

IV.7 Carbopalladation of Allenes

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A. INTRODUCTION

There are, in principle, two pathways for the carbopalladation reaction of allenes depending on the regiochemistry of the insertion reaction of the C—Pd bond into one of the two cumulated C=C bonds (**Scheme 1**). Following **Path I**, the reaction would afford a C_{sp}²—Pd species **1**, while a π -allylpalladium species **2** could be formed via **Path II**.

A.i. Formation of π -Allylpalladium Species via Stoichiometric Reactions of Carbon–Palladium Species with Allenes: Regiochemistry of Carbopalladations of Allenes

Schultz discovered the first example of a carbopalladation of allenes when PdCl₂(PhCN)₂ was added to 1,2-propadiene to form the π -allylpalladium complex **3**, which was confirmed by the ¹H NMR spectra (**Scheme 2**).^{[1],[2]} In this case the first step is the chloropalladation of propadiene to form the π -allylpalladium complex **4**,^[3] of which the C_{sp}²—Pd bond reacted further with another molecule of propadiene to afford the final product **3**.

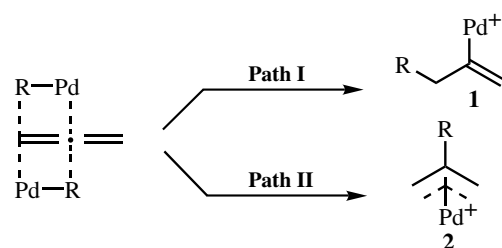
In 1968, van Helden and co-workers studied the corresponding carbopalladation reaction of 1,2-propadiene with the π -allylpalladium species **5**, affording η^3 -(2-(2'-alkenyl)allyl)palladium complex **6** (**Scheme 3**).^{[4]–[6]} Similar results were observed by Hughes and Powell.^{[7],[8]} The rate-determining step for these insertion reactions is the actual insertion step, not the coordination of the 1,2-diene onto Pd.^[9]

The stoichiometric reactions of palladium species other than π -allylpalladium complexes with allenes have also been observed with similar regioselectivity to afford π -allylpalladium species (**Scheme 4**).^{[10]–[14]}

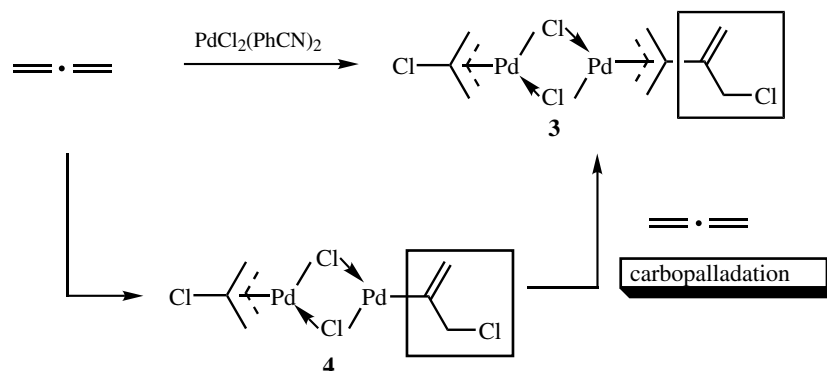
The regiochemistry of this carbopalladation has been further confirmed by the X-ray crystal structure analysis of complex **10**, which was formed by the reaction of the methylpalladium chloride complex **9** with propadiene (**Scheme 5**).^[15]

A.ii. Reactivities of π -Allylpalladium Species Formed via Carbopalladation of Allenes: Outline of Possible Reactions

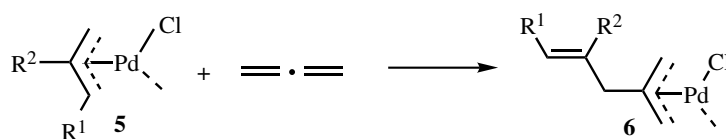
Based on the above stoichiometric reaction of organypalladium species with allenes, it is believed that, in most cases, the carbon atom originally connected with Pd in the initial



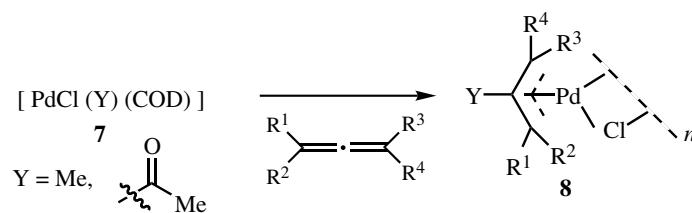
Scheme 1



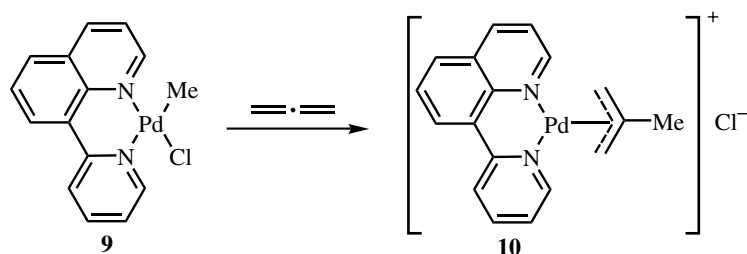
Scheme 2



Scheme 3

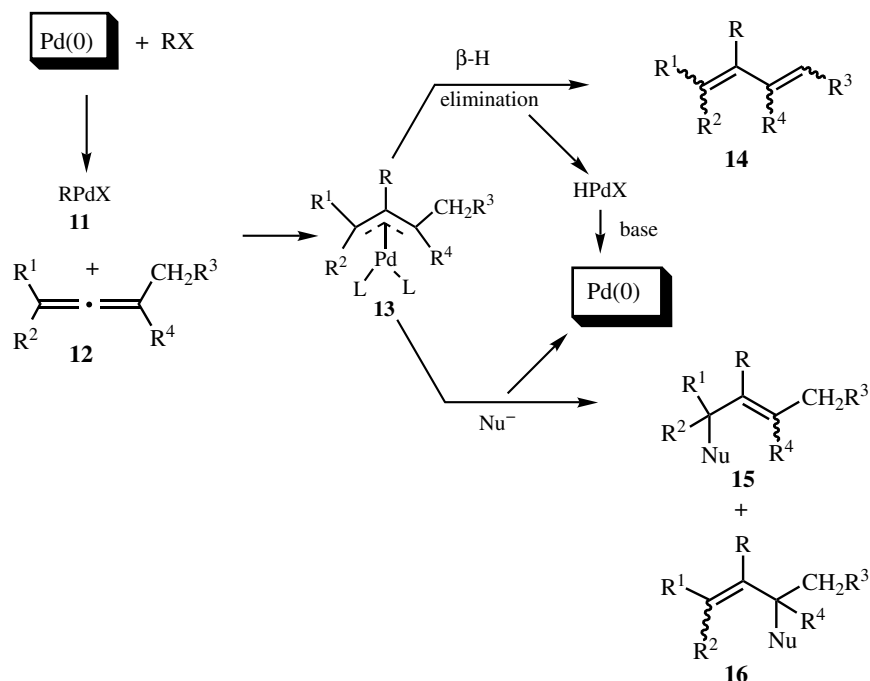


Scheme 4



Scheme 5

Pd species forms a C,C bond with the central carbon atom of the allene moiety; thus, the carbopalladation reaction of allenes provides an efficient entry to versatile and reactive π -allylpalladium species. Extensive studies have been carried out for the Pd-catalyzed reactions involving allenes (**Scheme 6**).



Scheme 6

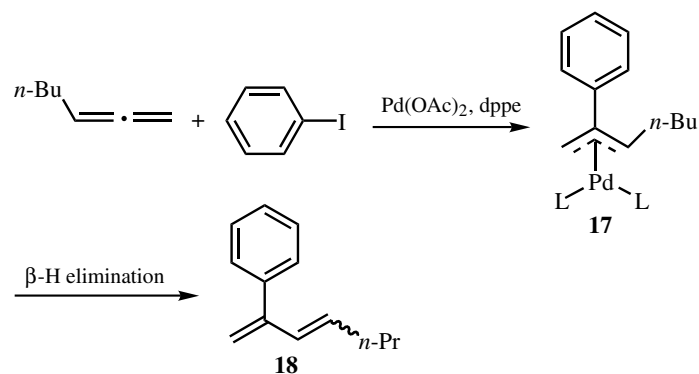
Palladium intermediates of type **11** can easily be generated via an oxidative addition of suitable organic halide onto a zerovalent palladium complex. The insertion reaction of **11** into a double bond of the allene **12** affords the π -allyl complex **13**, which can undergo either a β -hydride elimination or a nucleophilic substitution to afford organic product(s) and regenerate the zerovalent palladium species. Thus, new methodologies based on catalytic intermolecular or intramolecular reactions involving allenes can be designed. In limited cases, **Path I**-type carbopalladation reactions have also been observed (*vide infra*).

B. INTERMOLECULAR CARBOPALLADATION OF ALLENES FOLLOWED BY β -HYDRIDE ELIMINATION REACTION

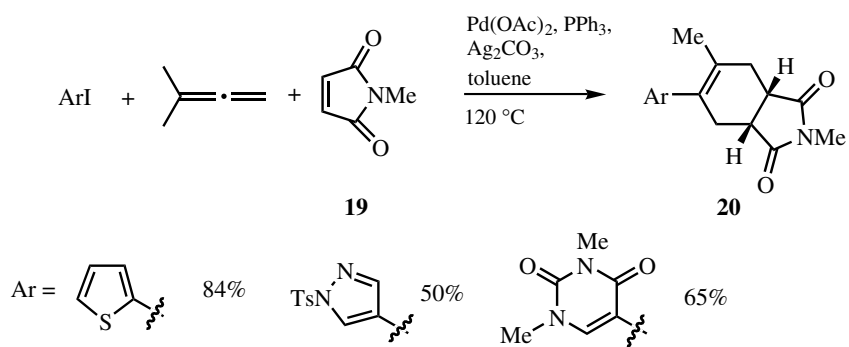
Shimizu and Tsuji reported the first catalytic carbopalladation reaction of allenes in 1984. The reaction of PhI with 1,2-heptadiene in the presence of $\text{Pd}(\text{OAc})_2$, dppe , and *N*-methylpyrrolidine (NMP) as the base gave 2-phenyl-1,3-heptadiene **18** (**Scheme 7**) via the β -hydride elimination from the π -allylpalladium intermediate **17**.^[16]

The 1,3-dienes formed could be trapped *in situ* with a dienophile to form an additional six-membered ring via a Diels–Alder reaction (**Scheme 8**).^[17]

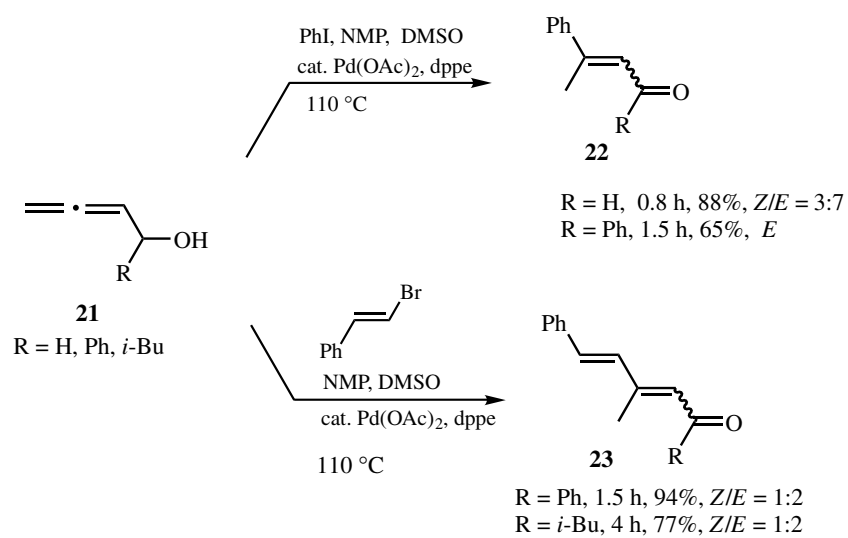
The corresponding reaction with 2,3-dienyl alcohols **21** provided a new entry to substituted enal/enone **22**, dialal/dienone **23** (**Scheme 9**).^[18]



