

II.4 Palladium Complexes Containing Pd(I), Pd(III), or Pd(IV)

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A. INTRODUCTION

Although the organometallic chemistry of palladium is dominated by oxidation state +2 for palladium, Pd(0) complexes play a significant role in organic synthesis and there is a rapidly developing field of Pd(IV) chemistry of potential and demonstrated applications in catalysis. In contrast, the odd electron configurations, d⁹ and d⁷ for Pd(I) and Pd(III), respectively, have been less successfully developed and indeed elusive for Pd(III).

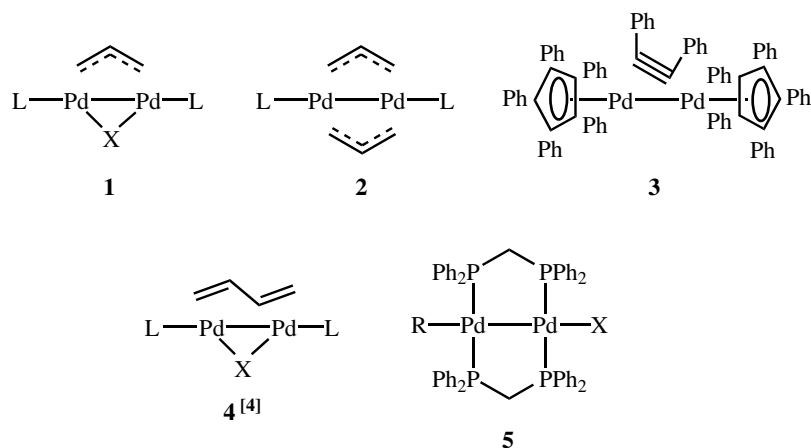
B. Palladium(I)

The odd electron configuration for Pd(I), as expected, generally gives rise to Pd—Pd bonding and there is an extensive chemistry of such complexes with π -bonding ligands.^{[1]–[4]} Typical structural types are shown as **1–4** in **Scheme 1**, and complexes with other ligands such as benzene, cyclopentadienyl, and indenyl^[2] have been characterized.

In view of the important role of allyl ligands in organic synthesis it is of interest to note that Pd(I) complexes of these ligands may be obtained in a similar manner to those of Pd(II) complexes,^{[5],[6]} for example, reaction of allyl acetate with Pd(0) reagents to give both **1** (L = PPh₃) and Pd(η^3 -C₃H₅)(O₂CMe)(PPh₃). Complexes are also formed on reduction of Pd(II) species, for example **1** (X = Cl, L = PPh₃) on reaction of [Pd(μ -Cl)(η^3 -C₃H₅)₂] with PPh₃ in the presence of sodium methoxide,^[7] and **2** (L = PPh₃) on reaction of Pd(η^3 -C₃H₅)₂ with PPh₃ at 0 °C via Pd(η^3 -C₃H₅)(η^1 -C₃H₅)(PPh₃).^[8]

Electrochemical studies of both π -bonded and Pd—C σ -bonded species have been reported,^{[9]–[14]} with evidence for Pd(I) species, although in these cases the assignment of oxidation state may be regarded as more of a formalism than for **1–4**, where there is at least the presence of a Pd—Pd bond to support assignment of oxidation state +1 at the metal center rather than electron transfer at the organic ligands. Typical examples include Pd(η^5 -C₅Ph₅)(η^4 -diene),^{[10],[11]} and closely related studies of **3**,^[9] which undergoes a three-step electron transfer process $3^{2+} \leftrightarrow 3^+ \leftrightarrow 3 \leftrightarrow 3^-$.

There is one report of the synthesis of η^1 -hydrocarbylpalladium(I) complexes,^[15] for example, **5** is formed by reaction of Al₂Me₆ with a Pd(I) precursor [PdCl(μ -dppm)]₂ at

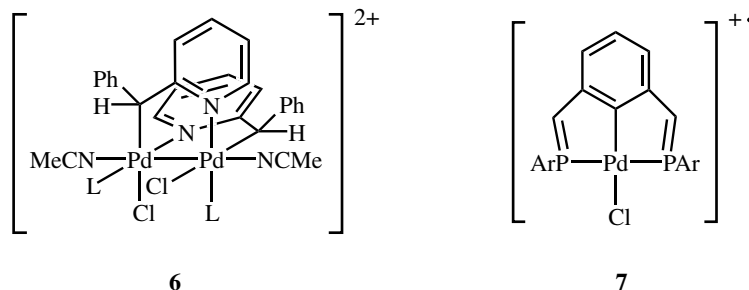


Scheme 1

−78 °C (**Scheme 1**, R = Me; X = Me, Cl). Complex **5** (R = Me, X = Cl) readily undergoes disproportionation to Pd(0) and Pd(II) species, and it is thus intriguing that a wide variety of pentahalogenophenylpalladium(I) complexes are formed in the reverse reaction,^{[12],[16],[17]} for example, the reaction of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ with *trans*-[PdX(C₆F₅)(η^1 -dppm)]₂ to form **5** (R = C₆F₅, X = Cl).^[16]

C. PALLADIUM(III)

Palladium(III) complexes are also expected to exhibit Pd—Pd bonding, but to date there appear to be no examples where this oxidation state or Pd—Pd bonding has been clearly demonstrated in the presence of “innocent” ligands.^{[12],[18]–[20]} For example, electrochemical oxidation of a (1'-phenyl)-2-pyridylmethylpalladium(II) dimer in acetonitrile may form **6** (**Scheme 2**), although it has not been established whether this contains a Pd—Pd bond.^[20] Oxidation of the pincer palladium(II) complex **7** has been shown by EPR spectroscopy to occur at the ligand rather than the metal atom.^[19] A series of mononuclear radical species for which assignment of formal oxidation state is problematic have been detected.^{[18],[19]}

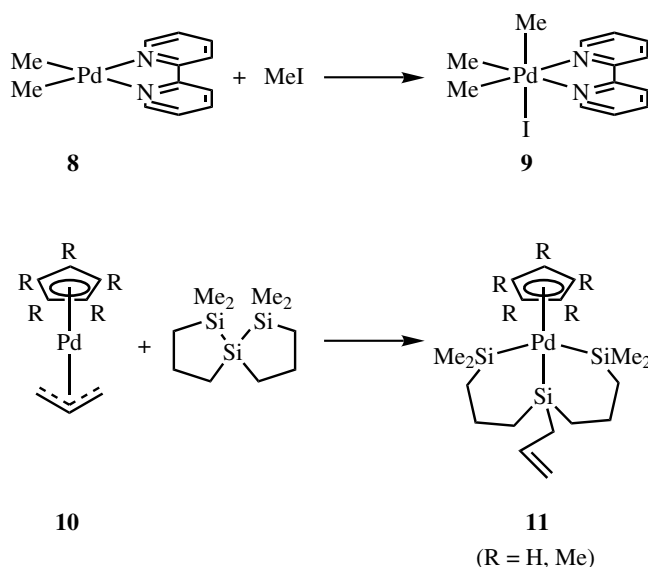


Scheme 2

D. PALLADIUM(IV)

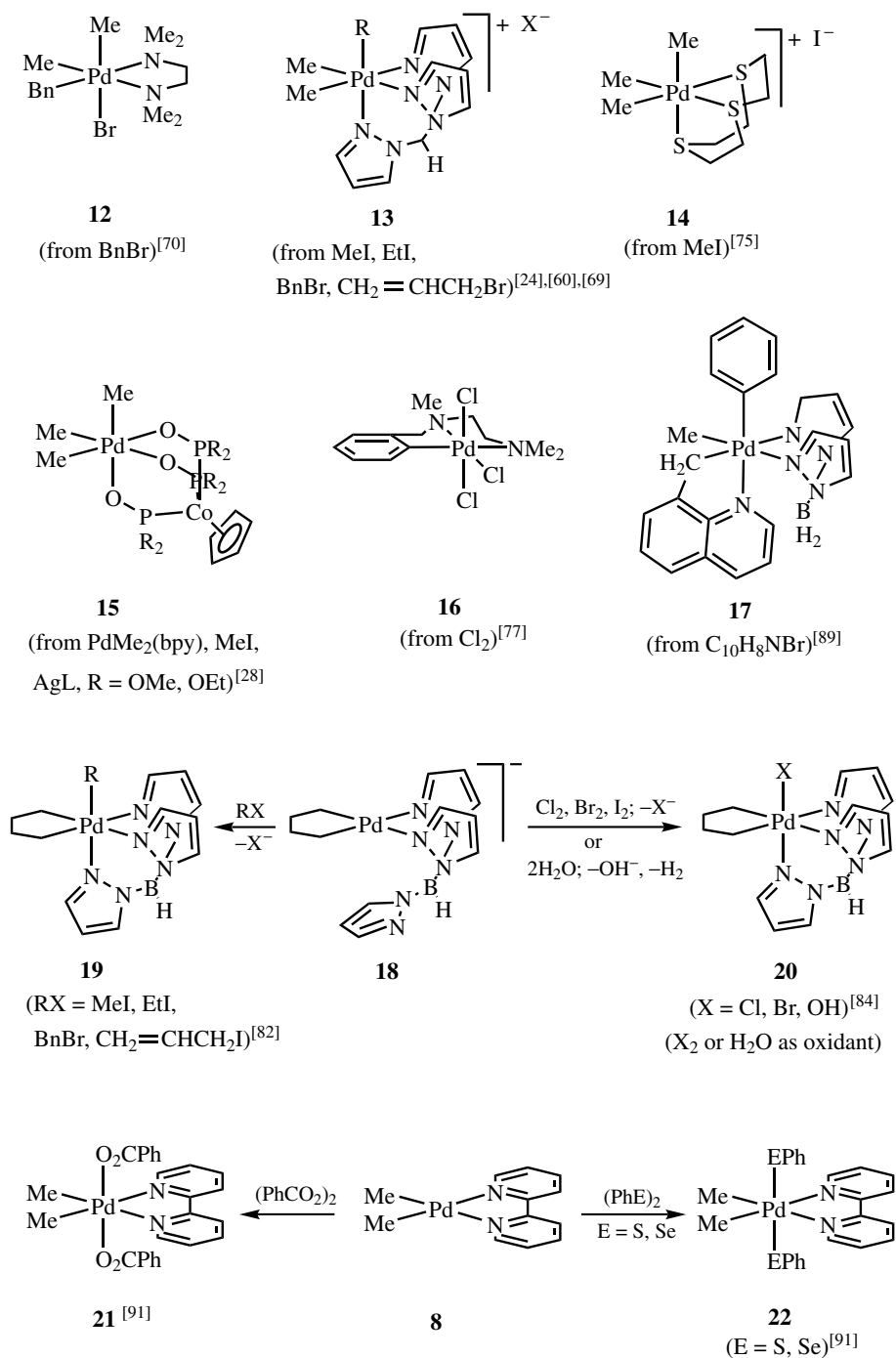
D.i. Synthesis and Structure

A series of pentafluorophenylpalladium(IV) complexes obtained on chlorine oxidation of Pd(II) substrates was reported in the 1970s.^{[17],[21],[22]} The first hydrocarbylpalladium(IV) complex was isolated by addition of MeI to PdMe₂(bpy) in 1986 (**Scheme 3**),^{[23],[24]} and the field developed rapidly thereafter.^{[12],[25],[26]} All of the Pd^{IV}—C σ -bonded complexes isolated, or detected in solution prior to decomposition, have been obtained via oxidation of organopalladium(II) complexes or, in a limited number of cases, via ligand exchange at Pd(IV) centers.^{[27],[28]} In a recent report the first examples of η^5 -bonded complexes have been described, obtained by complex reactions involving insertion into Si—Si bonds and Si—C coupling (**Scheme 3**).^{[29],[30]} There are many reports,^{[1],[31]–[59]} together with some referred to elsewhere in this section, that suggest the occurrence of undetected Pd(IV) species in reactions of Pd(II) complexes.



