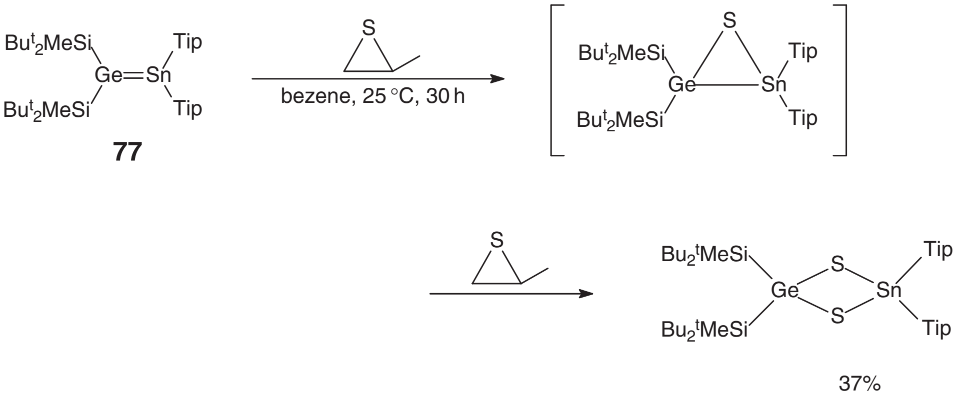
Table 21 Experimental data for Equation (137)

R groups	*Compound*	*Yield (%)*	*Ratio E : Z*
$R^1 = Me; R^2 = R^3 = R^4 = H$	**76a**	99	n.a.
$R^1 = R^2 = R^4 = H; R^3 = Me$	**76b**	98	65 : 35
$R^1 = R^4 = H; R^2 = R^3 = Me$	**76c**	86[a]	65 : 35
$R^1 = R^2 = Me; R^3 = R^4 = H$	**76d**	[a]	n.a.

[a] Compound **76d** was formed as a minor byproduct in the preparation of **76c** (**76c** : **76d** = 11 : 1).



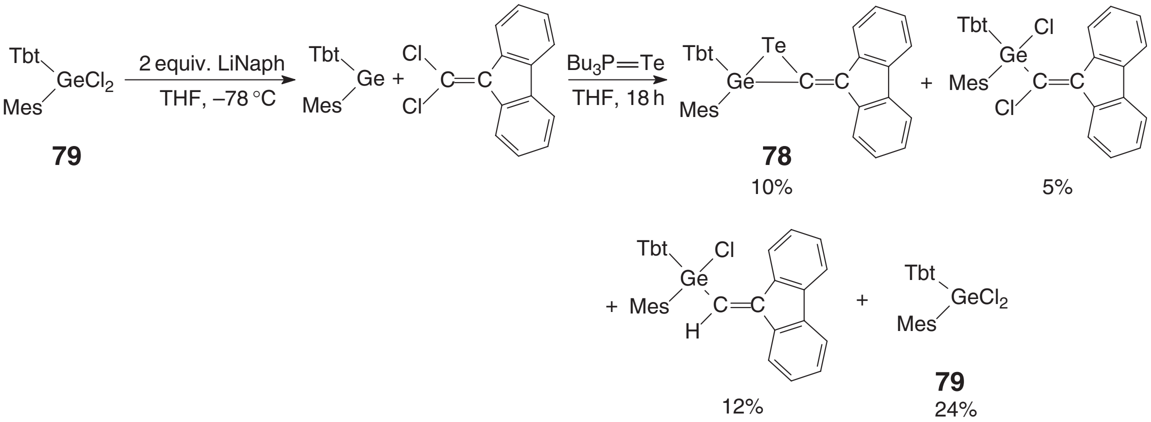
(138)



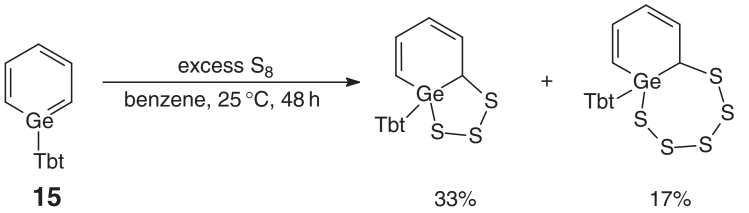
(139)

Complexes incorporating one[185] or two[186] chalcogenide bridges between germanium and carbon atoms have been prepared and characterized. The first alkylidenetelluragermane **78** was obtained from the bulky germylene **79** (Scheme 24), and the structure of this material indicates it exists as a π-complex consisting of a tellurium atom bonded to a germanium–carbon double bond.[185]

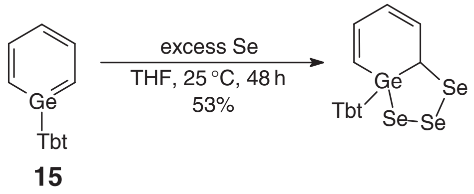
Polysulfide rings containing germanium and catenated sulfur atoms with ring sizes ranging from five to seven members are known and can be prepared from germanes and elemental sulfur.[187–189] The sterically encumbered germabenzene **15** reacts with elemental sulfur to yield both a trithiagermolane and a pentathiagermepane (Equation (140)).[188] However, reaction with elemental selenium yielded only the triselenagermolane with no evidence for formation of the larger cyclic species (Equation (141)).[188] A related species can be prepared starting with a sterically crowded germane proceeding via formation of the germylene intermediate **11** (Equation (142)).[190]



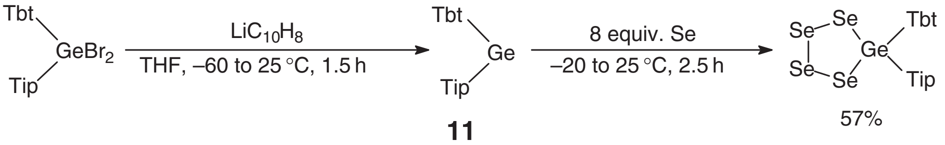
Scheme 24



(140)

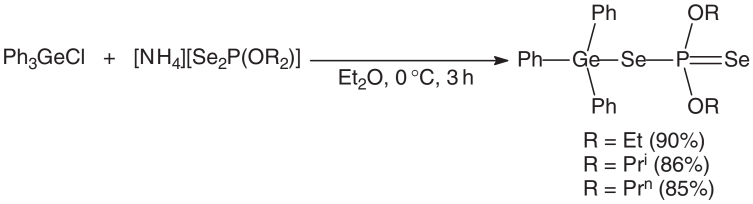


(141)



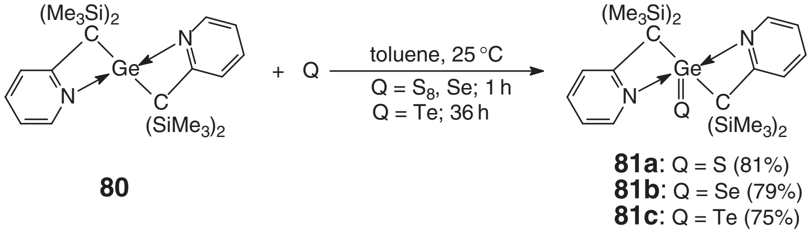
(142)

Several other complexes containing germanium bound to the heavier chalcogenides selenium and tellurium have been reported. A series of germanium diselenophosphates was prepared by nucleophilic attack of an anionic selenium reagent on a germanium halide (Equation (143)).[191] The base-stabilized germylene **80** undergoes reaction with elemental chalcogens to furnish the doubly bonded germanium chalcogenide species **81** (Equation (144)).[192] Heating **80** in the presence of sulfur or selenium at elevated temperatures yields the dihydropyridinato compounds **82** (Equation (145)).[192]

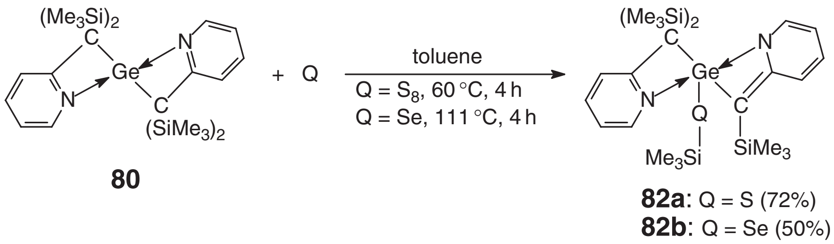


$$Ph_3GeCl + [NH_4][Se_2P(OR_2)] \xrightarrow[Et_2O,\ 0\,°C,\ 3\,h]{} Ph_3Ge{-}Se{-}P(=Se)(OR)_2$$

(143)



(144)



(145)

Germacyclopropabenzene **3** can react directly with elemental chalcogens to yield bicyclic chalcogenagermetes **83** (Equation (146)).[193] The structure of the tellurium derivative **83c** is shown in Figure 4 and structural information is

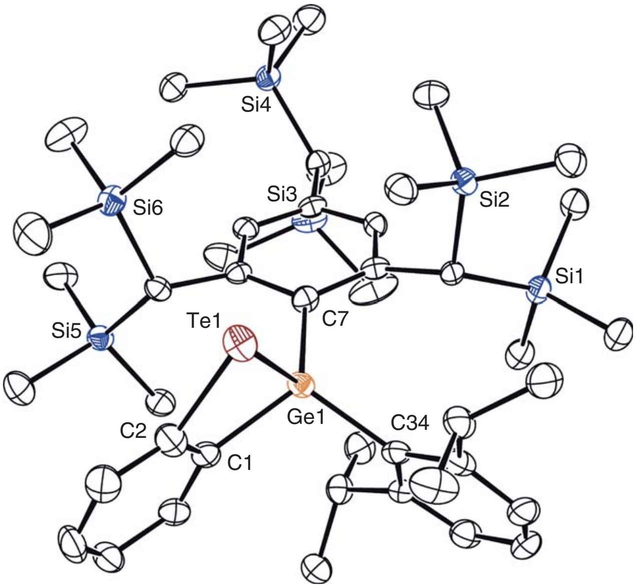
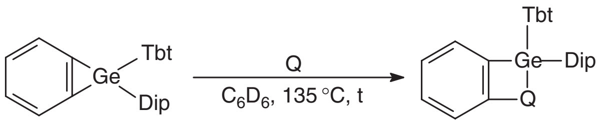


Figure 4 ORTEP diagram of the Ge–Te bonded species **83c**. Reproduced from Sasamori, T.; Sasaki, T.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 612–618.

Table 22 Selected bond lengths (Å) and angles (°) for **83c**

Ge(1)–Te(1)	2.6293(6)	C(7)–Ge(1)–Te(1)	114.0(1)
Ge(1)–C(1)	1.999(4)	C(34)–Ge(1)–Te(1)	120.9(1)
Ge(1)–C(7)	1.971(4)	C(7)–Ge(1)–C(34)	111.0(2)
Ge(1)–C(34)	1.999(4)	Ge(1)–Te(1)–C(2)	69.2(1)
Te(1)–C(2)	2.130(5)	C(1)–Ge(1)–Te(1)	76.4(1)
C(1)–C(2)	1.405(7)	Ge(1)–C(1)–C(2)	105.5(3)
		C(1)–C(2)–Te(1)	108.8(3)

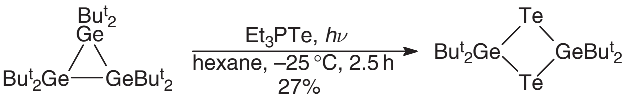
collected in Table 22. This represents the first stable germanium–tellurete derivative and has a Ge–Te contact of 2.6293(6) Å. A germanium–tellurium-bonded species was also obtained by the photolysis of a cyclic trigermane in the presence of triethylphosphine telluride (Equation (147)).[194]



3

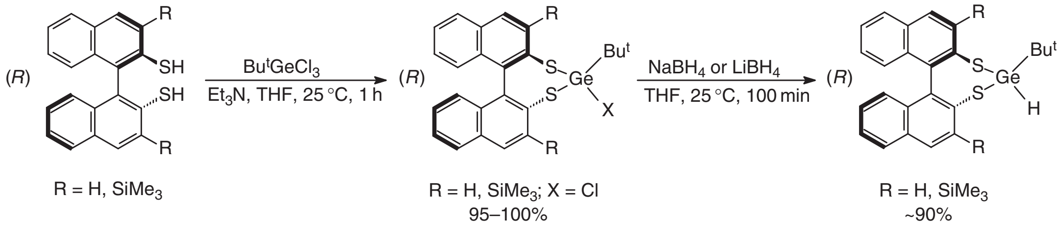
83a: Q = S_8, t = 120 h (63%)
83b: Q = Se, t = 216 h (56 %)
83c: Q = Te, t = 336 h (54%)

(146)



(147)

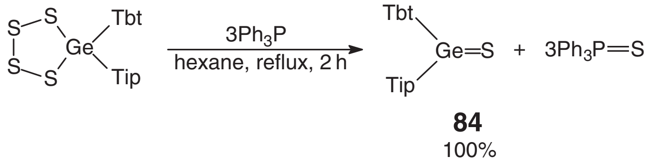
Another interesting group of compounds which have recently appeared are the chiral organogermanium hydrides which contain a resolved 1,1′-dithiobinaphthyl ligand (Equation (148)).[195]



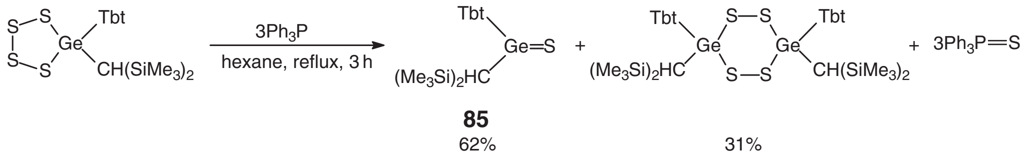
(148)

3.13.6.2 Reactivity of the Germanium–Chalcogen Bond

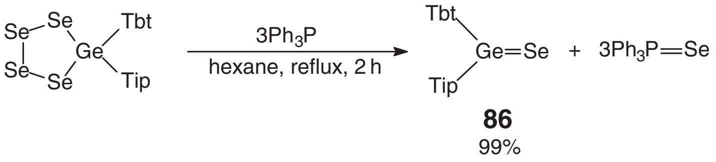
Heterocyclic compounds of germanium containing catenated chalcogen moieties undergo a variety of transformations. Tetrathiagermolanes react with triphenylphosphine to furnish the kinetically stabilized germanethiones[190,196] 84 and 85 in quantitative (Equation (149)) and good yield (Equation (150)), while a related selenium species gives the germane selenone 86 in excellent yield (Equation (151)).[190,197] Both 84 and 86 undergo [2 + 2]-cycloaddition reactions with phenylisothiocyanate and [3+2]-cycloaddition reactions with mesitonitrile oxide (Scheme 25).[190] The related tellurium-containing species 88 was obtained by thermolysis of the strained germirene 87 in the presence of tellurium metal (Equation (152)), and 88 undergoes cycloaddition reactions (Scheme 26).[198] Compound 87 can also be employed for the preparation of a 4-imino-1,3,2-dithiagermetane species (Equation (153)).[199]



(149)



(150)



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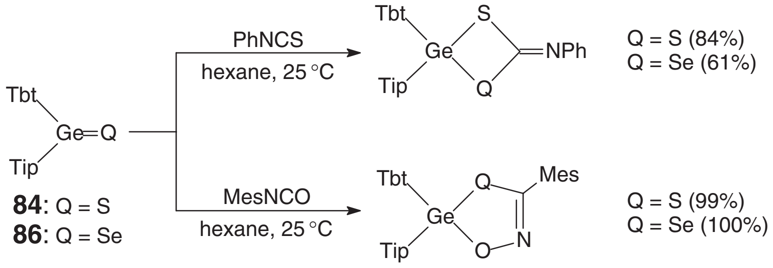
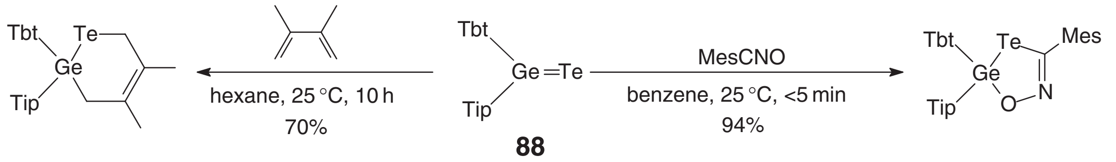
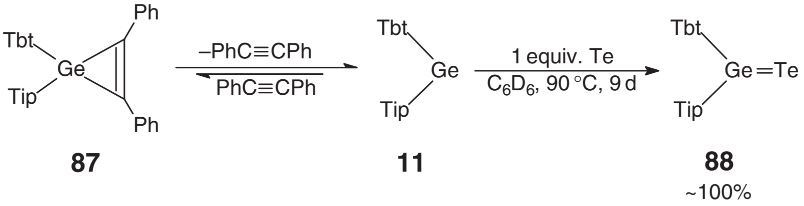


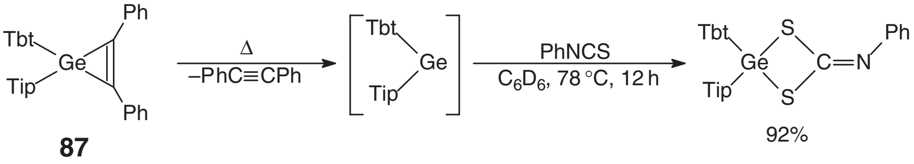
Scheme 25



Scheme 26



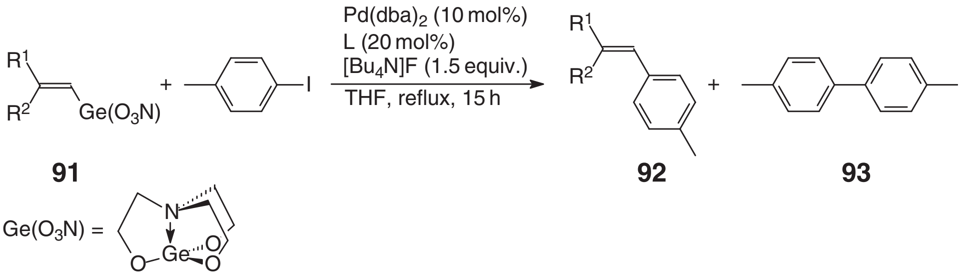
(152)



(153)

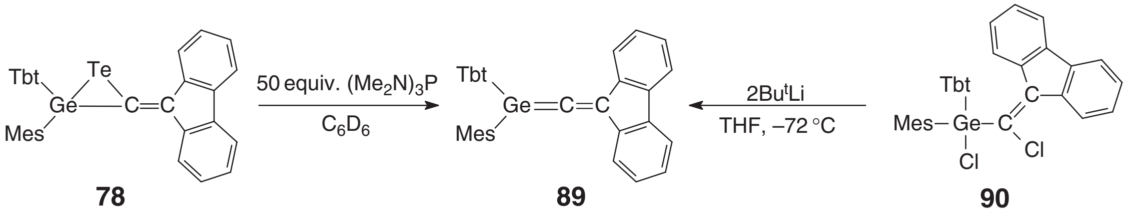
The first stable 1-germaallene **89** was obtained either from the detelluration of **78** or alternatively from the dechlorination of the chlorovinylchlorogermane **90** (Scheme 27).[200] The identity **89** was confirmed via trapping reactions with various reagents which yielded germanium-group 16 bonded species (Scheme 28).[200]

Organogermatranes can be employed in a variety of coupling processes.[201–203] Similar to their tin-containing analogs, these species can be used in the palladium-catalyzed cross-coupling reaction with aryl iodides (Equation (154), Table 23), but the germanium species are less reactive than related tin congeners.[202]

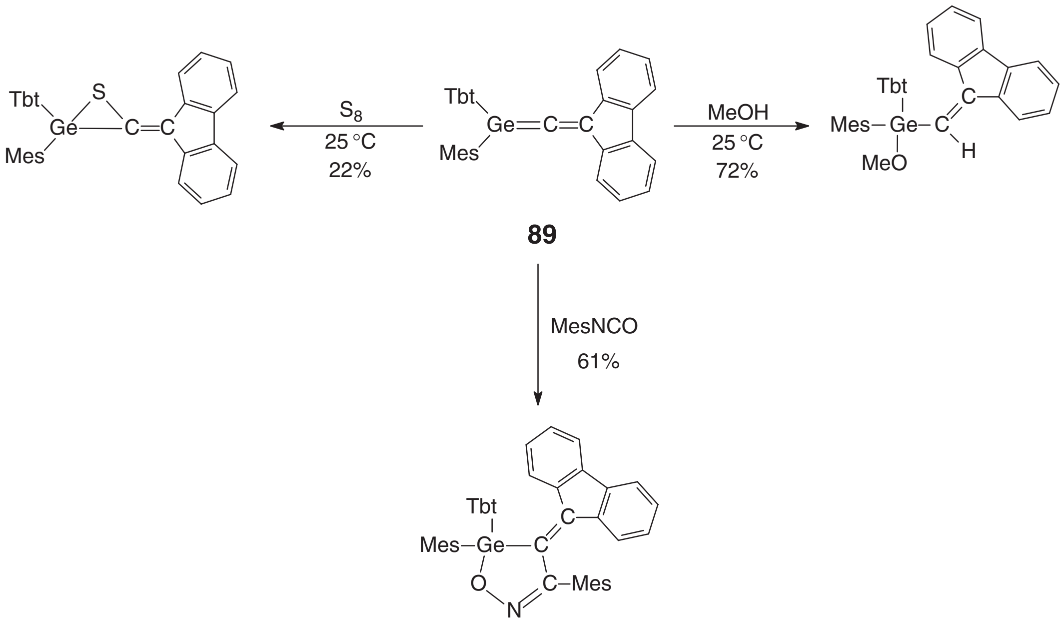


(154)

Thermolysis of the Ge–O–N-bonded species **94** produces the 1,3-digermaoxetane **95** (Equation (155)) via initial formation of a radical species (Scheme 29).[204]



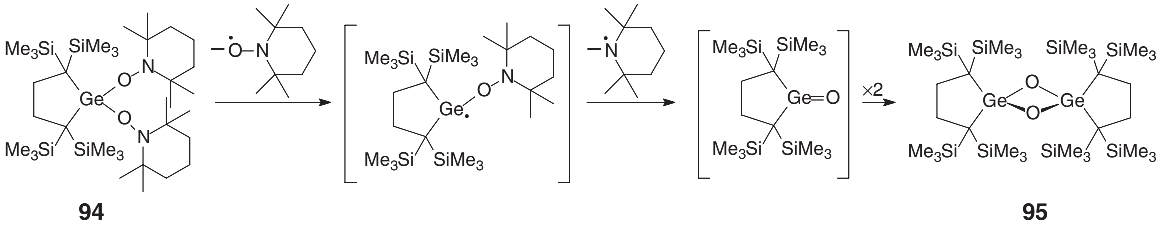
Scheme 27



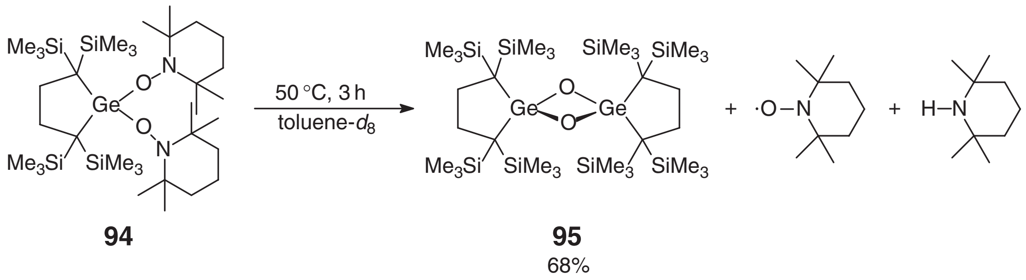
Scheme 28

Table 23 Experimental data for Equation (154)

*R*¹	*R*²	*L*	*Yield* **92** (%)	*Yield* **93** (%)
Ph	H	2-PBu$^t_2$-biphenyl	53	21
Ph	H	$AsPh_3$	64	16
H	Ph ($E:Z=1:3.5$)	$AsPh_3$	73 ($E:Z=1:2.6$)	15
H	*p*-tol ($E:Z=1:7.5$)	$AsPh_3$	71 ($E:Z=1:5.4$)	16
H	*p*-ClC_6H_4 ($E:Z=1:5.5$)	$AsPh_3$	73 ($E:Z=1:3.4$)	12



Scheme 29



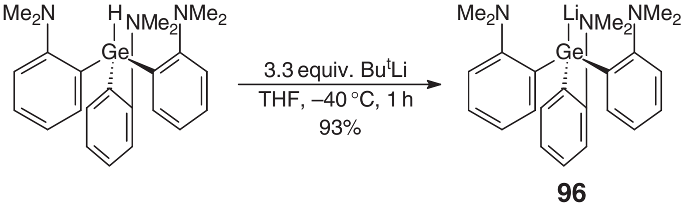
(155)

3.13.7 Compounds with Germanium–Metal (or Metalloid) Bonds

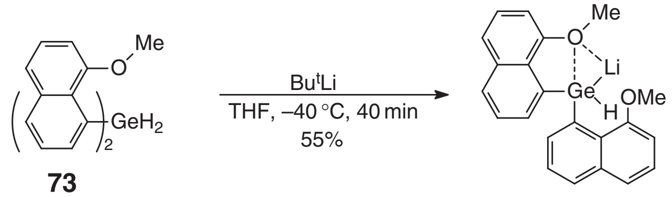
3.13.7.1 Preparation

3.13.7.1.1 Organogermyl–alkali metal compounds

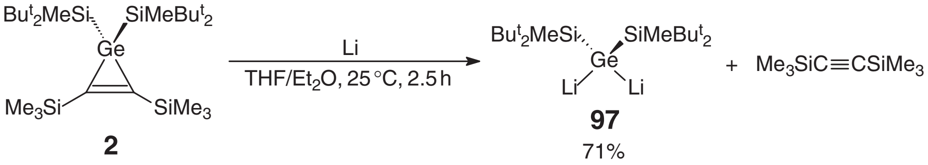
Germyllithium reagents are well-known species that function as useful synthons and a variety of new compound have appeared.[205] The germyllithium species **96** has a distorted structure induced by intermolecular coordination of the amino groups of the ligands (Equation (156)).[109] The Ge–Li bond length is very short (2.598(9) Å) and the Ge and Li atoms are part of a five-membered chelate ring, as shown in Figure 5. Monolithiation of the dihydride **73** yields a germyllithium species which is also stabilized by an intramolecular interaction (Equation (157)).[107] The first isolable dithiated germanium species **97** was prepared via the reaction of a germacyclopropene **2** with Li metal (Equation (158)).[12]



(156)



(157)



(158)

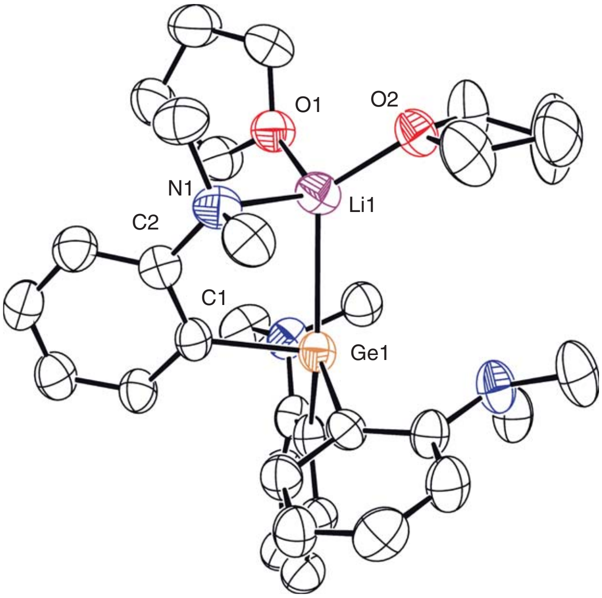
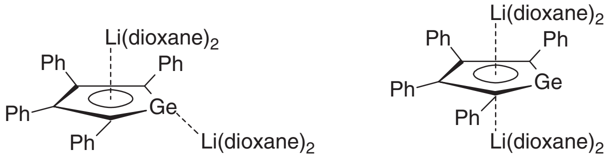


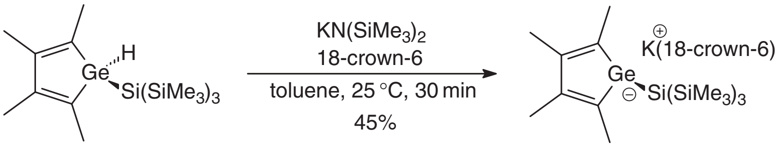
Figure 5 ORTEP diagram of the germyllithium species **96**. Reproduced from Kawachi, A.; Tanaka, Y.; Tamao, K. *Eur. J. Inorg. Chem*. **1999**, 461–464.



99a **99b**

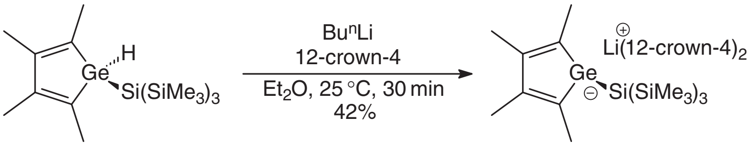
Figure 6 Illustration of the two isomorphic forms of **99**. Reproduced from West, R.; Sohn, H.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 1002–1004.

The synthesis of alkali salts of the sterically encumbered germole **98** (Equations (159) and (160)),[18] as well as the dilithio salt of tetraphenylgermole **99** (Equation (161)),[19] have been reported. The latter species crystallized in two isomorphic forms (**99a** and **99b**, Figure 6) and the dianion was shown to be aromatic.



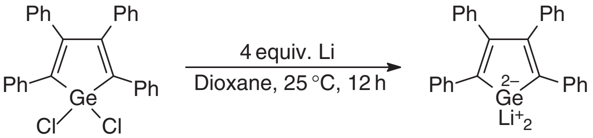
98

(159)



98

(160)

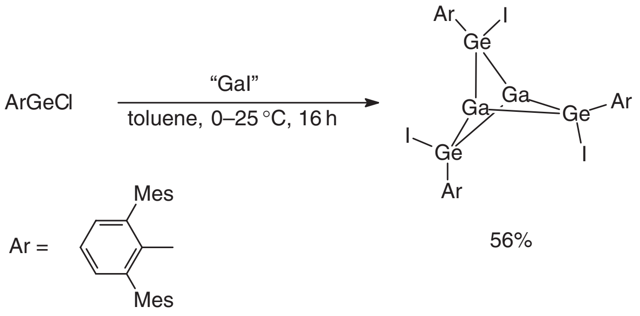


99

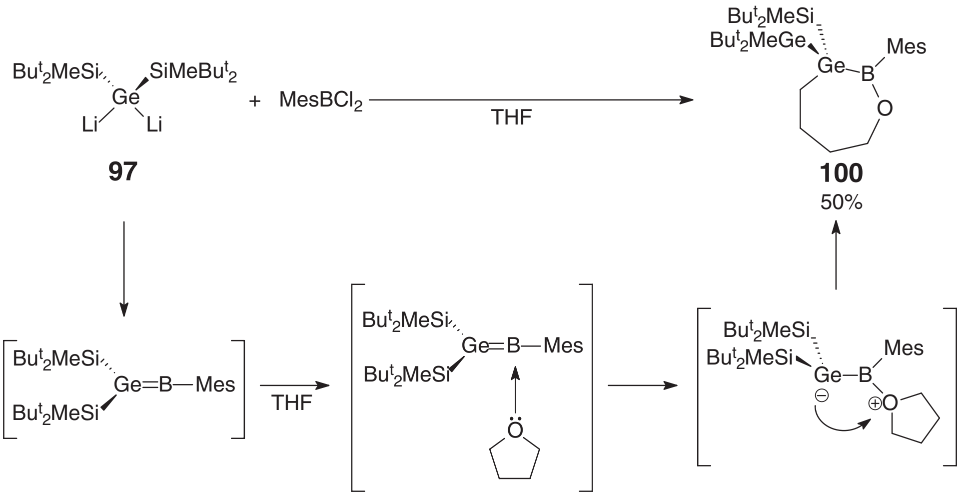
(161)

3.13.7.1.2 Organogermyl–group 13 metal (metalloid) compounds

Very few examples of these species have appeared since the field was last reviewed.[1] One species of interest is the seven-membered heterocycle **100**, which was obtained from the dilithiated species **97** via the formation of a Ge═B doubly bonded intermediate (Scheme 30).[206] A rare example of a germanium/gallium cluster complex has also been prepared (Equation (162)).[207]



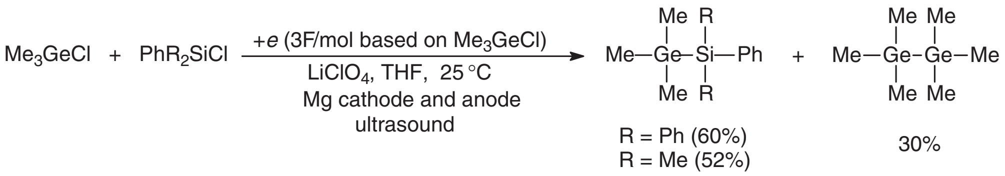
(162)



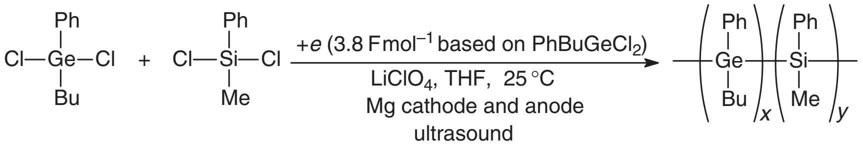
Scheme 30

3.13.7.1.3 Organogermyl–group 14 metal (metalloid) compounds

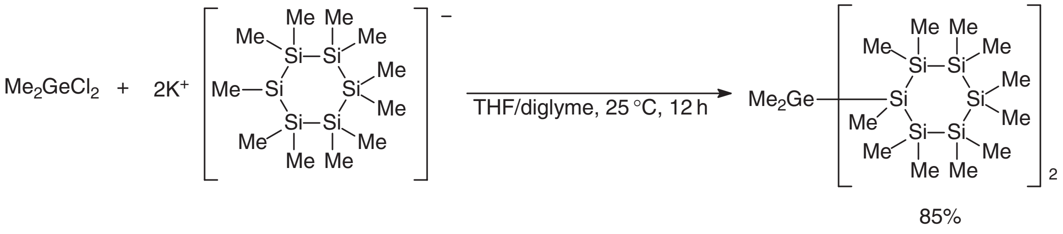
Compounds with a Ge–Si bond have been obtained through electroreductive synthesis[208,209] (Equations (163) and (164), Table 24)[209] and by metathesis using alkali metal salts of silanes[210–213] (Equations (165) and (166)).[211,212] The species **101** can subsequently be used for the formation of dendrimers with alternating Si and Ge atoms in the chain (Equation (167)).[212] Cyclic species such as the germatetrasilacyclopentane **102** can be formed employing germyllithium reagents (Equation (168)), and this species can be converted into a germatrisilacyclobutane by photolysis in the presence (Equation (169)) or absence of a trapping reagent (Equation (170)).[214]



(163)



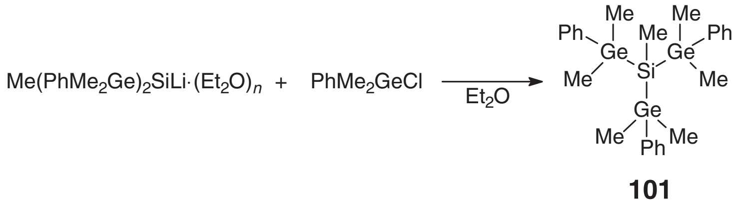
(164)



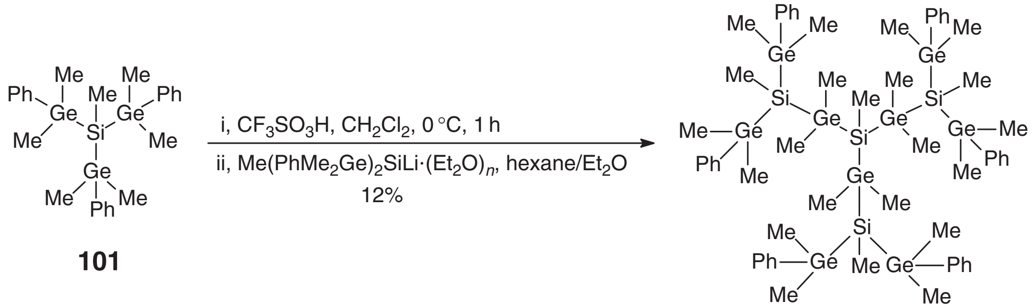
(165)

Table 24 Experimental data for Equation (164)

Ratio $PhBuGeCl_2 : PhMeSiCl_2$	*Yield* (%)	*Ge content in co-polymer (x/x + y)*	M_n (g/mol)
0.39	34	0.16	17,000
1.04	33	0.45	20,600



(166)



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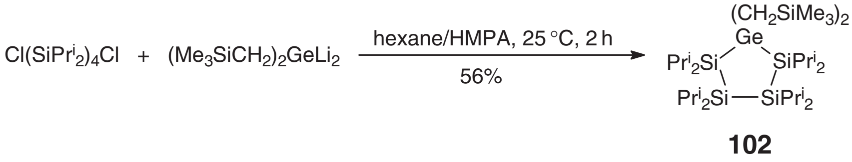
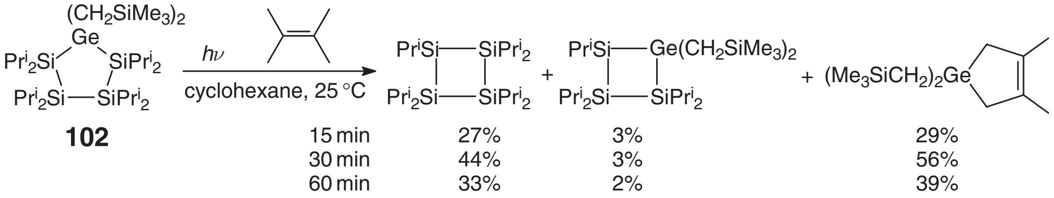


(168)



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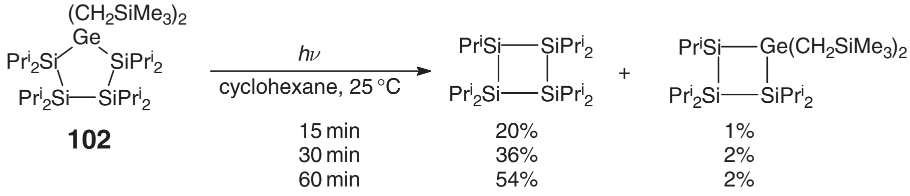
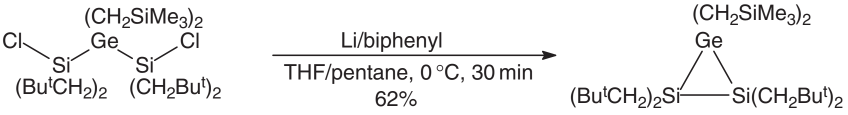
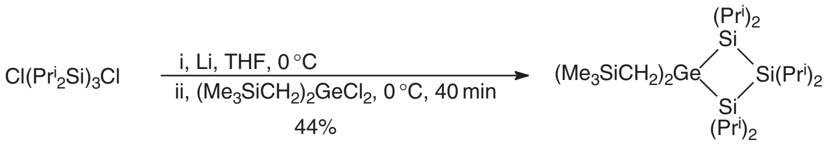


(170)

Cyclization of linear Ge/Si-containing precursors using Li metal furnishes a disilagermacyclopropane (Equation (171)), which can be photolyzed to give predominantly a disilene and a germylene (Scheme 31).[215] Lithium metal can also be used to affect cyclization of halogenated trisilanes by lithiation, followed by reaction with dichlorogermanes to give germatrisilacyclobutanes (Equations (172) and (173)).[216] Similarly, cyclization using base yields a germadisilaoxetane (Equation (174)), which upon phtolysis also releases a germylene and produces a disilaoxacycloproane (Scheme 32).[215]



(171)



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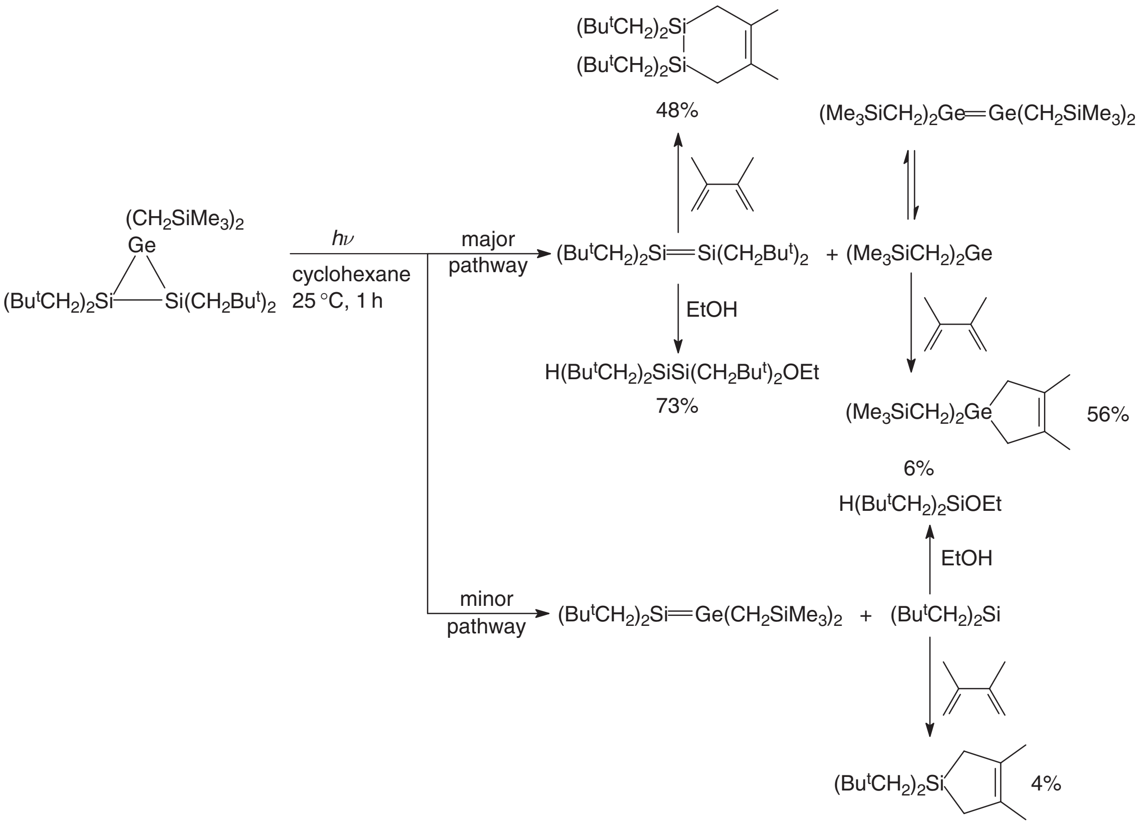
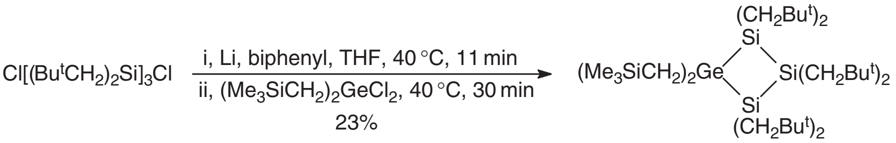
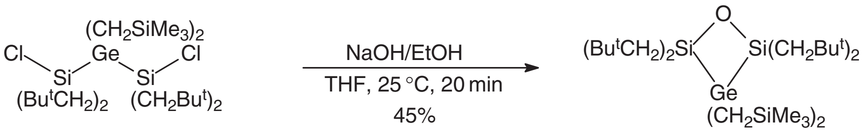


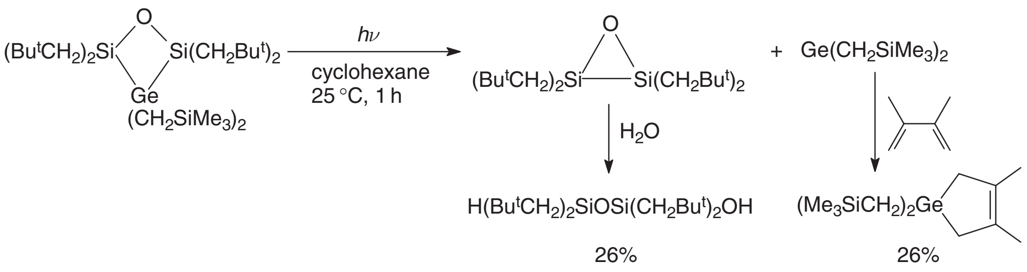
Scheme 31



(173)

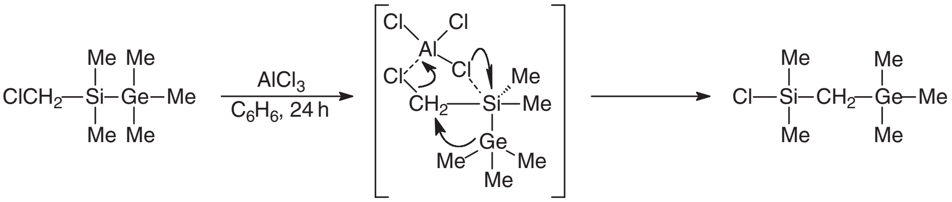


(174)

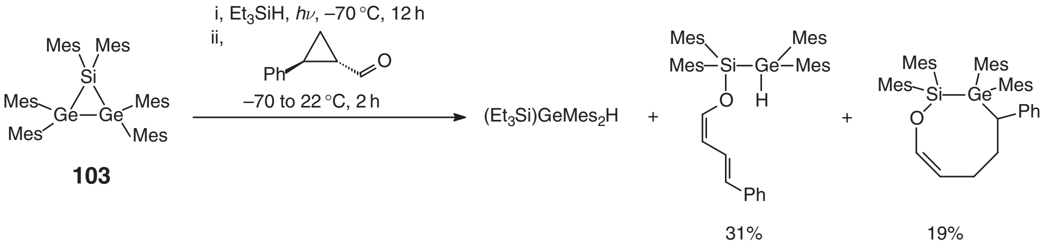


Scheme 32

The Si–Ge bond undergoes rearrangement in the presence of $AlCl_3$ to give a species with a methylene unit bridging the Si and Ge centers (Equation (175)), which is favored due to the formation of stronger Si–Cl and Ge–Cl bonds versus the weaker C–Cl bond.[217] Photolysis of the digermasilacyclopropane **103** in the presence of an aldehyde results in cleavage of the Ge–Si bond and leads to the formation of linear and cyclic adducts (Equation (176)).[218]

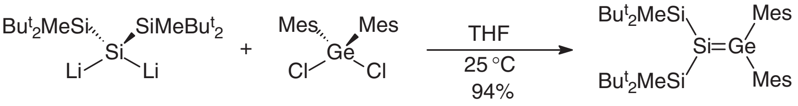


(175)

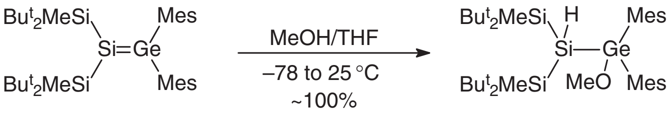


(176)

A similar process employing the silicon analog of **97** results in a compound with a Ge=Si double bond (Equation (177)), and reaction of this species with MeOH results in a product where the methoxy group is unexpectedly attached to germanium (Equation (178)).[219]

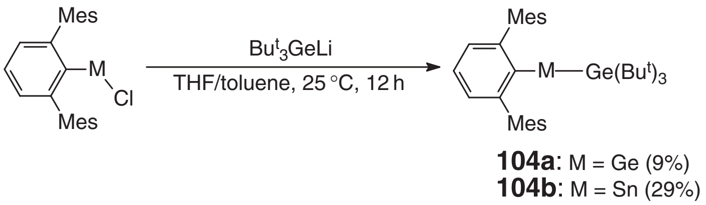


(177)

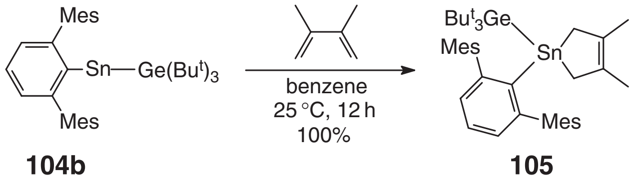


(178)

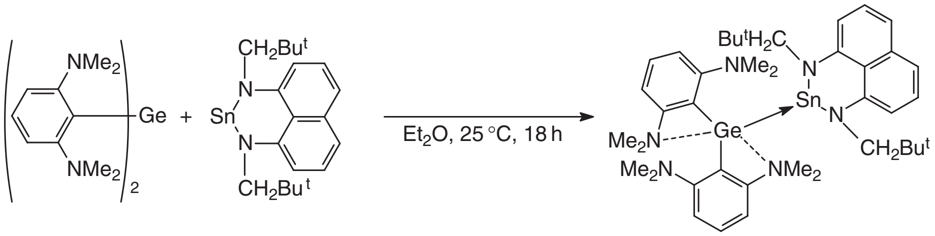
Several mixed germanium/tin species have also been prepared and characterized.[220–223] The compound **104** can be obtained from the appropriate heteroleptic germylene or stannylene precursor to furnish complexes with one metal in the divalent state and the other in the tetravalent state (Equation (179)).[224] Compound **104b** allowed the first determination of a tin(II)/germanium(IV) bond length, which was determined to be 2.722(1) Å. Compound **104b** undergoes oxidative trapping with 2,3-dimethylbutadiene to give the tin(IV)/germanium(IV) species **105** (Equation (180)).[224] The thermally stable complex **106** has also been prepared from germylene **107** which contains both germanium and tin in the divalent state (Equation (181)).[225]



(179)

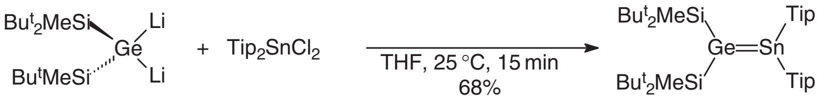


(180)

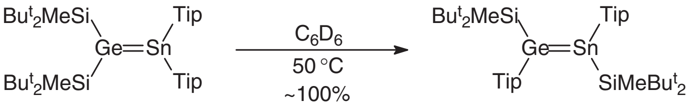


107 **106** (181)

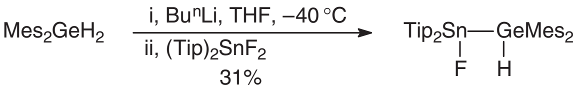
The dilithiated species **97** can be used to obtain a Ge═Sn doubly bonded species (Equation (182)), which undergoes a thermal isomerization involving migration of the bulky Tip group (Equation (183)).[184] The germanium/tin compound **108**, which contains a fluoride functionality at tin, can be prepared from Mes_2GeH_2 (Equation (184)), and this can subsequently be converted into the doubly bonded species **109** which can undergo several additional transformations (Scheme 33).[226]



97 (182)



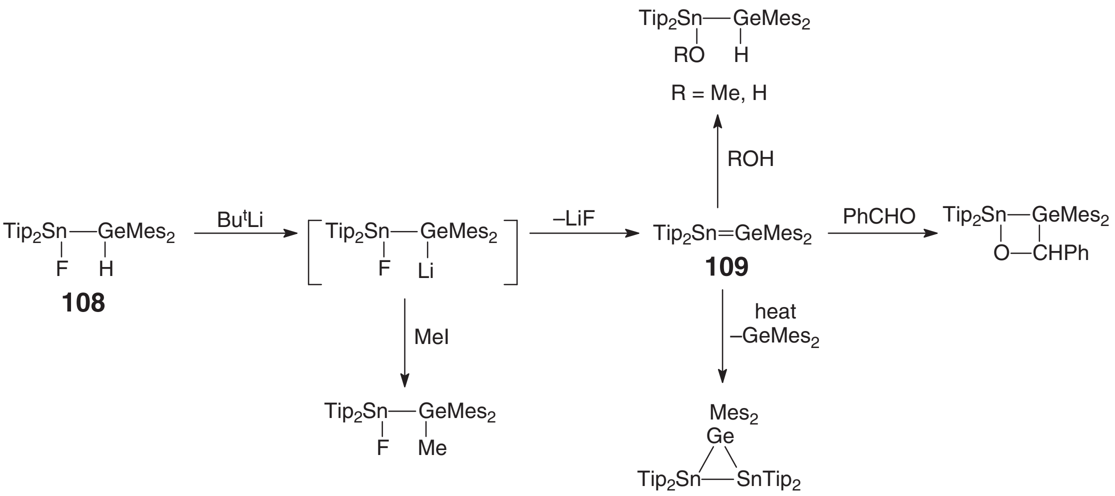
(183)



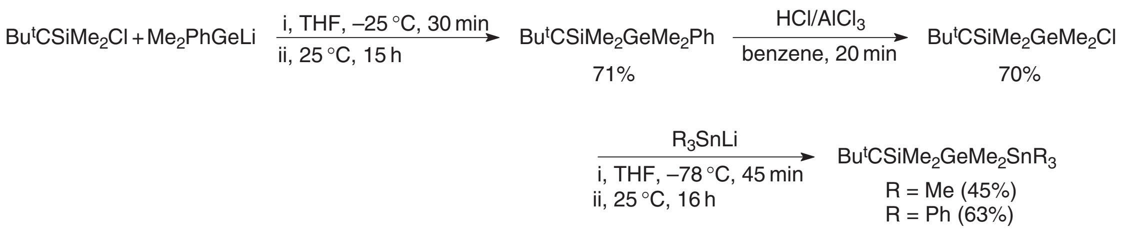
$$Mes_2GeH_2 \xrightarrow[\text{ii, (Tip)}_2\text{SnF}_2\ \ 31\%]{\text{i, Bu}^n\text{Li, THF, }-40\,^\circ\text{C}} \underset{\text{F}}{Tip_2Sn}-\underset{\text{H}}{GeMes_2}$$

108 (184)

Two compounds with a chain of four different group 14 elements have also been prepared (Scheme 34).[227]



Scheme 33



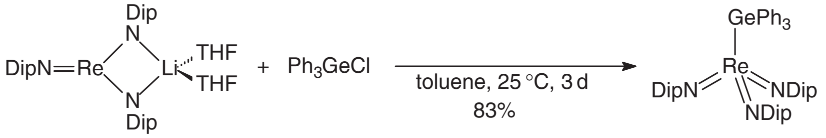
Scheme 34

3.13.7.1.4 Organogermyl–transition metal complexes

3.13.7.1.4.(i) Non-cyclic organogermyl transition metal complexes

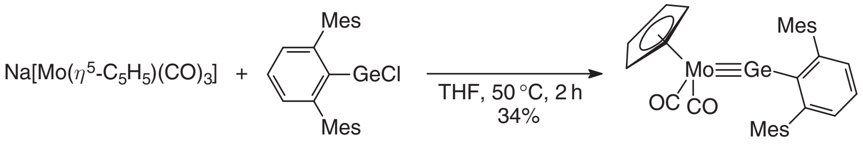
3.12.7.1.4.(i).(a) Preparation from germyl halides

The reaction of a transition metal anion with a halogermane is often a facile method for the formation of Ge–M bonds.[228–232] The rhenium imido complex **110** was prepared by this method (Equation (185)),[229] as was the molybdenum-containing species **111** which contains an Mo–Ge triple bond (Equation (186)).[230] Complexes containing a digermane moiety are also accessible by this method (Equation (187)),[233] including a species which undergoes a photolytic rearrangement to a germyl(germylene) complex (Equations (188) and (189)).[234] Cationic germylene/iron complexes which exhibit partial Ge–Fe double bond character are also accessible by this method (Scheme 35),[235] where monosubstitution on a dihalogermane is the first synthetic step.



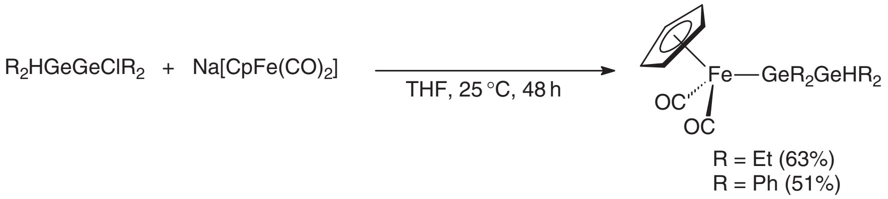
110

(185)

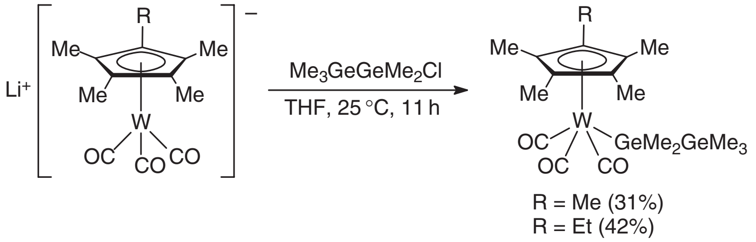


111

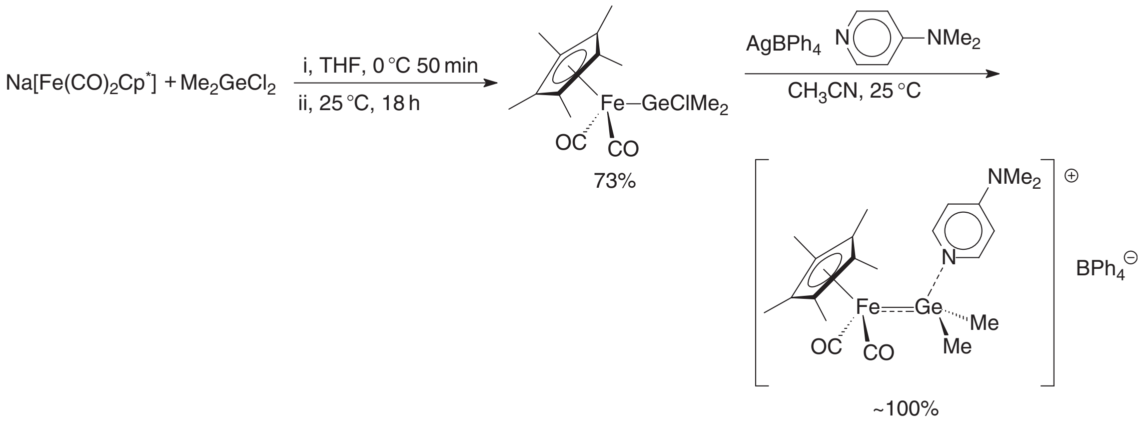
(186)



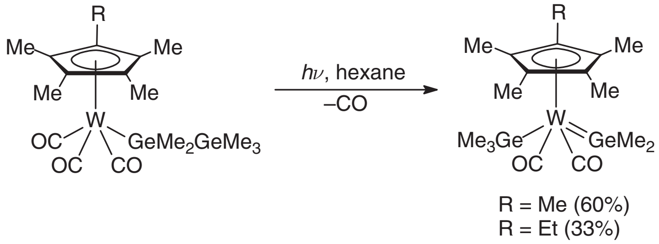
(187)



(188)



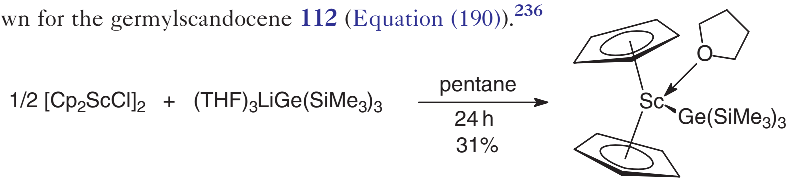
Scheme 35



(189)

3.12.7.1.4.(i).(b) *Preparation from organogermyl anions*

Organogermyl anions are readily available and can be used for the preparation of a variety of transition metal complexes, as shown for the germylscandocene **112** (Equation (190)).[236]



112

(190)

3.12.7.1.4.(i).(c) *Preparation via protonolysis reactions*

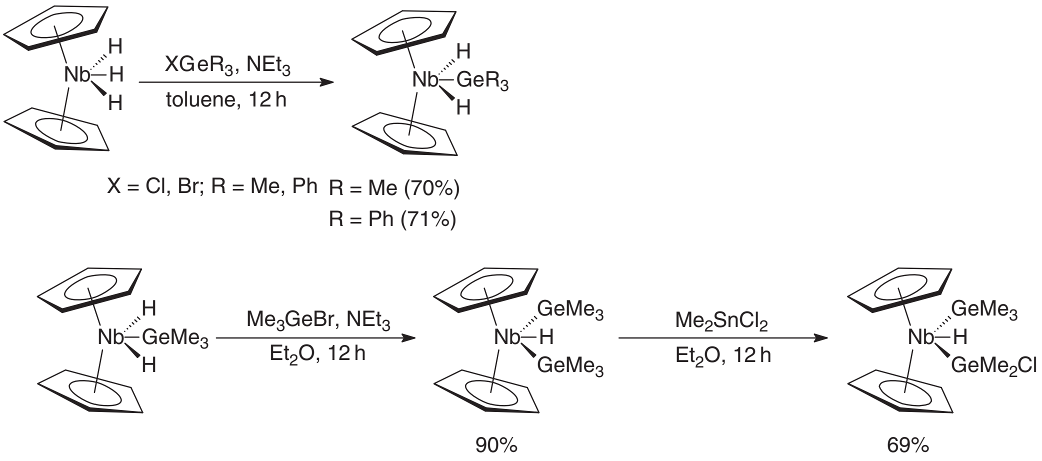
Germanium hydrides can undergo protonolysis reactions with both nitrogen- and oxygen-containing functional groups, or transition metal hydrides can react with germanes containing an appropriate leaving group. Both of these reactions can be facilitated by the addition of a base. The germanium/copper complexes **113** and **114** were prepared by the former method (Equations (191) and (192)),[237] while three different germanium/niobium species were obtained by the latter (Scheme 36).[238]

$$\mathrm{Ph_3GeH} + \mathrm{Bu^tOCu} + 3\mathrm{Ph_3P} \xrightarrow[50\,^\circ\mathrm{C},\ 2\,\mathrm{h}]{\text{dimethoxyethane}} \underset{\mathbf{113}}{\mathrm{Ph_3Ge{-}Cu(PPh_3)_3}} + 3\mathrm{Bu^tOH} \tag{191}$$

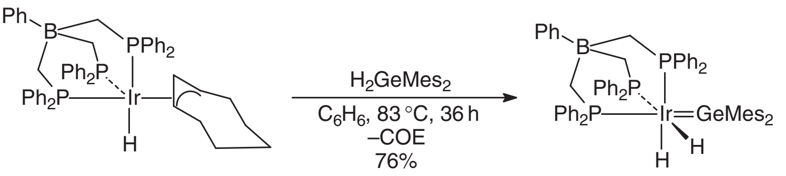
$$\mathrm{(C_6F_5)_3GeH} + \mathrm{Bu^tOCu} + 2\mathrm{Ph_3P} \xrightarrow[50\,^\circ\mathrm{C},\ 2\,\mathrm{h}]{\text{dimethoxyethane}} \underset{\mathbf{114}}{\mathrm{(C_6F_5)_3Ge{-}Cu(PPh_3)_2}} + 2\mathrm{Bu^tOH} \tag{192}$$

3.12.7.1.4.(i).(d) *Reductive substitution*

Germylenes can be released thermally in the presence of a transition metal complex leading to the formation of a germanium–metal bond (Equation (193)).[239] The reaction occurs at room temperature when a germylsilane is used as the synthon (Equation (194)).[240]



Scheme 36

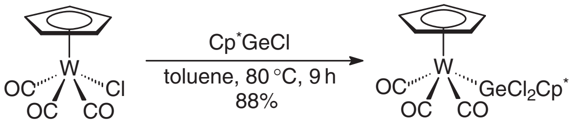


(193)

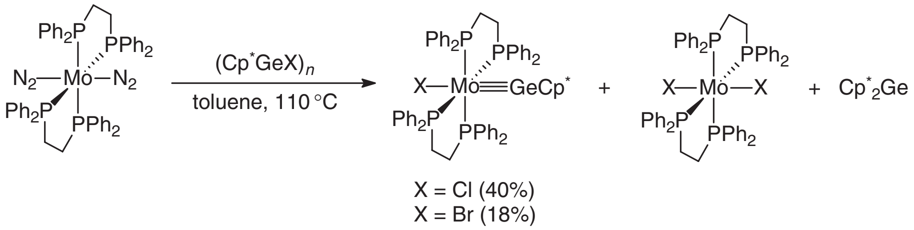
$$\mathrm{Ph_3GeSiEt_2H + Co_2(CO)_8 \xrightarrow[25\,°C,\ 3\,weeks]{petroleum\ spirits} [Co_4(CO)_{12}] + \underset{18\%}{Ph_2Ge[Co(CO)_4]_2} + PhEt_2SiCo(CO)_4} \tag{194}$$

3.12.7.1.4.(i).(e) Preparation from germylenes

Germylenes can react with transition metals in a variety of fashions to furnish germanium–metal bonds including complexes with germanium–metal double and triple[241–244] bonds. For example, oligomeric half-sandwich germylenes can insert into W–Cl bonds to give a W–Ge single bond (Equation (195))[245] and these species were also employed for the preparation of an Mo–Ge (Equation (196))[241] or a W–Ge triple bond (Equations (197) and (198)).[241,242] The tungsten complexes formed in Equation (198) each contain an η^1-Cp* ring.



(195)



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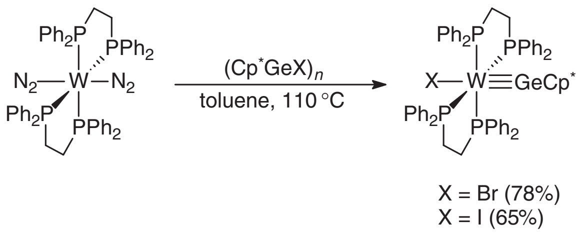
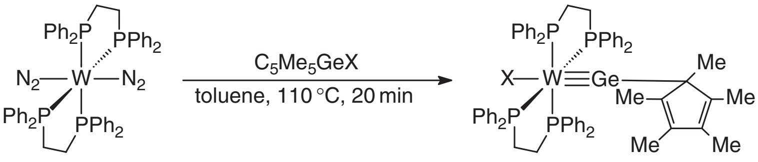


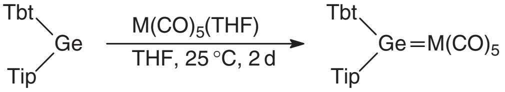
(197)



X = Cl, 67%
X = Br, 78%
X = I, 65%

(198)

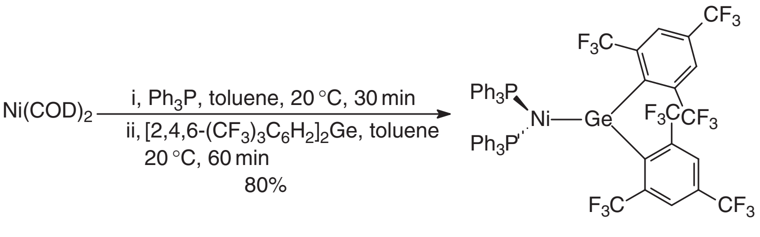
The first base-free diarylgermylene–transition metal complexes were prepared employing a bulky heteroleptic germylene, as shown in Equation (199).[246] A germylene bearing fluorinated *ortho*-substituents on the aryl rings displaces the cyclooctadiene ligands of Ni(COD)$_2$ to yield **115**, which exhibits partial double bond character in the Ni–Ge bond (Equation (200)),[247] and a related species containing the germylene Ge[CH(SiMe$_3$)$_2$]$_2$ **50** as a ligand has been prepared.[113]



11

M = Cr (5.5%)
M = W (6.3%)

(199)

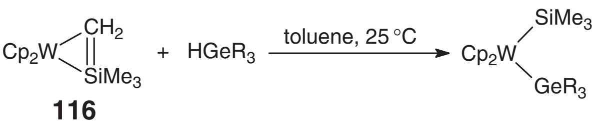


115

(200)

3.12.7.1.4.(i).(f) Addition of germanium hydrides to ligand double bonds

Various alkylgermanes add across the Si–C double bond in the silylene complex **116** to yield germyl(silyl)tungsten complexes (Equation (201), Table 25).[248]



116

(201)

3.12.7.1.4.(i).(g) Oxidative addition of halogermanes

Oxidative cleavage of the Ge–Cl bond in chloromethylgermanes can be achieved using complexes of Pt(0) yielding Pt(II) complexes containing organogermanium ligands. A series of such species was obtained by reaction of a platinum phenanthroline complex with Me$_n$GeCl$_{3-n}$ ($n = 1 - 3$) and Ph$_2$GeCl$_2$.[249]

Table 25 Experimental data for Equation (201)

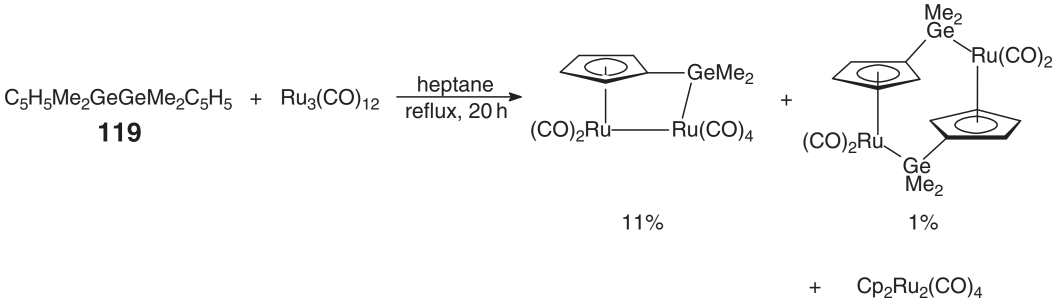
Germane	*Reaction time*	*Yield* (%)
Me$_3$GeH	18 h	62
Me$_2$GeH$_2$	18 h	71
Bu$^t{}_2$GeH$_2$	5 d	65
Ph$_2$GeH$_2$	12 h	80

3.13.7.1.4.(ii) Cyclic organogermyl transition metal complexes

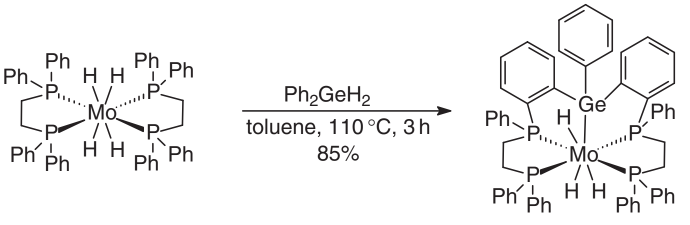
The incorporation of bridging germanium ligands into high-nuclearity transition metal clusters has been accomplished.[250–252] Thermal reaction of Ph_3GeH with rhodium carbonyl yields a mixture of germanium/rhodium cluster complexes **117** and **118** (Equation (202)), while **117** can be formed exclusively if the reaction is carried out under an H_2 purge (Equation (203)).[252] Reaction of the digermane **119** with ruthenium carbonyl yields two different heterobimetallic species arranged in either a four- or six-membered ring (Equation (204)).[253] Thermal reaction of Ph_2GeH_2 with a molybdenum bis(dppe) complex leads to the formation of **120** in high yield via Ge–H bond cleavage coupled with activation of the *ortho*-C–H bonds of the dppe ligands (Equation (205)),[254] and several related complexes have been prepared and studied.[255]

$$Ph_3GeH \xrightarrow[\text{heptane, reflux, 3 h}]{0.1\ \text{equiv.}\ Rh_4(CO)_{12}} \underset{\substack{\mathbf{117}\\ 12\%}}{Rh_8(CO)_{12}(\mu_4\text{-}GePh)_6} + \underset{\substack{\mathbf{118}\\ 18\%}}{Rh_3(CO)_5(GePh_3)(\mu\text{-}GePh_2)_3(\mu_3\text{-}GePh)(\mu\text{-}H)} \tag{202}$$

$$Ph_3GeH \xrightarrow[\substack{\text{heptane, reflux, 3 h}\\ H_2\ \text{purge}\\ 42\%}]{0.1\ \text{equiv.}\ Rh_4(CO)_{12}} \underset{\mathbf{117}}{Rh_3(CO)_{12}(\mu_4\text{-}GePh)_6} \tag{203}$$



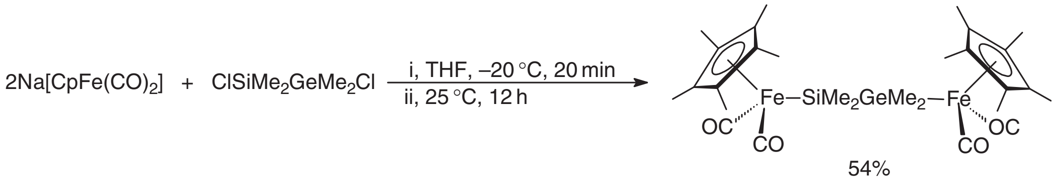
(204)



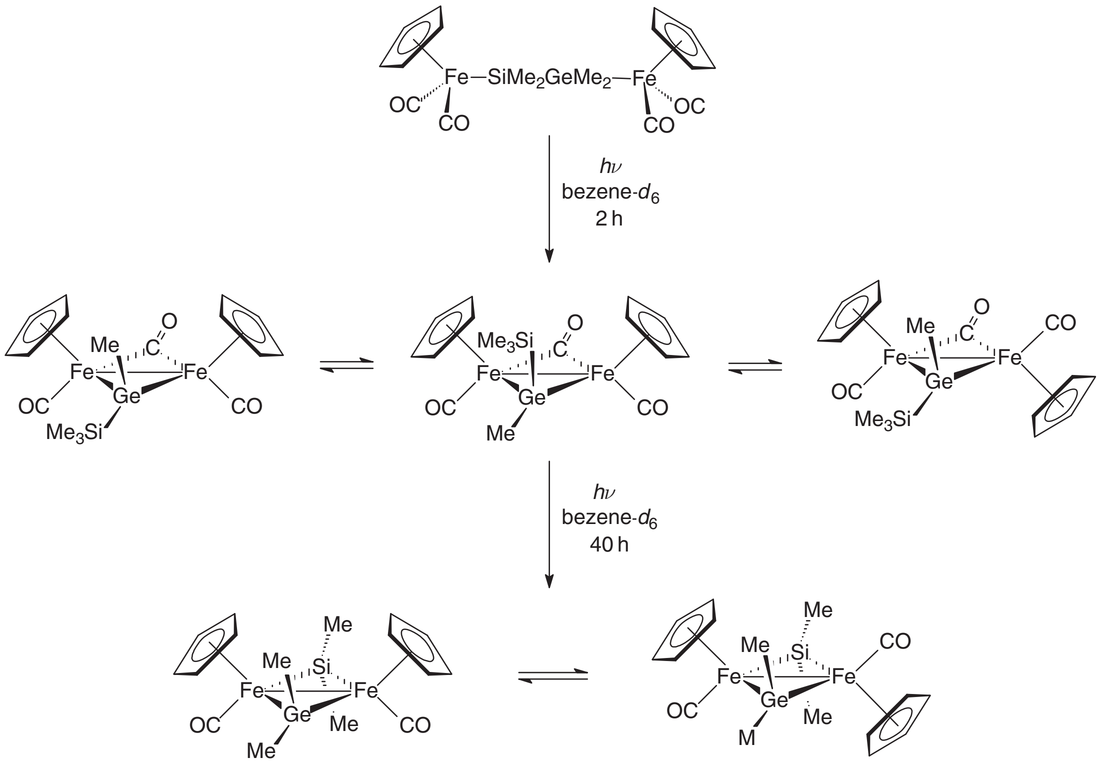
120

(205)

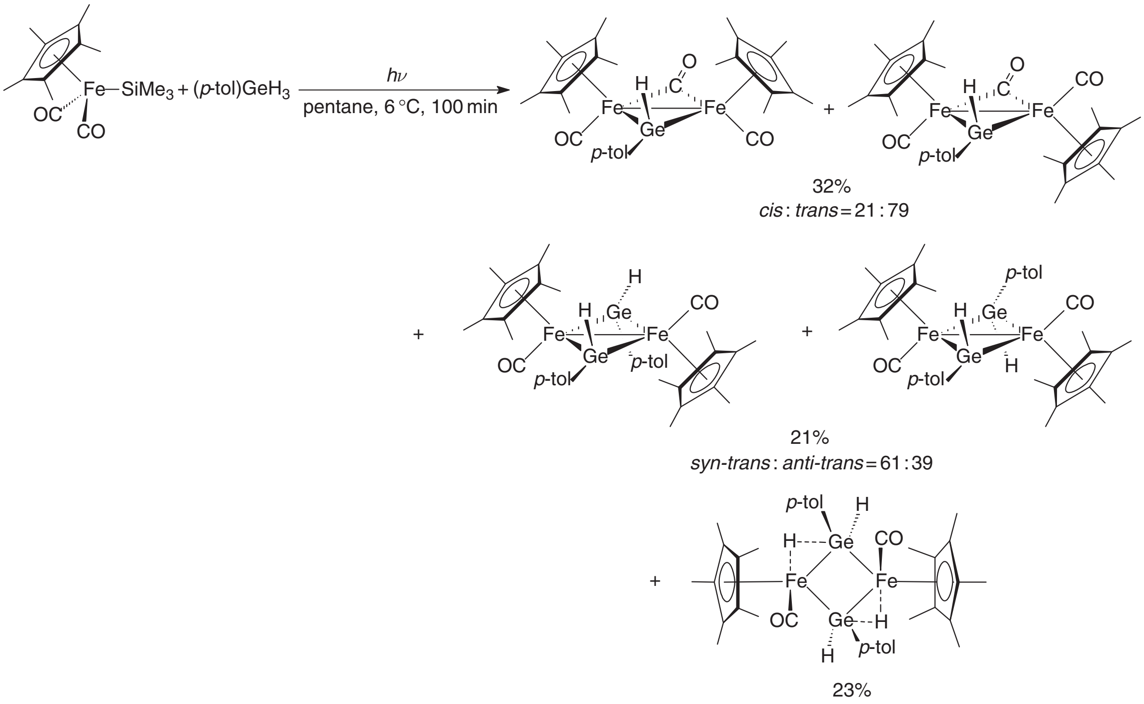
Diiron complexes often employ germylenes or related species as bridging ligands.[256–260] A germylsilyl-bridged diiron complex can be obtained from a mixed group 14 dihalide and a transition metal anion (Equation (206)) which undergoes several photolytically induced interconversions (Scheme 37).[258] A mixture related to these complexes has been prepared by a photolytic process resulting in the formation of five different products containing bridging germylene ligands (Scheme 38).[259]



(206)