Scheme 7



Scheme 8



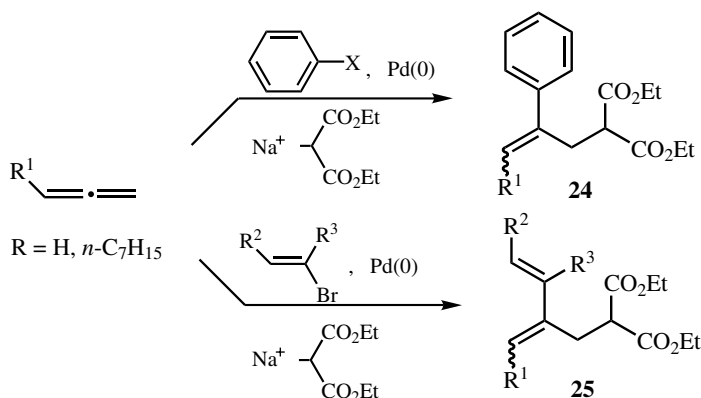
Scheme 9

C. INTERMOLECULAR CARBOPALLADATION OF ALLENES FOLLOWED BY INTERMOLECULAR NUCLEOPHILIC TRAPPING

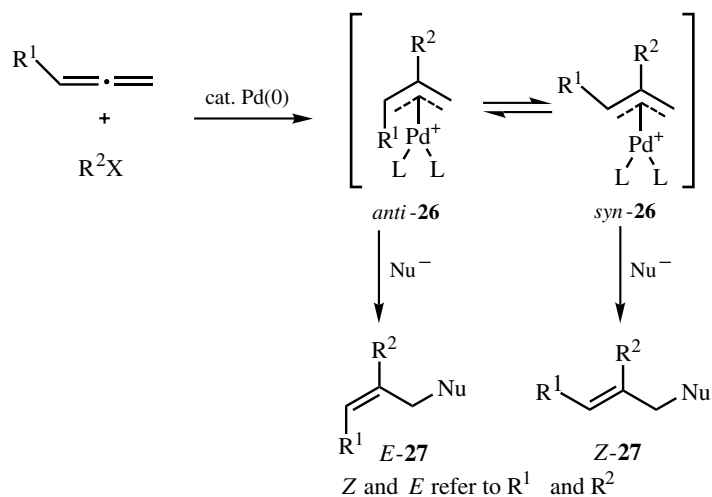
In **Sect. B**, the intermolecular carbopalladations of allenes are followed by a β -hydride elimination to afford a 1,3-diene. However, in the presence of a nucleophile, a Tsuji–Trost-type nucleophilic substitution of the intermediate π -allylpalladium species^{[19]–[21]} has been fully established (**Scheme 6**).

Shimizu and Tsuji^[16] and Cazes, Goré, and co-workers^{[22]–[25]} reported the first examples of such transformations in 1984. The Pd(0)-catalyzed reactions of either an aryl halide (bromide or iodide) or an alkenyl bromide with a 1,2-diene in the presence of sodium diethyl malonate afforded styrene derivatives **24** and 1,3-diene derivatives **25**, respectively (**Scheme 10**).^{[22]–[25]}

In these kinds of transformations, the configuration of the newly formed carbon–carbon double bond in either **24** or **25** depends on the relative stabilities of the two π -allylpalladium species *anti*-**26** and *syn*-**26** (**Scheme 11**).^{[25],[26]}

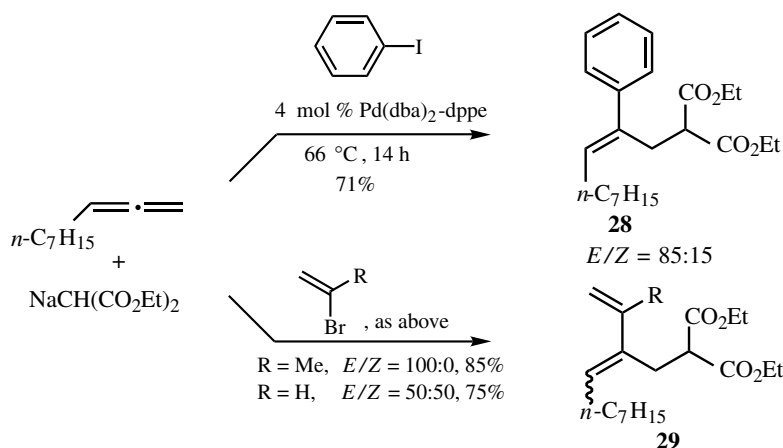


Scheme 10



Scheme 11

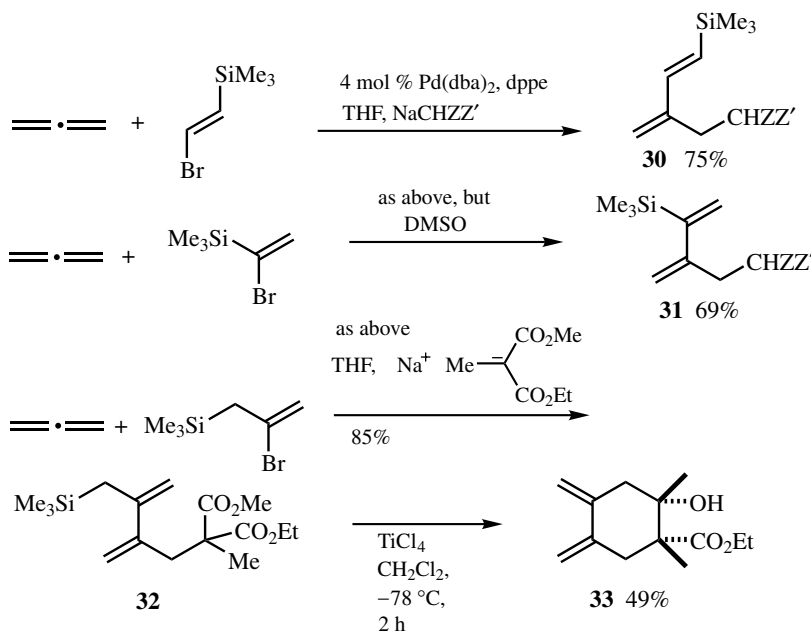
In these cases the interactions between R^1 and R^2 play the major role to determine the stereochemical outcome of the sequence of an intermolecular carbopalladation and an intermolecular nucleophilic trapping. Some typical results are listed in **Scheme 12**. In the case of **29**, the methyl group at the 2-position of the alkenyl bromide clearly shifts the equilibrium between *anti*-**26** and *syn*-**26** exclusively to *anti*-**26** (**Scheme 12**).^[23]



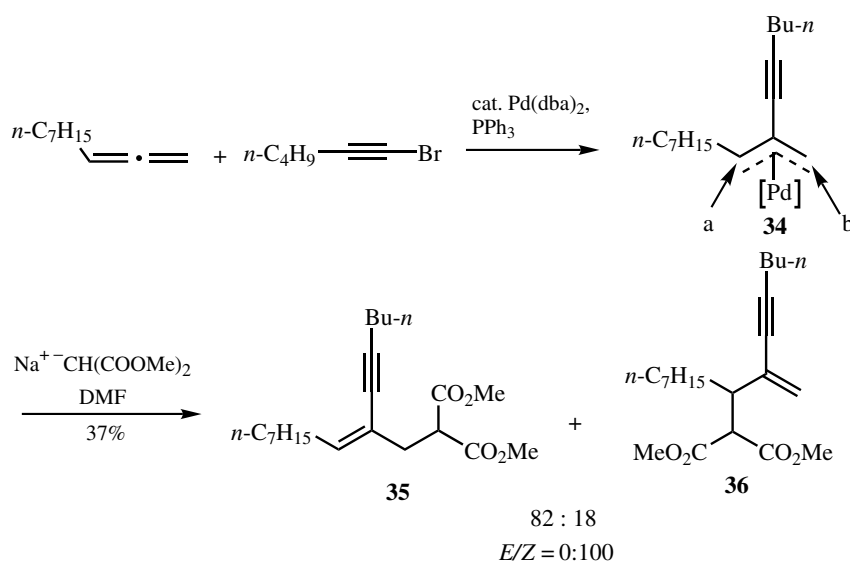
Scheme 12

Using trimethylsilyl-substituted vinyl bromides, the carbopalladation–intermolecular trapping protocol afforded trimethylsilyl-substituted 1,3-dienes **30/31** and 2-alkenyl-allyl silane **32**, which could be used for further elaboration (**Scheme 13**).^[27]

Under the catalysis of $\text{Pd}(\text{dba})_2$ and PPh_3 , the reaction of 1-hexynyl bromide with deca-1,2-diene and nucleophiles afforded enyne derivatives such as **35** and **36** (**Scheme 14**).^[28]

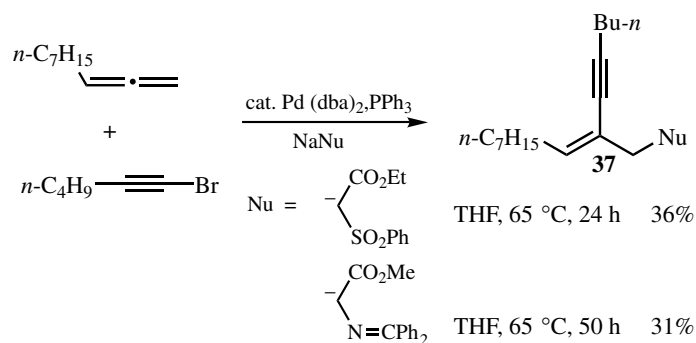


Scheme 13



Scheme 14

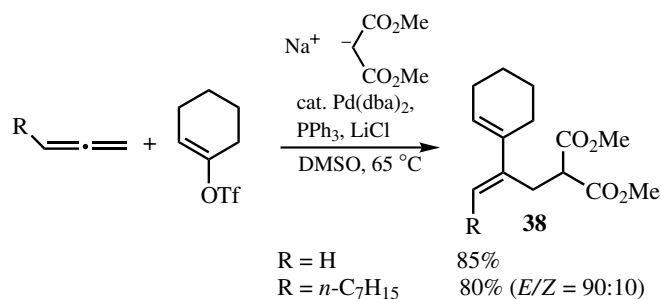
The following points should be noted.^[28] (i) The yield is usually low in this reaction, mainly due to a homocoupling reaction of the 1-alkynyl bromide and polymerization. (ii) The configuration of the carbon–carbon double bond in **35** is exclusively *Z* (not *E*), indicating that the effect of the interaction between R^1 and R^2 in **26** (Scheme 11) on the stereochemical outcome is replaced by that between R and the Pd residue^[26]; that is, due to the linear spatial arrangement of R^2 , *syn*-**26** is exclusively formed in the reaction mixture. (iii) The regioselectivity is somewhat lower; however, with a less reactive nucleophile, the regioselectivity is 100% (Scheme 15).



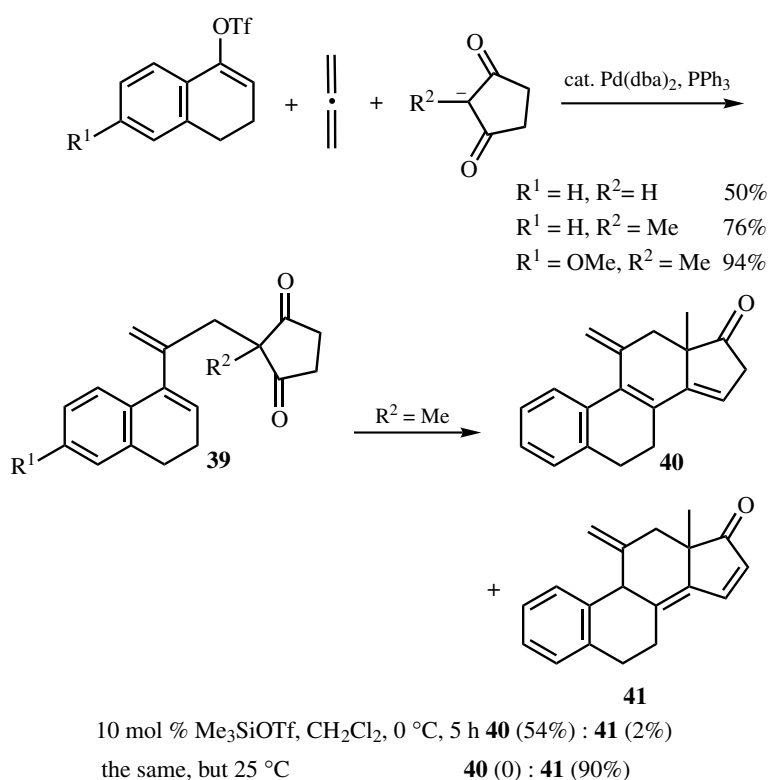
Scheme 15

Enol triflates, which can easily be prepared by trapping regiospecifically generated enolates with triflic anhydride or *N*-phenyl triflimide,^{[29],[30]} have also been applied in carbopalladation reactions of allenes (Scheme 16).^{[31],[32]}

