Element−Element Additions to Unsaturated Carbon−Carbon Bonds Catalyzed by Transition Metal Complexes

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1. Introduction

Additions of homoelement−element and heteroelement−element linkages to unsaturated substrates catalyzed by the platinum group metals constitute synthetically highly versatile processes. Two identical or different functionalities, which can undergo a multitude of further synthetic transformations, are added to the unsaturated moiety in one single step. Interelement linkages add to alkynes and alkenes in a 1,2-manner, whereas they usually add to allenes and conjugated dienes via 1,2- and 1,4-addition, respectively. Under certain conditions, additions to alkynes and 1,3-dienes are accompanied by dimerization of the unsaturated compound, and additions to diynes, enynes, and bisdienes may lead to carbocyclization. Reaction conditions are often possible to control, leading to high chemoselectivity. Recently a number of enantioselective additions have been achieved, thus expanding the synthetic utility of this type of catalytic processes.

Activation of the interelement linkage is usually achieved by group 10 metal compounds, but a few reactions are catalyzed by other transition metal complexes, in particular complexes containing Rh or Ru. Phosphites and isocyanides were originally employed as ligands, although later phosphines and other types of phosphorus ligands as well as ligand-free complexes have proven to constitute successful catalyst components.

The term "interelement linkage" was introduced for chemical bonds such as mutual linkages within the heavy main group elements and linkages between the main group elements and the transition metals.[1] For the individual reactions and reagents, there seems to be no agreement regarding nomenclature, however. For example, in American

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Irina Beletskaya received her Diploma degree in 1955, her Ph.D. degree in 1958, and her Doctor of Chemistry degree in 1963 from Moscow State University. The subject for the latter was Electrophilic Substitution at Saturated Carbon. She became a Full Professor at Moscow State University in 1970, and in 1974 she became a Corresponding Member of the Academy of Sciences (USSR), of which she became a full member (Academician) in 1992. She is currently Head of the Laboratory of Organoelement Compounds, Department of Chemistry, Moscow State University. Irina Beletskaya is Chief Editor of the *Russian Journal of Organic Chemistry*. She was President of the Organic Chemistry Division of IUPAC from 1989 to 1991. She was a recipient of the Lomonosov Prize (1979), the Mendeleev Prize (1982), The Nesmeyanov Prize, (1991), the Demidov Prize (2003), and the State Prize (2004). She is the author of more 600 articles and 4 monographs. Her current scientific interests are focused on (i) transition metal catalysis in organic synthesis, (ii) organic derivatives of lanthanides, and (iii) carbanions and nucleophilic aromatic substitution.

Christina Moberg received her undergraduate education from the Stockholm University and her Ph.D. degree from the Royal Institute of Technology, KTH, in Stockholm. She became Full Professor at KTH in 1997. She has been a member of the Royal Swedish Academy of Sciences since 1998. She is the author of approximately 135 scientific papers. Her current scientific interests are focused on asymmetric metal catalysis and include the development of new chiral catalysts and their application in asymmetric synthesis. Current interests also concern the use of microreactor technology and methods for high throughput screening for the development of new metal catalysts.

Chemical Society (ACS) journals, silastannation, silylstannation, silastannylation, and silylstannylation are all used for the addition of Si−Sn bonds to unsaturated compounds. We decided to generally employ nomenclature in accordance with the first of these, but exceptions are made when widely accepted nomenclature for particular compounds and reactions exists.

Several reviews covering the field have appeared lately. Two of them, both from 1995,[2,3] include the addition of disilanes to unsaturated compounds. Our own review from 1999 covers additions of interelement compounds to alkynes.[4] In a review on palladium-catalyzed reactions of allenes, which appeared one year later, stannylations, silylations, and germanylations of allenes are included.[5] The same year, an excellent review covering all types of additions of homo- and heteroelement compounds with silicon appeared.[6] A feature article from 1999 provides a brief summary of the field.[7] In addition to these broader summaries, a number of more specialized accounts have appeared dealing with disilylations,[8] silaborations,[9,10] and diborations[11,12,13] of carbon−carbon multiple bonds, processes including interelement linkages with sulfur and selenium,[14] and silylations and germylations of carboranes.[15]

In our opinion, there is a need, however, to consider recent results. The field is very important and develops fast, and many interesting results have appeared lately. Until now, no review covering the entire field has appeared. There is a need to compare the results from additions to different types of substrates as well as within a group of substrates, since, even for simple reactions of E−E compounds with alkynes, unexpected results may be achieved depending on the structure of the compounds and, in particular, the nature of the transition metal catalyst. Other important issues concern the mechanism of the additions and their chemo-, regio-, and stereoselectivities.

This review summarizes homo- and heterointerelement additions to alkynes, 1,3-dienes, 1,2-dienes, and alkenes, as well as additions to methylenecyclopropanes and vinylcyclopropanes, with the latter being covered together with alkenes. It does not deal with additions to carbon−heteroatom unsaturated compounds such as carbonyl compounds or imines, and it does not deal with 1,4-additions to unsaturated carbonyl compounds. The literature up to 2005 is covered, although some earlier literature covered by previous reviews has been omitted.

2. Additions to Alkynes

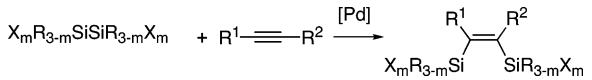
The literature concerning interelement additions to alkynes was covered in detail up to 1999 in our previous review.[4] Many of the products obtained serve as important building blocks in organic synthesis. Several vinyl compounds can be used for formation of carbon−carbon bonds, thus giving access to tri- and tetrasubstituted olefins. Vinylsilanes undergo substitutions with a wide range of electrophiles,[16] vinylstannanes are important building blocks in natural product chemistry,[17] and vinylboron compounds are versatile carbon−carbon bond forming tools undergoing Suzuki−Miyaura coupling reactions.[18] Addition of heteroelement compounds opens up wide synthetic possibilities, in that two consecutive functionalizations of the product from interelement addition can be achieved.

2.1. Si–Si

Transition metal-catalyzed disilylations of alkynes, which constituted the first examples of element−element additions to unsaturated compounds, were pioneered by Japanese scientists in the beginning of the 1970s. Due to great efforts by the groups of Kumada[19] and Sakurai,[20] many new reactions of organosilicon compounds were discovered and many new organosilicon compounds, including silicon-containing polymers, were synthesized utilizing these reactions. For a long time, this research field was a Japanese domain, and contributions from other groups such as that of Seyferth[21] appeared only in the 1980s.

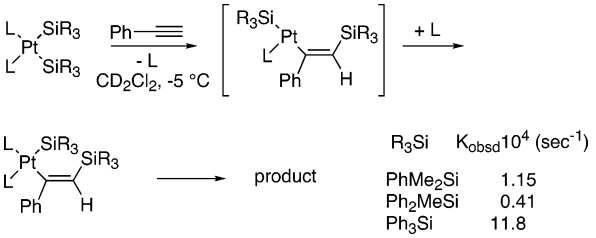
It was shown that the addition of interelement compounds to terminal as well as internal alkynes catalyzed by palladium complexes takes place with high syn selectivity (Scheme 1).

Scheme 1



The reaction proceeds smoothly with differently substituted disilanes, X = F, Cl, or OMe (Scheme 1), sometimes even at room temperature, with palladium phosphine complexes.[22,23] Surprisingly, disilanes with phenyl substituents have an accelerating effect on these reactions. That this influence is rather complicated can be seen from a kinetic study of the stoichiometric reaction between *cis*-$Pt(PPh_3)_2(SiR_3)_2$ and phenylacetylene. To shed light on the mechanism of the catalytic process, the insertion of acetylenes into the silicon−platinum bonds was studied by Ozawa.[24] In the presence of excess phenylacetylene, pseudo-first-order rate constants (k_{obsd}) were measured for insertion into the silicon−platinum bond of $(PMe_2Ph)_2Pt(SiR_3)_2$ compounds (Scheme 2).[25] The rate constants for insertion of phenylacetylene into

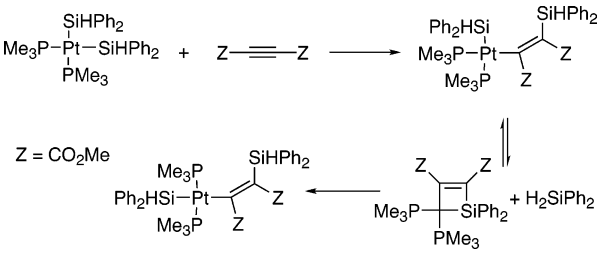
Scheme 2



Pt−Si bonds in Pt(II) disilyl complexes revealed a reactivity order inconsistent with the steric and electronic nature of the silyl substituents.[26] A detailed kinetic investigation showed that the first step is dissociation of one of the phosphine (L) ligands to form an unsaturated complex, which undergoes rate determining migratory insertion via prior coordination of the acetylene to the vacant site.