Scheme 37

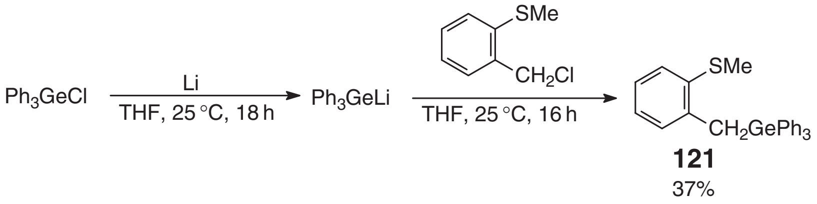


Scheme 38

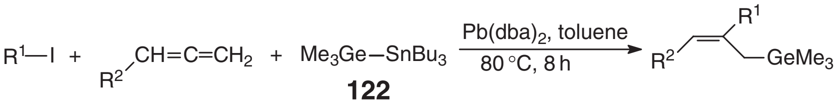
3.13.7.2 Chemical Properties of the Germanium–Metal Bond

3.13.7.2.1 Reactions involving cleavage of the Ge–metal bond

Germyllithium reagents are useful for the formation of bonds from germanium to other elements.[261] The germole dianaion **99** can be converted into various Ge-substituted germoles (Scheme 39).[19] The *ortho*-arylthioanisole **121**, which contains a five-coordinate Ge center, was obtained employing Ph_3GeLi (Equation (207)).[262] Various catenated germanium and germanium-containing species serve as germylation reagents.[263–265] The mixed germanium/tin catenate **122** undergoes highly selective carbogermylation of allenes (Equation (208), Table 26)[265] and intramolecular coupling can also be achieved (Equation (209)).[265]



(207)



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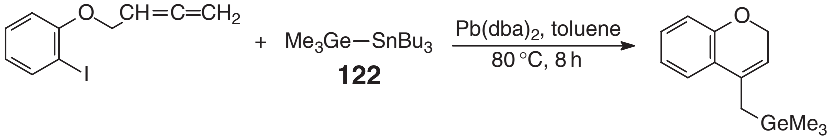

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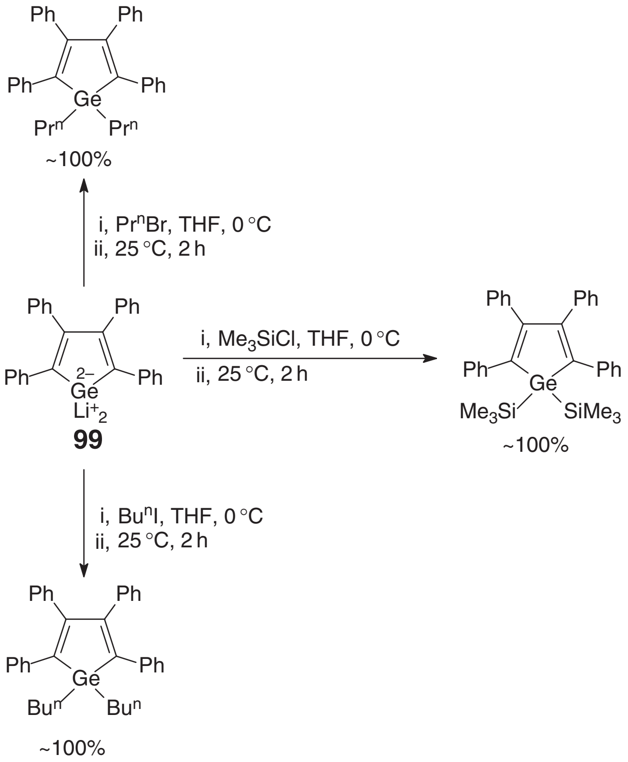


Scheme 39

Table 26 Experimental data for Equation (208)

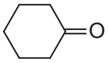
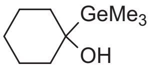
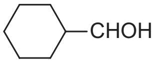
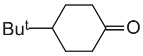
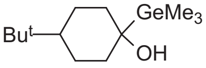
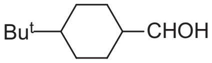
R^1	R^2	Ratio $Z:E$	Yield (%)
4-OMe-phenyl–	Cyclohexyl–	99 : 1	88
2-OMe-phenyl–	Cyclohexyl–	99 : 1	82
4-NO_2-phenyl–	Cyclohexyl–	99 : 1	89
4-$COCH_3$-phenyl–	Cyclohexyl–	98 : 2	90
Phenyl–	Cyclohexyl–	98 : 2	88
1-Naphthyl–	Cyclohexyl–	98 : 2	80
2-Thienyl–	Cyclohexyl–	94 : 6	81
4-Br-phenyl–	Cyclohexyl–	98 : 2	83
4-OMe-phenyl–	Cyclopentyl–	98 : 2	88
4-OMe-phenyl–	*n*-Butyl–	94 : 6	84
4-OMe-Phenyl–	*t*-Butyl–	99 : 1	82

The Ge–Ge bond can undergo cleavage in reactions with $[Bu_4N]F$ to yield metal-free germyl anions, which can be employed in subsequent reactions with alkyl halides (Equation (210), Table 27) and carbonyl species (Equation (211), Table 28).[266]

Table 27 Experimental data for Equation (210)

RX	Me_3GeR (% yield)	RH (% yield)
BuCl	Me_3GeBu (3.7)	BuH (n.a.)
BuBr	Me_3GeBu (34.3)	BuH (n.a.)
BuI	Me_3GeBu (36.7)	BuH (n.a.)
C_6H_5F	$Me_3GeC_6H_5$ (trace)	C_6H_6 (0)
C_6H_5Cl	$Me_3GeC_6H_5$ (5.4)	C_6H_6 (1.6)
C_6H_5Br	$Me_3GeC_6H_5$ (45.3)	C_6H_6 (5.3)
C_6H_5I	$Me_3GeC_6H_5$ (46.2)	C_6H_6 (5.8)
o-MeC_6H_4Cl	Me_3Ge(*o*-MeC_6H_4) (5.2)	C_6H_5Me (1.2)
m-MeC_6H_4Cl	Me_3Ge(*m*-MeC_6H_4) (4.9)	C_6H_5Me (trace)
p-MeC_6H_4Cl	Me_3Ge(*p*-MeC_6H_4) (5.0)	C_6H_5Me (trace)
o-MeC_6H_4Br	Me_3Ge(*o*-MeC_6H_4) (42.5)	C_6H_5Me (6.9)
m-MeC_6H_4Br	Me_3Ge(*m*-MeC_6H_4) (38.2)	C_6H_5Me (5.8)
p-MeC_6H_4Br	Me_3Ge(*p*-MeC_6H_4) (36.5)	C_6H_5Me (6.5)

Table 28 Experimental data for Equation (211)

$RR^1C{=}O$	$RR^1(Me_3Ge)COH$ (% yield)	RR^1CHOH (% yield)
$Et_2C{=}O$	$Et_2(Me_3Ge)COH$ (98.2)	Et_2CHOH (trace)
$BuMeC{=}O$	$BuMe(Me_3Ge)COH$ (97.8)	$BuMeCHOH$ (0)
$Pr^n{}_2C{=}O$	$Pr^n{}_2(Me_3Ge)COH$ (79.5)	$Pr^n{}_2CHOH$ (0)
$PhMeC{=}O$	$PhMe(Me_3Ge)COH$ (74.8)	$PhMeCHOH$ (0)
$Ph_2C{=}O$	$Ph_2(Me_3Ge)COH$ (12.3)	Ph_2CHOH (17.8)
	 (81.5)	 (0)
	 (90.5)	 (0)

$$\mathrm{Me_3Ge{-}SiMe_3} + \mathrm{[Bu_4N]F} \xrightarrow[\substack{\text{HMPA, 25 °C, 5 min}\\ -\mathrm{Me_3EF}}]{} \mathrm{[Bu_4N]^+\,[Me_3Ge]^-} \xrightarrow[\text{ii, H}_2\text{O}]{\substack{\text{i, RX,}\\ \text{24 h}}} \mathrm{Me_3GeR} + \mathrm{RH} + \text{Other products} \tag{210}$$

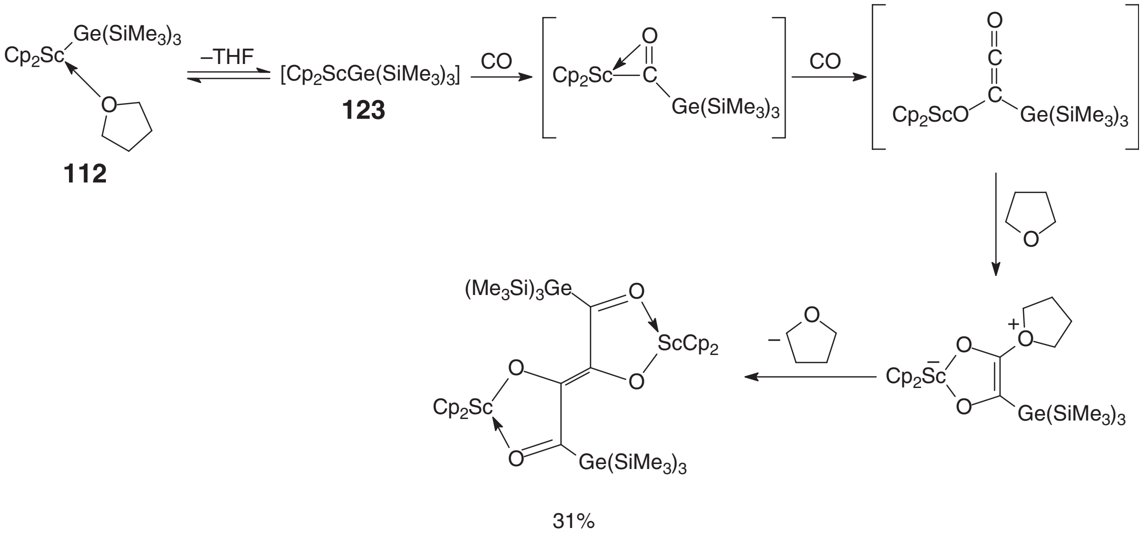
$$\begin{aligned}\mathrm{Me_3Ge{-}SiMe_3} + \mathrm{[Bu_4N]F} &\xrightarrow[\substack{\text{HMPA, MeCN, 25 °C, 5 min}\\ -\mathrm{Me_3EF}}]{} \mathrm{[Bu_4N]^+\,[Me_3Ge]^-} \xrightarrow[\text{ii, H}_2\text{O}]{\text{i, RR}^1\text{C=O, 25 °C, 5 h}} \\ &\mathrm{RR^1(Me_3Ge)COH} \quad + \quad \mathrm{RR^1CHOH}\end{aligned} \tag{211}$$

3.13.7.2.2 Carbonylation reactions

Carbon monoxide inserts into the Sc–Ge bond of **123**, leading to a scandium enedione diolate via a proposed ketene-type intermediate (Scheme 40).[236]

3.13.7.2.3 Coupling reactions

The coupling of aryl aldehydes and ketones to give chiral diols can be achieved by reaction with the tetraphenylgermole dianion **99** (Equation (212), Table 29).[17] Hexamethyldigermane can be employed to generate synthetically important allylgermanes with high stereoselectivity (Equation (213), Table 30), and the reaction pathway for this process has been proposed.[267]



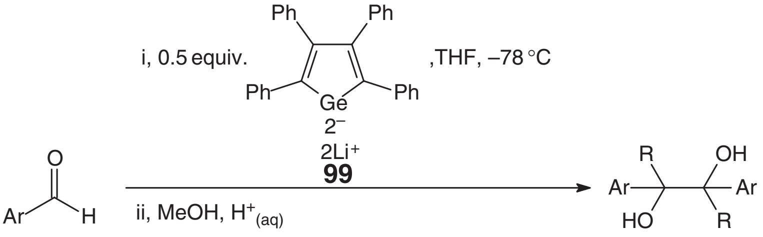
Scheme 40

Table 29 Experimental data for Equation (212)

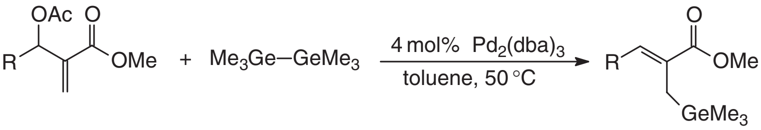
Ar	*R*	*Diol yield (%)*	*Dl* : *meso*
Ph	H	88.6	5 : 2
Ph	Me	92.5	3 : 1
p-ClPh	Me	30.7	4 : 1
o-MeOPh	Me	26.5	1 : 1
p-MeOPh	Me	17.6	3 : 1
m-MeOPh	Me	60.0	3 : 1
2-Naphthyl	Me	47.9	4 : 1

Table 30 Experimental data for Equation (213)

R	*Yield* (%)	*Z:E ratio*
Ph	84	100
p-Methylphenyl	82	98 : 2
p-Methoxyphenyl	85	97 : 3
p-Chlorophenyl	80	92 : 8
o-Chlorophenyl	70	95 : 5
1-Furyl	81	100
1-Naphthyl	76	100
n-Octyl	64	85 : 15



(212)

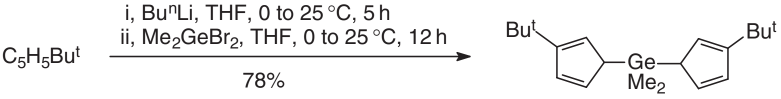


(213)

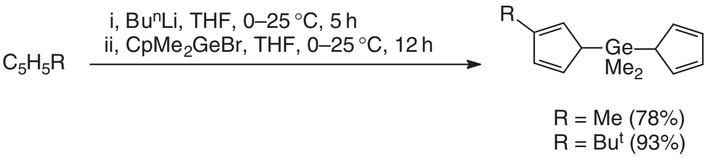
3.13.8 Organogermanium-containing Complexes and Polymers

3.13.8.1 Organogermanium-containing Complexes

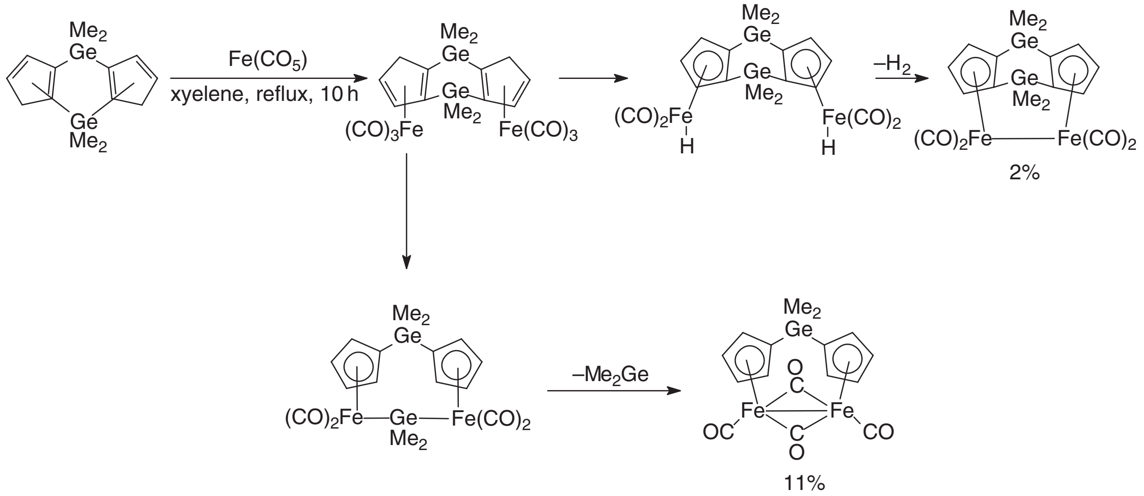
A number of species containing an organogermanium moiety as part of a ligand system have been reported. Compounds containing two Cp rings bridged by a dimethylgermanium fragment can be readily prepared (Equations (214) and (215)), and *ansa*-ferrocenophanes of the group 4 metals can subsequently be constructed[268,269] employing these species as ligands (Equations (216)–(218)), which can serve as highly active ethylene polymerization catalysts.[269] Germanium-containing ligands have also been utilized to bridge two iron centers[270–272] (Scheme 41),[271] and silyl/germyl-containing mono-[273] and bimetallic[217,274] systems have been reported which undergo various migrations and rearrangements of the silyl/germyl ligand. An example is illustrated in Scheme 42.[217]



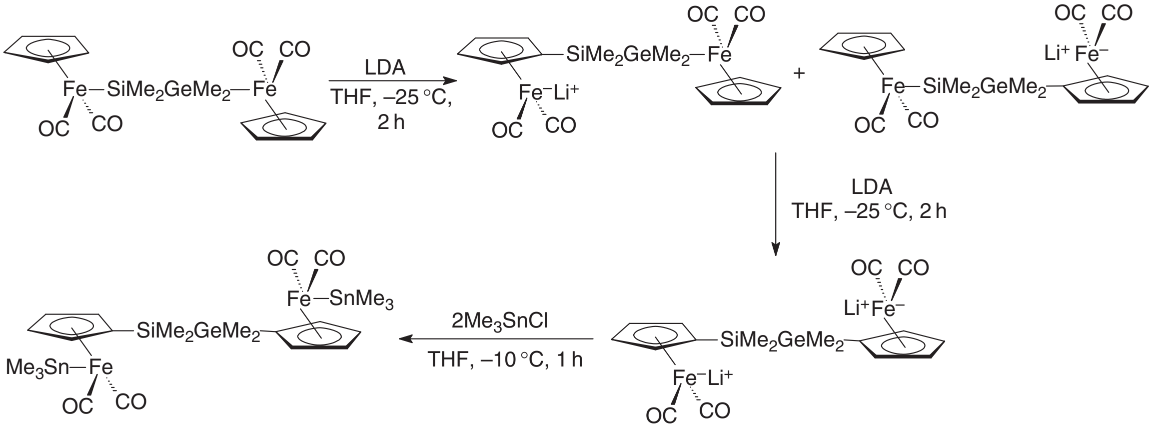
(214)



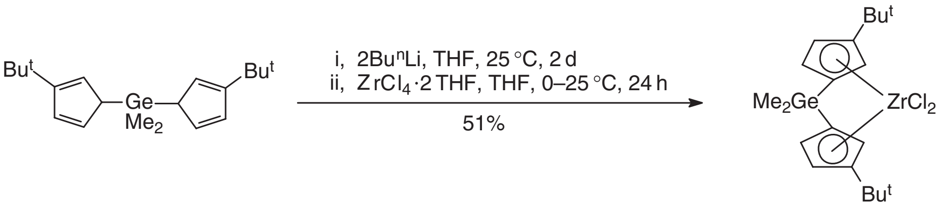
(215)



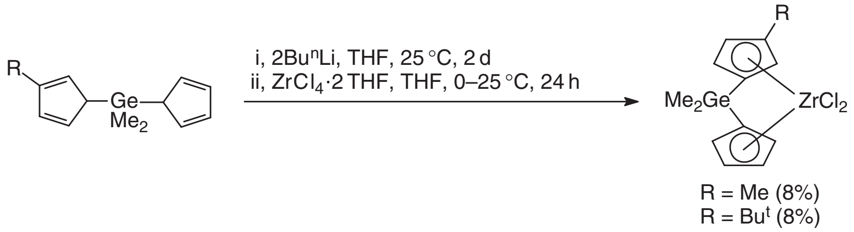
Scheme 41



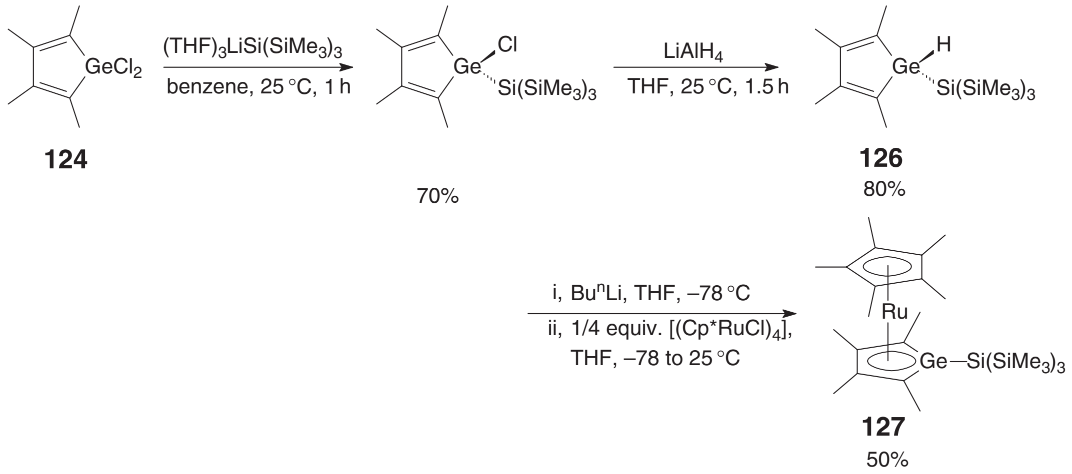
Scheme 42



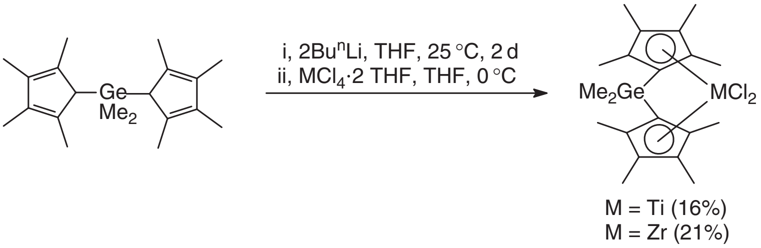
(216)



(217)

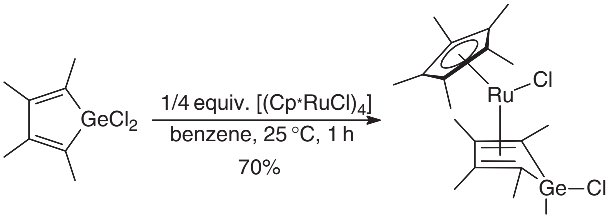


Scheme 43



(218)

Germoles have also been employed as ligands for heterometallocene complexes. The 1,1-dichlorogermole **124** yields a ruthenoncene-type complex **125** where the germolyl ring is η^4-bound to the metal center (Equation (219)), whereas **126** can be deprotonated to provide a complex with an unusual η^5-bound germolyl ligand (**127**, Scheme 43).[275]



124 **125**

(219)

3.13.8.2 Organogermanium-containing Polymers

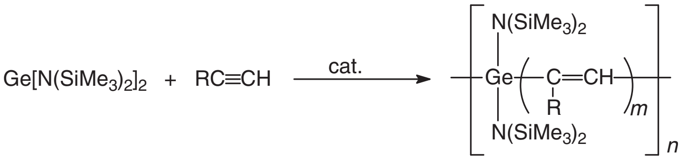
The electronic properties of germanium have led to an interest in incorporating the element into extended polymeric chains due to the intrinsic properties of the polymers themselves or in their use as precursors for material synthesis.[276–280] Catalytic co-polymerization of the germylene Ge[N(SiMe$_3$)$_2$]$_2$ with various substituted acetylenes leads to the polymeric systems **128** (Equation (220), Table 31).[277] This germylene has also been co-polymerized with various cyclic ketones (Equations (221)–(223)), and some of the products of these reactions can be cast as transparent thin films.[278] A group of poly(germylene)diacetylenes yields ceramic residues upon pyrolysis,[279] and a series of highly conjugated oligomeric fluorenylethynylene germylenes have been synthesized (Equation (224)) and polymerized

Table 31 Experimental data for Equation (220)

Ge[N(SiMe$_3$)$_2$]$_2$ (mmol)	*R*	*Catalyst* (mmol)	*Solvent* (ml)	*Time*	*Yield* (%)	M_n (× 10^3) (g/mol)	M_n/M_w	*Germylene/olefin ratio*
1.10	Ph	0	Toluene (4.0)	48 h	0			
0.84	Ph	0.012	NEt$_3$ (6.0)	5 min	30	21.6	2.1	1 : 8.3
1.11	Ph	0.017	Toluene (4.0)	1 h	36	16.7	6.6	1 : 5.0
1.10	Ph	0.017[a]	NEt$_3$ (4.0)	21 h	10	10.2	1.5	1 : 1.5
0.49	Bu^n	0.0054	Toluene (3.0)	13 h	35	4.9	2.3	1 : 2.6
1.22	C$_5$H$_{11}$^{n}	0.021	NEt$_3$ (4.0)	5 h	31	4.4	2.1	1 : 2.9
0.97	C$_6$H$_{13}$^{n}	0.021	NEt$_3$ (4.0)	5 h	30	3.9	1.8	1 : 2.5

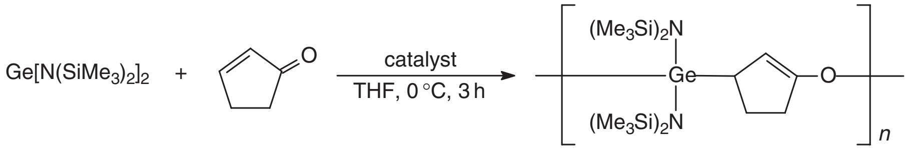
[a] [Rh(norbornadiene)Cl]$_2$ was used as the catalyst.

with organoplatinum reagents to furnish metallopolymers (Equation (225)).[280] The presence of the germylene bridges enhances the phosphorescence properties of the metallopolymers compared to their silicon-containing congeners.



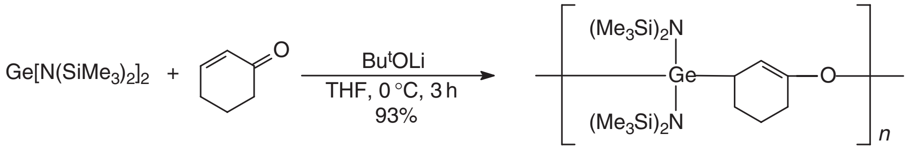
128

(220)



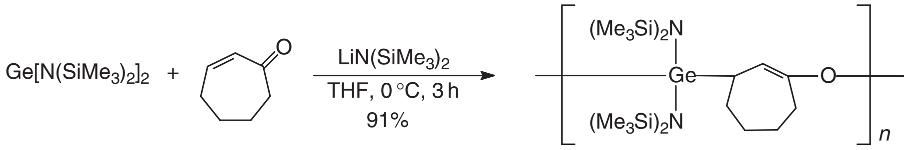
(221)

Catalyst = EtOLi, 99%, M_w/M_n = 2.56
Catalyst = LiI, 99%, M_w/M_n = 1.69



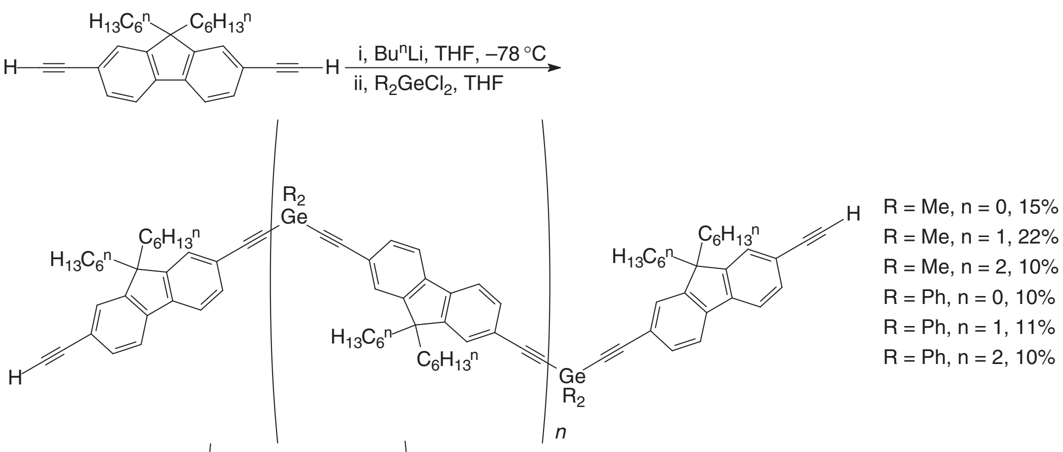
(222)

M_w/M_n = 1.95



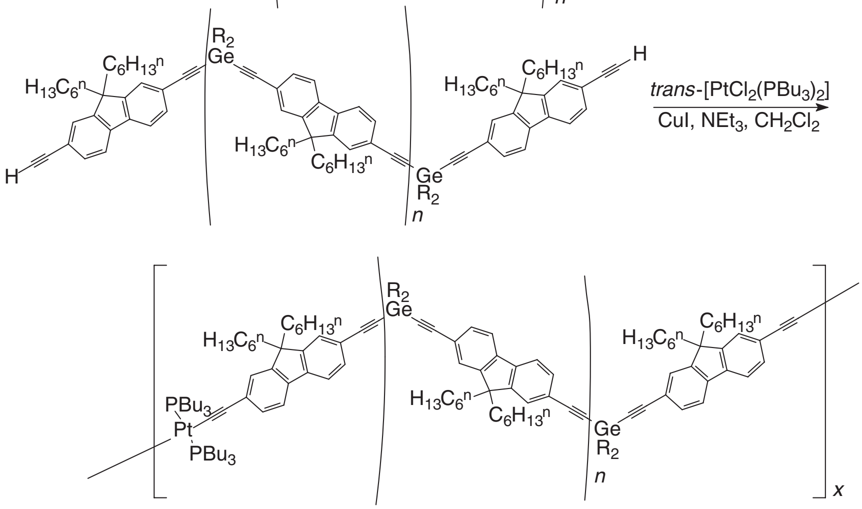
(223)

M_w/M_n = 1.73



R = Me, n = 0, 15%
R = Me, n = 1, 22%
R = Me, n = 2, 10%
R = Ph, n = 0, 10%
R = Ph, n = 1, 11%
R = Ph, n = 2, 10%

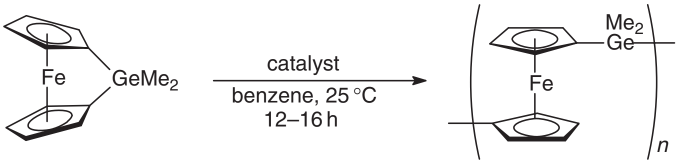
(224)



(225)

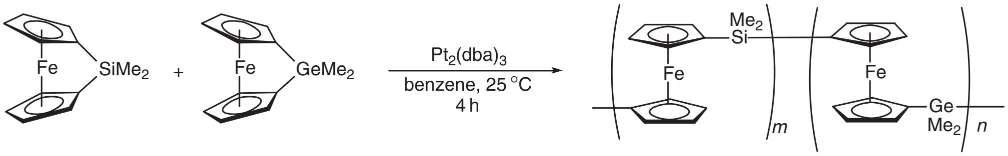
R = Me, n = 0, 71%
R = Me, n = 1, 52%
R = Me, n = 2, 47%
R = Ph, n = 0, 44%
R = Ph, n = 1, 41%
R = Ph, n = 2, 65%

Germanium-bridged [1]ferrocenophanes undergo a number of ring-opening polymerization reactions to yield ferrocene-containing polymers,[281,282] and the versatility of this interconversion has been reviewed.[283] A $–GeMe_2-$bridged [1]ferrocenophane yields high molecular weight Ge-bridged polyferrocenylene (Equation (226)), and a similar co-polymerization employing both germanium- and silicon-bridged [1]ferrocenophanes yields products with both group 14 elements serving as bridges (Equation (227)).[284] Both processes give the products in excellent yields. The incorporation of germanium into cobalt-containing polymers has also been achieved.[285]



(226)

Catalyst = $Pt(cod)_2$, $M_w = 1.1 \times 10^6$ g/mol, $M_w/M_n = 5.2$, 91%
Catalyst = $Pt_2(dba)_3$, $M_w = 2.3 \times 10^5$ g/mol, $M_w/M_n = 9.7$, 79%



(227)

$m:n = 1:1$, $M_w = 6.8 \times 10^5$ g/mol, $M_w/M_n = 13.5$, ~100%

3.13.9 Germylenes

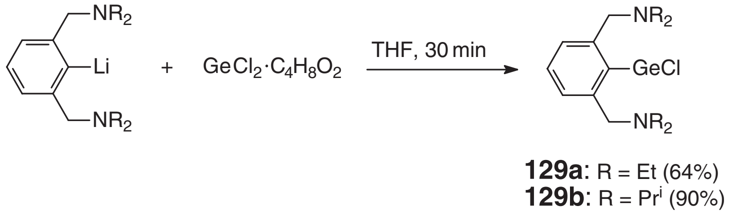
Interest in divalent compounds of germanium has increased steadily over the past several years, and many new species have been prepared. In particular, unsymmetrical heteroleptic species GeLL′ have become much more prevalent. Several reviews covering the synthesis and chemistry of germylenes have appeared,[163,286–295] and the chemistry of several reactive germylene intermediates R_2Ge (R = Me, Ph, etc.) has been investigated.[296–301]

3.13.9.1 Preparation

3.13.9.1.1 Heteroleptic germylenes

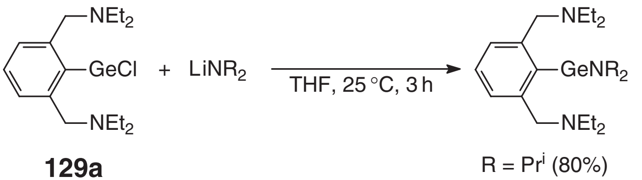
3.13.9.1.1.(i) Heteroleptic germylenes stabilized by side-chain donors

Intramolecular stabilization has allowed the preparation of a number of novel heteroleptic germylenes.[302] The 2,6-dialkylaminomethylphenyl ligand reacts with $GeCl_2$(dioxane) to furnish the arylchlorogermylenes **129** where the aryl ligand is bound in a tridentate fashion to germanium (Equation (228)).[303] Compound **129a** can be converted into arylaminogermylenes (Equation (229)), which subsequently react with protic reagents to yield a variety of products (Equation (230), Scheme 44).[304] The more bulky Mamx ligand contains only one side-chain functionality and also results in a stabilized heteroleptic arylchlorogermylene **130** with the arene bound in a bidentate fashion (Equation (231)), which undergoes reaction with a variety of substrates to yield various other heteroleptic species (Scheme 45).[305]



129a: R = Et (64%)
129b: R = Pr^i (90%)

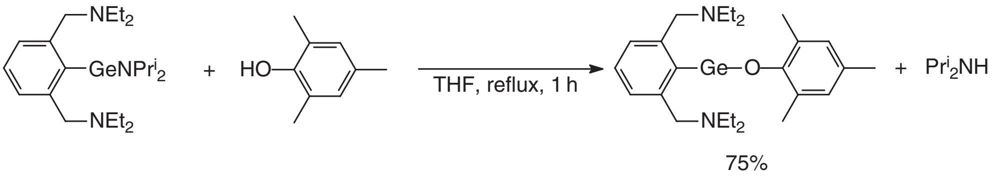
(228)



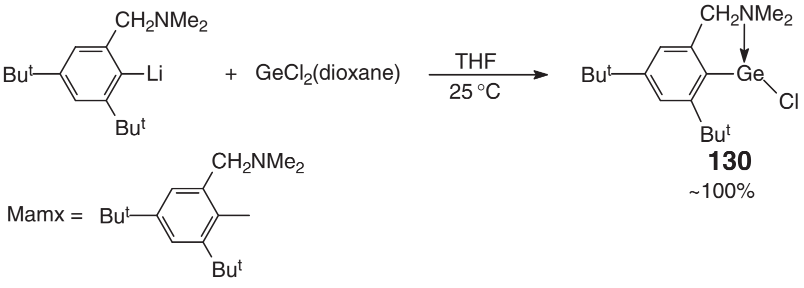
129a

R = Pr^i (80%)
R = $SiMe_3$ (41%)

(229)



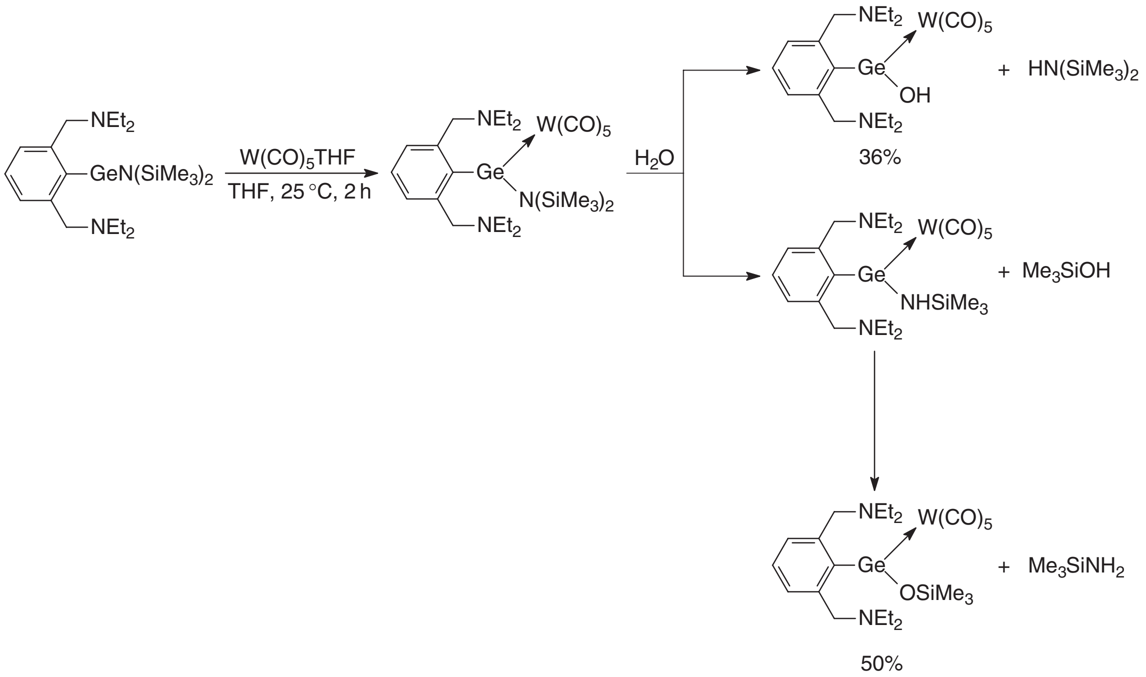
(230)



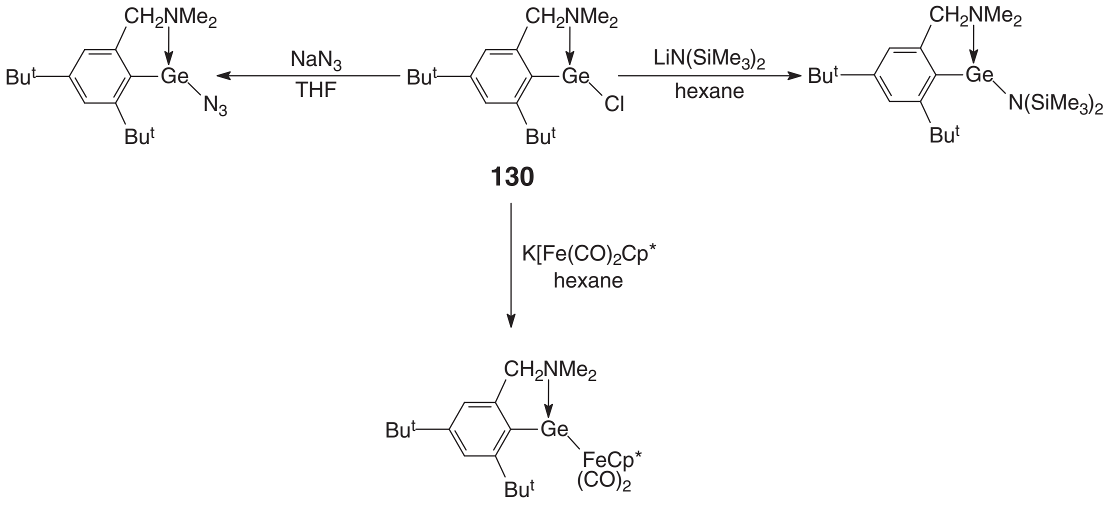
130
~100%

(231)

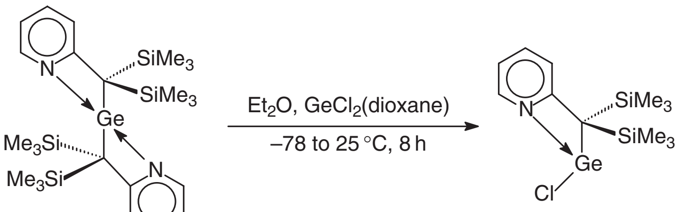
The heteroleptic species **131** was obtained via a redistribution reaction of $GeCl_2$(dioxane) (Equation (232)) and also can be converted into other heteroleptic germylenes (Equation (233)).[306] A chlorogermylene has also been reported which utilizes the 1,8-methoxyanthracenyl ligand as the stabilizing moiety (Equation (234)).[307]



Scheme 44

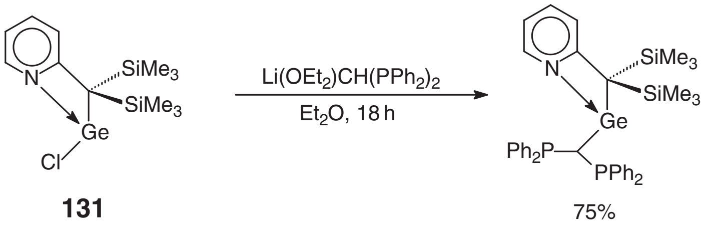


Scheme 45



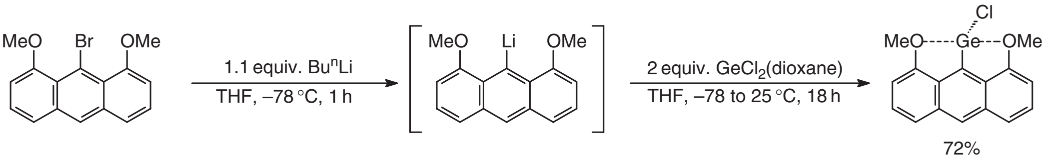
131
80%

(232)



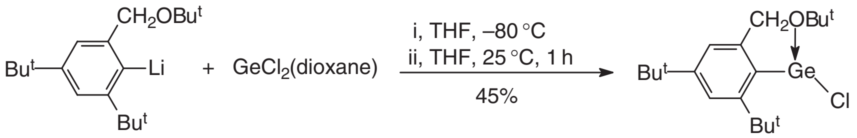
131

(233)



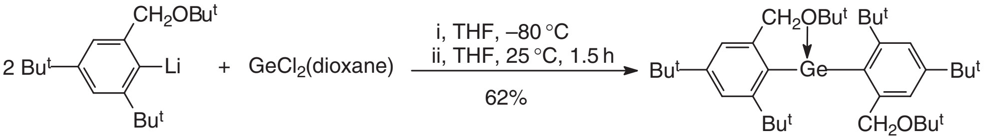
(234)

The stabilization of germanium(II) centers by oxygen donors has also been investigated. Reaction of $GeCl_2$(dioxane) with the lithium salt of the Bu^t-substituted ligand **132** gives both hetero- (Equation (235)) and homoleptic (Equation (236)) germylenes depending on the reaction stoichiometry.[308] Interestingly, when the substituent on oxygen is reduced in steric bulk from Bu^t– to Me–, the complex undergoes an oxidative addition to the H_3C–O bond of the ligand to generate a germanium(IV) species (Equation (237)).[308]



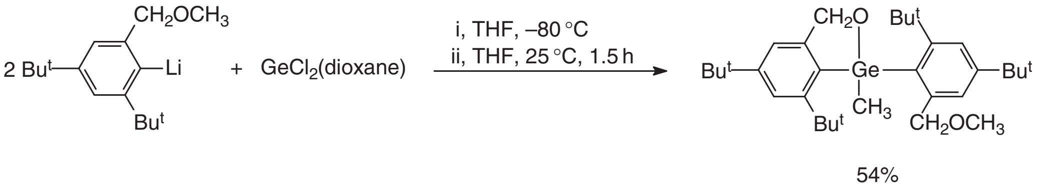
132

(235)



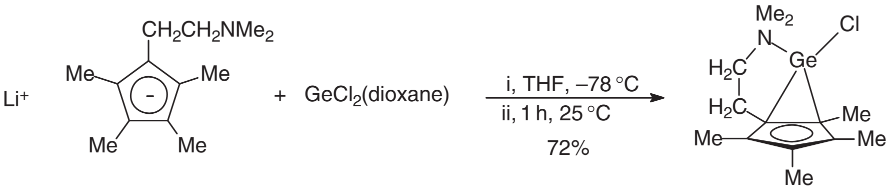
132

(236)



(237)

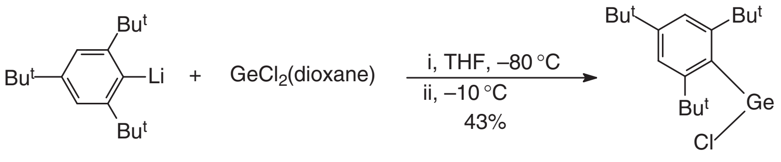
A stabilized heteroleptic germanium cyclopentadienyl complex was obtained which has an extremely long (2.369(1) Å) Ge–Cl bond and an η^2-bound Cp ring (Equation (238)).[309]



(238)

3.13.9.1.1.(ii) Heteroleptic germylenes without side-chain donors

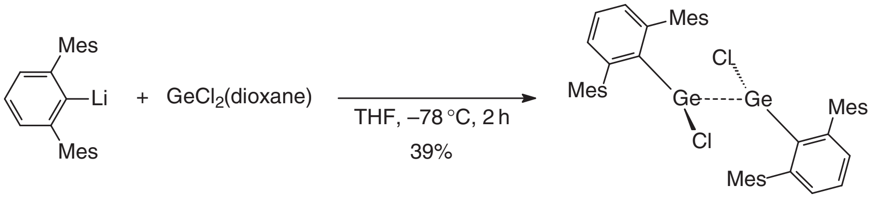
The use of sterically encumbering ligands also allows for the preparation of heteroleptic germylenes, as the ligand size can block introduction of a second group onto the Ge(II) center during reactions with germanium(II) dihalides. Reaction of 1 equiv. of supermesityllithium with $GeCl_2$(dioxane) affords the isolable supermesitylchlorogermylene **133** (Equation (239)).[228] Incorporation of germanium(II) into heterocyclic species also can impart stabilization.[310]



133

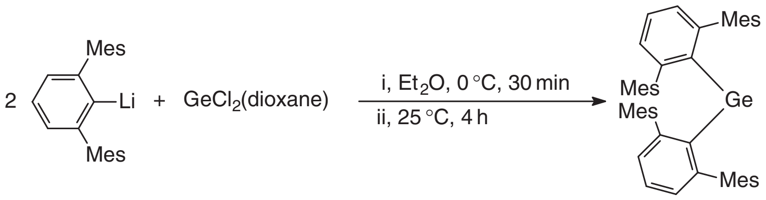
(239)

Reaction of 1 equiv. of the lithium salt of the bulky 2,6-dimesitylphenyl ligand with $GeCl_2$(dioxane) affords germylene **134** (Equation (240)), which is dimeric in the solid state and held together by a long (2.443(2) Å) Ge–Ge bond, while reaction with 2 equiv. of the lithium salt yields the homoleptic species **135** (Equation (241)).[311] Germylene **134** can also be obtained by reaction of 1 equiv. of $GeCl_2$(dioxane) with **135**.[311] Similarly, the larger 2,6-(Trip)$_2$phenyl ligand affords a monomeric heteroleptic germylene **136** (Equation (242)).[312]



134

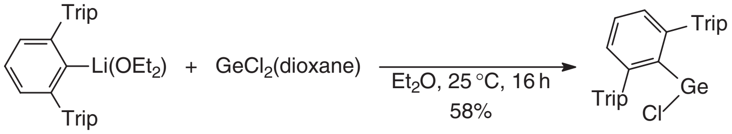
(240)



135

45%

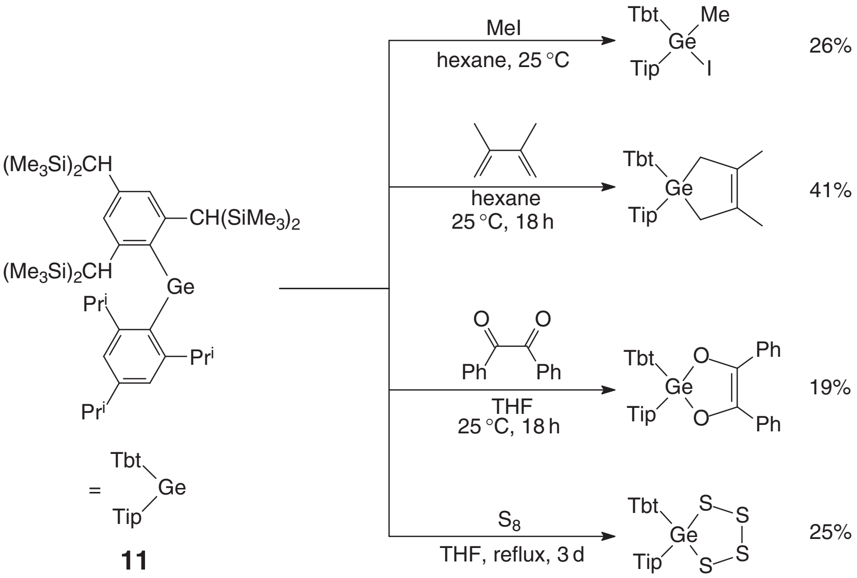
(241)



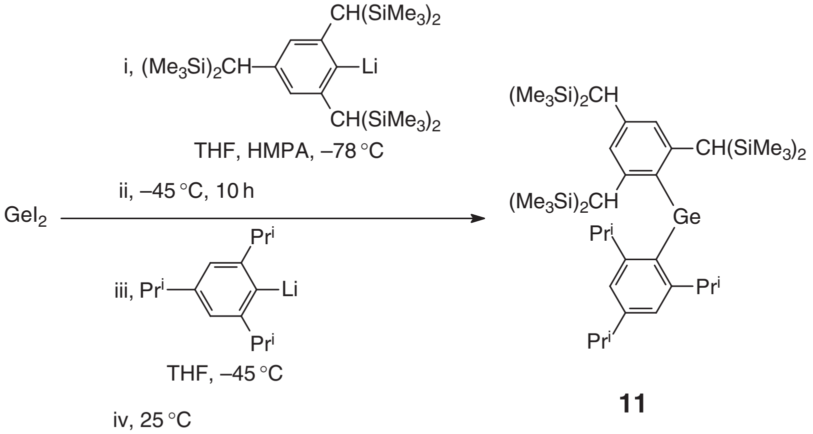
136

(242)

The chemically significant heteroleptic germylene **11** (Tbt)(Tip)Ge was prepared in two steps (Equation (243)) and undergoes reactions with typical trapping reagents (Scheme 46).[246]



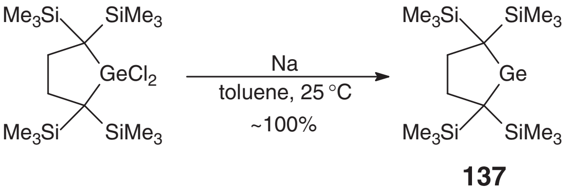
Scheme 46



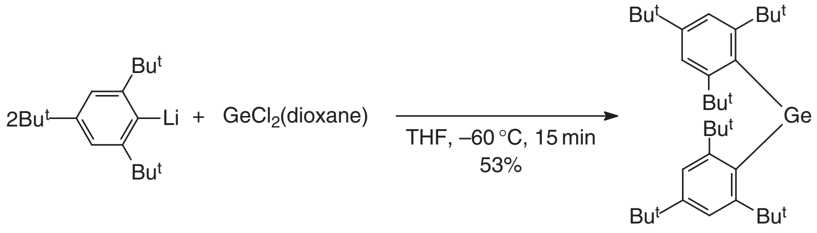
(243)

3.13.9.1.2 Homoleptic germylenes

Some new homoleptic divalent germanium compounds have appeared. A number of symmetric five-membered heterocyclic germylenes have been reported.[313–315] The cyclic germylene **137** was obtained via the Na-metal reduction of the corresponding dichloride (Equation (244)).[316] Germylenes containing sterically encumbering ligands have been prepared including the supermesityl species **138** (Equation (245))[26] and the triphenyl- and dinaphthyl-stabilized compounds **139** and **140** (Equations (246) and (247), respectively).[317] The structure of **140** is shown in Figure 7. The C(1)–Ge–C(2) bond angle is 102.72(9)° and the Ge–C(1) and Ge–C(2) distances are 2.036(2) and 2.030(2) Å, respectively. These values are very close to the values calculated for the parent diarylgermylene Ph_2Ge (101.6° and 2.006 Å).[317]

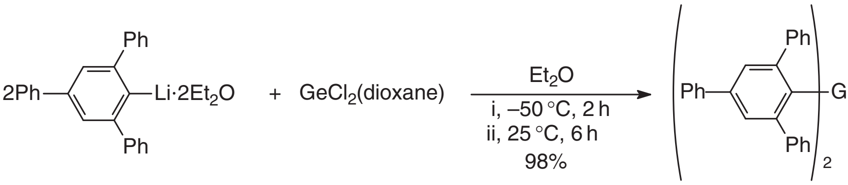


(244)



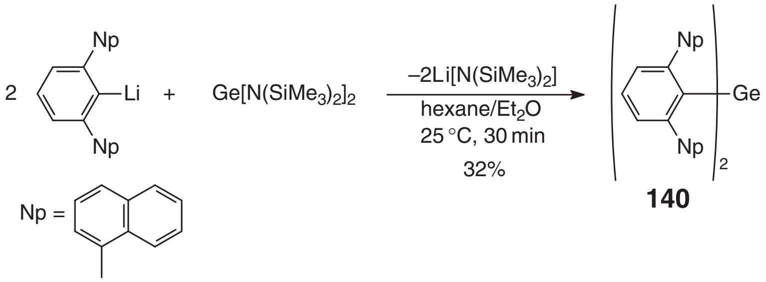
138

(245)



139

(246)



140

(247)

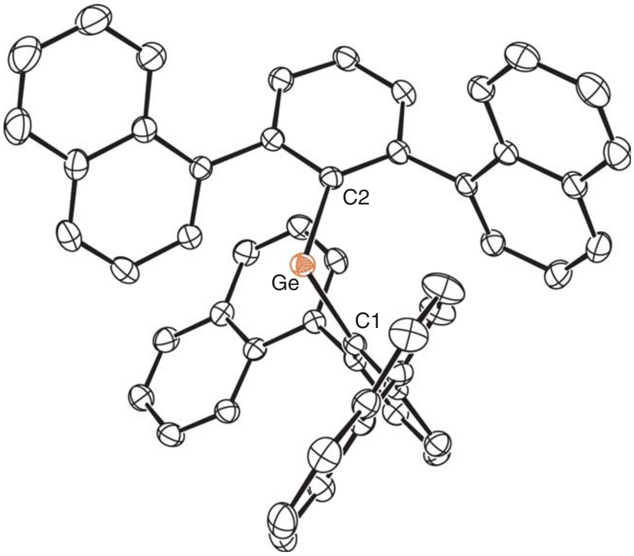
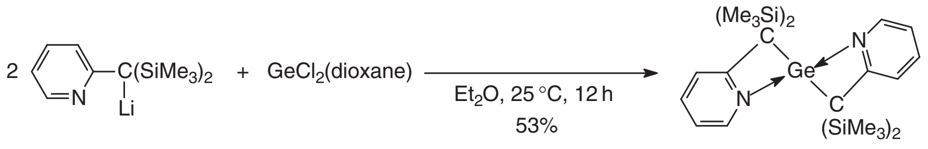


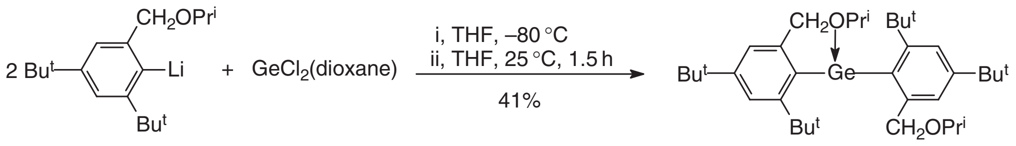
Figure 7 ORTEP diagram of **140**. Reproduced from Wegner, G. L.; Berger, R. J. F.; Schier, A.; Schmidbaur, H. *Organometallics* **2001**, *20*, 418–423.

Intramolecular stabilization via side-chain donor ligands has also been employed in the nitrogen-stabilized germylene **80** (Equation (248))[192] and the oxygen-stabilized species **141** (Equation (249)).[308] The tris(trifluromethyl)phenyl-substituted germylene is a stable monomer in the solid state and in solution (Equation (250)), and contains electron-withdrawing groups instead of electron-donating groups.[114] The *o*-trifluoromethyl substituents do provide a slight internal stabilization.



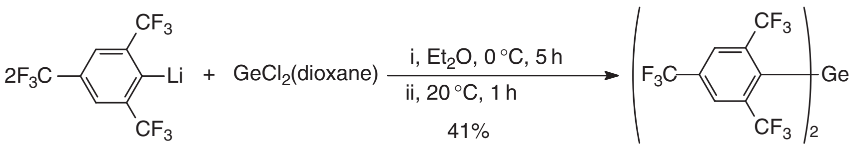
80

(248)



141

(249)

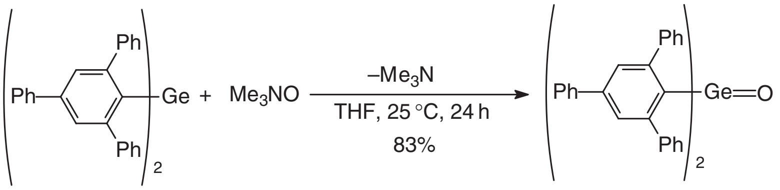


(250)

3.13.9.2 Reactions of Germylenes

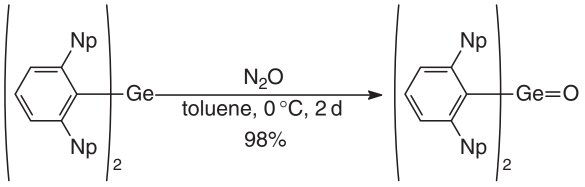
3.13.9.2.1 Oxidation reactions

The bulky germylenes **139** and **140** undergo oxidation with Me_3NO to yield the stable germanones **142** (Equation (251)) and **143** (Equation (252)), respectively,[317] while oxidation of the less-encumbered supermesityl germylene **138** yields an unstable germanone which rapidly interconverts to the germaindanol **144** (Equation (253)).[26] The cyclic germylene **137** reacts with 2 equiv. of the radical species TEMPO to yield the oxidized product **145** through formation of an intermediate Ge-centered radical species (Equation (254)),[318] and a related reaction of **137** with the galvinoxyl radical has also been reported.[319]



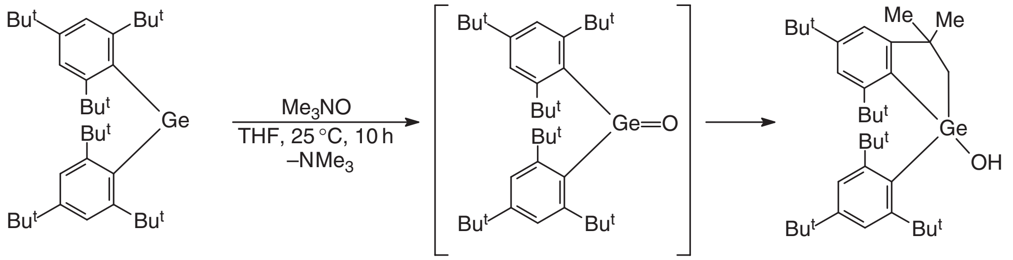
139 **142**

(251)



140 **143**

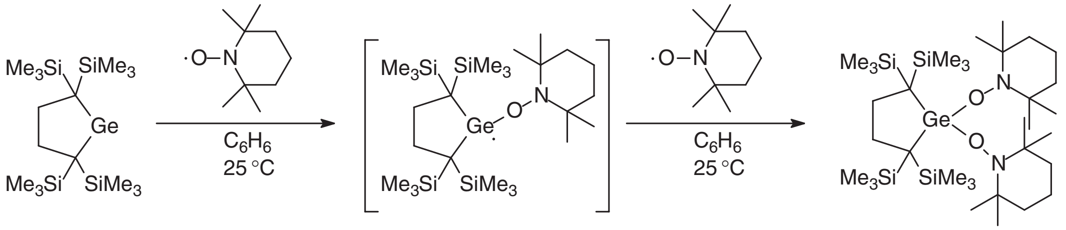
(252)



138 **144**

59%

(253)

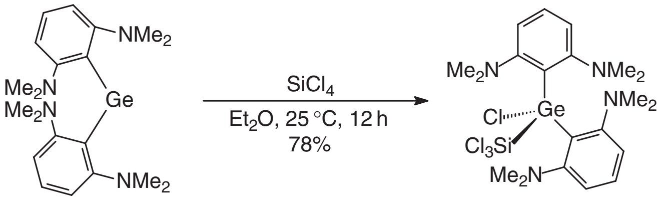


137 **145**

70%

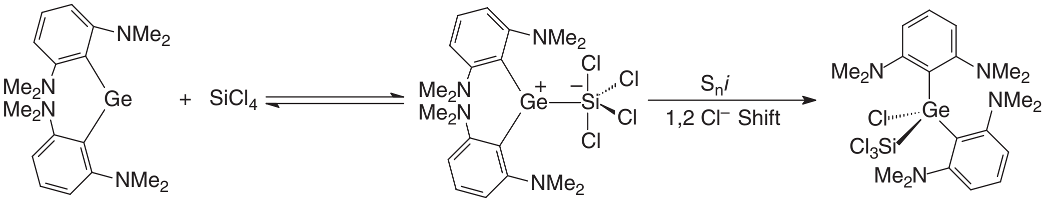
(254)

The germylene **107** undergoes an oxidative insertion into an Si–Cl bond of $SiCl_4$ (Equation (255)), and the reaction pathway of this process has been proposed (Equation (256)).[320]



107

(255)



107

(256)

3.13.9.2.2 Reduction reactions

The reduction of germylenes can be employed for the generation of germylene anion radicals. Treatment of $Ge[CH(SiMe_3)_2]_2$ **50** with sodium metal for 10–15 s generates the monoanionic radical **146** (Equation (257)) which has a half-life in solution of $t_{1/2} = \sim 1.5$ h, an absorption maximum at $\lambda_{max} = 666$ nm (THF), a g value of 2.0125, and a hyperfine splitting of $a = 2.6$ G.[321] Kinetic studies suggest that **146** dimerizes to **147** (Equation (258)).[321] Treatment of $Ge[CH(SiMe_3)_2]_2$ with sodium metal for longer times (1–2 min) results in the formation of the diamagnetic anion **148** (Equation (259)).[321]

$$\underset{\mathbf{50}}{[(Me_3Si)_2CH]_2Ge} + Na \xrightarrow[20\,^\circ C]{THF} \underset{\mathbf{146}}{Na^+[(Me_3Si)_2CH]_2Ge^{\overset{\cdot}{-}}} \qquad (257)$$

$$2Na^+[(Me_3Si)_2CH]_2Ge^{\overset{-}{\bullet}} \xrightarrow{THF} [(Me_3Si)_2CH]_2\ddot{Ge}\text{—}\ddot{Ge}[CH(SiMe_3)_2]_2 \qquad (258)$$

146 **147**

$$Na^+[(Me_3Si)_2CH]_2Ge^{\overset{-}{\bullet}} + Na \xrightarrow[20\,°C]{THF} Na_2[(Me_3Si)_2CH]_2Ge^{2\bullet 2-} \qquad (259)$$

146 **148**

Reduction of bulky organohalogermylenes leads to the formation of pentametallic germanium clusters **149** and **150** (Equations (260) and (261), respectively).[322] The structure of **149** is shown in Figure 8, and selected structural data are collected in Table 32. The five germanium atoms are held together by six two-center, two-electron bonds, and a lone pair resides on the unsubstituted Ge(5) atom.

$$Ge(Cl)CH(SiMe_3)_2 + 0.5\ \text{equiv.}\ GeCl_2{\cdot}(dioxane) \xrightarrow[THF,\ <0\,°C,\ 8\,h]{Mg} Ge_5[CH(SiMe_3)_2]_4 + MgCl_2 + Dioxane \qquad (260)$$

149
12%

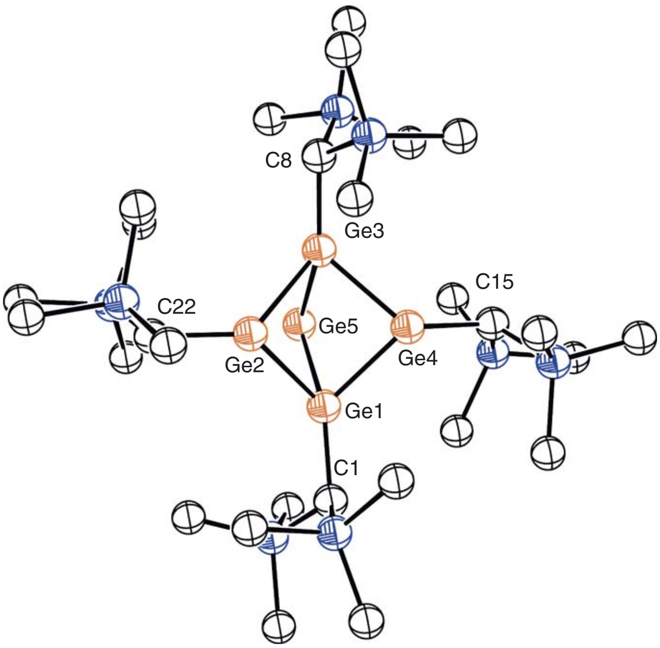


Figure 8 ORTEP diagram of the pentametallic cluster **149**. Reproduced from Richards, A. F.; Brynda, M.; Olmstead, M. M.; Power, P. P. *Organometallics* **2004**, *23*, 2841–2844.

Table 32 Selected bond lengths (Å) and angles (°) for **149**

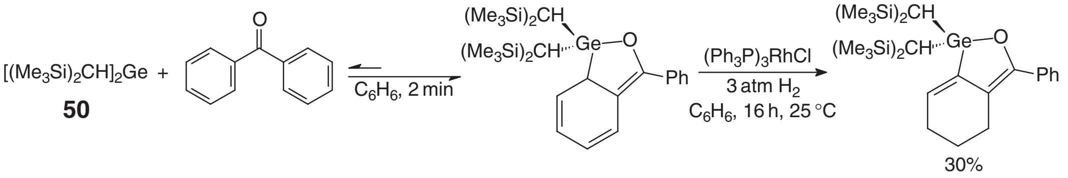
Ge(1)–Ge(2)	2.422(1)	C(1)–Ge(1)–Ge(5)	137.7(2)
Ge(1)–Ge(4)	2.4013(9)	Ge(4)–Ge(1)–Ge(5)	76.69(3)
Ge(2)–Ge(3)	2.4320(9)	Ge(2)–Ge(1)–Ge(5)	77.18(3)
Ge(3)–Ge(4)	2.4163(9)	Ge(4)–Ge(1)–Ge(2)	87.29(3)
Ge(1)–Ge(5)	2.464(1)	Ge(1)–Ge(2)–Ge(3)	83.52(3)
Ge(3)–Ge(5)	2.458(1)	Ge(2)–Ge(3)–Ge(4)	86.73(3)
Ge(1)–C(1)	1.960(5)	Ge(1)–Ge(4)–Ge(3)	84.30(3)
Ge(3)–C(8)	1.962(6)		
Ge(2)–C(22)	2.004(6)		
Ge(4)–C(15)	2.006(6)		

$$\mathrm{Ge(Cl)C_6H_3\text{-}2,6\text{-}Mes_2} \xrightarrow[\text{THF, 25 °C, 20 h}]{\mathrm{KC_8}} \underset{\substack{\mathbf{150}\\ 20\%}}{\mathrm{Ge_5(C_6H_3\text{-}2,6\text{-}Mes_2)_4}} + \mathrm{KCl} + \mathrm{C} + \text{Other products} \qquad (261)$$

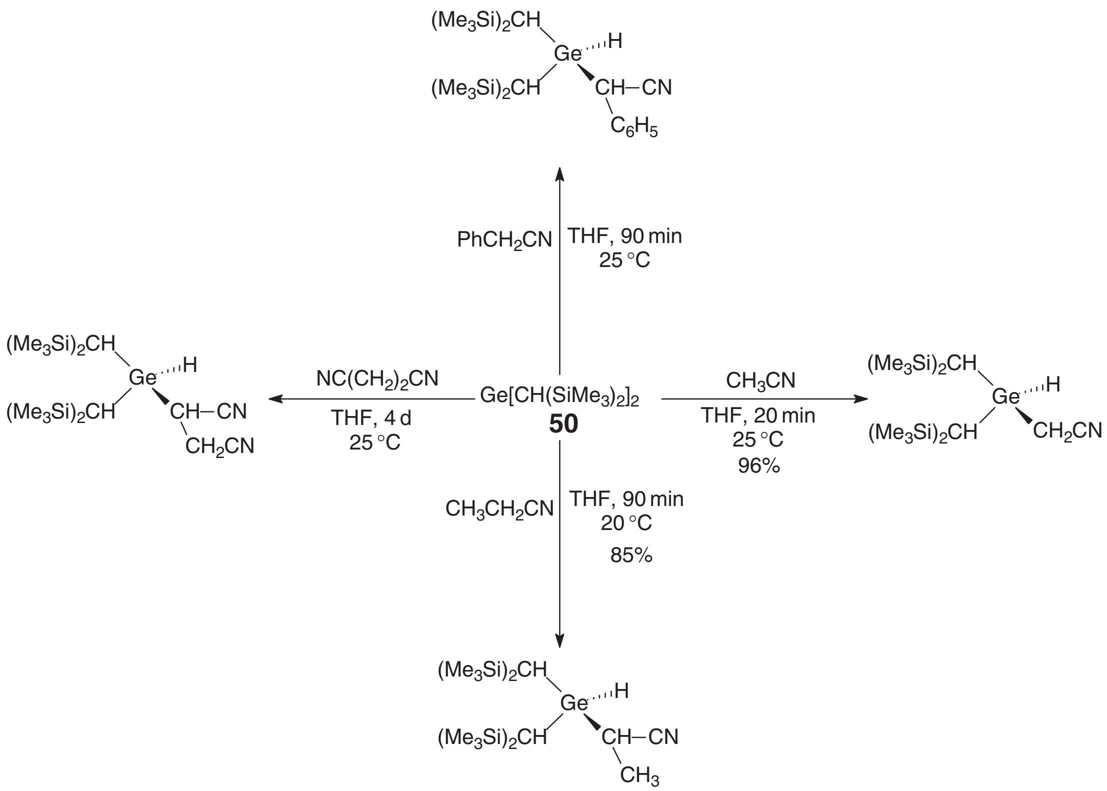
3.13.9.2.3 Insertion reactions

The insertion reaction chemistry of the well-known germylene $Ge[CH(SiMe_3)_3]_2$ **50** is very diverse.[154,323–328] This species inserts readily into the C–H bonds of mono- and dinitrile substrates (Scheme 47),[154] the C–H bonds of ethers and alkanes in the presence of PhI (Scheme 48),[323] the C–H bonds of ketones in the presence of $MgCl_2$ (Scheme 49) and the O–H bonds of the tautomer enols in the absence of $MgCl_2$ (Scheme 50),[324] and the C–H bonds of diketones resulting in cyclic products (Scheme 51).[326]

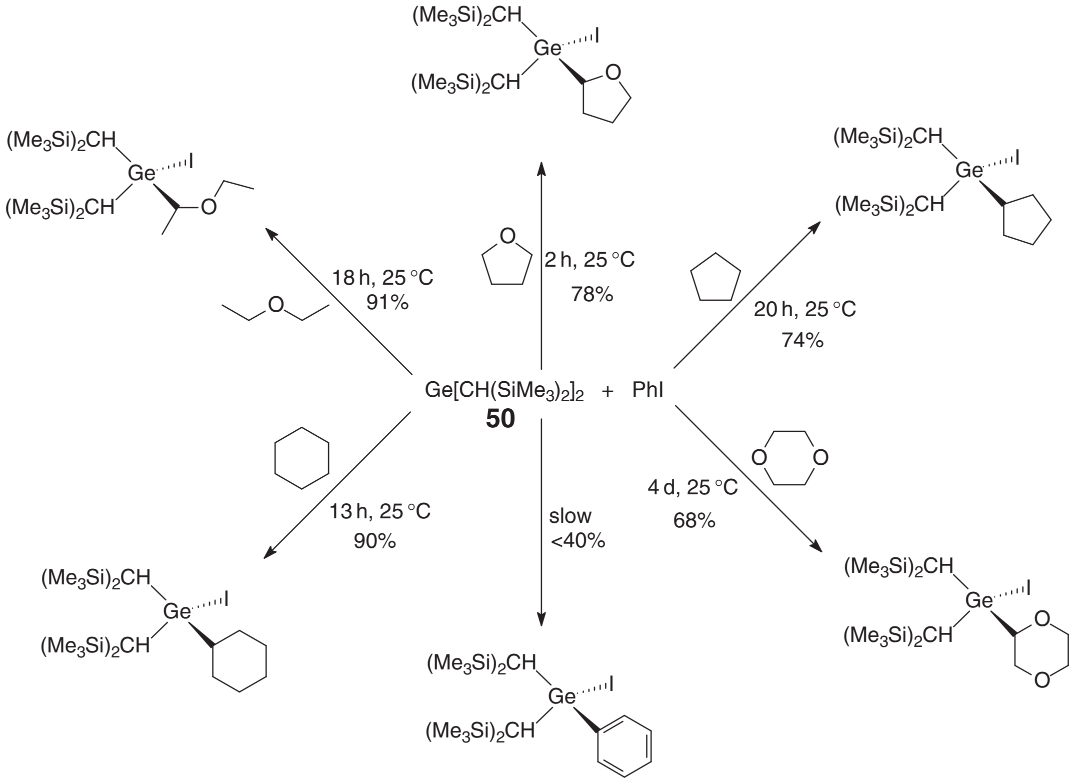
The mechanism for the addition of **50** to anthraquinone (Scheme 52), 1,4-diacetylbenzene (Scheme 53), and 1,2-diacetylbenzene (Scheme 54) has been proposed.[326] The addition of **50** to benzophenone followed by reaction with Wilkinson's catalyst formally results in the hydrogenation of a double bond (Equation (262)).[325] This species also undergoes stereospecific inertion into the vinyl chloride bond of various halogenated alkenes with high yields in most cases (Equations (263)–(267)).[329]



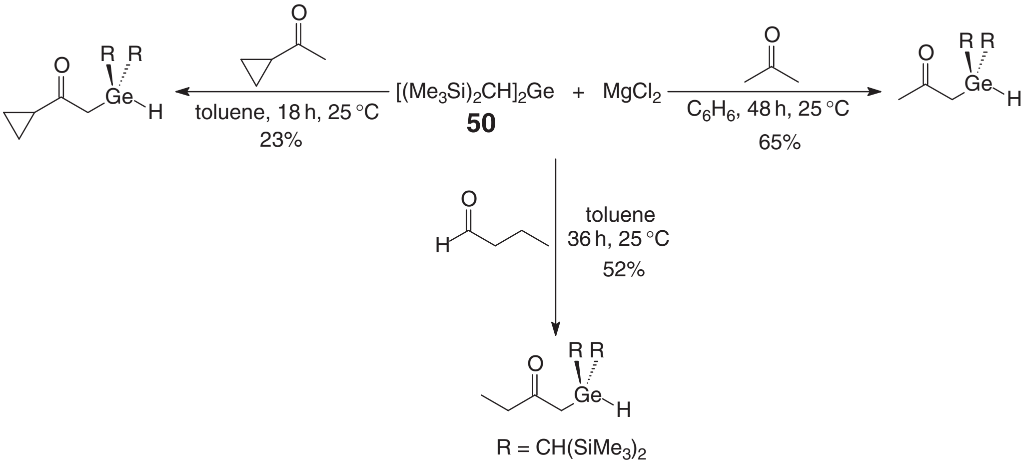
(262)