The Pd(0)-catalyzed reaction of the enol triflate of α -tetralone with 1,2-propadiene in the presence of the enolate of 1,3-cyclopentadione afforded bicyclic precursors to the steroid skeleton **39**. Under the catalysis of 10 mol % of Me_3SiOTf at different temperatures, **39** ($R^1 = \text{H}$, $R^2 = \text{Me}$) could be highly selectively converted into compounds **40** or **41** (Scheme 17).^{[33]–[35]}



Scheme 16

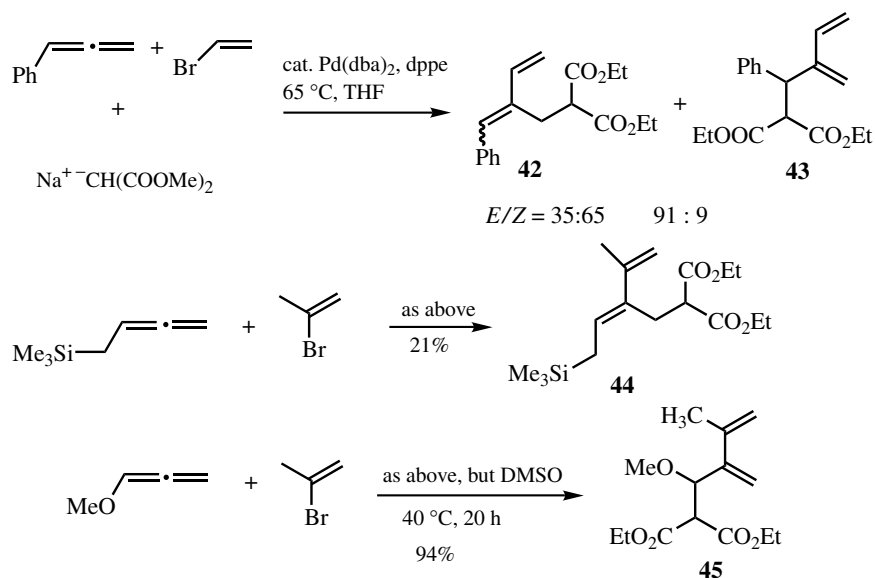


Scheme 17

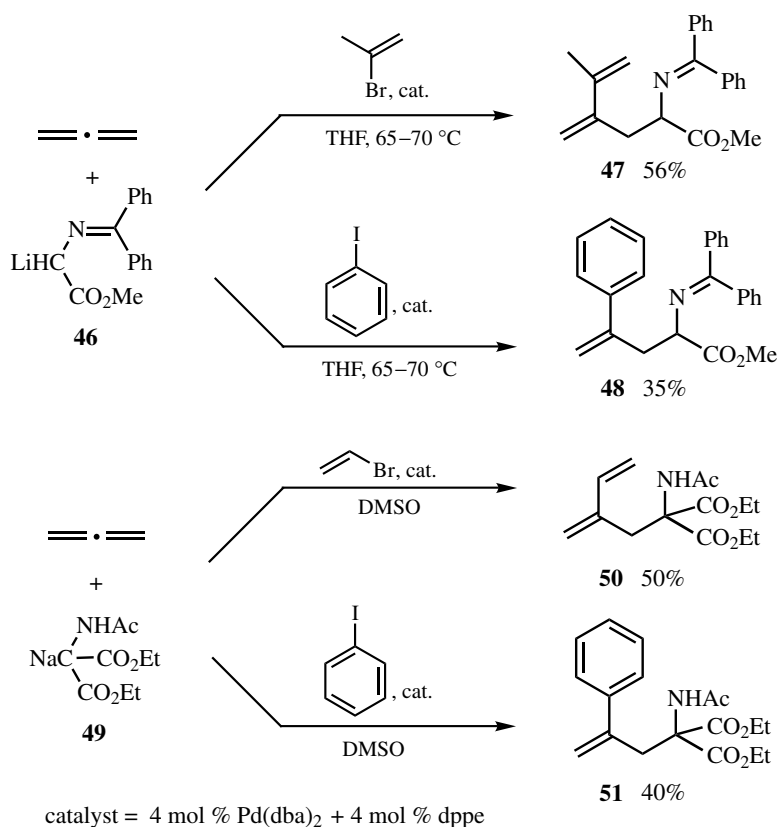
Functional groups in allenes such as phenyl, Me_3SiCH_2 , and methoxy are tolerated to afford the correspondingly functionalized 1,3-dienes in the $\text{Pd}(0)$ -catalyzed reactions of the respective allenes with alkenyl bromides (Scheme 18).^[36]

Using the enolate of the glycine equivalent methyl diphenylmethyleaminoacetate **46** or of diethyl acetamidomalonate **49** as nucleophiles, novel amino acid derivatives have been prepared from allenes (Scheme 19).^{[24],[25],[37]}

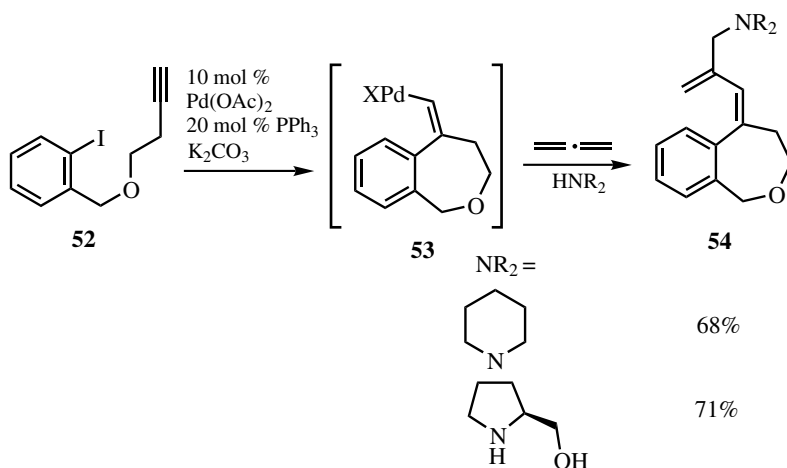
Amines have also been applied as nucleophiles.^{[6],[38]} Under the catalysis of the palladium, the *o*-iodobenzyl homopropargyl ether **52** formed the seven-membered ring vinyl-palladium intermediate **53**, which subsequently reacted with 1,2-propadiene in the presence of a secondary amine to eventually afford **54** (Scheme 20).^[38]



Scheme 18



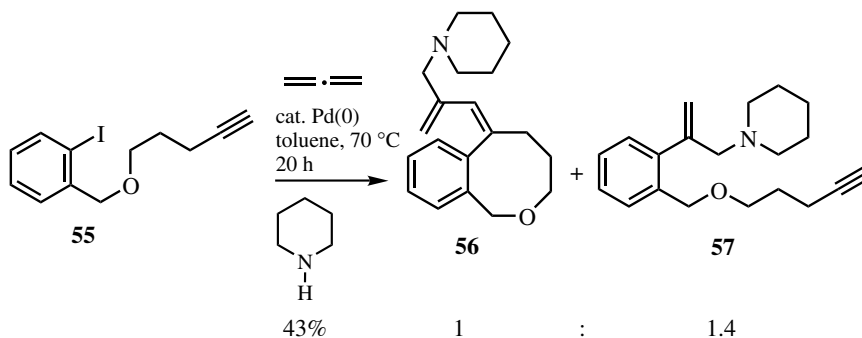
Scheme 19



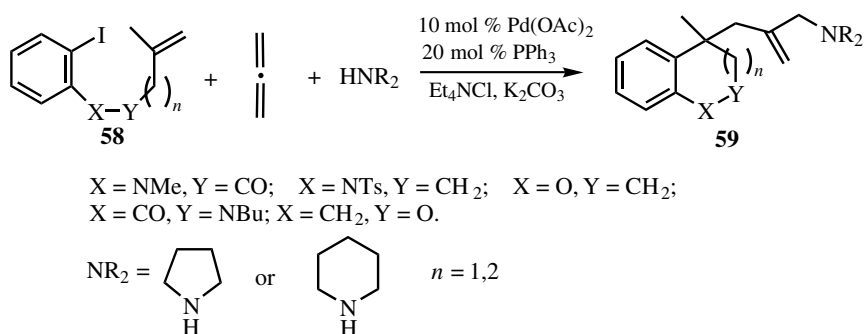
Scheme 20

In a similar way, even the benzoxacyclooctene derivative **56** with an eight-membered ring could be prepared, albeit in low yield along with the premature trapping product **57** (Scheme 21).^[38]

Similar results involving *o*-(ω -alkenyl)phenyl iodides have also been reported to afford benzolactams and benzoannulated cyclic amines or ethers (Scheme 22).^[39]



Scheme 21

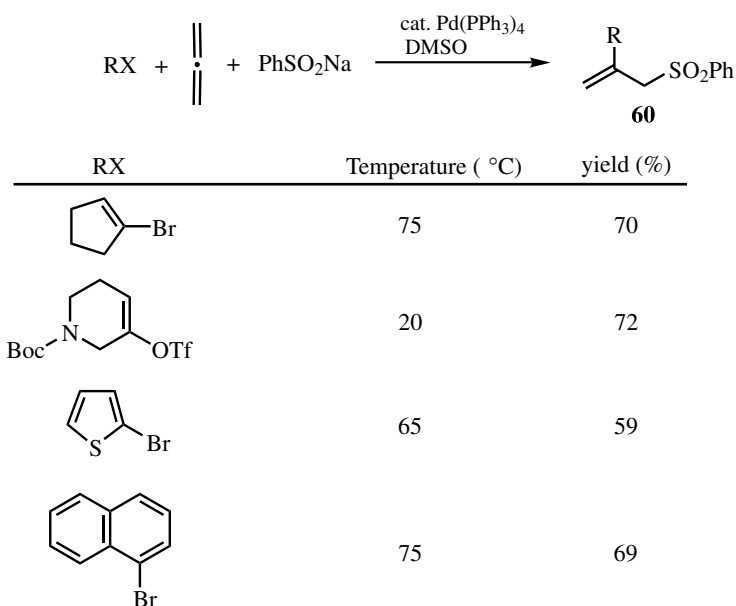


Scheme 22

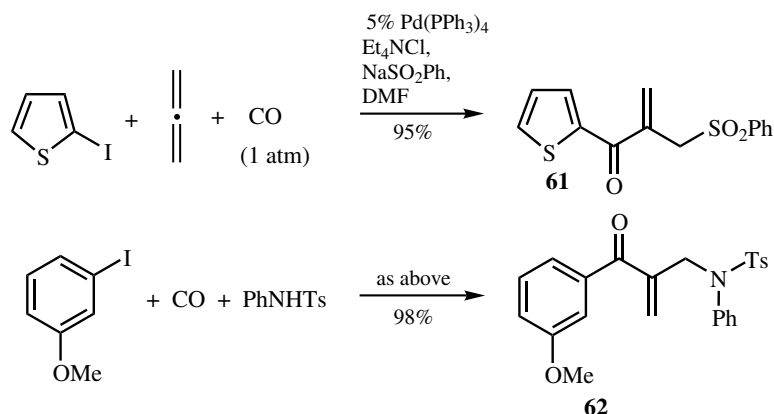
Sodium benzenesulfinate is also a nucleophile of choice (**Scheme 23**). The reaction provided an efficient route to allyl phenylsulfones **60**, which are of synthetic importance.^[40]

Acylpalladium species formed *in situ* via the insertion of CO can also react intermolecularly with an allene to form the corresponding π -allylpalladium intermediate, which could be trapped with NaSO₂Ph or *N*-phenyltosylamide to afford the α,β -unsaturated ketones **61** and **62** with an allylsulfone and an allylamine moiety, respectively (**Scheme 24**).^[41]