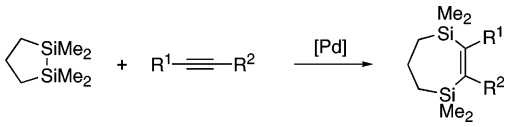
Insertion of dimethyl acetylenedicarboxylate in a silylplatinum(II) phosphine complex afforded products which were isolated and characterized. The initially formed cis complex was shown to be in equilibrium with a 4-sila-3-platinacyclobutane, which ring opened to yield the trans complex (Scheme 3).[27]

Scheme 3



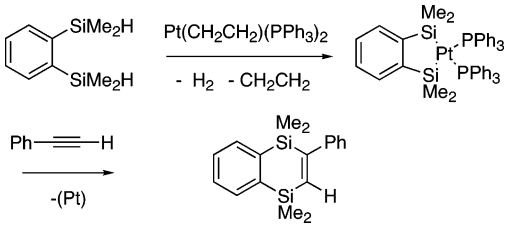
Other disilanes and other palladium complexes with less donating phosphine ligands were found not to be efficient as catalysts. However, with cyclic disilanes having strained Si−Si bonds, additions could be achieved with silanes lacking activating substituents using conventional palladium catalysts such as $PdCl_2(PPh_3)_2$ under mild conditions (80 °C, Scheme 4).[20,23,28]

Scheme 4



The majority of the reactions were catalyzed by palladium complexes, but also other type of catalysts, based on platinum and nickel, were able to catalyze the addition of disilanes to alkynes. The most efficient systems were obtained using $Pt(CH_2{=}CH_2)(PPh_3)_2$, $NiCl_2(PEt_3)_2$, and $Ni(PEt_3)_4$ as precatalysts. They were, in particular, used for dehydrogenative addition with compounds having two SiR_2H groups (Scheme 5). These reactions include in some cases the formation of

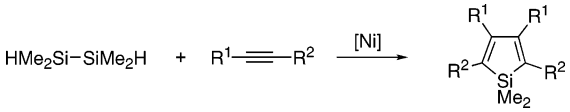
Scheme 5



strained silicon−silicon bonds possessing particular properties.[29]

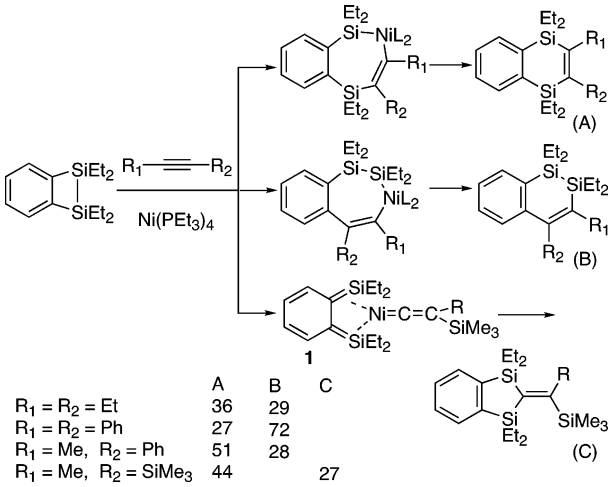
The dehydrogenative reaction of 1,1,2,2-tetramethyldisilane with alkynes catalyzed by Ni complexes was followed by dimerization and formation of silacyclopentadienes (Scheme 6).[19b,30]

Scheme 6



The insertion of disubstituted acetylenes into 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene was shown to lead to two isomers, A and B, via insertion of the alkyne into Ni−Si and Ni−C bonds, respectively (Scheme 7).[31] The

Scheme 7

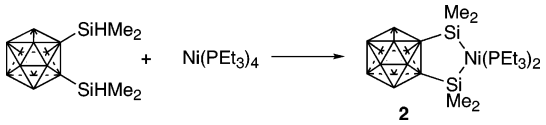


analogous reactions catalyzed by Pd and Pt were previously known to afford only the first type of adducts.[29,32] Monosubstituted alkynes did not afford the same products but resulted in oligomerization of the unsaturated compounds.

With trimethylsilyl-substituted alkynes, a vinylidene nickel complex (**1**) was, according to the authors, formed as an intermediate after migration of the trimethylsilyl group, resulting in formation of a product (C) having a carbon atom carrying two silyl substituents, in addition to A.[31]

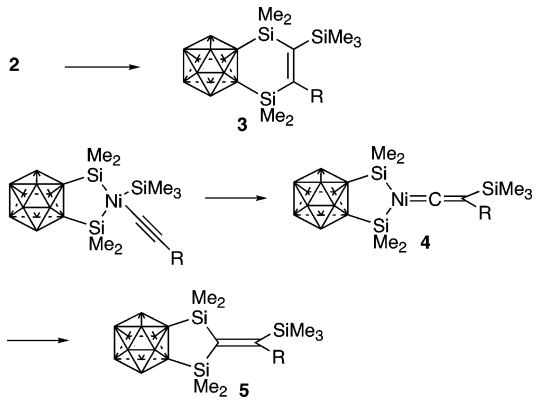
A disilyl nickel complex (**2**) was obtained by reaction of $Ni(PEt_3)_4$ with 1,2-bis(dimethylsilyl)carborane (Scheme 8).[33]

Scheme 8



It reacted with alkynes in two different ways, via ordinary insertion of the alkyne into the silicon−nickel bond, leading, after reductive elimination, to **3**, and via Ni-insertion into the carbon−(sp)−silicon bond (with formation of Ni(IV)!) followed by shift of a trimethylsilyl group to form a vinylidene nickel intermediate **4** and, finally, the second type of product (**5**, Scheme 9).

Scheme 9



The authors who studied the reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene preferred to write the product from oxidative addition to Ni(0), implying equilibrium between two intermediates (Scheme 10),[32a]

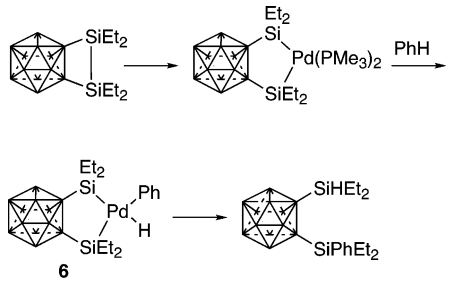
Scheme 10

whereas the authors who studied reaction of the carborane[33b] wrote a catalytic cycle involving Ni(0), Ni(II), and Ni(IV), although this was not discussed by the authors.

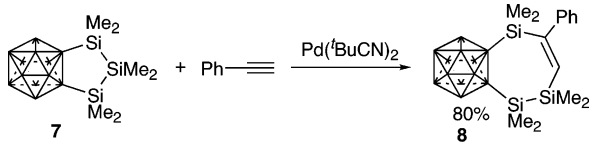
A similar reaction, catalyzed by palladium, was studied for 1,2-bis(diethylsilyl)carborane.[15] The palladium complex formed by insertion of palladium into the Si−Si bond had sufficient activity to activate an sp^2-carbon−hydrogen bond in benzene to yield **6**, which was transformed into a product with Si−H and Si−Ph bonds (Scheme 11).

Carborane derivative **7**, with a five-membered ring with three silyl groups, reacted with phenylacetylene in the presence of a palladium catalyst. The sole product was 6,7-*o*-carboranylene-1,1,4,4,5,5-hexamethyl-2-phenyl-1,4,5-trisilacyclohept-2-ene (**8**), with the acetylene inserted into one of the Si−Si bonds (Scheme 12).[34] The structure of the product was determined by X-ray crystallography.

Scheme 11

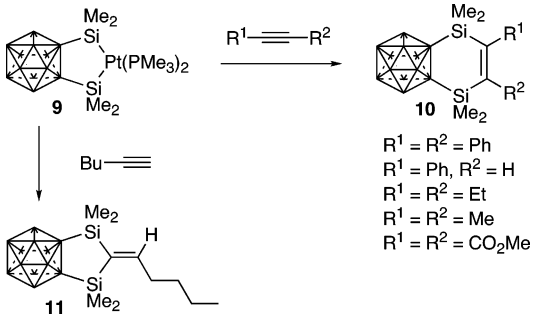


Scheme 12



The formation of these two types of compounds was observed also in a stoichiometric reaction of alkynes with 1,2-bis(dimethylsilyl)carborane platinum complex **9** (Scheme 13).[35] Heating (120 °C) with acetylenes gave six-membered

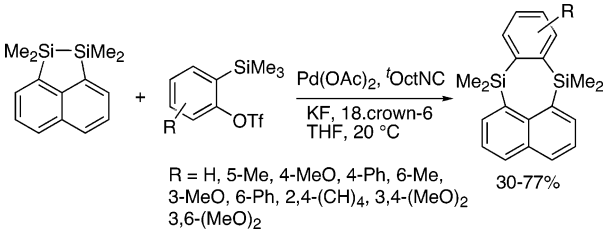
Scheme 13



2,3-disubstituted 5,6-carboranylene-1,1,4,4-tetramethyl-1,4-disilacyclohex-2-enes. Thus, from 2-hexyne **10** (R^1 = Me, R^2 = Pr) was obtained. From 1-hexyne, however, five-membered ring compound **11** was obtained under the same conditions.

Yoshida presented the first example of palladium-catalyzed disilylation of arynes, generated in situ from 2-(trimethylsilyl)aryl triflates (Scheme 14).[36] The adducts were suggested

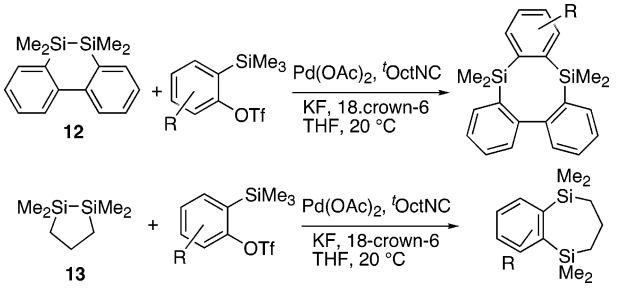
Scheme 14



to be formed via normal oxidative addition of the disilane to Pd(0), insertion of the triple bond, and reductive elimination. It is interesting to note that no addition products were formed in the absence of Pd.

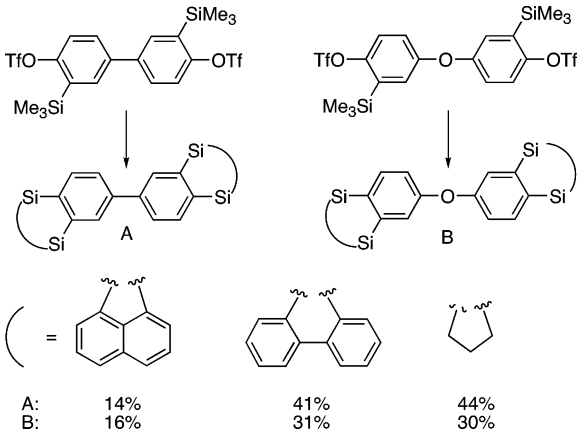
The reaction was applied to a variety of arynes using Ito's catalyst $Pd(OAc)_2$/^{t}OctNC to give products in good to high yields. Two other cyclic disilanes, **12** and **13**, were also employed in the process, thus affording eight- and seven-membered ring compounds (Scheme 15).[37]

Scheme 15



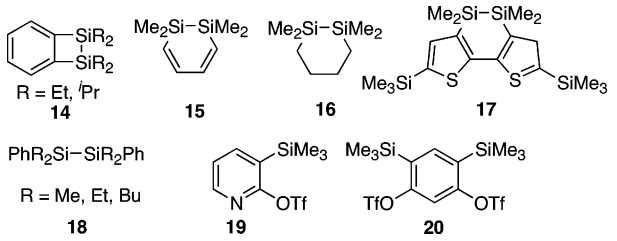
Tetrasilylated products were obtained from bisarynes (Scheme 16).