Scheme 3

Examples of the oxidants used to date for the synthesis of Pd^{IV}—C σ -bonded complexes are shown in **Schemes 3** and **4** (with the oxidants shown in parentheses). Thus, organic halides oxidize diorganopalladium(II) complexes^{[23],[24],[60]–[90]} to form triorganopalladium(IV) species; halogens form mono- or diorganopalladium(IV) species;^{[77],[79],[84]} dibenzoylperoxide, diphenylsulfide, and diphenyldiselenide oxidize diorganopalladium(II) complexes^{[91],[92]}; and even water will oxidize electron-rich tris(pyrazol-1-yl)borate complexes.^{[84],[93]} There is one report of the oxidation of a monoorganopalladium(II) complex by an alkyl halide,^[77] and an earlier reaction for which NMR spectra indicated that an unstable Pd(IV) complex may have been formed.^[94] Other examples of isolated or spectroscopically detected complexes are shown in later schemes [diagrams **23** and **26** (**Scheme 6**), **27**, **29**, **31**, and **32** (**Scheme 7**), and **40** (RX = Br₂, **Scheme 11**)].



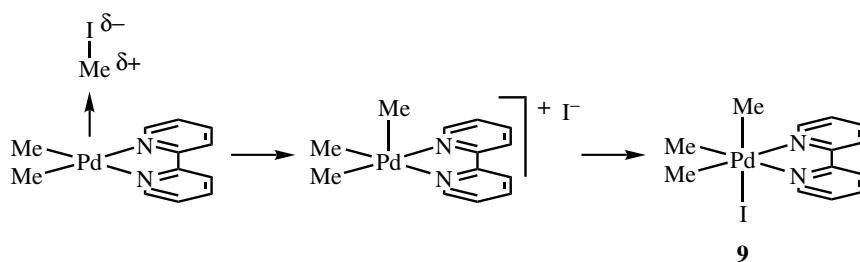
Scheme 4

All Pd(IV) complexes examined crystallographically are octahedrally coordinated,^{[23],[24],[28],[30],[60],[71],[73],[82],[84],[87],[89],[91]} as expected for the d^6 configuration, and the di- and triorganopalladium(IV) complexes have *cis*-PdR₂^{[84],[91]} and *fac*-PdR₃ configurations,^{[24],[28],[60],[61],[71],[73],[82],[87],[89]} respectively. Both neutral^{[23],[24],[28],[30],[71],[73],[82],[84],[87],[89],[91]} and cationic^{[24],[60],[84]} complexes have been examined crystallographically, including **9**, **11**, **13** (RX = MeI), **15**, **17**, **20** (X = OH), and **22** (X = Se). All complexes detected have a bidentate or tridentate ligand, including intramolecular coordination systems such as [C(sp²)~N~N]⁻ (**16**), [C(sp³)~N~N]⁻,^[77] or [C(sp³)~N]⁻ (**17**). The polydentates may be either hard or soft donor ligands, for example bidentate nitrogen in phen^{[24],[62],[64],[67],[71],[73],[74],[76],[78],[88],[91]} or TMEDA,^{[65],[70]} or tripodal oxygen (**15**) or sulfur (**14**). Examples of compounds containing these ligands are shown in **Schemes 3** and **4**. Although all complexes contain polydentates, for those complexes containing an additional unidentate ligand there is a wide range of ligands that will support Pd(IV), including halogens (F, Cl, Br, I), pseudohalogens and carboxylates,^[27] arenethiolate and areneselenolate,^{[91],[92]} and hydroxo and aqua ligands.^[84]

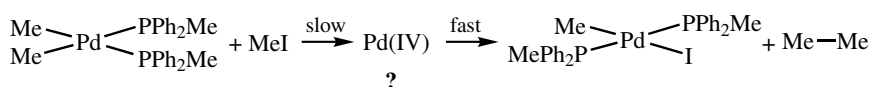
Organic groups bonded to Pd(IV) include alkyl, benzyl, allyl, propargyl, allenyl, aryl, and the cyclic systems shown in **Scheme 4** and **29** (**Scheme 7**).^[86] Organopalladium(IV) motifs PdAr (**16**); PdMe₂ (**21**, **22**)^{[79],[91],[92]}; PdMe₂R (R = Me,^{[23],[24],[28],[60],[61],[63]–[66],[73],[75],[79],[81],[82],[87]} Et,^{[61],[68],[69],[82]} Pr,^[69] Bn,^{[61],[64],[69]–[72],[77],[79],[82],[83]} CH₂CH=CH₂,^{[61],[68]–[70],[82]} Ar,^{[80],[82],[95]} ArCOCH₂,^[73] CH₂C≡CR and CH=C=CH₂,^[88] 8-methylquinolinyl,^[89] PdMeArR (R = Et,^[89] Bn^{[80],[82],[85],[90],[95]} including a periphery palladated dendrimer,^[89] 8-methylquinolinyl,^[89] CH₂CH=CH₂,^[82] Pd(CH₂CH₂CH₂CH₂)R (R = Me, Et, Bn, allyl, CF₃)^{[82],[86],[96]}; the palladacyclic system shown in **27** (**Scheme 7**) for oxidative addition of methyl, benzyl, and allyl halides^{[62],[67],[74],[76]}; Pd(2-CH₂OC₆H₄-C,C)R (R = Bn, CH₂=CH₂)^[78]; Pd{C(sp³)~N~N}Me₂^[77]; and dibromopallada(IV)-cyclopentadienes as in **40**^[55] (**Scheme 11**) have been detected. In all cases the formation of additional Pd—C bonds on oxidation of Pd(II) substrates occurs via oxidative addition of methyl, ethyl, propyl, allyl, benzyl, naphthylmethyl, phenacyl, propargyl, or 8-methylquinolinyl halides, or methyl triflate at Pd(II) centers.^[65] Arylpalladium(IV) complexes such as **16** and **17** (**Scheme 4**), **23** (**Scheme 6**), and **27** (**Scheme 7**) are obtained on oxidative addition of chlorine or C(sp³)—X (X = halogen) bonds to arylpalladium(II) complexes.

Detailed kinetic studies of the oxidation of Pd(II) substrates have been reported only for the reactions of PdMe₂(L₂) (L₂ = bpy, phen) with MeI^{[63],[69],[81]} and BnBr.^[64] The reactions exhibit second order kinetics with activation parameters typical for the classical S_N2 mechanism, for example, highly negative values for ΔS[‡] consistent with the mechanism shown in **Scheme 5**. In agreement, solvento-intermediates can be detected in many cases. Thus, for the reaction of **Scheme 5**, low-temperature NMR studies have shown the intermediacy of [PdMe₃(bpy)]⁺ in (CD₃)₂CO (where the cation is assumed to be solvated).^[73] Also, the complex PdIme₃(bpy) forms an equilibrium with [PdMe₃(bpy)(NCCD₃)]⁺ in CD₃CN^[24] and PdMe₂(TMEDA) reacts with methyl triflate in CD₃CN to form [PdMe₃(TMEDA)(NCCD₃)]⁺.^[65]

Similar kinetic parameters have been reported by Stille and co-workers for the reaction of *cis*-PdMe₂(PPh₂Me)₂ with MeI to form *trans*-PdIme(PPh₂Me)₂ and ethane (**Scheme 5**),^[36] except that this reaction is ~6000–7000 times slower than the reaction of PdMe₂(bpy). In the case of *cis*-PdMe₂(PPh₂Me)₂, oxidative addition is slow compared with reductive elimination of ethane and hence the Pd(IV) intermediate is not detected spectroscopically. The detection of a cation intermediate for the reaction of PdMe₂(bpy)



In acetone at 20 °C: $k_2 = 3.23 \pm 0.08 \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a = 25.3 \pm 0.6 \text{ kJ mol}^{-1}$,
 $\Delta S^\ddagger = -148 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$



In acetone at 20 °C: $k_2 = 4.9 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$, $E_a = 68 \pm 4 \text{ kJ mol}^{-1}$,
 $\Delta S^\ddagger = -85 \pm 13 \text{ J K}^{-1} \text{ mol}^{-1}$

Scheme 5

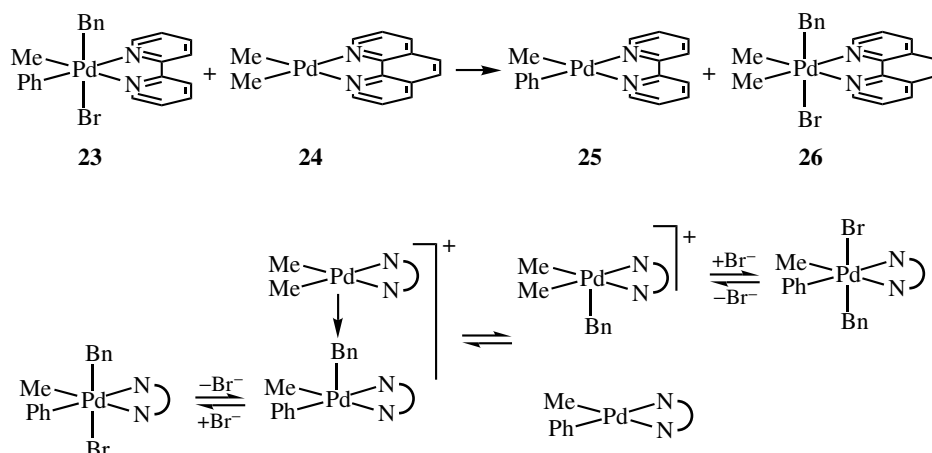
(**Scheme 5**) and the requirement of ligand dissociation in reductive elimination (see **Sect. D.ii**) imply that the intermediate phosphine complex may be $[\text{PdMe}_3(\text{PPh}_2\text{Me})_2]^+$ or $[\text{PdMe}_3(\text{PPh}_2\text{Me})_2(\text{solvent})]^+$ rather than $\text{PdIMe}_3(\text{PPh}_2\text{Me})_2$. Thus, the development and study of isolable Pd(IV) complexes, in particular of the archetypal reaction of **Scheme 3**, support the pioneering work of Stille suggesting the formation of transient undetected Pd(IV) species in reactions of alkyl halides or halogens with diorganopalladium(II) complexes containing phosphine donor ligands.^{[31],[32],[34]–[36]}

D.ii. Reactivity

Organopalladium(IV) complexes are stable toward water and oxygen and toward any excess oxidant used in their synthesis.

In almost all reactions of Pd(IV) complexes it appears that loss of a donor group to give a five-coordinate intermediate is required, although the potential involvement of a weak solvent coordination interaction cannot be discounted at present. Solvated cations have been detected by NMR spectroscopy^{[64],[65],[73]} and these species are known to be fluxional when they contain the *fac*-PdMe₃ unit, for example a ΔG^\ddagger of 53 kJ mol⁻¹ has been estimated for exchange of axial and equatorial methyl group environments in $[\text{PdMe}_3(\text{TMEDA})(\text{NCCD}_3)]^+$.^[65] Silver(I) salts may be employed at low temperature to exchange bromide in $\text{PdBrMe}_2\text{Bn}(\text{bpy})$ to form a series of complexes $\text{PdXMe}_2\text{Bn}(\text{bpy})$ (X = F, Cl, I, O₂CMe, N₃, OCN, SeCN, O₂CPh, O₂CCF₃)^[72] and to effect the exchange of both iodide and bpy to form **15**^[28] (**Scheme 4**).