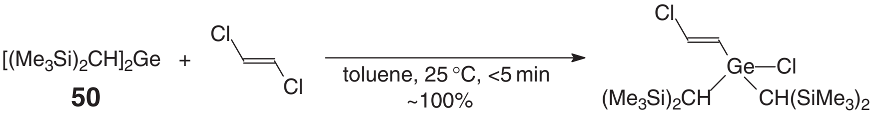
Scheme 47



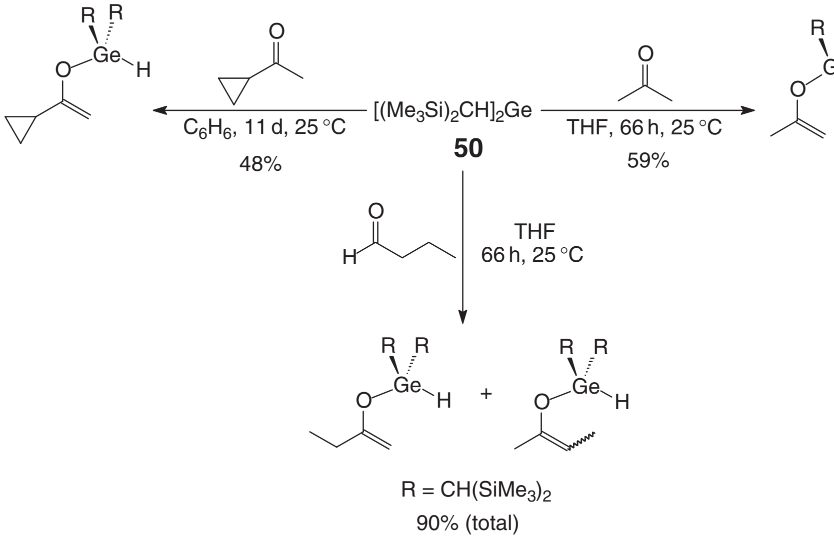
Scheme 48



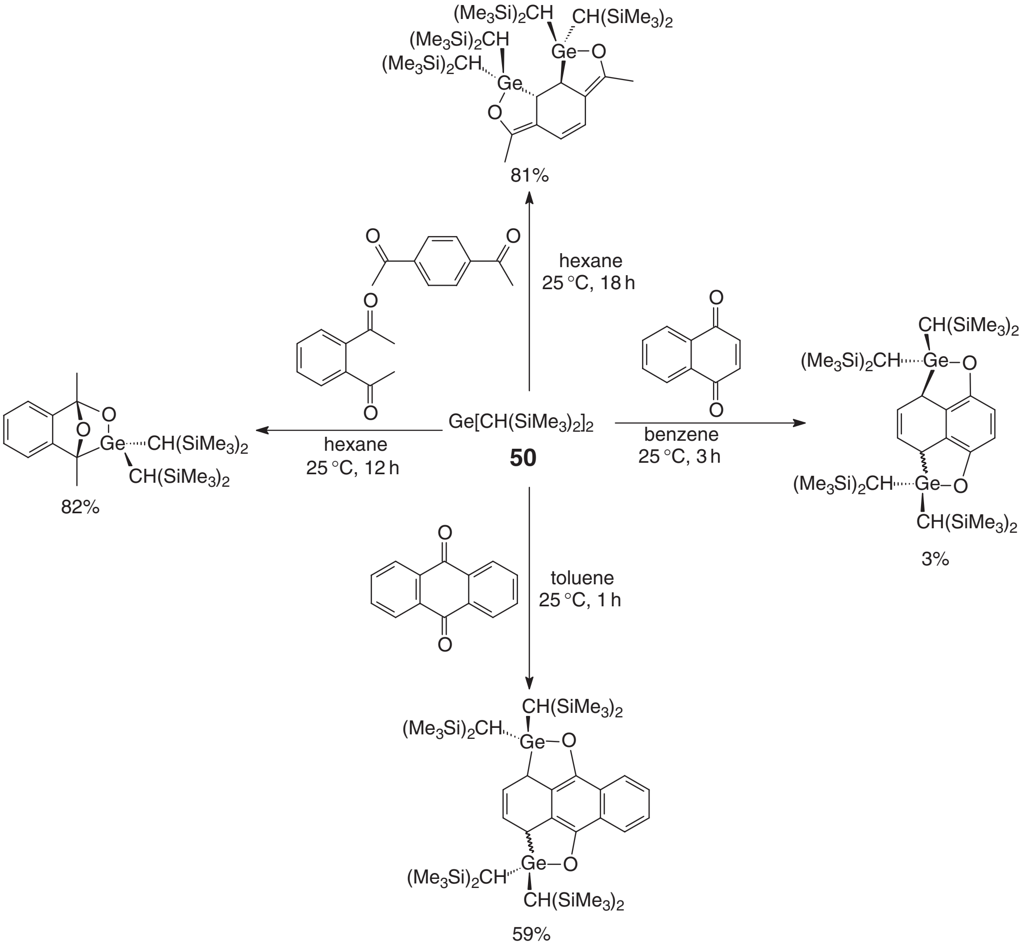
Scheme 49



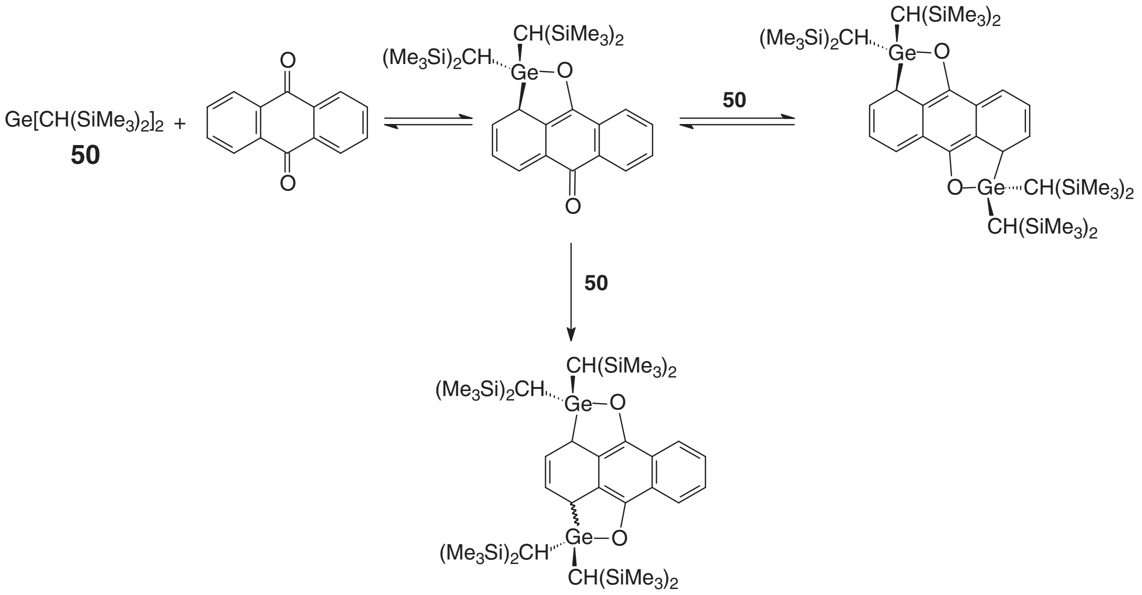
(263)



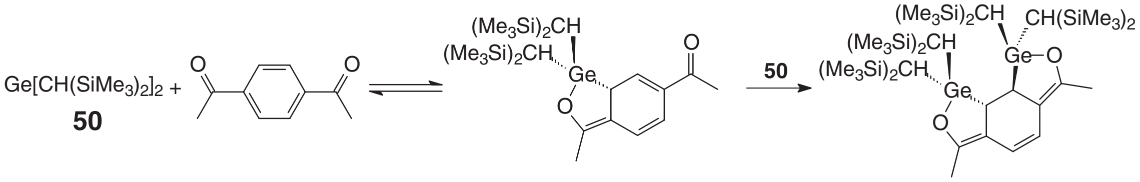
Scheme 50



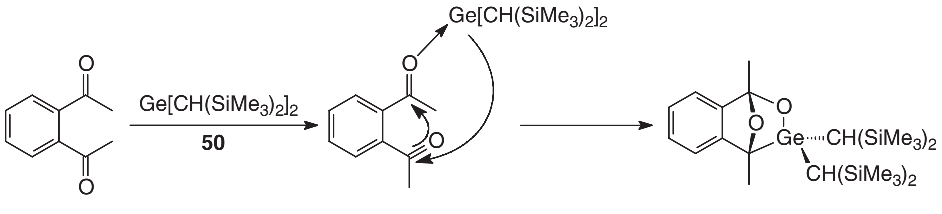
Scheme 51



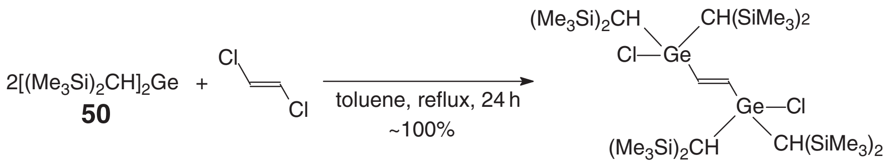
Scheme 52



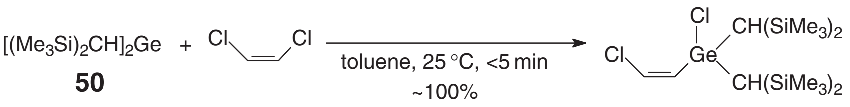
Scheme 53



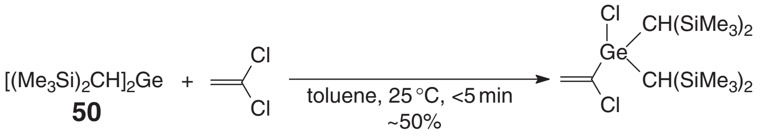
Scheme 54



(264)



(265)



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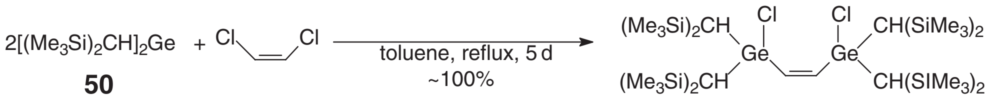
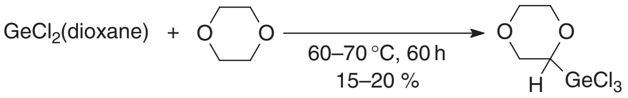
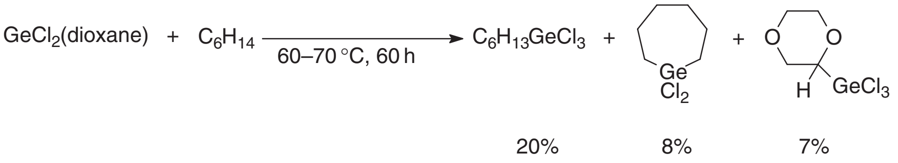


(267)

The insertion of $GeCl_2$(dioxane) into the C–H bonds of dioxane (Equation (268)), hexane (Equation (269)), and hexamethyldisilane (Equation (270)) has been reported.[330]



(268)



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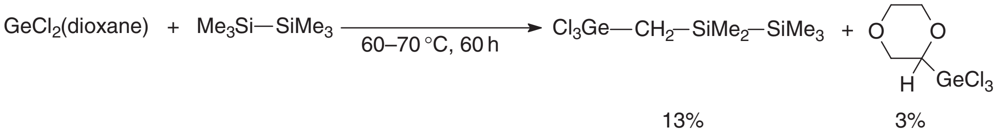
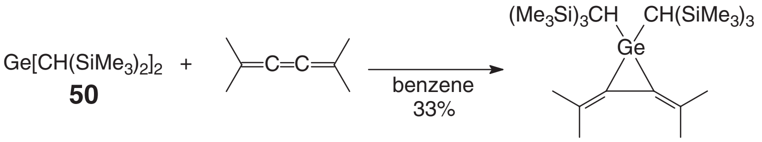


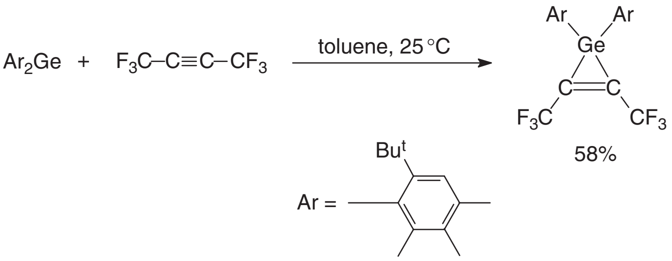
(270)

3.13.9.2.4 Addition to unsaturated compounds

The addition reaction of germylenes to unsaturated compounds is well known.[331] Addition of germylene **50** to tetramethylbutatriene furnishes a germacyclopropane with two exocyclic C=C double bonds (Equation (271)).[332] A sterically encumbered diarylgermylene undergoes addition to the C–C triple bond of an electron-poor alkyne to yield a germacyclopropene (Equation (272)).[333]



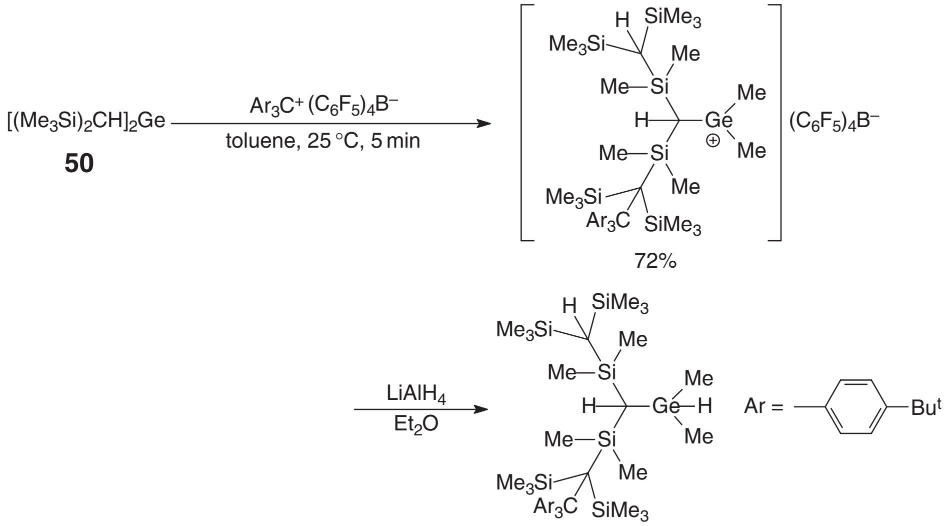
(271)



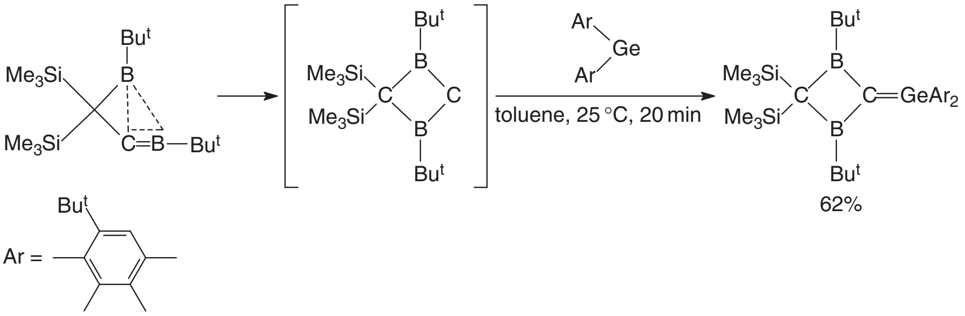
(272)

3.13.9.2.5 Miscellaneous reactions

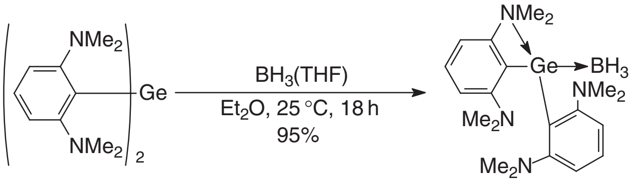
The germylene **50** reacts with the tris(4-*tert*-butylphenyl)methylium cation to yield a germyl cation which was identified by its reduction product (Equation (273)).[334] The preparation of a diboracyclobutane with an exocyclic Ge=C double bond employing a germylene has been described (Equation (274)).[335] Germylene **107** reacts with borane to yield an adduct where the removal of electron density from the germylene by complexation to boron is compensated by intramolecular base stabilization from the ligands (Equation (275)).[336]



(273)



(274)



107

(275)

3.13.10 Compounds with Germanium–Germanium Single Bonds

Since the field was last reviewed,[1] a number of linear and cyclic oligogermanes have been reported, as have a number of new methods for the synthesis of polygermanes. The Ge–Ge single bond length is typically considered to be approximately 2.45 Å, which is twice the atomic radius of germanium.

3.13.10.1 Preparation

The Wurtz-type coupling reactions, which were one of the original methods for the formation of Ge–Ge bonds, are still in use.[337] Various other synthetic techniques have been developed and improved upon in recent years as well.

3.13.10.1.1 Synthesis of linear oligogermanes and polygermanes

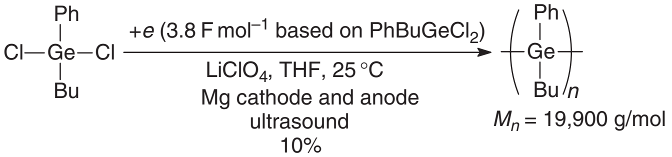
Electroreductive synthesis has been employed for the preparation of polygermanes from haloorganogermanes. Use of a platinum cathode in the reduction afforded some high molecular weight polygermanes when the substituents on germanium were relatively long-chain alkyl groups (Equation (276), Table 33).[338] Use of a magnesium cathode and

Table 33 Experimental data for Equation (276)

Monomer	*Yield* (%)	λ_{max} (nm)	M_w	M_n	M_w/M_n
Et_2GeCl_2	18	293	860	220	4.0
$Pr^n{}_2GeCl_2$	6.8	312	1,600	1,300	1.2
$Bu^n{}_2GeCl_2$	31	325	14,000	2,000	7.1
$(C_5H_{11})^n{}_2GeCl_2$	20	327	11,000	3,900	2.8
$(C_6H_{13})^n{}_2GeCl_2$	41	325	10,000	6,100	1.7
$PhMeGeCl_2$	11	327	9,400	1,700	5.7
$PhBuGeCl_2$	16	337	3,900	1,600	2.5

anode provided poly(butylphenyl)germane in high molecular weight (Equation (277)) and could also be used for the high yield synthesis of $Me_3GeGeMe_3$ (Equation (278)).[209]

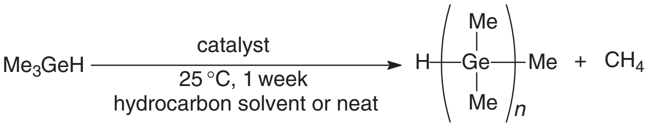
$$n\,R^1R^2GeX_2 \xrightarrow[\text{DME, voltage = 20 V}]{\text{Pt cathode}\atop +\,2n\,e^-} (R^1R^2Ge)_n + 2nX^- \tag{276}$$



$$Cl{-}Ge(Ph)(Bu){-}Cl \xrightarrow[\text{LiClO}_4\text{, THF, 25 °C; Mg cathode and anode; ultrasound; 10\%}]{+e\ (3.8\ \text{F mol}^{-1}\ \text{based on PhBuGeCl}_2)} {-}\!\left(Ge(Ph)(Bu)\right)_n\!{-} \quad M_n = 19{,}900\ \text{g/mol} \tag{277}$$

$$Me_3GeCl \xrightarrow[\text{LiClO}_4\text{, THF, 25 °C; Mg cathode and anode; ultrasound; 84\%}]{+e\ (3\ \text{F mol}^{-1}\ \text{based on Me}_3\text{GeCl})} Me_3Ge{-}GeMe_3 \tag{278}$$

Organogermanium hydrides can be polymerized by transition metal catalysts.[98,339–341] A ruthenium-containing catalyst was used for the polymerization of Me_3GeH, yielding high molecular weight polygermanes (Equation (279), Table 34).[340] The mechanism of the polymerization process was proposed (Scheme 55), and the steps determining the structural outcome of the process (i.e., formation of linear vs. branched polygermanes) were identified (Scheme 56). Similarly, demethanative polymerization of dimethylarylgermanes can be achieved using a ruthenium catalyst (Equation (280), Table 35).[98] A polygermane system containing hydrolyzable cross-linking sites was also obtained using an Ru-based catalyst via demethanative coupling (Equation (281)).[341]

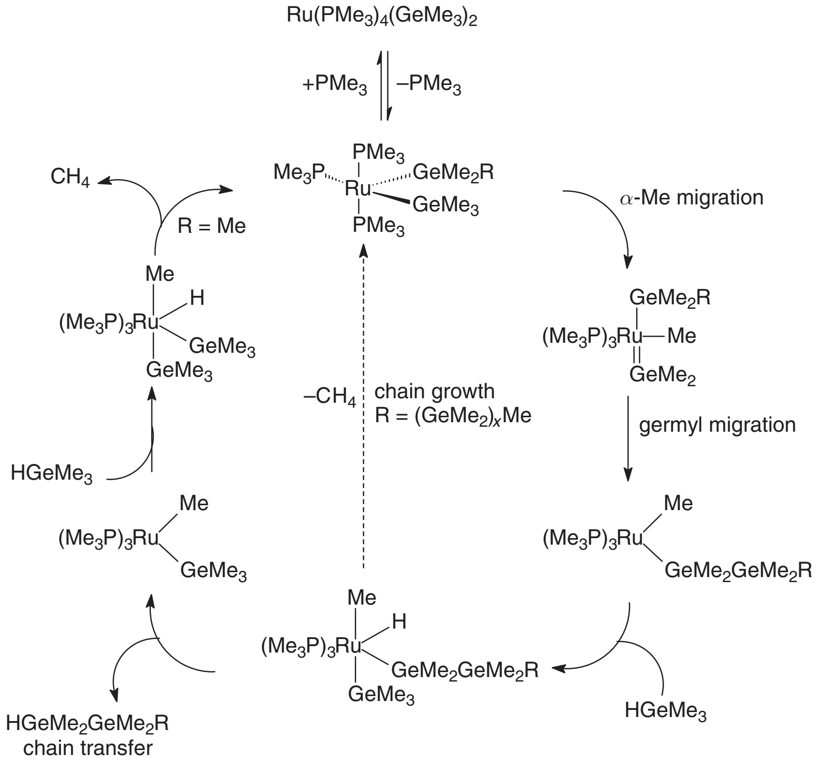


$$Me_3GeH \xrightarrow[\text{25 °C, 1 week; hydrocarbon solvent or neat}]{\text{catalyst}} H{-}\!\left(Ge(Me)(Me)\right)_n\!{-}Me + CH_4 \tag{279}$$

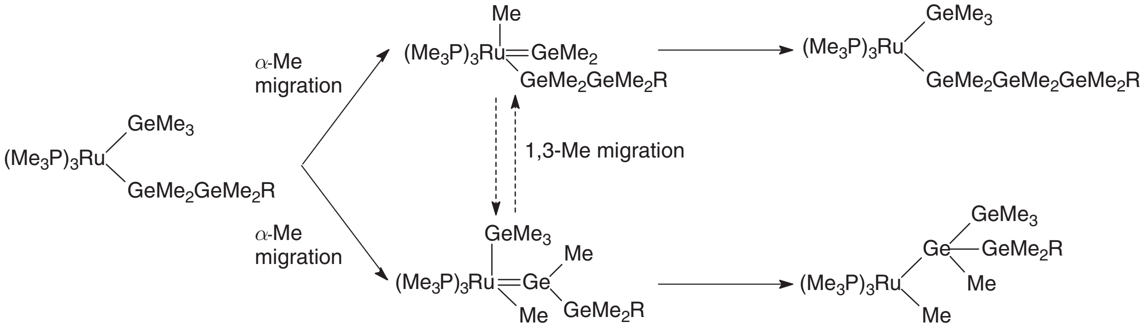
Table 34 Experimental data for Equation (279)

Catalyst (mol%)	*Yield* (%)	M_w (GPC)(g/mol)	M_n (GPC)(g/mol)
$Ru(PMe_3)_4(GeMe_3)_2$ (1.0)[a]	85	5.4×10^4	2.8×10^4
$Ru(PMe_3)_4(GeMe_3)_2$ (0.1)	97	6.6×10^4	1.8×10^4
$Ru(PMe_3)_4Me_2$ (1.0)	82	3.8×10^4	1.9×10^4
$Ru(PMe_3)_4Me_2$ (0.1)	92	7.4×10^4	3.7×10^4
$Ru(PMe_3)_4Me_2$ (1.0)[b]	81	2.0×10^4	0.9×10^4

[a] Reaction time = 1 d.
[b] $T = 60\,°C$.



Scheme 55

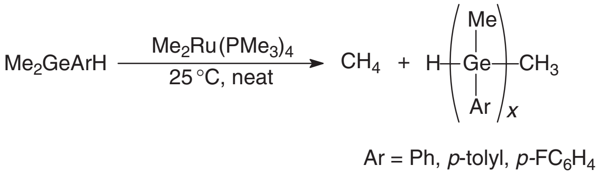


Scheme 56

Table 35 Experimental data for Equation (280)

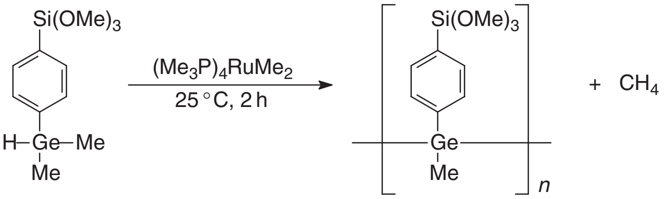
	Precipitation from MeOH				*Air workup*			
Ar	*Yield* (%)	M_w (g/mol)	M_n (g/mol)	*DP*[a]	*Yield* (%)	M_w (g/mol)	M_n (g/mol)	*DP*[a]
Ph	52	7,900	6,500	40	68	6,200	4,300	25
p-FC$_6$H$_4$	51	10,100	8,800	48	82	5,700	5,000	27
p-MeC$_6$H$_4$	54	5,500	4,700	26	100	4,600	3,200	18

[a] DP = M_n/(MW of repeat unit).



$$\mathrm{Me_2GeArH} \xrightarrow[\text{25 °C, neat}]{\mathrm{Me_2Ru(PMe_3)_4}} \mathrm{CH_4} + \mathrm{H}\left(\begin{array}{c}\mathrm{Me}\\ | \\ \mathrm{Ge}\\ | \\ \mathrm{Ar}\end{array}\right)_x\mathrm{CH_3} \qquad (280)$$

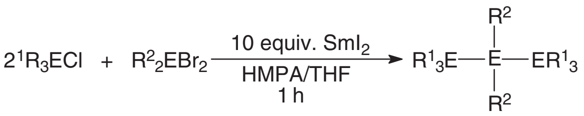
Ar = Ph, *p*-tolyl, *p*-FC_6H_4



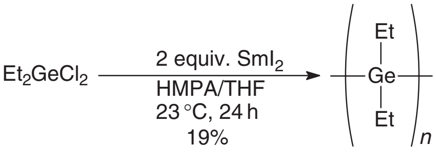
(281)

$M_n = 13{,}900$ g/mol
$M_w = 18{,}500$ g/mol
$M_w/M_n = 1.3$
37%

Both oligo- (Equation (282), Table 36) and polygermanes (Equations (283) and (284)) could be obtained using an excess of SmI_2,[342] and three different substituted polygermanes were obtained by reaction of $GeCl_2$(dioxane) with organolithium reagents (Equation (285), Table 37).[343]

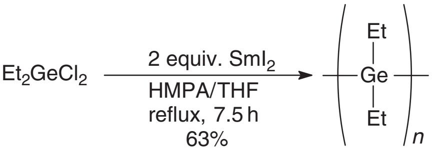


$$2^1\mathrm{R_3ECl} + \mathrm{R^2{}_2EBr_2} \xrightarrow[\text{HMPA/THF, 1 h}]{\text{10 equiv. SmI}_2} \mathrm{R^1{}_3E}-\overset{\mathrm{R^2}}{\underset{\mathrm{R^2}}{\mathrm{E}}}-\mathrm{ER^1{}_3} \qquad (282)$$



$$\mathrm{Et_2GeCl_2} \xrightarrow[\text{HMPA/THF, 23 °C, 24 h, 19\%}]{\text{2 equiv. SmI}_2} \left(\begin{array}{c}\mathrm{Et}\\ | \\ \mathrm{Ge}\\ | \\ \mathrm{Et}\end{array}\right)_n \qquad (283)$$

$M_w = 2{,}380$, $M_n = 2{,}030$, $M_w/M_n = 1.17$



$$\mathrm{Et_2GeCl_2} \xrightarrow[\text{HMPA/THF, reflux, 7.5 h, 63\%}]{\text{2 equiv. SmI}_2} \left(\begin{array}{c}\mathrm{Et}\\ | \\ \mathrm{Ge}\\ | \\ \mathrm{Et}\end{array}\right)_n \qquad (284)$$

$M_w = 1{,}562$ g/mol, $M_n = 1{,}393$ g/mol, $M_w/M_n = 1.12$

$$\mathrm{GeCl_2(dioxane)} + \mathrm{RLi} \xrightarrow[\mathrm{Et_2O}]{} \left(\mathrm{GeR_2}\right)_n \qquad (285)$$

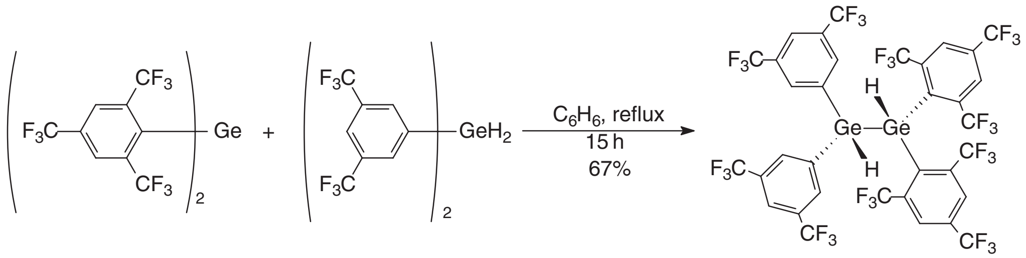
Table 36 Experimental data for Equation (282)

$R^1{}_3ECl$	*$R^2{}_2EBr_2$*	*Product*	*Yield (%)*
Et_3GeCl	Ph_2GeBr_2	$Et_3GeGePh_2GeEt_3$	94
Me_3GeCl	Ph_2GeBr_2	$Me_3GeGePh_2GeMe_3$	87
$Pr^i{}_3GeCl$	Ph_2GeBr_2	$Pr^i{}_3GeGePh_2GePr^i{}_3$	30
Et_3GeCl	$PhMeGeBr_2$	$Et_3GeGeMePhGeEt_3$	70
Et_3SiCl	Ph_2GeBr_2	$Et_3SiGePh_2SiEt_3$	50
Et_3SnCl	Ph_2GeBr_2	$Et_3SnGePh_2SnEt_3$	42

Table 37 Experimental data for Equation (285)

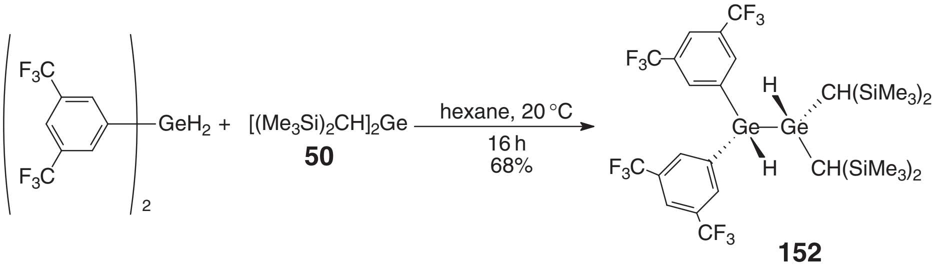
R	*Temp.* (°C)	*Time* (h)	*Yield* (%)	M_w ($\times 10^3$)(g/mol)	M_w/M_n
Me	−78	2	45	31.0	7.76
Bu^n	0	2	95	1.3	1.09
Bu^n	0	2	39	1.5	1.31
Bu^n	−78	1	98	17.9	2.88
Ph	0	1	83	0.7	1.17
Ph	−78	3	58	1.0	1.21

The unsymmetrically substituted digermanes **151** and **152** were obtained by insertion of a germylene into a Ge–H bond of a germane (Equations (286) and (287), respectively).[115] The synthesis of hexaethyldigermane was also reported employing a telluride reagent (Equation (288)).[164] A trigermole **153** containing three catenated germanium atoms was obtained in quantitative yield by lithiation of a dichlorogermole followed by reaction with MeI (Equation (289)).[344]



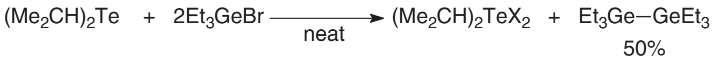
151

(286)



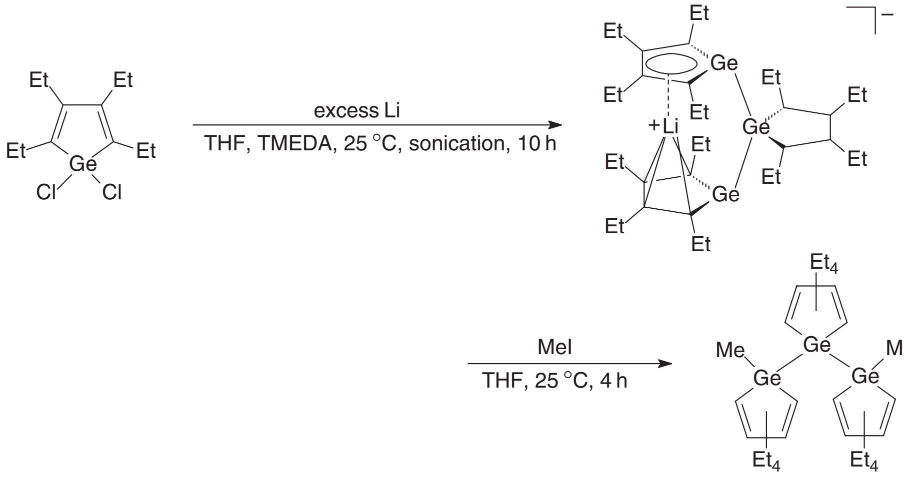
152

(287)



$$(Me_2CH)_2Te + 2Et_3GeBr \xrightarrow[\text{neat}]{} (Me_2CH)_2TeX_2 + \underset{50\%}{Et_3Ge{-}GeEt_3}$$

(288)



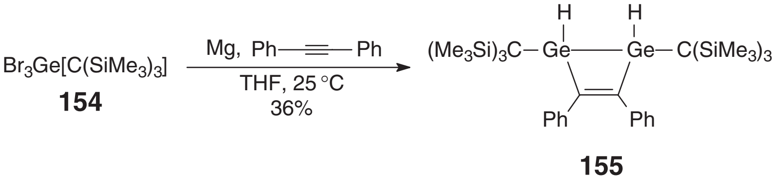
153

~100%

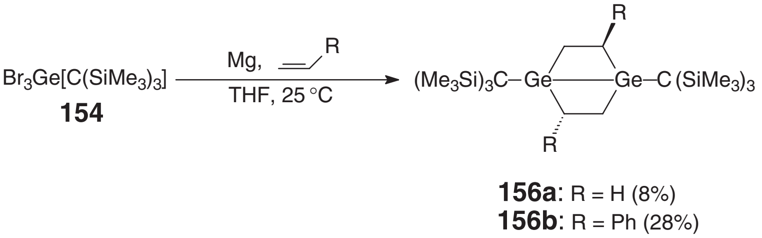
(289)

3.13.10.1.2 Synthesis of cyclic oligogermanes

Some reviews on this subject have appeared,[345,346] and several cyclic species containing two or more catenated germanium atoms have been reported. Reduction of the bulky bromogermane **154** with magnesium in the presence of diphenylacetylene yields the four-membered species **155** (Equation (290)), whereas reduction in the presence of alkenes yields the bicyclic products **156** (Equation (291)).[347] Both processes occur via initial formation of a stable germylene **157**, which was identified by its trapping product (Equation (292)), and it was elucidated that formation of **155** occurs via single-electron transfer from Mg to the halogermylene (Scheme 57).

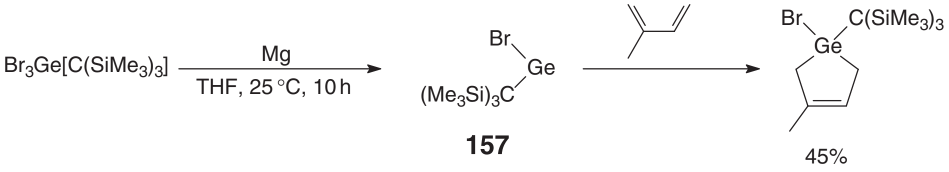


(290)



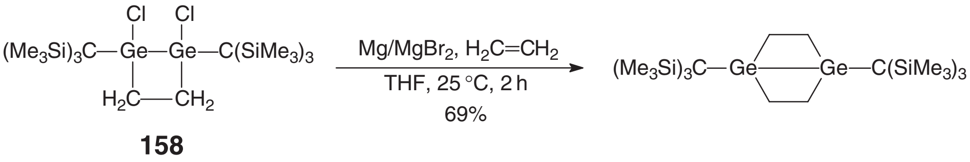
156a: R = H (8%)
156b: R = Ph (28%)

(291)

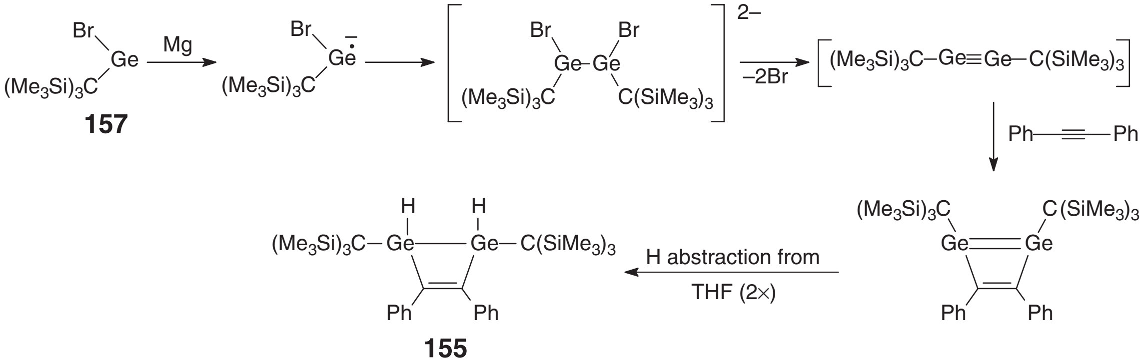


(292)

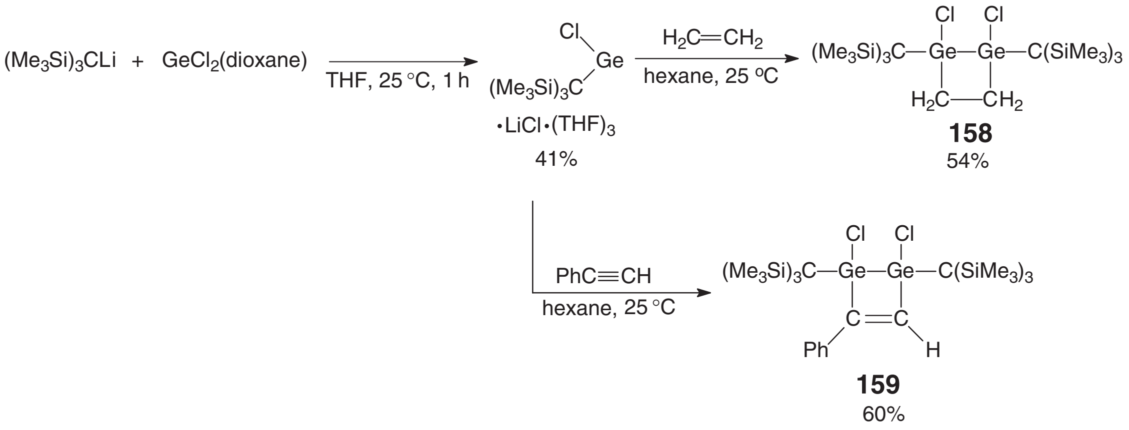
The chloride analog of **157** can be employed in similar processes to generate digermacyclobutanes **158** and **159** (Scheme 58), and **158** can be converted into a bicyclic species (Equation (293)).[348] The germylene **50** reacts with ethylene to yield a related germacyclobutane **160** via a germirane intermediate (Equation (294)).[349]



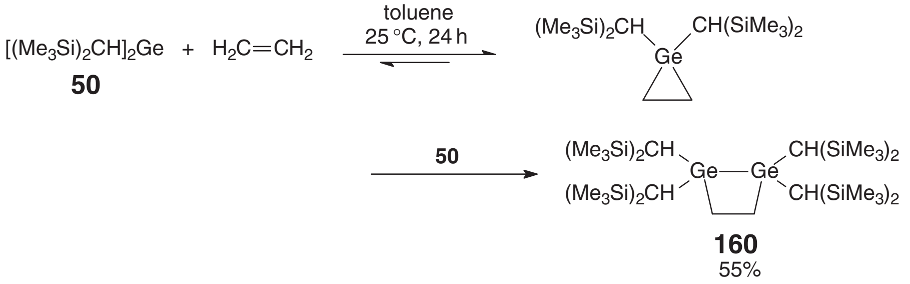
(293)



Scheme 57

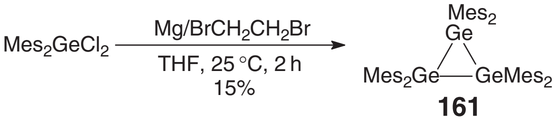


Scheme 58

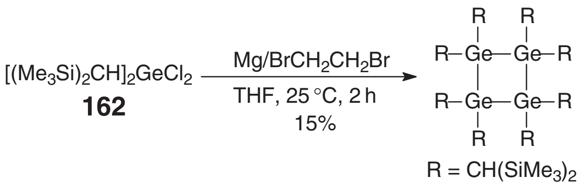


(294)

Compounds containing only germanium atoms in the ring have also been prepared. The permesityl-substituted cyclotrigermane **161** was obtained by reduction of Mes_2GeCl_2 in moderate yield (Equation (295)), while reduction of the bulky germane **162** yields a cyclotetragermane (Equation (296)).[350]

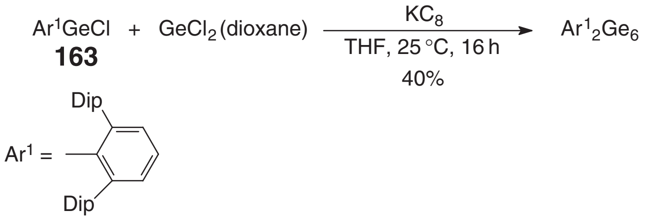


(295)

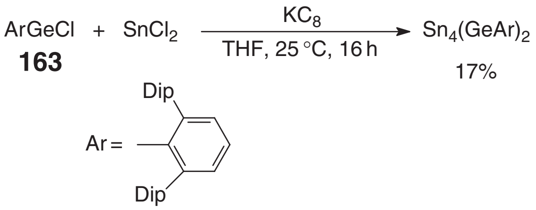


(296)

The preparation of both homo- (Equation (297)) and heteronuclear (Equation (298)) hexametallic clusters containing unsubstituted group 14 elements from germylene **163** was achieved using KC_8 as the reducing agent.[351]



(297)



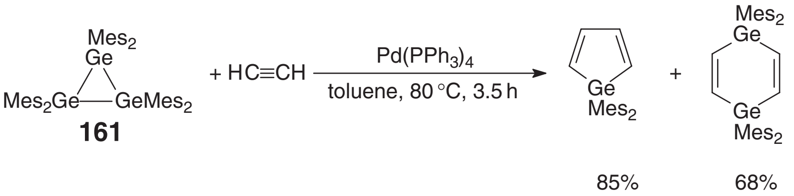
(298)

3.13.10.2 Reactivity of the Ge–Ge Bond

3.13.10.2.1 Photochemical and thermal reactions

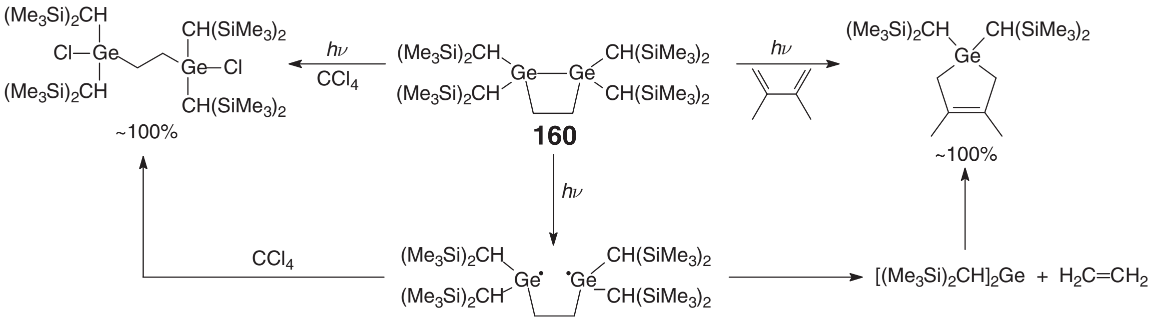
The digermacyclobutane **160** undergoes photolytic trapping reactions, which proceed via a biradical intermediate (Scheme 59),[349] and has been attached to C_{60} via a photolytic process.[352] Laser flash photolysis of organopolygermanes induces chain contraction by germylene extrusion and also Ge–Ge bond homolysis to produce polygermyl radicals,[353,354] and the latter process has been identified as occurring in the photolytic decomposition of polygermane thin films in air.[355]

Cyclotrigermanes are thermally or photolytically decomposed to generate digermenes and a germylene.[356] The cyclotrigermane **161** exhibits a wide variety of interconversions.[350,357–359] This compound thermally produces two different adducts in the presence of 2,3-dimethylbutadiene (Scheme 60).[350] In the presence of paraformaldehyde the oxadigermetane is generated (Scheme 61), and in the presence of thiobenzophenone a thiagermetane was obtained (Scheme 62).[350] In the latter case, a dithiagermolane was also produced from the germylene fragment. Furthermore, reaction of the cyclotrigermane **161** with acetylene in the presence of a catalytic amount of palladium catalyst furnishes a germole and a digermacyclohexadiene (Equation (299)).[350]

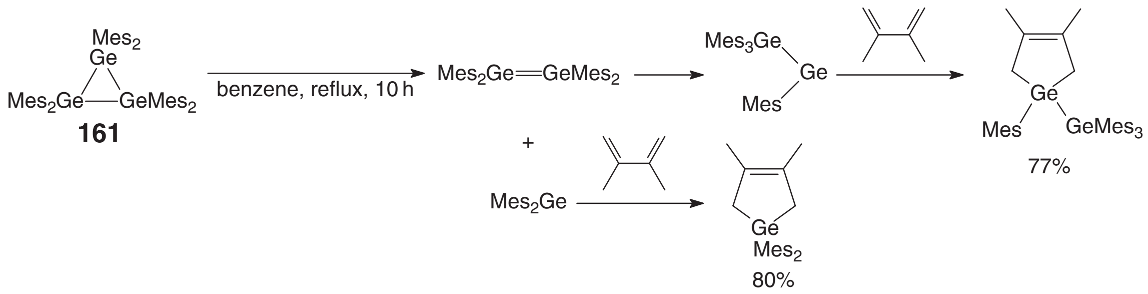


(299)

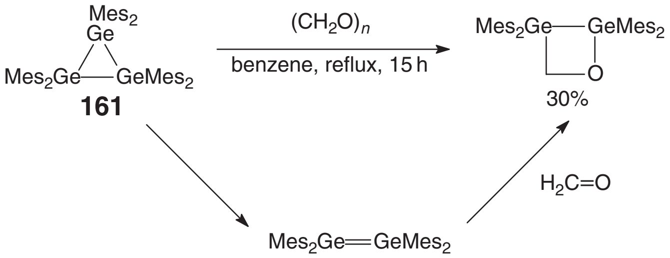
Cyclotrigermane **161** also reacts with carbonyl compounds[358,360] to produce a variety of products (Equations (300)–(302)),[358] and this material undergoes a diverse group of photolytic or thermal reactions in the presence of organolithium or Grignard reagents,[359,361] and some examples are shown in Equations (303)–(305).[359] Three-membered rings containing a Ge–Ge bond and a silicon atom bound to each germanium atom also exhibit similar reactivity with Grignard reagents,[362] and these species react with a variety of other substrates including electron-rich alkenes,[363] dienes,[364] protic reagents,[364,365] and other carbonyl compounds.[366]



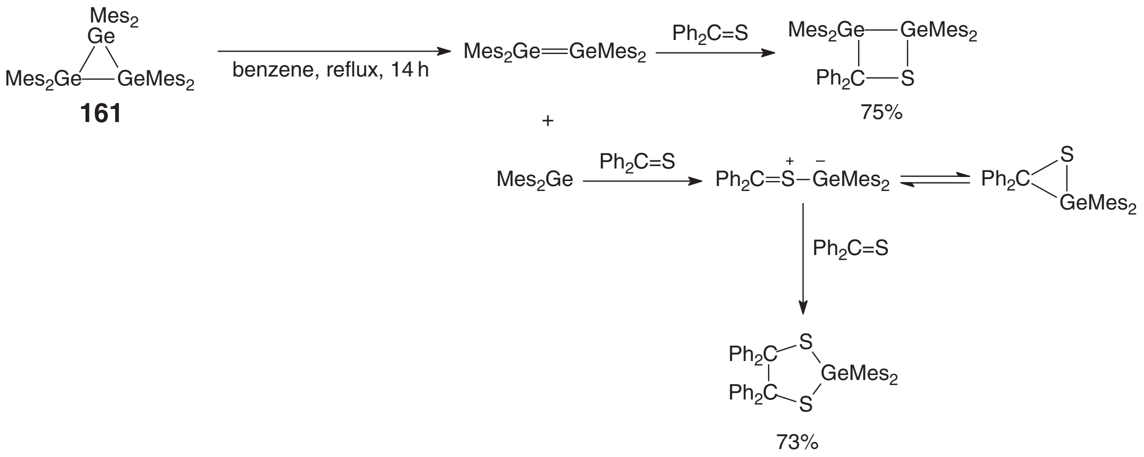
Scheme 59



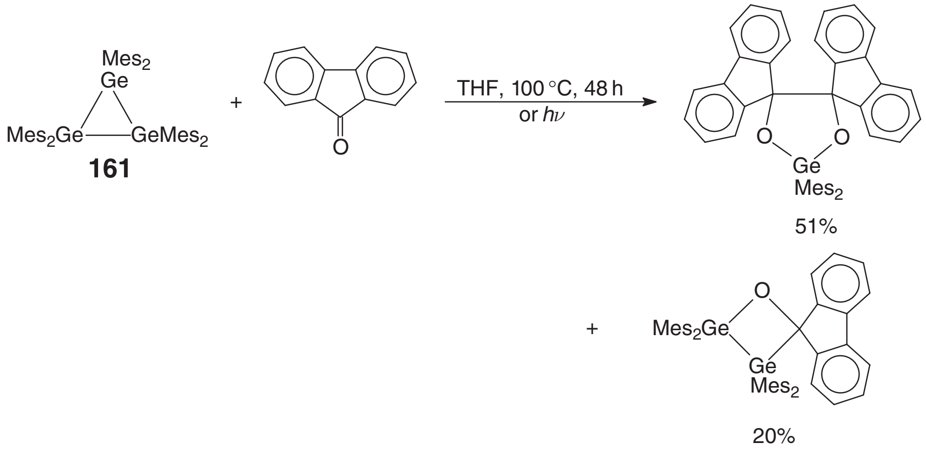
Scheme 60



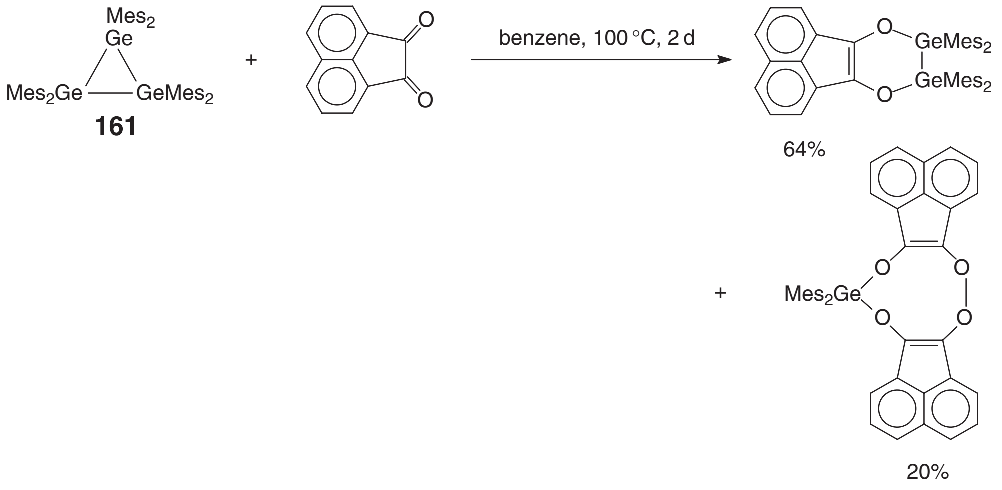
Scheme 61



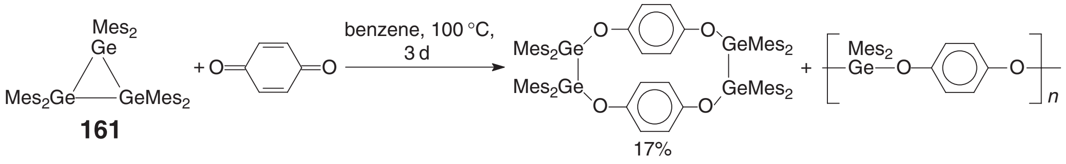
Scheme 62



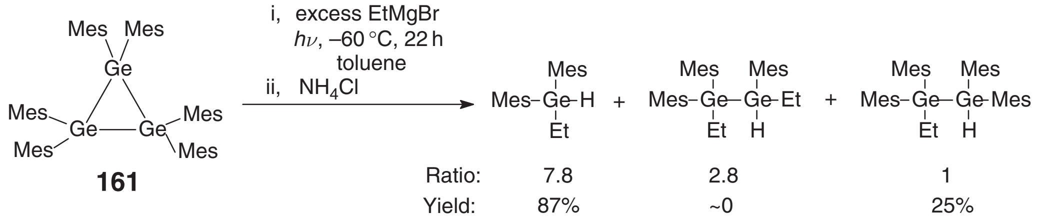
(300)



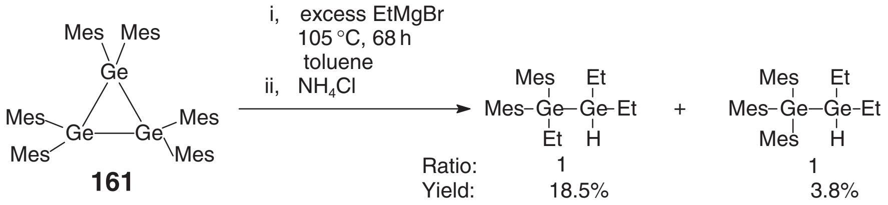
(301)



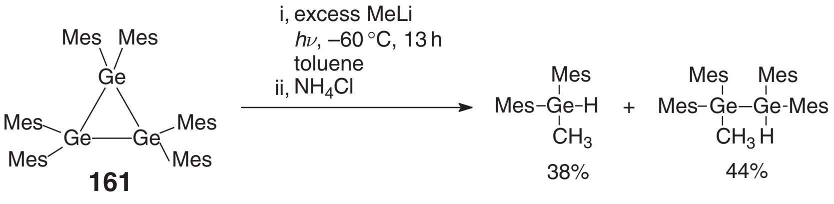
(302)



(303)

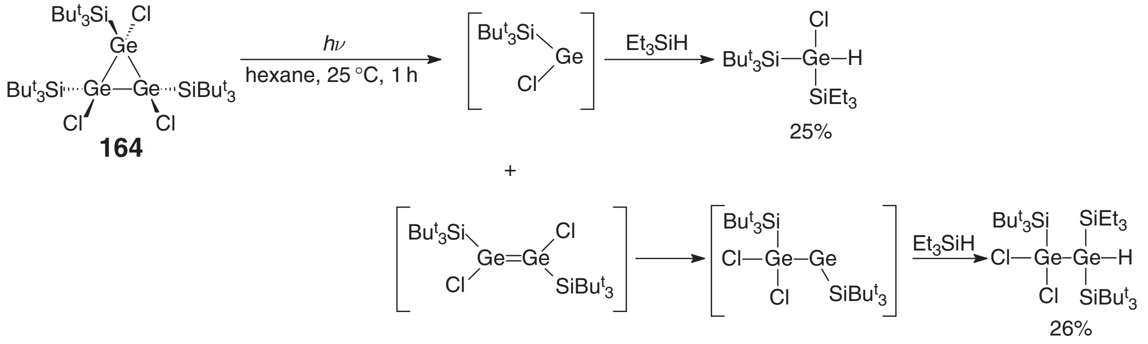


(304)

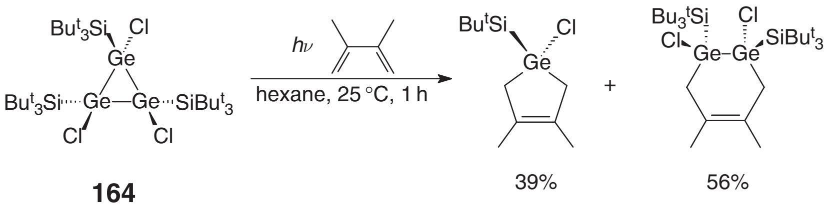


(305)

Photolysis of cyclotrigermane **164** in hexane in the presence of 2,3-dimethylbutadiene furnishes two different cycloadducts (Equation (306)), while photolysis in the presence of Et_3SiH yields silyl-substituted mono- and digermanes (Scheme 63).[367]

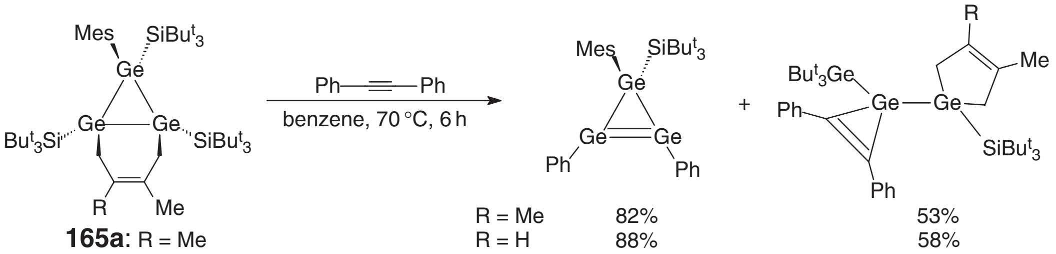


Scheme 63



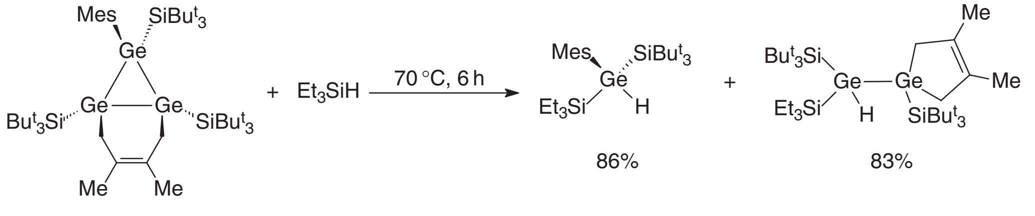
(306)

Thermolysis of the bicyclic cyclotrigermanes **165** in the presence of diphenylacetylene leads to ring contraction, giving a germacyclopropene and a dicyclic digermane species (Equation (307)).[368] The dimethyl-substituted compound **165a** also produces a bicyclic digermaoctadiene, and the mechanism of this interconversion was proposed (Scheme 64). Thermolysis of **165a** in the presence of Et_3SiH produces a germane and a digermane derivative (Equation (308)).[368]



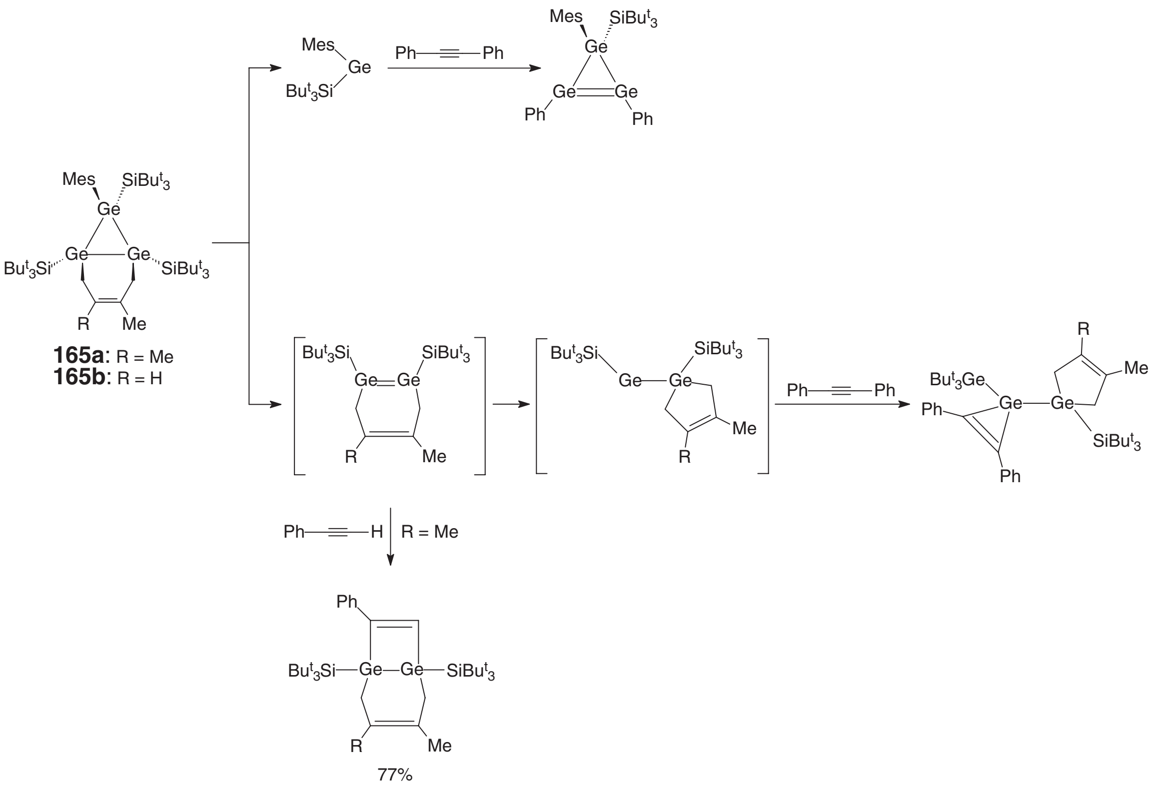
165a: R = Me
165b: R = H

(307)



165a

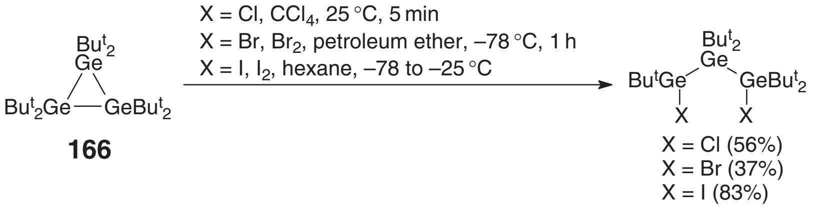
(308)



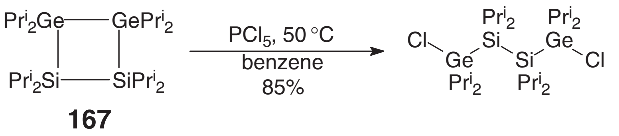
Scheme 64

3.13.10.2.2 Oxidation and halogenation reactions

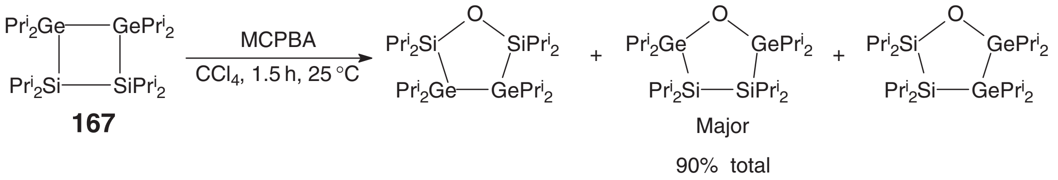
Cyclic trigermane **166** undergoes ring-opening halogenation by CCl$_4$, Br$_2$, or I$_2$ to yield a series of linear dihalotrigermanes (Equation (309)),[194] and the disiladigermacyclobutane **167** undergoes this reaction in the presence of PCl$_5$ to give a mixed group 14 element dihalide (Equation (310)).[369] Compound **167** can also be oxidized by *m*-chloroperoxybenzoic acid (MCPBA) to provide three oxadisiadigermacyclopentanes (Equation (311)).[369]



(309)



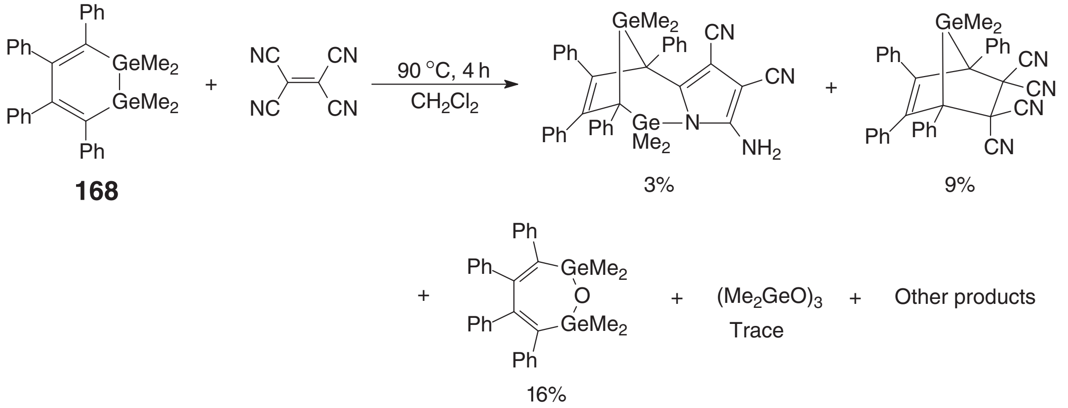
(310)



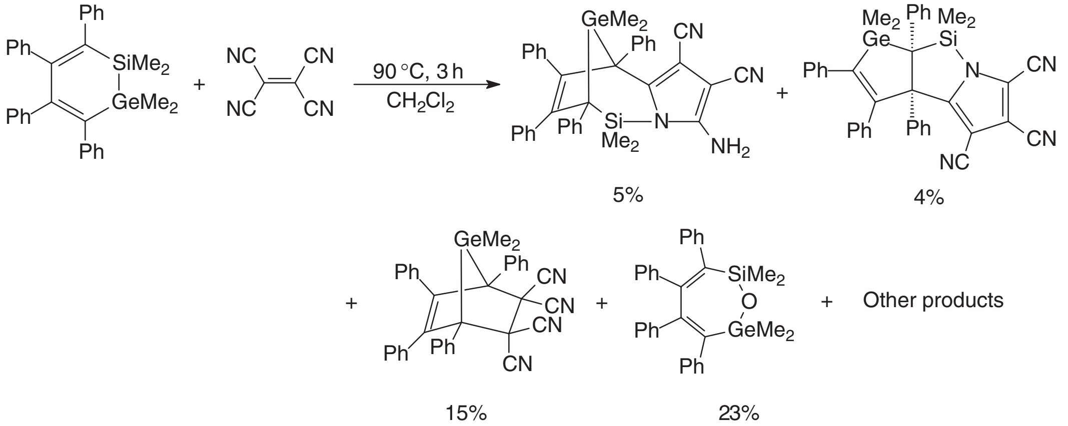
(311)

3.13.10.2.3 Electron-transfer reactions

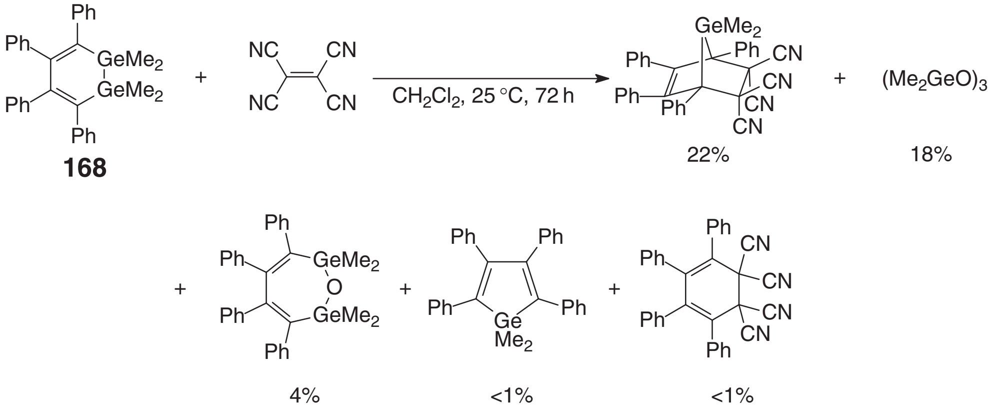
Singly bonded oligo- and polygermanes undergo various electron-transfer processes.[370–373] The digermacyclohexadiene **168** participates in a thermal electron-transfer reaction with tetracyanoethylene (TCNE) to yield a mixture of products (Equation (312)), and its silicon-containing analog also exhibits similar reactivity (Equation (313)).[372] Compound **168** produces a different mixture of products, when reacted with TCNE at room temperature (Equation (314)).[373]



(312)



(313)



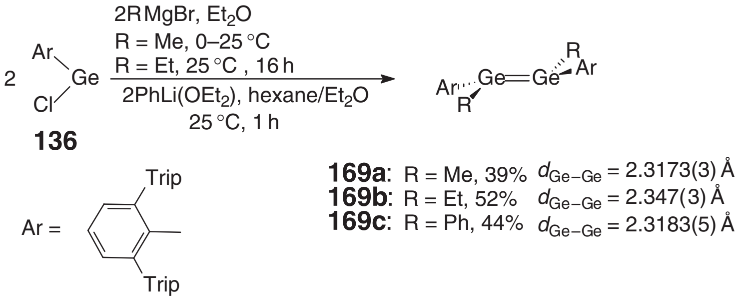
(314)

3.13.11 Compounds with Germanium–Germanium Multiple Bonds

Several reviews covering this area have appeared since 1993.[374–376] Doubly bonded Ge–Ge species have bond lengths which fall in the range of approximately 2.20–2.45 Å.[377–380] The substituents have an effect on the shape of Ge–Ge double bonds,[381] and some reports of Ge–Ge triple bonds have appeared.[382–385] These have been the subject of theoretical investigations.[386]

3.13.11.1 Linear Multiply Bonded Species

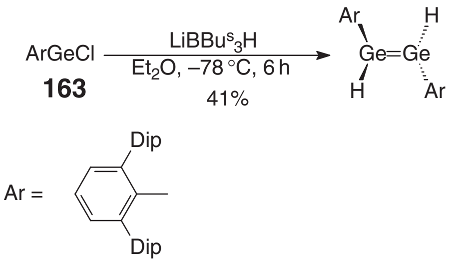
The digermenes **169** were obtained via reaction of the germylene **136** with Grignard reagents providing unusual digermene species **169a** and **169b** which contain alkyl substituents (Equation (315)).[387] These digermenes exhibit *trans*-bent structures which are retained in solution. A digermene bearing a hydride substituent at each Ge center with a Ge–Ge double bond length of 2.372(1) Å has also been prepared (Equation (316)).[388] Introduction of PMe_3 into the reaction produces compound **170** (Equation (317)) which contains germanium in both the Ge(I) (the monosubstituted Ge) and Ge(III) (the trisubstituted Ge) oxidation states.[388] The Ge–Ge bond in **170** is very long (2.5304(7) Å), and examples of this type of interaction are rare.[224,389]



136

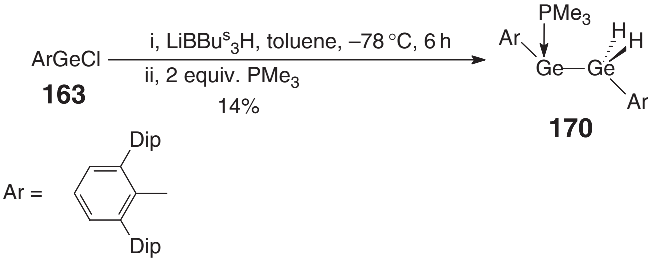
169a: R = Me, 39% d_{Ge-Ge} = 2.3173(3) Å
169b: R = Et, 52% d_{Ge-Ge} = 2.347(3) Å
169c: R = Ph, 44% d_{Ge-Ge} = 2.3183(5) Å

(315)



163

(316)

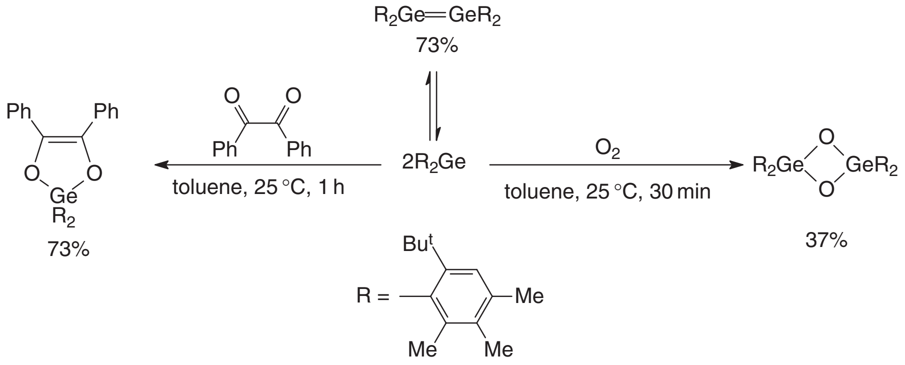


163

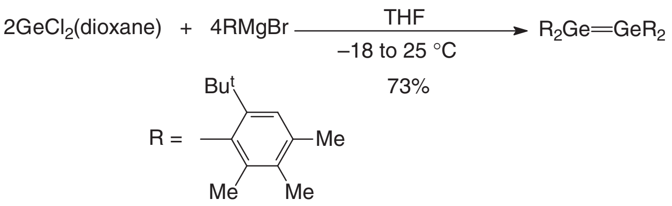
170

(317)

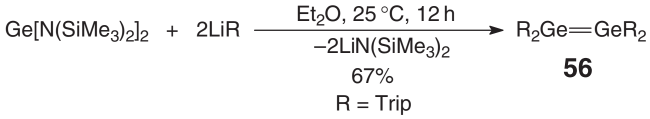
A planar peraryldigermene with a similar structure to **169** was prepared from $GeCl_2$(dioxane) (Equation (318)), which contains a short (2.2521(8) Å) Ge=Ge bond. This species undergoes dissociation to the germylene which was identified by trapping experiments (Scheme 65).[390] The digermene **56** which has a shorter Ge=Ge bond length of 2.213(1) Å was obtained using an organolithium reagent to abstract the amido groups of $Ge[N(SiMe_3)_2]_2$ (Equation (319)).[158]



Scheme 65



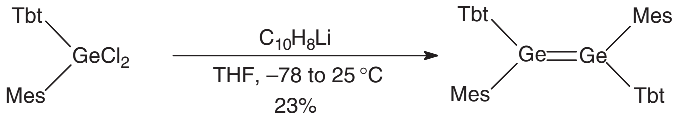
(318)



$$\mathrm{Ge[N(SiMe_3)_2]_2} + \mathrm{2LiR} \xrightarrow[\substack{-2\mathrm{LiN(SiMe_3)_2} \\ 67\% \\ \mathrm{R = Trip}}]{\mathrm{Et_2O,\ 25\ °C,\ 12\ h}} \mathrm{R_2Ge{=}GeR_2} \tag{319}$$

56

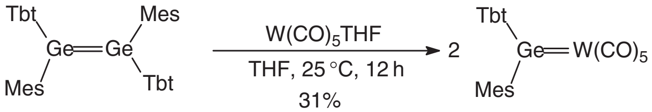
The highly hindered digermene **171** containing a long Ge═Ge (2.416(2) Å) was obtained by treatment of the corresponding diaryldichlorogermane with lithium naphthalenide (Equation (320)), and this species exhibits reversible thermochromism in hexane solution resulting in complete dissociation to the germylene (Scheme 66).[391,392]



171

(320)

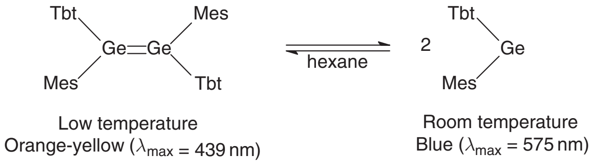
Intermolecular reactions of **171** proceed via the germylene as shown in the oxidation process (Scheme 67) and in complexation with W(CO)$_5$THF (Equation (321)).[392]



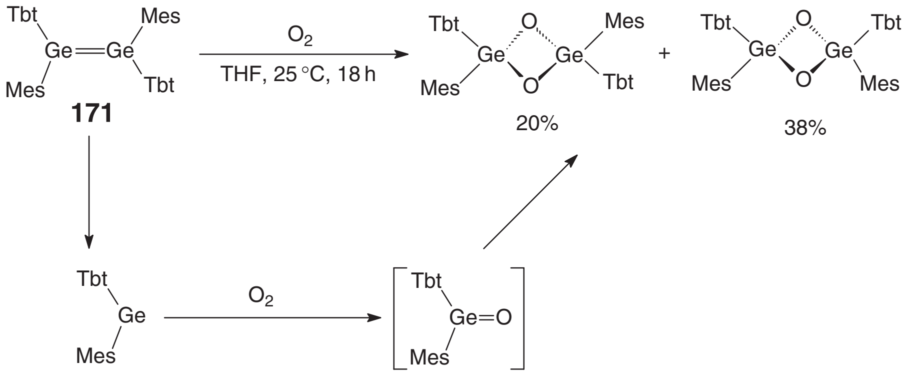
171

(321)

Efforts to prepare germanium analogs of alkynes which contain Ge–Ge triple bonds have also met with some success.[382–385] Reduction of the germylene **163** with a slight excess (~5%) of potassium metal affords the germyne **172** (Equation (322)), which contains only one substituent at each germanium and a Ge–Ge distance of 2.2850(6) Å



Scheme 66



Scheme 67

and a *trans*-bent structure.[383] The structure of **172** is shown in Figure 9, and structural data are collected in Table 38. The reaction stoichiometry is crucial to obtain the neutral species, as when **163** is reacted with a substoichiometric amount (1.5 equiv.) of potassium, the monoanionic radical **173** is produced (Equation (323)),[384] which exhibits a Ge–Ge distance of 2.3331(4) Å. The dianionic lithium salt **174** was obtained by reacting **163** with a 10-fold excess of Li powder (Equation (324)), and this species has a Ge–Ge bond length of 2.455(9) Å,[384] which is similar to that of a Ge–Ge single bond, and two long Ge–Li contacts.

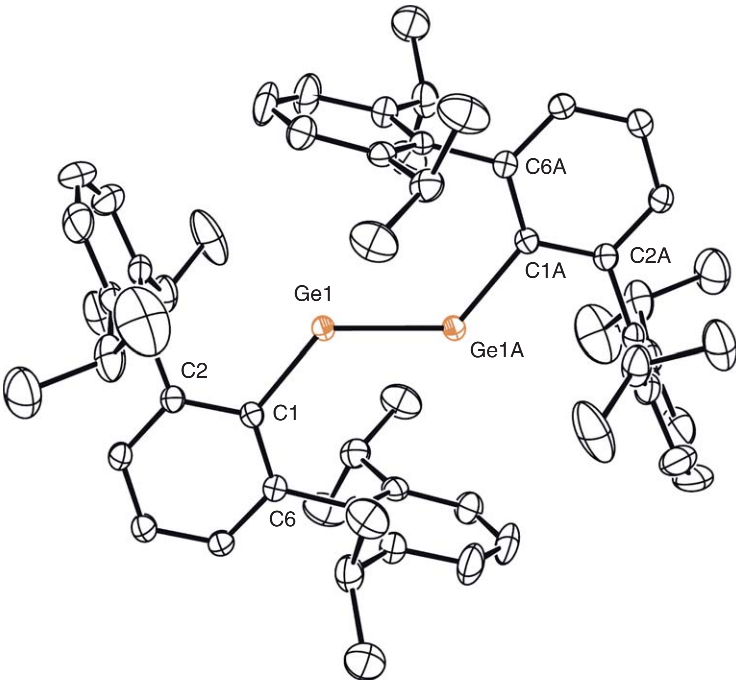
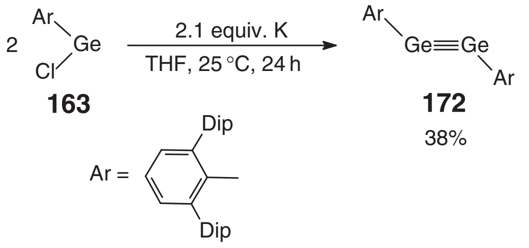


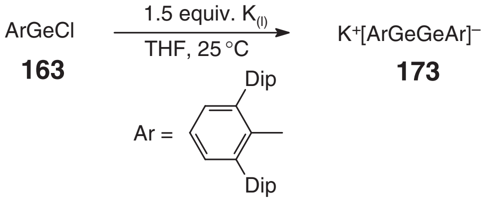
Figure 9 ORTEP diagram of the germyne **172**. Reproduced from Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed. Engl*. **2002**, *41*, 1785–1787.