Scheme 16



The four-membered disilanes **14** decomposed under the reaction conditions, and no reaction was observed with cyclic disilanes **15**−**17** and acyclic disilanes **18** (Chart 1). No

Chart 1

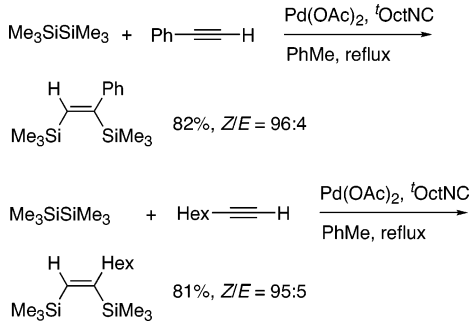


products were obtained from arynes generated from **19** and **20**.

An ab initio study of the oxidative addition of SiH_4 and $H_3Si-SiH_3$ to $Pt(PPh_3)_2$ showed that addition of the Si−Si bond is more exothermic than that of the Si−H bond (46.4 and 25.8 kcal/mol, respectively) but that the activation barrier was higher for the first type of process (17.4 and 0.7 kcal/mol for Si−Si and Si−H, respectively).[38] Therefore, the two types of reactions can compete with compounds containing both types of bonds, with the actual result being dependent on structure and reaction conditions. In another study it was shown that the oxidative addition of $H_3Si-SiH_3$ to Pd(0) is less exothermic than that to Pt(0), although the former process has a slightly lower activation energy.[39]

Important contributions to palladium-catalyzed reactions were made by Ito, who introduced an efficient catalytic system comprising $Pd(OAc)_2$−1,1,3,3-tetramethylbutyl isocyanide (Scheme 17),[40] and by Tanaka,[41] who discovered the efficiency of $Pd(dba)_2-P(OCH_2)_3CEt$ (4-ethyl-2,6,7-

Scheme 17



trioxa-1-phosphabicyclo[2.2.2]octane, etpo). These two types of catalysts allowed additions of any type of disilane, including nonactivated disilanes such as $Me_3Si-SiMe_3$, to be performed.

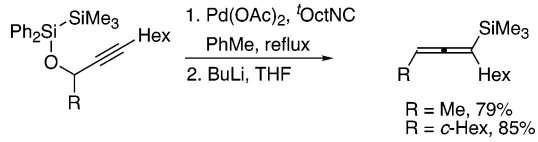
The first catalytic system was widely employed by Ito and co-workers for intramolecular variations, $(RNC)_nPd(0)$, with allylic and propargylic alcohols to provide access to allyl-, alkenyl-, and propargylsilanes, which are valuable reagents in organic synthesis.[8] They performed stoichiometric reactions of isolated $(^tBuNC)_2Pd$ with cyclic disilanes to give disilylpalladium complexes.[40b]

The disilanes obtained have been employed in a variety of synthetic applications. These include intramolecular versions of the disilylation with subsequent transformations of the Si-containing cyclic compound into useful organic derivatives.

The second catalytic system was widely used by the group of Tanaka for the synthesis of Si-containing polymers and oligomers, as a result of insertion of the alkyne into Si−Si bonds of polysilanes.[41b]

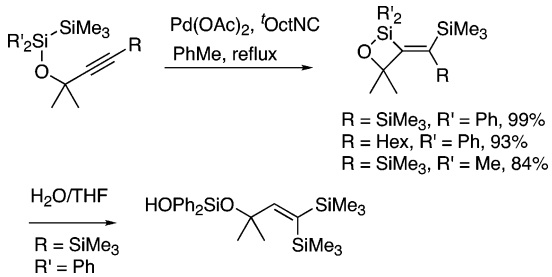
An illustrative application of palladium-catalyzed intramolecular disilylation of triple bonds is the stereospecific reaction of a bissilyl derivative of chiral secondary alcohols, leading, after Peterson elimination, to chiral allenes (Scheme 18).[8]

Scheme 18



The reaction with tertiary propargylic alcohols under the same conditions afforded rather stable products which were hydrolyzed (Scheme 19).[42]

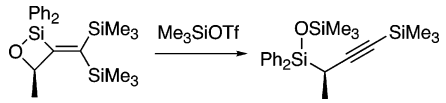
Scheme 19



Another reaction with 1,2-migration of the silyl group, proceeding with retention of configuration, was observed by

treatment of the four-membered cyclic silyl ether with trimethylsilyl triflate (Scheme 20).

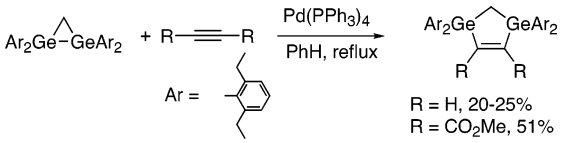
Scheme 20



2.2. Ge–Ge

The first additions of Ge−Ge bonds to triple bonds were reported by Ando, who used digermanes which inserted alkynes into Pd−Ge bonds to give cyclic products in rather modest yields (Scheme 21).[43]

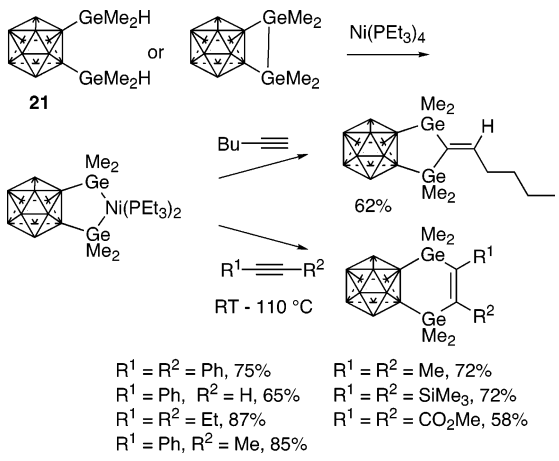
Scheme 21



In the same way as for disilanes, only activated digermanes react with alkynes in the presence of $Pd(PPh_3)_4$. Thus, reaction of bis(chlorodimethylgermane) with phenylacetylene gave the product in 88% yield.[44] For nonactivated compounds, such as $Me_3GeGeMe_2GeMe_3$, Tanaka's ligand was used, but even for phenylacetylene, a higher temperature, 120 °C, was required for reaction to proceed.[45]

1,2-Digermylcarborane **21** was shown not to behave in the same way as its disilyl analogue[33] in additions to alkynes. A digermylnickel(II) complex was generated by dehydrogenation of *o*-bis(dimethylgermyl)carborane[46] or by oxidative addition of 3,4-carboranylene-1,1,2,2-tetramethyl-1,2-digermacyclobutane[47] to tetrakis(triethylphosphine)nickel(0) (Scheme 22). Digermacyclohexenes were obtained in sto-

Scheme 22

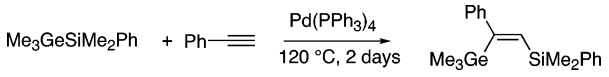


ichiometric reactions of the digermylnickel(II) complex with alkynes, except for 1-hexyne, which provided a vinylidenedigermacyclopentane as the major product. X-ray crystal structures for the Ni(II) complex and several insertion products were determined. Yields were higher than those observed in the analogous disilylations.

2.3. Si–Ge

Additions of Si−Ge bonds to alkynes are essentially unknown. However, the product from reaction of $Me_3GeSiMe_2Ph$ with phenylacetylene was obtained in moderate yield (48%) under rather harsh conditions (120 °C), although with high regioselectivity (Scheme 23).[48]

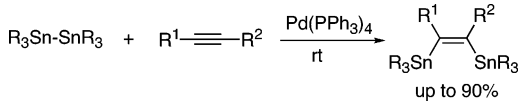
Scheme 23



2.4. Sn–Sn

Distannation of terminal alkynes catalyzed by $Pd(PPh_3)_4$ was achieved for the first time in modest to high yields by Mitchell.[49] Alkynes having functional groups ($R^2 = CO_2R$, $CONMe_2$, OR; Scheme 24) also underwent reaction.[50] As

Scheme 24

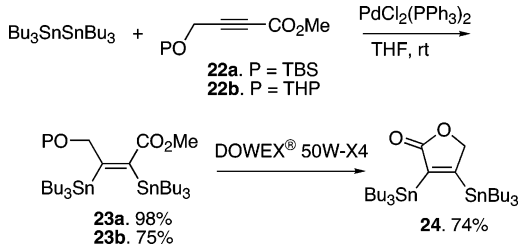


for other element−element additions, the reactions are syn additions and proceed under milder conditions than those necessary for disilylations.

However, the conversion in the reaction with more bulky $Bu_3Sn-SnBu_3$ using $Pd(PPh_3)_4$ was not complete. Recently, Lautens showed that the reaction could be performed under mild conditions using Ito's catalyst.[51] The reaction tolerated a variety of functional groups, such as carbamates, amines, sulfonamides, ethers, esters, and alcohols. Reactions with internal alkynes, with the exception of dimethyl acetylene dicarboxylate, were unsuccessful, however.