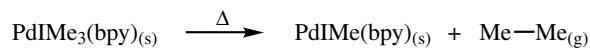
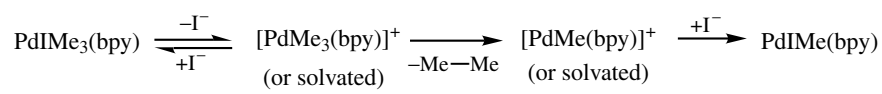
Preliminary halide loss is also implicated in alkyl halide exchange reactions of Pd(IV) complexes with Pd(II)^{[80],[85]} and Pt(II) complexes,^[64] for which an example is shown in **Scheme 6**. The reactions are strongly retarded by added halide ion, and kinetic studies of the reaction of $\text{PdBrMe}_2\text{Bn}(\text{phen})$ with $\text{PtMe}_2(\text{phen})$ reveal second order kinetics and a strong inverse dependence on $[\text{Br}^-]$.^[64] Together with the observed selectivity for



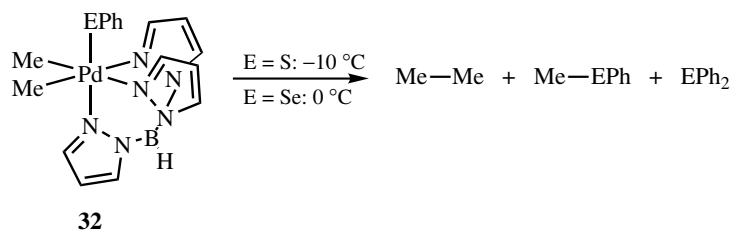
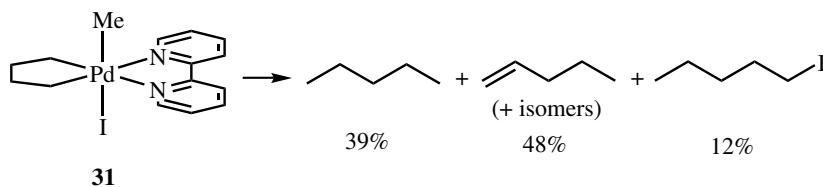
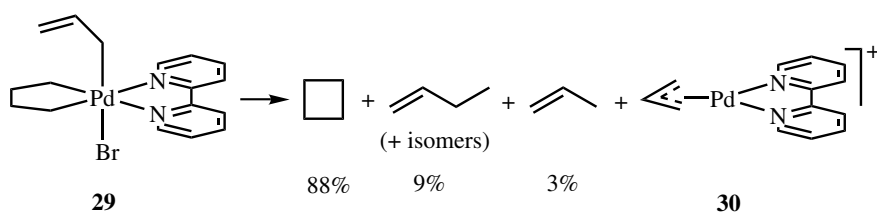
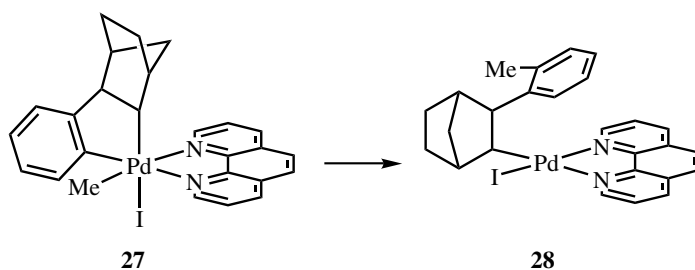
Scheme 6

exchange, $\text{BnI} > \text{MeI}$, a mechanism (**Scheme 6**, where cations may be solvated) directly related to the oxidative addition process (**Scheme 5**) is anticipated. Methyl group exchange between Pd(II) and Pd(IV) presumably occurs also during reactions of $[\text{PdMe}_2\{(\text{pz})_3\text{BH}\}]^-$ with halogens or water to form $\text{Pd}^{\text{IV}}\text{Me}_3\{(\text{pz})_3\text{BH}\}$ and “ $\text{Pd}^{\text{II}}\text{Me}\{(\text{pz})_3\text{BH}\}^-$ ”.^[84] These reactions are directly analogous to reactions of the pallada(II)cyclic complex **18** in **Scheme 4**, except that in the latter cases the product $\text{Pd}^{\text{IV}}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{X})\{(\text{pz})_3\text{BH}\}$ ($\text{X} = \text{OH}, \text{Cl}, \text{Br}, \text{I}$) cannot undergo alkyl group exchange reactions with the reagent nucleophile $[\text{Pd}^{\text{II}}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\{(\text{pz})_3\text{BH}\}]^-$ because of the constrained nature of the palladacycle rings.

Kinetic studies of the decomposition of $\text{PdIme}_3(\text{bpy})$ reveal first order behavior and a strong inverse dependence on $[\text{I}^-]$, again consistent with preliminary halide loss (**Scheme 7**).^{[63],[81]} Decomposition of triorganopalladium(IV) complexes occurs almost exclusively via C—C coupling and is generally “clean” in the solid state unless the Pd(IV) complex is exceptionally stable. Studies of the reductive elimination of ethane from $\text{PdIme}_3(\text{L}_2)$ ($\text{L}_2 = \text{bpy}, \text{phen}$) have enabled the first estimates of Pd—C bond energies to be made (**Scheme 7**) and the values obtained are ~10% less than for the most practically comparable Pt(IV) complexes such as $\text{PtIme}_3(\text{PMe}_2\text{Ph})_2$.^{[63],[64]} A similar decomposition occurs in the solid state for $\text{PdBrMe}_2\text{Bn}(\text{L}_2)$ ($\text{L}_2 = \text{bpy}, \text{phen}$), giving predominantly ethane, and in solution the selectivity for ethane is enhanced (100% for bpy; 75% Me—Me and 25% Me—Bn for $\text{L}_2 = \text{phen}$).^[64] Reductive elimination generally, but not always, favors coupling $\text{Ar—Me} > \text{Me—Me} > \text{Me—Bn}$. Recent reports of decomposition are shown in **Scheme 7**.^{[62],[86]} Additional examples include $\text{PdBrMePhBn}(\text{bpy})$ (**23**) giving Me—Ph,^{[80],[85]} $\text{PdBrMe}_2\text{Bn}(\text{TMEDA})$ (**12**) giving Me—Me,^[70] and $\text{PdIme}_2\text{Ph}(\text{bpy})$ giving Me—Me and Me—Ph in 4:1 ratio for which a selectivity in favor of Me—Me rather than Ar—Me coupling is observed.^[80] η^1 -Allylpalladium(IV) complexes decompose to form η^3 -allylpalladium(II) complexes,^{[61],[68]–[70],[86],[97]} as illustrated in **Scheme 7**.^[86] Pallada(IV)cyclic complexes also undergo C—C bond formation as the first step in decomposition, for example, for the allylpalladium(IV) complex shown in **Scheme 7**, and for **31** (**Scheme 7**), where Me—CH₂ coupling is followed by decomposition of an undetected pentylpalladium(II) species.^[86]



$$\Delta H = -105 \pm 2 \text{ kJ mol}^{-1}; D(\text{Pd}-\text{Me}) \sim 130 \text{ kJ mol}^{-1}$$



Scheme 7

Higher stability is favored by ligands that appear to encourage retention of octahedral coordination rather than release of a donor group: ligands that do not create steric congestion at the Pd(IV) center,^{[24],[27],[66],[69]} rigid bidentate ligands,^{[24],[27],[66],[79]} tripod ligands,^{[24],[28],[60],[61],[69],[75],[82]} and the $[C\sim N]^-$ donor illustrated by **17**, which is the only arylpalladium(IV) complex examined crystallographically.^[89]

Carbon-halogen coupling at Pd(IV) centers occurs to a minor extent for some triorganopalladium(IV) species,^{[79],[98]} and may occur in the decomposition of **31** although other processes for formation of the C-I bond cannot be excluded for this reaction. However, for *monoorganopalladium(IV)* and *diorganopalladium(IV)* complexes, carbon-heteroatom coupling appears to be a more prominent process in decomposition. Thus, for diorganopalladium(IV) complexes containing arenethiolate and areneselenolate ligands, C-C coupling is accompanied by C-S and C-Se coupling^[92] as illustrated by **32** in **Scheme 7**. The undetected complex $Pd(O_2CPh)_2Me_2(bpy)$ (**21**) decomposes in a complex manner involving methyl group exchange to form $PdMe_3(bpy)(O_2CPh)$, contrary to the early report,^[91] $Pd(EPh)_2Me_2(bpy)$ (**22**) gives Me-Me and Me-EPh in 1:1 ratio,^[91] and **16** forms $PdCl_2\{2-CIC_6H_4CH_2NMeCH_2CH_2NMe_2-N, N'\}$ quantitatively.^[77]

E. PALLADIUM(I), PALLADIUM(III), AND PALLADIUM(IV) IN ORGANIC SYNTHESIS

The chemistry of palladium in organic synthesis is dominated by the 0 and +2 oxidation states, often with catalytic cycles involving two-electron oxidation and reduction steps. Assignment of mechanisms involving other oxidation states in Pd-catalyzed reactions is not straightforward in view of several reactivity characteristics of palladium complexes. These include facile reduction of Pd(II) to Pd(0) by solvents and reagents under mild conditions leading to Pd(0)-Pd(II) cycles, the ability of Pd(II) to facilitate aryl and alkyl group exchange between Pd(II) centers and between Pd(II) and organometal reagents, stabilization of Pd(0) catalytic species at low concentrations by a range of ligand/solvent conditions, catalysis by di- and polynuclear palladium complexes and clusters, and the documentation in other sections in this text of an extraordinary range of catalytic processes that are readily accomplished at Pd(0) and Pd(II) centers. All of these factors favor assignment of oxidation states $\leq +2$ in mechanisms, and thus the emphasis in this section is placed on consideration of proposals for the involvement of higher oxidation states.

Palladium(I) intermediates have been proposed for the telomerization of butadiene with acetic acid yielding acetoxyoctadienes,^[5] and in a recent review the involvement of Pd(I) has been suggested for processes in which Pd(II) had been formerly suggested.^[99] These processes include alkene isomerization, methoxycarbonylation of alkynes to acrylic esters, and the aryloxy carbonylation of allyl alcohol.