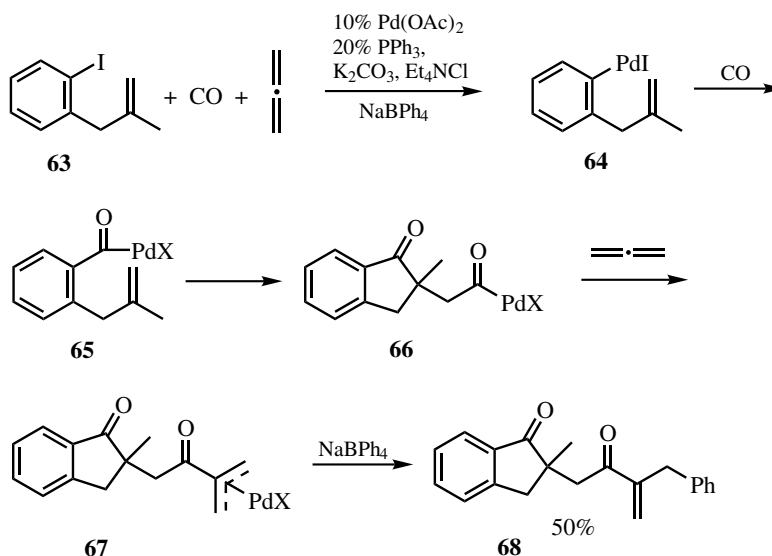
A five-component cascade reaction in which the last step is the trapping of a π -allylpalladium species with a nucleophile such as piperidine, pyrrolidine, morpholine, and NaBPh₄ afforded benzocyclopentenone derivatives **68** (**Scheme 25**).^[42]



Scheme 23

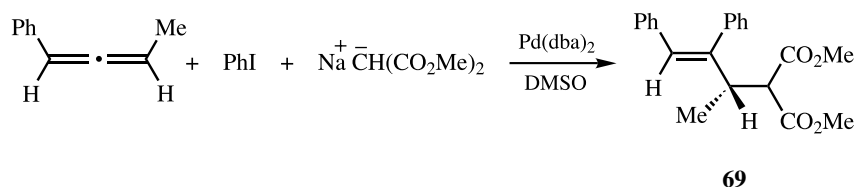


Scheme 24



Scheme 25

Using 4 mol % of Pd(dba)₂ plus 4 mol % of a chiral phosphine ligand such as BINAP, DIOP, MOD-DIOP, and ferrocenyl phosphines, the reaction of PhI, (±)-1-phenyl-1,2-butadiene, and sodium dimethyl malonate afforded chiral nonracemic (*S*)-dimethyl 1-methyl-2,3-diphenylallyl malonate **69** with up to 96% ee (Scheme 26).^[43]

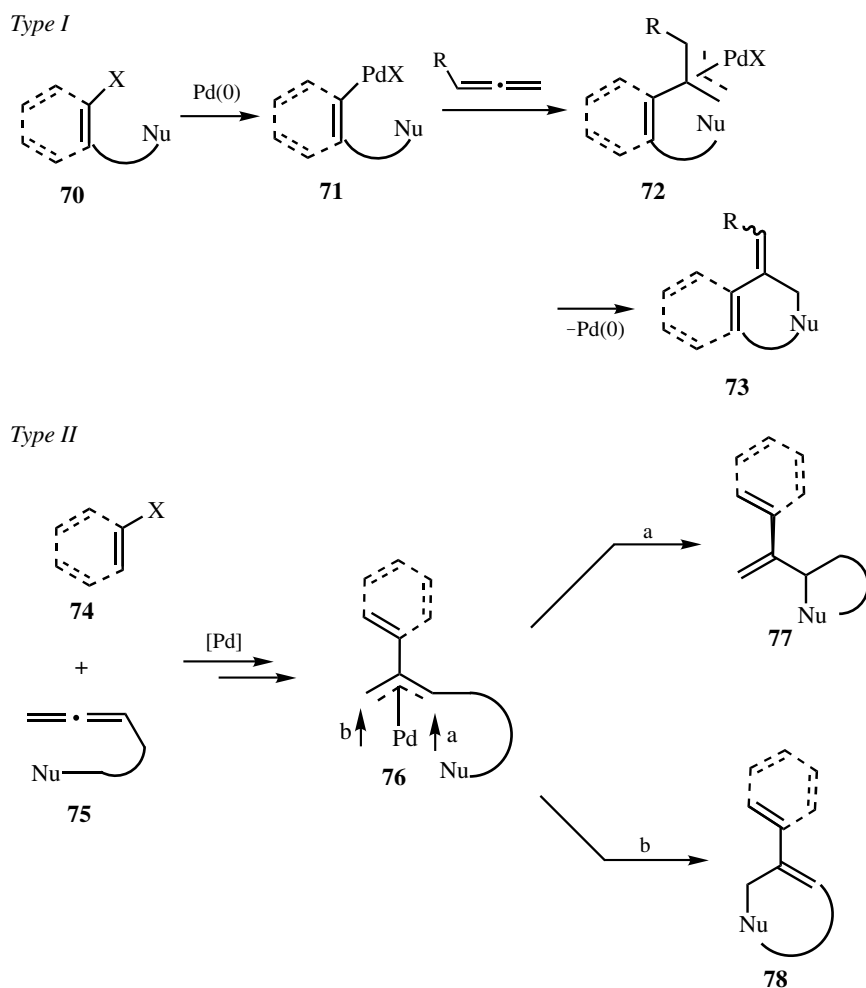


Ligand	Yield	(ee) %
(<i>S</i>)-BINAP	42	(96)
(+)-MOD-DIOP	89	(90)
(<i>R</i>)-(<i>S</i>)-BPPFOAc	77	(95)

Scheme 26

D. INTERMOLECULAR CARBOPALLADATION OF ALLENES FOLLOWED BY INTRAMOLECULAR NUCLEOPHILIC TRAPPING

As outlined in Sect. B and C, catalytic intermolecular carbopalladations of allenes followed by either β -hydride elimination or intermolecular nucleophilic trapping provide 1,3-dienes or allyl derivatives bearing the nucleophile moiety, respectively, while an intermolecular carbopalladation followed by intramolecular trapping sequential reaction provides cyclic skeletons (Scheme 27). In Type I, the nucleophilic moiety is connected with the C—X bond, and in Type II it is attached to the allene moiety.



Scheme 27

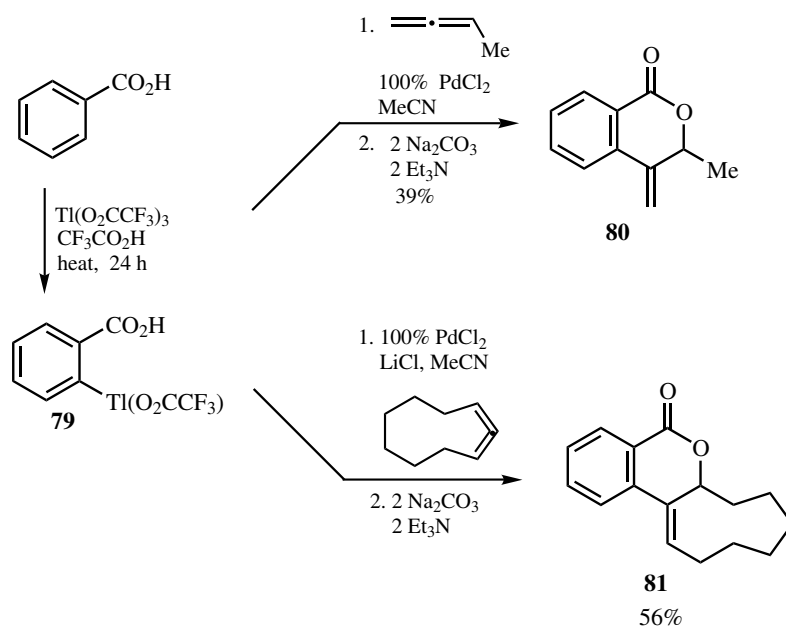
Larock and co-workers reported a stoichiometric Pd(II)-promoted cyclization of *ortho*-thalliated benzoic acid **79** with allenes to afford cyclic benzoannelated δ -valerolactones **80** and **81** (Scheme 28).^[44] In this reaction the first carbon–palladium bond is formed in a transmetalation reaction from Tl to Pd.

Based on these results, in 1991 Larock and co-workers developed a catalytic transformation starting from aryl iodides bearing potentially nucleophilic moieties in the *o*-position (Scheme 29).^[45]

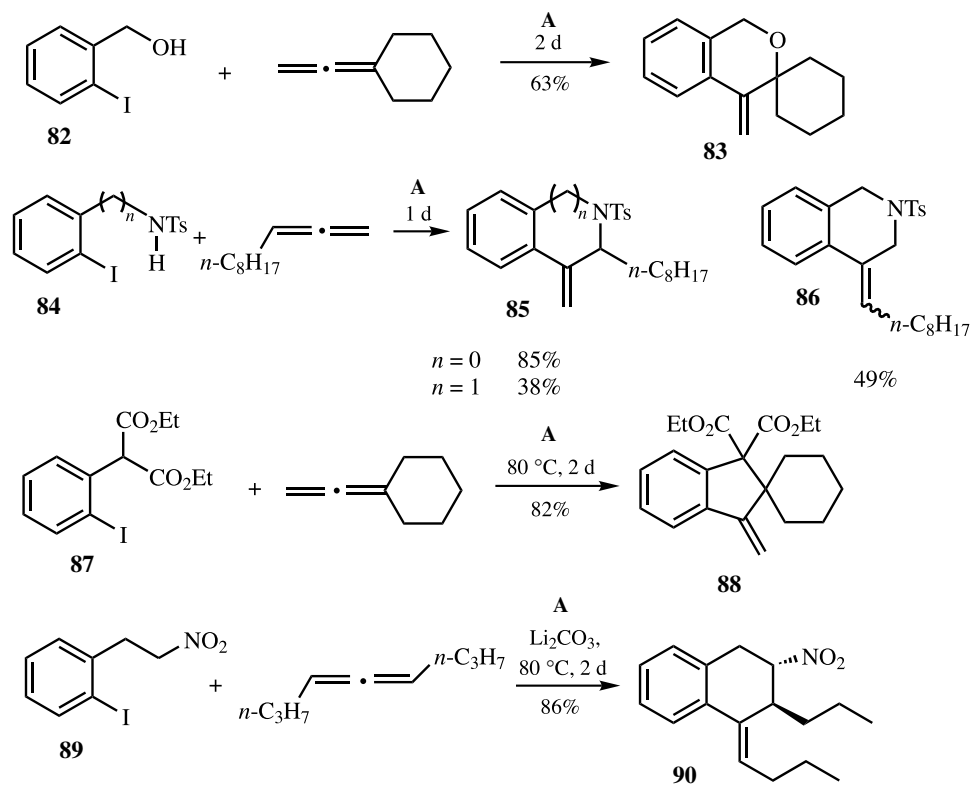
Similar results have also been reported by Desarbre and Méroux.^[46] The regioselectivity of the nucleophilic substitution depends exclusively on the electronic and steric effect of the substituent in the allene and the thus formed intermediate π -allylpalladium moiety (Scheme 30).

The Pd(0)-catalyzed reaction of iodoalkenes, bearing potentially nucleophilic groups, with allenes also afforded O- and N-containing heterocyclic products (Scheme 31).^[47]

Utilizing bisoxazoline **98** as a chiral ligand, the enantioselectivity in this carbopalladation–nucleophilic substitution sequence could be controlled with up to 82% ee (Scheme 32).^[48]