The bisstannylation of butynoates **22a** and **22b** was used for the preparation of **23a** and **23b**, respectively (Scheme 25). The latter compound was transformed into 3,4-bis-(tributylstannyl)-2(5H)-furanone (**24**).[52]

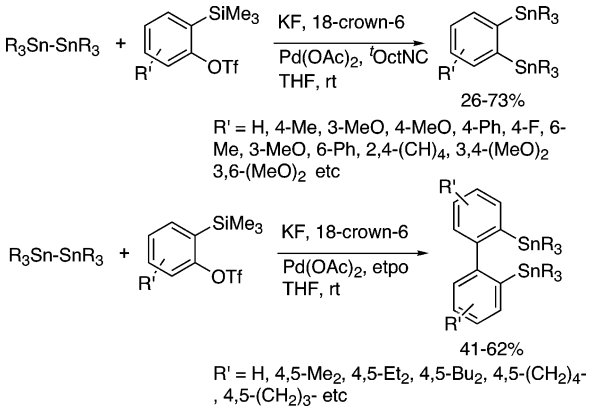
Scheme 25



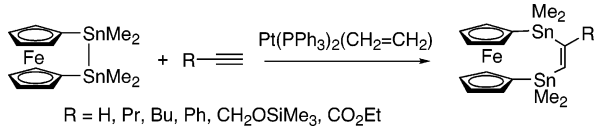
Quite recently, Yoshida reported that distannanes $R_3Sn-SnR_3$ (R = Me, Bu), in analogy to disilanes,[36] add to the strained carbon−carbon bonds of in situ generated arynes in the presence of palladium acetate and an isocyanide to yield 1,2-bis(trialkylstannyl)arenes (Scheme 26).[53] When the isocyanide was replaced by etpo, the addition was accomapanied by dimerization, affording biaryl derivatives as the major products.[54] The authors obtained the complex $Pd(^tOctNC)_2(SnBu_3)_2$ and performed stoichiometric reactions with aryne which gave the same results as the catalytic process (74% yield). This allowed them to propose a mechanism proceeding via oxidative addition of the distannane to Pd(0) followed by activation of the triple bond and its insertion into the Pd−Sn bond.[53] An alternative pathway, via activation of the triple bond by Pd(0), was suggested to afford the distannylbiaryls.[54]

The insertion of terminal alkynes into the tin−tin bond of 1,1,2,2-tetramethyl-1,2-distanna[2]ferrocenophane catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ was reported (Scheme 27).[55]

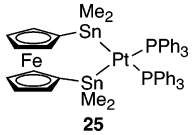
Scheme 26



Scheme 27



The same products as those formed in the catalytic reaction were formed in the stoichiometric reaction of platinum complex **25** and an acetylene. $Pt(PPh_3)_4$ as well as $Pd(PPh_3)_4$ and $Pd(dba)_2$ were not efficient catalysts for the reaction.

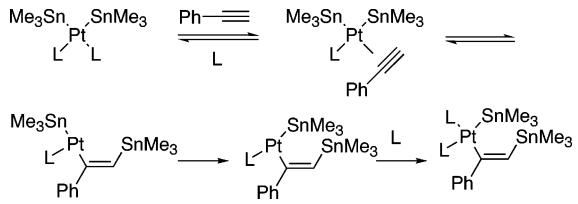


25

Structures of complexes obtained by oxidative additions of distannanes to Pt(0) and the following insertion of alkynes have been investigated. The Pt(II) complex obtained by oxidative addition of hexamethyldistannane to $Pt[P(C_6H_4Me)_3]_4$ was isolated and characterized and shown to be distorted from planarity and to exhibit fluxional behavior.[56]

A detailed experimental study of the insertion of phenylacetylene into Pt−Sn bonds was recently reported by Ozawa.[57] Oxidative addition of $Me_3Sn-SnMe_3$ to Pt(0) in the presence of PMe_2Ph afforded a 72:28 mixture of the cis- and trans-isomers, which rapidly interconverted in the presence of the ligand. By coordination of PMe_2Ph, the trans-isomer was converted to a five-coordinate species, $(PMe_2Ph)_3Pt(SnMe_3)_2$, which was isolated and fully characterized and shown to have trigonal bipyramidal geometry with the phosphine ligands in equatorial positions. Displacement of a phosphine ligand in the cis complex by the alkyne followed by migratory insertion into the Pt−Sn bond adjacent to the alkyne gave, for electronic reasons, the regioisomer shown in Scheme 28. Due to the strong trans influence of alkenyl

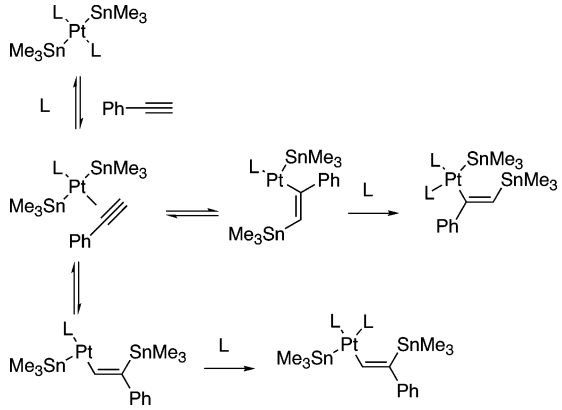
Scheme 28



and stannyl ligands, isomerization of the initially formed complex occurred before final coordination of phosphine.

Migratory insertion of the alkyne in the trans complex can take place in two ways due to two cis-positioned stannyl groups (Scheme 29). The complex having the bulky phenyl

Scheme 29



substituent at the remote position was considered to be favored, leading to the formation of a product different from that obtained from *cis*-$Pt(SnMe_3)_2(PMe_2Ph)_2$.

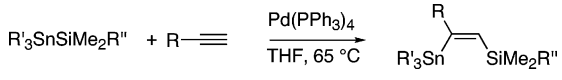
Distannation of triple bonds can also be performed starting from trialkyltin hydride as a result of metal-catalyzed decomposition of the hydride to give distannane and hydrogen.[58]

Applications of 1,2-bis(trimethylstannyl)-1-alkenes in reactions with electrophiles were studied by Mitchell and coworkers.[59]

2.5. Si–Sn

Among additions of interelement compounds to alkynes, those involving silicon−tin bonds have attracted most attention due to the possibility to prepare, in one step, compounds containing two elements with different reactivities. The first examples of this type of processes were reported by Chenard[60] and Mitchell.[61] They showed that the additions are catalyzed by $Pd(PPh_3)_4$ and proceed stereoselectively to afford syn products. Moreover, additions to terminal alkynes were shown to exhibit high regioselectivity, with tin attached to the more substituted carbon atom (Scheme 30).[60a,61a] Results from reactions with internal

Scheme 30



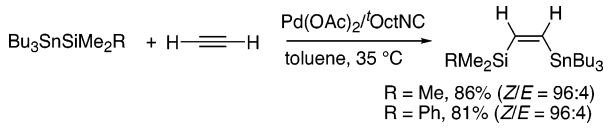
alkynes were less clear, regarding regioselectivity as well as the influence of substituents on the yield.[60b,61b]

No successful reaction was described for internal alkynes with alkyl substituents. Even with Ito's catalyst, which allowed the addition of different silicon−tin compounds $R_3Sn-SiMe_2R'$ (R = Me, Bu; R′ = Me, ^{t}Bu) to terminal alkynes at room temperature, ordinary internal alkynes failed to react.[62]

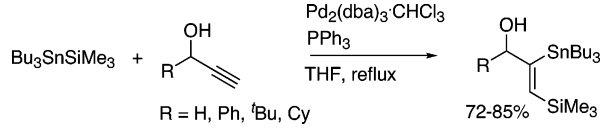
With acetylene itself, the reaction proceeded in a very stereoselective manner under mild conditions (1 atm) (Scheme 31).[63]

Palladium-catalyzed silastannation was applied to a variety of terminal propargylic alcohols and their derivatives, leading to regio- and stereoselective formation of high yields of product bearing tin at the internal vinylic position (Scheme 32).[64]

Scheme 31

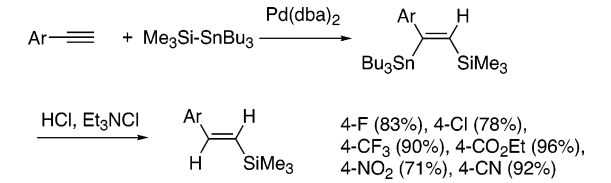


Scheme 32



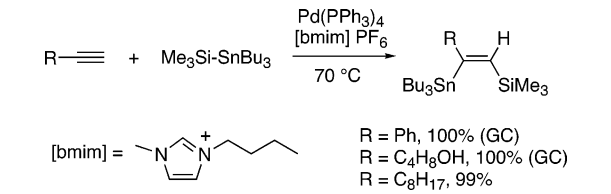
It was shown that addition of $Bu_3Sn-SiMe_3$ to arylacetylenes bearing electron-withdrawing substituents can be efficiently catalyzed by Pd complexes with phosphite ligands such as $(MeO)_3P$, $(^iPrO)_3P$, and $(PhO)_3P$.[65] Protodestannylation of the initially obtained 1-silyl-2-stannylalkenes afforded arylated vinylsilanes (Scheme 33).

Scheme 33



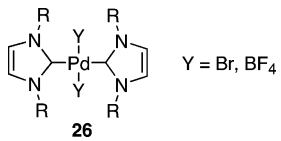
The reaction of $Bu_3Sn-SiMe_3$ with terminal alkynes in ionic liquids was studied.[66] Yields somewhat higher than those previously reported from reactions in THF[60b] were obtained, and the catalyst could be recycled up to 10 times without loss of activity. Thus, quantitative or close to quantitative yields were obtained with phenylacetylene, 1-decyne, and 5-hexyn-1-ol when the catalyst was recycled at least a few times (Scheme 34). *Z*-Alkenes were obtained

Scheme 34



in excellent yields with high regio- and stereoselectivity. Reaction times were usually longer than those required in THF. The activation of the catalyst involved mild heating in the first cycle, indicating that Pd(0) is different from PdL_4. A catalyst loading of 1 mol % proved to be sufficient, although the use of 5 mol % resulted in faster reactions.

Although the nature of the active catalyst is unknown, it was suggested that palladium−imidazolylidene carbene complexes (**26**) or possibly palladium metal nanoclusters may be responsible for the activation effects.