Table 38 Selected bond lengths (Å) and angles (°) for **172**

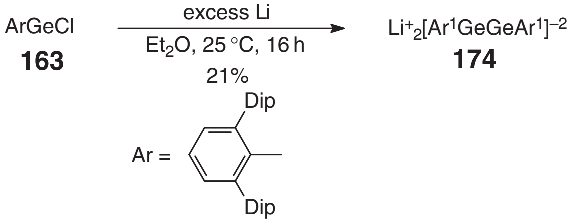
Ge(1)–Ge(1A)	2.2850(6)	Ge(1A)–Ge(1)–C(1)	128.67(8)
Ge(1)–C(1)	1.996(3)	Ge(1)–C(1)–C(2)	116.9(2)
C(1)–C(2)	1.412(4)	Ge(1)–C(1)–C(6)	124.6(2)
C(1)–C(6)	1.408(4)	C(1)–C(2)–C(6)	118.5(3)



(322)

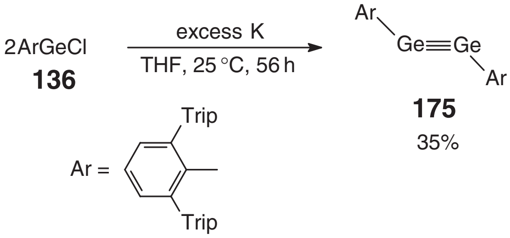


(323)

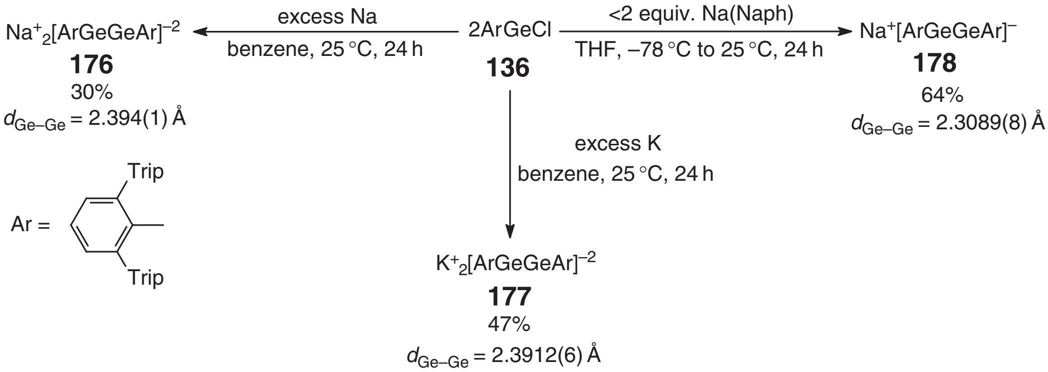


(324)

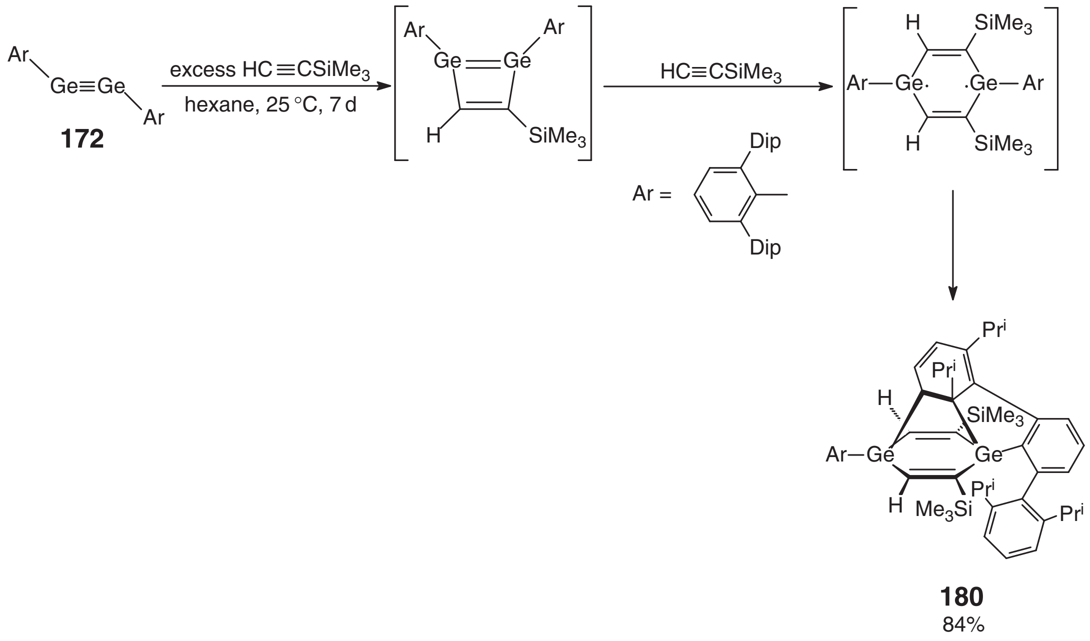
The germyne **175** with a slightly different ligand from **172** was prepared from the germylene **136** (Equation (325)).[384,385] Both mono- and dianionic sodium and potassium analogs of this species could be obtained by altering the reaction stoichiometry (Scheme 68), and the Ge–Ge bond distances vary accordingly depending on the charge on the anion.[384] The doubly reduced species **176** and **177** have Ge–Ge distances similar to the Ge–Ge single bond length. The position of the cation can have an effect on the Ge=Ge bond length as shown for the dilithium salt $[\{(\text{dioxane})_{0.5}(\text{Et}_2\text{O})\text{LiGeC}_6\text{H}_3\text{-2,6-Mes}\}_2]_\infty$.[393]



(325)

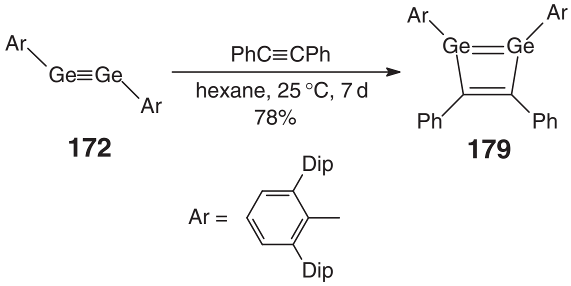


Scheme 68



Scheme 69

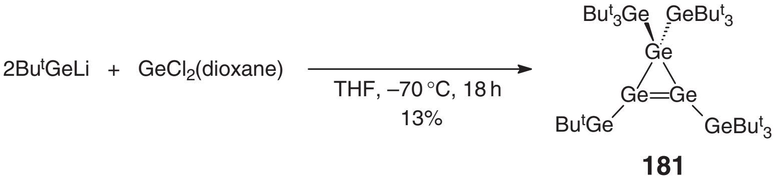
The reaction chemistry of germyne **172** has been investigated. Reaction with diphenylacetylene produces the digermacyclobutadiene **179** (Equation (326)), while treatment with excess trimethylsilylacetylene affords the bicyclic compound **180** (Scheme 69), which results from the formation of a biradical intermediate.[394]



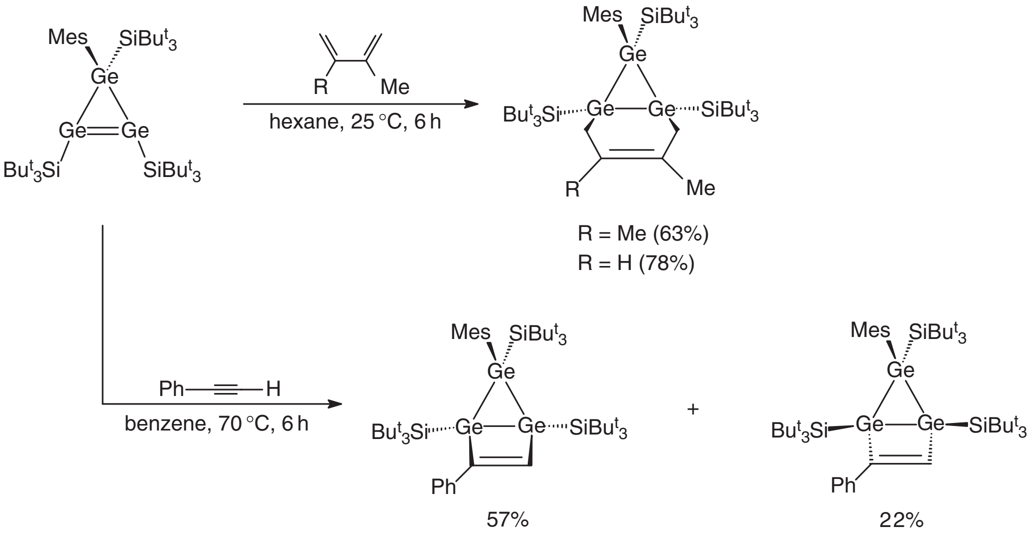
(326)

3.13.11.2 Cyclic Multiply Bonded Species

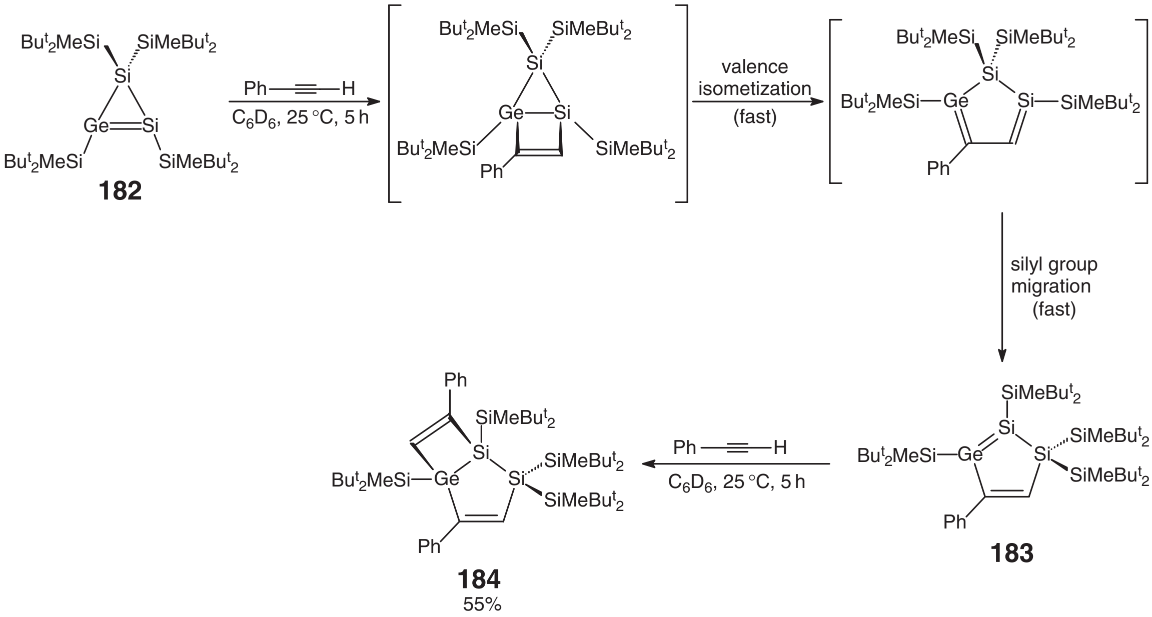
A number of cyclic species with Ge=Ge double bonds have appeared,[395,396] and several reviews have been published.[397] The cyclotrigermene **181** was obtained via reaction of $GeCl_2$(dioxane) with an organogermyl anion (Equation (327)), and the Ge–Ge distances within the ring are 2.522(4) and 2.239(4) Å.[396] Fused bicyclic cyclotrigermanes are available from cyclotrigermenes by reaction with dienes or acetylenes (Scheme 70).[398] Treatment of the disilagermacyclopropene **182** with phenylacetylene affords the disilagermacyclopentadiene **183**, which contains a Ge=Si double bond (Equation (328)). The reaction pathway for this interconversion has been proposed (Scheme 71), and the product **183** was also found to react with a second equivalent of phenylacetylene to give the bicylic product **184**.[399]



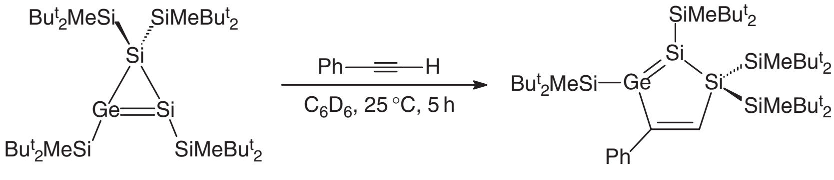
(327)



Scheme 70

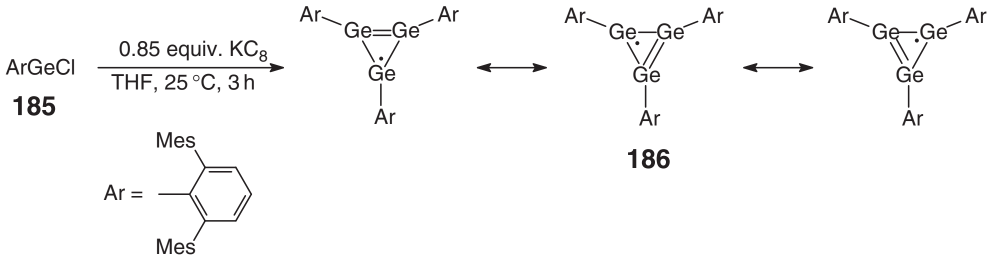


Scheme 71

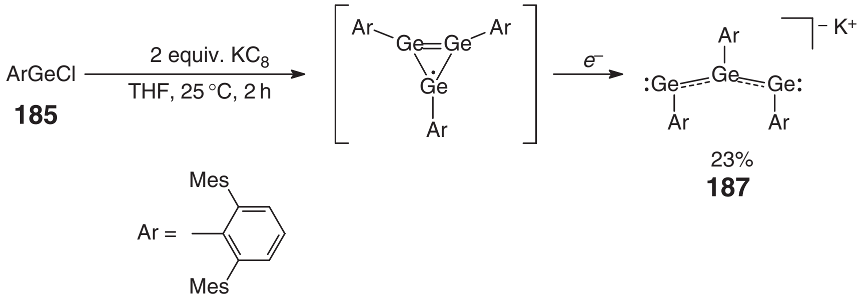


182 **183** (328)

Germylene **185** can be reduced with substoichiometric amounts of KC_8 to give the cyclotrigermenyl radical **186**, which has been structurally characterized (Equation (329)), while reaction of **185** with an excess (2 equiv.) of KC_8 produces **187** which is the germanium analog of the allyl anion (Equation (330)).[400] The structure of **187** has been obtained as well.



(329)



(330)

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3.14
Tin Organometallics

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3.14.1 Introduction

3.14.1.1 Developments in the Past Decade

Organotin chemistry continues to be a very active field, and there are more than 6,500 references in the past 10 years which refer to organotin compounds. The most active areas have been the use of $^{117/119}Sn$ NMR spectroscopy and X-ray crystallography for structural studies, the preparation of many complex cage structures of the stannoxanes, and the preparation of a variety of organotin species in low-valency states and low coordination numbers: the stannylenes (R_2Sn:), stannenes ($R_2Sn{=}CR^1{}_2$), heterostannenes ($R_2Sn{=}X$), distannenes ($R_2Sn{=}SnR_2$), the first distannynes ($RSn{\equiv}SnR$), and the stannonium ions (R_3Sn^+). Organotin compounds have continued to be used extensively in organic synthesis (see *Volumes 9* and *11*), particularly in reactions involving radical chain reactions, to the degree that complaints are made of the "tyranny of tin."

Applications of organotin compounds have been progressively restricted by environmental considerations; the major use continues to be in PVC stabilization, and the monoalkyl tin compounds are being increasingly used for coating glass with SnO_2.

3.14.1.2 Literature

Two editions of a monograph on *Organotin Chemistry* by A. G. Davies have been published in 1997 and 2004,[1,2] and P. J. Smith has edited the second edition of the *Chemistry of Tin* (1996).[3] Two volumes on *The Chemistry of Organic Germanium, Tin and Lead Compounds* (1995 and 2002) in Patai and Rappoport's series contain many articles on organotin chemistry, and emphasize the comparisons with the other metals in the group.[4,5] There is extensive coverage of the preparation of organotin compounds in the section on *Tin Compounds* in *Science of Synthesis, Vol. 5, Compounds of Group 14 (Ge, Sn, Pb)* (2003) with E. J. Thomas as section editor;[6] references to the individual articles are given in the sections below.

Five volumes of *Gmelin* have appeared since 1993,[7] and the whole series is available online. Structural data have been classified and analyzed in extensive reviews.[8–14]

There is still no recent monograph devoted to the use of organotin compounds in synthesis, but Pereyre, Quintard, and Rahm's book[15] has been supplemented with a chapter by Jousseaume and Pereyre in Smith's *The Chemistry of Tin*,[16] and there are substantial chapters in the two editions of Schlosser's *Organometallics in Synthesis*,[17,18] in Yamamoto and Oshima's *Main Group Metals in Organic Synthesis*,[19] and in Rappoport's *The Chemistry of Organic Germanium, Tin and Lead Compounds*.[20,21]

3.14.1.3 Physical Data

Physical data are available in the appropriate volumes of *Gmelin* (though only the references in the online version); the early volumes are now 20 years old, but the online version is kept up-to-date. Thermochemical data, critically evaluated by Simões, are in the National Institute of Standards and Technology's (NIST) web book,[22,23] which is freely available, and also gives details of IR, MS, and UV/VIS spectra. Theoretical methods for calculating physical properties have been greatly improved, particularly by the use of the DFT method.[24]

3.14.2 Spectroscopic Methods

3.14.2.1 NMR Spectroscopy

^{119m}Sn Mössbauer spectroscopy (reviewed by Barbieri[25]) was used extensively for investigating solid organotin compounds until about 1980, but is little used now that high resolution solid-state NMR spectroscopy and X-ray crystallography have become much more widely available. Instruments and methods for $^{117/119}$Sn NMR spectroscopy have improved considerably, and a number of good reviews are available, both for the solution[26–30] and the solid state.[31–34]

$^{117/119}$Sn NMR chemical shifts in organotin compounds cover a range of about 5,200 ppm, from +2,966 in (2,6-Mes$_2$C$_6$H$_3$)(Bu$^t{}_3$Ge)Sn: (Mes = mesityl) to −2,247 in (Me$_5$C$_5$)SnBF$_4$. Useful collections of data are in Wrackmeyer's and Marsmann and Uhlig's reviews.[27,30,35] This sensitivity of chemical shift to structure can be used to determine the enantiomeric purity of carboxylic acids, alcohols, and halides through their organotin derivatives, such as Bu$_2$SnR$^*{}_2$,[36,37] and solid-state NMR has been used to identify species such as $\equiv$SiOSnR$_3$ that can be formed in the surface of silica,[38–41] and for the qualitative and quantitative analysis of the different tin species in polymer-supported organotin reagents.[42]

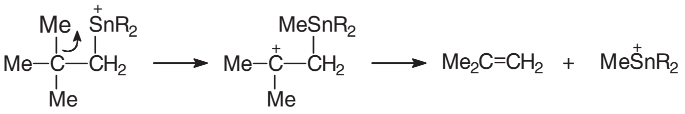
Chemical shifts for straightforward structures are best predicted by comparison with other structurally similar organotin compounds, and there are also useful correlations with the values of δ^{29}Si, ^{79}Ge, and ^{207}Pd in the corresponding silanes,[43] germanes,[44] and plumbanes.[43] DFT calculations reproduce the general trends in chemical shifts, but the accuracy is not high.[45]

$^{117/119}$Sn coupling constants[46,47] are more readily understandable.[48] Values of ^1J(Sn,X) increase with increasing *s*-character of Sn and of X in the SnX bond, resulting in sequences for $^1J(^{119}\text{Sn},^{13}\text{C})$, such as Me$_4$Sn −337, Me$_3$SnCl −380, Me$_2$SnCl$_2$ −468, MeSnCl$_3$ −696, (CH$_3$CH$_2$)$_4$Sn −330, (CH$_2$=CH)$_4$Sn −520, (C$_6$H$_5$)$_4$Sn −531, and (HC$\equiv$C)$_4$-Sn −1176 Hz. ^3J Values for the coupling of tin with a number of other nuclei show a Karplus-type angular dependence.[49]

3.14.2.2 Mass Spectrometry[50]

There are still rather few fundamental studies of the mass spectrometry of organotin compounds, but the fragmentation pathways of organotin compounds have been further elucidated by means of tandem mass spectrometry.[51,52]

Electrospray ionization has been used to study the hydrolysis products of organotin chlorides R_nSnCl_{4-n},[53] and a variety of complex SnOSn-bonded cage compounds have been identified from the difunctional and trifunctional compounds R_2SnX_2 and $RSnX_3$ (see Sections 3.14.16.2 and 3.14.16.3).[54] Trineopentyltin compounds fragment in the gas phase by migration of a β-methyl group, probably to form the stabilized β-stannylalkyl cation (Equation (1)).[55]



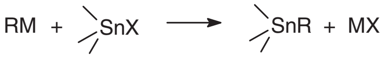
(1)

There are many references to the speciation of organotin compounds (particularly butyltin compounds) in marine sediments (see below), when compounds Bu_nSnR_{4-n} are separated by GLC or HPLC and analyzed by mass spectroscopy (MS),[56] sometimes with isotope dilution.[57–59]

3.14.3 Formation of the Tin–Carbon Bond[60–64]

3.14.3.1 Reaction of Organometallic Compounds with Tin(IV) Compounds

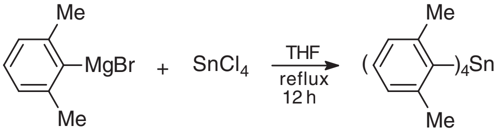
The reaction shown in Equation (2) provides the most common method of forming an RSn bond.



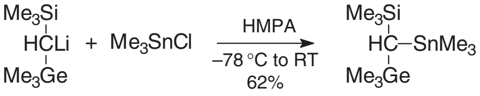
(2)

The metal M is commonly Mg, Li, Al, or Zn, and X is usually Cl or another halide.[64] When the tin substrate is a tetrahalide, SnX_4, Grignard reagents usually give peralkylation to R_4Sn unless steric hindrance is significant, when the organolithium reagents may be more effective. The organozinc reagents have the advantage that they are tolerant toward other functional groups such as CN, CO_2R, or OCOR, which are sensitive toward RMgX or RLi. Organoaluminum compounds, which are cheap and can be used in the absence of a solvent, are usually used on an industrial scale, and they often permit the reaction to be taken to the stage of incomplete alkylation. They have been recommended for the peralkylation of organotin residues R_nSnX_{4-n} in order to remove them from reaction mixtures. Organotin residues in environmental samples are usually monitored by peralkylation to $R_nSnR^1_{4-n}$, followed by separation by GLC or HPLC, and analysis by MS or AA, and $NaBEt_4$ is commonly used for the alkylation as it is insensitive to hydrolysis by water in the sample. There are a few examples of trifluoromethylation,[65] fluorovinylation,[66] allylation,[67] and alkynylation[68] by organosilanes in the presence of F^-.

Some recent examples of the reaction in Equation (2) are shown in Equations (3)–(7).[69–72]



(3)



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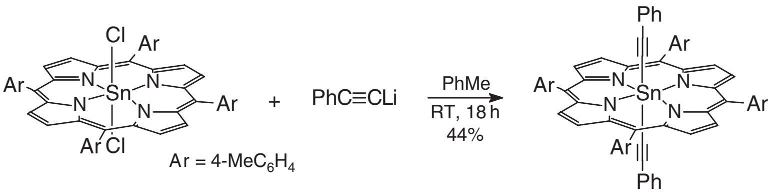
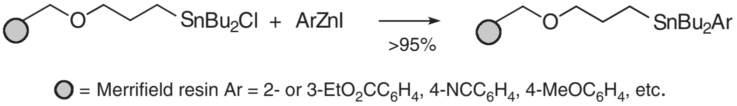


(5)



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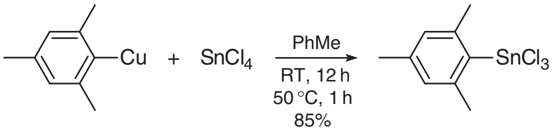
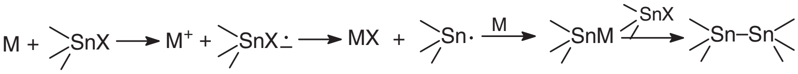


(7)

The Barbier process in which the organometallic reagent is generated *in situ* from a mixture of R^1X, R_nSnX_{4-n}, and M is experimentally simpler and more tolerant of functional groups (Equation (8)). Primary alkyl iodides will react with R_2SnCl_2 or R_3SnCl in the presence of zinc dust to give $R_2SnR^1{}_2$ or R_3SnR^1, respectively, but with primary alkyl chlorides or secondary alkyl iodides, the coupling fails, and SnSn-bonded compounds are the principal products, presumably because of competitive electron transfer to R^1X and to R_nSnX_{4-n} (Equations (8) and (9)).[73] The preparation of arylstannanes from aryl bromides and metallic zinc is catalyzed by $CoBr_2$ (though this process does not as yet appear to be successful for heteroaryl compounds).[74]

(8)



(9)

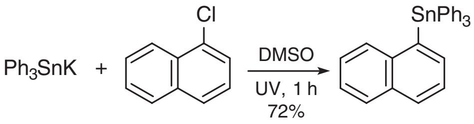
The reaction shown in Equation (9) can be minimized by using $(Bu_3Sn)_2O$ rather than a tin halide, and the stannanes Bu_3SnR^1 ($R^1 = p$- or *s*-alkyl, vinyl, allyl, benzyl, aryl, or hetaroaryl) can be prepared in good yield by treating a mixture of R^1Br and $(Bu_3Sn)_2O$ with magnesium powder and 1,2-dibromoethane under ultrasonic conditions.[75,76]

3.14.3.2 Reaction of Stannylmetallic Compounds with Electrophiles

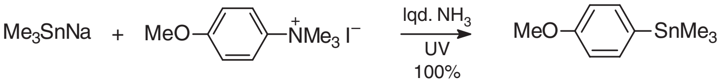
The reaction shown in Equation (10) is versatile, helped by the ready availability of R_3SnLi from $R_3SnH + LDA$, or $R_6Sn_2 + RLi$.[77] The group R can be alkyl, alkenyl, allyl, propargyl, aryl, or heteroaryl,[78] and X is commonly halide, but may be sulfonate, phosphate, or benzotriazolyl.[79] It provides a useful route to functionally substituted alkylstannanes by displacement of the halide from substrates such as $ClCH_2OBu$,[80] $ClCH_2SR$,[81] $ClCH_2CH_2NMe_2$,[82] or MeCOCl, of the PhS from $(PhSCH_2)_3N$[83] or PrCOSPh,[84] or of the PhO from $PhOCH(OEt)_2$.[2,85]

(10)

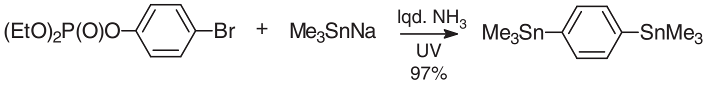
Triorganostannyl anions are excellent nucleophiles in $S_{RN}1$ processes with aromatic substrates,[86] and arylstannanes can be prepared from the photostimulated reactions of Ph_3SnNa or Me_3SnNa (from $R_3SnCl + Na$) and aryl halides in DMSO,[87] or of aryl amines, via their ammonium salts,[88] in liquid ammonia, or of phenols, via their phosphates, in liquid ammonia.[89] Examples are given in Equations (11)–(13).



(11)



(12)



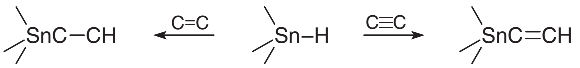
(13)

The reactions with non-aromatic substrates follow a variety of mechanisms. In the reaction of Bu_3SnK with *s*- and *t*-butyl bromides and iodides, a transient absorbing at 400 nm has been observed,[90] and the Bu_4Sn and $Bu_3SnSnBu_3$ that were formed showed a CIDNP effect, confirming the intermediacy of the $Bu_3Sn\cdot$ radical.[91]

Monosaccharides carrying hindered allylic bromide or methanesulfonate groups react with "Me_3SnCu" (from CuCN + BuLi, then Bu_3SnH) with retention of the allylic structure, but less-hindered derivatives give some allylic rearrangement.[78]

3.14.3.3 Hydrostannation

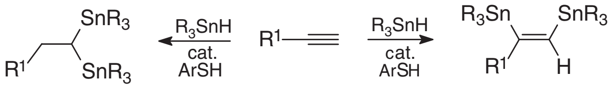
Hydrostannation of alkenes and alkynes (Equation (14)) can involve nucleophilic ($R_3Sn^-H^+$), electrophilic ($R_3Sn^+H^-$), or homolytic ($R_3Sn\cdot$) tin, or the hydride as a metal complex (R_3SnMH).



(14)

Stannane, SnH_4 (b.p. = −52.5 °C), can be prepared by reducing $SnCl_4$ with $LiAlH_4$. At −78 °C, a mixture of cobalt naphthenate and *t*-butyl peroxide, or palladium on charcoal, or hexachloroplatinic acid, will initiate its hydrostannation of alkenes to give the corresponding tetralkylstannanes. The yields are too low to make this a viable laboratory or industrial preparation (e.g., 1-butene gives tetrabutyltin in 33% yield), but there might be some potential in preparing the stannane by *in situ* reduction.[92]

Homolytic hydrostannation can also be initiated at room temperature by thiophenols, when a trace of oxygen may oxidize the thiol to the $ArS\cdot$ radical, which abstracts hydrogen from the stannane to give the stannyl radical (Equation (15)).[93] With azoisobutyronitrile (AIBN) initiation, alkynes undergo only monohydrostannation, but with the thiol, simple alkynes show bis(hydrostannation) or bis(stannation).

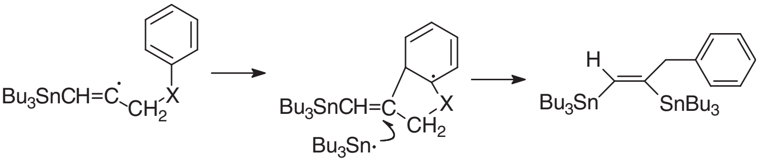


(15)

Geminal bis(hydrostannation) is attributed to quenching of the bis-2-tributylstannylethyl radical by the thiol, with polarity reversal catalysis (Equation (16)).

$$Bu_3SnCH{=}CHR \xrightleftharpoons{Bu_3Sn\cdot} (Bu_3Sn)_2CH\text{-}\dot{C}HR \xrightarrow[-ArS\cdot]{ArSH} (Bu_3Sn)_2CH\text{-}CH_2R \qquad (16)$$

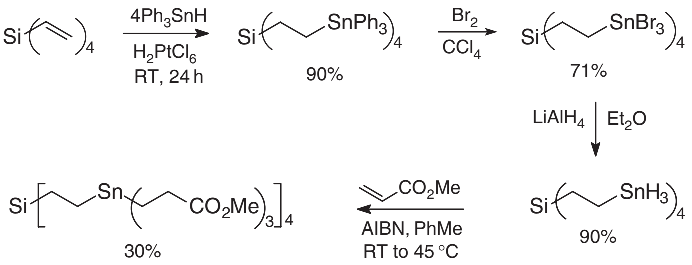
With a low concentration of thiol, propargyl aryl ethers or amines show vicinal bis(stannation), and it is suggested that this results from stabilization of the initial radical by cyclization onto the aromatic ring (Equation (17)).



(17)

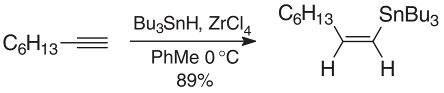
The regio- and stereo-selectivity of hydrostannation is sensitive to steric effects, and the bulky stannanes $(PhMe_2CCH_2)_3SnH$ (trineophyltin hydride) and $(PhMe_2SiCH_2)_3SnH$ have been designed with the aim of increasing the selectivity.[94,95] Under radical conditions, the former gave *anti*-addition to alkynes, but under catalysis with $Pd(PPh_3)_2Cl_2$, only *syn*-addition occurred. The latter hydride, under radical conditions, showed *anti*-addition, but with the alkynes $PhC{\equiv}CH$ and $PhC{\equiv}CPh$, long reaction times were needed (6 h at 85 °C or 7 h at 80 °C, respectively, with AIBN) and the *Z*-adduct isomerized into the *E*-adduct. Water-soluble organotin dendrimers, with potential applications as

X-ray contrast agents, have been prepared by reactions, one of which involves a 12-fold homolytic hydrostannation (Equation (18)).[96,97]



(18)

Hydrostannation can be catalyzed by Lewis acids. If a mixture of an alkyne, tributyltin hydride, and $ZrCl_4$ or $HfCl_4$ is stirred in hexane, the product of *anti*-addition is formed (Equation (19));[98] the hydride can be generated *in situ* from Bu_3SnCl and Et_3SiH, and $B(C_6F_5)_3$ is an alternative Lewis acid.[99,100] The mechanism of these reactions is still a matter of speculation.

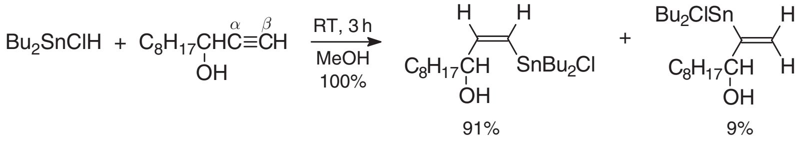


(19)

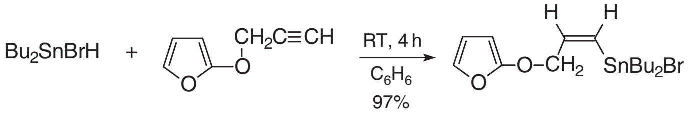
The principal developments in hydrostannation during the past decade are in the use of hydrides R_2SnXH, where X is an electronegative group such as halide, carboxylate, or sulfonate, and in the use of the hydrides complexed to a transition metal, particularly palladium.

The hydrides R_2SnXH have the advantage over Bu_3SnH, which is the more common reagent, that they allow hydrostannations to be carried out at room temperature or below, though Et_3B and 9-BBN have been used as initiators at −78 °C, and AIBN at room temperature or 60 °C. By varying the group X, a wide variety of reagents is available. Their higher Lewis acidity causes them to be more regio- and stereoselective, and makes available a series of anionic adducts R_2SnXYH^-, again with their own specific characteristics. This is a very active field, in which further developments can be expected.[101]

Most attention to date has been paid to the hydrostannation of propargyl alcohols and ethers where interaction of the Lewis-basic oxygen enhances the regio- and stereoselectivity and gives high yields of the Z-β-adducts (e.g., Equations (20) and (21)), whereas hydrostannation with Bu_3SnH gives only the Z-α-adducts.

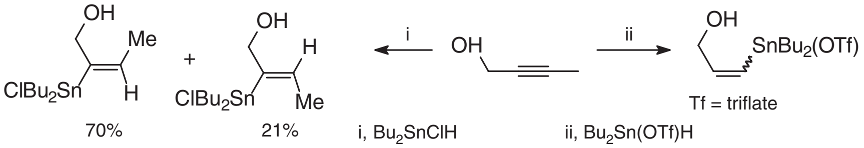


(20)



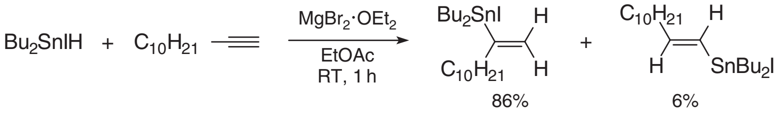
(21)

The control in regioselectivity that can be achieved by changing the Lewis acidity of the hydride is illustrated in Equation (22).[102,103]



(22)

Simple alkynes react with Bu_2SnIH only in the presence of an adduct such as $MgBr_2{\cdot}OEt_2$, when the active reagent is $Bu_2SnIBrH^-$ $MgBr^+$ (Equation (23)).[104] On the other hand, $Bu_2Sn(OAc)H$, which decomposes at room temperature to give dihydrogen and the diacetoxydistannane, is reported to react with *t*-butylacetylene by the addition of dihydrogen (Equation (24)).[105]



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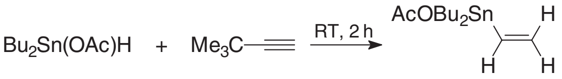
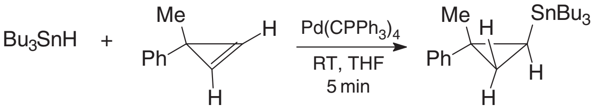


(24)

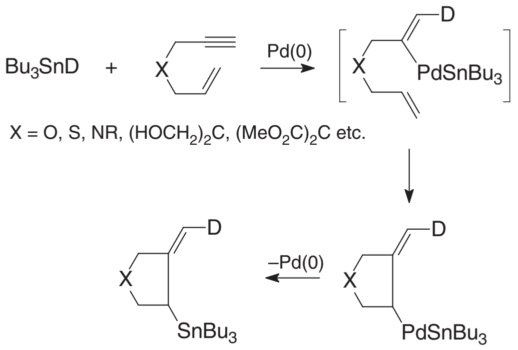
The hydrostannation of alkenes and alkynes can be catalyzed by a number of transition metals (Ni, Pd, Pt, Mo, etc.), but most studies have involved palladium.[106] The mechanism that is most commonly accepted is shown for an alkyne in Scheme 1; the model for an alkene is similar. This mechanism accounts for the observations that the reactions normally involve *cis*-addition, that the R_3Sn group enters so as to avoid steric hindrance by the largest substituent group on the alkene or alkyne, and that the regioselectivity depends on the polarization of the palladium–hydrogen bond in the sense $Pd^{\delta+}–H^{\delta-}$.

There are few reports of the hydrostannation of simple alkenes with metal catalysts in homogeneous solution, but steric strain in the ring causes cyclopropenes to be reactive even at −78 °C, with addition of Sn–H to the less sterically hindered face (Equation (25)). Distannation with $Me_3SnSnMe_3$ and silastannation with $Me_3SiSnBu_3$ could similarly be achieved with $Pd(OH)_2$ as catalyst.[107]

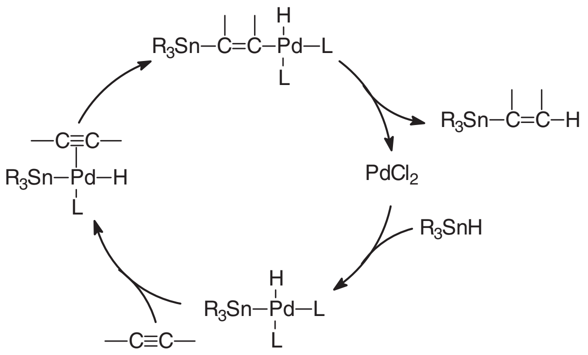


(25)

If the acceptor molecule contains both an alkene and an alkyne group, hydrostannation occurs at the alkyne moiety. 1,6-Enynes undergo ring closure initiated by addition to the alkyne, as shown by the fate of the deuterium in Equation (26).[108]

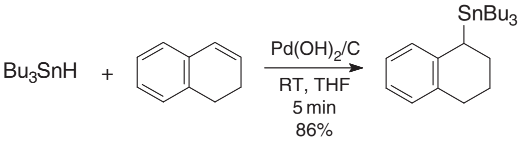


(26)

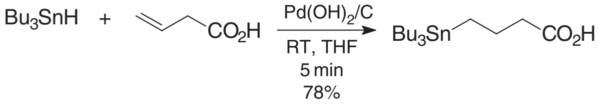


Scheme 1

Unactivated alkenes, however, can be hydrostannated in good yields, with $Pd(OH)_2/C$ as a heterogeneous catalyst (Equations (27) and (28)).[109]



(27)

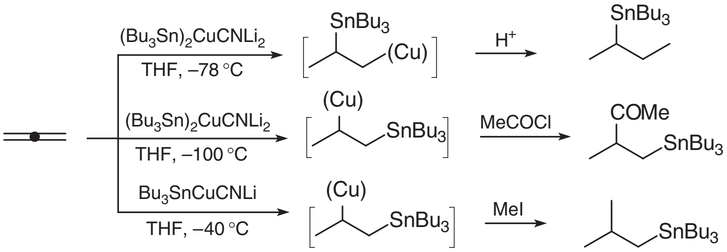


(28)

3.14.3.4 Metallostannation

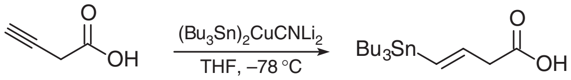
Metallostannation often gives a better regio- and stereoselectivity than does hydrostannation, and the vinylmetal group that is formed can often react further with suitable electrophiles such as halogens, acids, alkyl halides, acyl halides, metal halides, aldehydes, or epoxides.[110,111]

The use of stannylcuprate reagents is well established.[112,113] The reactions occur under mild conditions. They are reversible, and the reactivity and regio- and stereo-selectivity are sensitive to the structure and reaction conditions, as illustrated by the reaction of allene with the lower-order cuprate $Bu_3SnCuCNLi$ and, more readily, with the higher order cuprate $(Bu_3Sn)_2CuCNLi$ (Equation (29)).[114]

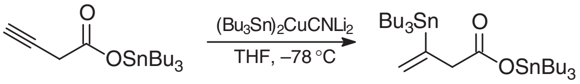


(29)

Alk-2- and alk-3-ynoic acids are stannylated with $Bu_3Sn(Bu)CuCNLi_2$ to give the 3- and 4-stannyl derivatives, respectively, but the tributylstannyl ester of but-3-ynoic acid gives the reverse regioselectivity (Equations (30) and (31)).[115]



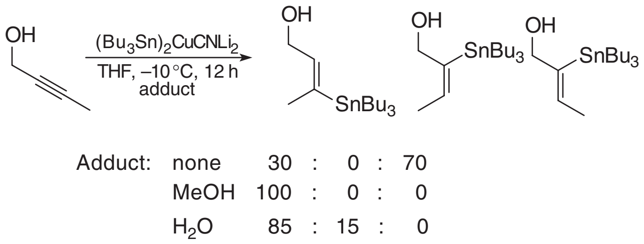
(30)



(31)

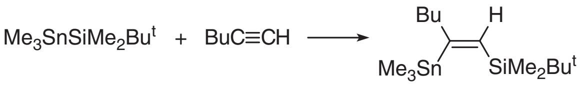
The reactions are faster in the presence of weak protic acids, which can quench the initial products under conditions where the stannylcuprate reagents are not affected. This is illustrated in Scheme 2. With no internal proton source, the thermodynamically more stable result of *trans*-addition is favored, but, in the presence of a proton source, the initial adducts resulting from *cis*-metallostannation are trapped.[116,117,118]

Borylstannation, catalyzed by palladium, has been established for alkynes, diynes, and enynes.[119,120] The reaction apparently occurs through the oxidative addition of B–Sn to the palladium to give the complex B–PdL$_n$–Sn, and one example of such an adduct has been isolated.



Scheme 2

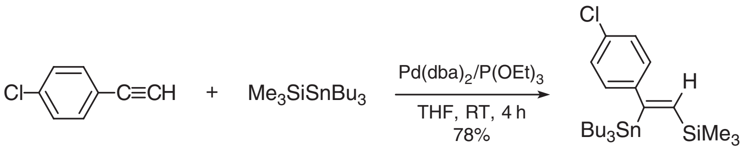
Silastannation similarly appears to involve intermediates based on Si–PdL$_n$–Sn complexes,[121] the rate-determining step being the insertion of the alkyne into the Sn–Pd bond (Equation (32)).[122]



Condition	*Temp.*	*Time* (h)	*Yield* (%)
Pd(OAc)$_2$/Bu^{t}CH$_2$CMe$_2$NC	RT	24	89
Pd(PPh$_3$)$_4$	RT	24	0
Pd(PPh$_3$)$_4$	70 °C	24	87

(32)

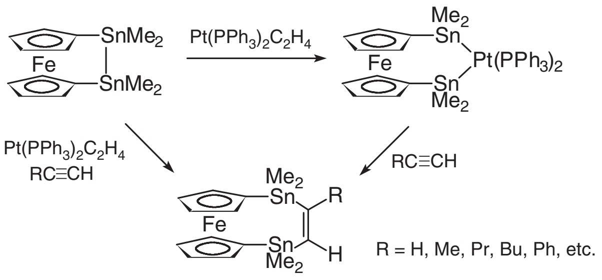
Palladium-phosphine catalysts have been used most commonly, but a Pd(OAc)$_2$/*t*-alkyl isocyanide[123] or Pd(dba)$_2$/P(OEt)$_3$ (cheaper)[124] catalyst is more effective, and will bring about silastannation at room temperature, for example, Equation (33).



(33)

The distannasilane Me$_3$SnSiMe$_2$SnMe$_3$ does not undergo a double insertion, but first rearranges in the presence of Pd(PPh$_3$)$_4$ to give Me$_3$SnSnMe$_2$SiMe$_3$, which then reacts to give the adduct Me$_3$SnSnMe$_2$(R)C=CHSiMe$_3$.[125]

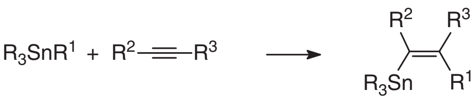
The intermediate Sn–Pd–Sn compound in distannation (Equation (34)) has recently been isolated in the reaction of an *ansa*-distannane.[126]



(34)

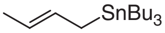
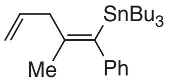
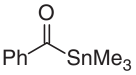
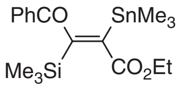
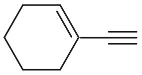
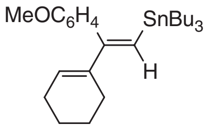
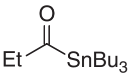
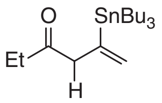
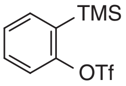
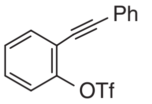
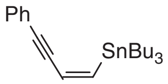
3.14.3.5 Carbostannation

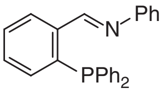
Carbostannation of alkynes and allenes has recently been developed and provides an important new route to stannylalkenes (Equation (35)).



(35)

Table 1 Carbostannation of alkynes and arynes

Carbostannane	*Alkyne*	*Catalyst*[a]	*Product*	*Yield (%)*	*References*
	Me—≡—Ph	Ni(cod)$_2$ 100 °C PhMe 14 h		64	127
	Me_3Si—≡—CO_2Et	Ni(cod)$_2$ 30 °C PhMe 3 h		85	128
4-$MeOC_6H_4$—≡—$SnBu_3$		Ni(cod)$_2$/DIBAL 80 °C PhMe 5 h		79	127
		Ni(cod)$_2$ 50 °C PhMe 15 h		67	129,130
Ph—≡—$SnBu_3$		Pd^{II}/IP 50 °C MeCN 3 h		54	131
Ph—≡—$SnBu_3$	≡	Pd^{II}/IP 50 °C THF 2 h		81	132

[a] Pd^{II} = [PdCl(π-allyl)]$_2$ IP = iminophosphine = 

The group R^1 can be allyl, acyl, or alkynyl, and arynes can also act as the acceptors. The catalysts are usually Ni(cod)$_2$, or ligated palladium. The mechanisms are not understood in detail, but a catalytic cycle involving the product of oxidative addition, Sn–M–R^1, is thought to be involved. The stannylalkenes that are formed can then be subjected to reaction with electrophiles (e.g., Ac_2O or RCH=O), or to coupling reactions in the presence of transition metals (e.g., the Stille reaction).

Examples of carbostannation are given in Table 1.

3.14.4 Alkylstannanes

Alkyl–tin bonds are generally less reactive than aryl–, alkenyl–, alkynyl–, or allyl–tin bonds, and often behave as spectator ligands as one of these other groups reacts. For example, Stille reactions that are aimed at the coupling of one of these groups, R, are often carried out with the tributyltin derivatives, Bu_3SnR, and the Bu_3Sn group stays intact as the group R reacts (Equation (36)).

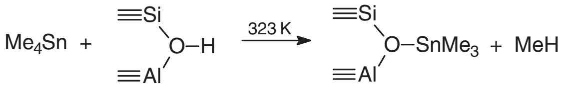
$$\mathrm{Bu_3SnR} + \mathrm{R^1X} \xrightarrow{\mathrm{Pd(0)}} \mathrm{Bu_3SnX} + \mathrm{RR^1} \qquad (36)$$

R = aryl, alkenyl, alkynyl, or allyl X = halide

Tetraalkylstannanes decompose in the gas phase at about 550 K to give mainly alkene and a little alkane, and in the presence of oxygen, the products are alkene, carbonyl compounds, carbon dioxide, and water.[133] They react with partially dehydroxylated silica at 200 °C to graft the R_3Sn group onto the surface (Equation (37)),[38] and tetramethyltin reacts with Hβ zeolite at temperatures as low as 183 K, to trimethylstannylate the surface, leaving the zeolite framework intact (Equation (38)).[134]

$$\mathrm{R_4Sn} + \equiv\mathrm{SiOH} \xrightarrow{473\ \mathrm{K}} \equiv\mathrm{SiOSnR_3} + \mathrm{RH} \qquad (37)$$

R = Me, Et, Pr^i, or Bu

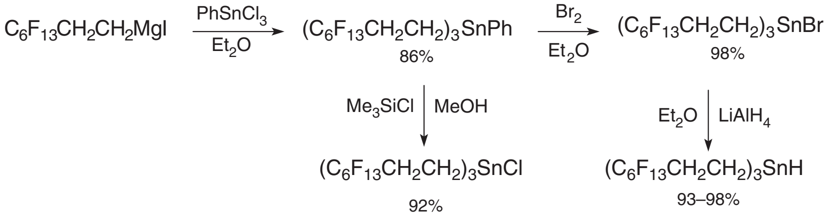


(38)

3.14.4.1 Fluorous Alkylstannanes

The many applications of organotin compounds in organic synthesis present problems in the separation and disposal of toxic organotin residues. One attempt to counter these problems has been to prepare heavily fluorinated ("fluorous") alkyltin reagents that are soluble in fluorinated solvents but relatively insoluble in organic solvents. The required reaction products can then be separated from the fluorous organotin residues by partition between fluorous and non-fluorous solvents that are mutually immiscible, and the reagents can be regenerated and reused. Purification has also been carried out by chromatography on fluorous reversed-phase silica gel.[135]

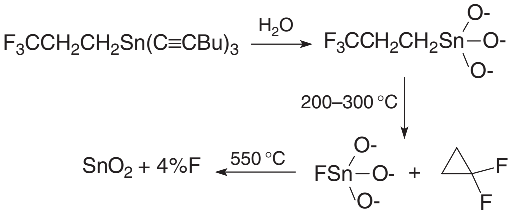
Fluorous stannanes typically carry the group $C_6F_{13}CH_2CH_2Sn$ (abbreviated to Rf_6h_2), in which the C_6F_{13} moiety confers suitable solubility characteristics but is sufficiently separated from the functional group on tin for the reagents to show their conventional properties. The fluorous solvents commonly used for the reactions and the separations are benzotrifluoride, $PhCF_3$, and perfluorohexanes (FC-72), but supercritical CO_2 (which is not reduced by the fluorous tin hydride) can also be used.[136] The route into tris(2-perfluorohexylethyl)tin reagents is shown in Equation (39).



(39)

Reactions that have been carried out with reagents $(Rf_6h_2)_3SnX$ include hydrostannolysis of halides (X = H) with either stoichiometric or catalytic (with $NaCNBH_3$) amounts of hydride,[137] Stille reactions (X = aryl),[138] allylation of aldehydes (X = allyl),[139] and cycloaddition reaction ($X = N_3$).[137] The distannoxanes $Cl(Rf_6h_2)_2SnOSn(Rf_6h_2)_2Cl$ have been used as catalysts for esterification and transesterification.[140]

Fluorous organotin compounds have also been designed with the purpose of producing F-doped SnO_2 by the sol–gel process (Equation (40)).[141]



(40)

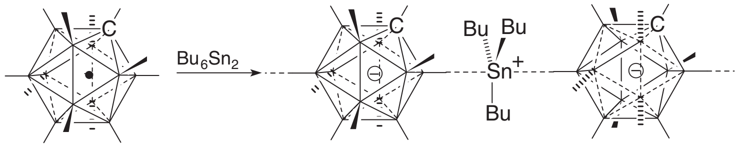
3.14.4.2 Cationic Alkyltin Species

In recent years, examples of stannylium ions, R_3Sn^+, and of stannylalkyl cations, R_3SnCC^+, have been isolated and characterized.

The search for stannylium ions has been long and controversial. The main criterion for their identity has been the Sn NMR chemical shift (usually in benzene or toluene solvent), which moves downfield with increasing ionic character of the $R_3Sn^{\delta+}–X^{\delta-}$ bond. Values that were obtained are: R_3SnClO_4 and $R_3SnB(C_6F_5)_3H$ δ 360,[142] $Bu_3SnB[3,5\text{-}(CF_3)_2C_6H_3]_4$ δ 360,[143] $Bu_3Sn[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)\}_2(\mu\text{-OMe})]$ δ 277,[144] $Bu_3Sn(PhMe)[B(C_6F_5)_4]$ δ 434,[144] Mes_3Sn^+ δ 806,[145] $PhTrip_2Sn^+$ (Trip = 2,4,6-triisopropylphenyl) δ 687,[145] and Dur_3Sn^+ (Dur = duryl) δ 720.[146]

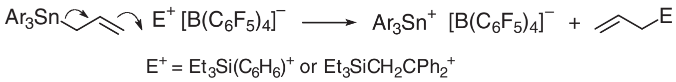
In all these compounds, there is some residual association between the R_3Sn cation and the counterion. Two recent attempts, however, have given crystalline compounds for which the crystal structures could be determined.

Michl prepared $Bu_3Sn^+CB_{11}Me_{12}^-$, δSn 453 (in cyclohexane), from the reaction of the stable radical $CB_{11}Me_{12}^{\cdot}$ with hexabutyldistannane.[147] X-ray crystallography shows a planar Bu_3Sn unit with *r* Sn–C 207 pm, shorter than the normal Sn–C(sp^3) length of 214 pm. Each Bu_3Sn^+ cation interacts with two $CB_{11}Me_{12}^-$ anions to give an infinite column of alternating units. The average Sn–C(Me) separation is 281 pm, much shorter than the sum (417 pm) of the van der Waals radii of a methyl group and tin. The ^{119}Sn chemical shift is little lower in solution than it is in the solid, suggesting that ion aggregation persists in solution (Equation (41)).



(41)

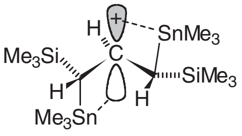
In Lambert's approach, the triarylstannylium ion is generated by the reaction of an electrophile with an allyltriarylstannane. The bulky aryl groups sterically protect the tin center in the stannylium ion from attack by nucleophiles, yet the allyl ligand permits unhindered conjugate electrophilic displacement of the tin (Equation (42)).[145]



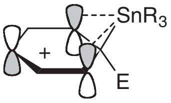
(42)

$Trip_3Sn^+B(C_6F_5)_4^-$ was obtained as a solvent-free crystalline solid, and X-ray diffraction showed that the $Trip_3Sn^+$ ion is planar about the tin, with the aryl rings twisted, propeller-fashion, by an average of 61.1°, and that there is no interaction with the anion or intramolecular agostic interaction.[148] In C_6H_6, the value of δSn is 714, similar to the values for the other Ar_3Sn^+ salts that were obtained previously only in solution.

The Sn–C bond is much more powerful than the H–C bond in hyperconjugating with a positive charge, or a radical, or π-electron system,[149] and a bis-β-stannyl cation has recently been isolated and characterized.[150] $Me_3Sn(Me_3Si)CHCH{=}CH(SiMe_3)$ reacts with Me_3SnCl in the presence of $ZrCl_4$ or $HfCl_4$ (i.e., in effect with the electrophile Me_3Sn^+) to give the first isolable secondary alkyl cation $[Me_3Sn(Me_3Si)CHCH^+CH(SiMe_3)SnMe_3]$ $M_2Cl_9^-$ (M = Zr or Hf) as colorless crystals with m.p. = 109 °C. The structure is as shown in **1**. The two Sn–C bonds eclipse the *p*-orbital so as to provide effective hyperconjugation, and the Sn–C bonds are lengthened and Cα–Cβ bonds are shortened.



1



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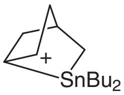


3

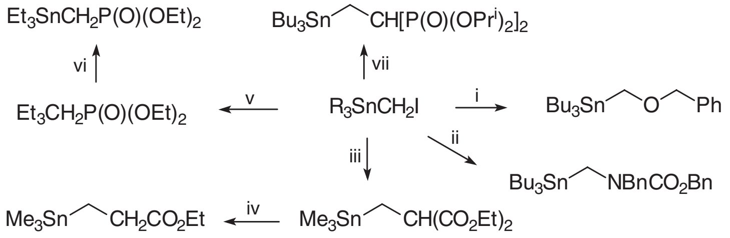
Sn–C hyperconjugation can similarly be invoked to account for the stability of the adducts between arenes and the stannonium ions, **2** (where the symmetry of the SOMO is shown), and of the 2-dialkylstannanorbornyl cation **3**.[151]

3.14.5 Functionally Substituted Alkylstannanes[1]

Iodomethyltrialkyltin compounds, R_3SnCH_2I (from R_3SnCl and ICH_2ZnI), provide an entry to other functionally substituted organotin compounds. Reaction with nucleophiles such as R^1O^-, R^1S^-, $R^1{}_2N^-$, or $R^1{}_3P$ gives further α-substituted derivatives, and carbon nucleophiles can be used to locate the functional groups at more distant positions on the alkyl chain. Some examples are shown in Scheme 3.

The stannylmetallic compounds R_3SnLi or R_3SnMgX give access to a variety of α-functional alkylstannanes. They react with alkoxyalkyl halides to give α-alkoxyalkylstannanes, and a convenient one-pot method is shown in Equation (43).[80]

$$Bu_3SnH \xrightarrow[\substack{THF \\ 0\,°C}]{LDA} Bu_3SnLi \xrightarrow[-78\,°C \text{ to RT}]{ClCH_2OBu} \underset{96\%}{Bu_3SnCH_2OBu} \qquad (43)$$



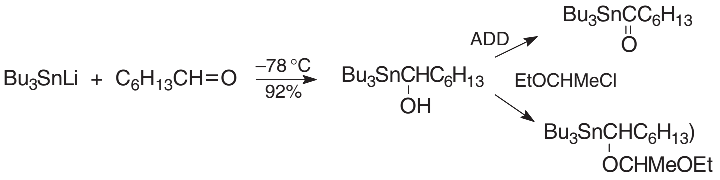
Reagents and references: i, $PhCH_2OH$, NaOH;[152] ii, $BnNHCO_2Bn$, BuLi;[153] iii, $NaCH(CO_2Et)_2$; iv, KOH;[154] v, $P(OEt)_3$ (Arbuzov reaction); vi, $LiAlH_4$;[155] vii, $NaCH(PO_3Pr^i{}_2)_2$.[154]

Scheme 3

Reaction with acyl halides, esters, or thioesters affords the acylstannanes $R^1{}_3SnCOR^2$, with thioesters giving the cleanest reactions (Equation (44)).[84,156]

$$Me_3SnLi + PhCOSMe \xrightarrow[-78\,°C,\ 1\ h]{THF} Me_3SnCOPh \qquad (44)$$

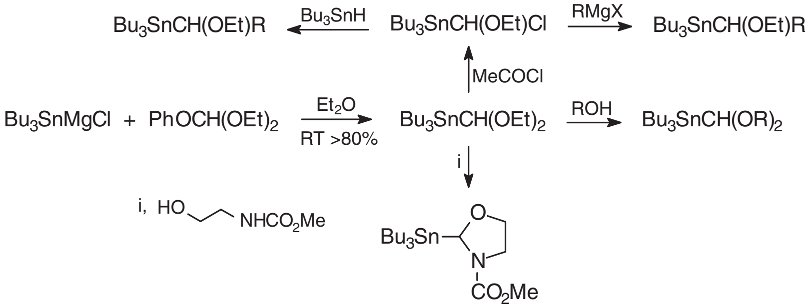
Addition to aldehydes or ketones gives α-hydroxyalkylstannanes,[18] which are rather unstable, but can be stabilized with an alkoxyalkyl protecting group, or can be oxidized with azodicarbonyldipiperide (ADD) to give the corresponding acyltin compounds (Equation (45)).[157]



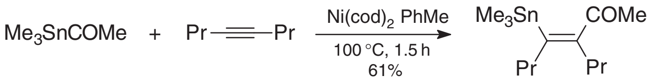
$$Bu_3SnLi + C_6H_{13}CH{=}O \xrightarrow[92\%]{-78\,°C} Bu_3Sn\underset{OH}{C}HC_6H_{13} \quad \xrightarrow{ADD} Bu_3Sn\underset{O}{\overset{}{C}}C_6H_{13}; \quad \xrightarrow{EtOCHMeCl} Bu_3Sn\underset{OCHMeOEt}{C}HC_6H_{13}) \qquad (45)$$

The formylstannane can be obtained as its diethylacetal by the reaction of the stannylmagnesium compound with diethyl phenyl orthoformate, and provides access to further α-substituted alkylstannanes (Scheme 4).[85,158,159]

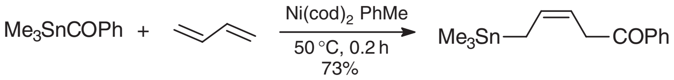
The acylstannanes are yellow-green liquids that are readily hydrolyzed to give the corresponding tin oxide or hydroxide and aldehyde, and are oxidized by air to the corresponding tin carboxylate. In the presence of a Ni(0) catalyst, they react with alkynes by *cis*-addition to give vinylstannanes, and with 1,3-dienes to give allylstannanes (Equations (46) and (47)).[127,160]



Scheme 4



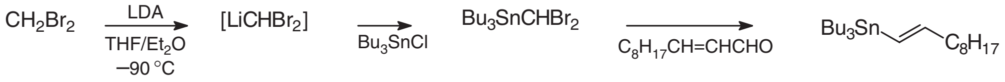
(46)



(47)

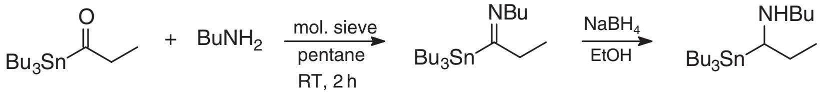
Their main application, however, continues to lie in their reduction with (*S*)-BINAL-H to give the corresponding carbinol in high enantiomeric excess.[161]

Dibromomethyltributyltin reacts with aldehydes in the presence of Cr(II)Cl$_2$ and LiI to give *E*-alkenylstannanes (e.g., Equation (48)). The reaction is tolerant toward ester, nitrile, and ketal groups, and is thought to take place through the formation of Bu$_3$SnCHI$_2$ (which is sensitive to light), and then Bu$_3$SnCH(Cr^{III})$_2$.[162]



(48)

Imidoylstannanes, R$^1_3$SnCR^2=NR^3, can be prepared from the reaction of stannyllithium compounds with the corresponding imidoyl chlorides (ClCR^2=NR^3; R^2 and R^3 = aryl),[163] or, more generally, from the reaction of an acylstannane with an amine.[164] The imidoylstannane can then be reduced to an α-aminostannane (Equation (49)).[165]

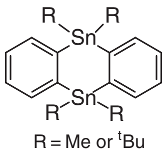


(49)

3.14.6 Arylstannanes

Methods for the synthesis of aryltin compounds are described in Sections 3.14.3.1 and 3.14.3.2. Promising advances in recent years include the syntheses from aromatic halides, amines, or phosphates by S$_{RN}$1 reactions (Equations (11)–(13)), and from aryl bromides and bis(tributyltin) oxide by a Wurtz–Barbier process with sonic assistance (Equation (8)). An aryl group on tin is usually more reactive than is an alkyl group, and a compound R$_3$SnAr is often prepared *en route* to the synthesis of a compound ArR^1 (e.g., in the Stille coupling reaction), or of R$_n$SnX$_{4-n}$ (e.g., Equation (18)). Very large aryl groups such as 2,4,6-trimethylphenyl (mesityl, Mes), or 2,4,6-triisopropylphenyl (Trip) sterically stabilize lower valence states of tin, and are often introduced with the aim of obtaining kinetically stable stannylenes (Ar$_2$Sn:), distannenes (Ar$_2$Sn=SnAr$_2$), distannynes (ArSn≡SnAr), and related compounds (see Sections 3.14.24.3–3.14.24.6).

Tetraalkyl-9,10-dihydrodistannaanthracenes **4** have been prepared via the lithiation[73] or the magnesiation of 1,2-dibromobenzene,[166] followed by reaction with R$_2$SnCl$_2$. The tetramethyl derivative is butterfly shaped with a dihedral angle of 142°, but the tetra-*t*-butyl derivative is planar.[73] The stannepin **5** and stannolane **6** were obtained as byproducts of the former reaction.



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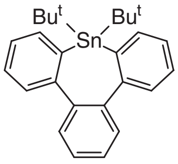

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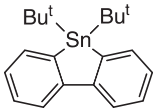
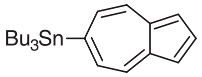


6

6-Tributylstannylazulene **7** is formed by the Pd(0)-catalyzed reaction of 6-bromoazulene and hexabutyldistannane, and has been used in Stille condensations with aryl, acyl, and azulenyl halides.[167]



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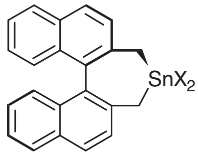
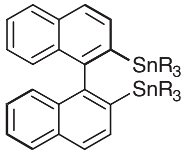


X = Br, OTf

8

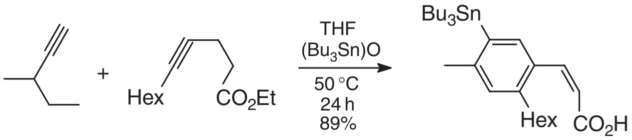


$R_3 = Me_3, Me_2Cl, MeCl_2, Me_2Ph,$
$PhCl_2, Me_2(OTf), Me(OTf)_2$

9

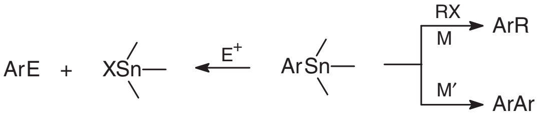
A number of optically active 1,1′-binaphthyl compounds, **8**[168] and **9**,[169] have been prepared with a view to use them as asymmetric catalysts. Compounds **8** (X = Br and OTf)[170,171] and **9** [$R_3 = Me(OTf)_2$][169] have been used to resolve diols in their reaction with benzoyl chloride. Tin hydrides based on structure **8** ($X_2 = MeH$,[172] Bu^tH,[173] and Me_3CCH_2H[174]) have been designed for carrying out enantioselective reductions.

The classical Diels–Alder cycloaddition reaction is seldom used for the construction of the aromatic ring in arylstannanes, but a promising palladium-catalyzed cycloaddition reaction of two similar or different enynes (Equation (50)) has recently been published.[175]



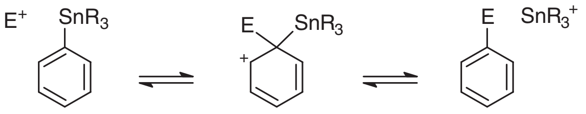
(50)

The two most important reactions of aryltin compounds are: first, their reaction with electrophiles, when either the tin or the non-tin product may be the aim, or, second, the coupling reactions that they show in the presence of certain transition metals (Equation (51)).



(51)

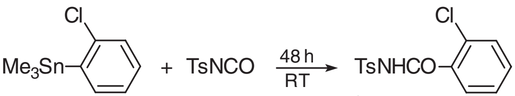
The arylstannanes undergo electrophilic substitution more readily than do the parent protic compounds, through a similar Wheland intermediate (Equation (52)).



(52)

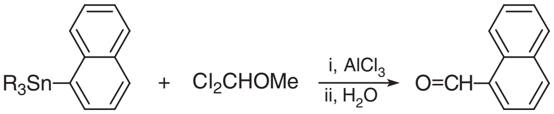
Part of the reason for this enhanced reactivity is the stabilization that accrues from hyperconjugation of the C–Sn bond with the LUMO of the pentadienyl cation, which is much more powerful than C–H hyperconjugation. This is illustrated above in formula **2** where it is presented in terms of the solvation of a stannonium ion by an arene.[149]

This reactivity enables *ipso*-substitution to be carried out at a specific position in the ring, irrespective of the presence of other contra-directing groups, and it allows the reaction to be carried out under mild conditions, or with weak electrophiles such as diazonium ions.[2] Recent additions to the extensive list of electrophiles that have been used are toluene *p*-sulfonylisocyanate and ethoxycarbonyl isocyanate (Equation (53)),[176] sulfonyl chloride,[177] arene[178] and silane sulfonyl chlorides,[179] and dichloromethyl methyl ether (Equation (54)).[180]



Ts = toluene *p*-sulfonyl

(53)

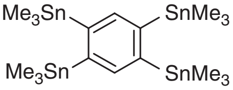
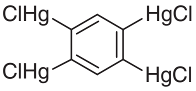
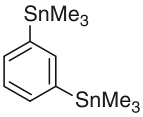
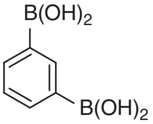
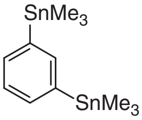
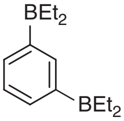
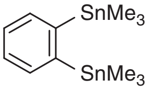
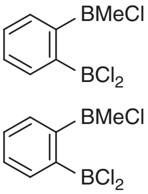
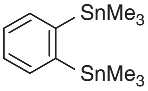
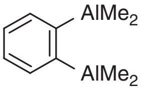
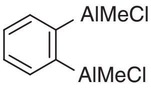
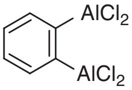
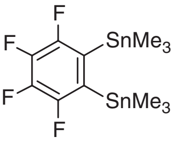
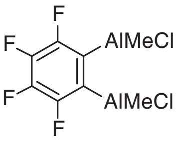
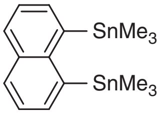
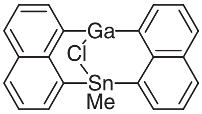


(54)

Transmetallation with metallic electrophiles has also received a lot of attention, often with the aim of making polyfunctional Lewis acids. Examples are shown in Table 2.

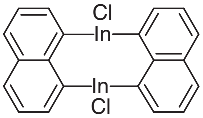
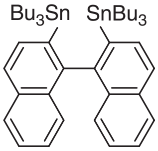
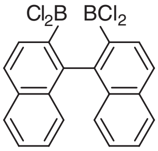
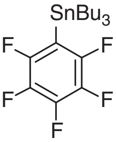
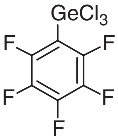
Some of the reactions (e.g., that of dimethylaluminum chloride in Table 2) involve redistribution of alkyl and halide groups between the metals. The boronic acids, $ArB(OH)_2$, prepared by Sn/B transmetallation, have been used in Suzuki coupling reactions. It is remarkable that the bistributyltin derivative of 1,1′-binaphthyl undergoes

Table 2 Reaction of arylstannanes with metal electrophiles

Reactant	*Reagent*	*Product*	*Yield (%)*	*References*
	$HgCl_2$ THF, RT		84	181
	i, $BH_3THF\cdot$ reflux ii, H_2O		82	182,183,184
	Et_2BCl 50 °C		>78	182
	BCl_3 Pentane, −78 °C			182
	Me_2AlCl Hexane RT		89	182
	$MeAlCl_2$ PhMe RT		85	182
	$AlCl_3$ PhMe RT		97	182
	Me_2AlCl Hexane RT		95	185
	$GaCl_3$ PhMe 65 °C		55	186

(*Continued*)

Table 2 (Continued)

Reactant	*Reagent*	*Product*	*Yield (%)*	*References*
	$InCl_3$ MeCN RT		65	187
	BCl_3 CH_2Cl_2 RT		71	188
	$GeCl_4$ 150 °C AIBN		73	189

conventional *ipso*-substitution, but the bistrimethyltin analog reacts under the same conditions to undergo cleavage of the tin–methyl rather than the tin–naphthyl bond, to give the Me_2SnCl derivative in 56% yield. The bistrimethylsilicon and bistrimethylgermanium compounds behave similarly.[188] A further surprising observation is that the reaction of $C_6F_5SnBu_3$ with $GeCl_4$ is accelerated by AIBN, implying that the mechanism may not be that of a simple electrophilic substitution.

In the Stille reaction, an organotin compound R^1SnR_3 and an organic electrophile R^2X are treated with a palladium(0) or palladium(II) catalyst, to generate the coupled product R^1R^2 (Equation (55)).[190]

$$R^1SnR_3 + R^2X \xrightarrow[Pd^{II}\,L_2X_2]{Pd^0\,L_2 \text{ or}} R^1R^2 + R_3SnX \qquad (55)$$

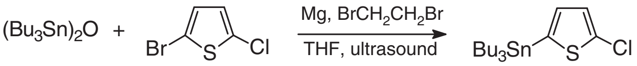
The reactivity of the group R^1 on tin follows the sequence alkynyl > alkenyl > aryl > benzyl ≈ allyl > acetonyl > alkyl; usually, only one of the groups on tin is transferred, and in the reaction of aryl compounds, the reactant is usually $ArSnMe_3$ or $ArSnBu_3$, the methyl or alkyl groups acting as spectator ligands. The reagent R^2X is usually an alkenyl, aryl, acyl, benzyl, or propargyl halide or triflate; simple alkyl halides are normally inert.[18]

3.14.7 Heteroarylstannanes

The heteroarylstannanes bear the same relation to the arylstannanes as do the heteroarenes to the arenes, with the extra factor that the Lewis acidity of the stannyl group may cause the heteroarylstannanes to have self-associated structures.

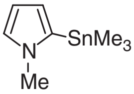
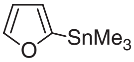
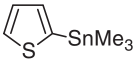
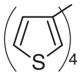
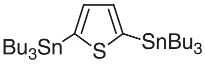
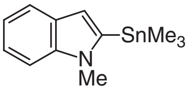
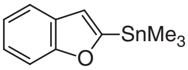
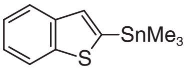
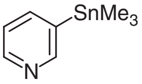
The heteroarylstannanes are usually prepared by the reaction of a heteroaryllithium or heteroaryl Grignard reagent with a tin(IV) halide, and all the simple examples in Table 3 have been prepared by this method.

Grignard reagents usually give poorer yields than do the alkali metal reagents, but some reactions give good yields under Barbier conditions with ultrasonic assistance (Equation (56)).[76]

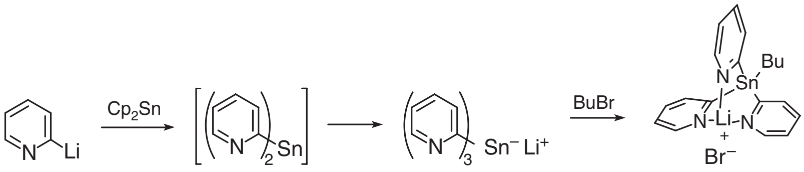


(56)

Table 3 Heteroarylstannanes

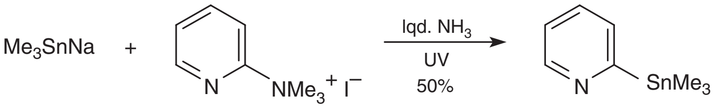
Stannane	*Yield m.p.* (°C) *or b.p.*/mmHg	*References*
	70% 90/10	191
	57% 87–89/55	193
	71% 97–99/33	195
	104	196
	220–222	196
	80%	192
	78% 105/0.07	194
	78% 91/0.05	194
	82%	194
	35% 75/13	194

Butyl(tri-2-pyridyl)stannane can be prepared from 2-lithiopyridine and butyltin trichloride, and also from the reaction of 2-lithiopyridine with stannocene. The product acts as a tridentate ligand, and the complexes with Li^+, $Mo(CO)_3$, and $W(CO)_3$ have been characterized (Equation (57)).

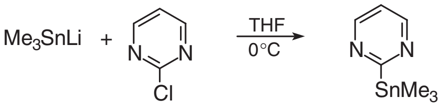


(57)

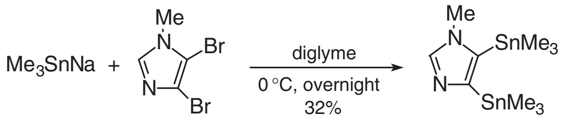
There is a limited number of examples of preparations involving the reaction of stannyl-alkali metal compounds with a substituted heteroarene, for example, Equations (58)–(60).[88,197,198] Some of these reactions (e.g., Equation (58)) occur only with photoirradiation, showing that they involve $S_{RN}1$ processes, but others may be straightforward nucleophilic heteroaromatic substitutions.



(58)

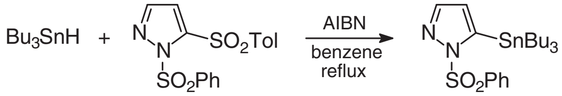


(59)



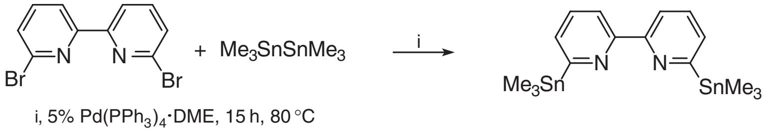
(60)

Tolylsulfones of indoles, pyrroles, pyrazoles, furans, thiophenes, indolines, and dibenzofurans react with tributyltin hydride under radical conditions by *ipso*-substitution. The most likely mechanism appears to be addition of the $R_3Sn\cdot$ radical to the ring, followed by elimination of the sulfonyl group, but an electron-transfer mechanism cannot be excluded (Equation (61)).[199]



(61)

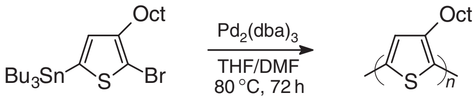
Pyridylstannanes have also been prepared by the reaction of halogeno pyridines with hexamethyldistannane in the presence of a palladium catalyst (Equation (62)).[200]



(62)

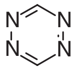
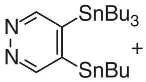
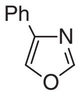
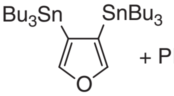
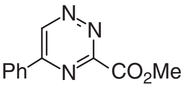
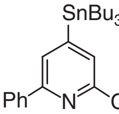
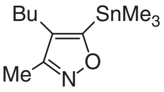
The heteroaromatic rings can sometimes be built up by a cycloaddition reaction, similarly to the ways in which the protic heteroaromatic parents can be formed. Frequently, a retro-Diels–Alder reaction is involved. Some examples are given in Table 4.

The heteroaromatic stannanes undergo the normal electrophilic substitution reactions of their protic precursors, and often to an enhanced degree. They are often prepared with the aim of a subsequent Stille cross-coupling reaction, and oligothiophenes with potentially useful optical and electron properties have been prepared by coupling between stannyl- and bromo-thiophenes, for example, Equation (63).[204]



(63)

Table 4 Preparation of heteroarylstannanes by cycloaddition reactions

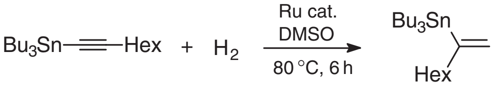
Reactants		*Products*	*References*
$Bu_3Sn{-}C\equiv C{-}SnBu_3$		 + N_2	201
$Bu_3Sn{-}C\equiv C{-}SnBu_3$		 + PhC≡N	202
$Bu_3Sn{-}C\equiv CH$		 + N_2	202
$Me_3Sn{-}C\equiv C{-}Bu$	MeC≡NO		203

3.14.8 Alkenylstannanes

3.14.8.1 Preparation

General methods for the formation of a tin–alkenyl bond are described in Section 3. This section considers only those reactions in which the tin–carbon bond is already formed, and the alkenyl group is generated by modification of the organic group that is already present.