There is little speculation on the role of Pd(III) in synthesis, although its involvement in the reactivity of electrochemically generated Pd(I) species has been canvassed^[13] as well as its possible role in oxidatively induced decomposition of Pd(II) species by organic halides to generate reactive intermediates.^[100]

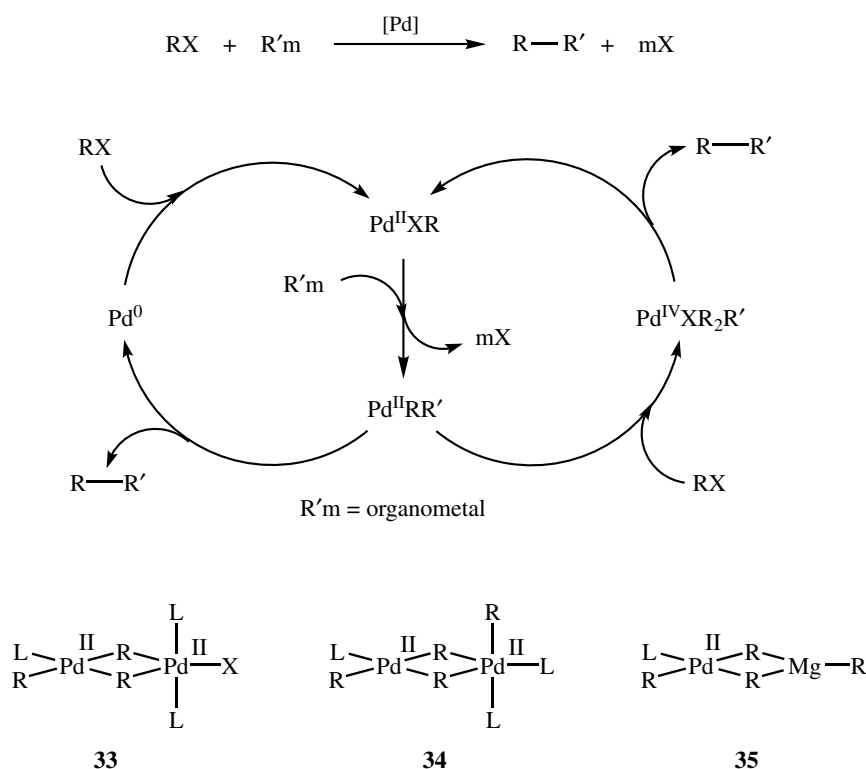
Synthetic procedures for which Pd(IV) intermediates have been proposed, usually with reservations by the authors on the potential involvement of Pd(0) and/or Pd(II) as alternative intermediates, include the synthesis of triphenylenes and related compounds formed by linking norbornene with aryl groups,^{[101]-[113]} benzo[*e*]pyrenes,^{[104],[108],[110]}

2,6-disubstituted arenes and vinylarenes,^{[111],[114],[115]} 6*H*-dibenzo[*b,d*]pyrans,^{[116]–[118]} acenaphthylenes,^{[117],[119]} annulated pyrans and furans,^[120] dihydrocyclobutabenzenes,^[121] benzo[*b*]furans,^{[117],[122]} 2-substituted indoles,^{[123],[124]} 2-aryldimethylaminomethylarenes,^[37] 2,6-dialkylated benzaldehydes,^[125] 2-arylphenols,^[126] indenones,^[127] polyfused heterocycles,^{[128],[129]} substituted pyrrolidines,^[130] cyclopentenes,^[131] esters and diynes from terminal acetylenes and oxalate esters,^[132] stannoles from ethyne and SnR₂^[133]; the Heck^{[118],[134]–[140]} and Suzuki reactions^[141]; coupling of terminal alkynes with aryl bromides,^[142] coupling of β -bromostyrene with norbornadiene,^[143] reactions of 2-bromobenzaldehyde with methyl acrylate,^[144] exchange and isomerization reactions of alkenes,^{[145]–[150]} dimerization of alkenes,^{[151]–[153]} dimerization of allenyl ketones,^{[154],[155]} cooligomerization of butadiene with 1-azadienes,^[156] addition of vinyl compounds to dimethylacetylenedicarboxylate,^[157] acetoxylation of arenes^{[158],[159]} and related reactions^[51] forming C—O bonds, chlorination of azobenzenes,^[160] orthoalkylation of acetanilide,^[41] reaction of arylazoxyarylsulfones with norbornene,^[161] cyclization and cycloisomerization of enynes,^{[117],[130],[131],[162]–[175]} cycloisomerization of alkynyl *N*-acylenamines,^[169] addition of terminal alkynes to acceptor alkynes,^{[176],[177]} double carbonylation of prop-2-ynal acetals with subsequent reactions to give vinyl ethers,^[178] carbonylation of iodomethane and methanol to methyl acetate^[179]; the synthesis of conjugated dienes from alkynes, tetramethyltin, and an organic halide;^{[55],[57]} the preparation of poly-*p*-phenylene,^[180] and reactions of Si—Si bonded reagents with alkynes^[181] and Si—Si bond metathesis.^{[29],[182]}

Examples of some of these reactions are discussed below to illustrate key principles, reactions that have support for Pd(IV) intermediacy from model reactions, and reactions that are frequently interpreted by some researchers (but not others) as involving Pd(IV) intermediates. In most of the mechanistic schemes presented below, an estimate of the full coordination sphere of palladium species has not been attempted.

Classic examples of the difficulties in assigning a mechanism include that for C—C coupling reactions (**Scheme 8**), where the Pd(0)–Pd(II) cycle appears to exclude homocoupling, but is apparently readily achievable for Pd(II)–Pd(IV) cycles (R—R from Pd^{IV}R₂R') and for which there is ample precedent, for example, oxidative additions in **Scheme 3** (to form **9**) and **Scheme 4** (to form **12–14**, **17**, and **19**) and reductive eliminations from Pd(IV) complexes. However, there is evidence for the formation of bridging species such as **33–35** in Pd(II) chemistry,^{[100],[183]–[188]} thus allowing homocoupling via Pd(0)–Pd(II) catalysis by, for example, Ar group exchange between Pd^{II}XAr and Pd^{II}ArAr' via L(Ar)Pd^{II}(μ -Ar')(μ -Ar)Pd^{II}XL₂ (as **34**) to form Pd^{II}Ar₂, which may decompose to Ar—Ar and Pd(0). Exchange of organic groups has also been demonstrated to occur between monoorganopalladium(II) complexes and organometal reagents^{[188],[189]} and via the formation of palladates, for example, NMR spectra indicate the formation of [PdPh₂Me(PEt₃)][–] and [PdPh₂Me₂]^{2–} on the reaction of *trans*-PdPh₂(PEt₃)₂ with LiMe.^[190]

Although there are ample precedents for the formation and decomposition of Pd(IV) complexes, including for undetected phosphine complexes (**Scheme 5**), where the oxidants involve C(sp³)—X bonds, *two-electron* oxidative addition of aryl halides has not been definitively demonstrated. Alternatives to oxidative addition may include one-electron oxidation giving [ArX]^{•–} and decomposition of “Pd(III)” species thus formed leading to Pd(0) involvement, formation of bridging species after oxidative addition of ArX to traces of Pd(0), and heterogeneous catalysis at Pd(0) or Pd(0)/Pd(II) species adsorbed at Pd(0) surfaces. Despite these reservations, two-electron oxidative addition of

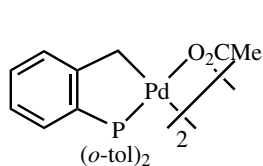
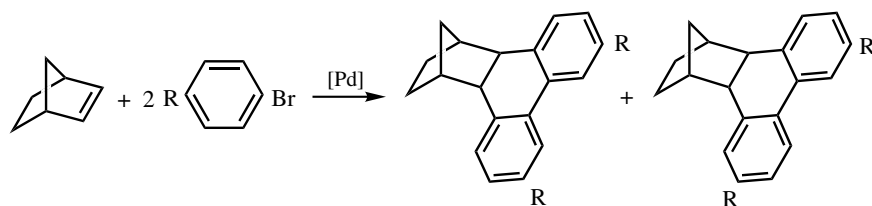


Scheme 8

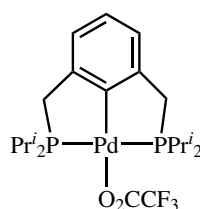
aryl halides to Pd(II) provides the simplest rationale for many observations, particularly for systems where formation of Pd(0) or of bridging species appears difficult, for example, the reaction of $PdPh(P\sim C\sim P)$ with PhI to form $PdI(P\sim C\sim P)$ and biphenyl $[P\sim C\sim P]^- = 2,6-(Pr^i_2PCH_2)_2C_6H_3]^-$.^[136] However, even in this case, the formation of bridging intermediates cannot be completely excluded.

Systems for which suggestions of intermediate Pd(IV) species formed by aryl halide oxidative addition have been proposed include reactions such as that of **Scheme 9** developed by Catellani, Chiusoli and co-workers^{[62],[74],[76],[102],[105],[111],[115]} and de Meijere and co-workers.^{[104],[108]-[110]} In this proposal,^{[62],[74],[76],[102],[105],[111],[115]} oxidative addition of aryl halide to Pd(0) is followed by alkene insertion to give pallada(II)cyclic $Pd(C_6H_3Y-C_7H_{10}-C,C')(PPh_3)_2$, followed by oxidative addition of aryl halide to give the putative palladium(IV) complex $PdBr(C_6H_4Y)(C_6H_3Y-C_7H_{10}-C,C')(PPh_3)_2$ and subsequent reductive elimination by C—C bond formation. Subsequent cyclization at Pd(II) and reductive elimination generates the products and Pd(0). The potential role of Pd(IV) is modeled by the formation of **27** (formed by oxidative addition of MeI) and its decomposition to form **28**.^{[62],[74]} A similar model sequence has been demonstrated for *p*-nitrobenzyl bromide.^[76]

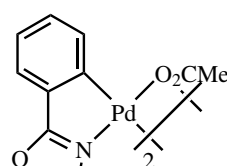
There has been extensive discussion of the possible role of Pd(IV) in Heck and related reactions catalyzed by Pd(II) intramolecular coordination complexes such as **36–38**.^{[118],[134]-[139],[180],[191],[192]} The proposals for Pd(IV) involvement require oxidative addition by aryl halides. Opinion is currently divided on whether Pd(IV) is involved and,



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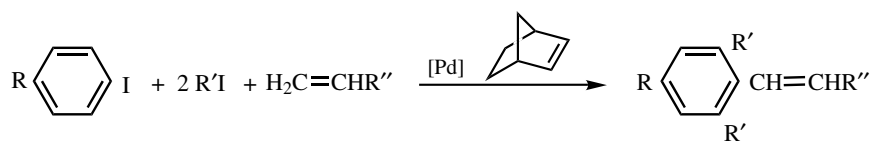


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Scheme 9

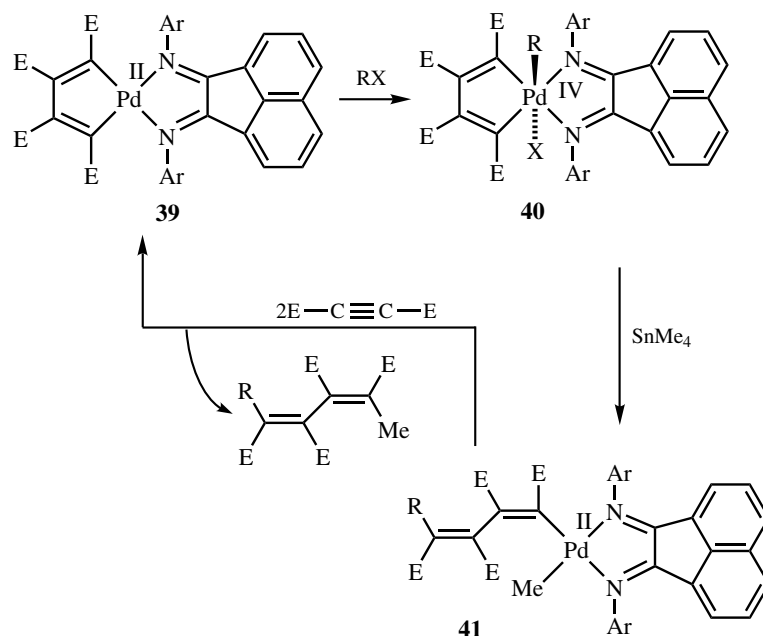
as noted by Herrmann in particular,^[135] further research is needed to resolve whether a Pd(0)–Pd(II) or Pd(II)–Pd(IV) pathway occurs.