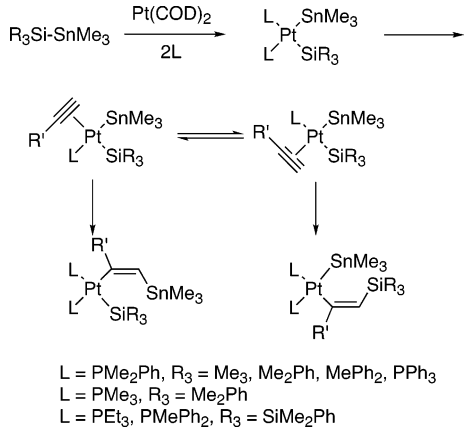
26

Silastannylated products derived from acetylene were used for a variety of transformations including reactions with aldehydes and cross-couplings, leading to functionalized vinylsilanes.[63]

Competitive insertion of phenylacetylene into the platinum−silicon and the platinum−tin bonds was observed under kinetic conditions in $(PMe_2Ph)_2Pt(SiR_3)(SnMe_3)$, whereas under thermodynamic conditions only products obtained by insertion into the Pt−Si bond were formed.[67]

A detailed mechanistic study of alkyne insertion into cis-silyl(stannyl)platinum complexes was performed by Ozawa and co-workers.[68] $(PhMe_2P)_2Pt(SiPh_3)(SnMe_3)$ was found to exhibit fluxional behavior involving a twist rotation via a pseudotetrahedral transition state. Competitive insertion of the alkyne into the Pt−Si and Pt−Sn bonds was observed, with the ratio of the two types of products being dependent on the substituents on Si and the ligand (Scheme 35). The

Scheme 35



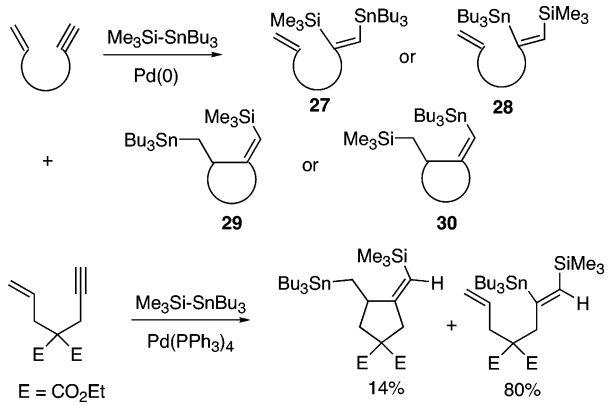
structure of the product obtained from insertion of dimethyl acetylene dicarboxylate into the carbon−silicon bond ($SiR_3 = SiMe_2Ph$) was determined by X-ray crystallography.

In a theoretical study concerning the regioselectivity of palladium-catalyzed silastannations, Ito, Nakatsuji, and co-workers showed that, for all types of alkynes, insertion into the Pd−Sn bond should be favored for kinetic reasons, with attack of Sn at the terminal position.[69] The fact that the theoretically suggested regiochemistry was observed experimentally only for alkoxyacetylenes[62b] was explained by the larger steric bulk of triphenylphosphine compared to *tert*-octyl isocyanide and the possibility of thermodynamic control in the case of unstable products.

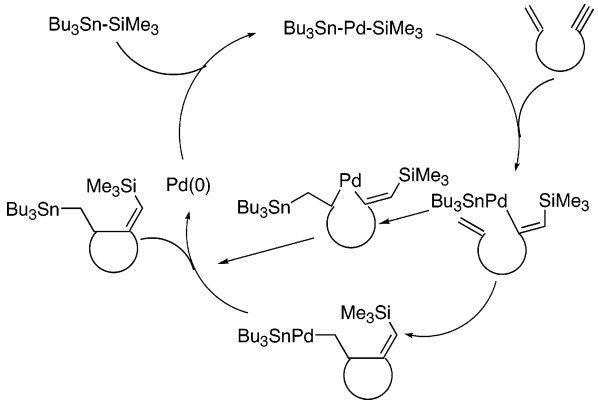
Palladium-catalyzed bismetalative cyclization of enynes was achieved by Mori upon reaction with $Bu_3Sn-SiMe_3$.[70] Products from metalation of the triple bond (**27** or **28**) were expected to accompany the formation of the desired cyclized compounds (**29** or **30**). Only compounds with structures **28** and **29** were observed. The formation of bismetalated alkynes was favored in the presence of phosphines (Scheme 36). Best results were obtained using phosphine-free complexes, e.g. $Pd_2(dba)_3$. Heterogeneous complexes such as Pd/C or $Pd(OH)_2/C$ also provided high yields of the desired products, although prolonged reaction times were required. Only terminal alkene and alkyne functions provided good results.

With the future goal of achieving asymmetric induction in the process, different types of ligands were tested. *N*-Heterocyclic carbenes were found to serve as suitable ligands, although no chiral induction was observed when asymmetric carbene ligands were employed.[71] A catalytic cycle for the reaction was proposed (Scheme 37). It included the formation of a palladium intermediate formed by insertion of the acetylenic moiety into the Pd−Si bond, followed by

Scheme 36



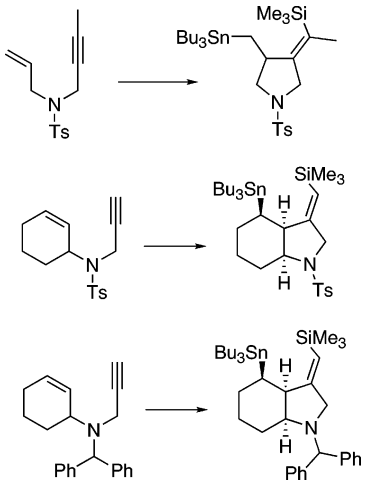
Scheme 37



the addition of the resulting vinyl−palladium fragment to the remaining olefinic bond.

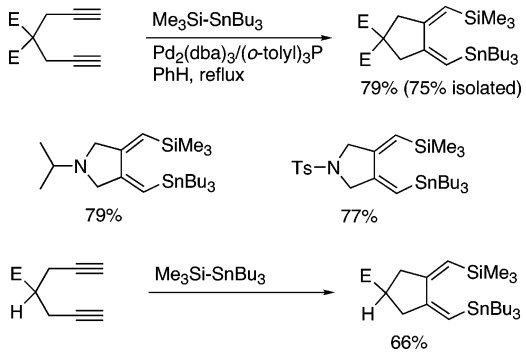
The synthetic utility of the bismetalated products was also explored.[72] A variety of *N*-containing heterocycles with vinylsilyl and alkyltin substituents, some of them with defined stereochemistry, were prepared (Scheme 38).

Scheme 38



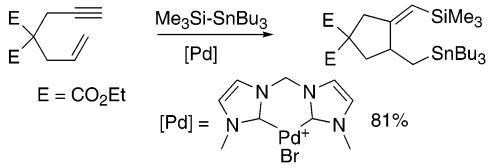
Sn−Si-mediated carbocyclizations of 1,6-diynes proceeded with high regio- and stereoselectivities to yield 1,4-disubstituted (*Z*,*Z*)-1,3-dienes (Scheme 39).[73] The sterically demanding substituents forced the molecules to be nonplanar and thus to exhibit axial chirality, as observed by X-ray crystallography as well as by low-temperature NMR spectroscopy.[74]

Scheme 39



Recently, carbocyclization of 1,6-enynes via silylstannations to yield cyclopentane and pyrrolidine derivatives was repeated by Lautens, who employed homogeneous cationic palladium complexes and performed reactions providing high yields of product (Scheme 40).[75]

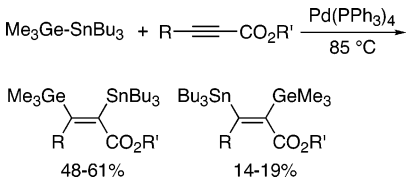
Scheme 40



2.6. Ge–Sn

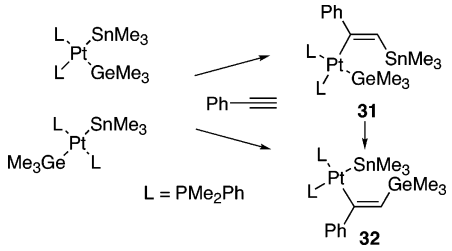
Studies of the addition of germastannanes to triple bonds are limited to propargylic esters.[76] As in the case of silastannation,[62a] the products were formed with poor stereoselectivity due to isomerization of the *Z*-isomer to the *E*-isomer and, in contrast to the former type of reactions, also with poor regioselectivity (Scheme 41).

Scheme 41



Recently, the insertion of phenylacetylene into [Pt(GeMe$_3$)(SnMe$_3$)(PMe$_2$Ph)$_2$], obtained as a cis−trans mixture from Me$_3$Ge−SnMe$_3$ and Pt(cod)$_2$, was studied.[77] The reaction afforded a 80:20 mixture of two isomers. In solution the thermodynamically less stable isomer **31** was converted into the more stable **32** (Scheme 42).

Scheme 42



2.7. B–B

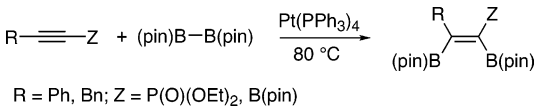
The first addition of diboron compounds to alkynes was reported by Miyaura, Suzuki, and co-workers in 1993.[78]

Various Pt(0) complexes such as $Pt(PPh_3)_4$, $Pt(PMe_3)_4$, PtL_2-(CH_2=CH_2), and $Pt(CO)_2(PPh_3)_2$ served as catalysts for the additions, whereas Pd and Rh complexes were found to be inactive. Terminal and internal acetylenes reacted at elevated temperatures (120 °C, but phenylacetylene at 50 °C), the latter to form adducts with *Z*-configuration.[79] The catalytic cycle proposed for the reaction included oxidative addition of the diborane to Pt(0) and insertion of the alkyne into the Pt−B bond.[80] That syn addition took place was supported by stoichiometric reactions between *cis*-$(PPh_3)_2Pt[B(pin)]_2$ and alkynes (hexyne and phenylacetylene).[79] Products obtained from diborations were employed in cross-coupling reactions to give trisubstituted alkenes.[81]

Automated screening of the influence of different monophosphine ligands on the addition of bis(pinacolato)diboron to alkynes was performed at ambient temperature.[82] For this purpose, phosphines with different properties were added to labile platinum(0) olefin catalyst precursors. The best phosphines for the addition to bis[4-(trifluoromethyl)phenyl]-ethyne were PCy_3 and PPh_2(*o*-Tol). The optimum ligand-to-metal ratio was found to be 1:1, and a 2:1 ratio turned out to be even less efficient than phosphine-free platinum. These findings support a mechanism in which the rate determining step is insertion of the alkyne. This conclusion was also supported by a kinetic study of catalytic as well as stoichiometric additions of bis(catecholato)diboron to alkynes.[83] An inverse dependence on [PPh_3], a first-order dependence on [alkyne] and [catalyst], and the absence of a dependence on [diborane] were observed.