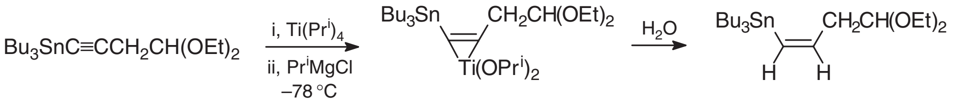
Direct hydrogenation of alkynylstannanes with hydrogen over a metal catalyst is difficult, presumably because the catalyst is poisoned, but Shirakawa has recently described the hydrogenation over a ruthenium catalyst in the presence of tributylphosphine, (($Ru_3(CO)_{12}/PBu_3$ or $RuH_2(CO)(PPh_3)_3/PBu_3$), which gives the alkenylstannane with migration of the stannyl group (Equation (64)). It is suggested that the rearrangement may imply that an intermediate vinylidene complex, $Ru{=}C(SnBu_3)R$, is involved. Hydrogenation with D_2 similarly gives access to 1,1′-dideuterio-2-stannylalkenes, $Bu_3Sn(R)C{=}CD_2$.[205]



(64)

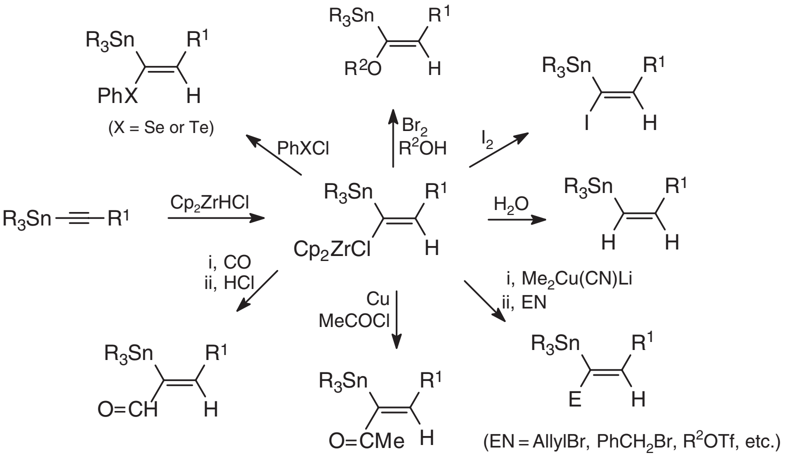
Hydrogenation can also be achieved through zirconium or titanium chemistry. Schwartz's reagent, Cp_2ZrHCl, effects *cis*-addition to an alkyne to give a 1-stannyl-1-zirconylalkene, in which the zirconyl group can then be hydrolyzed off with water to give the corresponding stannylalkene,[206] or displaced with a variety of other electrophiles.[207–209] Alkylation, allylation, benzylation, and acylation can be carried out in the presence of a copper catalyst,[210] giving a versatile, if expensive, route to a variety of α-substituted stannylalkenes by overall *cis*-addition (Scheme 5).

Alternatively, titanation of the triple bond, followed by hydrolysis, gives the *Z*-stannylalkene (Equation (65)).[211]



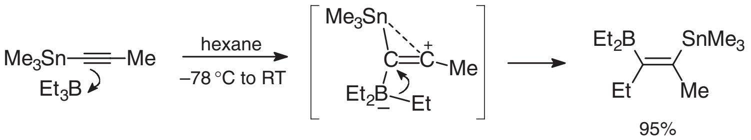
(65)

Trimethyl- and triethylborane react with alkynylstannanes exothermically at room temperature to bring about 1,1-organoboration with migration of the stannyl group, to give the alkenylstannane with *cis*-boryl and stannyl groups (e.g., Equation (66)). The reaction can be rationalized in terms of electrophilic attack by the borane at the α-alkynyl position being assisted by hyperconjugative stabilization of the developing positive charge on the β-position by the



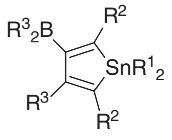
Scheme 5

C–Sn bond; then, complete transfer of the tin to the β-position is accompanied by a 1,2-nucleophilic shift of an alkyl group from boron to carbon, as occurs in so many reactions of organoboranes.[212]

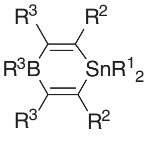


(66)

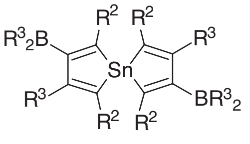
Similar but more complicated reactions occur when two or more alkynyl groups are present. Dialkyldialkynylstannanes can give stannacyclopentadienes **10** or 1-bora-4-stannacyclohexadienes **11**, and tetraalkynylstannanes give principally the spirostannanes **12**.



10

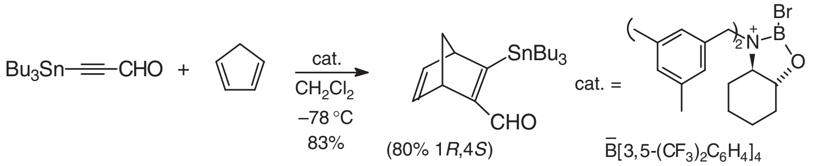


11



12

The Diels–Alder reaction of cyclopentadiene with β-stannylpropynal is much faster than that with β-alkylpropynals, and can be made enantioselective in the presence of a chiral Lewis acid catalyst (Equation (67)).[213]



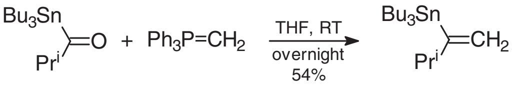
(67)

The relative reactivity of stannylbutadienes toward *N*-methylmaleimide anhydride as a dienophile, to give 1-cyclohexenylstannanes, is given in Scheme 6. The stannylbutadiene **13** and the chlorostannylbutadiene **15** may be reactive enough to be used in preparative chemistry. Steric hindrance between the two stannyl groups, destabilizing the planar structure, may be relevant in **14**, and hyperconjugation between the C–Sn bond and a double bond may be relevant in **13** and **15**.[214]

Tributyl-1,1-diiodomethylstannanes react with aldehydes in the presence of $CrCl_2$ to give *E*-alkenylstannanes.[162,215,216] The reaction proceeds probably through the formation of $Bu_3SnCH(Cr^{III})_2$ (Equation (68)).

$$Bu_3SnCHI_2 + O{=}CHC_8H_{17} \xrightarrow[\substack{2.5\,h,\ 25\,°C \\ 85\%}]{CrCl_2,\ DMF} Bu_3SnCH{=}CHC_8H_{17} \qquad (68)$$

Little use has been made of the reaction between acylstannanes and phosphorus ylides as a route to alkenylstannanes, though the feasibility of these reactions is well established, for example, Equation (69).[217]



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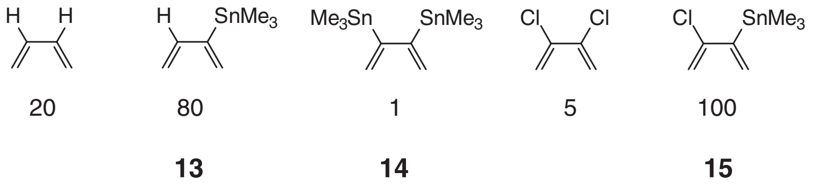


Scheme 6

3.14.8.2 Properties

Ionization energies of the alkenes $H_3MCH{=}CH_2$ are M═C 9.73, Si 10.3, Ge 10.2, Sn 10.1 eV; the orbital involved is mainly the C═C π-orbital with a small interaction with the π-component of the SnH_3 group.[218]

A survey of NMR data for vinylstannanes shows that the best criterion for assigning structures is the value of $^3J(^{117/119}Sn–^{13}C)$, which, for the (*E*)-γ-carbon, is between 75.0 and 40.0 Hz, and, for the (*Z*)-γ-carbon, has the lower value of 45.0 to 30.0 Hz.[219]

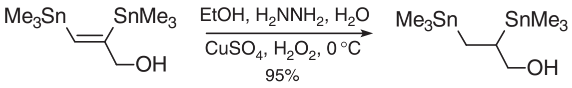
In organic synthetic procedures, alkenyltin compounds are often prepared with a view to subsequent transmetallation with lithium, or to the Stille coupling reaction with a palladium catalyst (Equations (70) and (71)).

$$R_3SnCH{=}CH_2 + BuLi \longrightarrow R_3BuSn + LiCH{=}CH_2 \qquad (70)$$

$$R_3SnCH{=}CH_2 + RX \xrightarrow{\text{Pd cat.}} RCH{=}CH_2 \qquad (71)$$

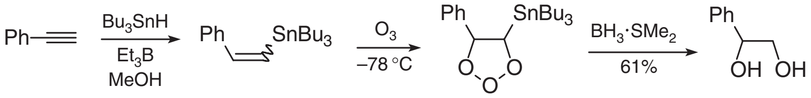
These reactions are covered in Section 3.14.20.1.

Alkenylstannanes are usually reported to be resistant to hydrogenation with typical metal catalysts, though a rhodium(I) catalyst has been used at 100 atm to reduce 3-hydroxy-1-alkenylstannanes.[220] Diimine has been used to reduce some acyclic and cyclic methylstannylalkene compounds, but lower yields were obtained with tributylstannylalkenes (Equation (72)).[221,198]



(72)

Little use has been made of the methenylenation of alkenylstannanes as a route to cyclopropylstannanes,[222] though reasonable yields have been achieved with some stannylated alcohols using amalgamated samarium and diiodomethane.[223] Epoxidation with *m*-chloroperoxybenzoic acid is well established, and has been extended to the reactions of 1,2-distannyl- and 1-silyl-2-stannylalkenes.[223] Ozonation of stannylalkenes gives primary ozonides that are surprisingly stable, providing a one-pot conversion of alkynes into 1,2-diols (Equation (73)).[224]



(73)

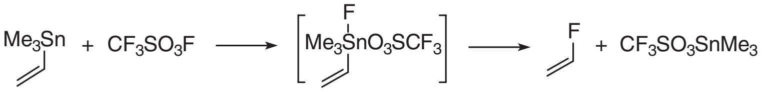
The vinyl–Sn bond can be cleaved with a wide variety of electrophiles to give the derivates vinyl–E. Some recent examples are given in Table 5.

Table 5 Reaction of alkenylstannanes with electrophiles

Reagent	*E*	*References*
BBr_3, BCl_3	BCl_2 or BBr_2	225
$HgCl_2$	HgCl	227
XF_2, AgOTf	F	228
RNCO	CONHR	230
Cl_2CHOMe	CH═O	226
Me_3SiSO_2Cl	SO_3H	226
I_2, Br_2	I, Br	229
SO_2Cl_2	SO_2NH_2	177,226

The fluorodestannylation with XeF_2 takes place rapidly at room temperature in the presence of 2,6-di-t-butyl-4-methylpyridine, fast enough for introducing the short-lived ^{18}F isotope, and is thought to involve the initial formation of triflic hypofluoride, F_3CSO_3F, and then its adduct with the vinyltin compound (Equations (74)–(76)).[228]

$$\mathrm{CF_3SO_3Ag + XeF_2 \longrightarrow AgF + Xe(0) + CF_3SO_3F} \qquad (74)$$



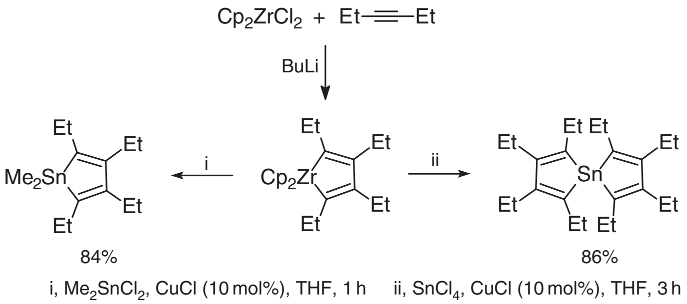
(75)

$$\mathrm{CF_3SO_3SnMe_3 + XeF_2 \longrightarrow CF_3SO_3F + Me_3SnF + Xe(0)} \qquad (76)$$

3.14.9 Stannacyclopentadienes (Stannoles)

The stannacyclopentadienes (stannoles) can be regarded as a special group of alkenylstannanes. In the past they have been prepared by reactions similar to those which are used for acyclic alkenylstannanes, for example, by the reaction of LiPhC=CPh–CPh=CPhLi with Me_2SnCl_2. In recent years, however, some methods have been developed that are special to the cyclic compounds, and involve transition metal chemistry.

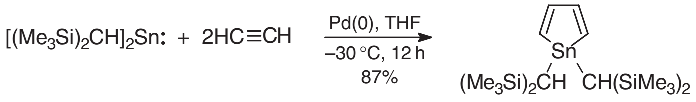
The most versatile synthesis involves the transmetallation of a zirconiacyclopentadiene[231,232] with a tin halide under catalysis with CuCl[233] (and an equivalent reaction occurs with other halides of other elements of Groups 13, 14, 15, and 16) (Equation (77)). Stannacyclopentenes can be prepared by analogous reactions of zirconacyclopentenes.[233]



(77)

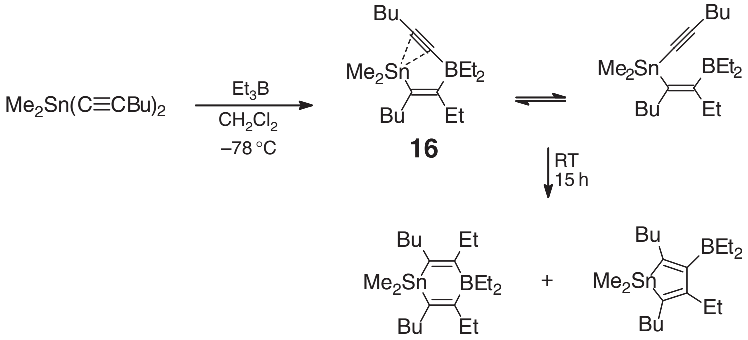
A variety of boron-substituted stannoles such as those shown in formulas **10 and 12** have been prepared by Wrackmeyer's 1,1-organoboration of dialkynes.[234]

Unsubstituted or 2,3-disubstituted stannoles can be prepared from the palladium-catalyzed reaction of an alkyne with the stable stannylenes $[(Me_3Si)_2CH]_2Sn$: and $\{CH_2C(SiMe_3)_2\}_2Sn$:. The mechanism has been traced by the isolation of intermediates,[235] and by *ab initio* calculations (Equation (78)).[236]



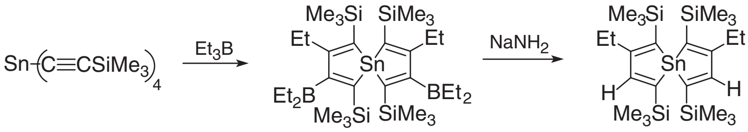
(78)

Wrackmeyer's alkylboration reaction of dialkynylstannanes can lead to ring closure, as shown in Equation (79). The initial product has the unusual structure **16**, in which the remaining ethynyl group is unsymmetrically bonded to the tin (rSnC = 233.9(4) and 252.3(5) pm). Migration of an alkyl group from boron then gives a stannacyclopentadiene, or migration of a vinyl group from boron gives a borastannacyclohexadiene.[212,234]



(79)

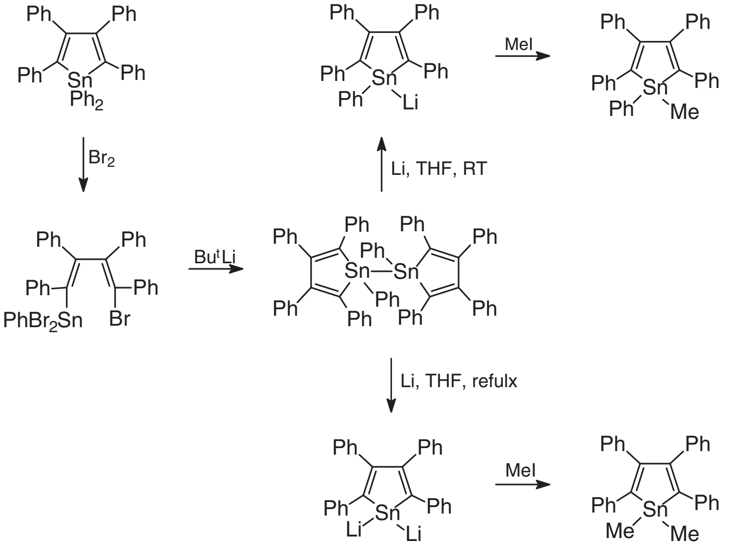
Similarly, alkylboration of a tetraalkynylstannane gives a *spiro*-stannole (Equation (80)).



(80)

The monoanion (δSn = −30.3) and dianion (δSn = 186.7) of the phenylstannoles have been prepared through the bis(stannole) as their lithium derivatives as shown in Scheme 7.[237,238] The 1-t-butyl-2,3,4,5-tetraphenylstannole anion is oxidized in air to the corresponding bis(stannole).[239]

Ab initio calculations indicate that there is an increased pyramidality at tin in $C_4H_4SnH^-$ and C_4H_4SnHLi, resulting in reduced aromaticity. The metallole dianions $C_4H_4Sn^{2-}$ (M = C, Si, Ge, Sn, or Pb) are more aromatic, the aromaticity staying remarkably constant down the group.[240]



Scheme 7

3.14.10 Alkynylstannanes

3.14.10.1 Preparation

The acidity of terminal alkynes makes available routes to alkynylstannanes that do not apply to alkenylstannanes. Thus, alkynylstannanes can be made by the acidolysis of aminostannanes with alkynes,[234,241] and the *N*-stannylpyrroles are recommended for this purpose as they can be readily prepared by azeotropic dehydration of the trialkyltin oxide and pyrrole, and the amine that is liberated is non-basic.[242]

Ethynylmagnesium bromide can be made from the reaction between acetylene and ethylmagnesium bromide, and then reaction with a tin halide gives the alkynylstannane. To avoid the formation of BrMgC≡CMgBr, the first reaction is usually carried out by adding the Grignard react to the acetylene, but details have now been published of how the reaction can be carried out more simply by passing acetylene into the Grignard reagent (Equation (81)).[243]

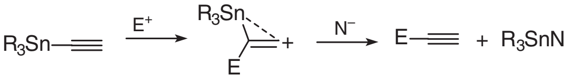
$$\mathrm{EtMgBr + HC{\equiv}CH \xrightarrow[10\,^{\circ}C]{THF} HC{\equiv}CMgBr \xrightarrow[R\,=\,Me,\ 70\%;\ R\,=\,Bu,\ 88\%]{R_3SnCl} HC{\equiv}CSnR_3} \qquad (81)$$

Alkynylsilanes will react with bis(tributyltin) oxide in the presence of fluoride ion as catalyst to give the stannylalkynes in excellent yield and hexamethyldisiloxane, which can be removed under reduced pressure (Equation (82)).[68,244]

$$\mathrm{PhC{\equiv}CSiMe_3 + (Bu_3Sn)_2O \xrightarrow[60\,^{\circ}C,\ 2.5\,h]{THF,\ TBAF} \underset{98\%}{PhC{\equiv}CSnBu_3} + (Me_3Si)_2O} \qquad (82)$$

3.14.10.2 Properties

Addition reactions at the alkyne bonds are dealt with in the section on alkenylstannanes that are produced. The alkynyl–tin bond is more readily cleaved by both electrophiles and nucleophiles than is the alkenyl– or alkyl–tin bond. Strong electrophiles such as halogens or halogen acids attack at the *ipso*-position of the triple bond to give a β-stannyl cation that is stabilized by C–Sn hyperconjugation, but this is followed by cleavage of the C–Sn bond (Equation (83)).

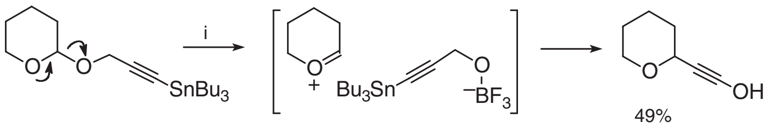


(83)

Dinitrogen tetroxide reacts with phenylethynyltrimethyltin to give benzoyl cyanide, probably by rearrangement of (dimeric) phenyl(nitroso)ethyne (Equation (84)).[245]

$$\mathrm{PhC{\equiv}C{-}SnMe_3 \xrightarrow{NO^+} PhC{\equiv}C{-}N{=}O \xrightarrow{o} PhC(O)C{\equiv}N} \qquad (84)$$

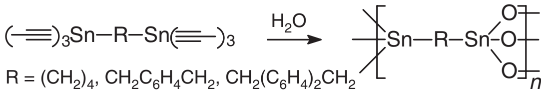
The reactivity of alkynylstannanes toward electrophiles is one element in the oxygen-to-carbon rearrangement of alkynylstannane derivatives of furanyl and pyranyl lactols (e.g., Equation (85)). The cleavage of the anomeric C–O bond is assisted by the Lewis acid to give an oxonium ion, which is trapped *in situ* by the nucleophilic stannylalkyne. The utility of this process has been demonstrated in the synthesis of the natural product muricatetrocin C, and the drug substance CMI-977.[246]



i, CH_2Cl_2, $BF_3{\cdot}OEt_2$

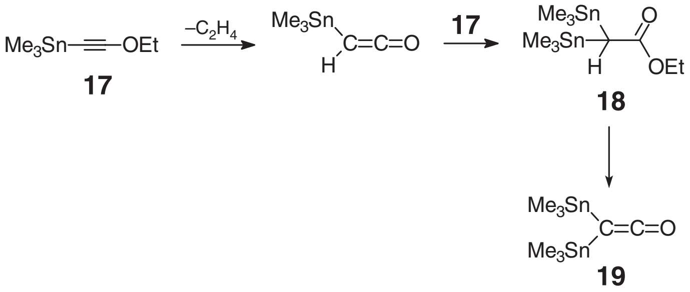
(85)

Nucleophiles react by attack at the tin center. The reaction of the trialkynyltin compounds $RSn(C{\equiv}CR^1)_3$ with primary or secondary alcohols gives the alkyltin trialkoxides, $RSn(OR^2)_3$, and controlled hydrolysis gives the *closo*-clusters $[(RSn)_{12}(\mu_3O)_{14}(\mu_2OH)_6](OH)_2$ (Equation (86)).[247] The spacer-bridged hexaalkynyldistannanes are hydrolyzed under microemulsion conditions to give hybrid organic–inorganic materials with promising potential applications.[248,249]



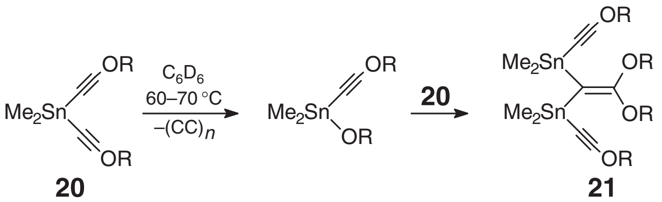
(86)

The alkoxyalkynylstannanes show the familiar instability associated with alkoxyalkynes. The decomposition of a trialkyl(ethoxyalkynyl)stannane, **17**, can be rationalized as follows. Elimination of ethene and rearrangement gives the stannylketene, which reacts with the alkoxyalkyne to give the ester **18** and the distannylketene **19** as the observed products (Equation (87)).[241,250]



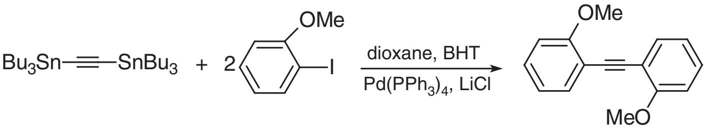
(87)

Dialkylbis(alkoxyalkynyl)stannanes **20** instead leave the alkoxy group intact and lose ethyne to give the distannyl compound **21**, probably by the route shown in Equation (88).[241]



(88)

Alkynyltin compounds also take part in Stille coupling reactions with alkyl, aryl, or acyl halides or triflates (e.g., Equation (89)).[251] These reactions are covered in *Volume 11*.



(89)

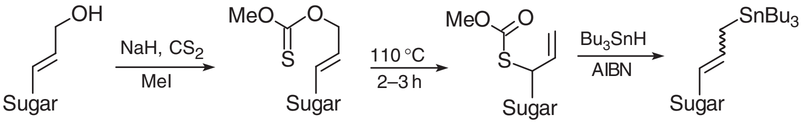
3.14.11 Allylstannanes

3.14.11.1 Preparation

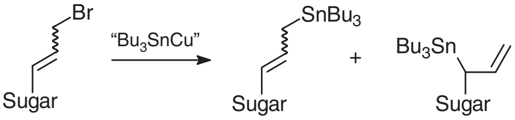
Allyltin compounds are important in organic synthesis because they provide a source of mildly nucleophilic allyl groups that are used particularly in the allylation of carbonyl compounds, and they are available through a number of routes. They are commonly prepared by the allylation of a tin halide with an allylic Grignard reagent, but this has the disadvantage that the preparation of the Grignard reagent often leads to the formation also of biallyl. This problem is often reduced by preparing the Grignard reagent in the presence of the tin halide (Wurtz conditions). Thus, crotyl bromide reacts with triphenyltin chloride in the presence of magnesium to give allyltriphenyltin in 85% yield,[252] and allyl bromide or chloride react with bis(tributyltin) oxide in THF in the presence of magnesium and 1,2-dibromoethane in an ultrasonic cleaning bath (39 kHz) to give allyltributyltin in 90% and 81% yields, respectively.[76] With zinc instead of magnesium, the reaction can be carried out in a mixed water/organic co-solvent containing ammonium chloride[253], or in liquid ammonia.[254]

Allylsilanes in the presence of fluoride ion can be used in place of the Grignard reagents, the reaction of allyltrimethylsilane and bis(tributyltin) oxide giving allyltributyltin in 96% yield.[68]

Sugar allylstannanes have been prepared by the homolytic reduction of allylic dithiocarbonates,[255] and by the reaction of "Bu_3SnCu" with an allylic mesylate or bromide;[256,257] the relative yields of isomers depend on the steric demands of the sugars (Equations (90) and (91)).

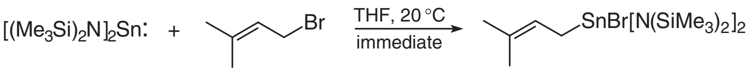


(90)



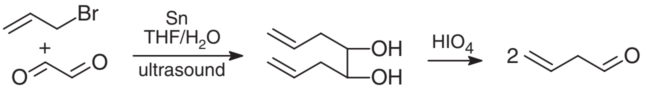
(91)

Allylstannanes for use in palladium-catalyzed coupling reactions can readily be made from Lappert's stannylene, $[(Me_3Si)_2N]_2Sn$:, with an allyl bromide or iodide. The reaction is immediate at room temperature, and the product can be used without further purification (Equation (92)).[258]



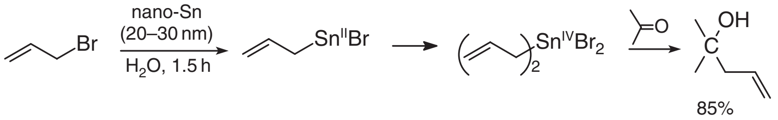
(92)

For the purpose of carrying out carbonyl addition reactions, allylstannanes can be prepared *in situ* from metallic tin and an allyl halide (Barbier conditions),[259] for example, Equation (93).[260]



(93)

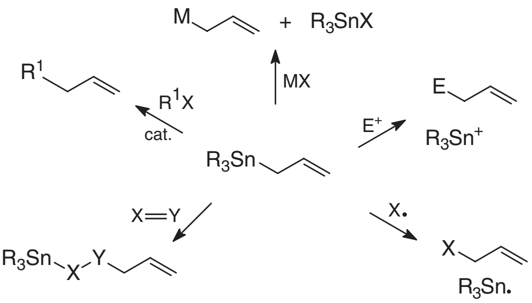
The reaction can be carried out in water[261] or in the absence of a solvent.[262] Nanoparticle tin gives a faster reaction and higher yield than powdered tin, and, under aqueous conditions, the allyltin(II) and allyltin(IV) intermediates have been identified by ^1H NMR spectroscopy (Equation (94)).[263]



(94)

Similar reactions can be carried out by using a tin(II) compound rather than metallic tin.[264–266]

The allylstannanes are still easily handled but are much more reactive than the simple alkylstannanes, and their principal modes of reaction are summarized in Scheme 8. All these reactions, and particularly the carbonyl addition reactions ($X{=}Y = R_2C{=}O$), are important in organic synthesis, and are covered in that respect in *Volume 9*. Only

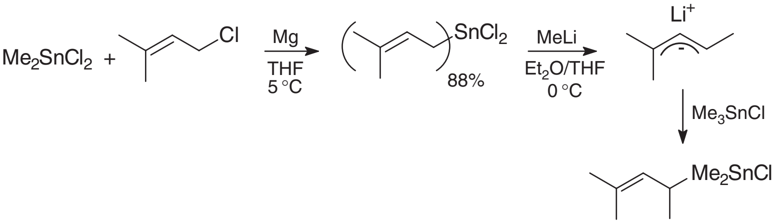


Scheme 8

some particular aspects of the reactions will be picked out here. The transmetallation with metal halides MX and the addition reactions of reagents X═Y can be considered to be within the classification of reactions with electrophiles, but a subdivision is useful here (Scheme 8).

3.14.11.2 Transmetallation Reactions[19,267]

Transmetallation with RLi is used to prepare pure organolithium compounds for structural and spectroscopic studies. Examples of the preparation of pure allylstannanes by this route are given in Equations (95)[268] and (96).[269]



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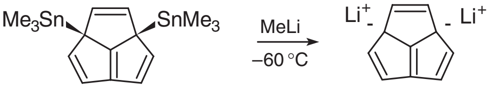
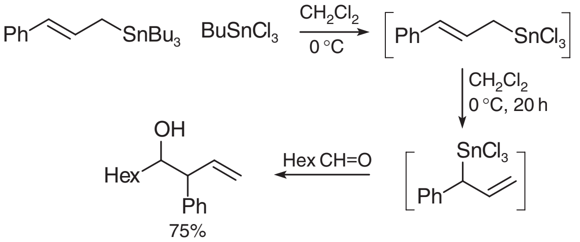


(96)

These Sn/Li transmetallations involve nucleophilic attack of an alkyl anion at the tin center. Transmetallations with metal halides on the other hand involve electrophilic attack of the metal at the allylic double bond.

Allyltin chlorides, allylSnR$_n$Cl$_{3-n}$, are more reactive in carbonyl addition than are the allyltrialkylstannanes, allylSnR$_3$, and for this purpose, the latter can be converted into the former by the Kocheshkov redistribution reaction with BuSnCl$_3$ or SnCl$_4$; the *trans*-stannylation can be carried out with the carbonyl compound *in situ* in a one-pot process (Equation (97)).[270]



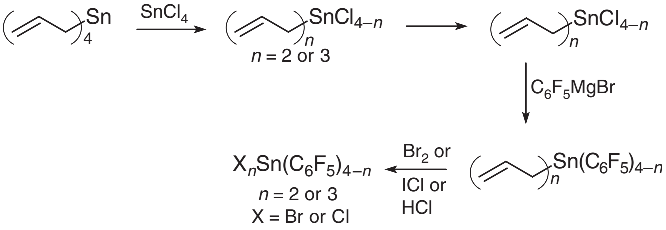
(97)

Analogous transmetallation reactions with other metal halides occur rapidly to give the corresponding allylmetallic compounds: BCl$_3$,[271,272] InCl$_3$,[261] PCl$_3$, AsCl$_3$, and SbCl$_3$.[273] Tris(pentafluorophenyl)borane can be used for catalyzing nucleophilic allylation with allylstannanes, when it operates through the allylborane $[(C_6F_5)_3BCH_2CH{=}CH_2]^-$.[274]

Lead tetracarboxylates react to give the corresponding allyl carboxylates, perhaps by reductive elimination by allylPb(OCOR)$_3$.[275]

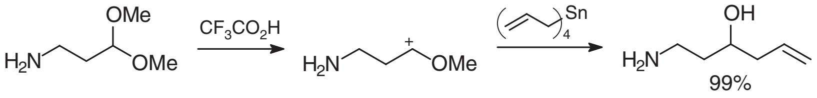
3.14.11.3 Reaction with Electrophiles

Mayr has reviewed the nucleophilicity parameters of allylstannanes and related compounds.[276] The allyl–tin bond is easily cleaved, and this has been exploited in the preparation of pentafluorophenyltin chlorides and bromides (Equation (98)).[277]

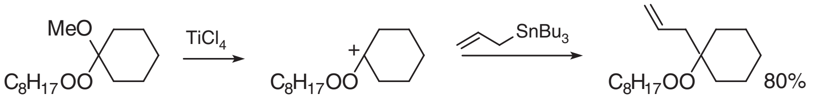


(98)

Homoallylic alcohols can readily be prepared from commercially available tetraallytin and acetals or aminoacetals in the presence of trifluoroacetic acid on silica gel; this provides an alternative to the reaction of an allylstannane with an aldehyde.[278] By a similar mechanism, homoallylic peroxides can be prepared from monoperoxyacetals (Equations (99) and (100)).[279]



(99)

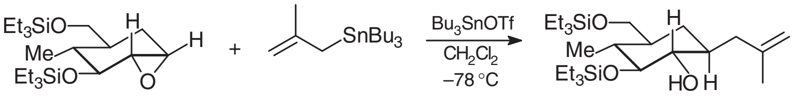


(100)

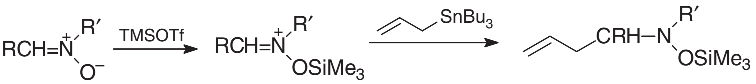
Lambert has exploited γ-attack by an electrophile to bring about conjugate substitution at a tin center that is too highly sterically hindered to allow attack at the tin center itself (see Section 3.14.04.2).[145]

The Michael allylation of *N*-enoyloxazolidinones with allyltributyltin proceeds in good yield with Sn(OTf)$_4$, ZrCl$_4$, or Sm(OTf)$_3$ as Lewis acid catalyst.[280]

β-*C*-Allyl glycosides can be prepared by the reaction of glycal epoxides with allyltributyltin in the presence of tributyltin triflate as a Lewis acid,[281] and aldonitrones can be allylated with trimethylsilyl triflate as a catalyst (Equations (101) and (102)).[282]



(101)



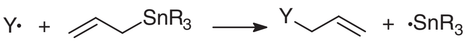
(102)

3.14.11.4 Reaction with Radicals[283,284]

The use of allylstannanes for homolytic allylation depends on the rapid conjugate displacement of R$_3$Sn· by attack of a radical at the γ-position of the allyl group. The rate constants for this reaction by primary alkyl radicals with the allylstannanes **22** and **23** in Scheme 9 are close to the value that was estimated previously for allyltributyltin.[285,286]

The attacking radical may be formed in a substitution reaction (Equations (103) and (104)), or in an addition reaction (Equations (105)–(107)). Initiation may be by AIBN at 80 °C, or by Et$_3$B/O$_2$ at lower temperature.

$$R_3Sn\cdot + X{-}Y \longrightarrow R_3SnX + Y\cdot \tag{103}$$

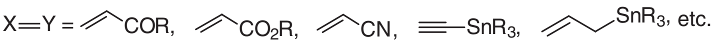


X–Y = R–Cl, R–Br, R–I, R–SPh, R–SePh, ROC(S)SMe,
OC(S)imidazole, RHgCl, etc.

(104)

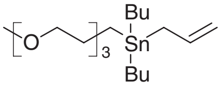
$$R_3Sn\cdot + X{=}Y \longrightarrow R_3SnX{-}Y\cdot \tag{105}$$

(106)



(107)

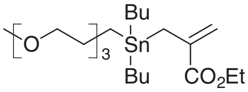
22:



$\log(k/\mathrm{l\,mol^{-1}\,s^{-1}}) = 8.6 \pm 0.9 - (32.1 \pm 5.9)/\theta$

$k(80\,°\mathrm{C})/\mathrm{l\,mol^{-1}\,s^{-1}} = 1.5 \times 10^3$

23:



$\log(k/\mathrm{l\,mol^{-1}\,s^{-1}}) = 8.5 \pm 0.3 - (19.1 \pm 2.6)/\theta$

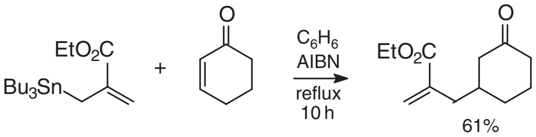
$k(80\,°\mathrm{C})/\mathrm{l\,mol^{-1}\,s^{-1}} = 1 \times 10^3$

$(\theta = 2.303\ RT\ \text{in kJ mol}^{-1})$

Scheme 9

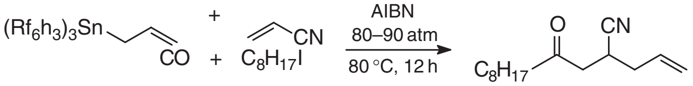
A number of modifications of the structure of the allylstannane have been prepared with the aim of facilitating the removal of tin from the product. These include Curran's fluorous allylstannane (see Section 3.14.04.1), Pereyre's monoallylstannane AllylXSn[N(TMS)$_2$]$_2$ (Equation (92) above),[258] allylstannanes with a polar (oligoethylene oxide) tail (e.g., **23** and **24**),[287] and the allylstannyl group bonded to a soluble[288] or insoluble[289] (cross-linked) polystyrene. The reaction using the allylstannane bonded to a soluble, uncross-linked, polystyrene resin occurs about 100 times faster than that on the cross-linked, insoluble resin, and the polymer can be recovered by recrystallization from methanol.

Allylstannanes are unreactive toward weakly electrophilic enones such as cyclohexenone, but enone additions have been established with the more electrophilic 2-ethoxycarbonylallylstannane (Equation (108)).[290]



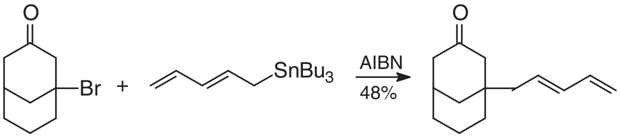
(108)

By suitable tailoring of the reactivities, cascade reactions can be designed (Equation (109)).[291,292]



(109)

Pentadienylstannanes show analogous reactions by addition to the ε-position (Equation (110)).[293]

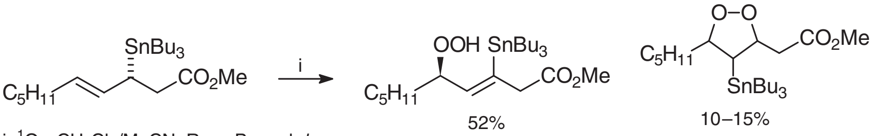


(110)

3.14.11.5 Additions to Multiple Bonds

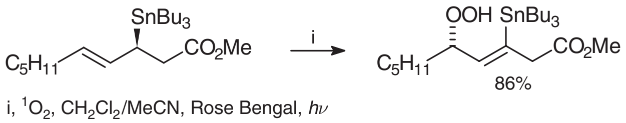
The addition of allylstannanes to multiple bonds covers a wide range of acceptors (X=Y = O=O, RN=NR, R$_2$CO, R$_2$C=CR$_2$, RC≡CR, etc.). The reactions of primary allylstannanes with non-polar acceptors such as singlet oxygen (the ene reactions) usually involve principally the transfer of tin (the M–ene reaction) through a cyclic transition state, but secondary allylstannanes can give mainly hydrogen transfer (the H–ene reaction).[112] Many of these reactions are strongly catalyzed by high concentrations of lithium perchlorate.[294,295]

The enantiomeric allylic stannanes in Equations (111) and (112) show only the H–ene reaction, and proceed with complete stereoselectivity.[279,296] The former compound gives also some dioxastannolane, and if an electron-donating group is present, this dioxastannolane can be the only product (Equation (113)).[297]

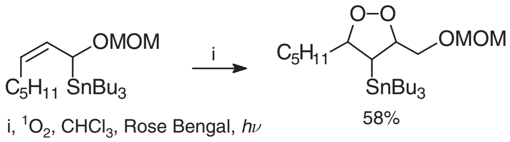


(111)

i, $^1O_2$, CH_2Cl_2/MeCN, Rose Bengal, $h\nu$



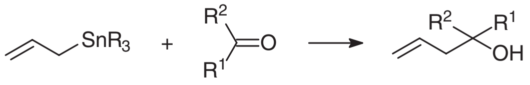
(112)



(113)

The ene reaction with diethyl azodicarboxylate has been used for removing unreacted allylstannanes from solution.[298]

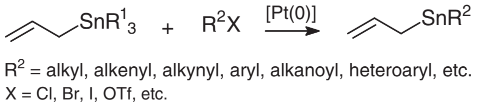
Most of the current interest, however, is directed toward the use in synthesis of the formation of a carbon–carbon bond by the addition of an allylstannane to carbonyl groups (Equation (114)). These reactions have been thoroughly reviewed,[16,18,19,299–301] and are covered in Section 9.08.3 of this series, and will not be considered in detail here.



(114)

3.14.11.6 Cross-coupling Catalyzed by Transition Metals

Similarly, the Migita–Kosugi–Stille cross-coupling reaction (Equation (115)) is important in organic synthesis and has been thoroughly reviewed.[18,190,302,303] These reactions are covered again in Volume 12, and are not considered here.

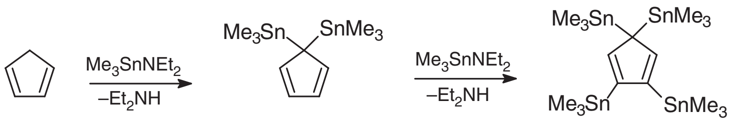


(115)

3.14.12 Cyclopentadienylstannanes[304]

Interest in the cyclopentadienylstannanes continues to be high, particularly in the field of the stannylated metallocenes.

Cyclopentadiene is acidic enough to react with aminostannanes, and at 80 °C, four stannyl groups can be introduced into the ring (Equation (116)).[305]

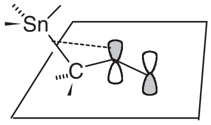


(116)

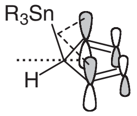
Pentaphenylcyclopentadienyl chloride reacts with $SnCl_2$ to give $C_5Ph_5SnCl_3$, but pentaphenylcyclopentadienyl bromide gives the persistent pentaphenylcyclopentadienyl radical.[306]

C–Sn hyperconjugation is much more effective than C–H hyperconjugation, and is significant in neutral compounds such as allylstannanes, where the equivalent C–H hyperconjugation is negligible. It is strongest when the C–Sn bond eclipses the LUMO of the π-system **24**, falling to zero when it is orthogonal.

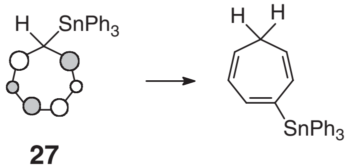
In the butadiene system of a cyclopentadienylstannane, the LUMO has the same phase at the 1- and 4-positions **25**, and it is argued that this results in enhanced hyperconjugation through the Whiffen effect,[307] which was first recognized in the ESR spectra of conjugated cyclic radicals and radical ions. In cycloheptatrienylstannanes, where the LUMO has the opposite phase at the terminal positions **26**, the hyperconjugation is effectively zero.



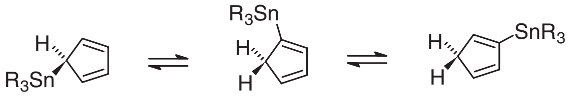
24



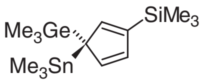
25



27



26

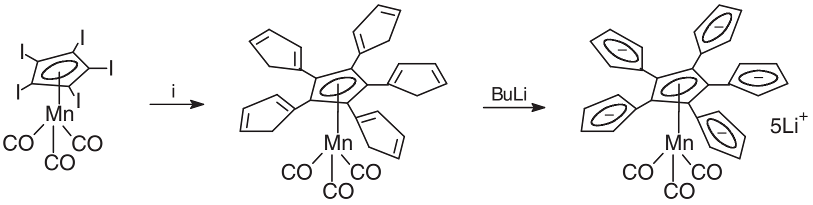


28

This model can account for the fact that in a cyclopentadienylstannane the tin is bonded to the sp^3- rather than sp^2-hybridized carbon **26**, although sp^2 C–Sn bonds are stronger than sp^3 C–Sn bonds, and why, in a cycloheptatrienylstannane, the 1-stannyl isomer **27** rearranges to the 3-stannyl isomer. Similarly, in a distannylcyclopentadiene, both stannyl groups are bonded to the sp^3-hybridized carbon, where both can hyperconjugate, and the silylgermylstannyl cyclopentadiene has the structure **28**, as the hyperconjugative interaction falls in the sequence Sn > Ge > Si.[308]

In $C_5Ph_5SnCl_3$, the C–Sn bond forms an angle of 99.5° with the centroid of the ring, which again will facilitate the hyperconjugation,[306] and the situation is similar in $Ph_3CC_5H_4SnMe_3$, where the tin is attached out of the plane at the allylic position where it can best hyperconjugate.[309]

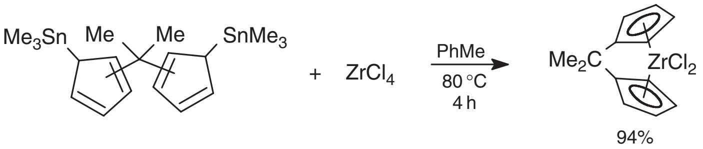
Cyclopentadienylstannanes can be used in the Migita–Kosugi–Stille reaction with organic iodides, RI, to give the cross-coupled product Cp–R, for example, Equation (117).[310]



i, $Me_3SnC_5H_5$, $Pd(MeCN)_2Cl_2$

(117)

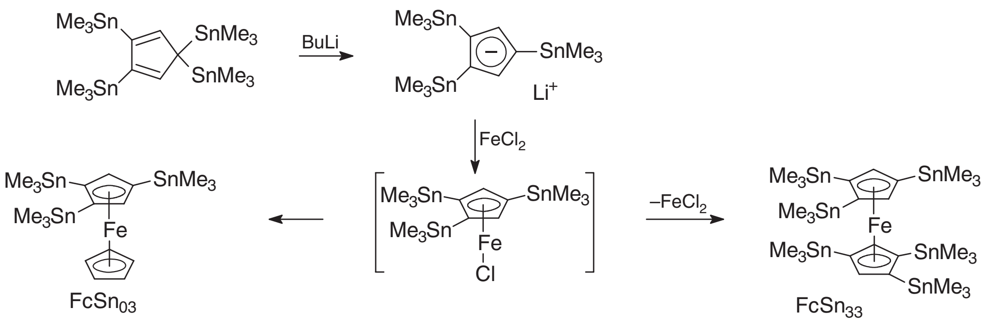
Transmetallation with metal halides (e.g., Re,[311] $TiCl_4$,[309] $ZrCl_4$,[312–315] or $HfCl_4$[314]) provides a route to other metallocenes, for example, Equation (118).[314]



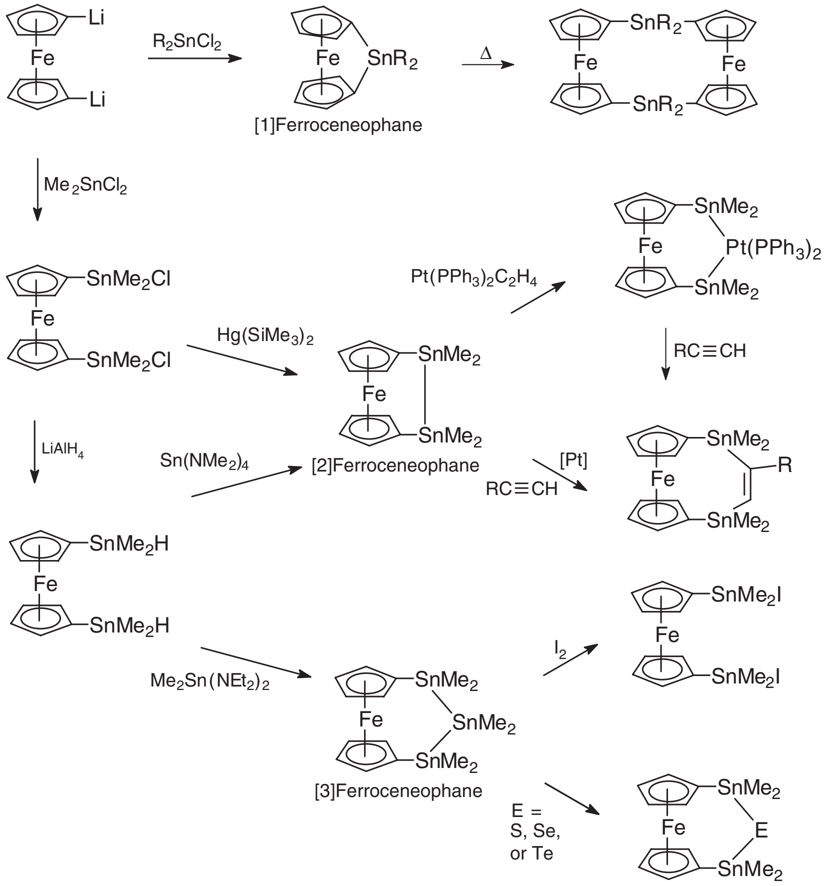
(118)

Stannylated ferrocenes can be prepared by the reaction of a lithiated ferrocene with an organotin chloride, or of a lithiated stannylcyclopentadiene with $FeCl_2$, for example, Scheme 10.[305] The products can be described by the shorthand $FcSn_{xy}$, where x and y indicate the number of stannyl substituents in each of the two rings.

Ferroceneophanes (*ansa*-ferrocenes) have been prepared where the cyclopentadienyl rings are bridged through one, two, or three stannyl groups.



Scheme 10



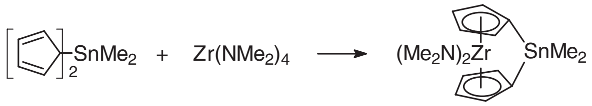
Scheme 11

Scheme 11 illustrates the chemistry of the stanna[1]-, 1,2-distanna[2]-, and 1,2,3-tristanna[3]ferroceneophanes. The stanna[1]ferroceneophanes are stable only when the groups R are large; when R = Bu^t or mesityl, the rings subtend angles of 14.1(2)° and 15.2(2)°, respectively. At elevated temperatures, or in the presence of acid or base, the monomer decomposes to give polymer and the cyclic dimer.[316–318]

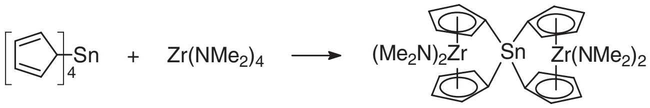
The distanna[2]ferroceneophane[319,320] shows the characteristic behavior of a distannane, inserting platinum into the SnSn bond,[321] and adding to an alkyne in the presence of a platinum catalyst.[126,322]

In the tristanna[3]ferroceneophane, the cyclopentadienyl rings are parallel but twisted, and reaction with a chalcogen gives a 1,3-distanna-2-chalcogena[3]ferroceneophane.[319,321]

Stanna[1]zirconocenes have been prepared by an alternative approach, taking advantage of the protic acidity of cyclopentadienylstannanes to bring about the acidolysis of tetrakis(dimethylaminyl)zirconium (Equations (119) and (120)).[323]



(119)

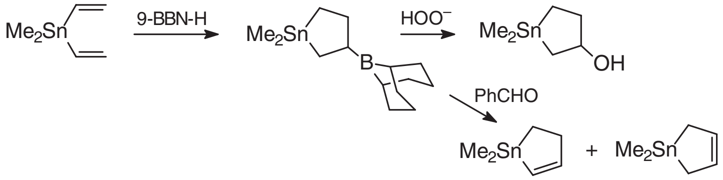


(120)

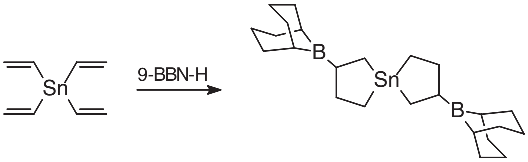
3.14.13 Stannacycloalkanes

Wrackmeyer’s organoboration of dialkynylstannanes to give borylstannacyclopentadienes is referred to above. By this type of reaction, *spiro*-stannacycloalkanes and cycloalkenes have been prepared (Scheme 12).[324]

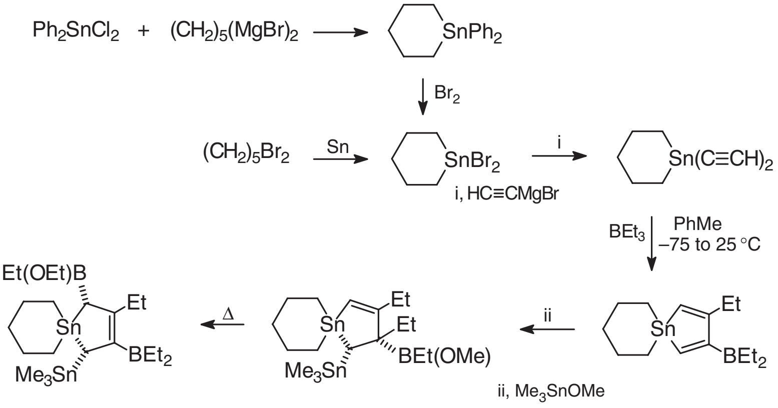
Related chemistry occurs when di- or tetravinylstannanes are treated with 9-borabicyclononane (Equations (121) and (122)).[325]



(121)

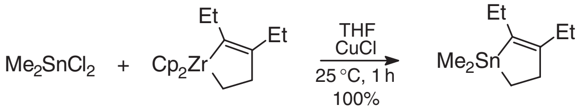


(122)

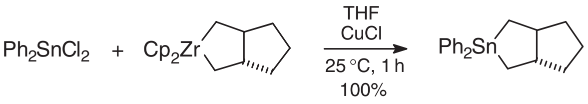


Scheme 12

The remarkable effect that CuCl has on the reaction of the zirconacyclopentadienes with R_2SnCl_2 or $SnCl_4$ (Section 3.14.9) extends to reactions involving zirconacyclopentenes and zirconacyclopentanes, providing a route to stannacyclopentenes and stannacyclopentanes (Equations (123) and (124)).[233]



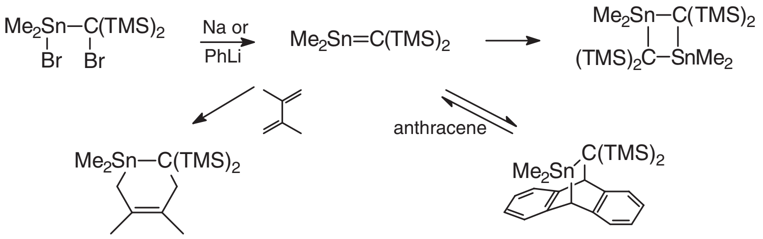
(123)



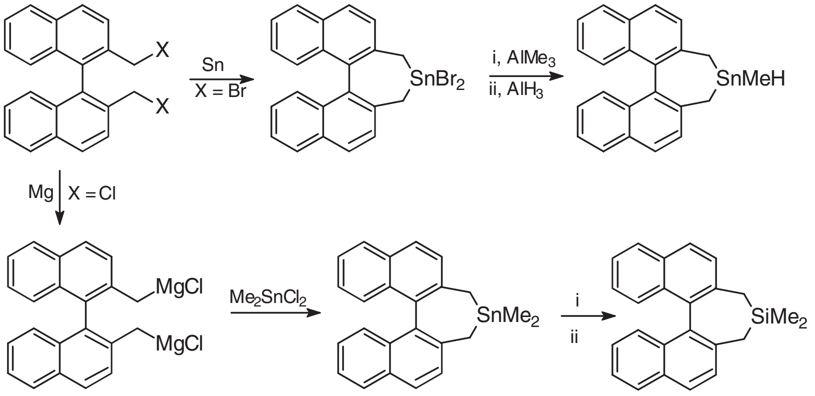
(124)

The reaction of an α-bromoalkyltin halide (Scheme 13) with sodium or phenyllithium gives a transient stannene, which self-reacts to give the dimer, or gives an adduct with anthracene, which dissociates into its precursors on heating.[326]

The stannepins which encompass the 2,2′-positions of 1,1′-binaphthyl are interesting because, in their enantiomeric forms, they can bring about stereoselective reactions. Scheme 14 shows the synthesis of the methyltin hydride, which has been used in asymmetric reduction,[172] and of the dimethyltin compound, which, via lithiation, can act as the precursor for further derivatives such as the silepins.[327]



Scheme 13

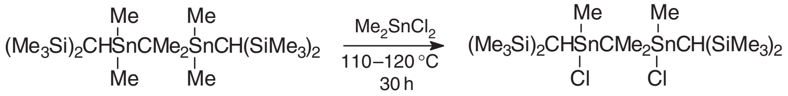


i, MeLi ii, Me_2SnCl_2

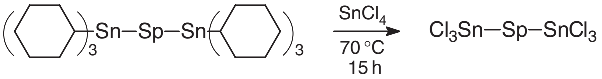
Scheme 14

3.14.14 Organotin Halides

Organotin halides are commonly prepared by the Kocheshkov redistribution reaction, where an organic group on tin (e.g., in SnR_4) exchanges (reversibly) with a halide group on tin (e.g., in $SnCl_4$).[64] Two recent examples are shown in Equations (125) and (126).[248,328] The first reaction exploits the high reactivity of the Sn–Me bonds, and the second depends on the low reactivity of the Sn–cyclohexyl bond.



$$(Me_3Si)_2CH\overset{Me}{\underset{Me}{Sn}}CMe_2\overset{Me}{\underset{Me}{Sn}}CH(SiMe_3)_2 \xrightarrow[\text{110–120 °C, 30 h}]{Me_2SnCl_2} (Me_3Si)_2CH\overset{Me}{\underset{Cl}{Sn}}CMe_2\overset{Me}{\underset{Cl}{Sn}}CH(SiMe_3)_2 \quad (125)$$



(126)

For preparing organotin trichlorides by this route, the slowest step is the reaction of R_2SnCl_2 with $SnCl_4$, and it has been shown that this reaction (and that of R_4Sn) is catalyzed by platinum and palladium compounds, for example, Equation (127).[329]

$$Bu_2SnCl_2 + SnCl_4 \xrightarrow[\substack{12\,h \\ 80\%}]{100\,°C} BuSnCl_3 \quad (127)$$

The redistribution reaction of $MeSnCl_3$ to give Me_2SnCl_2 and $SnCl_4$ in solution at 50 °C follows second-order kinetics, and is faster in coordinating solvents and in the presence of alcohols or amines, suggesting a nucleophile-assisted electrophilic mechanism.[330]

The second major route to the halides is the reaction of a tin hydroxide or oxide with a halogenating agent such as HCl or $SOCl_2$. The reaction of dialkyltin oxides with saturated NH_4X (X = F, Cl, Br, I) in refluxing dioxane gives high yields of the distannoxanes, $XR_2SnOSnR_2X$.[331]

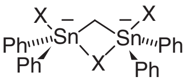
Conversion of the organotin chlorides into fluorides, bromides, or iodides is usually carried out with the sodium halide in acetone, and residual organotin compounds are often removed as the insoluble organotin fluorides. The fluorides can then be converted back into the bromides, chlorides, or iodides (and exchanges by other halides can be brought about with aqueous ammonium halides at room temperature).[332] A 2 : 1 mixture (solid solution) of CsF and CsOH, mixed with silica gel, also provides a very convenient way of removing organotin halide byproducts from solution.[333]

The structural chemistry of the organotin halides is dominated by their Lewis acid properties and their propensity to form five- and six-coordinate complexes. Self-association may give oligomers or polymers in the solid state, which usually dissociate in solution. The structure of tricyclohexyltin chloride in the crystal is temperature-dependent. At 108 K, it has the form of a rod-like polymer with distorted trigonal-bipyramidal tin and Sn–Cl separations of 245.6(7) and 300.77(7) pm, but at 298 K, the structure is best regarded as consisting of near-tetrahedral discrete molecules.[334]

The fluorides, R_3SnF, are usually zigzag polymers with non-linear bonds about the fluorine when R is small (e.g., butyl), and rod-like polymers when R is large (e.g., cyclohexyl), or monomers if R is very large (e.g., mesityl). Me_2PhSnF, rather surprisingly, has a low melting point (ca. 125 °C), but is polymeric in the solid state. $(Me_3SiCH_2)_3SnF$, also having the melting point at ca. 125 °C, is a monomer.[335]

With a functional substituent in the alkyl group, the self-association may be intramolecular. Thus, in the ω-hydroxyalkyltin trihalides, $HO(CH_2)_nSnCl_3$, when $n = 3$ or 4, the molecules are intramolecularly coordinated, whereas when $n = 5$, they form a linear polymer.[336] Similarly, $MeCO_2(CH_2)_nSnCl_3$ forms a cyclic monomer when $n = 3$, but a cyclic dimer when $n = 2$, and an oligomer when $n = 4$.[337]

Bis(stannyl halides) of suitable geometry can act as bidentate Lewis acids. The compounds $XPh_2Sn(CH_2)_nSnPh_2X$, $n = 1$, 2, or 3, all form 1 : 1 adducts **29** with halide ion, preferentially chelating F^- rather than Cl^- or Br^-.



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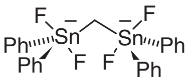

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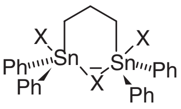

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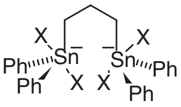


32

When $n = 1$, the fluoride reacts further to give the dianion **30**. When $n = 2$, the 1 : 1 adducts are particularly stable and do not react further. When $n = 3$, the fluoride and chloride give both the 1 : 1 and the 1 : 2 adducts **31** and **32**. In all these compounds, the structure about tin is approximately trigonal bipyramidyl.[338]

It is rather surprising that the bis(tin trichlorides), $X_3Sn(CH_2)_nSnX_3$ (X = Cl or Br, $n = 1$, 3, 4, or 8), behave as bis(monodentate) Lewis acids toward halide ions, giving $[X_4Sn(CH_2)_nSnX_4]^{2-}$ (X = Cl or Br) or $[F_5Sn(CH_2)_nSnF_5]^{2-}$, and there is no evidence for chelation.[339]

The *ortho*-phenylene bis(monochlorides), o-$C_6H_4(SnMe_2X)_2$ (X = Cl or F), act as bidentate Lewis acids toward chloride and fluoride ions (Y^-) to give the stable chelate complexes o-$C_6H_4(SnMe_2X)_2Y^-$, where X = Y = Cl, X = Y = F, and X = Cl, Y = F.[340]

Hydrolysis of the tin halides gives a family of important organotin oxides and hydroxides that have attracted a lot of attention in recent years. These compounds are considered in Section 3.14.16.

3.14.15 Organotin Carboxylates

Organotin carboxylates are usually prepared by treating the appropriate organotin oxide or hydroxide with a carboxylic acid. The reaction between a dialkyltin oxide $(R_2SnO)_n$ and a carboxylic ester, $R^1CO_2R^2$, gives the (alkoxy)(carboxylato)distannoxane, $(R^1CO_2)R_2SnOSnR_2(OR^2)$.[341] These and related carboxylates of tin oxides are covered in Section 3.14.16.2.

Alternatively, a tin–phenyl or tin–alkynyl bond can be cleaved with a carboxylic acid, for example, Equations (128) and (129).[342,343]

$$(Me_3CCH_2)_2SnPh_2 + ClCH_2CO_2H \xrightarrow[\substack{2\,h \\ 90\%}]{160\,°C} (Me_3CCH_2)_2Sn(OCOCH_2Cl)_2 \qquad (128)$$

$$RSnC{\equiv}C(CH_2)_3Me + 3R^1CO_2H \longrightarrow [RSn(O)OCOR^1]_6 \qquad (129)$$

Alkyl–tin bonds can be cleaved with lead tetraacetate, the reactivity falling in the order Ar ≈ Me > Et > Bu >> Pr^i (Equation (130)) and the reaction of $ArSnBu_3$ provides a convenient route to the aryllead triacetates, $ArPb(OAc)_3$.[344]

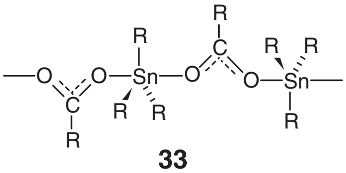
$$Me_4Sn + Pb(OAc)_4 \xrightarrow[\substack{28\,°C \\ 3\,h}]{CHCl_3} Me_3SnOAc \xrightarrow{3\,h} Me_2Sn(OAc)_2 \qquad (130)$$

The Sn–allyl bond (but not Sn–alkyl, Sn–vinyl, Sn–benzyl, or Sn–aryl) reacts with CO_2 in the presence of a palladium catalyst to give a tin buteneoate. A mechanism can be envisaged which involves the formation of the Sn–Pd–allyl structure, which undergoes CO_2 insertion to give Sn–Pd–OCO–allyl, followed by reductive elimination of the tin carboxylate (Equation (131)).[345]

$$Bu_3SnCH_2CH{=}CH_2 \xrightarrow[\substack{CO_2,\ THF \\ 70\,°C,\ 24\,h}]{Pd(PPh_3)_4} \underset{90\%}{Bu_3SnOCOCH_2CH{=}CH_2} + \underset{10\%}{Bu_3SnOCOCH{=}CH_2CH_3} \qquad (131)$$

A large variety of organotin carboxylates have been prepared, and their structures determined by X-ray diffraction. Part of the impetus for this work has been the search for anticancer drugs, and the aim of relating activity to structure. The early work on structure has been thoroughly reviewed,[346] as well as recent developments,[347] including the structural work on the organotin derivatives of amino acids and peptides.[348]

In the solid state, the most common structure of the monocarboxylates, in the absence of any major steric demands, is that of a linear polymer **33**, but tributyltin 2,6-difluorobenzoate forms a cyclic tetramer, $(Bu_3SnOCOAr)_4$.[349]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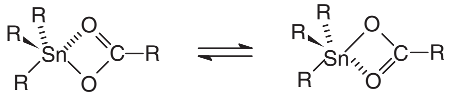
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In solution, the ^{17}O NMR spectra of tributyltin acetate and dibutyltin diacetate show a single signal in a variety of solvents over the range 200–300 K. This is interpreted to imply the existence, in solution, of a cyclic monomer in which the carboxylate groups are anisobidentate, and are undergoing rapid intramolecular exchange **34**.[350]

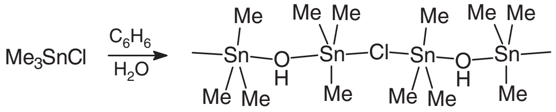
Interest in the organotin derivatives of the acids and thioacids of phosphorus arises from their potential biological action and the wide variety of structures that have been identified by X-ray diffraction. These structures are often particularly complex when the compounds are derived from the partially hydrolyzed mono- or diorganotin compounds, and words such as cubes, drums, crowns, butterflies, clusters, oxygen-capped clusters, and extended clusters have been use to describe them. References to the early work are given in Ref:**351**, and a recent review is available.[352]

3.14.16 Organotin Oxides and Hydroxides

The various tri-, di- and monoorganotin hydroxides and oxides that can be obtained by partial or complete hydrolysis of the corresponding halides or carboxylates often behave as catalysts for reactions such as esterification or transesterification, and it is partly with the aim of obtaining better and more selective catalysts that a lot of work has been carried out on these compounds in the past decade.[347]

3.14.16.1 Triorganotin Oxides and Hydroxides

The triorganotin oxides and hydroxides are relatively straightforward. The complete structure of trimethyltin hydroxide has not yet been determined, but exposure of a solution of trimethyltin chloride to moisture gives the half-hydrolysis product $Me_3SnCl{\cdot}Me_3SnOH{\cdot}H_2O$, in which trigonal-planar Me_3Sn units are alternately bridged by Cl and OH, with rSnO = 212.5(2) and 212.1(2) pm, and rSnCl = 290.7(3) and 289.2(3) pm (Equation (132)).[353]



(132)

Co-hydrolysis of Me_3SnCl in the presence of Me_2SnCl_2 gives the dimeric tristannoxane $[ClMe_2OSnMe_2OSnMe_2OSnMe_3]_2$, which is described below.[354]

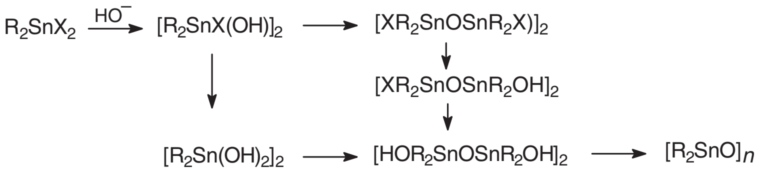
The oxonium salt $(Me_3Sn)_3O^+Cl^-$ has been isolated as a crystalline solid from the reaction of bis(trimethyltin) oxide and trimethyltin chloride. The three tin atoms are coplanar about the oxygen, and the chloride anion bridges three tin atoms in three $(Me_3Sn)_3O^+$ units to form graphite-like layers.[355] In the salt $(Et_3Sn)_2OH^+B(C_6H_5)_4^-$, the Sn–O bond is lengthened and the Et_3Sn group is flattened (CSnC 117.7°), indicating substantial stannylium ion character.[356]

The triaryltin hydroxides and the bis(triaryltin) oxides are readily interconverted, and have sometimes been confused. Tris(*o*-methoxyphenyl)tin hydroxide can be identified in solution, but when it is isolated, it rapidly loses water to give the oxide.[357]

Bis(tribuyltin) oxide reacts with carboxylic esters in ether at room temperature to give the corresponding tributyltin carboxylate and tributyltin alkoxide, and this reaction is recommended for removing protecting ester groups in the presence of other functional substituents.[358–360]

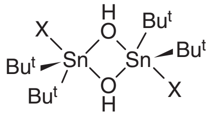
3.14.16.2 Diorganotin Oxides and Hydroxides

Hydrolysis of compounds R_2SnX_2 gives the dialkyltin oxide via a number of intermediates (Scheme 15).



Scheme 15

The dihydroxide is new on this list; di-*t*-butyltin dihydroxide exists in the crystal as a hydroxide-bridged dimer **35**,[361] and the diprotonated form has been isolated as the triflate, again as a dimer **36**.[362]



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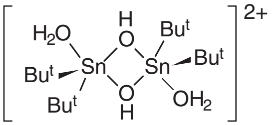

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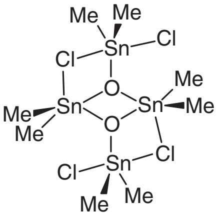
The difunctional distannoxanes $XR_2SnOSnR_2X$ can also be prepared from the reaction of $(R_2SnO)_n$ with R_2SnX_2, or from $(R_2SnO)_n$ and the appropriate amount of the acid HX. A further alternative is to heat the dialkyltin oxide with saturated aqueous NH_4X ($X = F$, Cl, Br, I, OAc) in refluxing dioxane, and this probably provides the best route to the fluorides $FR_2SnOSnR_2F$.[331]

The alkoxycarboxylates, $(R^1O)R_2SnOSnR_2(OCOR^2)$, can also be prepared by heating together the oxide $(R_2SnO)_n$ and the ester R^1OCOR^2,[341] and, under similar conditions, diphenyl carbonate reacts to give the diphenoxide, presumably via the phenoxy phenyl carbonate $(R^1O)R_2SnOSnR_2(OC(O)OR^2)$.[363] This type of reaction might well provide a useful new route to the dialkoxydistannoxanes, $(R^1O)R_2SnOSnR_2(OR^1)$, and thence to the dialkoxides, $R_2Sn(OR^1)_2$.

Unless the organic groups are very large, the difunctional distannoxanes are dimeric in the solid state, with all the tin atoms rendered at least five coordinate. The two most common structural motifs are represented by the dichloride **37**, where there are two four-membered rings about the central distannoxane core, and the dicarboxylate **38**, where there are four six-membered rings about the center, but a number of variants on these basic models have been identified.[347]



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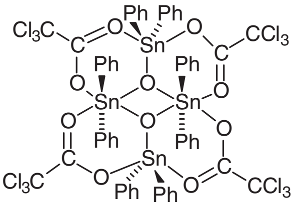

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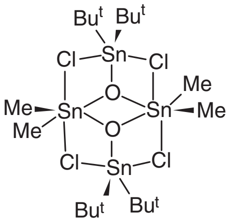
Distannoxanes with two different organic groups, $[XR_2SnOSnR^1{}_2X]$, can be formed from the reaction of equimolar R_2SnX_2 and $R^1{}_2SnO$, when the larger of the organic groups is bonded to the exocyclic tin, for example, **39**.[364]



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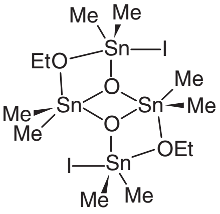
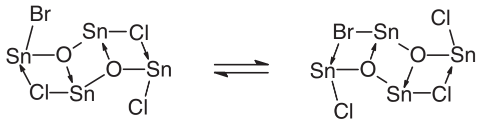


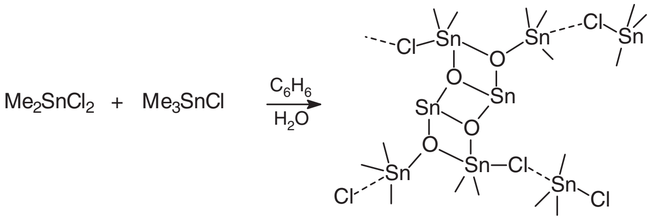
40

When two different electronegative ligands are involved in compounds $[XR_2SnOSnR_2Y]_2$, the strongest ligand is bonded to the endocyclic tin, for example, **40**.[365] When the two ligands X and Y have similar donor strength, their positions become randomized in solution, and a mixture of $[Bu_4Sn_2Cl_2O]_2$ and $[Bu_4Sn_2Br_2O]_2$ in solution shows ^{119}Sn NMR signals for the two parents and for five further isomers, $Bu_8Sn_4Cl_mBr_nO_2$ where $m + n = 4$, less than the theoretically possible number, because rapid equilibration between isomers such as **41a** and **41b** renders them equivalent on the NMR timescale.[366]



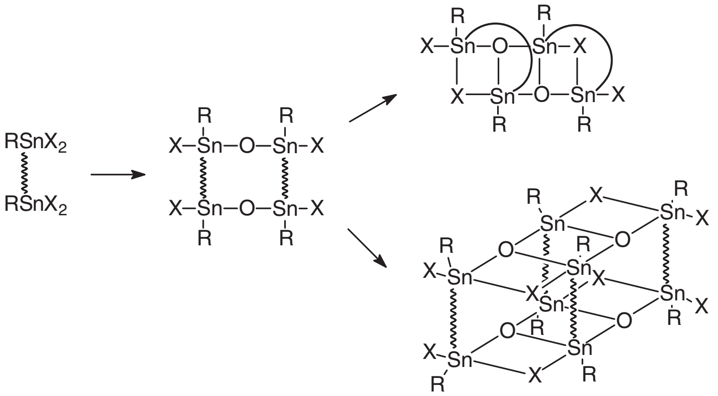
41a **41b**

Hydrolysis of a mixture of Me_2SnCl_2 and Me_3SnCl gives the tristannoxane $[ClMe_2SnOSnMe_2OSnMe_3]_2$, which crystallizes with two molecules of Me_3SnCl that link the tristannoxane into infinite bands (Equation (133)).[354]



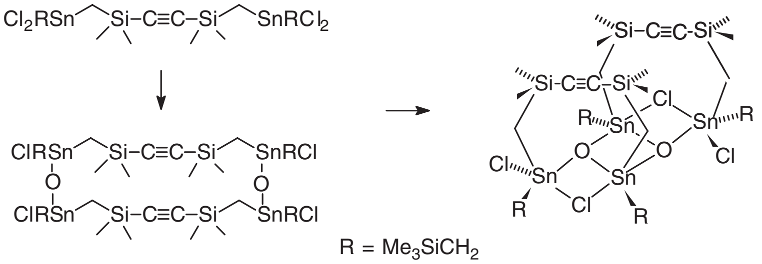
(133)

If bridged bis(dichlorodistannoxanes), $X_2RSn{\sim}{\sim}{\sim}SnRX_2$, are converted into the distannoxanes (usually by reaction with $Bu^t{}_2SnO$), the products have a more complex structure, with the alternatives shown in Equation (134).



(134)

The acetylene-bridged tris(dichlorostannane) (Equation (135)) achieves five-coordination by intramolecular association of the distannoxane, according to the former of these two possibilities.[367]



(135)

Most of the other compounds that have been studied usually have an oligomethylene bridge and have been studied by Dakternieks's group. They give tetradistannoxanes by intramolecular association; examples of these compounds are given in Table 6, and more are to be found in Chandrasekhar's review.[347]

Entry 2 was obtained by treating entry 1 with aqueous ethanolic KOH.[369] The acetate (entry 8) was obtained by treating the chloride (entry 1) with silver acetate. Entry 9 represents a mixture of the five possible isomers which are formed when the mixed bridged tetrachloride $Cl_2PhSn(CH_2)_3Sn(CH_2SiMe_3)Cl_2$ is treated with $(Bu^t{}_2SnO)_3$.

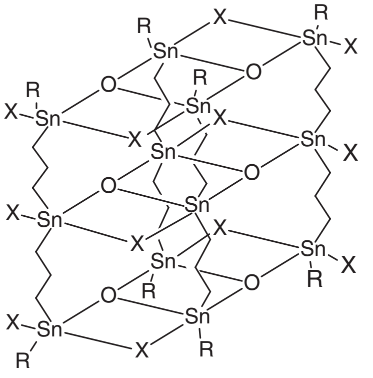
Table 6 Bridged tetradistannoxanes

Entry	*R*	*X*	*Bridge*	*References*
1	Me_3SiCH_2	Cl	$CH_2CH_2CH_2$	368,368,369
2	Me_3SiCH_2	Cl, OH	$CH_2CH_2CH_2$	369
3	Me_3CCH_2	Cl	$CH_2CH_2CH_2$	368
4	Me_3SiCH_2	Cl	$CH_2CH_2CH_2CH_2$	368
5	Me_3CCH_2	Cl	$CH_2CH_2CH_2CH_2$	368
6	Me_2CHCH_2	Cl	$CH_2CH_2CH_2CH_2$	368
7	Me_3SiCH_2	Cl	$CH_2SiMe_2CH_2$	368
8	Me_3SiCH_2	OAc	$CH_2CH_2CH_2$	368
9	Me_3SiCH_2, Ph	Cl	$CH_2CH_2CH_2$	370
10	Me_3CCH_2, Me_2CHCH_2	Cl	$CH_2CH_2CH_2CH_2$	370
11	Me_3CCH_2, Me_3SiCH_2	Cl	$CH_2CH_2CH_2CH_2$	370
12	Me_3SiCH_2	Cl	*p*-$(CH_2SiMe_2)_2C_6H_4$	371
13	Me_3SiCH_2	Cl	*m*-$(CH_2CH_2)_2C_6H_4$	371
14	Ph	I, OH	CH_2	372

Entries 10 and 11 were obtained by the reaction of the bridged tetrachlorides $Cl_2RSn(CH_2)_4SnRCl_2$ with the polymeric bridged oxides $[R^1(O)Sn(CH_2)_4Sn(O)R^1]_n$. In the crystal, the neopentyl groups occupy the outer four corners of the tetrameric block; in solution, the tetramers are in equilibrium with their corresponding mixed dimers.