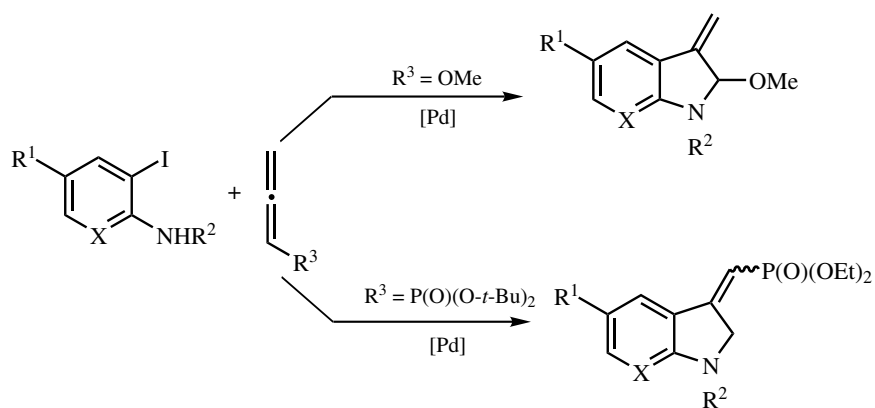


Scheme 28



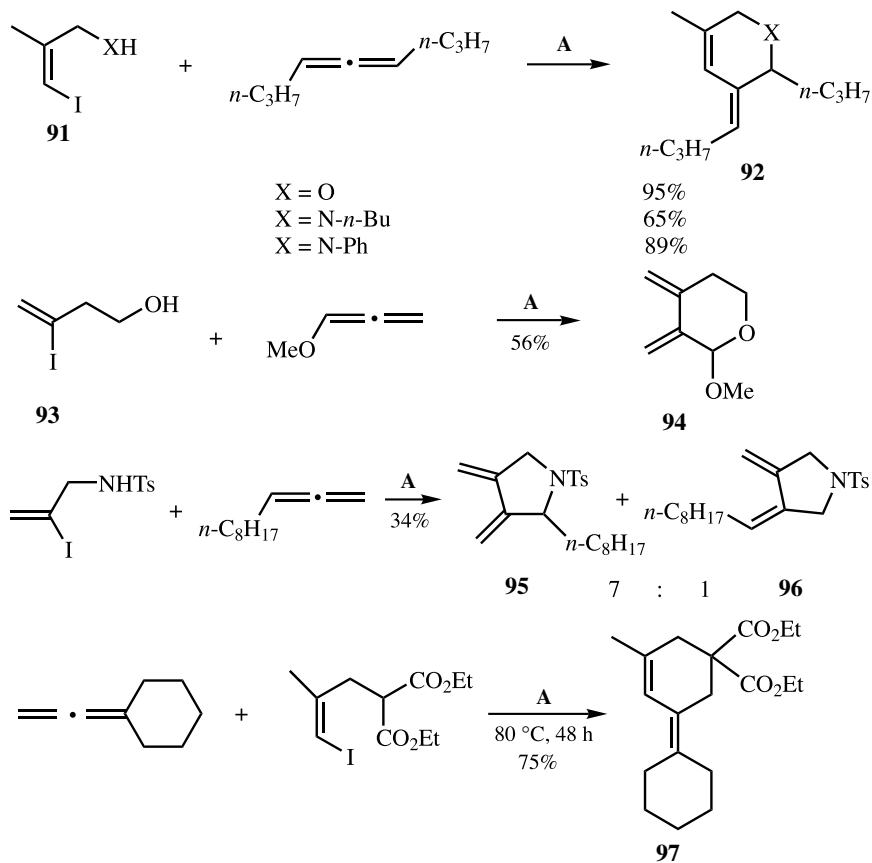
A = 5 mol % $\text{Pd}(\text{OAc})_2$, PPh_3 , Na_2CO_3 , $n\text{-Bu}_4\text{NCl}$, DMF, 100 °C

Scheme 29



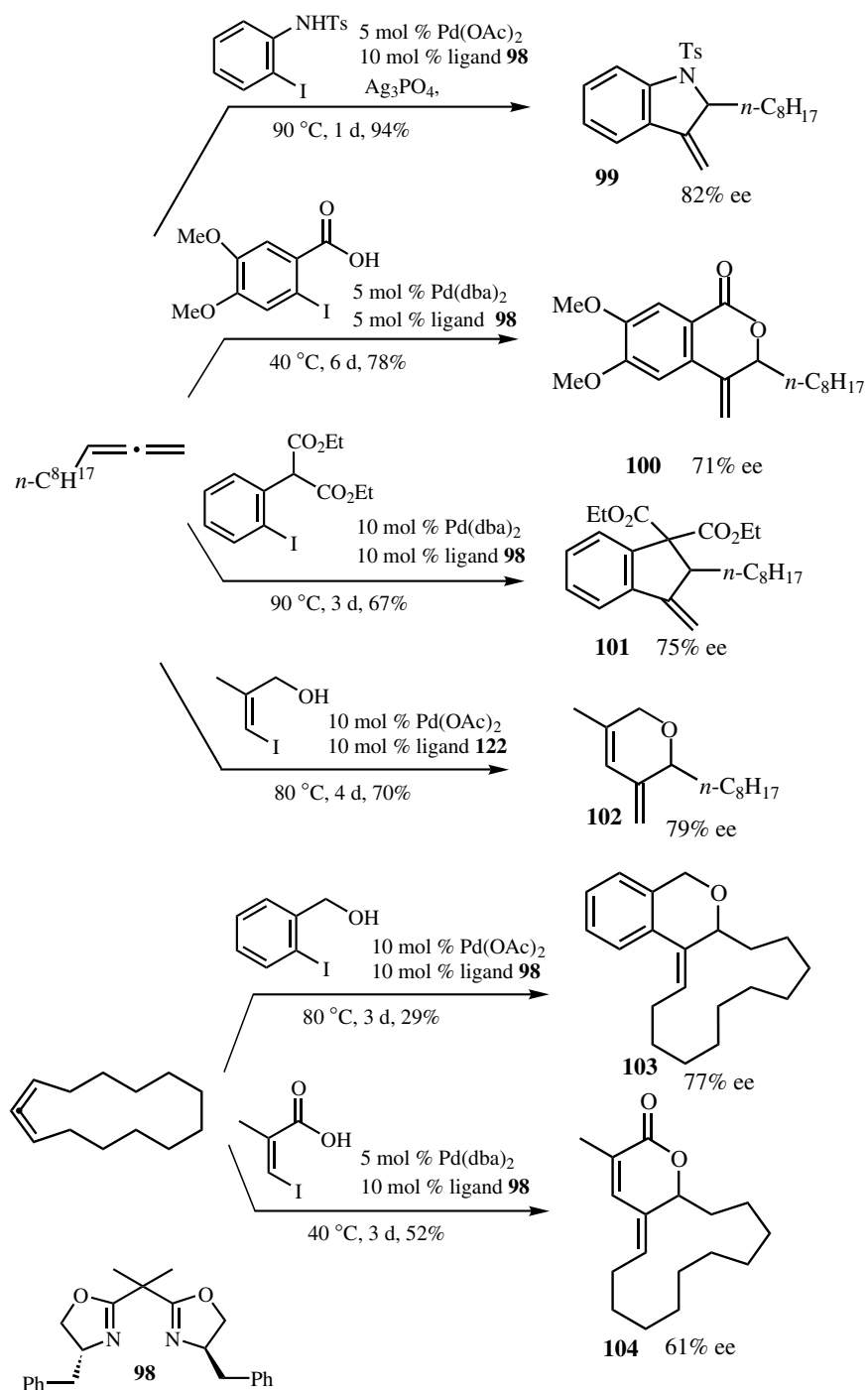
$R^1 = H, Br$; $R^2 = Ts, Boc$; $[Pd] = Pd(OAc)_2, Pd(PPh_3)_2Cl_2$; $BnEt_3^- N^+Cl$
 Base = Na_2CO_3 ; Solvent = DMF or MeCN

Scheme 30



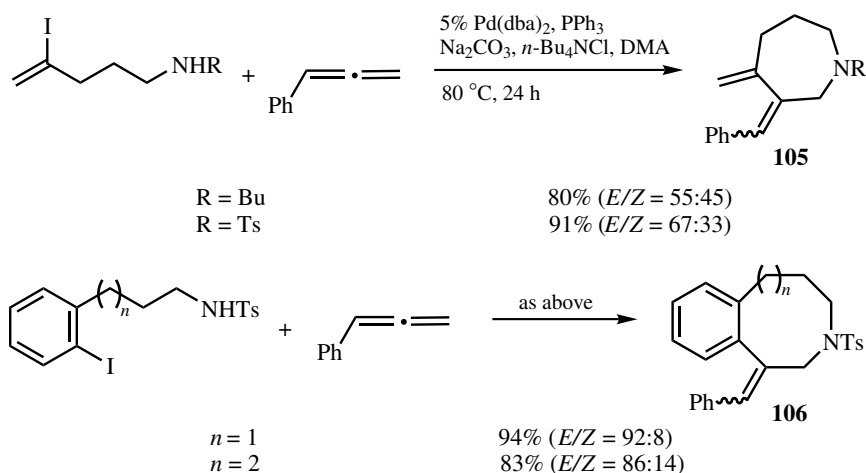
$A = 5 \text{ mol } \% Pd(OAc)_2, 5 \text{ mol } \% PPh_3, n-Bu_4NCl, Na_2CO_3, DMF$

Scheme 31



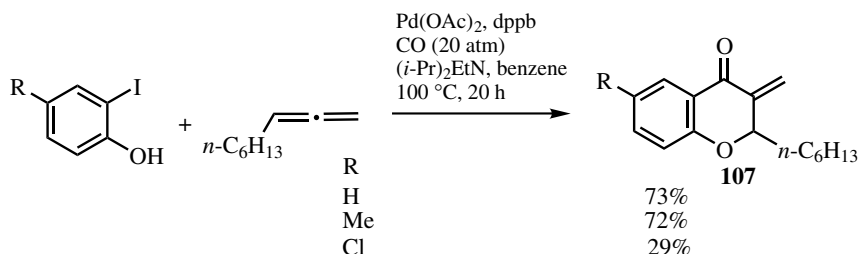
Scheme 32

Recently, Larock and co-workers reported the Pd(0)-catalyzed cyclization of 5- or 6-amino-2-iodo-alkenes or *o*-(2-/3-aminoalkyl)phenyl iodides with 1,2-dienes to afford N-containing seven- to nine-membered compounds. Some typical examples for the preparation of seven- and eight-membered heterocyclic products are listed in **Scheme 33**.^[49]



Scheme 33

The Pd(OAc)₂/dppb-catalyzed cascade reaction of *o*-iodophenol with 1,2-nonadiene and CO starts with a CO insertion which is followed by carbopalladation of the allene and subsequently terminated by an intramolecular nucleophilic substitution to afford O-containing six-membered α -methylenebenzo- γ -dihydropyrones (**Scheme 34**).^[50]

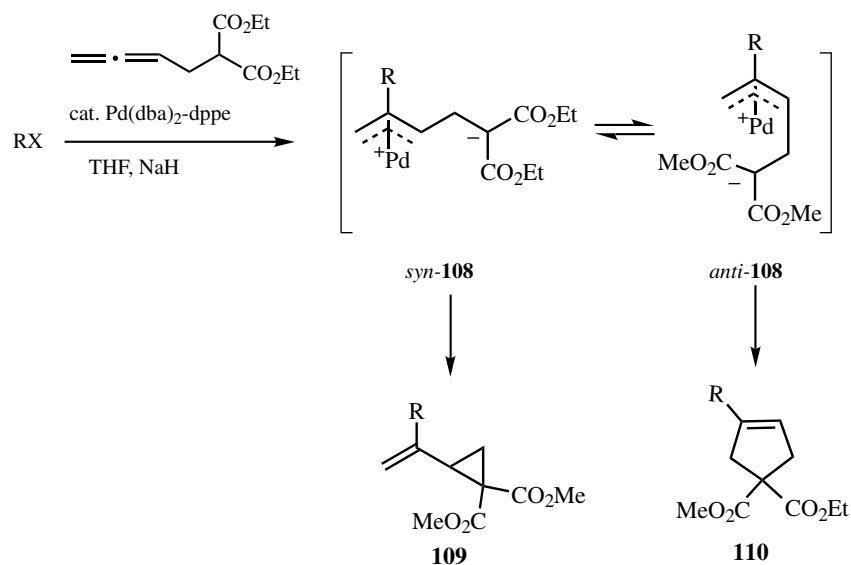


Scheme 34

On the other hand, the nucleophilic moiety can also be incorporated in the 1,2-dienyl derivative, which will lead to Type II cyclization products (see **Scheme 27**).