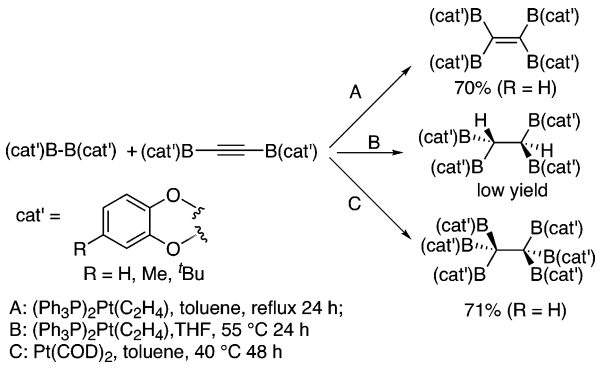
The platinum-catalyzed addition of bis(pinacolato)diboron to 1-alkynylphosphonates and 1-alkynylboronates allowed cis-1,2-diboronated vinylphosphonates and trisboronated alkenes to be synthesized in high yields (Scheme 43).[84]

Scheme 43



Catechol-substituted diborylacetylenes reacted with bis-(catecholato)diboron in the presence of $Pt(cod)_2$ to give tetraborylethane, whereas in the presence of $Pt(PPh_3)_2(CH_2$=$CH_2)$ or $Pt(PPh_3)_4$ tetra- and hexaborylethane derivatives were obtained (Scheme 44).[85]

Scheme 44



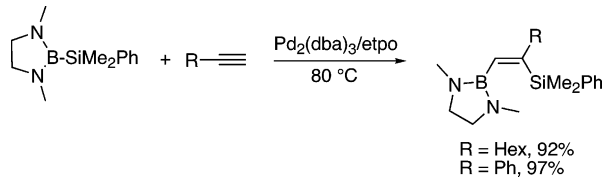
Products obtained from the addition of bis(pinacolato)-diboron to alkynes were recently subjected to electrophilic fluorination to yield α-fluorinated and α,α-difluorinated carbonyl compounds.[86]

Theoretical calculations demonstrated that reactions catalyzed by Pd(0) and Pt(0) should proceed via the same type of mechanism but that palladium complexes are inactive as catalysts due to the instability of the Pd(II) complex formed by oxidative addition.[87]

2.8. B–Si

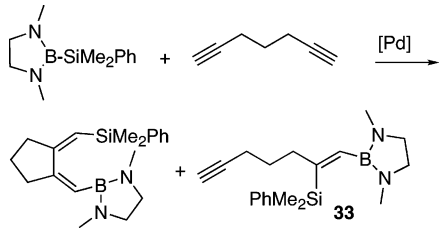
Silaborations of alkynes and silaborative carbocyclizations of diynes and enynes were reported first by Ito[88] and somewhat later by Tanaka.[89] Tanaka's catalyst[41] showed excellent results, providing products with high regioselectivity in high yields (Scheme 45).

Scheme 45



The reaction was applied to carbocyclizations of 1,6- and 1,7-diynes and a 1,6-enyne. Despite the fact that palladium complexes with PMe_3 and PPh_3 served as efficient catalysts for the reaction, etpo was required to obtain the cyclic compound as the major product (Scheme 46).[89] The structure

Scheme 46

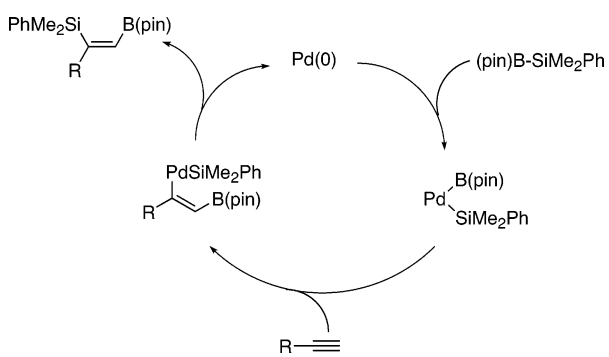


of **33** shows that insertion proceeds into the Pd−B bond.

Ito demonstrated that his catalyst also was efficient for the process, and the same results were obtained for additions of $PhMe_2Si-B(pin)_2$ and $PhMe_2Si-B(NMe_2)_2$ to 1-octyne (50 and 110 °C, 94 and 92%).[88,90] The reactions exhibited high regio- and stereoselectivities. It is interesting to note that $Pd(PPh_3)_4$ was a poor catalyst for the reaction, whereas $Pt(PPh_3)_4$ was efficient at 100 °C. The reaction was applied to a variety of alkynes bearing functional groups, and the products obtained were employed in palladium-catalyzed cross-couplings and Rh-catalyzed 1,4-additions to vinylketones to form vinylsilanes.

The general catalytic cycle for interelement additions was suggested (Scheme 47). A cyclic silylborane added to

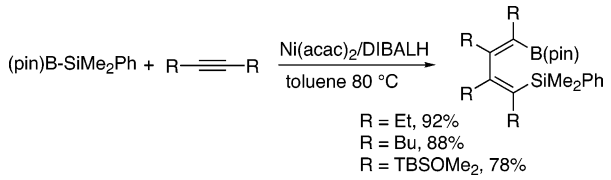
Scheme 47



1-octyne in the presence of a palladium catalyst to give the product with boron attached to the terminal alkyne carbon atom.[91] The reaction with an internal alkyne also exhibited high regioselectivity.

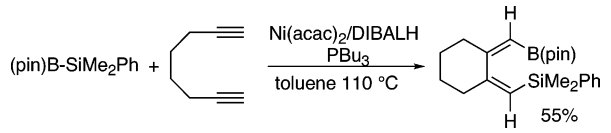
The nickel-catalyzed reaction of $PhMe_2Si-B(pin)$ with alkynes led to regio- and stereoselective silaborative dimerization (Scheme 48).[92]

Scheme 48



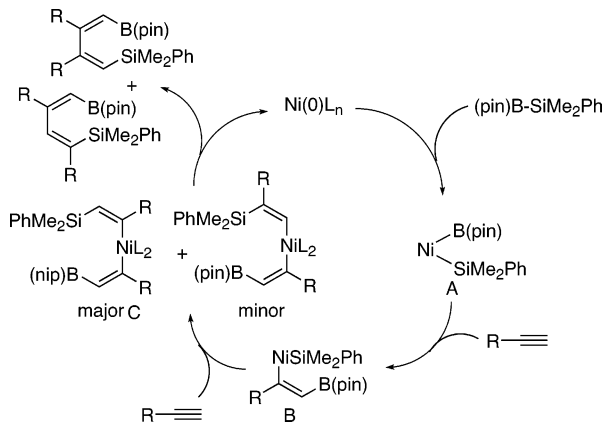
With terminal alkynes, mixtures of isomers, with the boryl group at the terminal position, were obtained. Carbocyclization of diynes was also achieved (Scheme 49).

Scheme 49



The catalytic cycle shown in Scheme 50 was proposed

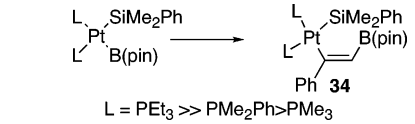
Scheme 50



for the reaction. Regioselective insertion of the alkyne into the Ni−B bond of the complex obtained by initial oxidative addition of the silylborane to Ni(0) (A) gave intermediate B. Insertion of a second alkyne was suggested to take place into the Ni−Si bond to give intermediate C. The possibility that the second alkyne inserts into the Ni−C bond of B was excluded.

Four new cis-silylborylplatinum(II) complexes with either B(pin) or B(dmeda) groups and with phosphine ligands were prepared by oxidative addition to in situ generated Pt(cod)-L_2 complexes.[93] Insertion of phenylacetylene afforded selectively complexes **34** (Scheme 51). Insertion into the

Scheme 51

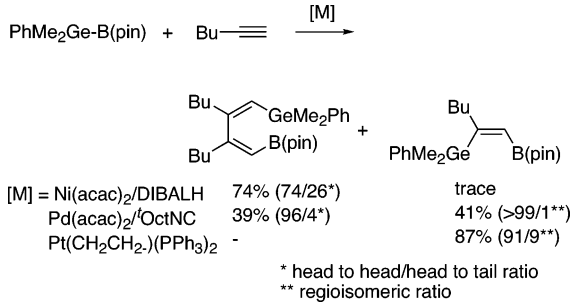


platinum−boron bond was favored both kinetically and thermodynamically.

2.9. B–Ge

Germaboration of 1-hexyne was demonstrated by Ito, who obtained the product from dimerization with Ni. With Pd and Pt catalysts the same compound was obtained along with the normal addition product (Scheme 52).[92]

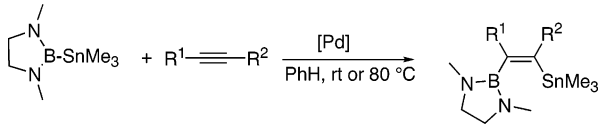
Scheme 52



2.10. B–Sn

The first stannaboration of an alkyne was reported by Tanaka, who studied the addition of 1,3-dimethyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentane to terminal and internal alkynes (Scheme 53).[94] Several palladium complexes

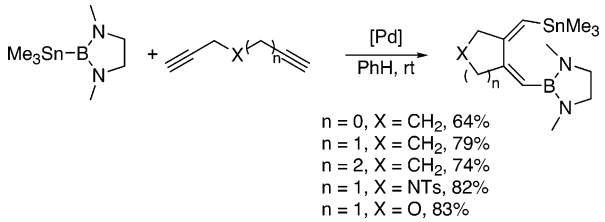
Scheme 53



were found to catalyze the reaction, although some of them required elevated temperatures. It is interesting to note that $Pd(PPh_3)_4$ did not serve as a catalyst for the addition.