In entry 12, which includes a *p*-phenylene unit in the bridge, the top ladder layer is twisted with respect to the bottom layer, resulting in a helical structure with no center of symmetry, and in which all eight tin atoms are chiral. In the *m*-phenylene equivalent (entry 13), on the other hand, the top and bottom layers are parallel. Entry 14 can be obtained solvent free, but also forms a 4THF and a $3CH_2Cl_2$ complex, and all three forms have a twist angle of 28–29°.

The doubly bridged tristannane $Cl_2RSn(CH_2)_3SnCl_2(CH_2)_3SnRCl_2$ ($R = Me_3SnCH_2$) reacts with $(Bu^t{}_2SnO)_3$ to give the three-layered chlorostannoxane **42** and $Cl_2RSn(CH_2)_3SnCl_2CH_2SiMe_2CH_2SnCl_2(CH_2)_3SnRCl_2$ gives the double-layered compound **43**.[373]



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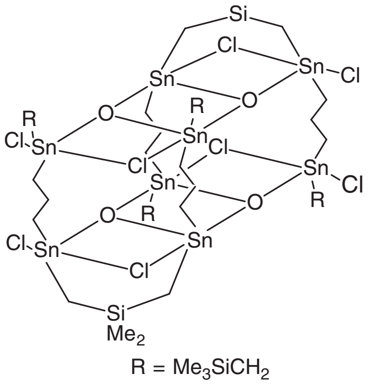

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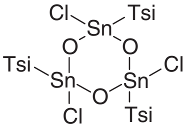
3.14.16.3 Monoorganotin Oxides and Hydroxides

Extensive hydrolysis of the trifunctional monoorganostannanes $RSnX_3$ tends to give cage oligomers with complex structures, but with a bulky group R, the degree of condensation is limited. When R is the tris(trimethylsilylmethyl) group, $(Me_3Si)_3CH_2$ (Tsi), hydrolysis of $(Me_3Si)_3CH_2SnCl_3$ gives cyclic trimeric chloride **44** and then the hydroxide **45**,[374] but with Na_2O in liquid ammonia, the adamantyl-like tetramer **46** is formed.[375]



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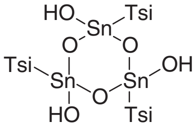

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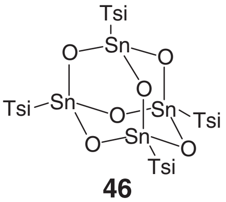

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Hydrolysis of the trialkoxides $\mathrm{BuSn(OR^1)_3}$, or of the trialkynyl compounds $\mathrm{RSn(C{\equiv}CR^1)_3}$ ($\mathrm{R = Bu}$, $\mathrm{4\text{-}(CH_2{=}CH)C_6H_4(CH_2)_4}$, $\mathrm{MeCO_2(CH_2)_5}$), or azeotropic dehydration of a mixture of butylstannonic acid and toluene *p*-sulfonic acid[376] gives a ball-shaped cluster $\mathrm{[(RSn)_{12}O_{14}(OH)_6]X_2}$, $\mathrm{X = OH}$ or Tos; metal ions such as $\mathrm{Na^+}$ can be enclosed within the cage, and up to six of the RSn groups can be replaced with VO groups.[377] Hydrolysis of the bridged bis(tin chloroacetate), $\mathrm{(RCO_2)_3Sn(CH_2)_3Sn(OCOR)_3}$, gives again an $\mathrm{Sn_{12}}$ complex, now with the composition $\mathrm{[Sn(CH_2)Sn]_6(ClCH_2CO_2)_{14}(OH)_2O_{10}}$, in which the $\mathrm{Sn_{12}}$ core is almost planar rather than spherical.[378]

3.14.17 Organotin Alkoxides

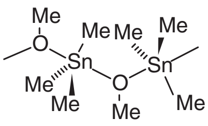
New routes to the alkoxides have been established, starting from the hydrido-, allyl-, or alkynylstannanes. Allyltributyltin and tributyltin hydride react with alcohols in the presence of triflic acid to give the tributyltin alkoxides in good yields,[379] and the alkyltrialkynylstannanes are cleaved by alcohols under neutral conditions to give the trialkoxides (Equations (136)–(138)).[247]

$$\mathrm{Bu_3SnH + MeOH \xrightarrow[\substack{RT,\ 16\,h\\ 82\%}]{\substack{CH_2Cl_2\\ CF_3SO_3H}} Bu_3SnOMe} \tag{136}$$

$$\mathrm{Bu_3SnCH_2CH{=}CH_2 + Pr^iOH \xrightarrow[\substack{RT,\ 1\,h\\ 98\%}]{\substack{CH_2Cl_2\\ CF_3SO_3H}} Bu_3SnOPr^i} \tag{137}$$

$$\mathrm{BuSn\left(\!-\!\!\equiv\!\!-Me\right)_3 + Bu^iOH \xrightarrow[\substack{60\,^{\circ}C,\ 16\,h\\ 76\%}]{C_6H_{12}} BuSn(OBu^i)_3} \tag{138}$$

Few X-ray diffraction data are available for the organotin alkoxides. Trimethyltin methoxide in the crystal is a five-coordinate linear polymer **47**,[380] and both tin atoms in the methanol solvate, $\mathrm{CH_2(SnPh_2OMe)_2{\cdot}MeOH}$, are five coordinate, one by intramolecular coordination, and the other by solvation **48**.[381] Dimethyltin dimethoxide **49**,[382] dimethyltin diphenoxide **50**,[383] and isopropyltin triisopropoxide **51**[384] are five-coordinate oxygen-bridged dimers. All these compounds are monomers in solution.



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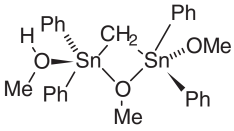

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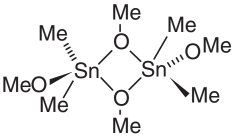

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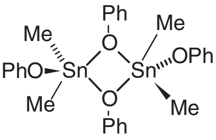

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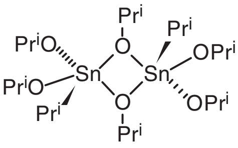
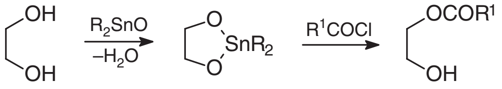


51

A potential "green" route to dimethyltin carbonate can be based on the reaction of methanol and carbon dioxide, catalyzed by dimethyltin dimethoxide. In supercritical CO_2 as solvent, the dimethoxide reacts to give the monocarbonate, which at 180 °C and 300 atm pressure gives dimethyl carbonate, probably by an intramolecular rearrangement, with regeneration of the dimethoxide (Equation (139)).[385,386]

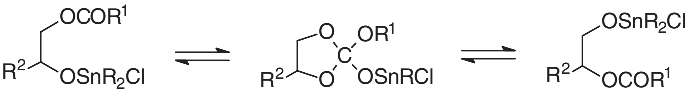
$$Me_2Sn(OMe)_2 \xrightarrow{CO_2} Me_2Sn(OMe)(OCO_2Me) \xrightarrow[-H_2O]{MeOH} (MeO)_2CO + Me_2Sn(OMe)_2 \tag{139}$$

The 1,3,2-dioxastannolanes are important in organic synthesis because they can readily be derived from dialkyltin oxide and 1,2-diols, as in carbohydrates; the reaction can be carried out in toluene in a few minutes under microwave irradiation.[387] The dioxastannolanes can then be subjected to regioselective reaction with an electrophile such as an acyl chloride (Equation (140)) or sulfonyl chloride, or an isocyanate. The acylation or sulfonation can be carried out with catalytic amounts of the dialkyltin oxide, including the recoverable $(C_6F_{13}CH_2CH_2)_2SnO$.[388]



(140)

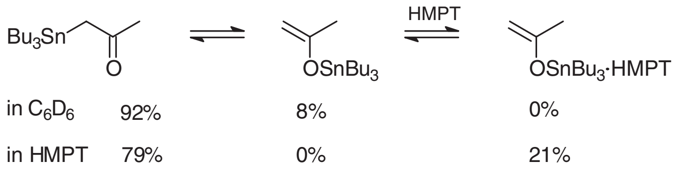
Factors that determine the regioselectivity are the deactivation of one of the two oxygen nucleophiles by stereochemically controlled dimerization of the dioxastannolane, and by equilibration of the possible isomeric products (Equation (141)).[389–391]



(141)

The reactions can be carried out under mild conditions in the presence of triethylamine or an inorganic base such as potassium carbonate,[388] and under the latter conditions, the kinetic resolution of $PhCH(OH)CH_2CH_2OH$ has been achieved using a chiral stannoxane based on 1,1′-binaphthyl.

The keto/enol ratio in organotin enolates is dependent on the enol structure and on the environmental conditions, a good ligand for the tin shifting the equilibrium toward the enolate, and increasing its reactivity (Equation (142)).[392]



(142)

These enolates are important in organic synthesis in providing a source of nucleophilic enol for use in aldol and related reactions, and this is covered in *Volume 9*.

3.14.18 Organotin Hydrides

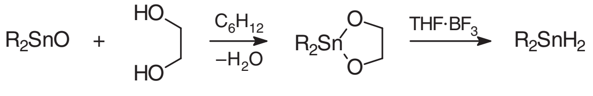
Much of the interest in the organotin hydrides derives from their applications in organic synthesis, often in radical chain reactions. The hydrostannation of alkynylstannanes to give alkenylstannanes, and of alkenylstannylanes to give alkylstannanes, has been covered in earlier sections of this chapter, and other uses in synthesis are considered in Volume 9. This section covers other aspects of tin hydride chemistry, though much of that is directed toward finding better reagents, or better routes to known reagents, for use in synthesis.

3.14.18.1 Preparation

The tin hydrides are usually prepared by reduction of a tin halide, oxide, or alkoxide with a metal hydride such as $NaBH_4$, $LiAlH_4$, or poly(methylhydrosiloxane) $[(MeHSiO)_n$; (PMHS)].

The reduction of trialkyltin halides by PMHS is catalyzed by aqueous KF and can be used *in situ* for free radical- or palladium-catalyzed reactions of the stannanes, and this protocol probably provides the best way of carrying out reductions with the volatile and toxic Me_3SnH.[393,394] If bis(tributyltin) oxide is reduced *in situ* with PMHS in the presence of an azide and AIBN as a free radical initiator, the corresponding amine is formed in good yield.[183]

An improved route to the dihydrides is the reduction of the dioxastannolanes (see above) with $THF{\cdot}BH_3$. The byproducts are easily removed by washing with water, and yields are very good (Equation (143)).[395]



yields: R = Bu 91%, Oct 85%, Cy 77%

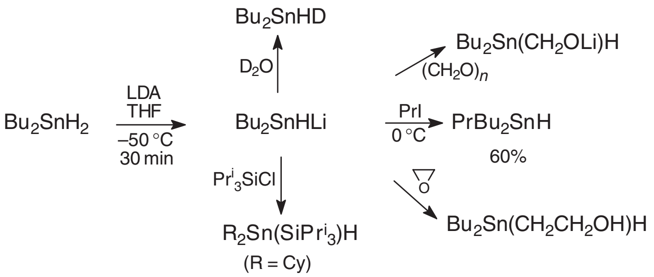
(143)

Deprotonation of the dihydrides with lithium diisopropylamide gives R_2SnHLi, which reacts with electrophiles to provide access to unsymmetrical trialkyltin hydrides. Examples of the reactions of this versatile reagent are shown Scheme 16. The reagent can also be used for attaching a stannylhydride group to a polymer, such as poly(4-chlorobutylstyrene).[396,397]

The use of halide hydrides such as Bu_2SnClH or $Bu_2SnIBrH^-MgBr^+$ ($Bu_2SnIH + MgBr_2$) is referred to in Section 3.14.03.3. If LiI in THF is added to Bu_2SnIH ($\delta Sn = -76.3$), the complex $Bu_2SnI_2H^-Li^+$ ($\delta Sn = -117.9$) is formed with presumably a trigonal-bipyramidal structure with apical iodine atoms. Its reaction with hex-2-enal is compared with other dibutyltin hydrides in Scheme 17.[398]

A novel route to organotin hydrides is provided by the reaction of Lappert's stannylene, $[(Me_3Si)_2CH]_2Sn$:, with water or methanol, which gives the hydroxy- or methoxy-hydrides, $[(Me_3Si)_2CH]_2Sn(OH)H$ and $[(Me_3Si)_2CH]_2Sn(OMe)H$.[399] The X-ray structure determination of the former compound gives an Sn–H bond length of 173(2) pm, as opposed to the value of 170.5(6.7) pm that was found for Me_3SnH by electron diffraction,[400] and 179(4) pm for $HBu^t_2SnSiPr^i_2SnBu^t_2H$ by X-ray diffraction.[125]

The use of tin hydrides for preparing pharmaceuticals is limited by the risk of toxic organotin compounds surviving into the products, and many special hydrides have been designed to overcome this problem. The five nitrogen-containing hydrides **52–56**[401,402] can be washed out with acid. Coordination of nitrogen to the tin enhances the reactivity of the hydride toward alkyl radicals, but reduces the activity of the radical toward organic halides. The ketal

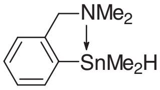


Scheme 16

Bu_2SnH_2	12%	6%	15%
$Bu_2SnI_2H^-Li^+$	80%	9%	trace
$Bu_2SnH_2{\cdot}HMPA$	18%	18%	10%

Scheme 17

57 can be hydrolyzed to a carboxylic acid, which is soluble in base.[403] The pyrene-based hydride **58**[404] can be removed by adsorption on activated carbon.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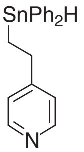
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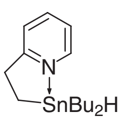
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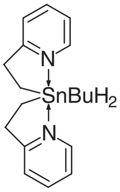
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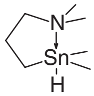
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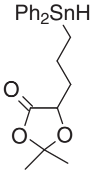
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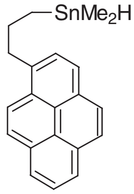
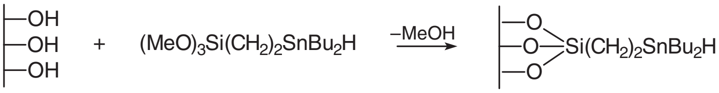

58

The fluorous tin hydrides show a reactivity similar to that of tributyltin hydride,[405,406] and the residues can be extracted into a fluorinated solvent.

Polymer-supported tin hydrides are being increasingly used to avoid the separation problem,[407–412] and the reagent Bu_2SnHLi, described above, is useful for attaching a stannyl hydride group to a polymer such as poly(4-chlorobutylstyrene).[397] The use of a non-cross-linked, soluble polystyrene has also been recommended.[288]

By the reactions shown in Equations (144) and (145), tin hydride can also be bonded to a silica surface, and the product has hydride-carrying capacities as good as the polymer-supported hydrides.[413]

$$Bu_2SnH_2 + CH_2{=}CHSi(OMe)_3 \xrightarrow{AIBN} Bu_2SnH(CH_2)_2Si(OMe)_3 \tag{144}$$



$$\text{|—OH, —OH, —OH} + (MeO)_3Si(CH_2)_2SnBu_2H \xrightarrow{-MeOH} \text{|—O}_3Si(CH_2)_2SnBu_2H \tag{145}$$

3.14.18.2 Properties

Sn–H bond lengths as measured by X-ray diffraction vary widely. Recent values are $[(Me_3Si)_2CH]_3SnH$ (in which the sum of the CSnC angles is 134.2°) −190(4), $[(Me_3Si)_2CH]_2Sn(OH)H$ −173(2), $Me_2Si(Bu^t{}_2SnH)$ −179(4) and 178(4), Bu^t(menthyl)(8-dimethylaminonaphthyl)SnH −152(5) and 165(5), $Si(CH_2CH_2SnH_3)_4$ −160(7) pm.

Hydrolysis of Bu_2SnHLi with D_2O gives Bu_2SnH_2, Bu_2SnHD, and Bu_2SnD_2 in a ratio of 1 : 2 : 1;[397] the NMR spectra of these and the tributyltin hydride isotopomers[414] are given in Table 7.

Most of the many applications of the tin hydrides in organic synthesis proceed by radical chain reactions in which one step involves the reaction of a radical X· with the tin hydride to abstract hydrogen and generate a stannyl radical,

Table 7 NMR spectra of Bu_3SnH and Bu_2SnH_2 isotopomers

Tin hydride	δ^nH	δSn	$^1J(^{117/119}Sn^nH)$/Hz
Bu_3Sn^1H	4.7	−89.2	1501/1575
Bu_3Sn^2H	4.7	−91.0	231/242
Bu_3Sn^3H	4.7	−91.9	1610/1685
$Bu_2Sn^1H_2$	4.58	−204.0	
$Bu_2Sn^1H^2H$		−205.2	
$Bu_2Sn^2H_2$		−206.4	

Table 8 Rates of reactions of radicals with tributyltin hydride

$$\text{X}\cdot + \text{Bu}_3\text{SnH} \longrightarrow \text{XH} + \text{Bu}_3\text{Sn}\cdot$$

X·	k/M^{-1} s^{-1} (T/°C)	*Rate expression*, log k[a]	*References*
Ph·	7.8×10^8 (RT)		417
p-R^f·	2.0×10^8 (20)		418
RCH·CO$_2$Et	3×10^6 (20)	$(8.1 \pm 0.6) - (2.2 \pm 0.6)/\theta$	419
RCMe·CO$_2$Et	2×10^5 (20)	$(8.5 \pm 0.9) - (4.3 \pm 1.2)/\theta$	419
RCMe·CN	3×10^5 (20)	$(6.8 \pm 0.8) - (1.7 \pm 0.8)/\theta$	419
RC·=O	4.1×10^5 (23)	$8.2 - 3.5/\theta$	420
EtC·=O	3.0×10^5 (23)		421
ROC·=O	1.7×10^5 (3)		422
^{1}(Me$_2$C=O)*	1.0×10^9		423
^{3}(Me$_2$C=O)*	5.4×10^8		423
^{1}(RN=NR)*	9.8×10^8		423
^{3}(RN=NR)*	3.5×10^7		423
PhCMe$_2$OO·	1.6×10^3 (72.5)		424
TEMPO	2.5×10^{-2} (60)		425
R$_2$C=N·	3×10^3 (25)		426
R$_2$N·	4.3×10^5 (20)		416

[a] $\theta = 2.3RT$ kcal mol^{-1}.

and it is important to know the rates of this process in order to design synthetic reactions. A selection of recent rate measurements is given in Table 8. A more extensive list covering the literature up to 1999 is given in a review by Chatgilialoglu and Newcomb.[415]

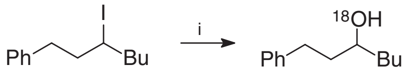
Aryl radicals are much more reactive than alkyl radicals (k ca. 2×10^6 M^{-1} s^{-1}), and rather more reactive than cyclopropyl radicals (ca. 8×10^7) or vinyl radicals (ca. 3×10^8). Fluoroalkyl radicals are also about 100 times more reactive than alkyl radicals, because of contributions from structures $\text{R}^{f\ \delta-} \cdots \text{H} \cdots {}^{\delta+}\text{SnR}_3$ to the transition state. Singlet-excited acetone is twice as reactive as triplet-excited acetone, which shows a similar reactivity to that of the t-butoxyl radical (k ca. 2×10^8 M^{-1} s^{-1}).

As befits a process that is extensively involved in organic synthesis, a number of empirical,[427] semi-empirical, and *ab initio*[428–430] models have been used with the aim of understanding the rates of the abstraction of hydrogen from tin hydrides.

A number of hydrides which carry chiral groups have been prepared with the aim of using them in asymmetric synthesis.[284] One family of these hydrides carries the (1*R*,2S,5*R*)-menthyl (Men*) group,[431] as in, for example, Men*Me$_2$SnH,[432] Men$^*_2$MeSnH,[433] Men*Ph$_2$SnH, and Men$^*_2$PhSnH,[431] and a second family is based on the chirality of the 1,1′-binaphthyl derivatives.[172–174]

3.14.18.3 Reactions

The tin hydrides react with oxygen to give tin hydroxides, presumably via the tin hydroperoxides, and this reaction has been used for converting alkyl halides into ^{17}O- and ^{18}O-labeled alcohols (Equation (146)).[434,435]



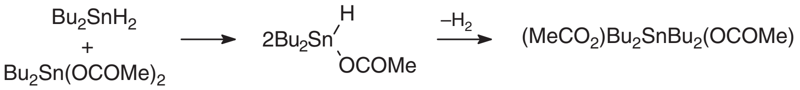
i, ^{18}O$_2$, 5 mol% Bu^{t}Bu$_2$SnCl, 1 mol% AIBN, NaBH$_3$CN, ^{t}BuOH, 60 °C

(146)

The tetraorganostannanes, R$_4$Sn, react with butyllithium to form, in solution, the anions R$_4$SnBu$^-$Li$^+$. On the other hand, butyllithium reacts with tin hydrides to form the anions Bu$_n$SnH$_{3-n}$$^-Li^+$, and there are as yet no reports of species such as Bu$_3$SnH$_2$$^-Li^+$, though five-coordinate halide hydride ate complexes of the type Bu$_2$SnIBrH$^-$ are known in solution.[104]

Transmetallation, in the sense that SnH and MX react to give SnX and MH, is common for many metals M. The reaction of R_2SnH_2 with R_2SnX_2 (M = Sn) to give R_2SnXH proceeds rapidly when X is, for example, halide, carboxylate, or sulfonate, and the use of these stronger Lewis-acidic hydrides for hydrostannation is described in Section 3.14.3.3. The stability of the compounds R_2SnXH depends on the nature of X. Dibutyltin hydride halides are fairly stable at room temperature, but, in the presence of pyridine, hydrogen is evolved and the distannane, $XBu_2SnSnBu_2X$, is formed (Equation (147)). The hydride acetate is less stable, and decomposes in the absence of any catalyst.

The decomposition of both the chloride and acetate hydride is halted by a phenolic inhibitor, indicating a radical mechanism, but the details are not clear.[436] $BuSnCl_2H$, which is believed to be formed when $BuSnH_3$ and $BuSnCl_3$ are mixed, is similarly unstable.[437]



$$Bu_2SnH_2 + Bu_2Sn(OCOMe)_2 \longrightarrow 2Bu_2Sn(H)(OCOMe) \xrightarrow{-H_2} (MeCO_2)Bu_2SnBu_2(OCOMe) \qquad (147)$$

When M is a metal other than hydrogen, reduction of the halides by tributyltin hydride often provides a route to the metal hydrides, such as vinylHgH,[438] vinylAsH_2 and ethylidyneAsH_2,[439] vinylSbH_2,[440] $HMe_2SiMeHSiMe_2H$,[441] and $(\mu\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}H)_2Cl_4$.[442] Other transition metals such as palladium or gold induce the formation of distannanes or oligostannanes;[443] these reactions are discussed in Section 3.19.1 on Sn–Sn bonded compounds.

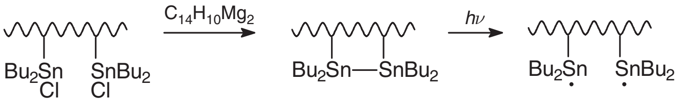
3.14.19 Tin–Tin Bonded Compounds

3.14.19.1 Distannanes

Most of the examples of tin–tin bonding involve the distannanes, R_3SnSnR_3, and oligostannanes, $R_3Sn(SnR_2)_nSnR_3$, that are considered in this section. Tin–tin bonding occurs also in the distannenes, $R_2Sn{=}SnR_2$ (Section 3.14.24.3), and in the few examples of the distannynes, $RSn{\equiv}SnR$ (Section 3.14.24.6), and mono- and distannylstannylenes, R_3SnSnR and $R_3SnSnSnR_3$ (Section 3.14.24.2), that are presently known.

Hexabutyldistannane, which is an important reagent in many organic syntheses, can be prepared very conveniently by reducing bis(tributyltin) oxide with sodium borohydride in ethanol at room temperature. After 5 min, the only tin species present is tributyltin hydride, but in 2 h, its decomposition is catalyzed by the ethoxide ion that is formed to give the distannane in 83% yield.[444] Hexaalkyldistannanes, R_3SnSnR_3 (R = Et, Pr, or Bu), are obtained in ca. 50% yield when the corresponding trialkyltin halides are treated with zinc powder in THF.[445]

Hexa(−)menthyldistannane, with potential applications in asymmetric synthesis, can be prepared in 40% yield by the reaction of (−)menthylmagnesium chloride with tin tetrachloride.[446] Polystyrene-supported distannane has been prepared by condensing together two neighboring $SnBu_2Cl$ groups on the polymer with magnesium/anthracene (Equation (148)), and used as a regeneratable photolytic source of stannyl radicals.[447]



(148)

When compounds R_2SnX_2 and R_2SnH_2 are mixed, redistribution takes place to give the compounds R_2SnHX, which have a stability that depends on the nature of X. The carboxylate hydrides decompose at room temperature with the evolution of hydrogen at a rate which increases with increase in the acidity of the acid HX (e.g., Equation (149)).

$$Bu_2SnH_2 + Bu_2Sn(OAc)_2 \longrightarrow 2Bu_2Sn(OAc)H \xrightarrow{-H_2} (AcO)Bu_2SnSnBu_2(OAc) \qquad (149)$$

The sulfonate hydrides are similarly unstable; the chloride hydrides are relatively stable but decompose in the presence of pyridine. These decompositions are quenched by phenolic inhibitors, and a free radical mechanism must be involved. The details are not clear, but it is important that they should be understood in relation to the use of these compounds in stannation and stannolysis reactions (see Sections 3.14.3.3 and Section 3.14.18.3).[105,436]

The SnSn bond is also formed, but with some complications, when $MeSi(SiMe_2SnBu^t{}_2H)_3$ is treated with LDA, giving $LiBu^t{}_2SnSnBu^t{}_2Li$, which can be hydrolyzed to $HBu^t{}_2SnSnBu^t{}_2H$.[448]

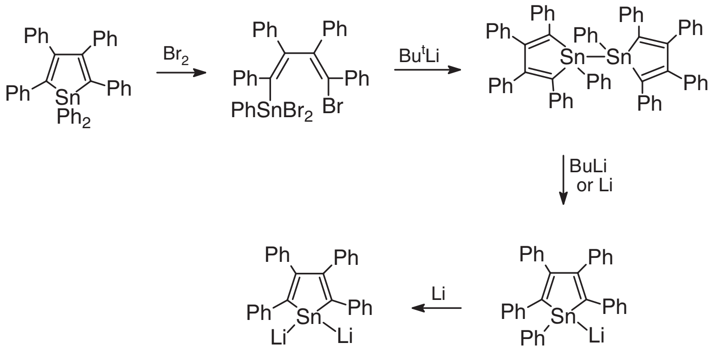
Recent interest has been focused more on the formation of distannanes by treatment of tin hydrides with transition metals, rather than on these more classic methods.[443]

A number of transition metal complexes will catalyze the dehydrogenative coupling of organotin tin hydrides, R_3SnH, to give the distannanes, R_3SnSnR_3.[443] These metals include palladium,[449] gold,[450], hafnium,[451] yttrium, and ruthenium.[452] The catalyst that is most commonly used is palladium, often as $Pd(PPh_3)_4$, and the most active catalysts appear to be the heterobimetallic Fe/Pd complexes, in which both metals are believed to be involved in the catalysis.[443]

The reaction of Cp_2HfClH with Mes_2SnH_2 gives the dihydrodimer, $HMes_2SnSnMes_2H$,[451] but, with other catalysts, dihydrides usually react to give stannane oligomers or polymers (see below).

The distannanes find application in organic synthesis as a source of stannyl radicals, which are usually generated by photolysis, often in the presence of a photosentizer.[453] By this radical mechanism, light induces the redistribution reaction between distannanes, R_3SnSnR_3, and the chalcogenides, R^1ZZR^1 ($Z = S$, Se, or Te), providing a mild route to the organotin chalcogenides R_3SnZR^1.[454] The distannanes react with oxygen under ambient conditions to give the distannoxanes via the distannyl peroxides, and the diacyloxydistannanes, $(R^1CO_2)R_2SnSnR_2(OCOR^1)$, which generate the distannoxanes, $(R^1CO_2)R_2SnOSnR_2(OCOR^1)$, on exposure to air, have been proposed as latent catalysts for the room-temperature vulcanization of silicones, and the preparation of polyurethanes from diols and diisocyanates.[449]

The bis(stannole) in Equation (150) reacts with *t*-butyllithium to give, first, the lithium derivative of the pentaphenylstannole anion ($\delta^{119}Sn = -99.3$), and then the dilithium derivative of the dianion ($\delta^{119}Sn = -30.3$).[237]



(150)

3.14.19.2 Oligo- and Polystannanes

Most of the reactions that can be used to prepare distannanes can be extended to the preparation of oligo- and polystannanes, which have attracted interest for potential use in electronic and optical devices.[455] The structures of the products are not necessarily those of completely linear catenanes, $(R_2Sn)_n$, and different degrees of branching confer different properties. The formation of polymers is also frequently accompanied by the formation of cyclic pentamers or hexamers, and samples prepared by different methods may show substantially different properties.

By creating new Sn–Sn bonds by the hydrostannolysis of SnX bonds by SnH, a series of oligomers, $EtO(CH_2)_2(Bu_2Sn)_m(Bu^t{}_2Sn)(Bu_2Sn)_n(CH_2)_2OEt$ (m and $n = 0-4$) and $EtO(CH_2)_2(Bu_2Sn)_n(CH_2)_2OEt$ ($n = 5-17$), have been prepared and used for characterizing the electronic and NMR spectra of the oligostannanes.[455–457] Tetrakis(trimethylstannyl)stannane can be prepared in low yield from the reaction of lithium with trimethyltin chloride.[458]

The diorganotin dihydrides react with catalysts based on the metallocenes of titanium, zirconium, or hafnium[459–462] to give oligo- and polystannanes.

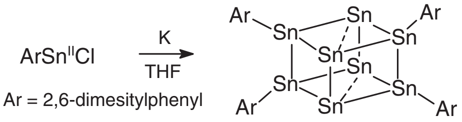
Samarium(II) diiodide reduces dialkyltin dichlorides, R_2SnCl_2 ($R =$ methyl, ethyl, or hexyl), under mild conditions to give polystannanes in good yield, with M.W. up to 4,800, and which are reactive toward oxygen.[463–465] Platinum[466] and rhodium[467] catalysts can give polystannanes free from small cyclic oligomers. Poly(dialkyl)stannanes have been obtained by electrochemical reduction of diorganotin dichlorides,[468] and network poly(monoalkyl)stannanes from the organotin trichlorides,[469] and similar methods can give silane-stannane and germane-stannane co-polymers.[470]

The poly(dialkyl)stannanes absorb at λ_{max} ca. 390–400 nm, and poly(diaryl)stannanes (with substituents in the aryl rings to increase the solubility) absorb at ca. 435 nm. This absorption is due to a σ–σ^* transition, although the apparent helical structure is not the optimum for σ-conjugation.[471,461] When poly(dialkyl)stannanes are cooled below about 273 K, they show thermochromism and a reversible phase change,[459,467,469] with a change of the broad ν(SnSn) Raman absorption at ca. 120 cm^{-1} to an intense sharp signal at ca. 145 cm^{-1}.[472] Linear polystannanes appear to behave as liquid crystals at room temperature, and give highly ordered films when they are sheared.[467]

3.14.19.3 Cage and Cluster Oligostannanes

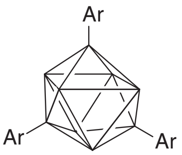
This field has been well supplied with review articles.[473–476] A variety of cluster geometries is known,[2] and the new structures that have been reported have all been discovered fortuitously.

No stannatetrahedrane, $(RSn)_4$, is yet known; in an effort to prepare $(ArSn)_4$ (Ar = 2,6-dimesitylphenyl), the dichloride Ar_2SnCl_2 was treated with potassium but the product was the unique, highly distorted cubane carrying only four aryl groups. The edge SnSn bonds have rSnSn = 285.3(2)–302.3(2) pm, but the diagonal SnSn separations, as marked, have r = 310.7(2) pm (Equation (151)).[477]



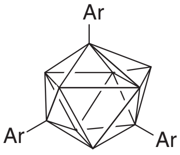
(151)

In an effort to make the distannyne, $Ar^*Sn{\equiv}SnAr^*$ (Ar^* = 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$), Ar^*SnH was heated in toluene; hydrogen was eliminated but SnC bonds also were cleaved, and gave the paramagnetic cluster $Ar^*_3Sn_9$ **59** (g = ca. 2.031), with a structure that is based on the 21-electron $[Sn_9]^{3-}$ cage that is known as a Zintl ion.[478]



$Ar^*_3Sn_9$

59



$Ar_3Sn_{10}^-$

60

In an attempt to prepare clusters containing both tin and a group 13 metal, ArSnCl (Ar = 2,6-dimesitylphenyl) was reduced with KC_8 in the presence of $AlCl_3$ or $GaCl_3$, but the product was the tin-only cluster $[Ar_3Sn_{10}]^+[AlCl_4]^-$ or $[Ar_3Sn_{10}]^+[GaCl_4]^-$, respectively **60**. The cation has the same structure in both compounds, and can be regarded as a mono-tin-capped, one-electron-reduced derivative of the Ar_3Sn_9 structure.[478]

3.14.20 Tin–Metal Bonded Compounds

The metallostannation reactions of alkynes are considered in Section 3.14.4, and compounds where tin is bonded to a transition metal are covered under the appropriate transition metal.

3.14.20.1 Sn–Li

Stannyllithium compounds are important as sources of nucleophilic stannyl anions, and the dialkyltin lithium hydrides, R_2SnLiH, have recently come to prominence as their reaction with electrophilic alkyl halides gives hydrides, R^1R_2SnH, with mixed alkyl groups (see Section 3.14.18.1).[397]

Me_3SnLi and Bu_3SnLi are monomeric in ether and THF and show large Li–Sn NMR couplings. In ether, Bu_3SnLi has $^1J(^7Li–^{119}Sn) = 402.5$ Hz. If HMPA is added, it forms first a solvated monomer, $Bu_3SnLi(HMPA)(OEt_2)_2$ ($J = 358$ Hz), then a solvated dimer, $(Bu_3SnLi)_2(HMPA)_3$ ($J = 486$ Hz), then solvent-separated ion pairs, $Bu_3Sn^-/Li(HMPA)_4{}^+$. Me_3SnLi behaves similarly.[479]

The compound Ph_3SnLi(PMEDETA) (PMEDETA = $(Me_2NCH_2CH_2)_2NMe$) in the crystal has a covalent bond with Sn–Li bond length 281.7 pm, slightly longer than the sum of the two covalent radii (274 pm). This bond is preserved in solution, and in HMPA at −90 °C it shows ^1J(SnLi) = 412 Hz. These large coupling constants probably imply a lot of 5s character in a highly polar bond.[480]

The ^{13}C NMR spectra of Ph_3SnM (M = Li or K) show that negative charge is built up on the *meta*- and particularly the *para*-position of the phenyl rings, implying that the interaction with the $Sn^{\delta-}$ center is inductive rather than hyperconjugative, and the same conclusion comes from studies of the electronic spectra.[481]

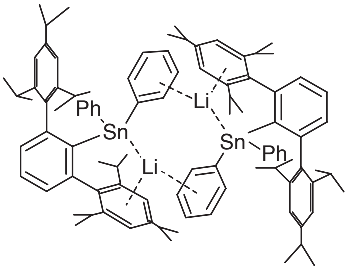
Tetraphenyltin reacts with lithium in liquid ammonia to give $(Ph_3Sn)_3Sn^-Li(NH_3)_4{}^+$. In the crystal, the $(Ph_3Sn)_3Sn^-$ anion has a trigonal-bipyramidal structure.[482]

Phenyllithium reacts with the stannylene, PhSnAr* (Ar* = 2,6-(2,4,6-$Pr^i{}_3C_6H_2)_2C_6H_3$), to give $(Ph_2Ar^*SnLi)_2$ **61** (Equation (152)). The molecule is tetrahedral about the tin (*r*SnLi = 280.9 pm), with the lithium intermolecularly η^6-bonded to one phenyl group and, more weakly, intramolecularly η^6-bonded to one Ar* group.[483]. The compound Ph_2Ar^*SnLi forms a monomeric solvate with ether (*r*SnLi = ca. 278 pm), in which the lithium is coordinated by tin, an ether oxygen, and an η^6-bond to an aryl ring.

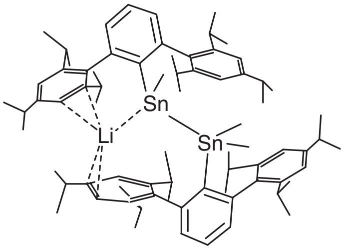
$$\text{Ar*SnPh} + \text{PhLi} \longrightarrow \text{Ar*SnPh}_2\text{Li}\cdot\text{OEt}_2 \longrightarrow (\text{Ar*SnPh}_2\text{Li})_2 \qquad (152)$$

The reaction with methyllithium is more complicated. Ar*SnCl (Ar* = 2,6-(2,4,6-$Pr^i{}_3C_6H_2)_2C_6H_3$) reacts with methyllithium to give, not Ar*SnMe or Ar^*SnMe_2Li, but the stannylstannylene $Ar^*Me_2SnSnAr^*$ and then its MeLi adduct $Ar^*Me_2SnSnMeLiAr^*$ **62**, in which the lithium is bonded to the tin (*r*SnLi = 268.5(8) pm) and η^2- or η^3-bonded to two aryl groups. The SnLi bond is maintained in solution, as shown by the large $^1J(^7\text{Li}–^{117/119}\text{Sn})$ value of 736 Hz. In contrast, the reaction of Ar*SnCl with *t*-butyllithium gives the monomeric stannylene Ar^*SnBu^t (Equation (153)).[484]

$$\begin{tikzcd}
\text{Ar*SnCl} + \text{MeLi} \arrow[r] & {[\text{Ar*SnMe}]} \arrow[r] & {[\text{Ar*SnMe}_2\text{Li}]} \arrow[d] \\
& \text{Ar*SnMe}_2\text{SnMeLiAr*} & \text{Ar*SnMe}_2\text{SnAr*} \arrow[l]
\end{tikzcd} \qquad (153)$$



61



62

This type of drastic redistribution of groups is not unusual when an organotin group is bonded to an electropositive metal; see, for example, the stannylcalcium compounds below. It probably results from insertion of the stannylene R_2Sn: into an RSn bond of R_3SnM.

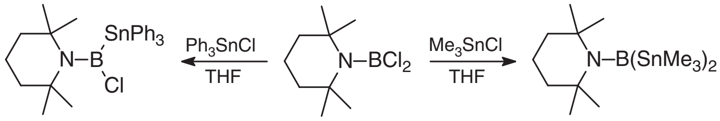
Trineopentylstannylpotassium can be prepared from the reaction of hexaneopentyldistannane with potassium naphthaleneate, and shows $J(^{119}\text{Sn}–^{39}\text{K})$ coupling of 289 Hz and, in the crystal, *r*SnK of 354.8 pm.[485]

3.14.20.2 Sn–Ca

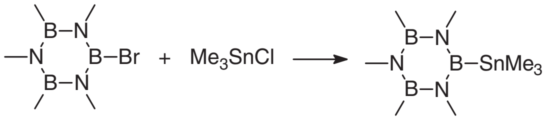
Bis(trimethylstannyl)calcium is formed when hexamethyldistannane reacts with calcium in THF during the course of 3 days, and can be isolated as crystalline $(Me_3Sn)_2Ca\cdot4THF$, which has an octahedral structure.[486] Further reaction with hexamethyldistannane then gives $[(Me_3Sn)_3Sn]_2Ca$. The reaction is faster (6 h at −33 °C) in liquid ammonia, and from the reaction of calcium, strontium, or barium with hexaphenyldistannane, $[(Ph_3Sn)_3Sn]_2Ca$(18-crown-6)$(HMPA)_2$, $[(Ph_3Sn)_3Sn]_2Sr$(18-crown-6)$(HMPA)_2$, and $(Ph_3Sn)_2Ba$(18-crown-6)$(HMPA)_2$ can be isolated as crystalline solids that are very sensitive to oxygen and moisture. The barium stannide has separated cations and pyramidal Ph_3Sn^- anions, and reacts with Ph_2SnCl_2 to give $Ph_3SnSnPh_2SnPh_3$. The calcium and strontium stannides similarly have separated metal cations and pyramidal $(Ph_3Sn)_3Sn^-$ anions, and they react with Ph_3SnCl to give $(Ph_3Sn)_4Sn$.[487]

3.14.20.3 Sn–B

The bond is most readily formed by reaction of SnLi with BCl. Me_3SnCl is more reactive than Ph_3SnCl; thus, tetramethylpiperidinodichloroborane reacts with Ph_3SnCl to give the monostannylborane, but Me_3SnCl gives the distannylborane, and pentamethylbromoborazine reacts with Me_3SnCl, but not with Ph_3SnCl, to give the stannylborazine (Equations (154) and (155)).[488]

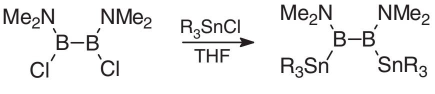


(154)



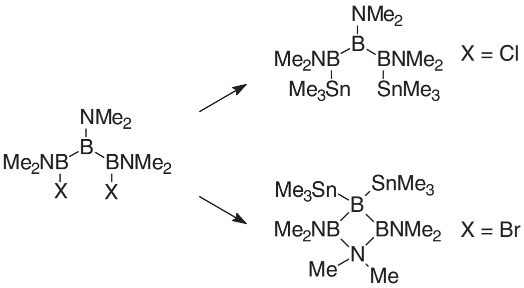
(155)

Trimethyltin lithium was reported to react with $BH_3{\cdot}THF$ to give Me_3SnBH_2,[489] but in a more recent study[488] only $(Me_3SnBH_3)^-Li(THF)_2^+$ was isolated, in which two molecules are connected through Li–H–B bridges. 1,2-Dichloro-1,2-bis(dimethylamino)diborane reacts with Me_3SnCl to give the 1,2-distannyldiborane. 1,3-Dichloro-1,2,3-tris(dimethylamino)triborane reacts in the same way, but the 1,3-dibromo compound, surprisingly, gives a cyclic isomer (Equations (156) and (157)).[490]



R = Me or Ph

(156)

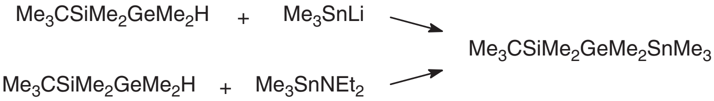


(157)

The stannyl derivatives of the higher boranes have been reviewed,[491] but there has been rather little new work in this field.

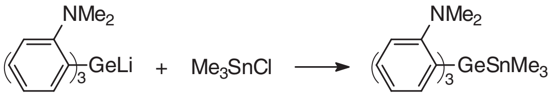
3.14.20.4 Sn–Si, Sn–Ge, Sn–Pb

The Sn–M bond (M = Si, Ge, Sn, or Pb) can be formed by the reaction SnLi + MX, SnX + MLi, SnH + MR_2, $SnNR_2$ + MH, or SnX + MX + Mg or Li. Recent examples of these reactions are given in Equations (158)–(162).[492–496]

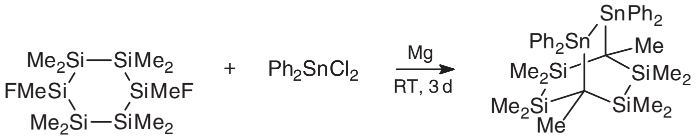


(158)

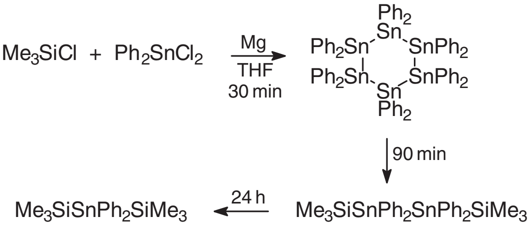
$$(Me_3Sn)_4Ge \xleftarrow[30\%]{GeCl_4} Me_3SnLi \xrightarrow[23\%]{SiCl_4} (Me_3Sn)_4Si \qquad (159)$$



(160)

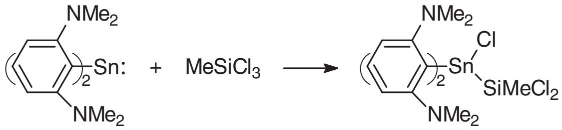


(161)



(162)

Stannylsilanes have also been made by the insertion of a diarylstannylene into an Si–Cl bond (Equation (163)).[497]

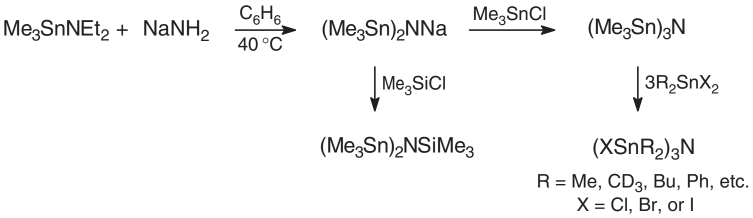


(163)

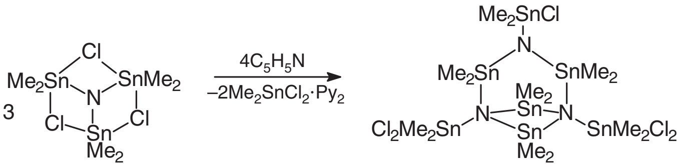
The reaction of dimethyldichlorosilane with di-*t*-butyl- or diphenyl-tin dichloride and magnesium gives the four- or six-membered rings with alternating Si–Sn sequences, but the former compound is apparently formed through the intermediate $ClMe_2Si(SnBu^t{}_2)_2SiMe_2Cl$, which can be isolated.[498] Electrochemical reduction of a mixture of Bu_2SiCl_2 or Bu_2GeCl_2 and Bu_2SnCl_2 gave Bu_2Si/Bu_2Sn or Bu_2Ge/Bu_2Sn co-polymers.[470]

3.14.21 Organotin Derivatives of Nitrogen and Phosphorus

New examples of the preparation of stannylamines, largely by established methods, are shown in Equations (164) and (165). Sodium bis(trimethylstannyl)amine can be prepared from sodium amide and a stannylamine,[499] and can act as the precursor to other bis- and tris(stannyl)amino compounds.[499,500] The tristannylamines are planar about the nitrogen, with the unshared pair in a 2*p* orbital. Tris(chlorodimethylstannyl)amine, with five-coordinate tin, is close to centrosymmetrical, and reacts with pyridine to give a tetrastannabicyclo[3.1.1]heptane.[501]

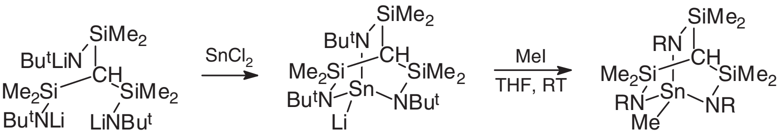


(164)



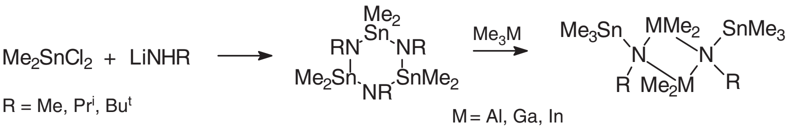
(165)

Similarly, the lithium triaminostannates provide a route into various organostannyltriamines, for example, Equation (166).[502]



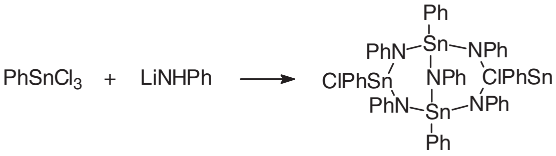
(166)

Lithium alkylamides react with dimethyltin dichloride to give the cyclotristannazane, which is methylated by trimethyl-aluminum, -gallium, or -indium, giving the metal stannylamides, which are coordinatively dimerized (Equation (167)).[503]



(167)

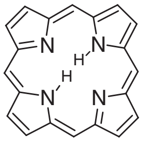
Lithium anilide reacts with phenyl- or methyltin trichloride to give polynuclear Sn–N compounds, in which the phenyltin derivatives are four-coordinate and bicyclic (Equation (168)), and the methyltin derivatives are five-coordinate and tetracyclic.[504]



(168)

3.14.21.1 Organostannyl Porphyrins and Corroles[505]

The diprotic porphyrins, H_2(Por) **63**, give rise to organotin(IV) derivatives, R_2Sn(Por) or RXSn(Por) (X = halide); Por represents a generalized porphyrin dianion, often with alkyl or aryl substituents in the peripheral positions.



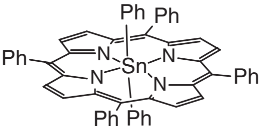
Porphyrin
H_2(Por)

63

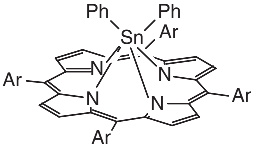
Dialkylstannylporphyrins, R_2Sn(Por), were prepared by the alkylation of Cl_2Sn(Por) with a Grignard[506] or dialkylzinc or organolithium reagent.[507] They are unstable at room temperature and are sensitive to light and to oxygen, reacting to give the peroxides R(ROO)Sn(Por), and then $(ROO)_2$Sn(Por).[508] On the other hand, the methyliodostannylporphyrins, which can be prepared by the oxidative addition of methyl iodide to the Sn^{II}(Por),[509] and methylbromostannylporphyrins, from Li_2(Por) and Me_2SnBr_2,[507] are relatively stable at room temperature.

The aryl- and alkynylstannylporphyrins can be isolated as stable compounds with six-coordinate tin. The reaction of diphenylmagnesium with *trans*-Cl_2Sn(Por) gives *trans*-Ph_2Sn(Por) **65**, and that of Li_2(Por) with diphenyltin dichloride gives *cis*-Ph_2Sn(Por) **66**. In chloroform, in the light, both compounds reacted to give PhClSn(Por).[510]

The alkynylstannyl compounds *trans*-$(PhC{\equiv}C)_2Sn(Por)$ and *trans*-$(Me_3SiC{\equiv}C)_2Sn(Por)$ can be prepared from the lithium acetylides and $Cl_2Sn(Por)$;[507] then, *trans*-$(PhC{\equiv}C)_2Sn(Por)$ reacts with alcohols, 1,2-diols, and phenols to give $(PhC{\equiv}C)(RO)Sn(Por)$, and then $(RO)_2Sn(Por)$.[507]

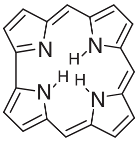


65



66

The triprotic corroles **64** form monoorganotin complexes of the type $RSn^{IV}(Cor)$. PhSn(Cor) is formed when octaethylcorrole reacts with diphenyltin oxide, or phenylmagnesium bromide reacts with ClSn(Cor). The tin is five-coordinate, and is placed 72.2(3) pm above the plane of the four nitrogen atoms, with the corrole assuming a domed structure. The compound is reversibly reduced by transfer of one electron into the π-system.[511]



Corrole
$H_3(Cor)$

64

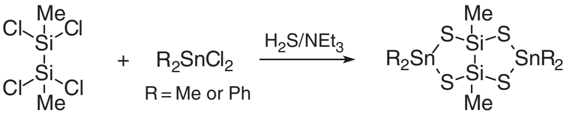
3.14.22 Organotin Derivatives of Sulfur, Selenium, and Tellurium

Phenyltin sesquisulfide, $(Ph_4Sn_4S_6)$, with an adamantine-like structure, reacts with Na_2S to give the sodium thiolate, $PhSnS_3{}^{3-}Na^{+}{}_3$, with near-tetrahedral tin.[512]

Trialkyltin thiolates R_3SnSR^1 are commonly made by the reaction between R_3SnCl and $NaSR^1$, but this may leave traces of sodium chloride in the product, which may impair its use in the MOCVD preparation of semiconductor materials. The photocatalyzed reaction of R_3SnSnR_3 and R^1SSR^1 gives a purer product that does not suffer from this disadvantage (e.g., Equation (169)). The reaction occurs rapidly in room light, and yields are essentially quantitative. Diphenyl diselenide reacts equally rapidly to give $R_3SnSePh$, and diphenyl ditelluride reacts similarly, though more slowly, to give $Me_3SnTePh$.[454]

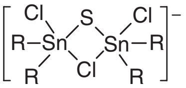
$$Me_3SnSnMe_3 + BuSSBu \xrightarrow[1.5\,h]{\text{room light}} 2Me_3SnSBu \qquad (169)$$

Diorganotin dichalcogenates can be prepared by the reaction of the dichlorides with H_2S in the presence of triethylamine, or with Li_2Se or Li_2Te; then, reaction *in situ* with a tetrachlorodisilane gives distannatetrachalcogenabicyclooctanes (Equation (170)).[513]

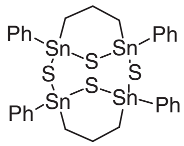


(170)

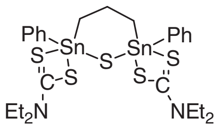
The difunctional distannthianes, $XR_2SnSSnR_2Cl$, do not associate to give the "ladder" dimers that have attracted so much interest in the corresponding distannoxanes, $XR_2SnOSnR_2Cl$. They are formed in equilibrium as four-coordinate monomers from the trimeric sulfides and the dialkyltin dichlorides, and add chloride ion which bridges the two tin atoms **67**,[514] and whereas hydrolysis of $Cl_2SnPh(CH_2)_3SnPhCl_2$ gave a double-laddered octanuclear distannoxane (Equation (134)), reaction of the same compound with Na_2S gave the tricyclic tetranuclear compound **68**. Substitution of two of the four chloro ligands with sodium diethyldithiocarbamate followed by substitution of the two remaining chlorines with sodium sulfide gave the tin sulfide **69**.[515]



67

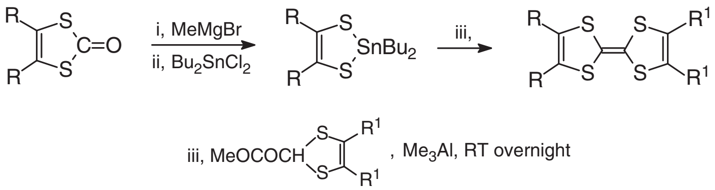


68



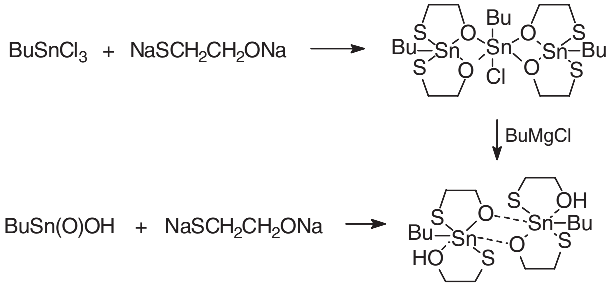
69

Equation (171) illustrates a route by which a double bond can be formed between two dithiole rings. By this type of reaction, a large variety of unsymmetrical tetrathia- and dithiadiselena-fulvalenes have been prepared in exploration of new molecular-based organic metals.[516]



(171)

Butyltin trichloride reacts with the sodium salt of 2-mercaptoethanol to give a trinuclear oxathiastannolane, which, with butylmagnesium chloride, gives an oxathiaststannolane dimer, which can be prepared also from the reaction of butanestannonic acid with 2-mercaptoethanol (Equation (172)).[517]



(172)

3.14.23 Stannyl Radicals[518]

Stannyl radicals are usually generated by homolytic substitution at hydrogen in a tin hydride, or at tin in a distannane, or, conjugatively, at the γ-carbon atom in an allylstannane.[453] The initiator is commonly AIBN at ca. 80 °C. In the presence of a trace of air, organoboranes are oxidized by a radical chain mechanism, and triethylborane is now commonly used as an initiator at temperatures down to −78 °C,[519] and it can be used in aqueous solution.[520] 9-Borabicyclo[3.3.1]nonane (9-BBN) has similarly been used to initiate the reaction of tin hydrides at 0 and −78 °C,[521] and diethylzinc works in the same way.[522]

Organotin radicals have been generated also by the photolysis of stannylcobaloximes[523,524] and of acylstannanes;[525] the latter reaction shows an ^{119}Sn CIDNP effect for the distannane that is formed, confirming the intermediacy of stannyl radicals. A CIDNP effect is also shown by the $Bu_3SnSnBu_3$ and Bu_4Sn that are formed when Bu_3SnK reacts with butyl bromide or iodide, confirming an electron-transfer mechanism,[90,91] and the UV spectrum of the $Bu_3Sn\cdot$ radical has been observed in the reaction of Bu_3SnK with *s*- and *t*-butyl bromide and iodide.[90]

There has been very little work published on the subject of ESR spectra of organotin radicals. The photolysis of the stannylene (2,3,4-Me_3-5-$Bu^tC_6H)_2Sn$: (Ar_2Sn:) in solution gave the persistent radical $Ar_3Sn\cdot$ with $g = 2.0012$, $a(^{13}C) = 1.8(1)$ mT, $a(^{117}Sn) = 175.6(6)$ mT, $a(^{119}Sn) = 182.7(6)$ mT.[526]

The first tin-centered radical has been isolated, though it is not strictly organometallic in the C–Sn bonded sense. It is prepared by the reaction shown in Equation (173), in which the $SnCl_2$ acts both as a substrate for forming the stannyl anion and as a one-electron oxidizing agent.

$$3\mathrm{Bu^t{}_2MeSiNa + SnCl_2{\cdot}dioxane} \longrightarrow \mathrm{(Bu^t{}_2MeSi)_3Sn^{\bullet}} \qquad (173)$$

The NMR spectrum shows $\delta Sn = 2653$, and the ESR spectrum shows $g = 2.0482$, $a(^{117/119}Sn) = 32.9\,mT$. This hyperfine coupling is about five times less than that which is usually found in triorganotin radicals, which have a pyramidal structure. The radical $(Bu^t{}_2MeSi)_3Sn\cdot$ can be isolated as brown crystals, and X-ray analysis shows that the molecule is planar about the tin. Oxidation with the trityl cation gives the stannyl cation, which also is planar at tin.[527]

The first example of an isotope effect on the reaction of stannyl radicals has been reported in the photolysis of 1-naphthyltrimethyltin. The excited singlet crosses to the triplet, which dissociates into the triplet radical pair. Within this pair, triplet-to-singlet reversion and recombination occurs more rapidly in the ^{117}Sn and ^{119}Sn isotopic species because of interaction of the electron spin with the spin-active nuclei; the $Me_3Sn\cdot$ radicals, which escape from the cage and go on to form Me_6Sn_2, are therefore enriched in the spin-inactive (mainly ^{120}Sn) isotope, and this is confirmed by ^{119}Sn NMR spectroscopy, which also shows spin-inactive depletion in the reactant (Scheme 18).[528]

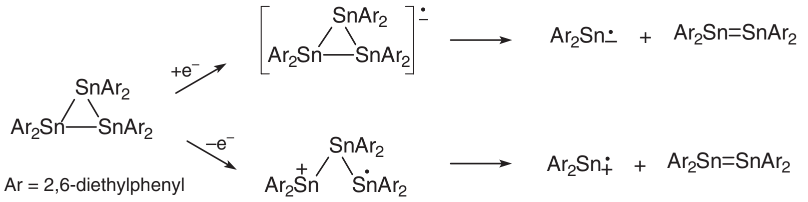
The kinetics of reactions involving the tributylstannyl radical have been refined by laser flash time-resolved UV spectroscopy. The measured extinction coefficient of the $Bu_3Sn\cdot$ radical in benzene was $1620 \pm 40\ M^{-1}\,cm^{-1}$ at 400 nm, the rate constant of the reaction of the *t*-butoxyl radical with Bu_3SnH was $(3.5 \pm 0.3) \times 10^8\,M^{-1}\,s^{-1}$, and the rate constant for the self-reaction of the Bu_3Sn radical was $(3.6 \pm 0.3) \times 10^9\,M^{-1}\,s^{-1}$.[529]

Electrochemical methods have been used to determine the thermochemical properties of the radicals $R_3M\cdot$ (M = C, Si, Ge, and Sn). The reduction potential for $Ph_3Sn\cdot$ is −0.54 V (vs. SCE) in DMSO and −0.46 V in MeCN. DFT computations for the species $R_3M\cdot$, R_3M^+, and R_3M^- have given the geometry of the species, the charge on M, and the spin density on M in the radical. The radicals $Ph_3Sn\cdot$ and $Bu_3Sn\cdot$ are calculated to be pyramidal, with a spin density at tin of 0.77 and 0.83, respectively.[530]

A number of radical ions of organotin compounds have also been detected in solution by ESR spectroscopy.[2] Most of these relate to compounds where the tin carries bulky organic groups that have been introduced to stabilize lower valence states, though there has been a good deal of previous work on the generation of radical ions of simpler organotin compounds in solid matrices.

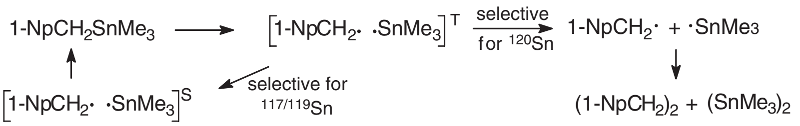
The first of these radical ions was the stannylene radical anion, $[(Me_3Si)_2CH]_2Sn^{\cdot-}$, which was obtained by the reduction of the stannylene with sodium in THF. In the ESR spectrum, it showed a broad singlet with $g = 2.0177$ and $a(^{117/119}Sn) = 11.6\,mT$, but the lifetime was only a few minutes at 20 °C.[531]

Electrochemical reduction of the hexaarylcyclotristannane shown in Equation (174) gave the radical anion of the stannylene with $g = 2.015$, $a(^{117/119}Sn) = 15.1\,mT$, and oxidation gave rise to two spectra, a singlet with $g = 2.020$, $a(^{117/119}Sn) = 11.2$ and 39.4 mT, which was ascribed to the ring-opened distonic radical cation, and a second singlet with $g = 2.022$, $a(^{117/119})Sn = 25.0\,mT$, which was tentatively ascribed to the stannylene radical cation.[532]



(174)

Radical anions have also been obtained recently from the tin equivalents of the alkynes, the distannynes (see Section 3.14.24.6). Reduction of 2,6-di(2,4,6-triisopropylphenyl)phenyltin(II) chloride (ArSnCl) with potassium in THF gave $[ArSnSnAr]^{\cdot-}K^+$, which showed $g = 2.0069$, $a(^{117}Sn) = 0.83\,mT$, $a(^{119}Sn) = 0.85\,mT$, and in the crystal, the radical anion adopts a *trans*-bent structure. The 2,6-di(2,6-diisopropylphenyl)phenyltin analog behaves similarly.[533,534]



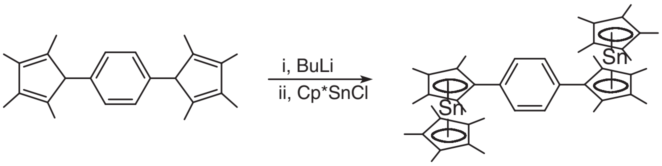
Scheme 18

3.14.24 Stannylenes, Stannenes, and Stannynes[304,535,536]

3.14.24.1 Stannocenes Cp_2Sn:

DFT calculations[537–539] reproduce the angular structure of Cp_2Sn: (stannocene; Cp = cyclopentadienyl), but show that the structure with parallel rings is less stable by not more than 2 kcal mol^{-1}, so that ring-substituted derivatives such as $[(Bu^tMe_2Si)C_5H_4]_2Sn$: may have parallel rings.[540]

New distannenes linked through phenylene, biphenylene, or thiophene spacers have been prepared by reactions of the type shown in Equation (175) (Cp^* = pentamethylcyclopentadienyl),[541] and the *ansa*-stannocene (Equation (176)) is formed in low yield when dimethylfulvene reacts with tin vapor.[542]



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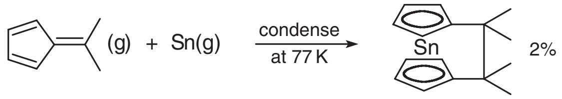
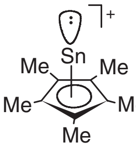


(176)

CpNa and Cp_2Mg react nucleophilically with Cp_2Sn at room temperature to give the paddle wheel Cp_3Sn^- anion 70.[543] Pentamethylcyclopentadienyltin chloride (Cp^*SnCl) reacts with $Li^+B(C_6F_5)_4^-$ to give the $CpSn^+$ cation 71, which is an effective co-catalyst, with Cp_2ZrCl_2, for Ziegler–Natta polymerizations,[544] and decamethylstannocene (Cp^*_2Sn) reacts directly with $Cp^*Sn^+B(C_6F_5)_4^-$,[545] or, indirectly, via Cp^*Sn^+, with $Ga(C_6F_5)_3$, to give the triple-decker cation $Cp^*SnCp^*SnCp^{*+}$ 72.[546]



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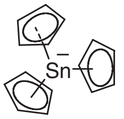

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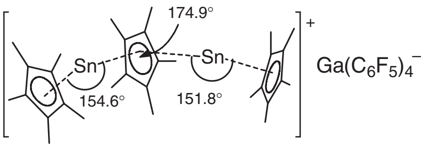
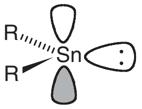


72

3.14.24.2 σ-Bonded Stannylenes, R_2Sn:[2,14,547–549]

This has been a very active field of research and over 60 σ-bonded stannylenes, R_2Sn:, have been isolated, most of them in the last decade. They are usually prepared from the reaction of RLi with $SnCl_2$, and can be rendered persistent by the presence of very bulky groups, or by intra- or inter-molecular coordination[549] that causes the tin to be three or four coordinate. If the unshared pair is regarded as a phantom ligand, the two-coordinate compounds, in solution, have a planar-trigonal structure 73, the three-coordinate compounds are tetrahedral 74, and the four-coordinate compounds are trigonal bipyramidal 75, notionally sp^2-, sp^3-, and sp^3d-hybridized, respectively.



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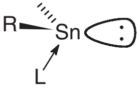

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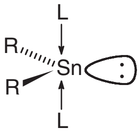
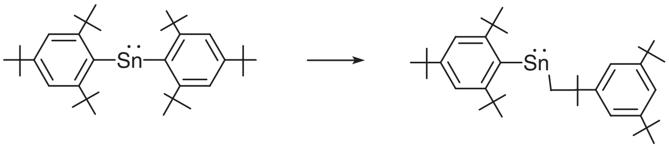


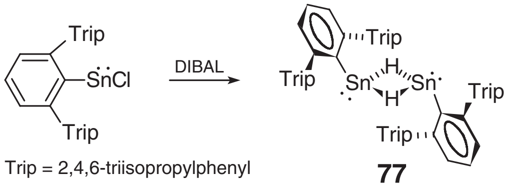
75

The compounds that are two coordinate in solution usually form SnSn-bonded dimers in the solid state, but the three- and four-coordinate stannylenes do not change their structures, and remain as monomers when they crystallize. Bis(2,4,6-tri-*t*-butylphenyl)stannylene is exceptional in that it is stable in the crystal, but in solution it rearranges to the aryl alkyl stannylene **76**.[550] The hydride (and deuteride) **77** is also unusual in that, in solution, it exists as a bright blue monomer, but it separates out as orange crystals in which the tin is rendered three coordinate by bridging hydrogen, with SnH bond lengths of 189(3) and 195(3) pm (Equations (177) and (178)).[551]



76

(177)

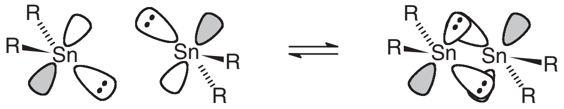


Trip = 2,4,6-triisopropylphenyl

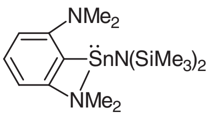
77

(178)

The NMR spectra of the two-coordinate stannylenes in solution show values of δSn ranging from about 1150 (e.g., in ArSnI) to 3750 (in $(Ar_3Sn)Sn$:), with a large anisotropy. The stannylenes behave as Lewis acids, for example, in the three- or four-coordinate complexes (e.g., **78**, **79**, and **80**), which are formed when the molecule carries an intramolecular ligand, and as Lewis bases, particularly in complexing to transition metals (e.g., **81**, **82**, and **83**). The dimerization of stannylenes to give distannenes can be regarded as a result of this amphoteric character (Equation (179)).



(179)



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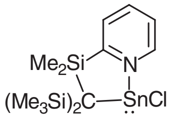

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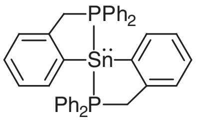
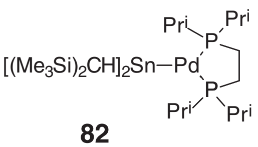


80

$[(Me_3Si)_2CH)_2Sn]_4Ni$

81



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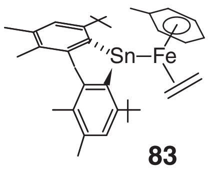
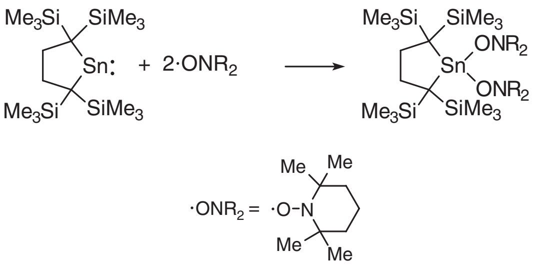
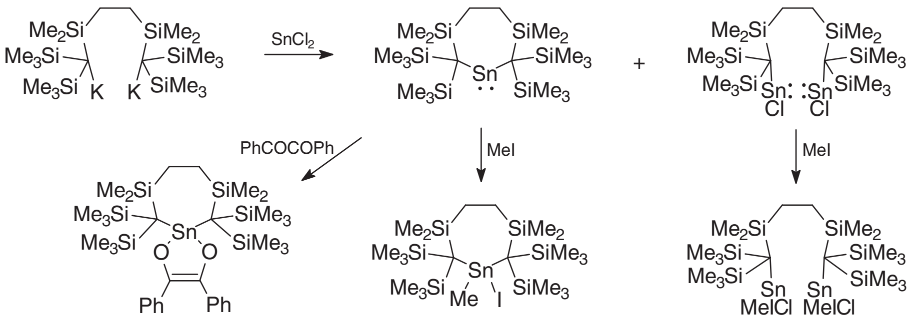


83

A second major characteristic of the stannylenes is their ability to undergo oxidative addition with reagents such as alkyl halides, enones, and 1,2-diones (e.g., Scheme 19)[552] and nitroxyl radicals (Equation (180)).[553]

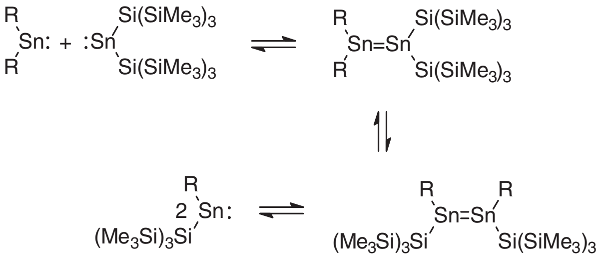


(180)



Scheme 19

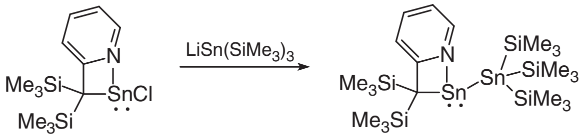
As two-coordinate stannylenes, R_2Sn:, dimerize to give distannenes, $R_2Sn{=}SnR_2$, two different stannylenes, $R^1{}_2Sn$: and $R^2{}_2Sn$:, might be expected to give $R^1{}_2Sn{=}SnR^2{}_2$. In fact, redistribution occurs to give the distannene, $R^1R^2Sn{=}SnR^1R^2$ (Equation (181)).[554,555]



R = 2,4,6-$(F_3C)_3C_6H_2$ or 2-Bu^t-4, 5, 6-Me_3C_6H

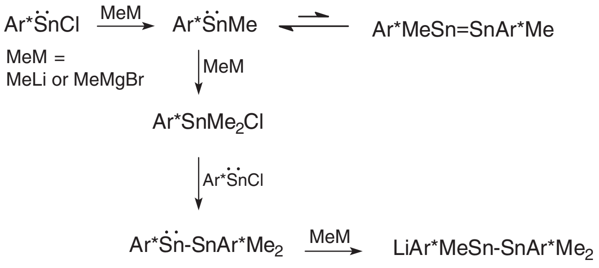
(181)

A number of stannylenes are now known that have a bond or bonds between divalent and tetravalent tin; an example is shown in Equation (182). The product is pyramidal at the stannylene center (δSn = 897) and tetrahedral at the stannyl center (δSn = −502), with $^1J(^{117}Sn)$ = ca. 6400 Hz and $^1J(^{119}Sn)$ = ca. 6700 Hz, and an SnSn bond length of 286.89(5) pm.[556]



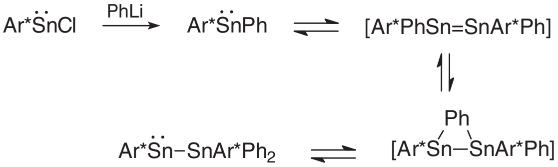
(182)

A similar type of Sn–Sn bonding is observed in $ClSnSn(C_6H_4CHPh_2\text{-}2)$[557] and in $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}Bu^t\text{-}C_6H_2\}SnSnR_3$ (R = Me or Ph).[558] The reaction of methyllithium or methylmagnesium bromide with 2,6-di(2,4,6-triisopropylphenyl)phenyl$Sn^{II}Cl$ (Ar^*SnCl) gives the stannylstannylene $Ar^*SnSnAr^*Me_2$ rather than the symmetrical stannene, $Ar^*MeSn{=}SnAr^*Me$. Presumably, the initial stannylene, Ar^*MeSn:, which is in equilibrium with the expected stannene, reacts further with MeM by oxidative addition to give Ar^*Me_2SnM (M = Li or MgBr); then, this reacts with the original tin(II) chloride to form the SnSn bond (Equation (183)).[484,559] In the crystal, the SnSn bond length is 289.09(2) pm, and the solution shows NMR signals at δSn = 2856.9 for stannylene and 257.4 for stannyl tin. Further reaction with MeLi gives $LiAr^*MeSnSnAr^*Me_2$ with *r*SnSn = 2850.8(4) pm and δSn = −431 and +151, $^1J(^{119}Sn\text{–}^{119}Sn)$ = 4437 Hz.



(183)

When the same Ar*SnCl reacts with PhLi, crystallization of the product at 25 °C gives the stannylene, Ar*SnPh, but crystallization at −30 °C gives Ar*SnSnAr*Ph$_2$ with *r*SnSn = 296.88(5) pm. In solution, the ^{119}Sn NMR spectrum shows that the two compounds are in equilibrium, with δSn = 1517 for Ar*SnPh, and 2800 (stannylene) and 246 (stannyl) in the Sn–Sn bonded compound. The migration of the phenyl group probably occurs though a phenyl-bridged intermediate (Equation (184)).[560]



(184)

2,6-Diisopropoxyphenyllithium, ArLi, reacts with SnCl$_2$ to give the distannylstannylene (Ar$_3$Sn)$_2$Sn: (and a trace of the propellane, (Ar$_2$Sn)$_3$Sn$_2$), perhaps through the formation of Ar$_2$Sn, then Ar$_3$SnLi, which reacts further with SnCl$_2$. In solution, the ^{119}Sn NMR spectrum shows δ(2Sn) = 1302, δ(1Sn) = −14, with $^1J(^{119}\text{Sn}/^{119}\text{Sn})$ = 9011 Hz. In the crystal, the SnSnSn angle is 110.7°, and *r*SnSn is 286.5(1) and 286.7(1) pm.[561] A similar compound is obtained, via Ar*Ph$_2$SnLi, when phenyl[2,6-di(2,4,6-triisopropylphenyl)phenyl]stannylene (Ar*SnPh) is treated with phenyllithium, and then SnCl$_2$. The product, (Ar*Ph$_2$Sn)$_2$Sn:, remains monomeric in the crystal; the SnSnSn angle is 115.19(1)°, and the central tin shows δ^{119}Sn = 3752, which appears to be the furthest downfield shift of any known organotin compound.[483]

3.14.24.3 Distannenes $R_2Sn{=}SnR_2$[14,547,562,563]

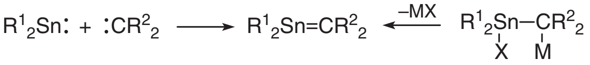
Most stannylenes, R$_2$Sn:, that are two coordinate in solution are in equilibrium with, and separate out as, the distannenes, R$_2$Sn=SnR$_2$. These are the distanna analogs of the alkenes, R$_2$C=CR$_2$, but the nature of the Sn=Sn bond is different from that of the C=C bond, and can be represented by the mutual coordination of the electron pair in the 5*sp*^{2} orbital of one stannylene unit into the vacant 5*p* orbital of the second stannylene unit, as illustrated in Equation (179).[564,565] The molecules are usually *trans*-bent ($\theta = \theta' =$ ca. 40°, $\phi = 0°$), but are easily distorted, and the binding is weak. The prototypical example is Lappert's stannylene, with the geometry shown in Table 9, and a bond dissociation energy of 90 kJ mol^{-1}.

When one of the stannylene partners is already four coordinate, and the second component stannylene carries electronegative substituents, the association may be more in the nature of a simple coordinate bond, R$_2$L$_2$Sn: → SnX$_2$.

Some examples of the stannylenes are given in Table 9. They show the reactions of the component stannylenes with which they are in equilibrium in solution.

3.14.24.4 Stannenes $R_2Sn{=}CR_2$

Stannenes, R$_2$Sn=CR$_2$, are usually prepared either by coupling of a stable stannylene with a stable carbene, or by an elimination reaction (Equation (185)).

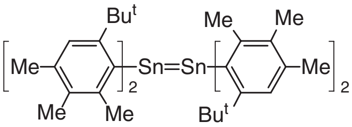
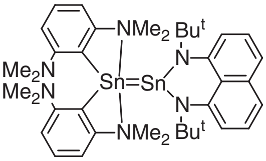
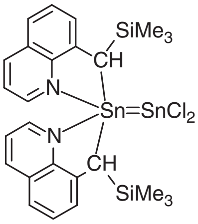


$$R^1{}_2Sn\colon + \colon CR^2{}_2 \longrightarrow R^1{}_2Sn{=}CR^2{}_2 \xleftarrow{-MX} \underset{X}{R^1{}_2Sn}-\underset{M}{CR^2{}_2} \qquad (185)$$

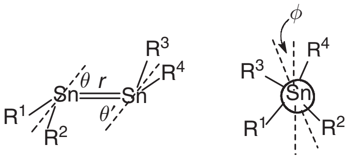
The first stannenes were obtained as reactive intermediates that were identified by their reaction products.[570,571] For example, Me$_2$Sn=C(SiMe$_3$)$_2$ (Scheme 20) was prepared by the 1,2-elimination of LiBr, or by a retro-Diels–Alder reaction, and was characterized by cyclodimerization, by ene reactions with alkenes, and by cycloaddition with 1,4-dienes.[572]

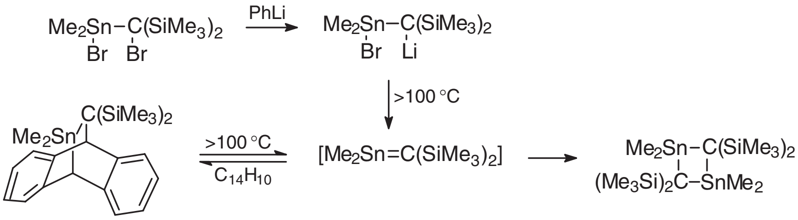
Persistency can be conferred on the stannenes by steric protection to hinder self-reaction. For example, bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene can be prepared as the ether complex (δ^{119}Sn = 288, δ^{13}C = 133.9, UV λ_{max} = 542 nm), as violet crystals, by dehydrofluorination as shown in Scheme 21.[573–576] At room temperature, it slowly converts into the head-to-tail dimer. Protic reagents and methyl iodide add across the double bond, and the bond is reduced by lithium aluminum hydride.