Systems for which Pd(II)–Pd(IV) cycles are consistent with model reactions involve alkyl halide oxidative addition or oxidation by strong inorganic oxidants. Thus, the reaction of **Scheme 10** may be explained by a process very similar to that for **Scheme 9** but involving alkyl halide (R'I) addition modeled by formation of **27** and its decomposition to **28**, cyclization and repetition of this process, and subsequent elimination of norbornene.^[114] In this proposal the sequence for the alkylation of the ortho positions of the aryl group in the intermediate “Pd(C₆H₄—C₇H₁₀—C,C')L₂,” involving Pd(IV),^{[118],[134]–[139],[180],[191],[192]} is similar to that proposed for the exchange of ortho hydrogen atoms of Pd(C₆H₅—C₇H₁₀—C,C')(NMe₂CH₂CH₂N(Me)CH₂CH₂NMe₂—N,N') with protons of the solvent where,^[49] in the latter case, the electrophile is H⁺ rather than Alk⁺.



Scheme 10

The reaction of **Scheme 11** is validated for RX = Br₂ by the NMR detection of all four species in the proposed cycle^[55] and illustrates again a system where aryl halide involvement is readily explained in the same way but with the severe reservations expressed above for other systems. Facile cyclopalladation of azobenzene, oxidation of Pd(II) by chlorine (e.g., formation of **16**), and reductive elimination via C—Cl coupling



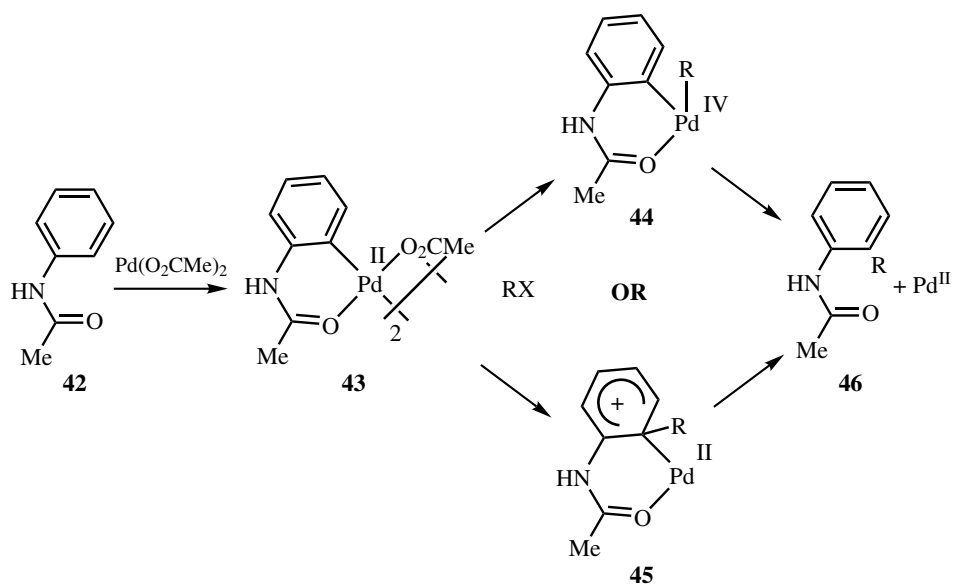
RX = Br₂ (**40** detected); E = CO₂Me; catalysis also occurs for RX = BnBr, MeI, PhI

Scheme 11

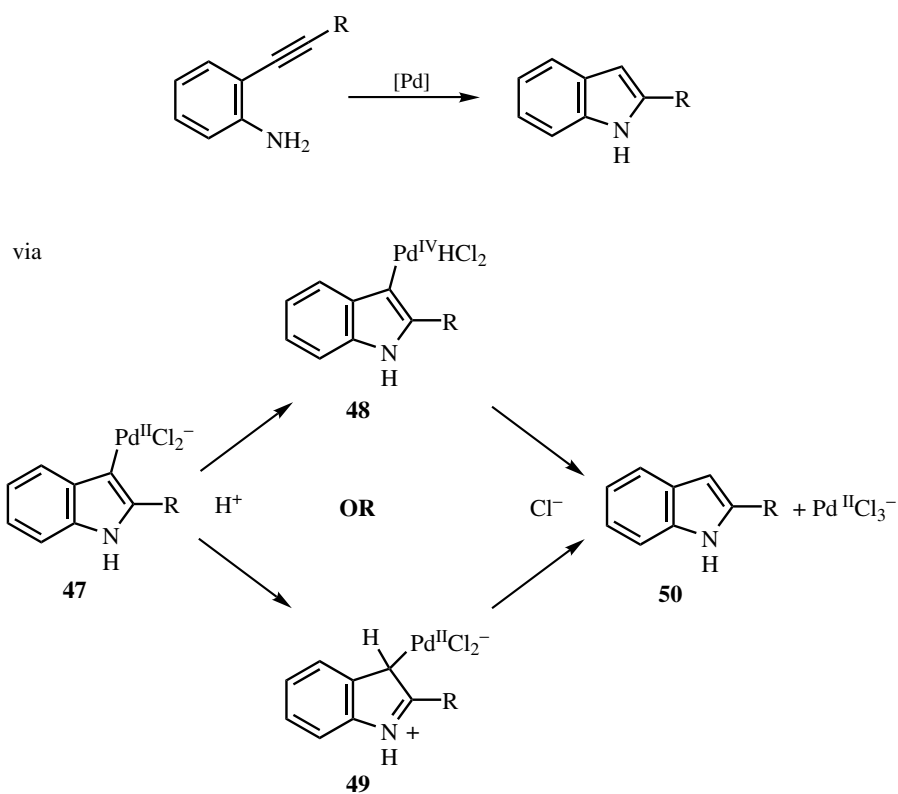
(e.g., decomposition of **16**) provide support for the proposal that Pd(IV) intermediates occur in the chlorination of azobenzene by PdCl₂/Cl₂ to form 2,6,2',6'-polychloro-azobenzenes.^[160]

In the reactions of **Schemes 10** and **11**, and in chlorination of azobenzene, electrophilic attack at Pd(II) is assumed to occur, leading to Pd(IV), but these syntheses and the proposals shown in **Scheme 12**,^[41] **Scheme 13**,^{[123],[124]} and **Scheme 14**^[127] illustrate typical dilemmas in assignment of mechanism, generally recognized by the authors of these proposals. Thus, electrophilic attack at Pd(II) [**43**→**44**, **47**→**48** giving Pd(IV)] or at carbon [**43**→**45**, **47**→**49**, remaining as Pd(II)] may give rise to acetanilides (**42**→**46**) or indoles (**47**→**50**); and C—H oxidative addition [**52**→**53** giving Pd(IV)] or cyclopalladation [**52**→**54** involving Pd(II)] may occur to give indenones (**55**). Cyclopalladation (**42**→**43**) is generally believed to occur via electrophilic attack by Pd(II) without involvement of Pd(IV) intermediates,^{[193],[194]} although in view of a recent report on cyclometallation at Rh(I),^[195] direct deprotonation from an agostically bonded arene ring cannot be discounted. Both experimental^[196] and theoretical studies^[197] indicate that, for platinum, formation of the stable Pt(II) arenonium species **58** (**Scheme 15**) most likely occurs via a Pt(IV) intermediate (**57**), suggestive of Pd(IV) involvement in the synthesis of *ortho*-substituted acetanilides but modified to give the sequence **42**→**43**→**44**→**45**→**46** (**Scheme 12**). The subtleties of electrophilic attack at metal or carbon atoms in M—C bonds for d⁸ metal centers, and the reverse reaction, relevant to **Schemes 12–15**, have been reviewed recently.^{[194],[195]}

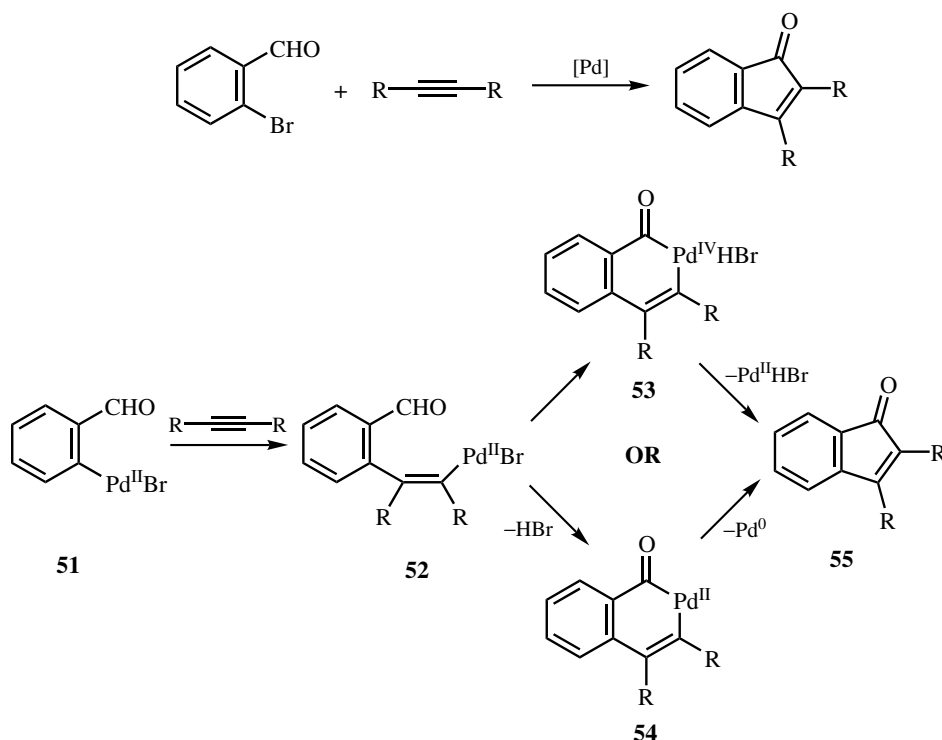
In addition to consideration of whether electrophiles interact with Pd or C atoms in Pd—C bonds, σ -bond metathesis (interaction of reagent X—Y across a Pd—C bond) may be appropriate for some systems.