In 1985, Ahmar Cazes, and Goré^[51] disclosed the cocyclization reaction of nucleophile-containing allenes with aryl and 1-alkenyl halides to form five-membered and/or three-membered carbocycles. With unsubstituted vinyl bromide, only the vinyl cyclopropane derivative **109** was formed (**Scheme 35**).^{[51]–[54]}

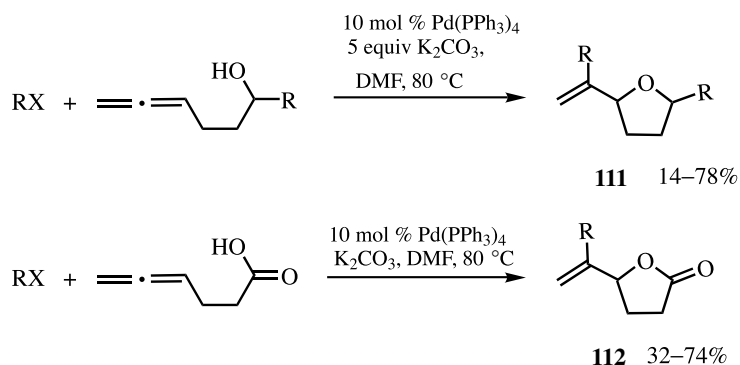
The regioselectivity of this reaction depends on the structure of the halide used and the type of nucleophilic moiety. According to a control study by Gamez and co-workers, the mechanism of this reaction did involve a corresponding π -allylpalladium intermediate (**Scheme 35**).^[54]



RX	Yield	(Ratio of 109/110)
1-Cyclohexenyl bromide	50%	(4:96)
Vinyl bromide	80%	(100:0)
Phenyl iodide	65%	(0:100)

Scheme 35

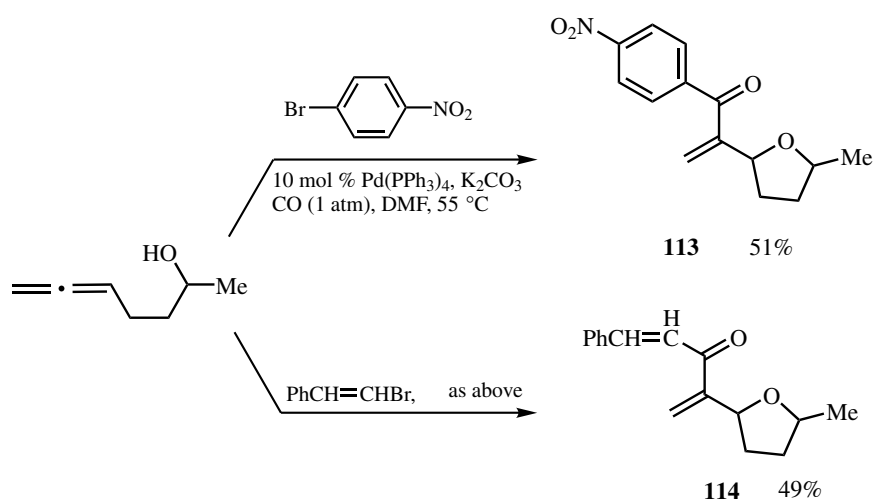
Walkup and co-workers developed new methodologies for the efficient synthesis of tetrahydrofurans **111** and γ -butyrolactone derivatives **112**, respectively, using the Pd(0)-catalyzed cyclization of organyl halides with 4,5-dienols and 4,5-dienoic acids, respectively (Scheme 36).^[55]



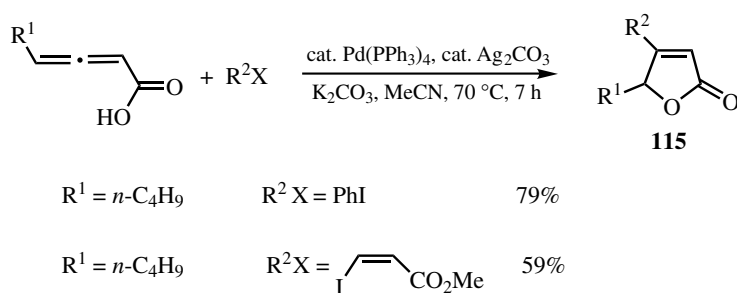
Scheme 36

In an atmosphere of CO (1 atm), the Pd(0)-catalyzed reaction of 5,6-heptadien-2-ol and organyl halides afforded 2-(1'-benzoylvinyl)-5-methyltetrahydrofurans **113** and **114** (Scheme 37).^[56]

Recently, Ma and Shi reported a one-step procedure for the efficient synthesis of butenolides via a Pd(0)- and Ag⁺-cocatalyzed carbopalladation–cyclization sequence of aryl/alkenyl halides with the easily available 3-substituted allenic acids (**Scheme 38**). In this reaction the presence of a catalytic amount of Ag⁺ is crucial, although its exact role is still unclear.^[57]



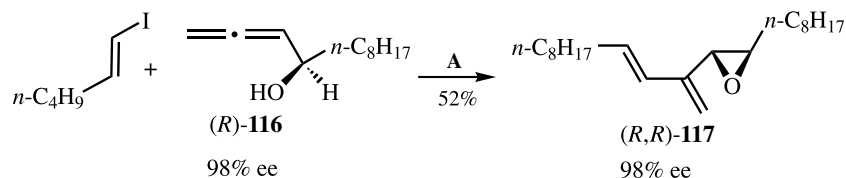
Scheme 37



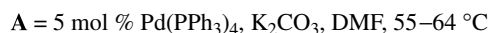
Scheme 38

With 3-hydroxy-1,2-dienes, alkenyl and aryl iodides formed only three-membered ring products, that is, vinyloxiranes, in a highly stereoselective manner (**Scheme 39**).^[58]

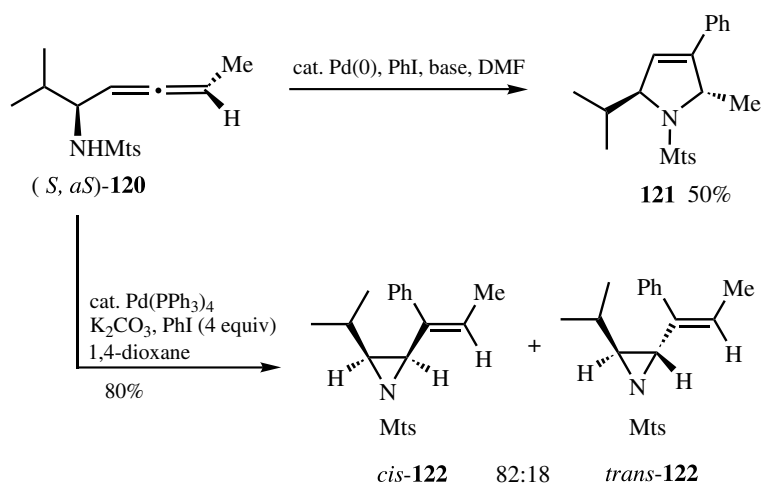
Ibuka and co-workers studied the Pd(0)-catalyzed cocyclizations of organyl halides with aminoallenes to afford 3-pyrrolines and aziridines with high selectivities under different reaction conditions (**Scheme 40**).^[59]



Scheme 39 (Continued)



Scheme 39 (Continued)



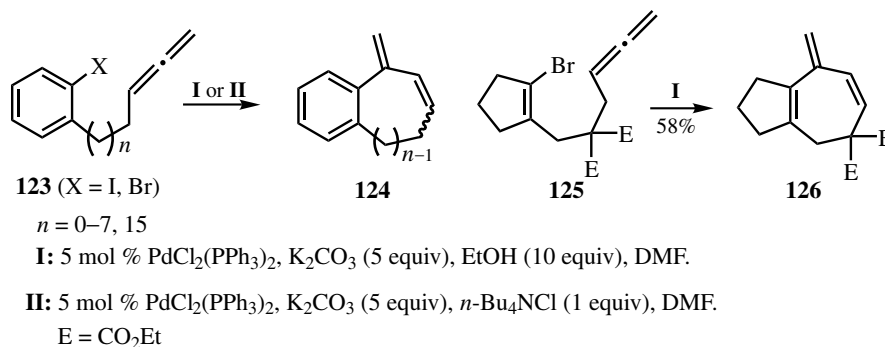
Scheme 40

E. INTRAMOLECULAR CARBOPALLADATION OF ALLENES FOLLOWED BY β -HYDRIDE ELIMINATION

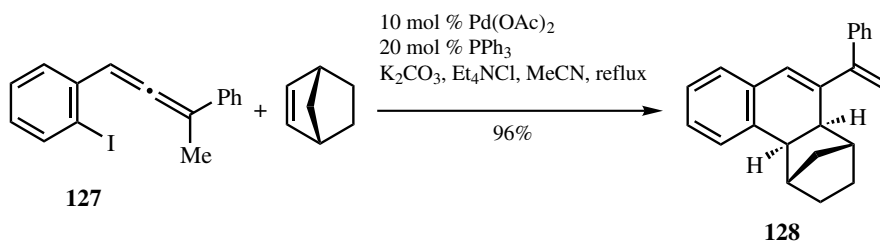
All the reactions discussed above involved an intermolecular carbopalladation. Recently, intramolecular carbopalladation reactions of allenes have received much attention. In 1994 Ma and Negishi found the first examples of a cyclizing carbopalladation of allenes and reported that this principle provides a general route to common, medium, and large ring compounds **124** (**Scheme 41**). The configuration of the endocyclic carbon–carbon double bond depends on the ring size and the nature of the substituents on the ring.^{[60],[61]}

Under palladium catalysis, the *o*-iodoallenylbenzene **127** first undergoes an intermolecular carbopalladation of the carbon–carbon double bond of norbornene; this is

followed by an intramolecular carbopalladation of the allene moiety and finally β -hydride elimination to provide the tricyclic compound **128** (Scheme 42).^[62]



Scheme 41



Scheme 42

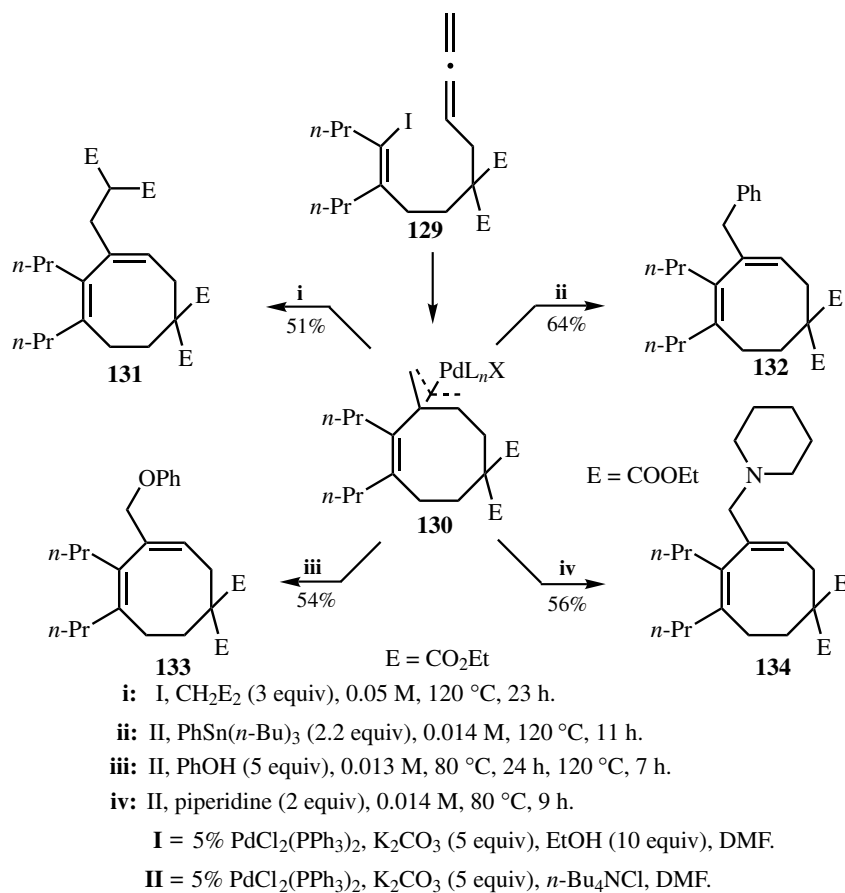
F. INTRAMOLECULAR CARBOPALLADATION OF ALLENES FOLLOWED BY NUCLEOPHILIC TRAPPING

The π -allylpalladium intermediate **130**, formed by the intramolecular carbopalladation of **129**, could be trapped with the enolate of diethyl malonate, with Bu_3SnPh , with piperidine, or with phenol to afford a variety of cycloocta-1,3-diene derivatives **131–134** (Scheme 43).^[61]

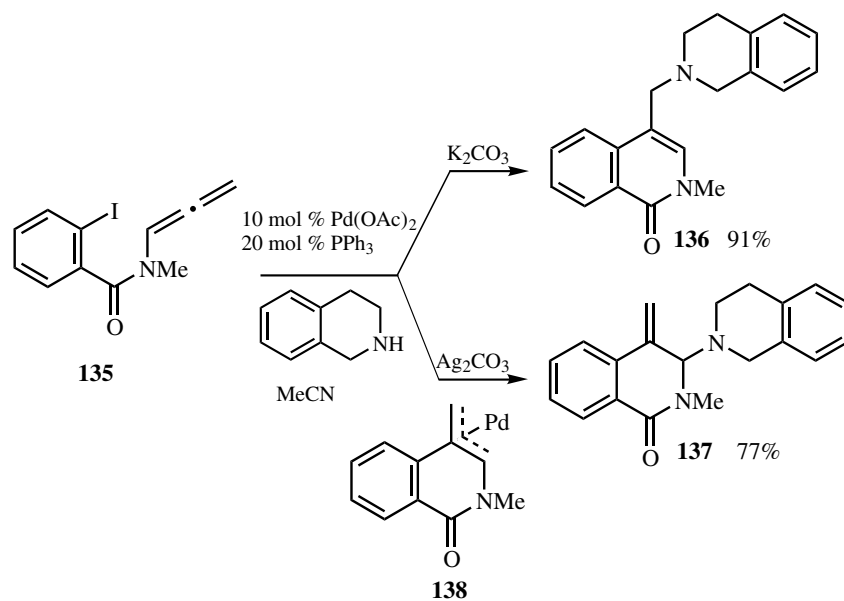
In 1995 Grigg and co-workers reported a similar cascade consisting of an intramolecular carbopalladation and intermolecular nucleophilic trapping (Scheme 44).^[63] The regioselectivity of the allylic nucleophilic substitution can be controlled completely by using different bases.