The products were obtained with high regio- and stereoselectivity, and yields were high. From terminal alkynes, essentially only the regioisomer having tin at the more substituted position was obtained. The results are in agreement with the accepted mechanism, with the alkyne inserting into the Pd−B bond. The reaction was used for stannaborative carbocyclization of 1,5-, 1,6-, and 1,7-diynes, including heterocontaining 1,6-diynes (Scheme 54).[95] The products

Scheme 54

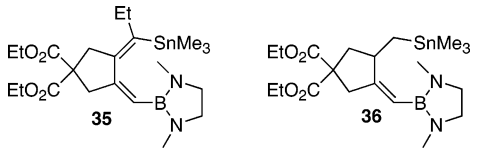


were isolated in good yields.

The structure of **35** supported the assumption that insertion proceeds into the Pd−B bond. Hept-6-en-1-yne underwent the same type of process, affording **36**, again in agreement with insertion occurring into the Pd−B bond.

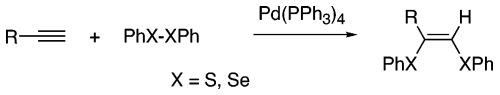
2.11. S–S and Se–Se

Additions of PhS−SPh and PhSe−SePh to triple bonds were first described by Ogawa and Sonoda.[96] Terminal



alkynes were shown to react with both types of compounds in the presence of $Pd(PPh_3)_4$ to provide high yields of *Z*-adducts (Scheme 55). The reactions tolerated a variety of

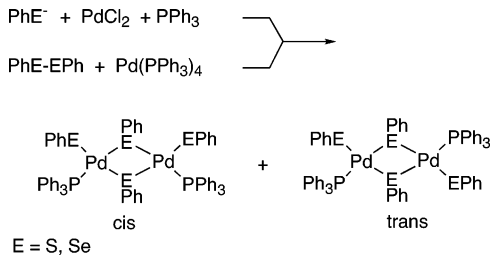
Scheme 55



functional groups. For some activated substrates, *E*-isomers were formed as a result of a noncatalyzed process. When 1,6-enynes were employed as substrates, addition took place only to the triple bond and no carbocyclization was observed. $Pt(PPh_3)_4$ and $Rh(PPh_3)_3Cl$ served as catalysts for the processes but were inferior to the palladium complex.

Recently, it was shown that binuclear palladium complexes[97] are formed under catalytic as well as stoichiometric conditions (Scheme 56).[98] These complexes may be obtained

Scheme 56



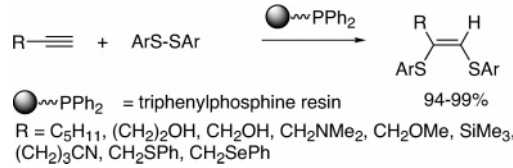
either by methathesis of σ-bonds or by oxidative addition of the disulfide or diselenide to Pd(0).

In the absence of phosphine, $Pd(XAr)_2$ undergoes polymerization. Additions of diphenyl disulfide and diaryl diselenides to a variety of alkynes catalyzed by $Pd(PPh_3)_4$ (1 mol %) and PPh_3 (15 mol %) performed at 80 or 100 °C without solvent in air afforded the products in essentially quantitative yields.[99] A dramatic acceleration of the reaction rate was observed, obviously as an effect of concentration. At 120 °C, the reactions were complete within 5 min, allowing the catalyst concentration to be decreased to 0.01 mol % (97% yield) and even to 0.001 mol % (70% yield after 300 min) at 140 °C. The catalysts, $[Pd_2(XAr)_4(PPh_3)_2]$, were stable in air and could be recycled without loss of activity. The reactions could conveniently be performed in gram scale. When triphenylphosphine was replaced by phosphite ligands, product purification was simplified at the same time as catalyst polymerization was avoided.[100] Key monomeric and dimeric palladium intermediates with a $P(O^iPr)_3$ ligand were isolated and characterized by X-ray crystallography. Additions of diaryl disulfides and diaryl diselenides were also performed using microwave heating.[101]

A theoretical study of the oxidative addition of disulfides and diselenides to Pd(0) and Pt(0) demonstrated that the activation barrier correlates with the E−E bond energy and is higher for E = S than for E = Se; the weaker the E−E bond, the smaller the oxidative addition barrier.[102] The overall exothermicity was also shown to decrease in the same order. The barrier was found to be higher for Pt than for Pd, in accordance with the experimentally observed reactivities.[96]

Recently, a polymer-supported palladium−phosphine complex was used for additions of diaryl disulfides to a variety of terminal alkynes (Scheme 57).[103] The products were

Scheme 57



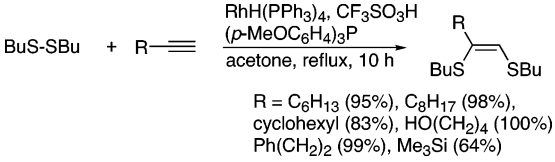
isolated in high yields by simple filtration, and catalyst activity was maintained during several catalytic cycles.

In contrast to palladium complexes, platinum phosphine complexes $(RS)_2Pt(PPh_3)_2$ are monomeric.[97] This is in accordance with theoretical calculations, which showed that dimerization is less feasible for Pt.[102]

Recently, selenium complexes $(RSe)_2Pt(dmphen)(olefin)$ (dmphen = 2,9-dimethylphenanthroline), obtained by oxidative addition of diselenides to Pt(0), were also isolated and characterized by X-ray crystallography.[104] The reactions were reversible, and the equilibrium could be tuned by varying the electronic and steric properties of the ligands. Although this study demonstrates that diselenides undergo oxidative addition to Pt(0), Pt complexes did not show catalytic activity in the addition of diselenides to alkynes. The explanation for this failure was provided by mechanistic studies showing that the cis-platinum complexes initially formed exhibited good catalytic activity but were isomerized to more stable and catalytically inactive trans complexes under the reaction conditions.[98]

Additions of dialkyl disulfides to terminal alkynes were successfully achieved in a highly stereoselective manner using $Rh(PPh_3)_4/(p\text{-}MeOPh)_3P$ in the presence of trifluoromethanesulfonic acid to give products with *Z*-configuration (Scheme 58).[105] The sulfonic acid was shown to dramatically

Scheme 58

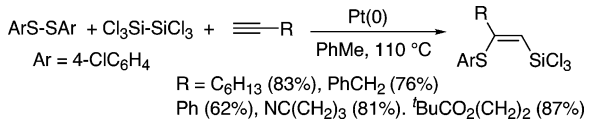


change the reactivity of the rhodium complex. Several other Rh and Pd catalyst precursors were tried, but they were found to be inefficient. Good to high yields were obtained with a variety of alkynes and disulfides.

2.12. Si–S, Si–Se, and Ge–Se

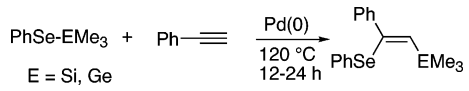
Oxidative additions of Si−X as well as Sn−X (X = S, Se, Te) bonds to Pt(0) are known and proceed more readily with the tin-containing compounds than with their silicon analogues.[106] No reactions of the complexes resulting from addition of Si−S or Sn−S bonds with alkynes have been observed, however, and so far no insertion of an alkyne into a metal−tellurium bond has been observed. The only successful result was obtained by Tanaka for activated silicon compounds $ArS-SiCl_3$, obtained in situ from ArS−SAr and $Cl_3Si-SiCl_3$ (Scheme 59).[107] It was tentatively suggested that insertion takes place into the platinum−sulfur bond.

Scheme 59



Ogawa reported that the additions of $PhSe-SiMe_3$ and $PhSe-GeMe_3$ to arylacetylenes catalyzed by $Pd(PPh_3)_4$ led to regio- and stereoselective formation of products having selenium at the internal position, albeit in poor yields (Scheme 60).[48]

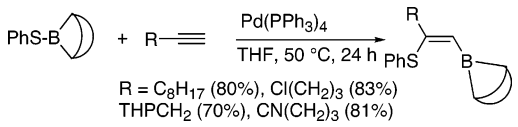
Scheme 60



2.13. B–S

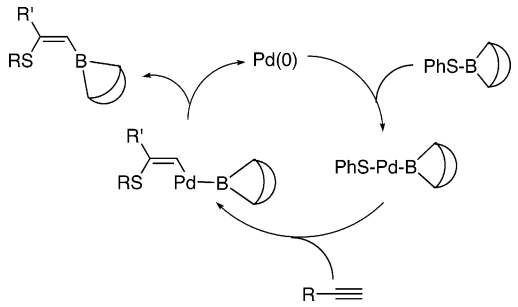
Miyaura and Suzuki found that the addition of boron−sulfur bonds to terminal alkynes was catalyzed by $Pd(PPh_3)_4$ under mild conditions to provide high yields of adducts with high regio- and stereoselectivities (Scheme 61).[108]

Scheme 61



The same regiochemistry as that observed in the addition of Si−S bonds was found, with sulfur being attached to the internal position. The authors were in favor of insertion taking place into the palladium−sulfur bond, with formation of the Markovnikov product (Scheme 62).

Scheme 62



No reaction was observed with $PdCl_2(PPh_3)_2$, probably due to difficulties in the reduction of Pd(II) to Pd(0) under the reaction conditions.

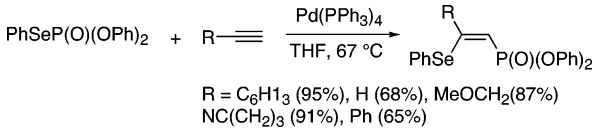
However, a theoretical study showed that oxidative addition of $HS-B(OR)_2$ or $CH_3S-B(OR)_2$ to Pd(0) is highly endothermic and does not take place.[109] The authors suggested a new mechanism for the thiaboration of alkynes with acetylene coordination to $Pd(PPh_3)_2$, phosphine dissociation, and addition of the S−B bond to the metal center via a methathesis-like transition state leading to a vinylpalladium complex, which after isomerization undergoes reductive elimination to form the final product.