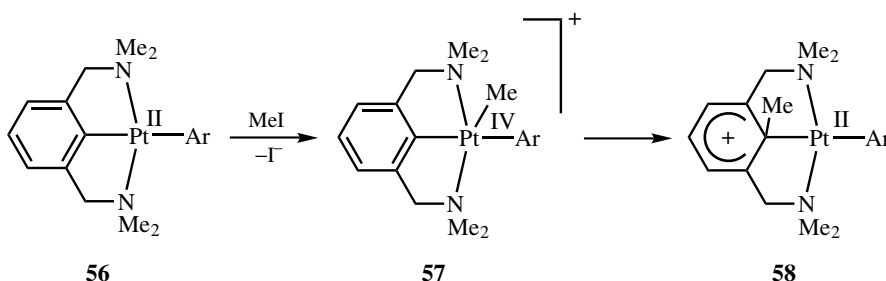
Scheme 12



Scheme 13



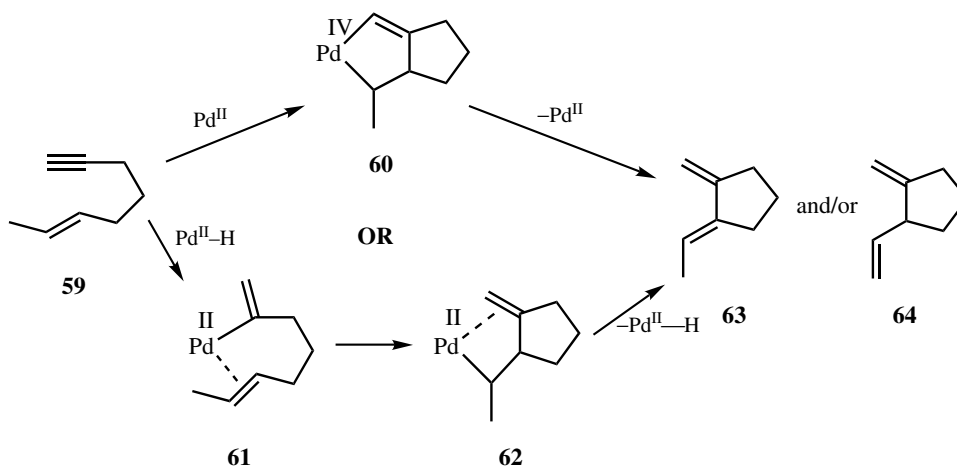
Scheme 14



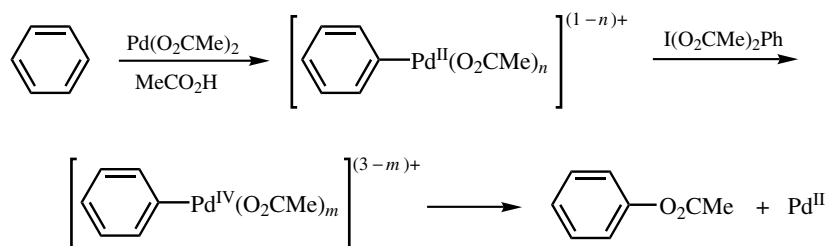
Scheme 15

A range of cyclization and cycloisomerization reactions of enynes, including enynes with heteroatoms in the skeleton, have been reported for which the possibility of Pd(IV) intermediates has been canvassed.^{[117],[130],[131],[162]–[175]} A typical example is shown in **Scheme 16**, where supporting ligands at palladium include palladacyclopentadienes, acetate, acetate/PPh₃, and acetate/P(*o*-tol)₃. An alternative pathway involving a Pd(0)–Pd(II) cycle has been acknowledged (**Scheme 16**), and different reaction conditions may favor each pathway.^{[166],[167],[172],[175]} Alkylidene complexes as intermediates have also been proposed for some reactions of enynes.^{[131],[165],[170]}

There is support for the occurrence of Pd(IV) species in the acetoxylation of arenes,^{[158],[159]} with the most recent proposal shown in **Scheme 17**, consistent with demonstrated palladation of benzene, for example, by Pd(O₂CMe)₂/SEt₂ to form



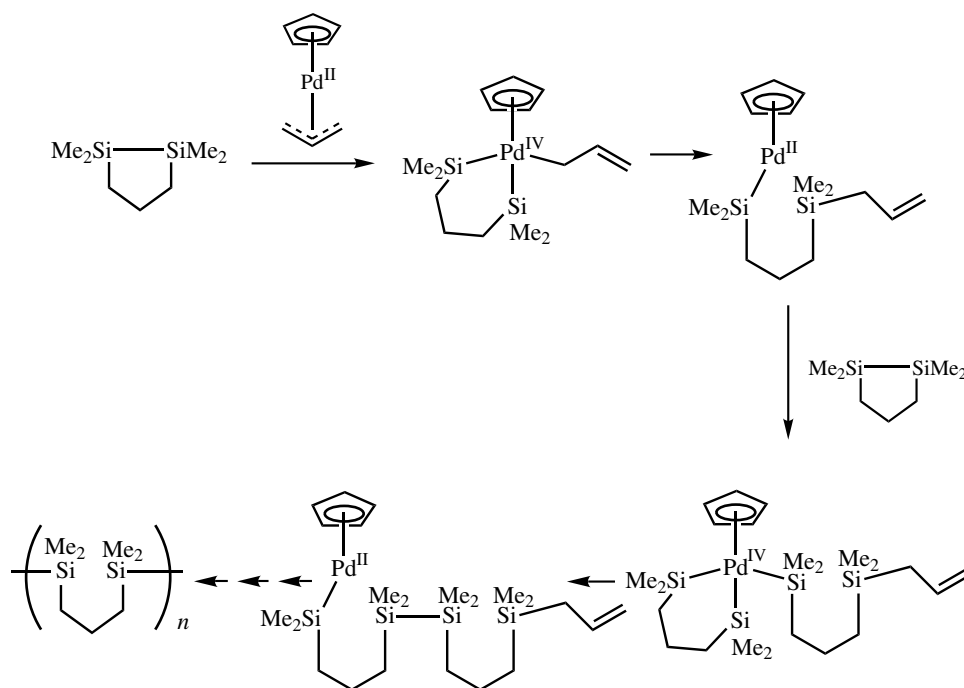
$\{\text{PdPh}(\text{SEt}_2)(\mu\text{-O}_2\text{CMe})_2\}_2\text{Pd}$.^[198] In related reactions, formation of alcohols and ethers in the presence of $\text{MoO}(\text{O}_2)_2 \cdot \text{HMPT} \cdot \text{H}_2\text{O}$ is proposed to occur via cyclopalladation, oxidation by Mo(VI) , and C—O bond formation involving an oxygen atom of the molybdenum species or methoxide from the methanol solvent.^[51]



The synthesis of **11** (Scheme 3)^{[29],[30]} and the related complex $\text{Pd}\{1,2\text{-(H}_2\text{Si)}_2\text{C}_6\text{H}_4\text{-Si,Si}\}_2(\text{dmpe-}P,P')$,^[199] both of which have been examined by X-ray diffraction, are relevant to the potential role of Pd(IV) in silane chemistry,^{[29],[30],[181],[182],[199]} and to the role of phosphine ligands in Pd(IV) catalysis. For example, **11** ($\text{R} = \text{H}$) is formed in the reaction shown in Scheme 3, and reactions of this type can be assumed to occur in the catalytic formation of $\{\text{SiMe}_2(\text{CH}_2)_3\text{SiMe}_2\}_n$ from $(\text{SiMe}_2\text{CH}_2)_2\text{CH}_2$ catalyzed by $\text{PdCp}(\eta^3\text{-C}_3\text{H}_5)$ or **11** (Scheme 18).^{[29],[182]}

F. CONCLUDING REMARKS

Oxidation state +4 is well established as a key oxidation state in the organometallic chemistry of palladium, but there are few reports of Pd(I) chemistry except for poly-halogenophenyl derivatives, and scanty evidence for Pd(III) chemistry. Catalysis involving palladium complexes is dominated by Pd(0) and Pd(II) species, with evidence for Pd(I)



Scheme 18

involvement in a few systems. There are several catalysis and organic synthesis procedures for which proposals of Pd(IV) intermediates are supported by studies of model reactions, and isolated or spectroscopically detectable complexes, in particular those involving reactions in the presence of strong inorganic oxidants and organosilicon chemistry. Organic syntheses involving alkyl halide oxidative addition to Pd(II) appear to be feasible and, in addition, there are a range of reactions for which Pd(IV) intermediacy is enticing but as yet not supported by model reactions. This group of reactions include elegant syntheses involving enynes and aryl halide reagents.

REFERENCES

- [1] P. M. Maitlis, P. Espinet, and M. J. H. Russell, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds., Pergamon, New York, **1982**, Vol. 6, Chap. 38.3, 265–278.
- [2] T. Tanase, T. Nomura, Y. Yamamoto, and K. Kobayashi, *J. Organomet. Chem.*, **1991**, 410, C26.
- [3] J. A. Davies, in *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, and G. Wilkinson, Eds. (R. J. Puddephatt, Vol. 9, Ed.), Pergamon, Oxford, UK, **1995**, Vol. 9, Chap. 6, 291–390.
- [4] T. Murahashi, N. Kanehisa, Y. Kai, T. Otani, and H. Kurosawa, *Chem. Commun.*, **1996**, 825.
- [5] A. Behr, G. v. Ilseemann, W. Keim, C. Krüger, and Y.-H. Tsay, *Organometallics*, **1986**, 5, 514.
- [6] K. Osakada, T. Chiba, Y. Nakamura, T. Yamamoto, and A. Yamamoto, *Organometallics*, **1989**, 8, 2602.

- [7] J. Sieler, M. Helms, W. Gaube, A. Svensson, and O. Lindqvist, *J. Organomet. Chem.*, **1987**, 320, 129.
- [8] P. W. Jolly, C. Krüger, K.-P. Schick, and G. Wilke, *Z. Naturforsch.*, **1980**, 35B, 926.
- [9] K. Broadley, N. G. Connelly, G. A. Lane, and W. E. Geiger, *J. Chem. Soc. Dalton Trans.*, **1986**, 373.
- [10] G. A. Lane, W. E. Geiger, and N. G. Connelly, *J. Am. Chem. Soc.*, **1987**, 109, 402.
- [11] J. A. DeGray, W. E. Geiger, G. A. Lane, and P. H. Rieger, *Inorg. Chem.*, **1991**, 30, 4101.
- [12] A. J. Canty, in *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, and G. Wilkinson, Eds. (R. J. Puddephatt, Vol. 9, Ed.), Pergamon, Oxford, UK, **1995**, Vol. 9, Chap. 5, 225–290.
- [13] R. van Asselt, C. J. Elsevier, C. Amatore, and A. Jutand, *Organometallics*, **1997**, 16, 317.
- [14] C. Amatore, E. Carré, and A. Jutand, *Acta Chem. Scand.*, **1998**, 52, 100.
- [15] S. J. Young, B. Kellenberger, J. H. R. Reibenspies, S. E. Himmel, M. Manning, O. P. Anderson and J. K. Stille, *J. Am. Chem. Soc.*, **1988**, 110, 5744.
- [16] J. Forniés, F. Martinez, R. Navarro, A. Redondo, M. Tomas, and A. J. Welch, *J. Organomet. Chem.*, **1986**, 316, 351.
- [17] R. Uson and J. Forniés, *Adv. Organomet. Chem.*, **1988**, 28, 219–297.
- [18] E. R. Milaeva, A. Z. Rubezhov, A. I. Prokof'ev, and O. Y. Okhlobystin, *J. Organomet. Chem.*, **1980**, 193, 135.
- [19] A. Jouati, M. Geoffroy, G. Terron, and G. Bernardinelli, *J. Chem. Soc. Chem. Commun.*, **1992**, 155.
- [20] A. M. Bond, A. J. Canty, J. B. Cooper, V. Tedesco, P. R. Traill, and D. M. Way, *Inorg. Chim. Acta*, **1996**, 251, 185.
- [21] R. Uson, J. Forniés, and R. J. Navarro, *J. Organomet. Chem.*, **1975**, 96, 307.
- [22] R. Uson, J. Forniés, and R. J. Navarro, *Synth. React. Met.-Org. Chem.*, **1977**, 7, 235.
- [23] P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc. Chem. Commun.*, **1986**, 1722.
- [24] P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *Organometallics*, **1990**, 9, 826.
- [25] A. J. Canty, *Acc. Chem. Res.*, **1992**, 25, 83–90.
- [26] A. J. Canty, *Platinum Metals Rev.*, **1993**, 36, 2–7.
- [27] A. J. Canty, P. R. Traill, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, **1992**, 433, 213.
- [28] W. Kläui, M. Glaum, T. Wagner, and M. A. Bennett, *J. Organomet. Chem.*, **1994**, 472, 355.
- [29] M. Suginome and Y. Ito, *J. Chem. Soc. Dalton Trans.*, **1998**, 1925–1934.
- [30] M. Suginome, Y. Kato, N. Takeda, H. Oike, and Y. Ito, *Organometallics*, **1998**, 17, 495.
- [31] P. K. Wong and J. K. Stille, *J. Organomet. Chem.*, **1974**, 70, 121.
- [32] J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, **1976**, 98, 5841.
- [33] T. Ito, H. Tsuchiya, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **1977**, 50, 1319.
- [34] A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, **1980**, 102, 4933.
- [35] M. K. Loar and J. K. Stille, *J. Am. Chem. Soc.*, **1981**, 103, 4174.
- [36] A. Moravskiy and J. K. Stille, *J. Am. Chem. Soc.*, **1981**, 103, 4182.
- [37] R. A. Holton and K. J. Natalie, *Tetrahedron Lett.*, **1981**, 22, 267.
- [38] H. M. McPherson and J. L. Wardell, *Inorg. Chim. Acta*, **1983**, 75, 37.
- [39] H. Kurosawa, M. Emoto, and A. Urabe, *J. Chem. Soc. Chem. Commun.*, **1984**, 968.
- [40] H. D. McPherson and J. L. Wardell, *Inorg. Chim. Acta*, **1984**, 81, 39.
- [41] S. J. Tremont and H. U. Rahman, *J. Am. Chem. Soc.*, **1984**, 106, 5759.