The intermediate π -allylpalladium species **138** (Scheme 44) could also be coupled with phenylboronic acid to yield mainly the benzopyridone derivative **139**; however, the regioselectivity depends largely on the base used (Scheme 45).^[64]

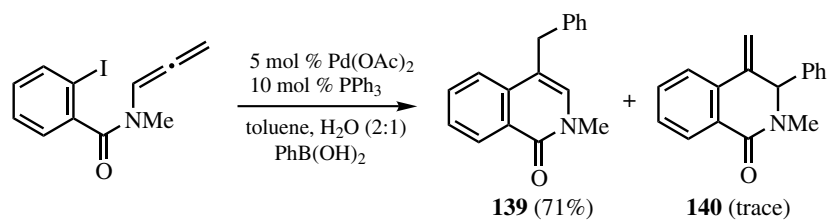
With sodium azide as the trapping reagent, **141** yields cyclic allyl azides, which can immediately undergo an intermolecular 1,3-dipolar cycloaddition with added norbornadiene and the adducts eventually cleave off cyclopentadiene in a retro-Diels–Alder reaction to provide triazoles (Scheme 46).^[65] Sodium benzenesulfinate can also be used as a nucleophile.^[65]



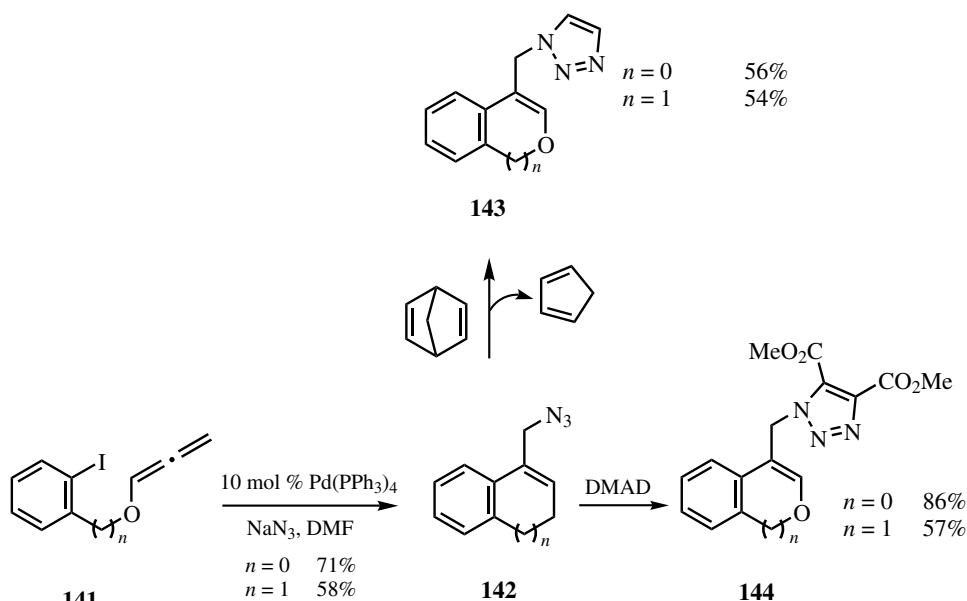
Scheme 43



Scheme 44



Scheme 45



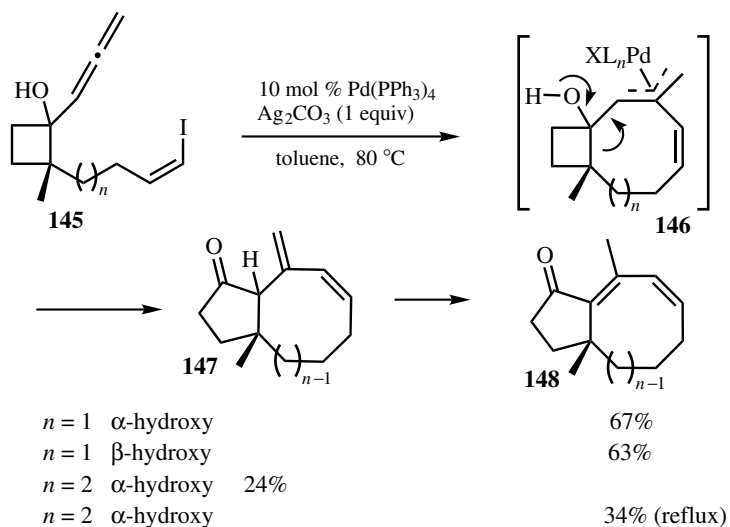
Scheme 46

G. CARBOPALLADATION OF ALLENES FOLLOWED BY SKELETAL REARRANGEMENT

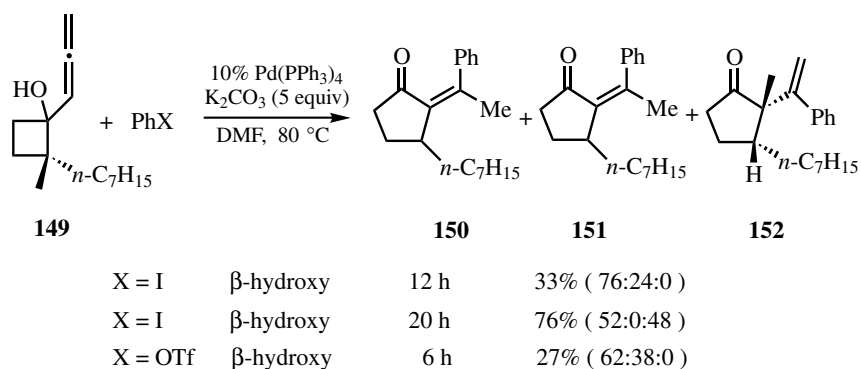
Under the catalysis of $\text{Pd(PPh}_3)_4$, 1-propadienyl-2-(Z- ω -iodo-(ω -1)-alkenyl)cyclobutanol **145** afforded the π -allylpalladium intermediate **146** after oxidative addition and intramolecular carbopalladation. Nemoto and co-workers observed that the ring strain of the four-membered ring in **146** was released by ring expansion to afford the bicyclo[6.3.0]undecane derivatives **147** and/or **148** with a cyclopentanone moiety (Scheme 47).^[66]

An analogous ring expansion was observed upon an intermolecular carbopalladation of the 1-propadienylcyclobutanol **149** with PhPdX formed from phenyl iodide or phenyl triflate (Scheme 48).^[66]

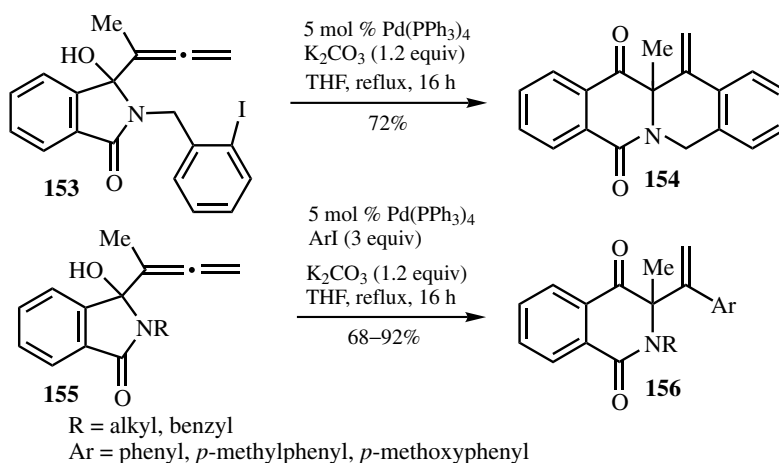
Recently, Jeong and Nagao observed a similar ring enlargement of a nitrogen-containing five-membered ring (Scheme 49).^[67]



Scheme 47



Scheme 48



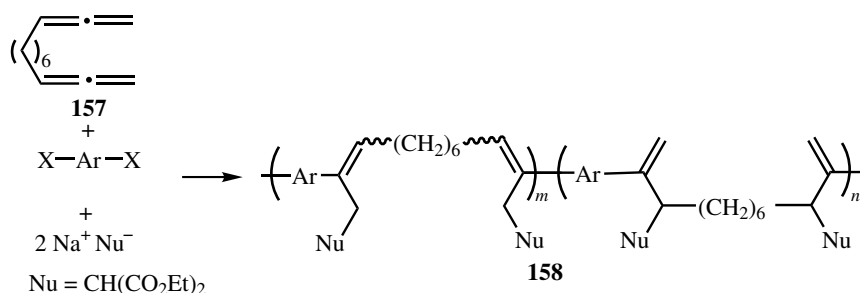
Scheme 49

H. POLYMERIZATION REACTIONS INVOLVING CARBOPALLADATIONS OF ALLENES

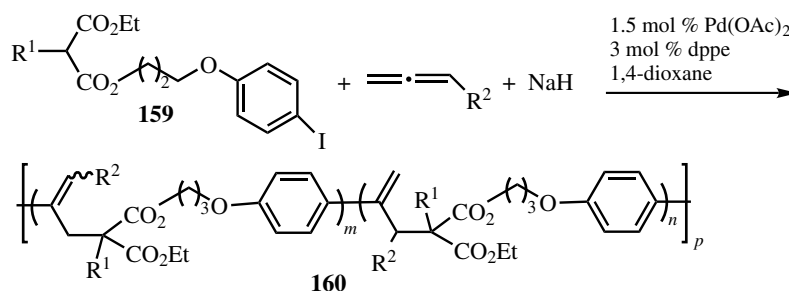
The Pd(0)-catalyzed reaction of bis(allene)s, dihaloarenes, and nucleophiles can be applied toward the synthesis of polymers (**Scheme 50**).^[68] The carbon chain between the two allene units ends up as the linker group in the polymer **158**.

Aryl halides containing an alkoxy-tethered malonate unit have also been reported to react with allenes yielding a class of polymers **160**, which, due to the two regioisomeric modes of the nucleophilic trapping reaction, contained two kinds of repeating units (**Scheme 51**).^[69]

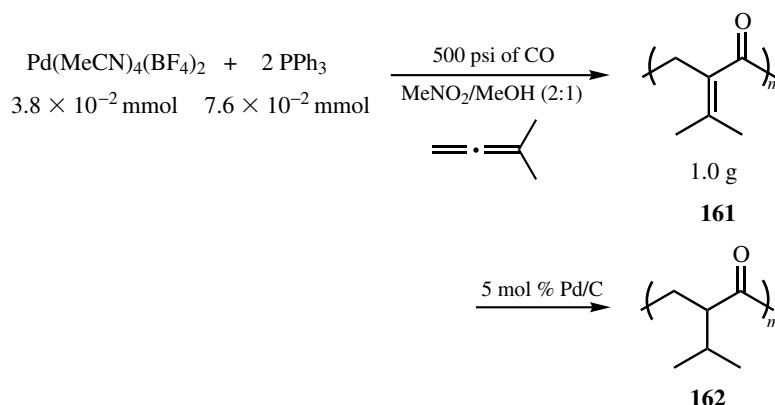
An alternating copolymerization of allene and CO initiated by an acyl- or methylpalladium complex was developed by Kacker and Sen (**Scheme 52**).^[70]