Table 9 Examples of distannenes

Distannene	*r*SnSn (pm)	*θ*, *θ*′ (°)	*ϕ* (°)	*δ*Sn	*References*
$[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_3)]_2$	276.8(1)	41	0	724 and 740	564
$(Bu^t{}_2MeSi)_2Sn{=}Sn(SiMeBu^t)_2$	266.830(10)			630	566
	291.0(1)	21 and 64°		819	526,567
	308.7(2)				568
	296.1(1)			−613.2 and 1264.4	569

Symbols:



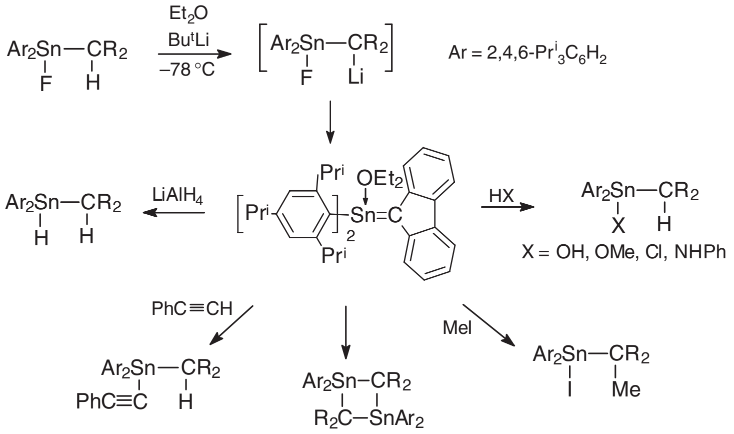


Scheme 20

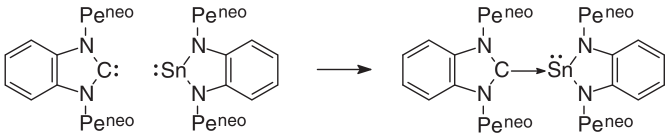
The formation of a stannene from the coupling of a stannylene and a carbene is illustrated in Scheme 22. The stannene is obtained as yellow crystals, and shows, in solution, $\delta^{119}Sn = 374$, $\delta^{13}C = 127$. It is close to planar at both Sn and C, but twisted through 36°, with rSn=C = 203.2(5) pm.

3.14.24.5 Heterostannenes $R_2Sn{=}X$

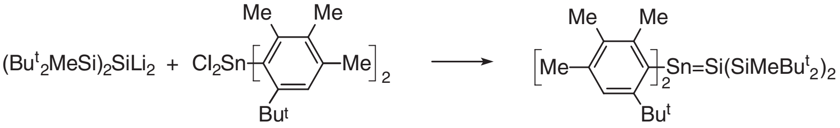
Of the heterostannenes of the other group 14 elements, the compounds $R_2Sn{=}MR_2$ (M = Si, Ge, and Sn) have been prepared,[577] but the plumbastannenes, $R_2Sn{=}PbR_2$, are still unknown. At the time of writing, one silastannene has been prepared (Equation (186)) as deep violet, air-sensitive, crystals. Unlike the distannenes, it does not dissociate in solution, and shows $\delta^{119}Sn = +516.7$. It is near planar at tin but significantly pyramidal at silicon, and twisted by 34.6°, with rSn=Si = 241.88(14) pm, 7% less than the length of an Sn–Si single bond. By analogy with the model described for the distannenes, the bonding can be described in terms of the structure **84** (Equation (187)).[578]

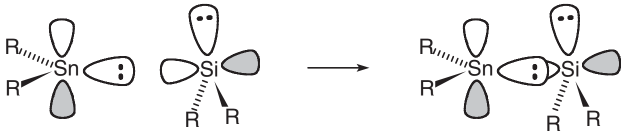


Scheme 21



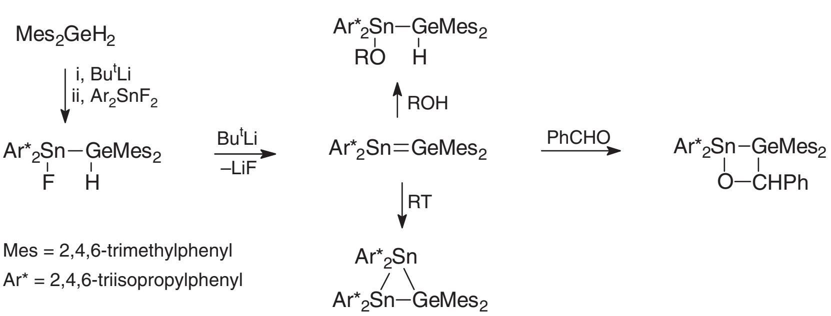
Scheme 22

 (186)

 (187)

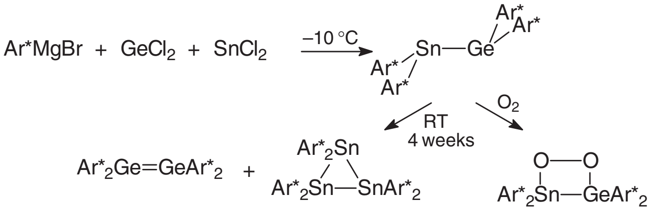
84

Four germastannenes and one disilagermadistannetene are known. Bis(2,4,6-triisopropylphenyl)(dimesitylgerma)stannene ($Ar_2Sn{=}GeMes_2$), with $\delta^{119}Sn = 360$, can be prepared by the reaction shown in Scheme 23. It is stable at −20 °C and reacts with water or methanol, and with benzaldehyde, by regiospecific addition across the double bond. At room temperature, it decomposes to give the corresponding distannagermirane, suggesting that like the distannenes, but unlike the one silastannene that is known (see above), it is in equilibrium in solution with its two components.[579]



Scheme 23

Replacing the mesityl by the larger triisopropylphenyl groups gave a germastannene that could be handled at room temperature. The Grignard reagent Ar*MgBr reacts with a mixture of $GeCl_2$ and $SnCl_2$ in dioxane/THF to give the germastannene as red crystals, with $\delta^{119}Sn = 268$. The Sn═Ge bond length is 255.5 pm, with a bending angle at tin of 43.3° and at silicon of 30.2° (Equation (188)).[580] In solution, it decomposes slowly into the digermene and the cyclotristannane, suggesting that it may dissociate into the germylene and stannylene, and it reacts with dry air to give the germastannadioxetane.

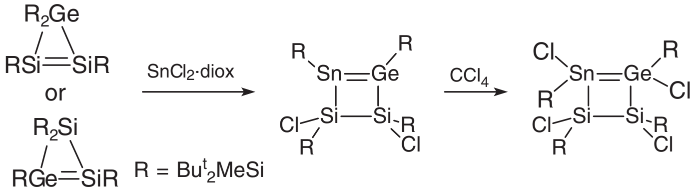


(188)

The corresponding bis(*t*-butyldimethylsilyl)germastannene, $Ar^*{}_2Sn{=}GeR_2$ ($\delta^{119}Sn = 525.1$), is stable in the solid state and in solution, but at 50 °C, it rearranges to the unsymmetrical germastannene, $Ar^*RSn{=}GeAr^*R$, with $\delta^{119}Sn = 373.4$ (Equation (189)).[581]

$$R_2GeLi_2 + Ar^*SnCl_2 \xrightarrow{THF} Ar^*{}_2Sn{=}GeR_2 \xrightarrow[50\,^\circ C]{C_6H_6} Ar^*RSn{=}GeAr^*R \qquad (189)$$

The disilagermirenes shown in Equation (190) react rapidly with $SnCl_2$ to give the disilagermastannetene as orange crystals, with $\delta^{119}Sn = 439.3$, which is indefinitely stable in solution and in the solid state. The Sn═Ge bond readily undergoes addition and cycloaddition reactions, and, with carbon tetrachloride, the tetrachloro derivative is formed.[582]



(190)

Table 10 gives the calculated Sn═X bond energies and bond lengths for the species $H_2C{=}X$ and $H_2Sn{=}X$ (X = O, S, Se, and Te). The difference between the strengths of the σ- and π-bonds shows how much thermodynamic advantage might be gained by oligomerization of the monomer. The bond distance, *r*, indicates how difficult it might be to build in steric hindrance against such oligomerization: the longer the bond, the larger must be the groups that replace the hydrogen atoms.[583]

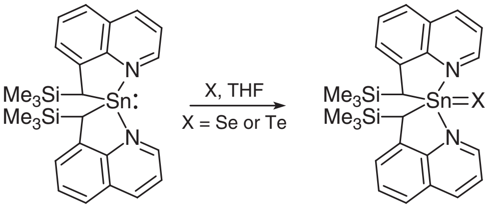
Research into these compounds has followed the usual pattern for the study of very reactive compounds.[584,585] First, the compounds are obtained only as transient intermediates that are characterized by their reactions, then longer-lived compounds are obtained that can be studied in solution at low temperature; finally, compounds are designed, usually by building in steric protection, that can be obtained as crystalline solids, the structures of which can be determined by X-ray crystallography. These advances have been made alongside related studies of the chalcogenides of the other group 14 metals.[584,585]

Heterostannenes can also be stabilized by intramolecular coordination by a nitrogen substituent. The four-coordinate stannylene shown in Equation (191) reacts with sulfur to give the dimeric thione, but with selenium or tellurium to give the five-coordinate monomeric yellow-orange selenone or red tellurone. The Sn═Se and Se═Te bonds, at 239.8 and

Table 10 Calculated σ- and π-bond energies (kcal mol^{-1}) and bond lengths *r* (pm) [B3LYP/TZ(*d*,*p*)] for the molecules $H_2C{=}X$ and $H_2Sn{=}X$

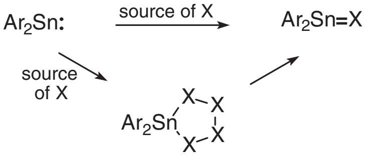
$H_2M{=}X$		X = O	X = S	X = Se	X = Te
$H_2C{=}X$	σ	93.6	73.0	65.1	57.5
	π	95.3	54.6	43.2	32.0
	r	120.00	161.7	175.8	194.9
$H_2Sn{=}X$	σ	94.8	69.3	64.3	56.4
	π	32.8	33.5	30.6	26.3
	r	180.2	222.2	234.6	254.3

261.9 pm, respectively, are shorter than Sn–Se or Sn–Te single bonds, and the Sn chemical shifts, at δ^{119}Sn = −111.55 and −350.34, are upfield from the values that are observed for equivalent two-coordinate tin compounds.[586]



(191)

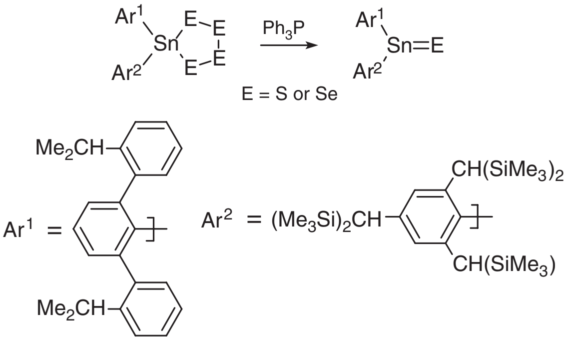
The stannane-thiones, -selenones, and -tellurones are usually prepared by addition of the element, or a source of the element such as a thiirane, to a stannylene, or by dechalcogenation of a tetrachalcogenostannolane with triphenylphosphine (Equation (192)).



(192)

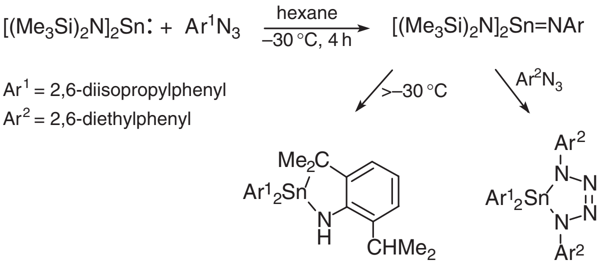
As yet, no monomeric stannaketone, R$_2$Sn=O, either with or without intramolecular coordination, has been reported (see Section 3.14.16.2), but, in recent years, both the two-coordinate stannathiones and stannaselenones have been isolated and characterized by using these reactions.[587] Early attempts with large, but not large enough, aryl groups on the tin gave transient thiones and selenones that could not be isolated, but were characterized by their cyclodimerization or other addition reactions.[588]

2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl(2,4,6-triisopropylphenyl)stannaselenone[589] and the corresponding thione[590] were obtained in solution in 1995 and 1996, respectively, and, with the aryl groups as 2,2′-diisopropyl-*m*-terphenyl and triisopropylphenyl, both the thione and the selenone have now been obtained as red crystals, with δ^{119}Sn as 531 and 440, respectively.[591] The selenone is trigonally planar about the tin, with rSnSe = 237.5(3) pm (Equation (193)).



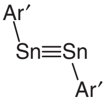
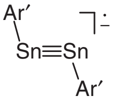
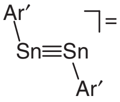
(193)

There has been little recent work on the stannaimines, R$_2$Sn=NR. The compound [(Me$_3$Si)$_2$N]$_2$SnNAr (Ar = 2,6-diisopropylphenyl) can be obtained as dark red crystals that are stable below −30 °C, and have an Sn=N bond length of 203.0(3) pm. Above −30 °C, cyclization slowly occurs by intramolecular addition of CH of an isopropyl group to the double bond. It reacts with 2,6-diethylphenyl azide to give the stannatetraazole (Equation (194)).[592]



(194)

Table 11 Diarylstannyne neutral molecule, radical anion, and dianion

			
*r*Sn–Sn (pm)	266.75	280.8	278.9
Sn–Sn–C (°)	125.2	97.9	104.8

The stannaphosphenes $R_2Sn{=}PAr$ (R = $(Me_3Si)_2CH$ or 2,4,6-triisopropylphenyl, Ar = 2,4,6-tri-*t*-butylphenyl) can be prepared by elimination of HF across the FSn–PH unit with *t*-butyllithium, but no crystal structures appear yet to have been reported. Protic reagents add across the Sn═P bond, and enones, 1,2-diones, and *ortho*-quinones react by [2 + 4] cycloaddition.[593–595]

3.14.24.6 Distannynes RSn≡SnR[596]

In recent years, the first distannynes have been obtained. Reduction of 2,6-di(2,6-diisopropylphenyl)phenyltin(II) chloride (Ar^*SnCl) or 2,6-di(2,4,6-triisopropylphenyl)phenyltin(II) chloride (ArSnCl) with sodium or potassium has given not only the stannynes $Ar^*Sn{\equiv}SnAr^*$ and ArSn≡SnAr, but also the radical anion $[ArSn{\equiv}SnAr]^{\cdot -}$, and the dianions $[ArSn{\equiv}SnAr]^{=}$ and $[Ar^*Sn{\equiv}SnAr^*]^{=}$.[534] The properties of the Ar compounds are as shown in Table 11.

The alkynes ArSn≡SnAr and $Ar^*Sn{\equiv}SnAr^*$ are obtained in 30–40% yield as purple or dark blue-green crystals, respectively, and show the same UV/VIS spectra in the crystals and on solutions. Unfortunately, the ^{119}Sn NMR signal could not be observed for either compound. Both are sensitive to air; ArSn≡SnAr is oxidized to the distannoxides ArSnOSnAr, and reacts with trimethylsilyl azide to give the distannazane $ArSnN(SiMe_3)SnAr$.[596] The molecules are *trans*-bent, and the Sn–Sn bonding can be represented in similar terms to those described above for the distannenes.[565,597] The SnSn bonds are much shorter than Sn–Sn single bonds ($Ph_3SnSnPh_3$, 279.1 pm), and shorter than any known bond in a distannene, and the bond order is estimated to lie beween 1.5 and 2.0.

Reduction of the distannynes with sodium or potassium gives the radical anions. $[Ar^*Sn{\equiv}SnAr^*]^{\cdot -}$ has the *trans*-bent geometry given in Table 11, and shows an ESR spectrum with $g = 2.0691$, $a(^{117}Sn) = 0.83\,mT$ and $a(^{117}Sn) = 0.85\,mT$, indicating a very low unpaired spin density on tin. The main line is about 0.6 mT wide, and no proton coupling is resolved.

Reduction of the aryltin(II) chlorides with lithium, sodium, or potassium for some days gives the dianions, with the alkali metals sandwiched between aryl rings from different terphenyl groups.

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3.15
Lead Organometallics

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3.15.1 Introduction

The interest in tetraorganolead compounds reached a climax about 30 years ago, when worldwide more than 600,000 tons of tetraethyllead as well as large quantities of tetramethyllead were produced annually and used mainly as efficient antiknocking additives in gasoline. With the restriction and, finally, abandonment of leaded gasoline in many countries, the production of tetraorganolead compounds declined. Seyferth described *The Rise and Fall of Tetraethyllead* in two fascinating essays.[1,2] The ready accessibility and easy decomposition of tetraethyllead into lead atoms and organic compounds have opened up promising new applications, such as, to mention just a few, chemical vapor deposition (CVD) of lead titanate, lead zirconate, and other lead-containing films,[3–12] as well as lead nanoclusters.[13]

In the last few years, the interest in organolead(IV) compounds has moved from preparative aspects more to the analytical detection of such compounds or their decomposition products. On the other hand, the synthesis and characterization of low-valent organolead compounds has experienced an impressive increase; numerous remarkable results have been achieved, and these constitute the major part of this survey.

3.15.2 Plumbanes and Diplumbanes

Hand in hand with the declining ecological significance of tetraorganolead compounds, the interest in such molecules is also decreasing, and comprises now mostly purely academic aspects. Most results in this field have been summarized in COMC(1982) and COMC(1995), as well as the five volumes of the Gmelin series *Organoelement Compounds* that appeared between 1987 and 1996.[14–18]

An X-ray diffraction study of tetramethyllead performed at 150 K showed the expected tetrahedral structure of the molecule, which crystallizes in the cubic SnI_4 type.[19] In contrast, the fluoromethylplumbanes Me_nPbF_{4-n} exhibit large distortions from tetrahedral symmetry. According to *ab initio* pseudo-potential calculations, the C–Pb–C angle in Me_2PbF_2 is widened to 135°; in Me_3PbF, on the other hand, the C_3Pb molecular fragment is almost planar.[20,20a]

Although the reaction of triphenyllead chloride with the THF adduct of tris(trimethylsilyl)silyllithium affords the lead compound **1** in 81% yield, the analogous reaction of diphenyllead dichloride affords two compounds that can be isolated in 21% and 30% yields, namely the plumbane **2** and the diplumbane **3**. Because of the steric demands of the silyl groups, the Pb–Pb bond in **3** has a length of 291.1(1) pm, somewhat stretched compared with that in hexaphenyldiplumbane (284.4(6) pm) (Equation (1)).[21]In the same way as molecules **1–3**, the corresponding tris(trimethylsilyl)germyl-substituted lead compounds **4–6** are also accessible (Equation (2)). An X-ray crystallographic study of **5** revealed a Ge–Pb–Ge angle of 135.0(1)°, thus clearly demonstrating the higher steric demands of the two germyl groups.[22]

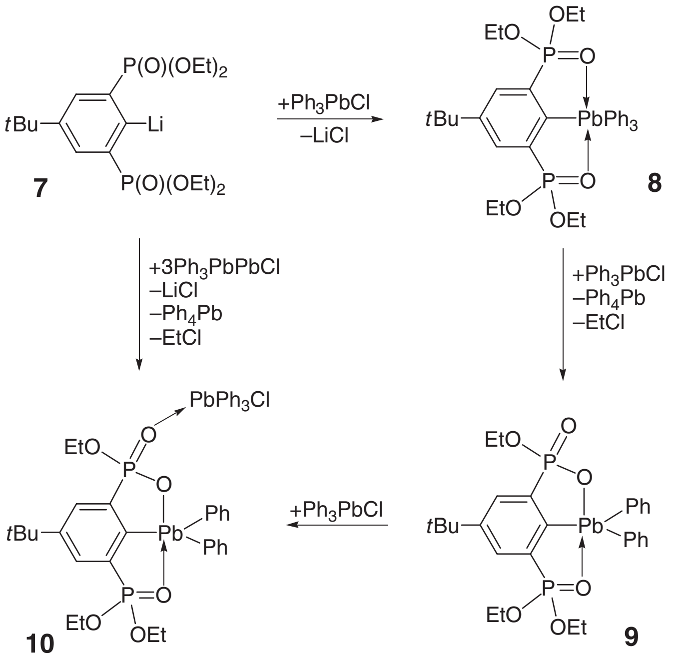
$$Ph_3PbCl + LiSi(SiMe_3)_3 \longrightarrow \underset{\mathbf{1}}{Ph_3PbSi(SiMe_3)_3} + LiCl$$

$$\underset{\mathbf{2}}{Ph_2Pb[Si(SiMe_3)_3]_2} \qquad \underset{\mathbf{3}}{[(Ph)_2Si(SiMe_3)_3]Pb{-}Pb[Si(SiMe_3)_3(Ph)_2]} \tag{1}$$

$$Ph_3PbCl + LiGe(SiMe_3)_3 \longrightarrow \underset{\mathbf{4}}{Ph_3PbGe(SiMe_3)_3} + LiCl$$

$$\underset{\mathbf{5}}{Ph_2Pb[Ge(SiMe_3)_3]_2} \qquad \underset{\mathbf{6}}{[(Ph)_2Ge(SiMe_3)_3]Pb{-}Pb[Ge(SiMe_3)_3(Ph)_2]} \tag{2}$$

Treatment of triphenyllead chloride with the lithium compound **7** afforded first the intramolecular [4 + 2]-coordinated tetraarylplumbane **8** as colorless crystals in 70% yield. Repeated treatment of **8** with triphenyllead chloride finally furnished the pentacoordinated compound **9** in the form of its triphenyllead chloride adduct **10** in 69% yield, also as colorless crystals. The compounds **8** and **10** were characterized by a complete NMR dataset, and by X-ray crystallography (Scheme 1).[23]



Scheme 1

The reactions of tri-*tert*-butylplumbyllithium with various phosphorus chlorides have been investigated. For example, reaction of the lithium compound with diphenylchlorophosphane afforded hexa-*tert*-butyldiplumbane and tetraphenyldiphosphane as the isolated products. Analogous reactions with *tert*-butyl-substituted phosphorus chlorides yielded (tri-*tert*-butylplumbyl)di-*tert*-butylphosphane or tri-*tert*-butylplumbyl(amino)-*tert*-butylphosphane. These and other molecules were characterized by multinuclear magnetic resonance spectroscopic studies.[24]

Treatment of the trialkyllead bromide **11** with magnesium results in the formation of compound **12**, a further hexaalkyldiplumbane with a very long Pb–Pb bond length of 296.8(2) pm in 7% yield (Equation (3)).[25]Unexpectedly, the reaction of diphenyllead dichloride with 2 equiv. of alkyllithium reagent does not give rise to the plumbane $Ph_2Pb[C(SiMe_3)_3]_2$; instead, the pentaphenyl[tris(trimethylsilyl)methyl]diplumbane **13** is obtained in 29% yield. Like compound **12**, this also possesses a long Pb–Pb bond length of 290.8(1) pm. The mechanism of formation of the unusual diplumbane **13** probably involves migration of a phenyl group and a radical coupling to form the Pb–Pb bond (Equation (4)).[26]

$$\underset{\mathbf{11}}{2[(Me_3Si)_3C]Me_2PbBr} + Mg \longrightarrow \underset{\mathbf{12}}{[(Me_3Si)_3C]Me_2Pb{-}PbMe_2[C(SiMe_3)_3]} \qquad (3)$$

$$Ph_2PbCl_2 + 2\,Li[C(SiMe_3)_3] \longrightarrow \underset{\mathbf{13}}{Ph_3Pb{-}PbPh_2[C(SiMe_3)_3]} \qquad (4)$$

Attempted syntheses of unsymmetrically substituted hexaaryldiplumbanes of the type $Ar_3Pb{-}PbAr'_3$ met with only partial success, since the resulting products were contaminated by the symmetrical diplumbanes $Ar_3Pb{-}PbAr_3$ and $Ar'_3Pb{-}PbAr'_3$, which could not be separated. In contrast, the germylplumbanes (p-tolyl)$_3$Pb–GePh$_3$ and (p-tolyl)$_3$Pb–Ge(p-tolyl)$_3$ were isolated in pure form, and characterized by X-ray crystallography.[27]

The reaction of biphenylmagnesium bromide with $PbCl_2$ gave rise to hexakis(biphenyl)diplumbane, the Pb–Pb bond length (286.97(10) pm) of which is only marginally longer than that of hexaphenyldiplumbane.[28]

In the presence of catalytic amounts of tri-*tert*-butylphosphane, tellurium smoothly undergoes insertion into the Pb–Pb bond of hexaphenyldiplumbane to furnish the corresponding diplumbyl telluride in 95% yield.[29]

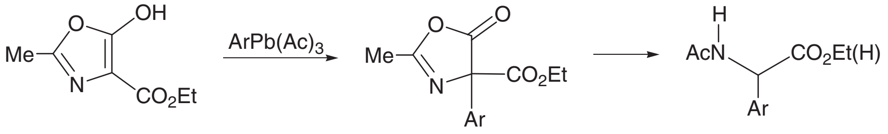
Nucleophilic cleavage of hexaphenyldiplumbane by potassium *tert*-butoxide results in the formation of the plumbyl anion $K^+PbPh_3^-$, which is principally characterized by the high field shift of the C-1 nuclei to 191.11 ppm in the NMR spectrum; hexaphenyldigermane and hexaphenyldistanne behave analogously.[30]

3.15.3 Applications in Organic Synthesis

3.15.3.1 C–C Bond Formation with Organolead Reagents

In the past few years, the use of organolead compounds in synthetic organic chemistry has increased remarkably. This is well documented in numerous original papers and two review articles that are principally devoted to the chemistry of organolead triacetates.[31,32] The latter compounds have proved to be relatively cheap and versatile reagents for the electrophilic alkylation, vinylation, and alkynylation of soft carbon nucleophiles. The aryllead triacetates occupy a prominent place, since they are simple to prepare, even when highly functionalized, and possess the ability to easily form C–C bonds, especially quaternary centers, in high yields and under extremely mild reaction conditions. They have proved to be equally useful in the synthesis of complex organic molecules as well as in diastereoselective and enantioselective reactions. On account of their very specialized nature, these topics are not included in this survey; moreover, they have recently been covered in a comprehensive review article.[32] (see also COMC III, Volume 11, Chapter 11).

The reactions of the 5-oxazolanes **14** with aryllead triacetates are examples of the typical arylation of heterocycles by which products **15** are formed. After hydrolysis and decarboxylation, heterocyclic compounds **15** are converted to the arylglycines **16** in yields of 81–93% (Equation (5)).[33]



14 **15** **16**

(5)

The arylation of phenols also proceeds smoothly. Even the sterically overcrowded 3,5-di-*tert*-butylphenol **17** reacts with 2,4,6-trimethoxyphenyllead triacetate **18** to furnish compound **19**, which is isolated in 87% yield, together with 10% of the monoarylation product (Equation (6)).[34]

17 **18** Ar = 2,4,6-$MeO_3(C_6H_2)$ **19**

(6)

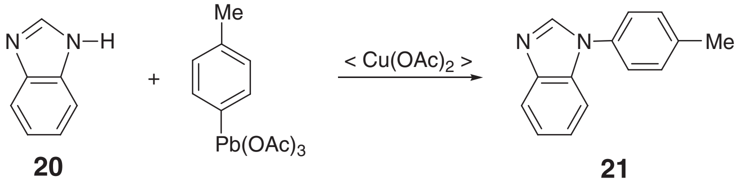
In order to determine whether or not these and similar reactions proceed through radical species, 2-(3,3-diphenylprop-2-enyloxy)phenyllead triacetate, a compound containing an internal radical trap, was prepared, and its behavior in base-catalyzed C-arylation reactions investigated. The absence of benzofuran derivatives among the products excluded the participation of radical species in these processes.[35]

3.15.3.2 N-arylations with Organolead Reagents

Similar to the above-mentioned C-arylations, the experimental results from copper-catalyzed N-arylations do not support the participation of radical species.[35]

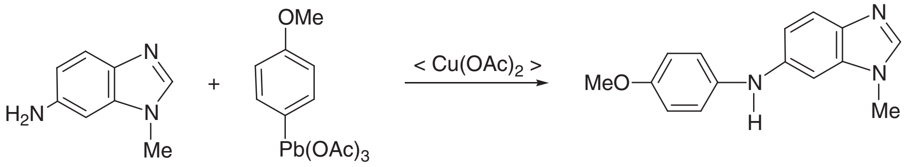
Only a few more recent examples of the numerous studies on N-arylations with aryllead triacetates will be discussed here. For earlier publications in this field, the interested reader is referred to the pioneering arylations of aliphatic and aromatic amines by Barton's group,[34,36–38] as well as the comprehensive review article by Elliott and Konopelski.[32]

Arylations of amines and nitrogen-containing heterocycles require the presence of a copper catalyst, usually 10% copper(II) acetate. For example, the reaction of 4-$MeC_6H_4Pb(OAc)_3$ with the benzimidazole **20** affords the arylation product **21** in 98% yield.[39,40] Similarly, the arylation of the amino groups of heteroaromatic compounds **22** and **23** gives rise to the corresponding products **24a** and **25** in good to excellent yields (Equations (7)–(9)).[41,42]



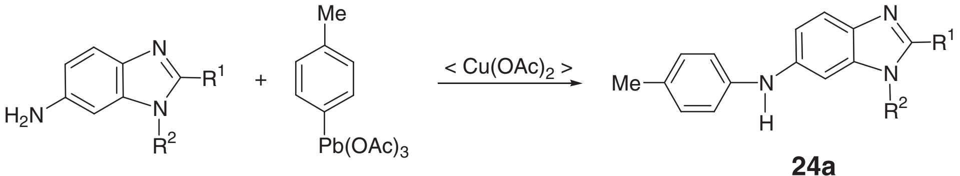
20 **21**

(7)



22 **24**

(8)



23 **24a**

(9)

Imines, sulfonamides, and hydantoins undergo copper-catalyzed arylation by aryllead triacetates in the same manner. In many cases, prior conversion of the N–H bonds into the corresponding sodium salts is recommended.[43,44]

3.15.3.3 Palladium-catalyzed Cross-couplings with Organolead Compounds

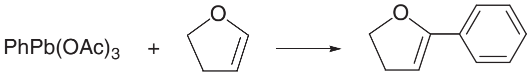
Aryllead triacetates can also serve as substitutes for organostannanes in the palladium-catalyzed Stille reaction or can be used in the palladium-mediated Suzuki–Miyaura reaction in place of the generally employed organoboron compounds. In Stille-type reactions, aryllead triacetates are used with tetraorganostannanes in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) as catalyst and copper(I) iodide as co-catalyst. Presumably, CuI slows down the competing homocoupling reaction. In all cases, it is important that sodium methoxide be used in excess. Under these conditions, the aryllead triacetates **25** react with vinyl- or furyltributylstannanes to afford the compounds **26** in good yields. Only traces of products of the homocoupling reactions are observed (Equation (10)).[45]

$$\underset{\textbf{25}}{\mathrm{ArPb(OAc)_3}} + \mathrm{RSnBu_3} \longrightarrow \underset{\textbf{26}}{\mathrm{Ar{-}R}} \qquad (10)$$

Ar = Ph, R = vinyl
Ar = 4-$MeOC_6H_4$, R = 2-furyl
Ar = 4-$MeOC_6H_4$, R = 3-furyl

Stille-type reactions can be performed under analogous conditions. For example, reactions of aryllead triacetates with arylboronic acids give rise to the respective biaryls in yields of around 75%.[46]

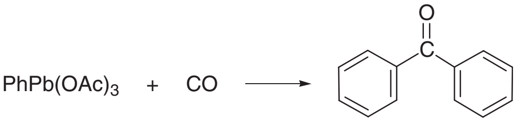
Reactions of aryllead triacetates with olefins (Heck-type reactions) proceed similarly but do not require CuI as co-catalyst. From the numerous reported reactions, that of phenyllead triacetate with 2,3-dihydrofuran is mentioned as a typical example. This affords the C–C coupling product **27** in 68% yield, together with 10% of the homocoupling product (Equation (11)).[47]



27

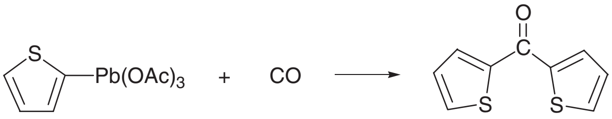
(11)

Carbonylations of organolead triacetates with CO (1 atm), which proceed in the presence of $Pd_2(dba)_3$ and an excess of sodium methoxide to furnish symmetrical ketones, such as compounds **28** and **29**, deserve special mention (Equations (12) and (13)).[48]



28

(12)

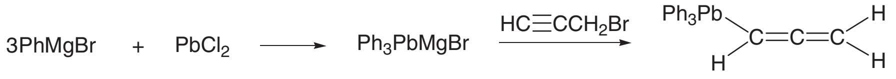


29

(13)

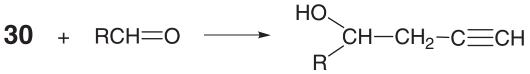
3.15.3.4 Miscellaneous

Apart from the organolead triacetates and, albeit more rarely, the diorganolead diacetates, only few other lead compounds have found their way into synthetic organic chemistry. One example is triphenyl(allenyl)lead that can act as a propargylating reagent. The reaction of triphenylplumbylmagnesium bromide with propargyl bromide affords as the main product triphenyl(allenyl)lead **30**, which, in the presence of Lewis acids such as $BF_3 \cdot OEt_2$ or $TiCl_4$, reacts with numerous alydehydes to give the corresponding homopropargylic alcohols **31** in good yields (Equations (14) and (15)).



30

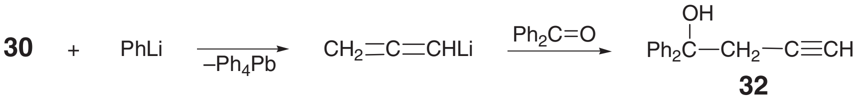
(14)



31

(15)

Benzophenone does not react under these conditions. However, when a prior transmetallation between **30** and phenyllithium is performed, and the new organolithium compound is allowed to react with benzophenone, the homopropagylic alcohol 1,1-diphenyl-3-butyn-1-ol **32** is obtained in 69% yield (Equation (16)).[49]



$$\mathbf{30} + \mathrm{PhLi} \xrightarrow[-\mathrm{Ph_4Pb}]{} \mathrm{CH_2{=}C{=}CHLi} \xrightarrow{\mathrm{Ph_2C{=}O}} \mathrm{Ph_2\overset{OH}{C}{-}CH_2{-}C{\equiv}CH} \tag{16}$$

32

3.15.4 Plumbocenes and Related Compounds

3.15.4.1 Formation and Structures of Plumbocenes

Subsequent to the parent plumbocene $(C_5H_5)_2Pb$, which was first synthesized in 1956 by Fischer and Grubert, a number of ring-substituted derivatives have been reported. The sterically congested plumbocenes $(1,2,4\text{-}t\mathrm{Bu}_3C_5H_2)_2Pb$, $(i\mathrm{Pr}_4C_5H)_2Pb$, and $(i\mathrm{Pr}_5C_5)_2Pb$ **33** were obtained from $PbCl_2$ and the corresponding lithium or sodium compounds. The structure of **33** could not be completely resolved owing to disorder of the isopropyl groups. The only feature that can be deduced is a slightly bent structure with a bending angle of approximately 170°.[50]

Depending on the spatial requirements of the ring substituents, other plumbocenes also exhibit differing angles for the ring centroid–Pb–ring centroid unit. These range from 139.7° for $(C_5Me_4H)_2Pb$[51] to 173.3° or, respectively, 172.9° for $[1,3\text{-}(SiMe_3)_2C_5H_3]_2Pb$.[52,52a] In the case of the highly sterically overloaded compound $(t\mathrm{BuMe_2SiC_5Me_4})_2Pb$[53] and, surprisingly, for the plumbocene $(i\mathrm{Pr_3H_2C_5})_2Pb$[54], which is sterically less crowded in comparison to **33**, strictly parallel rings have been observed.

Cyclopentadienyl ring metathesis with organocalcium or organopotassium compounds constitutes a further method for the synthesis of decamethylplumbocene **34** and, for example, furnishes compound **34** in 59% or, respectively, 35% yield[55] (Equation (17)).

$$(C_5Me_5)_2Ca{\cdot}4THF + (C_5H_5)_2Pb \longrightarrow \underset{\mathbf{34}}{(C_5Me_5)_2Pb} + (C_5H_5)_2Ca{\cdot}4THF \tag{17}$$

The above-mentioned examples clearly demonstrate that plumbocenes exist not only in the gas phase as monomers but also as such in the condensed phase when the substituents are sufficiently bulky. It has long been known that the parent compound $(C_5H_5)_2Pb$ exists as a polymer in the solid state. However, various polymorphous forms exist the formation of which depends on the conditions of growth and the solvent used. While crystal growth by crystal deposition from the gas phase results in the classical zigzag chain of orthorhombic plumbocene, crystallization from toluene at 5 °C gives rise to the solvate $(C_5H_5)_2Pb{\cdot}C_6H_5CH_3$ **35** as well as the hexamer $[(C_5H_5)_2Pb]_6$ **36**.[56]

Although a new determination of the structure of the zigzag modification of plumbocene **37**[57] confirmed the original configuration, it also exposed the unsatisfactory quality of the first structural analysis, which was, moreover, refined to an erroneous space group (Figure 1). In addition to these polymeric or oligomeric forms of plumbocene, a tetragonal, helical phase has been isolated and represents one of the rare examples of a helical metallocene.[58]

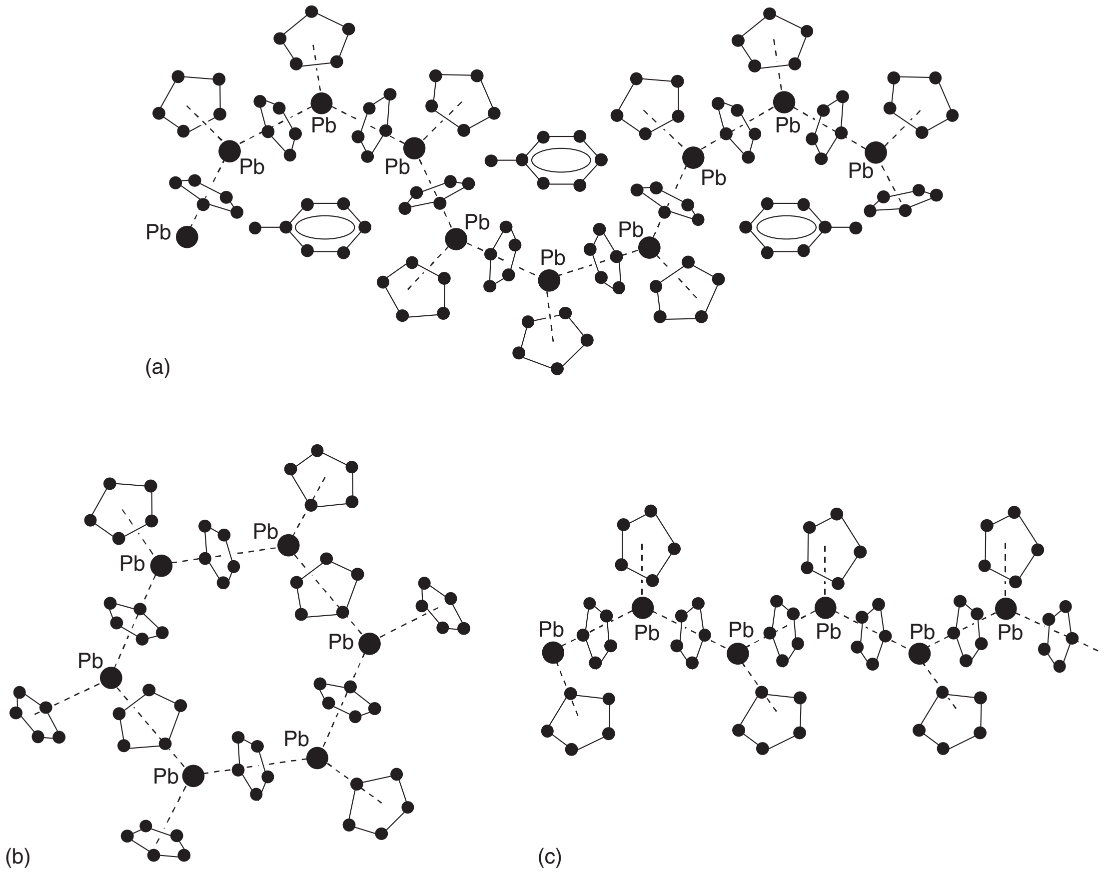
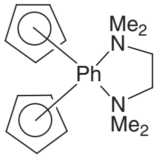


Figure 1 Modifications of plumbocene in the solid state. (a) Sinusoidal toluene solvate **35**. (b) Solvent-free hexameric form **36**. (c) Zigzag chain of solvent-free **37**.

3.15.4.2 Lewis Acid–Base Adducts

Although monomeric plumbocene exhibits an angled sandwich structure with 14 peripheral electrons, it behaves rather as a weak Lewis acid that forms loose adducts with Lewis bases. The weakly bound adducts 38 and 39 are obtained with the bidentate nitrogen bases tetramethylethylenediamine (TMEDA) and 4,4′-dimethyl-2,2′-bipyridyl, and both are characterized by extremely long Pb–N bonds. Surprisingly, the Cp groups in both compounds take up eclipsed conformations and are bonded, to a first approximation, in a η^3-mode to the lead atom. In solution 39 is, and 38 also is probably, dissociated into the starting compounds.[59] *Ab initio* MO calculations of 38 and 39 confirm that in spite of the presence of longer Pb–N bonds in the solid state structure of the TMEDA adduct, the association of TMEDA with the metallocene is more favorable than with bipyridyl. This finding is a consequence of the greater reorganization energy of 4,4′-Me_2bipy compared to TMEDA. The low association energies of both species can be rationalized in terms of metal lone pair/ligand lone pair repulsion.[60]



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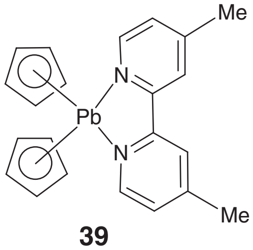

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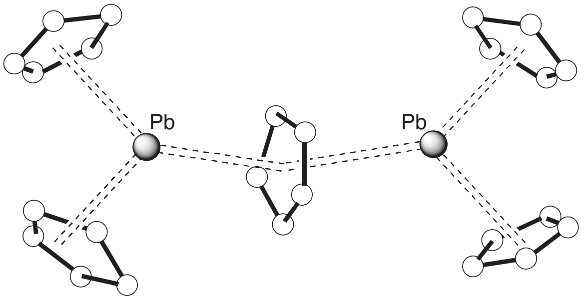


Figure 2 Anion of **40** in the crystal.

Nucleophilic additions of cyclopentadienide anions to polymeric $[Cp_2Pb]_n$ produce a range of anionic complexes. For example, the reaction of NaCp with plumbocenes in the presence of $(Me_2NCH_2CH_2)_2NMe$ (PMDETA) gives the ion-contacted complex $[Cp_2Pb(\mu\text{-}Cp)Na\cdot PMDETA]$, whereas the reaction of Cp_2Mg with Cp_2Pb in THF yields the ion-separated complex $\{[(\eta^3\text{-}Cp)_3Pb]_2{}^{2-}[Mg(THF)_6]^{2+}\}$. The $[Cp_3Pb]^-$ ions present in these complexes contain trigonal-planar Pb centers that can be regarded as an extruded segment of the polymeric $[Cp_2Pb]_n$ chain.[61]

Addition of alkali metal cyclopentadienides (MCp) to $(Cp_2Pb)_n$ produces π-anions of the general formula $[Cp_{2x+1}Pb_x]^-$. Multi-decker anions with $x > 1$ can be prepared if crown ether or cryptand ligands coordinate with the alkali metal cations. For example, the reaction of $(Cp_2Pb)_n$ with KCp in the presence of 2,2,2-crypt produces $[K(2,2,2\text{-crypt})]^+[Cp_5Pb_2]^-$ **40**, containing a dinuclear anion in which the Pb centers are linked by a μ-Cp ligand (Figure 2).[61]

The predominant anionic species formed with a broad range of alkali metals and crown ether and cryptand ligands is $[Cp_5Pb_2]^-$. This is consistent with the bonding in the anion $[Cp_9Pb_4]^-[Cp_5Pb_2]^-$, for which solid-state MAS NMR studies indicate that $[Cp_9Pb_4]^-$ is best regarded as a $[Cp_5Pb_2]^-$ anion loosely associated with two Cp_2Pb molecules.[62,63]

A compound with an unusual polymeric sheet structure of $[Cp_2PbCp(THF)Na]_3$ rings is obtained from the addition reaction of $[Cp_2Pb]_n$ to NaCp in THF.[64]

3.15.4.3 Theoretical Calculations

The unusual but experimentally confirmed molecular conformations of group 14 metallocenes, of which some are planar and some are bent to varying degrees, were examined within the framework of the MM3 force field theory. The experimental results are rationalized in terms of the non-bonding interactions, especially attractions between the Cp ligands. Crystal packings influence the bending to some extent, but they are neither the cause of the bending nor the major force in determining the degree of bending.[65]

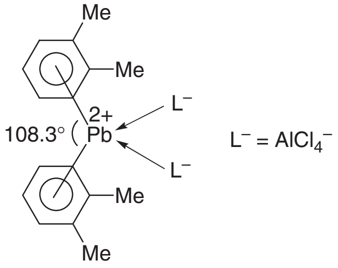
Ab initio calculations with density functional theory methods have confirmed that, at least in their isolated form, the group 14 metallocenes are most stable as slipped sandwich compounds with π-bound cyclopentadienyl rings. The difference in energy between the linear and bent forms for $(C_5H_5)_2Pb$ is small ($\sim$1 kJ mol^{-1}), and the stereochemical influence of the metal-centered lone pair of electrons is relatively slight. The fact that the heavier metallocenes are still strongly bent even though there is little energetic push from the metal-centered lone pair suggests that other bending mechanisms, such as core polarization, should be considered for these molecules.[66]

To shed light on the nature of the molecular crystal structure disorder observed in the orthorhombic zigzag polymorph of plumbocene $(C_5H_5)_2Pb$, plane wave density functional theory was applied. The energies obtained from the optimization of the idealized crystal lattice arrangements derived from the disordered cell have allowed crystallographic occupancy factors to be calculated by a quantum mechanical technique. This has revealed a very close agreement between experiment and theory at room temperature, whereas, at lower temperatures, one well-defined packing arrangement is increasingly favored. Furthermore, single-point energy calculations performed on plumbocene chains taken from the two different crystal lattices have highlighted the importance of chain–chain interactions in determining the greater stability of the staggered conformation.[67]

Improved energy values have been obtained by coupled-cluster theory at the CCSD(T) level. The nature of the metal–ligand bonding has been analyzed with an energy-partitioning method. A smooth trend of decreasing bond energies from Cp_2Si (547 kJ mol^{-1}) to Cp_2Pb (466 kJ mol^{-1}) is predicted for the group 14 compounds. The attractive interactions in the group 14 sandwich complexes Cp_2Si to Cp_2Pb have between 63% and 72% electrostatic character. The covalent bonding arises mainly (52–55%) from the e_{1u} orbitals. The metal–Cp bonds in the bent forms have a higher covalent character than in the linear D_{5d} structures.[68] These and similar results have been summarized in a comprehensive review on *Trends in Cyclopentadienyl–Main Group-Metal Bonding*.[69]

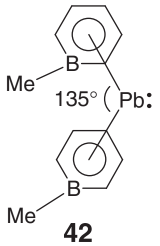
3.15.4.4 Related π-Complexes of Lead(II)

Treatment of lead(II) chloride with aluminum trichloride and *o*-xylene furnishes bis(*o*-xylene)lead(II) bis(tetrachloroaluminate) **41**. According to the results of an X-ray structure determination, **41** consists of a monomeric complex with two arene ligands in a distorted η^6-mode of coordination and two bidentate $AlCl_4^-$ ions at the central Pb^{2+} ion. The interaction of the lead center with the tetrachloroaluminate ligands is presumably highly ionic, suggesting that **41** is a triad of arene-stabilized ions, rather than a molecule.[70]



41

Bis(1-methylboratabenzene)lead **42** is synthesized in 63% yield by the reaction of $Li(C_5H_5BMe)$ with lead(II) chloride. The X-ray structure analysis of **42** reveals some remarkably short intermolecular contacts from the lead atoms to the *ortho*-carbon atoms of neighboring molecules which create a tetrameric packing unit. Compound **42** forms weak adducts such as **43** with nitrogen Lewis bases like TMEDA or 4,4′-dimethyl-2,2′-bipyridine.[71]



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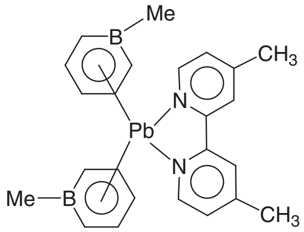
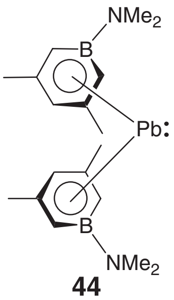


43

The analogous reactions of $PbCl_2$ with lithium 1-(dimethylamino)-3,5-dimethylboratabenzene or 1-[bis(trimethylsilyl)amino]-3,5-dimethylboratabenzene yield the corresponding sandwich compounds **44** and **45**. The lead atom of **45** displays a rather asymmetric bonding to the boratabenzene rings as evidenced by the fact that the lead-to-carbon/boron distances span the large range from 2.519 to 3.033 Å.[72]



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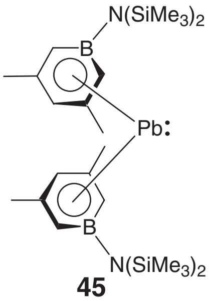
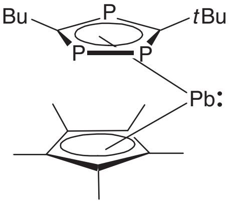
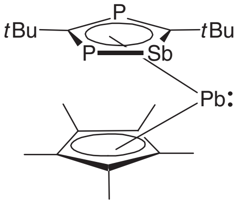


45

The reaction between a slurry of $\mathrm{PbCl_2}$ in THF with a 1 : 1 mixture of $[\mathrm{Li(dme)_2}][t\mathrm{Bu_2C_2P_3}]$ and $[\mathrm{Li(C_5Me_5)}]$ affords the heteroleptic complex **46** in 45% yield. Additionally, the analogous complex **47** is prepared in 25% yield by the reaction between $[\mathrm{Li(tmen)_2}][t\mathrm{Bu_2C_2P_2Sb}]$ and $\mathrm{(C_5Me_5)PbCl}$.

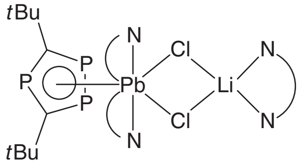


46



47

In the solid state, both **46** and **47** exist as bent monomeric sandwich complexes with ring centroid–lead–ring centroid angles of 152.2° in **46** and 144.2° in **47**. Interestingly, if the reaction between $\mathrm{PbCl_2}$ and $[\mathrm{Li(dme)_2}][t\mathrm{Bu_2C_2P_3}]$ is carried out in tmen rather than DME, the product formed is not a homoleptic plumbylene but rather the novel heterobimetallic compound **48**.[73]

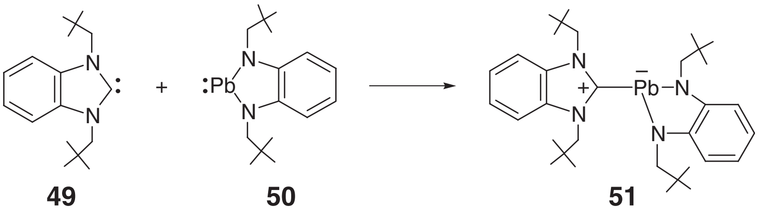


48

3.15.5 Low-valent Organolead Compounds

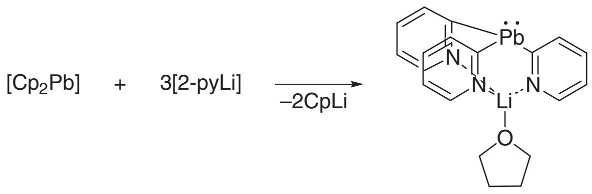
3.15.5.1 Donor-stabilized Low-valent Lead Compounds

The reaction of the diaminocarbene **49** with the diaminoplumbylene **50** furnishes dark red crystals of the zwitterionic adduct **51** in 71% yield. Compound **51** reveals a very long Pb–C bond length of 258.6(7) pm. While the C atom of the Pb–C bond is in an almost trigonal-planar environment (sum of angles 350.3°), the lead atom has a pyramidal environment with a sum of angles of 274.5°. This can be attributed to the presence of a stereochemically active lone pair at the lead atom (Equation (18)).[74]



49 **50** **51** (18)

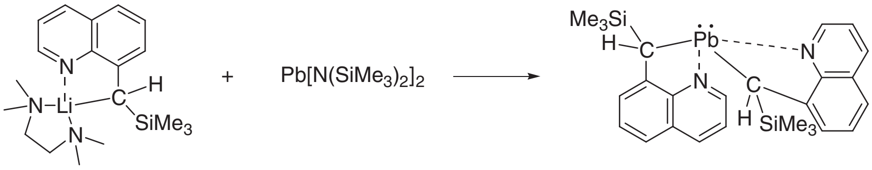
Treatment of the plumbocene $[\mathrm{Cp_2Pb}]$ with 2-pyLi produces yellow crystals of compound **52** in 56% yield. Compound **52** is the first example of a molecule of this type containing a low-valent group 14 element. The solid-state structure of **52** is that of a cage resulting from the symmetrical complexation of the Li^+ cation by the pyridyl-N centers of the $[Pb(2\text{-py})_3]^-$ anion (Equation (19)).[75]



52

(19)

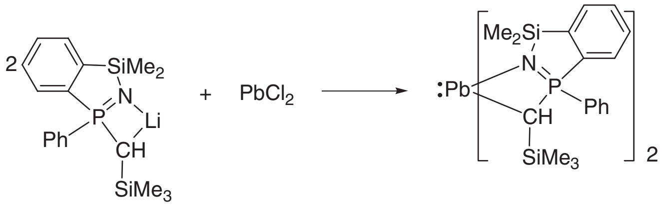
The donor-stabilized lead(II) dialkyl **54** is prepared in 65% yield by the reaction of the lithium compound **53** with $Pb[N(SiMe_3)_2]_2$. The orange-red crystals of **54** are stable in the solid state; in solution, they slowly decompose to deposit metallic lead at room temperature (Equation (20)).[76]



53 **54**

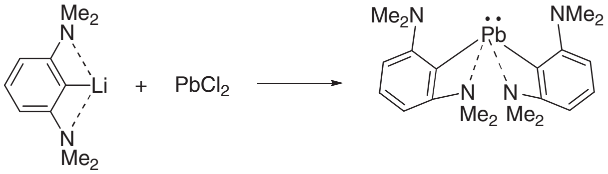
(20)

The reaction of the lithium compound **55**, accessible from the iminophosphorane $CH_2(SiMe_3)PPh_2{=}NSiMe_3$ and *n*BuLi, with $PbCl_2$ gives colorless crystals of the lead complex **56** in 50% yield (Equation (21)).[77] Similarly, treatment of $PbCl_2$ with the lithium compound **57** affords yellow crystals of the donor-stabilized lead(II) diaryl **58** in 70% yield (Equation (22)).[78]



55 **56**

(21)

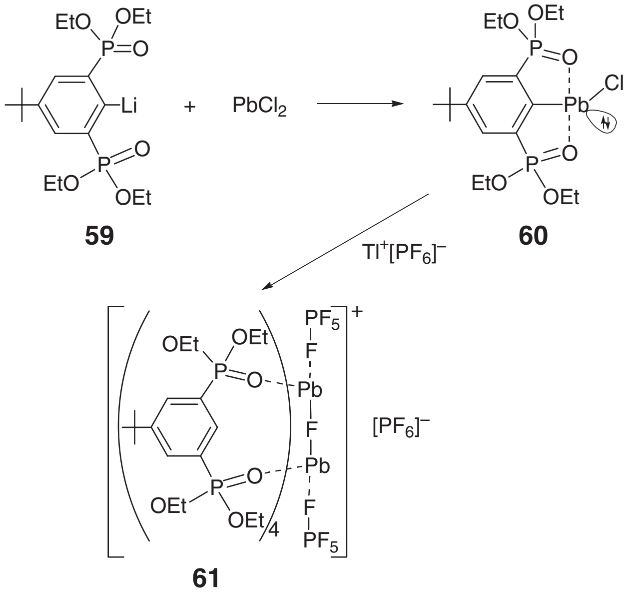


57 **58**

(22)

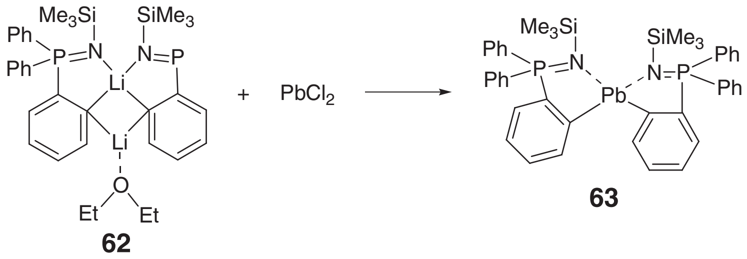
The organolithium compound **59** reacts with $PbCl_2$ to give the intramolecular coordinated plumbylene **60** as colorless crystals in 81% yield. Compound **60** adopts a polymeric chain structure through intermolecular Pb–Cl–Pb bridges, a structural motif previously unknown for organolead(II) derivatives. The reaction of **60** with $TlPF_6$ does not give the expected intramolecularly coordinated organolead(II) hexafluorophosphate. Instead, the unprecedented salt

61 is obtained, in which the $[(\mathrm{Pb{-}F{-}Pb})]^{3+}$ cation is stabilized by eight intramolecular P═O→Pb interactions (Equation (23)).[79]



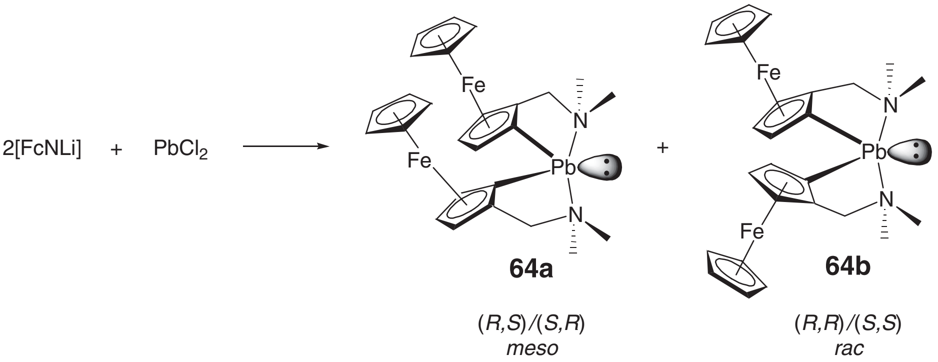
(23)

Lithiation of the iminophosphorane $\mathrm{Ph_3P{=}NSiMe_3}$ with MeLi gives the *ortho*-metallated species **62**. Reaction of the latter with $\mathrm{PbCl_2}$ furnishes the donor-stabilized diarylplumbylene **63** as colorless crystals in 47% yield. In this compound, the small C–Pb–C angle of 86.0(2)° indicates a ${}^1\sigma^2$ singlet carbene homolog electronic configuration at the lead atom with the lone pair in a spherical *s*-orbital and both bonding electron pairs in orthogonal *p*-orbitals (Equation (24)).[80]



(24)

The stable tetracoordinated diorganolead(II) compound **64** is obtained by the reaction of [FcN]Li with $\mathrm{PbCl_2}$ in 80% yield. The deep red crystals of **64** exist in the solid state only as the *meso*-diastereomer **64a**. The ratio of *meso*-/*rac*-diastereomers in solution is solvent and temperature dependent, consistent with an intermolecular exchange between diastereomers (Equation (25)).[81]



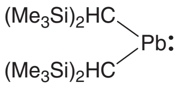
(25)

$[\mathrm{FcNLi}] = [\mathrm{Fc}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5H_3\text{-}2\text{-}CH_2NMe_2})]\mathrm{Li}$

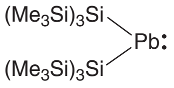
3.15.5.2 Plumbylenes, Plumbylene Dimers, Diplumbenes

Although Lappert *et al.* reported on the isolation of the purple dialkylplumbylene **65** as early as 1973, its structure has only recently been determined. In the solid state, compound **65** exists as a loosely bonded dimer with a second plumbylene molecule and has a Pb···Pb separation of 412.9 pm, with *trans*-bent angles between the PbC_2 plane and the Pb···Pb vector of 34.2°.[82]

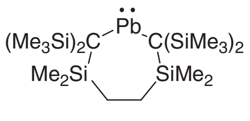
In contrast, the structurally similar molecules **66**[83,83a] and **67**[84] are strictly monomeric in the solid state, with large distances to the lead atoms of neighboring plumbylene molecules. The same holds for the diarylplumbylene **68**[85] and for the sterically extremely overcrowded plumbylenes **69**,[86] **70**,[87] as well as **71**.[88]



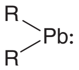
65



66

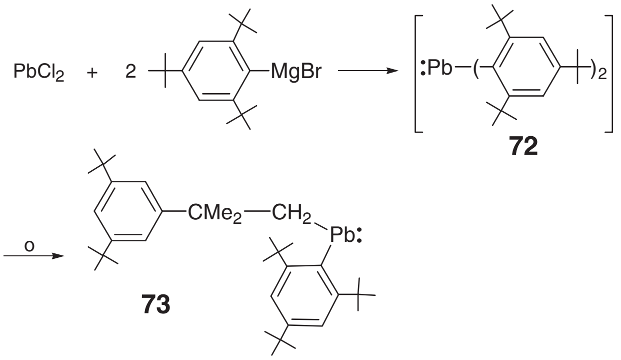


67



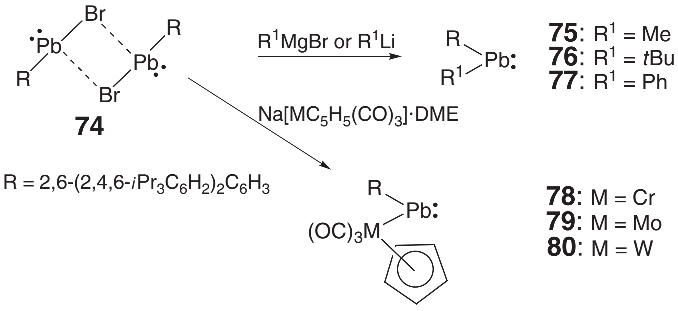
68: R = 2,4,6-$(CF_3)_3C_6H_2$
69: R = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-C_6H_2
70: R = 2,4,6-$[(SiMe_3)_2CH]_3C_6H_2$
71: R = 2-*t*Bu-4,5,6-Me_3C_6H

The reaction of $PbCl_2$ with 2,4,6-tri-*tert*-butylphenylmagnesium bromide follows an unexpected course, probably involving the diarylplumbylene **72** that rearranges to finally afford the isolated alkylarylplumbylene **73**[88] (Equation (26)).



(26)

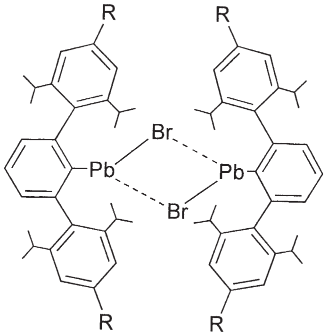
With the voluminous 2,6-bis(2,4,6-triisopropylphenyl)phenyl group, it is only possible to introduce one unit of this substitutent to lead to obtain an arylbromoplumbylene. In the solid state, this compound exists as the halogen-bridged dimer **74**.[89] Starting from **74**, not only the heteroleptic diorganylplumbylenes **75–77**,[89] but also the again heteroleptic metalloplumbylenes **78-80**[90] can be prepared (Equation (27)).



(27)

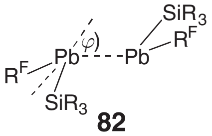
The reaction of $PbBr_2$ with the lithium compounds $Li[2,6(2,6\text{-}i\text{Pr}_2C_6H_3)_2C_6H_3]$ or $Li[2,6(2,6\text{-}i\text{Pr}_2\text{-}4\text{-}t\text{BuC}_6H_2)_2C_6H_3]$ also furnishes the bromide-bridged organolead(II) halides **81a and 81b**. Treatment of **81a** with methylmagnesium bromide results in a weakly bonded diplumbene (Pb═Pb: 316.01(6) pm), in which the bromine atoms are replaced by methyl groups. With 4-*tert*-butylphenylmagnesium bromide, a plumbylene dimer (Pb···Pb: 392.7(1) pm) with a weak

Pb···Pb interaction is formed. The reaction of the more crowded aryllead bromide [Pb(μ-Br)R]$_2$, R = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)C$_6$H$_3$, with 4-isopropylbenzylmagnesium bromide or LiSi(SiMe$_3$)$_3$, yielded strictly monomeric plumbylenes.[91]

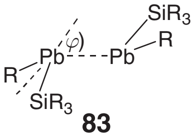


81a: R = H
81b: R = *t*Bu

These plumbylenes also exist as V-shaped singlet molecules without contacts to neighboring plumbylene molecules. A first breakthrough in the context of short Pb···Pb contacts was the isolation of the heteroleptic plumbylene dimer 82, exhibiting a Pb···Pb separation of 353.7(1) pm and a *trans*-bent angle φ of 40.8°.[92,92a] The plumbylene dimer 83 has a shorter Pb···Pb separation of 337.0(1) pm and a *trans*-bent angle φ of 46.5°.[88] Nevertheless, the observed Pb···Pb distances in 82 and 83 are markedly longer than the values 282–300 pm calculated for the parent compound Pb$_2$H$_4$ with a genuine Pb═Pb double bond.[93–95]



82

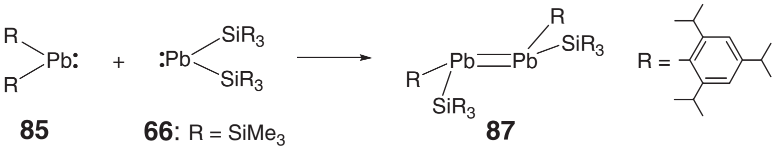


83

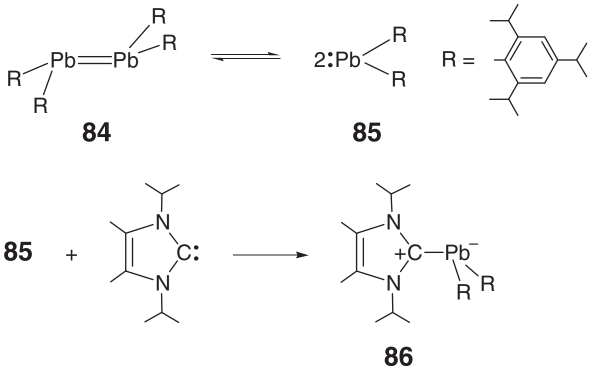
SiR$_3$ = Si(SiMe$_3$)$_3$, R^F = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, R = 2-*t*Bu-4,5,6-Me$_3$C$_6$H

The reaction of lead(II) chloride with 2,4,6-triisopropylphenylmagnesium bromide furnished red crystals of compound 84, the first molecule with a short Pb═Pb double bond length of 305.15(3) pm and *trans*-bent angles of 43.9° and 51.2°.[96,96a] Compound 84 is stable in the solid state. In solution, it dissociates into the plumbylene molecules 85 that, for example, react with a nucleophilic carbene to furnish the highly labile, zwitterionic adduct 86 (Scheme 2).[97]

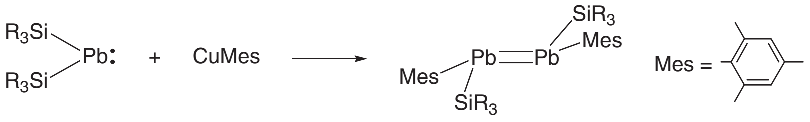
Substituent exchange between 85 and the disilylplumbylene 66[83] leads to the heteroleptic diplumbene 87 with a short double-bond length of 298.99(5) pm.[98] The diplumbene 88, with the shortest Pb═Pb bond length of 290.3 pm determined so far, was isolated from the reaction of 66 with mesitylcopper in low yield (Equations (28) and (29)).[99]



(28)

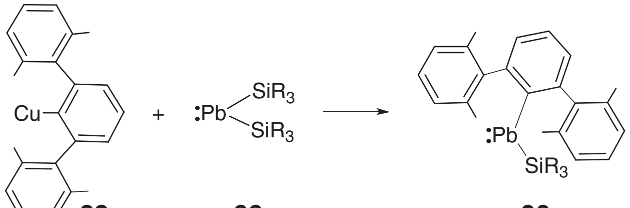


Scheme 2



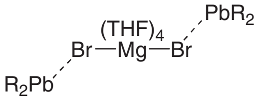
66 **88** (29)

However, reaction of the sterically congested arylcopper compound **89** with the disilylplumbylene **66** yielded the strictly monomeric plumbylene **90** (Equation (30)).[100]



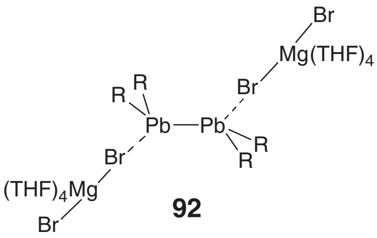
89 **66** **90** (30)

The diplumbenes **84**, **87**, and **88** demonstrate that in contrast to the homonuclear double bonds in disilenes, digermenes, and distannenes where increasing bond lengths require even larger substituents for shielding, lead–lead double bonds can be realized with smaller groups. Replacement of the above-mentioned groups by the markedly less voluminous 2,4,6-triethylphenyl group and reaction of the corresponding Grignard compound with lead(II) chloride furnished the compound **91**, in which two plumbylene molecules are linked by a magnesium bromide molecule.[101] Further reduction of the steric bulk of the substituents by replacement of the triethylphenyl by the even smaller mesityl group afforded black crystals of the plumbylene dimer **92**, that is stabilized by two magnesium dibromide molecules. Worthy of note are the lead–lead separation of 335.49(6) pm and the very large *trans*-bent angle of 71° at the mesityl group.[98]



91

R = 2,4,6-Et$_3$C$_6$H$_2$



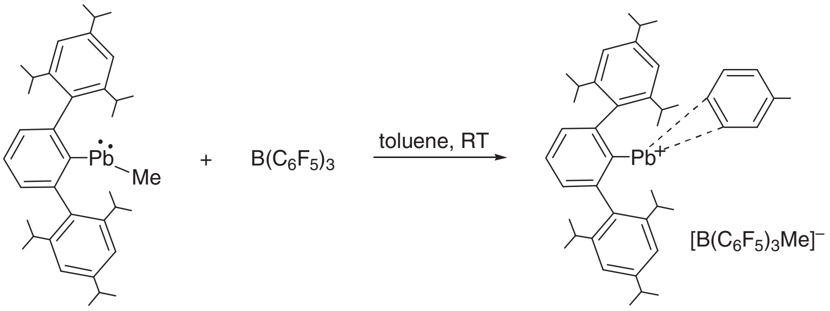
92

R = 2,4,6-Me$_3$C$_6$H$_2$

These, in part unexpected, results led to a re-examination of the reactions of lead(II) halides with phenylmagnesium bromide that have been known for more than 100 years to furnish tetraphenyllead and lead. It was later demonstrated that hexaphenyldiplumbane is also accessible by this route depending on the ratio of the starting materials. Repeating the reaction of phenylmagnesium bromide with PbBr$_2$ furnished yellow needles of the ionic compound **93**, the anion of which reveals some interesting features. The presence of a free electron pair at the lead atom results in a compression of the Pb–Pb–Pb bond angles and in stretched Pb–Pb bond lengths (Equation (31)).[102] Treatment of excess biphenylmagnesium bromide with PbCl$_2$ at −78 °C yielded the ionic compound [(THF)$_3$Mg(μ-Cl)$_3$Mg(THF)$_3$]$^+$[Pb(Pbbp$_3$)$_3$]$^-$ (bp = biphenyl) whose structure reveals similar structural parameters to those of **93**.[28]

$$\mathrm{PbBr_2} + \mathrm{PhMgBr} \xrightarrow{\mathrm{THF}} \underset{\textbf{93}}{[(\mathrm{THF})_5\mathrm{MgBr}]^+[\mathrm{Pb(PbPh_3)_3}]^-} \qquad (31)$$

Another unusual ion was obtained from the reaction of the arylmethylplumbylene **94** with B(C$_6$F$_5$)$_3$ to give the salt [Ar*Pb–η^2–PhMe]$^+$[MeB(C$_6$F$_5$)$_5$]$^-$ **95** (Ar* = 2,6-Trip$_2$C$_6$H$_3$, Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$) (Equation (32)).[103,103a]



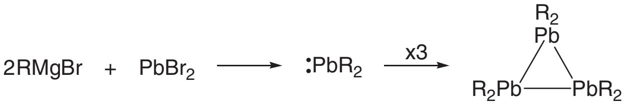
94 **95**

(32)

Compound **95** contains a quasi-one-coordinate lead cation, which is weakly solvated by a toluene molecule. In the reaction of **95** with excess pyridine, the weakly bonded toluene is replaced by pyridine to give the ionic compound $[\mathrm{Ar}^{*}\mathrm{Pb(py)_2}]^{+}[\mathrm{MeB(C_6F_5)_5}]^{-}$, in which the cationic lead center has a pyramidal environment composed of the aryl group and two pyridine molecules.[103,103a]

3.15.6 Homonuclear Ring Compounds

While the lighter elements of group 14 form numerous ring systems, a homonuclear ring of lead atoms was unknown until recently. To separate the $MgBr_2(THF)_4$ formed in the reaction between 2,4,6-triethylphenylmagnesium bromide and lead(II) bromide in THF, and thus suppress the formation of **91**, the reaction was performed in the presence of dioxane. This procedure yielded black crystals of the cyclotriplumbane **96**, containing the first and, as yet, only homonuclear ring of lead atoms (Equation (33)).[104]



96

(33)

With an average value of 318.4 pm, the Pb–Pb bond lengths are markedly longer than those of typical diplumbanes. Equally unusual is the orientation of the substituents at the lead atoms, since they are twisted by about 37° out of their ideal positions (Figure 3).[104]

These structural parameters are in fair agreement with those obtained from calculations on the parent compound *c*-Pb_3H_6, for example, Pb–Pb bond lengths of 323.1 pm and displacement angles of 50° for the hydrogen atoms.[105] The MP2 calculated structure of the more realistic hexaphenyl derivative reveals a Pb–Pb bond length 321.6 pm and a displacement angle of 50.2°.[106] The calculated and observed structures demonstrate that the Pb–Pb bonds in **96** are not classic single bonds but rather that the three-membered ring is held together by weak interactions between three singlet plumbylene molecules.

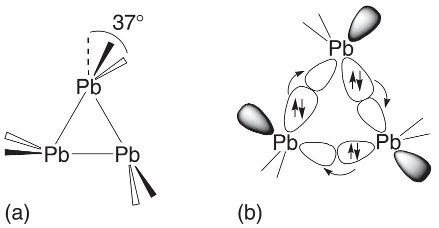
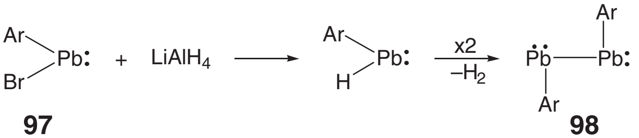


Figure 3 (a) Structure of **96**. (b) Interaction of three singlet plumbylenes.

3.15.7 Triple Bonds to Lead

The reaction of the arylbromolead compound **97** with $LiAlH_4$ furnished the dilead compound **98**, a formal lead analog of an alkyne (Equation (34)).[107] The Pb–Pb bond length of 318.81(1) pm and the Pb–Pb–C bond angles of 96.26(4)° clearly indicate that **98** does not contain a multiple bond, but should rather be considered as a diplumbylene with a weak Pb–Pb single bond and a free 6*s* electron pair on each of the lead atoms.[107] These experimental observations are supported by quantum chemical calculations that unequivocally show the diplumbylene form **98** to be an energy minimum.[108,108a]

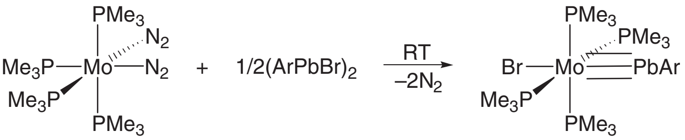


97 **98**

Ar = 2,6-(2,4,6-*i*$Pr_3C_6H_2)_2C_6H_3$

(34)

Although, triple bonds between the heavier atoms of group 14 and transition metal fragments were previously restricted to germanium and tin,[109–110a] recent reports have shown that lead is also able to form such bonds. Treatment of the dinitrogen complex **99** with aryllead(II) bromide[89] gave the plumbylidyne complex **100** (Equation (35)).[111,111a]

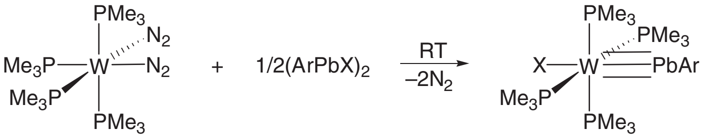


99 Ar = 2,6-(2,4,6-*i*$Pr_3C_6H_2)_2C_6H_3$ **100**

(35)

The very short Mo–Pb bond and the almost linear Mo–Pb–Ar arrangement suggest the presence of a triply bonded lead atom. Theoretical calculations provide additional evidence for the presence of an Mo–Pb triple bond.[111,111a]

Following an analogous route, the corresponding complexes **102 and 103** with a W–Pb triple bond were also synthesized. Reaction of the dinitrogen complex **101** with an aryllead(II) bromide[89] or aryllead(II) iodide, incidentally the first aryllead iodide to be structurally characterized, yielded the plumbylidyne complexes **102 and 103**, respectively. These isotypic complexes display almost linear C–W–Pb linkages and the shortest W–Pb bond lengths reported so far (Equation (36)).[112,112a]



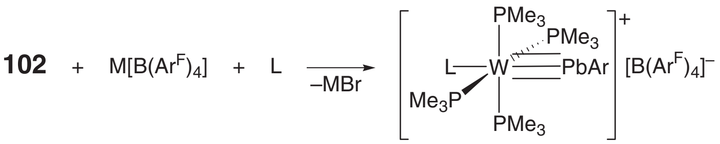
101

102: X = Br
103: X = I

Ar = 2,6-(2,4,6-*i*$Pr_3C_6H_2)_2C_6H_3$

(36)

Treatment of **102** with lithium or sodium borates in the presence of trimethylphosphane or benzonitrile gave the plumbylidyne complex salts **104 and 105** (Equation (37)).[112,112a]



(37)

104: L = PhCN, $Ar^F = 2,6\text{-}(CF_3)_2C_6H_3$
105: L = PMe_3, $Ar^F = C_6F_5$

The cations of **104 and 105** also reveal very short W–Pb bond lengths and an almost linear C–W–Pb arrangement.