- [42] P. Diversi, D. Fasce, and R. Santini, *J. Organomet. Chem.*, **1984**, 269, 285.
- [43] C. Cornioley-Deuschel and A. von Zelewsky, *Inorg. Chem.*, **1987**, 26, 3354.
- [44] R. P. Thummel and Y. Jahng, *J. Org. Chem.*, **1987**, 52, 73.
- [45] F. Maassarani, M. Pfeffer, G. Le Borgne, J. T. B. H. Jastrzebski, and G. van Koten, *Organometallics*, **1987**, 6, 1111.
- [46] W. de Graaf, S. Harder, J. Boersma, G. van Koten, and J. A. Kanter, *J. Organomet. Chem.*, **1988**, 358, 545.
- [47] A. Albinati, S. Affolter, and P. S. Pregosin, *J. Organomet. Chem.*, **1990**, 395, 231.
- [48] K.-C. Kong and C.-H. Cheng, *J. Am. Chem. Soc.*, **1991**, 113, 6313.
- [49] B. A. Markies, P. Wijkens, H. Kooijman, A. L. Spek, J. Boersma, and G. van Koten, *J. Chem. Soc. Chem. Commun.*, **1992**, 1420.
- [50] H. Nakazawa, Y. Matsuoka, I. Nakagawa, and K. Miyoshi, *Organometallics*, **1992**, 11, 1385.
- [51] P. L. Alsters, J. Boersma, and G. van Koten, *Organometallics*, **1993**, 12, 1629.
- [52] S. Strömberg, M. Oksman, L. Zhang, and K. Zetterberg, *Acta Chem. Scand.*, **1995**, 49, 689.
- [53] R. McCrindle, G. Ferguson, A. J. McAlees, G. J. Arsenault, A. Gupta, and M. C. Jennings, *Organometallics*, **1995**, 14, 2741.
- [54] J.-M. Valk, J. Boersma, and G. van Koten, *Organometallics*, **1996**, 15, 4366.
- [55] R. van Belzen, H. Hoffmann, and C. J. Elsevier, *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 1743.
- [56] J. Cámpora, C. Graiff, P. Palma, E. Carmona, and A. Tiripiccio, *Inorg. Chim. Acta*, **1998**, 269, 191.
- [57] R. van Belzen, R. A. Klein, H. Kooijman, N. Veldman, A. L. Spek, and C. J. Elsevier, *Organometallics*, **1998**, 17, 1812.
- [58] J. Cámpora, J. A. Lopez, P. Palma, P. Valerga, E. Spillner, and E. Carmona, *Angew. Chem. Int. Ed. Engl.*, **1999**, 38, 147.
- [59] K. Kamaraj and D. Bandyopadhyay, *Organometallics*, **1999**, 18, 438.
- [60] P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc. Chem. Commun.*, **1987**, 1093.
- [61] A. J. Canty and P. K. Byers, *J. Chem. Soc. Chem. Commun.*, **1988**, 639.
- [62] M. Catellani and G. P. Chiusoli, *J. Organomet. Chem.*, **1988**, 346, C27.
- [63] P. K. Byers, A. J. Canty, M. Crespo, R. J. Puddephatt, and J. D. Scott, *Organometallics*, **1988**, 7, 1363.
- [64] K.-T. Aye, A. J. Canty, M. Crespo, R. J. Puddephatt, J. D. Scott, and A. A. Watson, *Organometallics*, **1989**, 8, 1518.
- [65] W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek, and G. van Koten, *Organometallics*, **1989**, 8, 2907.
- [66] P. K. Byers, A. J. Canty, R. T. Honeyman, and A. A. Watson, *J. Organomet. Chem.*, **1990**, 385, 429.
- [67] M. Catellani and B. E. Mann, *J. Organomet. Chem.*, **1990**, 390, 251.
- [68] P. K. Byers, A. J. Canty, P. R. Traill, and A. A. Watson, *J. Organomet. Chem.*, **1990**, 390, 399.
- [69] D. G. Brown, P. K. Byers, and A. J. Canty, *Organometallics*, **1990**, 9, 1231.
- [70] W. de Graaf, J. Boersma, and G. van Koten, *Organometallics*, **1990**, 9, 1479.
- [71] P. K. Byers, A. J. Canty, B. W. Skelton, P. R. Traill, A. A. Watson, and A. H. White, *Organometallics*, **1990**, 9, 3080.
- [72] P. K. Byers, A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, **1992**, 433, 223.

- [73] P. K. Byers, A. J. Canty, B. W. Skelton, P. R. Traill, A. A. Watson, and A. H. White, *Organometallics*, **1992**, *11*, 3085.
- [74] M. Catellani and G. P. Chiusoli, *Gazz. Chim. Ital.*, **1993**, *123*, 1–7.
- [75] M. A. Bennett, A. J. Canty, J. K. Felixberger, L. M. Rendina, C. Sutherland, and A. C. Willis, *Inorg. Chem.*, **1993**, *32*, 1951.
- [76] G. Bocelli, M. Catellani, and S. Ghelli, *J. Organomet. Chem.*, **1993**, *458*, C12.
- [77] P. L. Alsters, P. F. Engel, M. P. Hogerheide, M. Copijn, A. L. Spek, and G. van Koten, *Organometallics*, **1993**, *12*, 1831.
- [78] D. J. Cárdenas, C. Mateo, and A. M. Echavarren, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2445.
- [79] R. van Asselt, E. Rijnberg, and C. J. Elsevier, *Organometallics*, **1994**, *13*, 706.
- [80] B. A. Markies, A. J. Canty, J. Boersma, and G. van Koten, *Organometallics*, **1994**, *13*, 2053.
- [81] C. Dücker-Benfer, R. van Eldik, and A. J. Canty, *Organometallics*, **1994**, *13*, 2412.
- [82] A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton, P. R. Traill, and A. H. White, *Organometallics*, **1995**, *14*, 199.
- [83] G.-X. Liu and R. J. Puddephatt, *Inorg. Chim. Acta*, **1996**, *251*, 319.
- [84] A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton, and A. H. White, *Organometallics*, **1996**, *15*, 5713.
- [85] D. Kruis, B. A. Markies, A. J. Canty, J. Boersma, and G. van Koten, *J. Organomet. Chem.*, **1997**, *532*, 235.
- [86] A. J. Canty, J. L. Hoare, N. W. Davies, and P. R. Traill, *Organometallics*, **1998**, *17*, 2046.
- [87] A. J. Canty, A. Dedieu, H. Jin, A. Milet, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, **1999**, *287*, 27.
- [88] A. J. Canty, H. Jin, and J. Penny, *J. Organomet. Chem.*, **1999**, *573*, 30.
- [89] A. J. Canty, J. L. Hoare, J. Patel, M. Pfeffer, B. W. Skelton, and A. H. White, *Organometallics*, **1999**, *18*, 2660.
- [90] N. J. Hovestad, J. L. Hoare, J. T. B. H. Jastrzebski, A. J. Canty, W. J. J. Smeets, A. L. Spek, and G. van Koten, *Organometallics*, **1999**, *18*, 2970.
- [91] A. J. Canty, H. Jin, B. W. Skelton, and A. H. White, *Inorg. Chem.*, **1998**, *37*, 3975.
- [92] A. J. Canty and H. Jin, *J. Organomet. Chem.*, **1998**, *565*, 135.
- [93] A. Milet, A. Dedieu, and A. J. Canty, *Organometallics*, **1997**, *16*, 5331.
- [94] E. L. Weinberg, B. K. Hunter, and M. C. Baird, *J. Organomet. Chem.*, **1982**, *240*, 95.
- [95] B. A. Markies, A. J. Canty, M. D. Janssen, A. L. Spek, J. Boersma, and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, **1991**, *110*, 447.
- [96] A. J. Canty and P. R. Traill, *J. Organomet. Chem.*, **1992**, *435*, C8.
- [97] A. J. Canty, P. R. Traill, R. Colton, and I. M. Thomas, *Inorg. Chim. Acta*, **1993**, *210*, 91.
- [98] A. J. Canty, A. A. Watson, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, **1989**, *367*, C25.
- [99] I. I. Moiseev and M. N. Vargaftik, *New J. Chem.*, **1998**, *22*, 1217.
- [100] F. Ozawa, M. Fujimori, T. Yamamoto, and A. Yamamoto, *Organometallics*, **1986**, *5*, 2144.
- [101] M. Catellani, G. P. Chiusoli, S. Ricotti, and F. Sabini, *Gazz. Chim. Ital.*, **1985**, *115*, 685.
- [102] M. Catellani and G. P. Chiusoli, *J. Organomet. Chem.*, **1985**, *286*, C13.
- [103] M. Catellani, G. P. Chiusoli, and S. Ricotti, *J. Organomet. Chem.*, **1985**, *296*, C11.
- [104] O. Reiser, M. Weber, and A. de Meijere, *Angew. Chem. Int. Ed. Engl.*, **1989**, *28*, 1037.
- [105] M. Catellani, G. P. Chiusoli, and M. Costa, *Pure Appl. Chem.*, **1990**, *62*, 623.
- [106] M. Catellani, G. P. Chiusoli, and C. Castagnoli, *J. Organomet. Chem.*, **1991**, *407*, C30.