Scheme 50



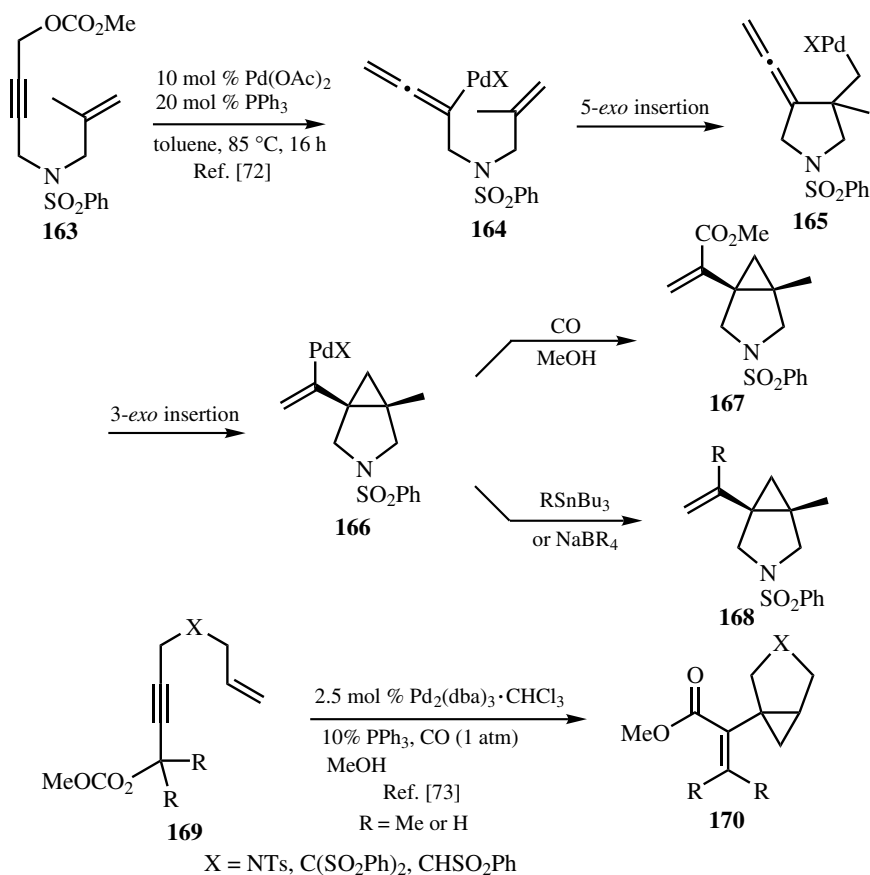
Scheme 51



Scheme 52

I. CARBOPALLADATION REACTION FORMING C_{sp^2} —Pd SPECIES

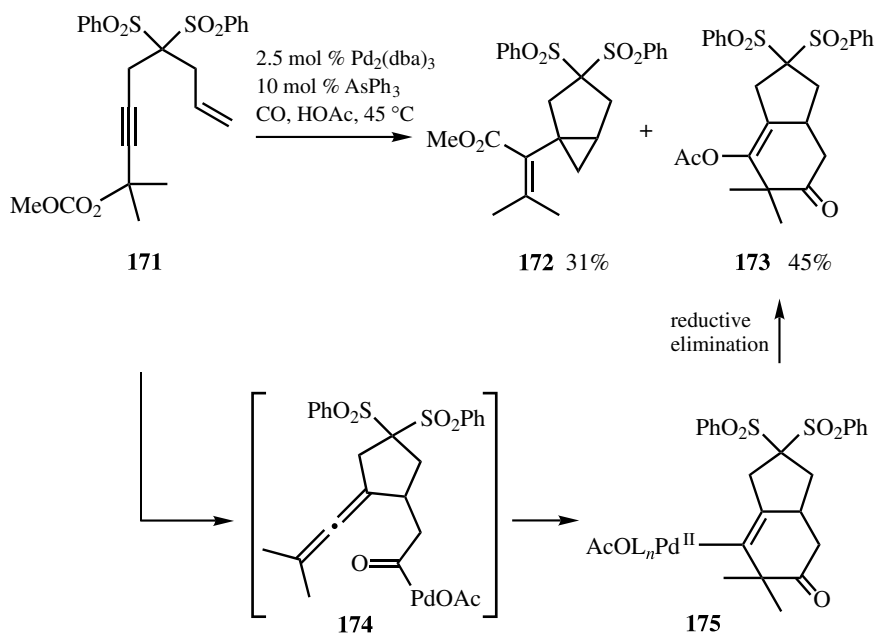
In all of the reactions discussed above, the carbopalladation of the allene occurred regioselectively in such a way that the substituent of the first formed organopalladium intermediate would be attached to the central carbon atom of the allene moiety to form a π -allylpalladium intermediate. However, Grigg et al.^[71] and later Oppolzer et al.^[72] observed that the intramolecular carbopalladation of the first formed allene **165** proceeded in a completely different manner (**Scheme 53**). Instead of the formation of a π -allylpalladium complex, a reverse regioselectivity to form a C_{sp2}—Pd intermediate was observed.



Scheme 53

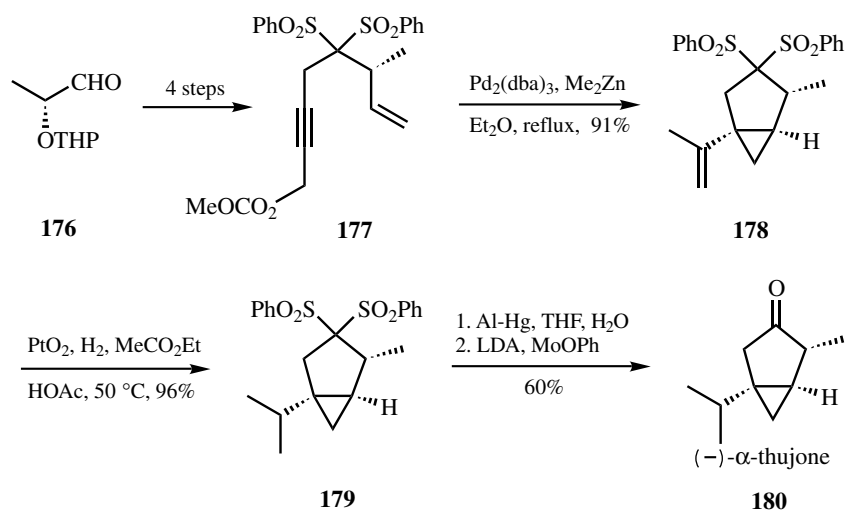
Obviously, in this case the normal regiochemical preference cannot be achieved due to the geometrical constraints exerted by the attachment of both reacting units to the five-membered ring. Instead, 3-*exo-dig* carbopalladation prevails, and the thus formed alkenylpalladium intermediate **166** is trapped by CO and MeOH to yield a bicyclic α -cyclopropylacrylate **167** and **170**. Other trapping reagents for the intermediate **166** can be applied as well (**Scheme 53**). In addition to the same type of product **172**, the reaction of the propargyl carbonate **171** with two methyl groups adjacent to the carbonate moiety gave

a bicyclo[4.3.0]nonenone derivative **173**, which must have been formed by CO insertion after the first intramolecular carbapalladation step affording **174**, followed by intramolecular acylpalladation to give **175** and reductive elimination, that is, by cyclization of the intermediate acylpalladium intermediate **175** (Scheme 54).^[72]



Scheme 54

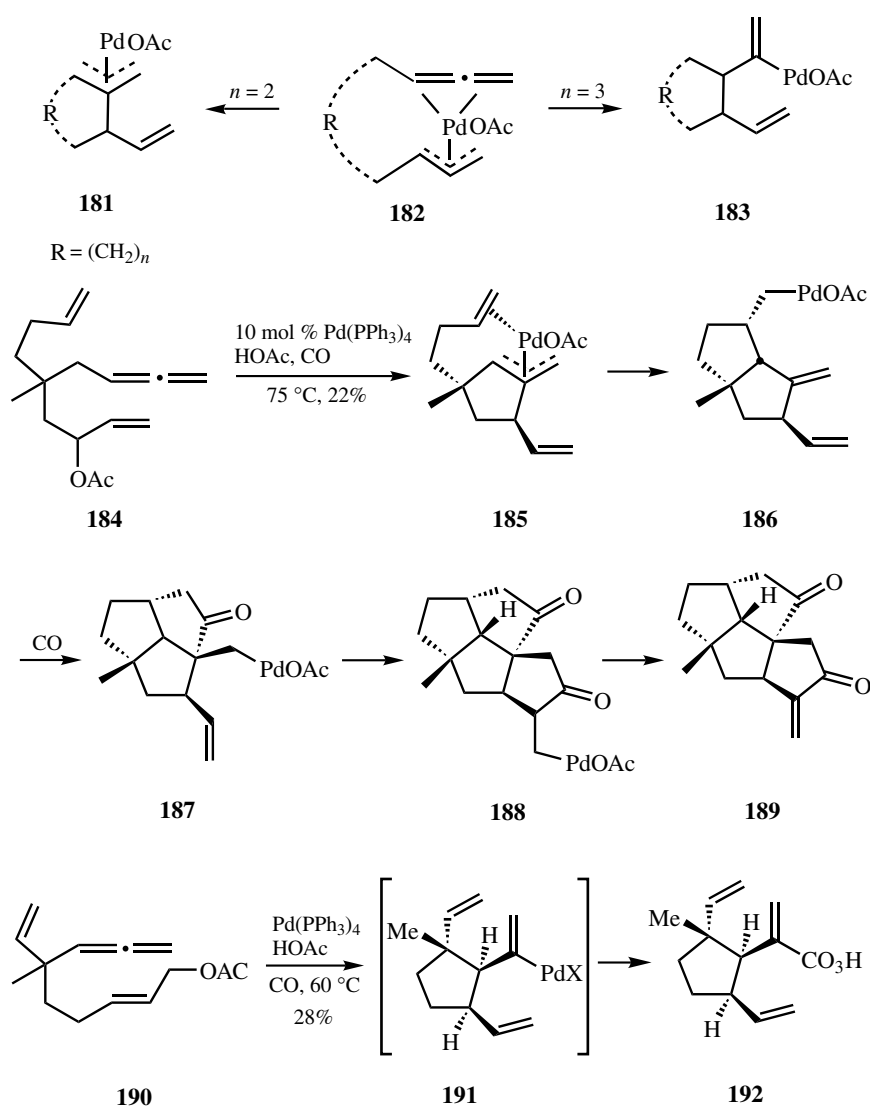
This reaction was utilized to synthesize (–)- α -thujone (Scheme 55).^[72] The two centers of chirality in the cyclopropane ring were controlled in a highly diastereoselective manner by the center of chirality originally present in the starting aldehyde **176**.



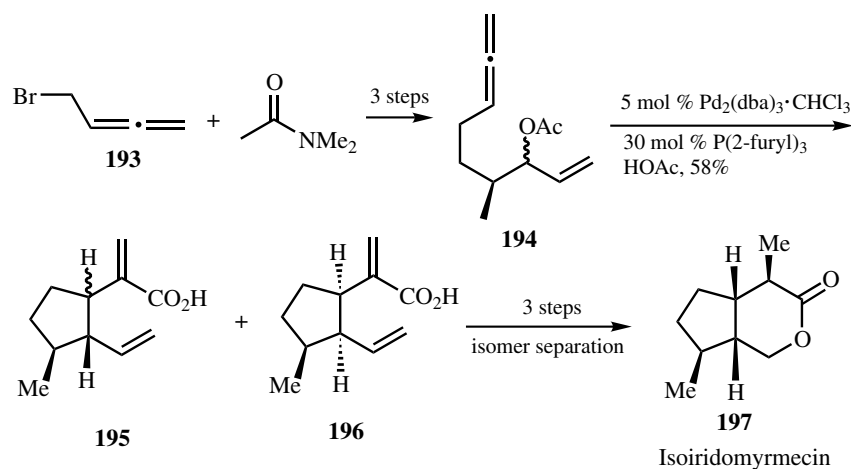
Scheme 55

In all of the stoichiometric intermolecular reactions of a π -allylpalladium complex with an allene to form a new π -allylpalladium intermediate, the type of insertion reaction was established by ^1H NMR spectroscopy as well as X-ray single crystal structure analysis.^{[1]–[15]} However, it is interesting to note that the corresponding intramolecular carbopalladations of allenes displayed two different modes to form either a $\text{C}_{\text{sp}^2}\text{—Pd}$ species or a new π -allylpalladium intermediate highly selectively depending largely on the length of the tether between the two moieties (**Scheme 56**).^{[73]–[75]}

This abnormal insertion mode was applied in a total synthesis of the natural product (\pm)-isoiridomyrmecin **197** in seven steps starting from 2,3-butadienyl bromide (**Scheme 57**).^[73]



Scheme 56



Scheme 57

J. SUMMARY

1. The intermolecular carbopalladation of allenes has been shown to form π -allylpalladium intermediates.
2. The intramolecular carbopalladations of allenes has been shown to afford either π -allylpalladium intermediates or $\text{C}_{\text{sp}^2}\text{--Pd}$ species, depending on the structure of the substrates.
3. π -Allylpalladium intermediates described in this section can undergo either a β -H elimination or a nucleophilic substitution reaction. Enantioselective nucleophilic substitution can afford the corresponding chiral compounds with high enantiomeric excesses.

In conclusion, with subtle design, carbopalladation of allenes will provide efficient access to dienes, alkenes, monocycles, and oligocycles with functional groups and will show its utility in the synthesis of specific target molecules.

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