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3.16
Arsenic, Antimony, and Bismuth Organometallics

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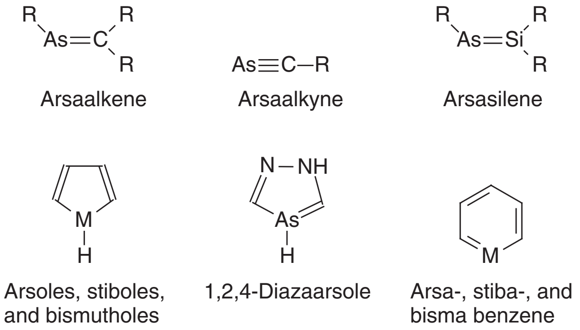
3.16.1 Introduction

The history and the general features of organoarsenic, -antimony, and -bismuth chemistry were given in COMC (1982)[1] and COMC (1995).[2] In this chapter, the focus is mainly on the results published between 1993 and 2004. Several overviews of the chemistry of organoarsenic, -antimony, and -bismuth compounds were presented in this period in books and annual reviews.[3–7] More specialized review articles featured homonuclear multiple bonding in heavier main group elements,[8] low-coordinated interelement compounds of the heavier group 15 elements,[9] the chemistry of organoantimony(III) halides,[10] coordination compounds with organometal ligands,[11–13] supramolecular organometallic compounds,[14,15] group 13 compounds with Sb, Bi,[16] low-coordination organoantimony and bismuth chemistry,[17] organoantimony and bismuth rings,[18,19] organometallic compounds with Sb–Sb or Bi–Bi bonds,[20–24] diheteroferrocenes of As, Sb, Bi,[25] microbial methylation of As, Sb, Bi,[26] and structural chemistry of organobismuth derivatives.[27]

3.16.2 Trivalent Compounds

3.16.2.1 Metal–Carbon Multiple-bonded Compounds

Double-bonded species (i.e., dicoordinate λ^3, σ^2 metal species) were reported for As, Sb, and Bi.[2] The stability of these species toward the formation of oligomers with metal–carbon single bonds is increased by steric protection with

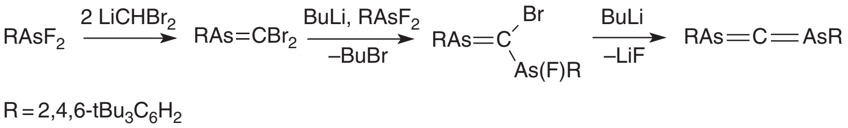


Scheme 1

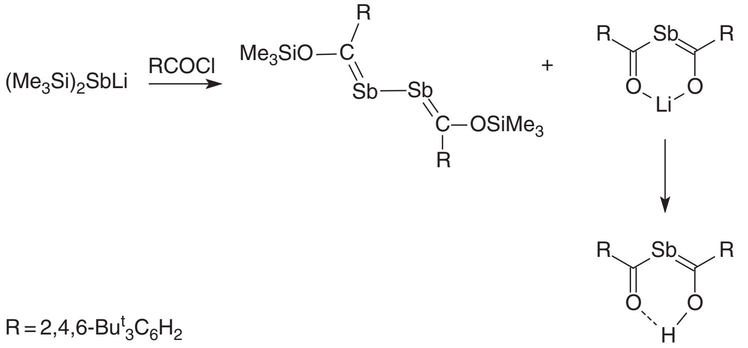
bulky organic ligands, for example, $(Me_3Si)_2CH$, $(Me_3Si)_3C$, 2,4,6-$Bu^tC_6H_2$, or by incorporating the M═C unit into a delocalized π-system. The chemistry of metal carbon multiple bonded species were reviewed in COMC (1995).[2] Examples are given in Scheme 1.

A sterically protected diarsaallene is formed in the sequence of reactions shown in Scheme 2. The final step is a 1,2-elimination of LiF from an arsaalkene precursor.[28]

The arsaallene, ArAs═C═CR_2 (Ar = 2,4,6-tri-*tert*-butylphenyl, CR_2 = fluorenylidene), has been synthesized by a one-pot procedure involving the successive addition of *n*-butyllithium and fluorenone to the new arsaalkene ArAs═C(Br)$SiMe_3$, which presents a *Z* configuration and a short As═C bond length (1.789(3) Å).[29] Reactions of the arsaalkene Me_3Si–As═C$(NMe_2)_2$ with chlorocarbyne transition metal complexes $Tp'(CO)_2M{\equiv}CCl$ [M = Mo, W; Tp′ = $HB(3,5\text{-}Me_2HC_3N_2)_3$] lead to the elimination of Me_3SiCl with the formation of the arsaalkenyl carbyne complexes $Tp'(CO)_2M{\equiv}C\text{–}As{=}C(NMe_2)_2$.[30] Adducts of the ferrioarsaalkene $[C_5Me_5(CO)_2Fe\text{–}As{=}C(NMe_2)_2]$ form in reactions with Me_3M^1 (M^1 = Al, Ga, In). The ferrioarsaalkene is coordinated to the Lewis acid via the arsenic atom.[31] A stibaalkene species $[2\text{-Pyr}(SiMe_3)_2CSb{=}C(SiMe_3)2\text{-Pyr})$ (Pyr = C_5H_4N) is formed by beta elimination of Me_3SiCl from $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$.[32,33] Reactions of bis(trimethylsilyl)lithium antimonide with RCOCl lead to mixtures of a remarkable distibabutadiene[34] and a stibadionato complex which is protonated to a stibaenol (Scheme 3).[35] Arsa- and stibadionato complexes of Li or Na[36] and 1,2,4-diazaarsole[37] were also characterized by structural methods.

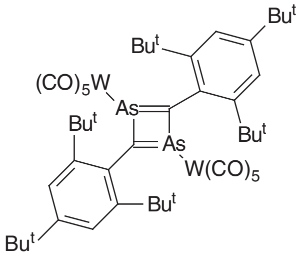


Scheme 2



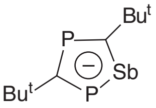
Scheme 3

A diarsacyclobutadiene is the ligand in the tungsten pentacarbonyl complex **1** which was characterized by X-ray crystallography.[38]

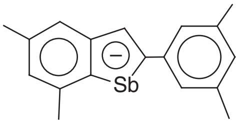


1

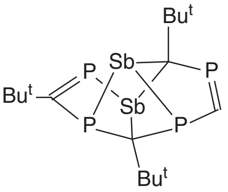
The reaction of $KSb(SiMe_3)_2$ with $Me_3SiP{=}C(Bu^t)(OSiMe_3)$ gives the potassium derivative of the diphosphastibolyl **2**,[39] which reacts in the presence of $FeCl_3$ with the formation of cage **4**.[40] The stibindolyl anion **3** is formed in a one-pot synthesis from trimesitylantimony and potassium.[41]



2



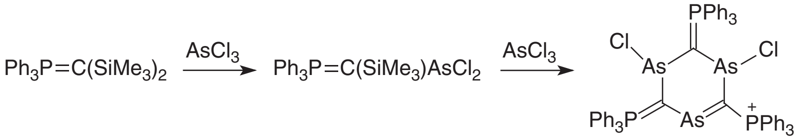
3



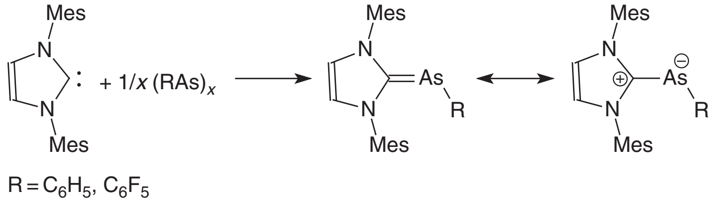
4

A triarsinenium cation is formed by the elimination of Me_3SiCl from ylide precursors and $AsCl_3$ (Scheme 4).[42]

Adducts between 1,3-dimesitylimidazol-2-ylidene and phenyl or (pentafluorophenyl) arsinidene are formed by the direct reaction of a stable nucleophilic carbene with the corresponding cyclic oligomers (Scheme 5). These carbene–arsinidenene adducts possess strongly polarized arsinidene–carbene bonds. The C–As–C angles are all typically small



Scheme 4



Scheme 5

at 97–102°, and there is only a 4% shortening of the nominal As═C double bond compared to the As–C single bond to the second substituent on the arsenic atom.[43]

3.16.2.2 Group 15 Metal–Metal Bonded Compounds

An extensive range of compounds with homonuclear or heteronuclear single or double bonds between As, Sb, or Bi is known. They include the simple tetraorganodimetallic species, R_2MMR_2, double bonded species RM═MR, linear tri- and tetra-metallated species, and mono- or polycyclic compounds. In addition, adducts with coordinative metal–metal bonds are known.[44–46,46a] Examples for cationic species with Sb–Sb bonds are $Me_2SbSbMe_2^+$ and $Me_3SbSbMe_3^{2+}$.[47]

3.16.2.2.1 Diarsines, distibines, and dibismuthines

The M–M bond can be formed by oxidizing alkali metal derivatives, R_2MM' with 1,2-dihaloethane, or reducing diorganometal halides with Mg.[48] Another method is the elimination of H_2 from the hydrides R_2MH. Tetrabenzoyldiarsane was obtained by the reaction shown in Scheme 6.[49]

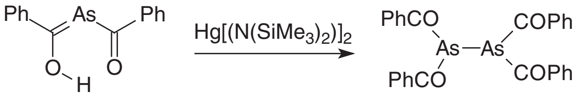
The tetraorganodimetal compounds are all air sensitive. Many tetraalkyldibismuth compounds decompose at room temperature. The sterical hindered diarsine R_2AsAsR_2 [R = $(Me_3Si)_2CH$] is remarkable because it dissociates on heating to give the radical $R_2As\cdot$, which is stable in solution at 25 °C.[50] In contrast, the analogous dibismuthine R_2BiBiR_2 [R = $(Me_3Si)_2CH$] is stable toward dissociation in solution at this temperature although the Bi–Bi bond is weaker than the As–As bond.[51] These differences can be explained by the consideration of the sterical situation. The driving force for the dissociation of the diarsine is the tension between bulky bis(trimethylsilyl)methyl substituents. The sterical tension is smaller for the dibismuthine than for the diarsine. Heating the dibismuthine above room temperature leads to the migration of the alkyl groups with the formation of trialkylbismuth and cyclobismuthines $(RBi)_n$ ($n = 3, 4$) [R = $(Me_3Si)_2CH$]. Attempts to form the diorganoantimony radical $R_2Sb\cdot$ [R = $(Me_3Si)_2CH$] by the elimination of hydrogen from the corresponding stibine failed.[51]

Many distibines and dibismuthines have lighter colors in solutions or melts than in the solid state. Crystals of these "thermochromic" distibines or dibismuthines consist of linear chains of the dimetal compounds with short intermolecular metal–metal contacts. Delocalization of electrons along the chains is possibly responsible for the bathochromic shift between fluid and solid phases. Usually, the *trans*-conformation is adopted by the tetraorganodimetal compounds in the solid state. $(CF_3)_4As_2$ shows the *trans*-conformation also in the gas phase. Photoelectrospectroscopic measurements on Me_4Sb_2 revealed the presence of *gauche*- (12%) and *trans*- (88%) conformers in the gas phase.[52]

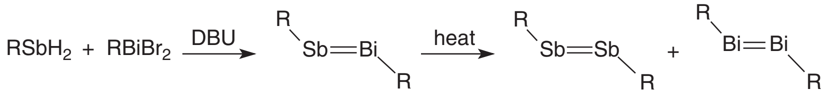
The M–M bonds of tetraorganodimetal compounds are cleaved by halogens, chalcogens, and other reagents with the reactivity increasing in the sequence As < Sb < Bi. The insertion of oxygen into the Sb–Sb bond of tetraaryldistibines gives the corresponding monoxides.[48] Dimetal compounds M_2R_4 react with Me_3M^1 (M^1 = Al, Ga, In) with the formation of heterocycles of the general type $[Me_2M^1MR_2]_3$ or adducts $[M_2R_4][M^1R_3]_2$.[53,54,54a] In addition, diarsines bearing halogen substituents, for example, 1,2-di-*tert*-butyl-1,2-diiododiarsine, which exists in the *meso*-form in the solid state, are known.[55]

3.16.2.2.2 Metal–metal double bonded compounds

The use of bulky organic groups permitted the isolation of several thermally stable compounds containing double bonds between arsenic, antimony, or bismuth.[8,9,56] Examples of homonuclear dimetal compounds, that is, diarsenes, distibenes, or dibismuthenes, include RAs═AsR (R = 2,4,5-$Bu^t_3C_6H_2$),[57] RM═MR {M = Sb, Bi; R = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$(Tbt)},[56,58,58a] R = 2,6-$(Me_3Si)_2CH]_2$-4-$[(Me_3Si)_3C]C_6H_2$(Bbt),[56,59] and the terphenyl-protected dipnicogen compounds RM═MR [M = As, Sb, Bi; R = 2,6-$Ar_2C_6H_3$ (Ar = 2,4,6-$Me_3C_6H_2$, 2,4,6-$Pr^i_3C_6H_2$)].[60] The



Scheme 6



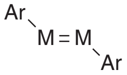
R = Bbt; DBU = diaza-bicyclo-undecene

Scheme 7

diarsene $(RAs)_2$ ($R = 2,4,5\text{-}Bu^t{}_3C_6H_2$) has been synthesized from the corresponding difluorarsine by reaction with $RAs(SiMe_3)Li$.[57] In addition, Arsa–Wittig complexes ($ArAs{=}PMe_3$) are intermediates for the synthesis of diarsenes, $ArAs{=}AsAr$.[61] The species $TbtM{=}MTbt$ (M = Sb, Bi) were obtained by deselenation of the heterocycles $(TbtMSe)_3$ by $(Me_2N)_3P$.[58] $TbtSb{=}SbTbt$ reacts with oxygen to form the dioxadistebetane $(TbtSbO)_2$.[58] The compounds of the type $(2,6\text{-}Ar_2C_6H_3M)_2$ were obtained by reduction of the corresponding organometal dihalides by K or Mg.[60]

In addition, a number of unsymmetric dipnictenes, $RP{=}AsR$, $RP{=}SbR$,[62] $RSb{=}BiR$,[59] and $RP{=}BiR$,[63] were reported. One example, the stibabismuthene $RSb{=}BiR$ (R = Bbt), was formed by the elimination of HBr from $RSbH_2$ and $RBiBr_2$. The stibabismuthene is stable at ambient temperature in hydrocarbon solvents in the absence of air and light. When a solution in benzene was heated, the symmetrical compounds are formed (Scheme 7).[59]

All the dipnictenes **5** display a *trans*-coplanar arrangement of the C–M═M–C fragment and the M═M bond is shorter than an M–M single bond. *cis*-Dibismuthenes are known only as ligands. Complexes **6** were formed by the reaction of cyclobismuthines, R_nBi_n ($n = 4$, 5; $R = Me_3CCH_2$, Me_3SiCH_2) with $W(CO)_5THF$.[64] A *trans*-distibene, $RSb{=}SbR$ ($R = Bu^t(CO)$)], was trapped as ligand in complex **7**.[65]



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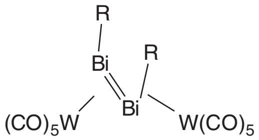

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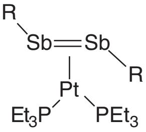

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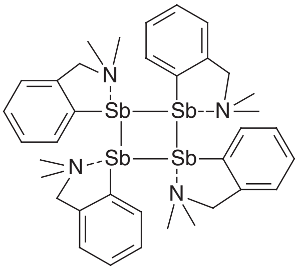
3.16.2.2.3 Polymetal compounds

Compounds have been characterized which contain three or more metal atoms in monocyclic or polycyclic arrays. Synthetic methods include the reduction of dihalides RMX_2,[66] or the elimination of H_2 from RMH_2. Extraordinary examples for cyclotriarsines are the carbine derivatives R_3As_3 ($R = Tp'(CO)_2M{\equiv}C\text{—}$) which are obtained by the reactions of arsaalkenyl carbine complexes $Tp'(CO)_2M{\equiv}C\text{–}As{=}C(NMe_2)_2$ [$Tp' = HB(3,5\text{-}Me_2HC_3N_2)_3$] with $Au(CO)Cl$.[67] The cyclotrimer R_3Sb_3 [$R = (Me_3Si)_2CH$] was obtained by photochemical ring contraction of cyclo-R_4Sb_4 [$R = (Me_3Si)_2CH$] or by reaction of $RSbCl_2$ with Li_3Sb.[68] Bismuth monocycles R_3Bi_3 and R_4Bi_4 [$R = (Me_3Si)_2CH$, $2\text{-}(Me_2NCH_2)C_6H_4$] exist in equilibria in solution but the cyclotetramers prevail in the solid state.[69,70] $(RSb)_4$ [$R = 2\text{-}(Me_2NCH_2)C_6H_4$] **8** is formed by the reaction of $RSbCl_2$ with Mg in THF.[71] Elimination of H_2 from $RBiH_2$ leads to equilibria mixtures of cyclopentamers and trimers $(RBi)_n$ ($n = 3$, 5; $R = Me_3CCH_2$, Me_3SiCH_2).[64,72] The analogous antimony rings are formed by the reaction of $RSbBr_2$ with Mg.[72] Cyclopentamers with known solid-state structures include $(p\text{-}TolAs)_5$ **9**[73] and $(Me_3CCH_2Sb)_5$.[72] Also a P_3As heterocycle **10**,[74] bicyclic arsines **11** and **12**,[75,75a] and the hexaarsine complex **13**[76] were characterized by crystallography. Four-membered cycles $Bu_4{}^tAs_nSb_{n-4}$ ($n = 0\text{–}2$) were formed from Bu^tSbCl, $AsCl_3$, and Mg.[77] The structure of the trisarsino phosphine **14** contains the central phosphorus atom in a pyramidal environment.[78] Air oxidation of $RSb(SiMe_3)_2$ gave $(RSb)_n$ (R = *o*-, *m*-, *p*-Tol), which exist as tetramers and pentamers in solution but as cyclohexamers in the crystalline state.[79] A pentaalkylchlorohexastibane **15** was obtained from $RSbCl_2$ and Na/K alloy.[80] Arsenic polycycles R_2As_7 ($R = PhCH_2$) were obtained from $As_7{}^{3-}$and RMe_3NBr.[81] The polycycle **16** is one of the products of the reduction of $RSbCl_2$ by Mg.[82]



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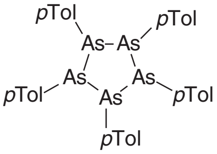

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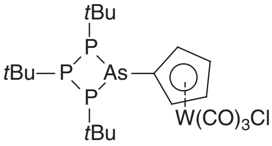

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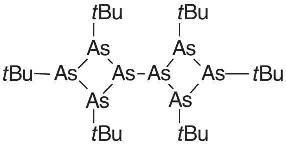

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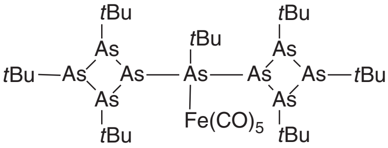

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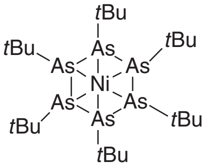

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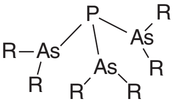

R = C(O)Ph

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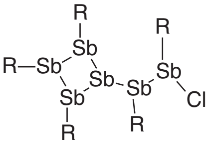

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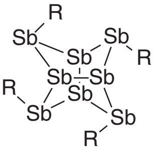

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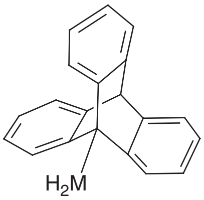
Chains of the type catena $(RM)_n$ exist as ligands in the coordination sphere of transition metal complexes. Examples are the four-membered arsenic or antimony chains in $[(PhAs)_4]_2[CuPPr_3]_4$[83] or $(Me_3CCH_2Sb)_4[Cr(CO)_2MeC_5H_5]_2$.[84] Catena tetrastibanes, $R_2Sb–SbR–SbR–SbR_2$, are formed by the reactions between distibanes and cyclostibanes, or by reactions of $RSbX_2$ and R_2SbX with Mg.[84] They can be trapped as bidentate ligands in transition metal carbonyl complexes.[85,85a] A triantimony species $[Me_2SbSbMe_2SbMe_2]^+[Me_2SbBr_2]^-$ was obtained from Me_4Sb_2 and Me_2SbBr.[86]

3.16.2.3 Organometal Hydrides

Many organometal hydrides of the types RMH_2 or R_2MH (M = As, Sb, Bi) are highly sensitive, thermally labile, and self-igniting compounds, for example, the primary cyclopentadienylarsine $C_5Me_5AsH_2$[87] decomposes at −70 °C. The hydrides are generally synthesized by the reactions of the corresponding organometal halides with complex hydrides.[88–93.] Examples are 6-methyl-2-(pyridyl)bis(trimethylsilyl)methylarsine and isobutylstibines R_2SbH and $RSbH_2$ (R = Me_2CH).[92,93] Primary unsaturated stibines, for example, ethenylstibine $H_2C{=}C(H)SbH_2$ and ethynylstibine $HC{\equiv}C–SbH_2$, are obtained from the corresponding chlorides and Bu_3SnH.[94] With appropriate protecting substituents, the stability toward heat and air can be enhanced considerably. A "user friendly" primary arsine is the air-stable compound $FcCH_2CH_2AsH_2$ (Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)), that has been prepared by reduction of the arsonic acid $FcCH_2CH_2As(O)(OH)_2$ using Zn/HCl.[95] Thermally stable primary arsines and stibines RMH_2 (M = As, Sb) were obtained with the triptycenyl **17**[96] or terphenyl **18**[97] groups as protecting substituents. Sterical protection with the bis(trimethylsilyl)methyl group was used for the stabilization of R_2SbH,[88] $RSbH_2$,[90] R(H)Sb–Sb(H),[89,90] and 2-(Me_2NCH_2)C_6H_4(R)SbH **19**[91] [R = $(Me_3Si)_2CH$].



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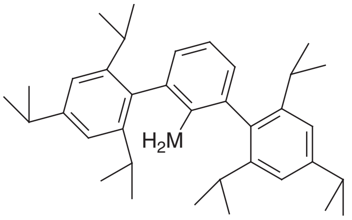

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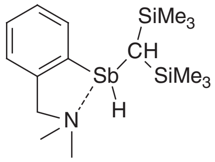

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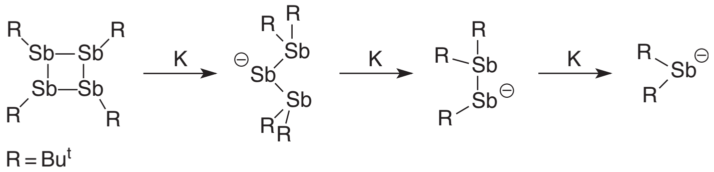
R_2BiH [R = $(Me_3Si)_2CH$] decomposes however at an ambient temperature with the formation of hydrogen and the corresponding dibismuthine $R_2Bi–BiR_2$.[88] The secondary bismuthine R_2BiH (R = 2,6-$Mes_2C_6H_3$) is stable up to 100 °C. Decomposition at higher temperatures gives RH and the corresponding dibismuthene RBi=BiR.[98]

3.16.2.4 Alkali Metal–Group 15 Element Compounds

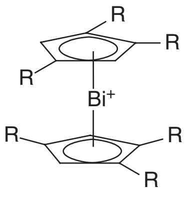
The alkali metal diorganometal compounds R_2MM^1 (M = As, Sb, or Bi; M^1 = alkali metal) are important reagents that can be prepared by the reaction of R_2MX (X = halogen) or R_3M with an alkali metal, or by treating the corresponding hydride R_2MH with an alkali metal (COMC (1995)).[2] The antimonides R(2-$Me_2NCH_2C_6H_4$)SbM [M = Li, Na; R = $(Me_3Si)_2CH$] are formed by the reaction of the corresponding hydride with BuLi or by transmetallation of the resulting lithium antimonide with *tert*-butoxide.[91] Metallation of $PhAsH_2$ with BuLi in toluene-thf gives the primary arsenide $[PhAsHLi\cdot 2thf]_\infty$ which crystallizes as helical polymers.[99] In contrast, metallation of $PhSbH_2$ with BuLi gave the Zintl compound Li_3Sb_7.[100] Metallation of the terphenyl-substituted primary pnictanes $ArMH_2$ with BuLi gave the metallated derivatives ArM(H)Li (Ar = C_6H_3-2,6-$Trip_2$; Trip = 2,4,6-triisopropylphenyl; M = As, Sb).[97] Alkali metal derivatives of $(Bu^t{}_2Sb)_2Sb^-$, and $Bu^t{}_2Sb(Bu^t)Sb^-$ and $Bu^t{}_2Sb^-$ are formed by the reactions of $Bu^t{}_4Sb_4$ with sodium or potassium in boiling tetrahydrofuran (Scheme 8).[77,100,101]

3.16.2.5 Cyclopentadienyl Compounds

Both monohapto (η^1) and pentahapto (η^5) coordination of cyclopentadienyl rings on As, Sb, or Bi were studied. Tetraisopropylcyclopentadienylarsenic dihalides, η^1-Cp^xAsCl_2, are formed by the reactions between AsX_3 and Cp^xK.[102] Tris(cyclopentadienyl)bismuth $(Cp)_3Bi$ was obtained by the reaction of tris(dialkylamino)bismuth compounds with cyclopentadiene.[103] Representatives of stibocenium species $[Cp'_2Sb]^+[AlCl_4]^-$ and $[Cp^*{}_2Sb]^+[AlI_4]^-$ (Cp′ = 1,2,4-tri(*tert*-butyl)cyclopentadienyl; Cp^* = pentamethylcyclopentadienyl) are formed by the reaction of Cp′Na with $SbCl_3$ and $AlCl_3$ or from Cp^*Al and SbI_3. The structure of $Cp^*{}_2Sb^+$ is angular (36°), that of Cp'_2Sb^+ almost coplanar.[104] Chloride abstraction from $Cp^x{}_2BiCl$ with $AlCl_3$ gives $[Cp^x{}_2Bi]^+[AlCl_4]^-$ (Cp^x = 1,2,4-$Bu^t{}_3C_5H_2$). The crystal structure shows a bismocenium cation **20** with almost parallel η^5-cyclopentadienyl rings.[105]



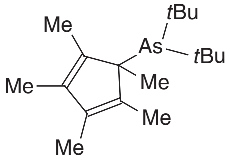
Scheme 8



R = Bu^t

20

The cyclopentadienyl arsines Cp^xAsR_2 ($Cp^x = Me_5C_5$; R = Et, Pr^i, Bu^t; $Cp^x = Me_3H_2C_5$; R = Cl, Et, Pr^i) were synthesized by the reactions between the corresponding dichlorides and RMgX or by the reaction of R_2AsX with Cp^xM (M = Li, K). The structure of $Me_5C_5AsBu^t_2$ **21**, $(Me_5C_5AsMe)_2$ **22**, and $(Me_5C_5AsNH)_4$ in the crystal shows a monohapto arrangement of the pentamethylcyclopentadienyl ligands.[87,106,107]



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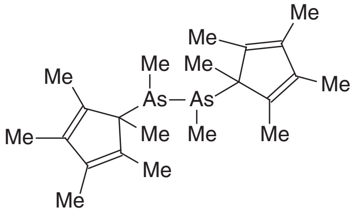

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3.16.2.6 Triorganometal(III) Compounds

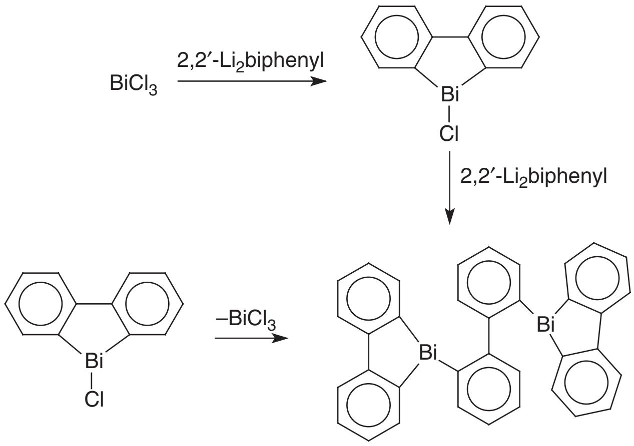
Triorganometal compounds of As, Sb, Bi are among the organometallic compounds with the longest history. They are generally stable at room temperature but the reactivity varies with the structure and the nature of the substituents. Alkyl compounds of the type R_3M are air sensitive and strong reducing agents in contrast to the aryl derivatives. Tertiary arsines, stibines, and bismuthines, R_3M, all have pyramidal structures as exemplified by the structure of tribenzylstibine.[108] The inversion barriers are high and chiral derivatives RR^1R^2M have been isolated and resolved using chiral transition metal complexes as auxiliary.[109,110]

Well-established routes to triorganometal compounds are the reactions of trihalides of arsenic, antimony, or bismuth with organolithium compounds or Grignard reagents. Examples for the use of organolithium reagents are the syntheses of R_3As (R = 8-(dimethylamino)-1-naphtyl,[111] $C\equiv CPh$)[112], R_3Sb [R = (2-C_4H_3O, 2-C_4H_3S),[113] R_3Bi [R = *p*-$C_6H_4(NMe_2)$; *p*-$C_6H_4CH_2N$-Pr^i_2; *p*-$C_6H_4CH_2N(2\text{-}Py)_2$,[114] 2,4,6-(triphenyl)phenyl,[115] 9-anthryl[116]], R_3M [M = As, Sb, Bi; R = *p*-(N-7-azaindolyl)phenyl),[117] CH_2PMe_2,[118] 2-[(dimethylamino)methyl]phenyl[119]]. A biphenylene (biph) complex of bismuth $Bi_2(biph)_3$ is formed both by reaction of $BiCl_3$ with a lithium reagent or by redistribution (Scheme 9).[120]

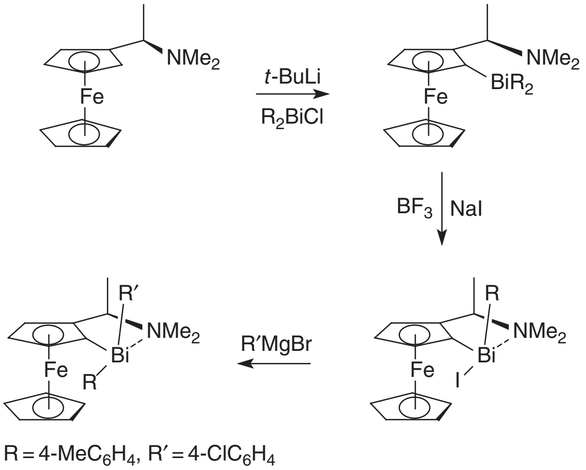
Tris(chlorodifluorovinyl)antimony, $Sb(CCl{=}CF_2)_3$, is formed in a one-pot reaction between CF_3CH_2Cl, BuLi (2 equiv.), and $SbCl_3$.[121] *cis*–Ph_2As–$CH{=}CH$–$AsPh_2$ was synthesized from Ph_2AsLi and *cis*-Cl-$CH{=}CH$-Cl.[122]

Grignard reactions between organomagnesium halides and MCl_3 have been used for the syntheses of R_3M [M = Sb, Bi, R = 2,6-$F_2C_6H_3$;[123] M = As, R = 3,5-$(CF_3)_2C_6H_3$[124]]. The Sb chiral triarylstibine $RR'R''Sb$ (R = tolyl, R′ = naphtyl, R″ = 1-dimethylaminoethylphenyl) was obtained by the stepwise substitution of the ethynyl groups on bis(phenylethynyl)-*p*-tolylstibine with Grignard and organolithium reagents.[110] Arylcopper reagents were employed to prepare tris(2,4,6-triisopropylphenyl) arsine, stibine, and bismuthine.[125] Good yields of tris(perfluoroalkyl) arsenic or antimony compounds were obtained by reacting $AsCl_3$ or $SbCl_3$ with cadmium reagents.[126] Me_3Sb is formed together with $MeSbBr_2$ by a scrambling reaction of Me_2SbBr.[127] Transmetallation of 2,6-$(F_2C_6H_3)_3Bi$ with Sb gives (2,6-$F_2C_6H_3)_3Sb$.[128] Bichiral ferrocenyl compounds were obtained as shown in Scheme 10.[129]

A new synthetic method for R_3M (R = Ph, *p*-Tol, 4-$Me_2NC_6H_4$; M = As, Sb, Bi) is composed of two-step reactions starting from the metal oxides and 2,6-dimethoxybenzenethiol yielding the corresponding thiolatometals which react with the aryllithium reagents RLi to give R_3Bi.[130] A novel dry route to *ortho*-functionalized triarylbismuthanes implies milling together bismuth shots and calcite grains in the presence of Cu powder and CuI using a laboratory ball-mill.[131] Triarylstibines bearing an amino side chain displaying hypervalent Sb···N bonding were studied by

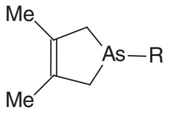


Scheme 9



Scheme 10

X-ray, NMR, and theoretical calculations.[119,132,133] Benzylamine-substituted stibines R_3Sb [R = 2-$Me_2NCCHR^1C_6H_4$, R^1 = H, Me] react with MeI or HBr to obtain the corresponding di-, or tri-, ammonium salts, for example, $[(2\text{-}Me_2HN^+CCH_2C_6H_4)_3Sb](Br^-)_3$.[119] Triorganometal compounds are frequently used as ligands in transition metal complexes.[11,12] Adducts of the type $R_3M–M^1R_3$ (M = As, Sb, Bi; M^1 = Al, Ga) are formed in reactions with triorganometals of Al or Ga.[134–139.] Crowded triarylmetal compounds, R_3M, tris(2,4,6-triisopropylphenyl) arsine, stibine, and bismuthine, were synthesized by the reaction of RCu with the corresponding metal trichlorides. Introduction of the three bulky aryl groups resulted in pyramidal structures with large bond angles around metal atoms (R_3As: 111.5°, R_3Sb: 109.2°, R_3Bi: 106.7°).[140] Reactions of zirconocene–butadiene complexes and $RAsCl_2$ give 3-arsolenes **23**.[141] The tetraarsacubane **24** was obtained by reacting $(Me_3Si)_2PLi$ with the arsaalkene $Me_3SiAs{=}C(OSiMe_3)Bu^t$ in the presence of $CoCl_2$.[142] The structure of diarsatriptycene **25** was reported.[143]



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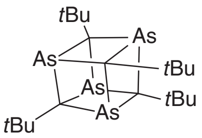

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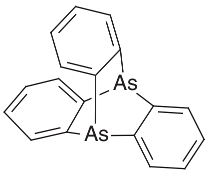

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Dentritic phenylene-bridged Bi_n bismuthanes were obtained from Ph_2BiCl and p-$Li_2C_6H_4$ and related reagents.[144]

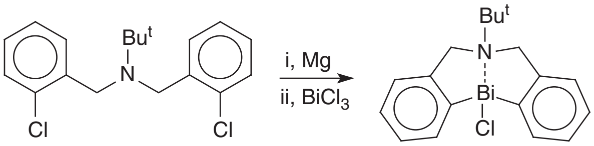
3.16.2.7 Diorganometal(III) Species

An established synthetic pathway to dialkylmetal halides, R_2MX, is thermolysis of R_3MX_2. A recent example for this route is the synthesis of $Bu^i{}_2SbI$ by thermal decomposition of $Bu_3{}^i SbI_2$.[93] Partial alkylation of MX_3 with RMgX or RLi is useful only for diorganometal halides with bulky substituents, for example, R_2BiCl ($R = (Me_3Si)_2CH$,[145] R_2MCl (M = As, Sb; R = 2,4,6-tris(trifluoromethyl)phenyl).[146] Organomagnesium reagents are also involved in the synthesis of a hypervalent azabismocine (Scheme 11). The eight-membered azabismuthine ring is highly flexible. The hypervalent Bi–N bond distance is 2.568(3) Å.[147]

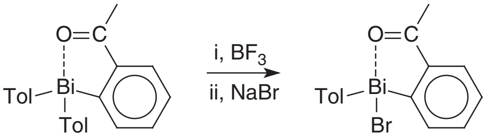
Dialkylbismuth chlorides or dimethylantimony chloride can be obtained in high purity by cleavage of dialkylphenylmetal compounds with gaseous HCl.[148] Redistribution reactions are particularly useful for the syntheses of diarylantimony or bismuth halides, for example, Mes_2BiBr.[149] However, dialkylantimony bromides, for example, $Bu^i{}_2SbBr$, are also obtained by this method.[93] Hypervalent R_2SbX (X = Cl, Br, I; R = 2-$Me_2NCH_2C_6H_4$) have been prepared by the reaction of RLi with SbX_3 and by exchange reactions between R_3Sb and SbX_3.[150] Chiral diarylbismuth halides RR^1BiCl can also be prepared by fluoro dearylation of unsymmetrical triarylbismuth R_2R^1Bi compounds with BF_3 followed by halogen exchange.[151–153] An example is given in Scheme 12.[154]

Chiral racemic RR^1MCl [M = Sb, Bi; R = 2-$(Me_2NCH_2)C_6H_4$; $R^1 = CH(SiMe_3)_2$] form by the reaction of R^1MCl_2 with RLi. Coalescence of the Me_3Si signals was observed at 45 °C in the ^{1}H NMR spectra of solutions of $RR'BiCl$ in $(CD_3)_2SO$.[91] Investigations on edge inversion at trivalent bismuth and antimony revealed great acceleration by intra- and intermolecular nucleophilic coordination of {2-$C_6H_4C(CF_3)_2OBi$(p-Tol)} and related trivalent organobismuth compounds in DMSO and other solvents.[155] Diphenylantimony iodide and dimethylantimony iodide are obtained from the corresponding chlorides by halogen exchange with NaI.[148,156]

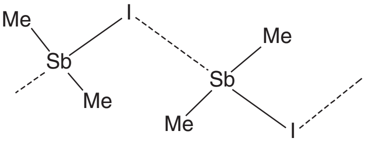
Generally, diorganometal halides are pyramidal molecules. This was confirmed by X-ray crystallography for dimesitylarsenic bromide,[157] 2,4,6-$[(F_3C)_3C_6H_2]_2MCl$ (M = As, Sb),[146] Me_2SbI,[148] Ph_2SbX (X = Cl, Br, I),[108,156–158] $[(Me_3Si)_2CH]_2MCl$ (M = Sb, Bi),[145,148] and dimesitylbismuth bromide.[159] In the crystals of dimethylantimony iodide **26** the molecules are associated to zigzag chains through intermolecular Sb···I contacts.[148] The compounds R_2MX are readily hydrolyzed or react with other nucleophiles such as RM, RO-, S^{2-}, RCO_2^-, $^-OSO_2CF_3$, RTe^-.[2,160] Hydrolysis of Mes_2BiBr gives $Mes_2BiOBiMes_2$.[161] The diphenylbismuth amide $Ph_2BiN(SO_2Me)_2$ is formed by the reaction of Ph_2BiCl with the corresponding silver salt.[162] Diarylmetal halides are Lewis acidic and several adducts were reported. The adducts Mes_2BiBrL ($L = OSPh_2$, $OPPh_3$) are monomeric, each bismuth atom having a four-coordinate disphenoidal geometry with axial bromine and ligand donor atoms and equatorial mesityl groups.[163] With ligands capable of intramolecular coordination, base-coordinated diarylmetal complexes of the types **27** and **28** were synthesized.[164]



Scheme 11



Scheme 12



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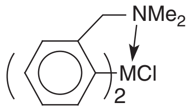

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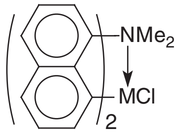

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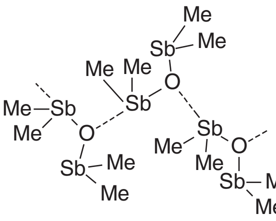
Anionic $[R_2MX_2]^-$ ($M = Sb$, Bi) species are formed from the appropriate halides R_2MX and onium halides.[2] Cationic, four-coordinate ten-electron bismuth(III) complexes, for example, $[BiPh_2(L)_2][BF_4]$, are formed by reactions between $BiPh_2Br$, $AgBF_4$, and 2 equiv. of the ligand L ($L = OPPh_3$, pyridine).[165,166] $[SbPh_2(L)_2][PF_6]$ is obtained in a phenyl migration reaction from $PhSbCl_2$ and $TlPF_6$.[168] Cationic complexes stabilized by intra- or intermolecular coordination of the type $[R_2M][PF_6]$ ($M = Sb$, Bi; $R = 2\text{-}Me_2NCH_2C_6H_4$) are formed by the reaction of R_2MCl with $TlPF_6$; the coordination geometry at the Sb or Bi centers is distorted trigonal bipyramidal.[167] In addition, in the chiral triphenylphosphine(methyl)phenyl arsenium salt, $[Ph_3P(Ph)(Me)As][PF_6]$, the central arsenic atom is situated in a trigonal bipyramidal (lone pair included) environment.[168] The cation $[Me_2Sb\text{–}SbMe_3]^+$ can be viewed as an example for a dimethylstibenium species, stabilized by coordination of Me_3Sb.[46]

Exchange reactions between diarsines or distibines $R_2M\text{–}MR_2$ and ditellurides $RTe\text{–}TeR$ ($M = As$, Sb; $R = Me$, Et) give the mixed compounds $R_2M\text{–}TeR$,[160] $R^1{}_2SbTeR$ [$M = Sb$, $R^1 = Me_3SiCH_2$, $R = Ph$].[169] $R_2SbS_2PR_2$ ($R = CH_3$) is formed from $Me_2Sb\text{–}SbMe_2$ and $Me_2P(S)\text{–}(S)PMe_2$.[170] Electron diffraction data of R_2SbER ($E = S$, Se; $R = CH_3$) reveal that the *syn*-conformer is predominant in the gas phase.[171]

Oxides $(R_2Sb)_2O$ ($R = Ph$, *o*-Tol, *p*-Tol)[48] or $(Mes_2Bi)_2O$[161,172] are formed by reactions of the corresponding distibines or dibismuthines with oxygen. The bismuth chalcogenides $(R_2Bi)_2E$ [$E = S$, Se, Te; $R = Me$, $(Me_3Si)_2CH$, Mes] are obtained by the reactions of R_2BiX with Na_2S or Na_2Te, or by the insertion of elemental chalcogens into the corresponding dibismuthines.[161,173] The structures of $(Me_2Sb)_2E$ ($E = O$, S, Te) were determined by electron diffraction and it was shown that *syn–syn* and *syn–anti* conformers exist in the gas phase.[174–177] The valence angles of the *syn–syn* conformers are $\angle SbSSb = 98.7(5)^\circ$ and $\angle SbTeSb = 91(2)^\circ$.[174]

The structures of $(Me_2Sb)_2E$ ($E = O$, S) were also determined in the solid phase where $(Me_2Sb)_2O$ molecules in the *syn–anti* conformation are associated to zigzag chains **29** through $Sb\cdots O$ contacts (2.58 Å). The structure of the sulfur analog **30** consists of a three-dimensional net where the molecules in the *syn–syn* conformation are linked together by $Sb\cdots S$ contacts (3.164 Å).[177] Me_4Sb_2 and Me_2SbBr react with air to form $[(Me_2Sb)_3O]Br$, **31**, a planar stibino oxonium salt.[178] $(Me_2Sb)_2S$ reacts, with the formation of Me_3Sb and $MeSb(SSbMe_2)_2$.[179]



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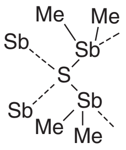

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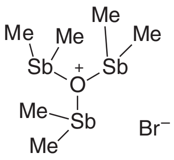

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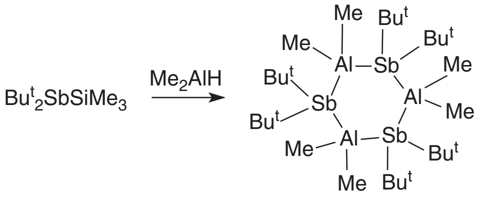
Tris(diphenylstibino)amine $(Ph_2Sb)_3N$ is formed by ammonolysis of Ph_2SbCl in liquid ammonia. The Sb_3N core is almost planar.[180] In addition, crystals of the analogous methyl derivatives $(Me_2M)_3N$ ($M = As$, Sb) contain molecules with planar M_3N cores.[181,182]

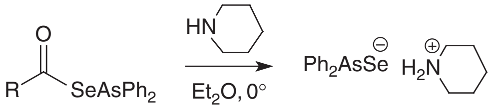
Monomeric arsinoboranes Mes_2BAsR_2 have been prepared via the reaction of $LiAsR_2$ with Mes_2BF.[183] It was shown that B–As π-bonding is difficult to achieve in arsinoboranes, because of the large inversion barrier at arsenic.[184] The heterocycles $[Bu^t{}_2SbAlR_2]_3$ ($R = Me$, Et) form in dehalosilylation reactions between diorganoaluminum hydrides and $Bu^t{}_2SbSiMe_3$ (Scheme 13).[185]

$[Me_2SbInR_2]_3$ is formed from $(Me_2Sb)_2$ and R_3Sb ($R = CH_2SiMe_3$).[186] Reactions of Ph_3Sb or Ph_3Bi with K_4Ge_9 lead to the anions $[Ph_2Sb\text{–}Ge_9\text{–}Ph]^{2-}$, $[Ph_2Sb\text{–}Ge_9\text{–}Ge_9\text{–}SbPh_2]^{4-}$,[187] or $[Ph_2Bi\text{–}Ge_9\text{–}BiPh_2]^{2-}$.[188]

Thioacylsulfanylarsines $(RCS_2)AsPh_2$ were synthesized by treating piperidinium dithiocarboxylates with Ph_2AsCl.[189] The reaction of a *Se*-diphenylarsanyl selenoester with piperidine gave diphenylselenoarsinous and diphenyldiselenoarsinic acid piperidinium salts (Scheme 14).[190]

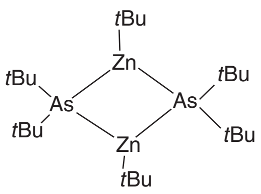


Scheme 13



Scheme 14

Four-membered heterocycles exist in the structures of dimeric di-*t*-butylarsino zinc complex **32** and in the related gallium compound **33**.[191,192] In contrast, the di-*t*-butylarsino beryllium complex $Bu^t_2As–BeCp^*$ **34** is monomeric.[193]



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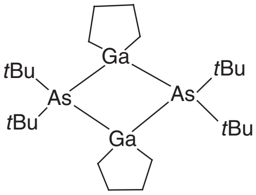

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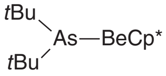

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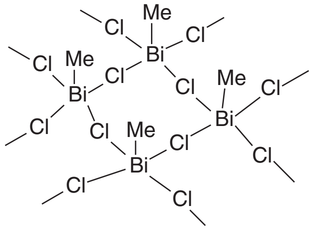
3.16.2.8 Monoorganometal(III) Compounds

The dihalides RMX_2 are important reagents in organometallic syntheses. They can readily be prepared by comproportionation between R_3M and MX_3. Examples for the use of this method are the syntheses of mesitylbismuth dichloride and dibromide.[194] The reduction of arsonic acids $ArAs(O)(OH)_2$ is useful for the synthesis of arylarsenic dihalides $ArAsX_2$.[2] For sterically protected monoorganometal(III) dihalides, the reactions between MX_3 and RLi are widely used. Examples are the preparations of triptycenylmetal dihalides, 2,4,6-triphenylphenylbismuth dichloride,[195] N-functionalized alkyl complexes R^1MCl_2 (M = As, Sb; R = 6-Me-2-Pyr $(SiMe_3)_2C^-$),[196] and intramolecular base-coordinated dihalides RMX_2 (M = As, Sb, Bi; R = 2-$(Me_2NCH_2)C_6H_4$, 8-$(Me_2NC_{10}H_6)$).[164]

Vinyl- or alkynylbutylstannanes have been used as reagents for the syntheses of primary unsaturated dichlorostibines from $SbCl_3$.[94] For the syntheses of alkylmetal dihalides of high purity, it is useful to react $MeMPh_2$ with gaseous HX. Examples are $MeMX_2$ (M = Sb, Bi; X = Cl, Br) and $RBiCl_2$ (R = $CH(SiMe_3)_2$).[146,197] Organometal diiodides are readily formed by halogen exchange reactions, for example, $MeSbCl_2$ or $MeSbBr_2$ react with NaI in acetone to form $MeSbI_2$.[198] However, $MeBiI_2$ is obtained from Bi and MeI.[199]

Due to the interactions between Lewis-acidic centers at the metals and Lewis-basic centers at the halogen atoms usually extended structures result. Examples for one- or two-dimensional frameworks where molecular units cannot be distinguished are the solid-state structures of $MeBiCl_2$ **35**[197] and $MeBiI_2$ **36**.[200] Intermolecular metal–halogen interactions between pyramidal molecules exist in the structures of *p*-tolylantimony(III) dichloride and dibromide,[158] Bu^tSbCl_2,[200] or $MesBiBr_2$.[194] In the presence of Lewis bases (L monodentate donor molecule) adducts of the types $[RMX_2L_2]$ **37** or $[RMX_2L]_2$ **38** containing five-coordinate square-based bismuth centers form. Examples are $[PhBiBr_2(OPPh_3)]_2$, $[PhBiBr_2(dmpu)_2]_2$, (dmpu = N,N′-dimethylpropylene urea),[163] $[PhSbCl_2bipy]$,[201] $[PhBiX_2(py)]_2$.[202] Organometal dihalides also accept readily an additional halide ion and anionic monomeric species

$[RMX_3]^-$, for example, $[MeAsCl_4]^-$ or dimeric species $[RMX_3]_2^{2-}$ with five-coordinate metal centers, for example, $(TolSbCl_3)_2^{2-}$, $[Me_3SiCH_2SbCl_3]_2^{2-}$, *cis*- and *trans*-$[PhSbI_3]_2^{2-}$ **39, 40** result.[203–206]



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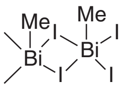

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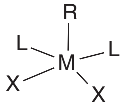

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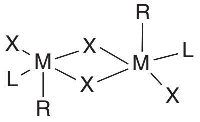

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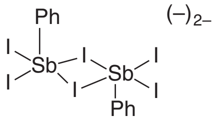

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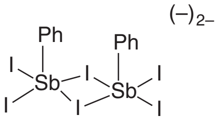

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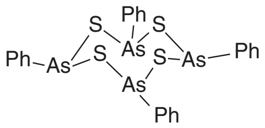
Reactions of organometal dihalides with chalcogenides or reactions of metal–metal bonded oligomers $(RM)_n$ with chalcogens lead to polymers or oligomers of the type $(RME)_x$. Examples are the well-defined cyclooligomers $(RSbE)_n$ [$R = (Me_3Si)_2CH$; E = O, S, Se, Te; $n = 2$–4] which were prepared by the reactions of $RSbCl_2$ with KOH, or with Na_2E.[71,173,207,208] Three types of sulfurization products containing two antimony atoms result in the reaction the distibene bearing 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups with elemental sulfur (Scheme 15).[209]

The structural chemistry of the $(RME)_n$ species is highly diverse as reflected in the crystal structures of $(PhAsO)_4$,[210] $(PhAsS)_4$ **41**,[303] $(RSbO)_4$ **42**,[207] $(RSbS)_2$ [$R = 2$-$(Me_2NCH_2)C_6H_4$] **43**, and $(RBiS)_2$ [$R = 2,6$-$(Me_2NCH_2)_2C_6H_3$] **44**.[211]



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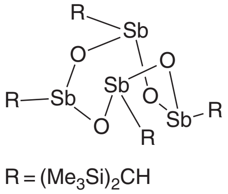

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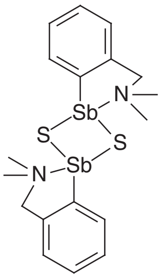

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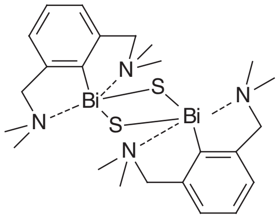

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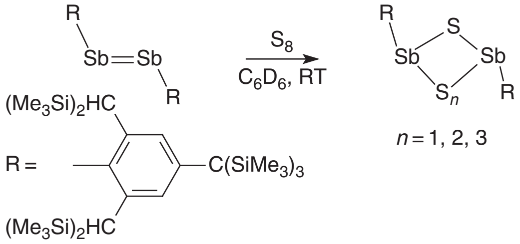
The $(RME)_n$ heterocycles can be used as sources for the unstable six-electron RM species. Deselenation of $(RSbSe)_3$ in the presence of 1,3-butadienes results in the formation of cycloadducts of the stibinidene RSb,



Scheme 15

$R = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$.[212] Interesting structures result when $(RME)_n$ species are reacted with main group or transition metal acceptors. The reaction of $(EtAsO)_4$ with KSCN gives $K[(EtAsO)_4]_2SCN$, a potassium complex where two asoxane ligands are coordinated on K^+ through the oxygen atoms.[213] Reaction of $(EtAsS)_4$ with $SbBr_3$ leads to the coordination of the As–S ring on Sb centers through the sulfur atoms.[214] Photolytic reactions of $(MeAsS)_n$ ($n = 3, 4$) with $M(CO)_6$ (M = Cr, W) give a series of complexes where the As–S ring system is expanded giving metal-stabilized rings of 8, 10, and 12 alternating As and S atoms.[215]

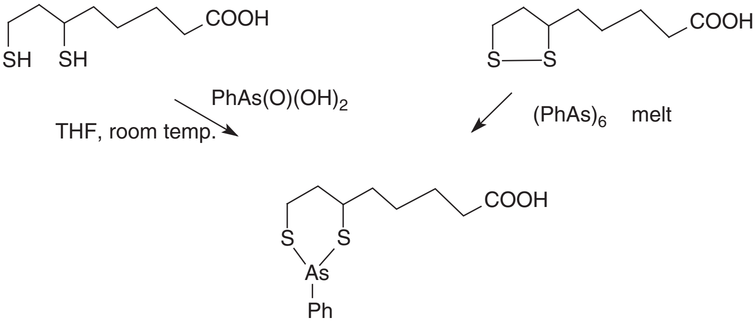
Organometal chalcogenides result also from the reactions of cyclic polymetal species with chalcogen derivatives. A ditellurostibine $RSb(TeR^1)_2$ is formed by the reaction of *cyclo*-$(RSb)_5$ with $R^1Te–TeR^1$ ($R = Me_3SiCH_2$).[205]

Several ionic or neutral derivatives of four-electron species of the type RM^{2+} stabilized by four two-electron donors have been studied. The resulting complexes generally adopt square pyramidal geometries as exemplified by $PhBiL_4^{2+}$ ($L = OP(NMe_2)_3$)[165] and $[PhBi(O_2CCF_3)_4]^{2-}$, a complex that was synthesized by the reaction of Ph_3Bi with trifluoroacetic acid and diamines or pyridine.[216] Square pyramidal environments result also when two anionic dichalcogen ligands are coordinated to a metal center. Examples are $MesBi(S_2PPh_2)_2$ formed by the reaction of Mes_2BiBr with $Ph_2PS_2NH_4$,[159] and methylbismuth complexes of the types $MeBi(S_2COR)_2$ (R = Me, Et, Pr^i), $MeBi(S_2CNR_2)_2$ (R = Me, Et, $1/2\,C_4H_8N$), and $MeBi(S_2P(OR)_2)_2$ (R = Me, Et, Pr^i).[217] A square pyramidal $CSbX_2S_2$ core exists also in the crystal structures of $PhSb[(XPPh_2)(SPPh_2)N]_2$ (X = O, S).[218] The structure of the thiobenzoate $PhSb(SOCPh)_2$ in the crystal is, however, distorted trigonal bipyramidal.[219] Organometal(III) dithiolates were obtained by different methods. Synthetic routes leading to a phenylarsenic lipoic acid derivative are shown in Scheme 16.[220]

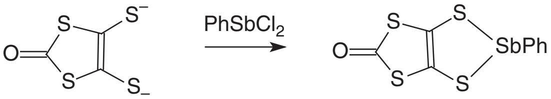
Thioacylsulfanylarsines $(RCS_2)_2AsPh$ were synthesized by treating piperidinium dithiocarboxylates with $PhAsCl_2$.[189] Reactions of $PhSbCl_2$ with dithiolato ligands gave dithiolene derivatives (Scheme 17).[221]

Organometal diamides $RM(NR_2)_2$ have also been studied. As an example, the reaction of $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ with 2-NHLiR (R = pyridyl) generating the dianion complex $1,3\text{-}[(RNLi)Sb]_2(\mu\text{-}NR)(CH_2)_3(RNHLi)_3THF$ is shown in Scheme 18.[222]

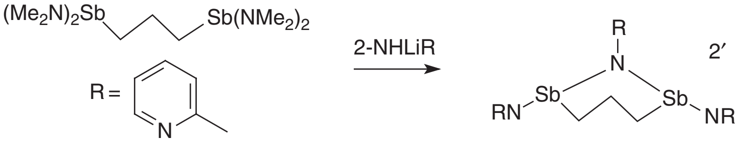
A phenylbismuth amide species $PhBi[N(SO_2Me)_2]_2$ is formed by metathesis of $PhBiBr_2$ and $AgN(SO_2Me)_2$.[162]



Scheme 16

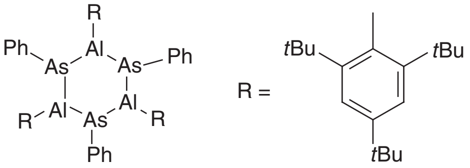


Scheme 17



Scheme 18

Trimethylsilyl organoantimony species have been used as reagents where the Me_3Si group can be exchanged by other organometal groups. *p*-$TolSb(M^1Me_3)_2$ (M^1 = Si, Ge, Sn) are formed by the reactions between *p*-$TolSb(SiMe_3)_2$ and Me_3MCl.[223] $PhSb(SiMe_3)_2$ and $CpFe(CO)_2X$ react to give derivatives of the triferriostibonium ion $[PhSb[CpFe(CO)_2X]_3]^+$.[224] The dianionic species $[MeSb\{Fe(CO)_4\}_3]^{2-}$ reacts with HOAc with the formation of $[Me(OAc)Sb\{Fe(CO)_4\}_2]^-$.[225] Reaction of $[HSb\{Fe(CO)_4\}_3]_2^-$ and methyl iodide gives $[Sb(Me)I\{Fe(CO)_4\}_2]^-$.[226] Formal valence analogs of borazine are formed by the reaction of $(Mes^*AlH_2)_2$ (Mes^* = 2,4,6-$Bu^t_3C_6H_2$) with H_2AsPh at ca. 160 °C. The resulting trimeric, six-membered ring compounds $(Mes^*AlAsPh)_3$ **45** adopt a nonplanar boat conformation. Little or no delocalization of the phosphorus or arsenic lone pairs is evident since the average Al–P and Al–As distances are consistent with single bond lengths. Moreover, pyramidal coordination is observed at all the pnictide centers.[227] Six-membered As–In heterocycles associated to dimers exist in the anionic cluster $[(Bu^t_3As_3In_3Cl_3)_2Cl_2]^{2-}$.[228]



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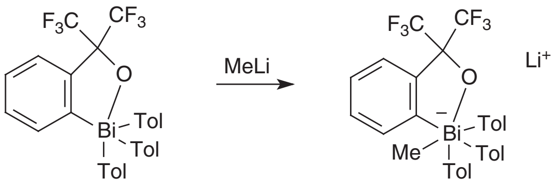
3.16.3 Pentavalent Compounds

3.16.3.1 Penta- and Hexaorganometallic Compounds

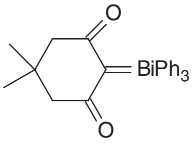
In contrast to the square pyramidal structure of Ph_5Sb, the structures of pentamethylantimony and pentamethylbismuth and $SbPh_3Me_2$ in crystals are regular trigonal bipyramidal with pronounced differences between axial and equatorial bond lengths in the case of Sb compounds.[229] The reaction of $BiPh_5$ with PhLi affords octahedral $BiPh_6^-$. In addition, the methyl derivatives MMe_6^- (M = Sb, Bi) are octahedral.[229] A blue crystalline 1 : 1 adduct is formed from $BiPh_5$ and pyridine.[230] The synthesis of a six-coordinate anionic pentaorganobismuth species is shown in Scheme 19.[231]

3.16.3.2 Ylides $R_3M{=}CR_2$ and Related Compounds

The ylides are described as hybrids of the pentacovalent and dipolar structures $R_3M{=}CR_2$ and $R_3M^+{-}C^-R_2$. Most work has been carried out on the arsonium ylides but antimony and bismuth analogs are also known.[2] Complexes with coordination of ylides on indium tribromide, $Ph_3MCH_2InBr_3$ (M = As, Sb), are formed by the reactions of InBr, CH_2Br_2, and Ph_3M.[232] Stabilized bismuth ylides, $Ar_3Bi{=}C(CO_2R^1){-}C(CO_2R^1){=}NR$, bearing a conjugated ylidic carbon atom were obtained by the reaction of $Ar_3Bi{=}NR$ (R = COR^2 or SO_2R^2) with dialkyl acetylenedicarboxylates.[233] The X-ray structure determination of the bismuth ylide **46** revealed that the Bi–C(ylide) bond is polarized as $C^-{-}Bi^+$ or $O^-{-}C{=}C{-}Bi^+$.[234,234a] A reversed ylide **47** is derived from 1,3-dimesityl-4,5-dichlorimidazol and tris(trifluoromethyl)antimony.[234]



Scheme 19



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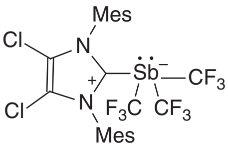

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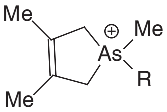
3.16.3.3 Tetraorganometal(v) Compounds

Tetraorganometal compounds exist as onium salts $R_4M^+X^-$ with tetracoordinate tetrahedral metal centers or as covalent R_4MX species with trigonal bipyramidal structures.

Salts containing the tetraphenyarsonium ion are well known. They can be synthesized by the reactions of triorganometal compounds and organo halides. Reactions of R_3M ($R = 2{,}6\text{-}(MeO)_2C_6H_3$, M = As, Sb) with alkyl halides, R^1X, give $[R_3R^1M]X$.[235] Other recently studied examples are $(Me_4M)^+$ (M = As, Sb),[236,237] Ph_4As^+,[238] Me_3AsR^+,[239] $(PhCH_2)_3SbMe^+$,[240] $Ph_3(p\text{-Tol})Sb^+$,[241] or the arsolene derivative 48.[141] Methods for the formation of arylstibonium salts from tertiary stibines and aryl halides are very limited. The intramolecular pentacoordinated tetraarylstibonium cation 49 was obtained as an iodocuprate salt by the reaction of the corresponding arylimino iodide and triphenylstibine in the presence of CuI.[242]



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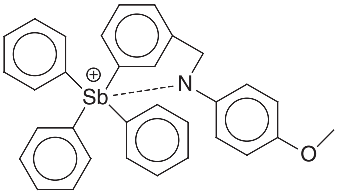

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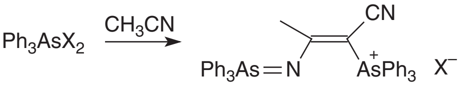
Also the reaction of triphenylarsenic dihalides with acetonitrile leads to the onium compounds.[243,244] An example is shown in Scheme 20.

Treatment of triarylbismuth difluorides with silylenolethers or siloxycyclopropanes in the presence of BF_3 gave oxoalkyltriarylbismuth tetrafluoroborates (Scheme 21).[245,246,246a]

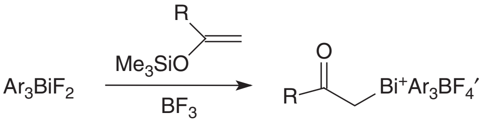
Alkenyltriphenylbismuthonium salts are formed by refluxing triphenylbismuth difluoride $BF_3{\cdot}OEt_2$ and alkenyltrimethylsilanes (Scheme 22).[247]

The quaternary bismuth(v) complex $BiR_4{}^+PF_6{}^-$ ($R = p\text{-}C_6H_4NMe_2$) was obtained by the reaction of R_3BiCl_2 with $AgPF_6$.[114] A zwitterionic species with a stibonium center is $Me_3Sb^+CH_2COO^-$, the antimony analog of betaine.[127]

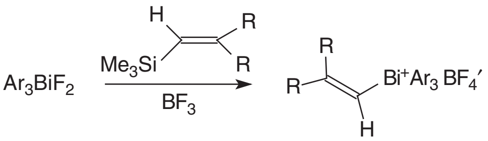
Covalent R_4MX species, that is, antimony(v) bromides R_4SbBr (R = Bu, Ph), were encapsulated as guests in hexameric resorcinarene hosts.[248] Pentavalent bismuth(v) alkoxides, Ph_4BiOR, and organoantimony(v) cyanoximates,



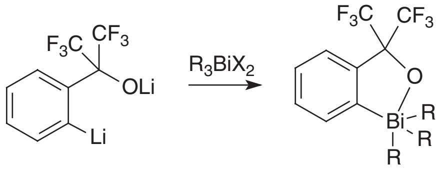
Scheme 20



Scheme 21



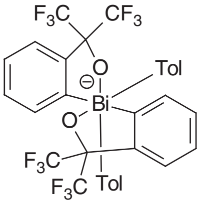
Scheme 22



Scheme 23

$Ph_4SbONC(CN)C(O)NH_2$,[249] possess trigonal bipyramidal geometries.[250] Reactions of the Martin ligand with triorganobismuth dihalides leading to cyclic tetraorganobismuth compounds are shown in Scheme 23.[251]

A six-coordinate bismuthate **50** with four Bi–C bonds is the anion.[128] Due to the intramolecular coordination, the compound is stable up to 150 °C but ^1H NMR spectra show coalescence due to an equilibrium between the CF_3 groups at 70 °C.[231]



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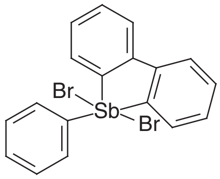
3.16.3.4 Triorganometal(v) Compounds

Triorganometal dihalides, R_3MX_2 (M = As, Sb, Bi), can be prepared by direct reaction of triorganometals with halogens in aprotic media.[252,252a] Various other halogenating agents have been used including $SOCl_2$, XeF_2[120] as well as metal halides. Competitive chlorination of various triarylbismuthines with SO_2Cl_2 revealed that the reactivity decreases with increasing electron-withdrawing abilities of the aryl groups.[253] Tris(pentafluoroethyl)arsenic and antimony difluorides and tris(2,6-difluorphenyl)bismuth dihalides are formed by the reaction of the corresponding trialkyl metal compounds with XeF_2.[129,130]

The compounds R_3MX_2 generally are non-ionic species with near trigonal bipyramidal geometries at the metal and axial halogen atoms, for example, Ph_3AsCl_2 and Ph_3AsBr_2,[254] Ph_3SbCl_2 and Ph_3SbBr_2,[255] Me_3SbBr_2,[256] R_3SbBr_2, R = Me_2CHCH_2,[66] R = $PhCH_2$.[108]

Square pyramidal geometries and Lewis-acidic behavior were found in $Sb(2,2'\text{-}C_{12}H_8)PhBr_2$ **51** and related compounds.[252]



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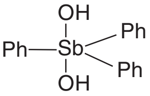
However, complexes of the types $[R_3MX]^+X^-$ (e.g., $[Me_3AsBr]^+Br^-$,[256] $[Pr^i{}_3AsOH]Cl$[257]) and $R_3M{-}I{-}I$ (e.g., $Me_3As\text{-}I\text{-}I$,[258] $Ph_3As\text{-}I\text{-}I$[259]) are also known. The trimethylarsonium ion Me_3AsH^+ was obtained as $As_4F_{11}{}^-$ salt.[260]

Triorganometal dihalides R_3MX_2 are valuable starting materials for further reactions. Hydrolysis leads to hydroxides $R_3M(OH)_2$ or oxygen-bridged species $[R_3MX]_2O$.[261–263] Examples are the derivatives $Me_3Sb(OH)_2$,[264] $(R_3SbBr)_2O$ ($R = Tol$),[265] or $(R_3BiCl)_2O$ ($R = p\text{-}C_6H_4NMe_2$).[118] Oxidative hydrolysis of $[Et_4N]^+[PhSbCl_2Br]^-$ gave $Ph_3Sb(OH)_2$ **52**.[266] Hydrolysis of R_3BiX_2 ($R = 2\text{-}MeOC_6H_4$) gives $(R_3Bi)_2O_2$.[267]



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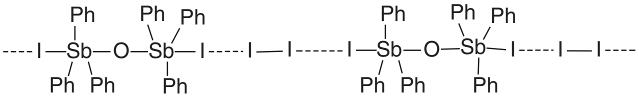
The compound $4(Ph_3SbI)_2O{\cdot}I_2$ is obtained by the addition of I_2 in acetonitrile/water to a solution of triphenylantimony. The crystal structure contains a one-dimensional chain **53** and $(Ph_3SbI)_2O$ molecules which are not coordinated to I_2. In the 1D chain, the distance between the iodine of the $(Ph_3SbI)_2O$ molecule and the diiodine molecule is 3.370(1) Å.[268]



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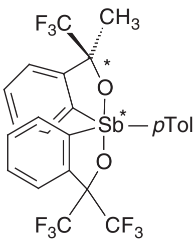
From R_3Sb [$R = 2\text{-}(Me_2NCH_2)C_6H_4$], I_2, and water, a hydroxide $[R_3SbOH]^+[I_3]^-$ was obtained.[150] The reaction of R_2SbX_2 with functionalized oximes gives complexes of the type $[R_3Sb\{ON{=}C(Me)Ar\}_2]$.[269] Reactions of $[SbR_3X]_2O$ with carboxylates lead to the formation of $[SbR_3(O_2CR)_2]_2O$.[270] Other compounds of the type $[R_3SbX]_2O$ are described in Refs: 261–263, and 271. Hydrates of the type $R_3M{\cdot}xH_2O$ ($M = As$, Sb) are obtained from R_3M and H_2O_2.[235] Oxidation of triphenylarsine with $[Bu^t{}_2Ga(\mu\text{-}OOBu^t)]_2$ gives the complex $[Bu^t{}_2Ga(OBu^t)OAsPh_3]$.[272]

Treatment of R_3M with N-bromosuccinimide in aqueous acetone gave $(R_3MOH)Br$.[235] The dimeric phenoxystibaneoxide $\{(2\text{-}PhOC_6H_4)O(C_6H_4)_2Sb]_2O_2$ is formed by air oxidation of the corresponding stibine.[273] α-Hydroxy carboxylic acids react with Ph_3SbCl_2 to afford cyclometallated complexes.[274]

Many diesters $MPh_3(O_2CR)_2$ ($M = Sb$, Bi) with trigonal bipyramidal structures are known.[275–278] The alkoxides $Ph_3Bi(OR)_2$ and $Ph_3BiBr(OR)$ were formed by salt elimination from Ph_3BiBr_2 and NaOR.[250] Treatment of triarylbismuth difluorides with silyl enol ethers in the presence of trifluoromethane sulfonate (triflate) gave the oxygen-bridged species $ROBiR_3{-}O{-}BiR_3{-}OR$ ($R =$ triflate).[245] In addition, oxygen- or sulfur-bridged heterotrinuclear compounds containing antimony(V) and arsenic or phosphorus are known. Examples are $R_3Sb(OAsR_2)_2$,[279] $Me_3Sb(OSPPh_2)_2$,[280] or $(Me_3SiCH_2)_3Sb(S_2PPh_2)_2$.[281] Hydrolysis of $Me_3Sb(O_2PPh_2)_2$ gave $Me_3Sb(OH)(O_2PPh_2)$.[282] Configurationally stable diastereomeric hypervalent compounds **54–56** and related compounds with an asymmetric antimony atom were prepared and characterized.[283–285]



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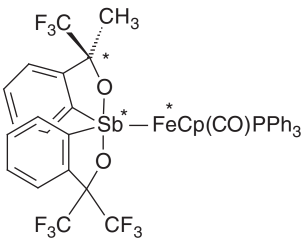

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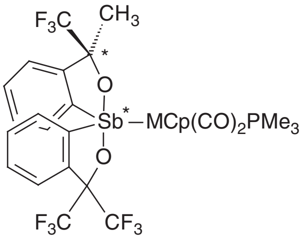

M = Cr, Mo, W

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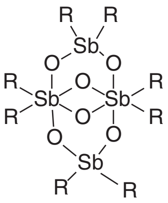
The dimeric complex $[Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2$ is formed from $PhCH_2CH_2NH_2$ and $Ph_3Sb(NMe_2)_2$.[286] $R_3Sb{=}NSO_2CF_3$ ($R = 2\text{-}MeC_6H_4$) is a monomeric imino-λ^5-stibane with an Sb=N bond length of 1.958 Å.[287] Reaction of Ph_3AsX_2 with $Me_3SiNPEt_3$ gives iminium salts $[Ph_3AsNPEt_3]X$ which react with acetonitrile to form derivatives of the type $[(Ph_3As)_2CCN]X$.[244] An acetyliminotriarylbismuth species $Ar_3Bi^+–N{=}C(CCl_3)O^-$ was characterized by crystallography.[288]

3.16.3.5 Diorganometal(v) Compounds

Diorganometal(v) compounds can be prepared by the oxidation of dimetal compounds R_2MMR_2 or halides R_2MX. Addition of Br_2 to R_2SbBr ($R = Me_3SiCH_2$) gives R_3SbBr_3.[281] Ph_2SbCl_3 forms a 1 : 1 adduct with $OPPh_3$.[289] Tetraaryldistibanes react with oxygen or H_2O_2 to form oxo- or peroxo-clusters $(R_2Sb)_4O_6$ **57** or $(R_2SbO)_4(O_2)_2$ **58** (R = Ph, *o*-Tol, *p*-Tol).[48] **58** is also formed by the reactions of $PhSb(SiMe_3)_2$ with air.[273] The multiply bridged organodiantimony compound **59** was obtained by treating $(SbPh_2BrO)_2$ which contains a four-membered Sb_2O_2 ring with NaO_2AsPh_2.[290]



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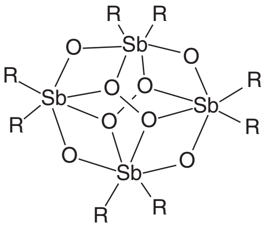

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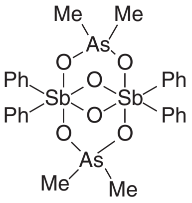

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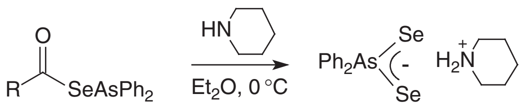
Methathesis reactions between Ph_2SbCl_3 and alkali metal salts of the corresponding imido diphosphinic acid gives $R_2Sb(Cl_2)OPPh_2(XPPh_2)N$ (X = O, S).[291]

Diphenyldiselenoarsinic acid piperidinium salt was synthesized by the reaction of an *Se*-diphenylarsanyl selenoester with piperidine as shown in Scheme 24.[190]

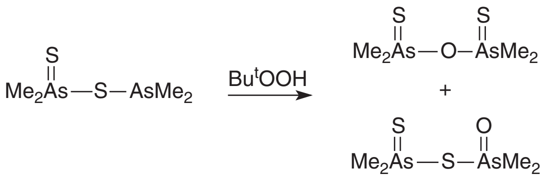
Oxodiphenylantimony phosphinates include the oxo-bridged derivatives $[Ph_2SbCl(O_2PR_2)]_2O$ and $[Ph_2Sb(O_2PR_2)]_2O$.[292,293] The structure of dihydroxodiphenylarsonium chloride $[Ph_2As(OH)_2]Cl$ was determined.[294] Oxidation of tetramethyldiarsinedisulfide with Bu^tOOH gave two isomeric products (Scheme 25).[295]

3.16.3.6 Monoorganometal(v) Compounds

The monoorganoarsenic compounds most readily prepared are the arsonic acids $RAs(O)(OH)_2$.[1,2,296] The ferrocenyl arsonic acid $FcCH_2CH_2As(O)(OH)_2$ [$Fc = C_5H_5(C_5H_4)Fe$] was obtained from $FcCH_2CH_2Br$ and sodium arsenite.[297] The tetrachloroorgano arsoranes $RAsCl_4$ can be produced by the reaction of $RAsCl_2$ with Cl_2. The cationic species $MeAsF_3{}^+$ was isolated as $AsF_6{}^-$ salt.[298] The alkyl compounds $RAsCl_4$ decompose readily but the aryl derivatives are more robust.[2] Arenestibonic acids are generally prepared by the reaction of diazonium salts $ArN_2{}^+X^-$ with Sb_2O_3 or $SbCl_3$.[2] Hypervalent monoantimony(v) porphyrine derivatives $[LSb(R)OH]^+$, $[LSbR]$, $[LSbR_2]^+$ (R = Me, Et) are

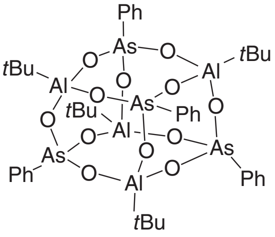


Scheme 24



Scheme 25

obtained by the reactions of LSbCl (L = octaethylporphyrin) with R$_3$Al and water.[299] Cyanomethyltrisselenido arsenate, CNCH$_2$AsSe$_3$$^{2-}$,[300] contains arsenic in a distorted tetrahedral environment with three terminal Se ligands. A cubane stucture is adopted by the phenylarsonato derivative (PhAsO$_3$AlBu^t)$_4$ **60**.[301] A unique square pyramidal coordination with five different atoms attached to the metal atom is found in the complex **61**.[302]



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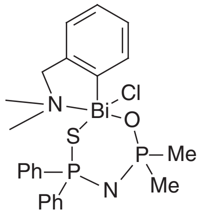

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