- [107] M. Catellani and M. C. Fagnola, *Gazz. Chim. Ital.*, **1992**, 122, 481.
- [108] K. Albrecht, O. Reiser, M. Weber, and A. de Meijere, *Synlett*, **1992**, 521.
- [109] A. de Meijere, and F. E. Meyer, *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 2379–2411.
- [110] K. Albrecht, O. Reiser, M. Weber, B. Knieriem, and A. de Meijere, *Tetrahedron*, **1994**, 50, 383.
- [111] M. Catellani, G. P. Chiusoli, and M. Costa, *J. Organomet. Chem.*, **1995**, 500, 69.
- [112] M. Catellani and L. Ferioli, *Synthesis*, **1996**, 769.
- [113] M. Catellani and E. Motti, *New J. Chem.*, **1988**, 759.
- [114] M. Catellani and M. C. Fagnola, *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 2421.
- [115] M. Catellani, F. Frignani, and A. Rangoni, *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 119.
- [116] G. Dyker, *Angew. Chem. Int. Ed. Engl.*, **1992**, 31, 1023.
- [117] G. Dyker, *Chem. Ber./Recueil*, **1997**, 130, 1567–1578.
- [118] G. Dyker and A. Kellner, *J. Organomet. Chem.*, **1998**, 555, 141.
- [119] G. Dyker, *J. Org. Chem.*, **1993**, 58, 234.
- [120] G. Dyker, *Chem. Ber.*, **1994**, 127, 739.
- [121] G. Dyker, *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 103.
- [122] G. Dyker, *J. Org. Chem.*, **1993**, 58, 6426.
- [123] D. E. Rudisill and J. K. Stille, *J. Org. Chem.*, **1989**, 54, 5856.
- [124] S. Cacchi, V. Carnicelli, and F. Marinelli, *J. Organomet. Chem.*, **1994**, 475, 289.
- [125] J. S. McCallum, J. R. Gasdaska, and L. S. Liebeskind, *Tetrahedron Lett.*, **1989**, 30, 4085.
- [126] T. Satoh, T. Itaya, M. Miura, and M. Nomura, *Chem. Lett.*, **1996**, 823.
- [127] R. C. Larock, M. J. Doty, and S. Cacchi, *J. Org. Chem.*, **1993**, 58, 4579.
- [128] D. Brown, R. Grigg, V. Sridharan, and V. Tambyrajah, *Tetrahedron Lett.*, **1995**, 36, 8137.
- [129] R. Grigg, V. Loganathan, and V. Sridharan, *Tetrahedron Lett.*, **1996**, 37, 3399.
- [130] B. M. Trost and S.-F. Chen, *J. Am. Chem. Soc.*, **1986**, 108, 6053.
- [131] B. M. Trost and A. S. K. Hashmi, *J. Am. Chem. Soc.*, **1994**, 116, 2183.
- [132] H. Alper and M. Saldana-Maldonada, *Organometallics*, **1989**, 8, 1124.
- [133] J. Krause, K.-J. Haack, K.-R. Pörschke, B. Gabor, R. Goddard, C. Pluta, and K. Seevogel, *J. Am. Chem. Soc.*, **1996**, 118, 804.
- [134] W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, and H. Fischer, *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 1844.
- [135] W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, and M. Beller, *Chem. Eur. J.*, **1997**, 3, 1357.
- [136] M. Ohff, A. Ohff, M. E. van der Boom, and D. Milstein, *J. Am. Chem. Soc.*, **1997**, 119, 11687.
- [137] B. L. Shaw, S. D. Perera, and E. A. Staley, *Chem. Commun.*, **1998**, 1361.
- [138] B. L. Shaw and S. D. Perera, *Chem. Commun.*, **1998**, 1863.
- [139] G. T. Crisp, *Chem. Soc. Rev.*, **1998**, 27, 427.
- [140] B. L. Shaw, *New J. Chem.*, **1998**, 77.
- [141] M. Beller, H. Fischer, W. A. Herrmann, K. Öfele, and C. Brossmer, *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 1848.
- [142] W. A. Herrmann, C.-P. Reisinger, K. Öfele, C. Brossmer, M. Beller, and H. Fischer, *J. Mol. Catal.(A)*, **1996**, 108, 51.
- [143] K. Albrecht and A. de Meijere, *Chem. Ber.*, **1994**, 127, 2539.
- [144] S. K. Meegalla, N. J. Taylor, and R. Rodrigo, *J. Org. Chem.*, **1992**, 57, 2422.
- [145] N. R. Davies, *Aust. J. Chem.*, **1964**, 17, 212.

- [146] J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **1966**, 88, 3491.
- [147] F. T. T. Ng and P. M. Henry, *J. Org. Chem.*, **1973**, 38, 3338.
- [148] B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, **1978**, 100, 3407.
- [149] A. D. Ryabov, A. V. Eliseev, and A. K. Yatsimirsky, *Appl. Organomet. Chem.*, **1988**, 2, 101.
- [150] J. W. Francis and P. M. Henry, *Organometallics*, **1991**, 10, 3498.
- [151] A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **1967**, 6, 657.
- [152] G. Oehme and H. Pracejus, *J. Prakt. Chem.*, **1980**, 322, 798.
- [153] I. Guibert, D. Neibecker, and I. Tkatchenko, *J. Chem. Soc. Chem. Commun.*, **1989**, 1850.
- [154] A. S. K. Hashmi, *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 1581.
- [155] A. S. K. Hashmi, T. L. Ruppert, T. Knöfel, and J. W. Bats, *J. Org. Chem.*, **1997**, 62, 7295.
- [156] H. tom Dieck, C. Müller, E. T. K. Haupt, and D. Bolze-Kuhrt, *Z. Naturforsch.*, **1987**, 42B, 853.
- [157] C. Stephan, C. Munz, and H. tom Dieck, *J. Organomet. Chem.*, **1993**, 452, 233.
- [158] L. M. Stock, K.-W. Tse, L. J. Vorvick, and S. A. Walstrum, *J. Org. Chem.*, **1981**, 46, 1757.
- [159] T. Yoneyama and R. H. Crabtree, *J. Mol. Catal.(A)*, **1996**, 108, 35.
- [160] D. R. Fahey, *J. Organomet. Chem.*, **1971**, 27, 283.
- [161] N. Kamigata, M. Satoh, and M. Yoshida, *J. Organomet. Chem.*, **1991**, 401, C26.
- [162] B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, **1985**, 107, 1781.
- [163] B. M. Trost and M. Lautens, *Tetrahedron Lett.*, **1985**, 26, 4887.
- [164] B. M. Trost and G. J. Tanoury, *J. Am. Chem. Soc.*, **1987**, 109, 4753.
- [165] B. M. Trost and G. J. Tanoury, *J. Am. Chem. Soc.*, **1988**, 110, 1636.
- [166] B. M. Trost, *Acc. Chem. Res.*, **1990**, 23, 34.
- [167] B. M. Trost, M. Lautens, C. Chan, D. J. Jebaratnam, and T. Mueller, *J. Am. Chem. Soc.*, **1991**, 113, 636.
- [168] B. M. Trost and M. K. Trost, *Tetrahedron Lett.*, **1991**, 32, 3647.
- [169] B. M. Trost and C. Pedregal, *J. Am. Chem. Soc.*, **1992**, 114, 7292.
- [170] B. M. Trost and A. S. K. Hashmi, *Angew. Chem. Int. Ed. Engl.*, **1993**, 32, 1085.
- [171] B. M. Trost, G. J. Tanoury, M. Lautens, C. Chan, and D. T. MacPherson, *J. Am. Chem. Soc.*, **1994**, 116, 4255.
- [172] B. M. Trost, D. L. Romero, and F. Rise, *J. Am. Chem. Soc.*, **1994**, 116, 4268.
- [173] J. Castro, G. Balme, and J. Goré, *J. Chem. Res.(S)*, **1995**, 504.
- [174] H. Yamada, S. Aoyagi, and C. Kibayashi, *J. Am. Chem. Soc.*, **1996**, 118, 1054.
- [175] B. M. Trost and M. J. Krische, *Synlett*, **1998**, 1.
- [176] B. M. Trost and A. S. K. Hashmi, *J. Am. Chem. Soc.*, **1987**, 109, 3486.
- [177] B. M. Trost, M. T. Sorun, C. Chan, A. E. Harms, and G. Rühter, *J. Am. Chem. Soc.*, **1997**, 119, 698.
- [178] A. Bonardi, M. Costa, B. Gabriele, G. Salerno, and G. P. Chiusoli, *J. Chem. Soc. Chem. Commun.*, **1994**, 2429.
- [179] J. Yang, A. Haynes, and P. M. Maitlis, *J. Chem. Soc. Chem. Commun.*, **1999**, 179.
- [180] F.-T. Luo, A. Jeevanandam, and M. K. Basu, *Tetrahedron Lett.*, **1998**, 39, 7939.
- [181] A. Naka, T. Okada, and M. Ishikawa, *J. Organomet. Chem.*, **1996**, 521, 163.
- [182] Y. Uchimarui and M. Tanaka, *J. Organomet. Chem.*, **1996**, 521, 335.
- [183] F. Ozawa, T. Ito, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **1981**, 54, 1868.
- [184] F. Ozawa, K. Kurihara, T. Yamamoto, and A. Yamamoto, *J. Organomet. Chem.*, **1985**, 279, 233.

- [185] D. A. Widdowson and Y.-Z. Zhang, *Tetrahedron*, **1986**, 42, 2111.
- [186] F. Ozawa, T. Hidaka, T. Yamamoto, and A. Yamamoto, *J. Organomet. Chem.*, **1987**, 330, 253.
- [187] F. Ozawa, K. Kurihara, M. Fujimori, T. Hidaka, T. Toyoshima, and A. Yamamoto, *Organometallics*, **1989**, 8, 180.
- [188] R. van Asselt and C. J. Elsevier, *Organometallics*, **1994**, 13, 1972.
- [189] N. Bumagin, A. B. Ponomarev, and I. P. Beletskaya, *J. Org. Chem. USSR*, **1987**, 23, 1215.
- [190] H. Nakazawa, F. Ozawa, and A. Yamamoto, *Organometallics*, **1983**, 2, 241.
- [191] J. Louie and J. F. Hartwig, *Angew. Chem. Int. Ed. Engl.*, **1996**, 35, 2359
- [192] M. Ohff, A. Ohff, and D. Milstein, *J. Chem. Soc. Chem. Commun.*, **1999**, 357.
- [193] A. D. Ryabov, *Chem. Rev.*, **1990**, 90, 403.
- [194] A. J. Canty and G. van Koten, *Acc. Chem. Res.*, **1995**, 28, 406.
- [195] A. Vigalok, O. Uzan, L. J. W. Shimon, Y. Ben-David, J. M. L. Martin, and D. Milstein, *J. Am. Chem. Soc.*, **1998**, 120, 12539.
- [196] J. Terheijden, G. van Koten, I. C. Vinke, and A. L. Spek, *J. Am. Chem. Soc.*, **1985**, 107, 2891.
- [197] J. V. Ortiz, Z. Havlas, and R. Hoffmann, *Helv. Chim. Acta*, **1984**, 67, 1.
- [198] Y. Fuchita, K. Hiraki, Y. Kamogawa, M. Suenaga, K. Tohgoh, and Y. Fujiwara, *Bull. Chem. Soc. Jpn.*, **1989**, 62, 1081.
- [199] S. Shimada, M. Tanaka, and M. Shiro, *Angew. Chem. Int. Ed. Engl.*, **1996**, 35, 1856.