In our opinion, this mechanism provides a better explanation for the experimentally observed regioselectivity, but the authors did not consider the problem of regiochemistry. They predicted that Pt(0) complexes, to which B−S bonds can add oxidatively, should not be good catalysts for thiaboration due to energetically unfavorable reductive elimination.

2.14. P–Se

The only addition of a phosphorus−heteroatom compound to an alkyne is that of phenylselenophosphonates to terminal alkynes described by Tanaka (Scheme 63).[110] The reaction

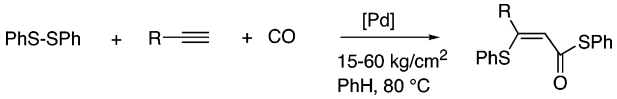
Scheme 63



was catalyzed by palladium(0) phosphine complexes. Platinum complexes, which, like their bis-selenium analogues,[98] are stable in their trans forms, did not catalyze the reaction.[110] High regio- and stereoselectivities were observed, with the regiochemistry being the same as that observed for other selenium−element additions. The authors considered the possibility of insertion into the Pd−Se bond as well as into the Pd−P bond.

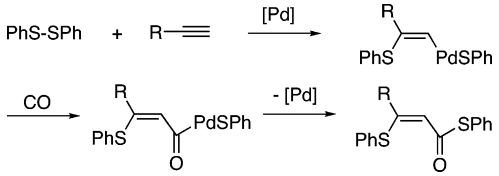
Although reactions with symmetrical E−E bonds do not allow conclusions to be drawn about whether Markovnikov or anti-Markovnikov products are formed, results from carbonylative additions by Ogawa and Sonoda[96] may provide insight into the regiochemistry, at least for additions of disulfides and diselenides. They showed that reaction of terminal alkynes in the presence of carbon monoxide led to vinyl carboxylate with the thiocarboxylic or selenocarboxylic group at the terminal position (Scheme 64).

Scheme 64



This can be considered as evidence that the reaction proceeds in the same manner as the addition of Si−S, Si−Se, Ge−Se, or B−S, in which a PdSePh or PdSPh fragment is attached to the unsaturated carbon atom (Scheme 65).

Scheme 65

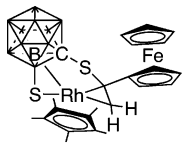


However, other possibilities, such as formation of an $PhXPd(COXPh)L_2$ (X = S, Se) intermediate and insertion of alkyne into the Pd−COXPh bond, cannot be excluded.

Reaction of ethynylferrocene with $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ afforded carborane **37**, which was subjected to X-ray structural analysis, in high yield via insertion of the alkyne into one Rh−S bond followed by Rh-induced hydrogen transfer from B via Rh to the terminal acetylene carbon atom.[111] The Se analogue did not undergo the same type of reaction.

2.15. Comments on Additions to Alkynes

(1) Additions of homo- and hetero-interelement compounds to alkynes have been extensively studied, particularly



37

those involving Si−Si, Ge−Ge, Sn−Sn, B−B, Si−Sn, and B−Si bonds. Several types of additions have emerged as synthetically versatile processes.

(2) A variety of palladium, platinum, and nickel complexes catalyze the additions of disilanes, digermanes, distannanes, and silylstannanes to alkynes. Diborations, on the other hand, are catalyzed only by platinum complexes (see results of theoretical calculations[87]).

(3) Terminal and internal alkynes can participate in the additions, although the latter require harsher reaction conditions.

(4) The mechanisms of most reactions involve oxidative addition of the interelement compound to the metal, insertion of the alkyne into the metal−element bond, and reductive elimination. Additions of B−S bonds catalyzed by Pd proceed via a different mechanism (see results of theoretical calculations[109]).

(5) The additions usually proceed with high syn selectivity. As a rule, the reactions with hetero-interelement compounds are also highly regioselective. In silastannations of terminal alkynes, Si becomes attached to the terminal position, whereas, in silaborations, B adds to the terminal position. In the former type of additions, the insertion of the alkyne proceeds into the Pd−Si bond of the Si−Pd−Sn complex, and in the latter type, the insertion proceeds into the B−Pd bond of the B−Pd−Si complex, with the Pd substituent ending up at the most substituted carbon atom. Some authors propose mechanisms with alkyne insertion taking place into the alternative metal−element bond. These would indeed lead to the same final product, but they do not take into account electronic and steric preferences.

(6) Reactions of interelement compounds with alkynes carrying an ω-unsaturated function, i.e., diynes and enynes, result in carbocyclizations to yield synthetically interesting carbo- and heterocyclic products.

(7) Nickel-catalyzed additions of strained cyclic disilanes lead to formation of two types of products, having the alkyne inserted in the Si−Si bond and in a Si−C bond, respectively.

(8) The regiochemistry of additions of RX−XR, X = S and Se, is different from that of other interelement compounds.

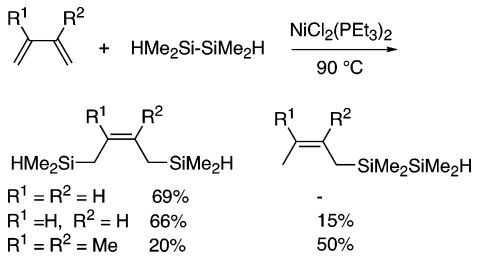
3. Additions to 1,3-Dienes

The catalytic addition of an interelement linkage to a 1,3-diene is a particularly important process, as it allows the preparation of compounds having two equal or different reactive allylic functionalities in one step. Additions providing access to allylsilane[112] and allylborane functionalities,[113] which both serve as important synthetic motifs, have been particularly well studied. Despite a rather long history, it is only recently that studies aiming at synthetic applications of the processes started. This development will be briefly presented here.

3.1. Si–Si

Additions of an interelement compound to dienes were first observed by Kumada and co-workers, who found that *sym*-tetramethyldisilane upon reaction with a variety of 1,3-dienes in the presence of $NiCl_2(PEt_3)_2$ afforded 1,4-disilylated alkenes along with products from hydrosilylation (Scheme 66).[19b]

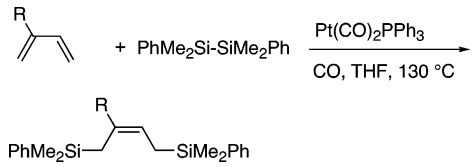
Scheme 66



$FMe_2Si-SiMe_2F$ was also shown to undergo addition to several substituted 1,3-dienes catalyzed by $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ to give as the major product that from 1,4-addition, with pure *Z*-configuration, and up to 25% of the head-to-head product from bissilylative dimerization.[114] Strained Si−Si bonds were shown by Sakurai to add to 1,3-dienes more easily.[115] Later Watanabe, Nagai, and co-workers[116] showed that reaction of $(Cl_nMe_{3-n}Si)_2$ catalyzed by $Pd(PPh_3)_4$ gave only 1,4-addition products, whereas Sakurai[117] observed only the product of bissilylative dimerization with high regio- and stereoselectivities in the presence of $PdCl_2(PhCN)_2$ or $Pd(OAc)_2$. The dimer obtained from butadiene and hexamethyldisilane was used in a synthesis of *rac*-muscone. A catalytic system, consisting of $Pd(dba)_2$ in DMF or dioxane, allowing the reaction to be performed at ambient temperature, was later found.[118] Bissilylative dimerization catalyzed by Pd complexes, which can be carried out even with $Me_3Si-SiMe_3$, has also been extensively studied.[21,119]

Selective 1,4-additions of disilanes to conjugated dienes were observed in the presence of $Pt(CO)_2(PPh_3)_2$ (Scheme 67).[120] Yields were good to high, but the *E*/*Z* ratio was

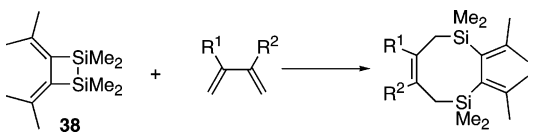
Scheme 67



strongly dependent on the substituents on silicon and the structure of the diene. The unexpected high reactivity of disilanes with a phenyl group on silicon was suggested to be due to π-coordination of the arene to platinum.

Addition of disilacyclobutane **38** to 2,3-dimethyl-1,3-butadiene was found to be catalyzed by a platinum complex, but it failed in the presence of palladium catalysts (Scheme 68).[121]

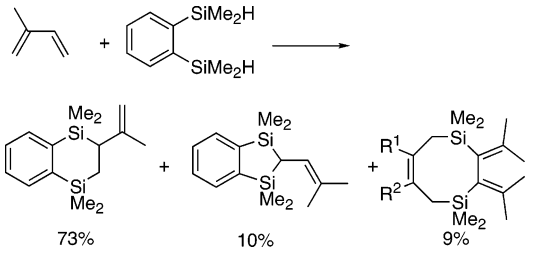
Scheme 68



38

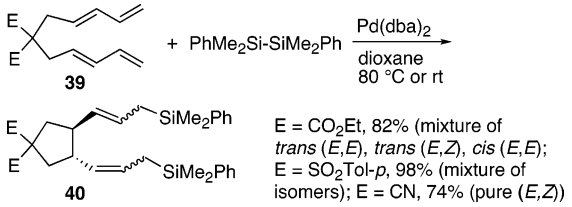
o-Bis(dimethylsilyl)benzene added in a 1,2-fashion mainly to the least substituted double bond of isoprene in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (Scheme 69).[122]

Scheme 69



Bisdienes **39** (E = CO_2Et, SO_2Tol-*p*) were shown to undergo the interesting process of carbocyclization−disilylation in the presence of $Pd(dba)_2$.[123] The reactions proceeded with high regioselectivity but low stereoselectivity, producing the trans-(*E*),(*Z*)-isomers of **40** as the main products along with stereoisomers (Scheme 70). In contrast,

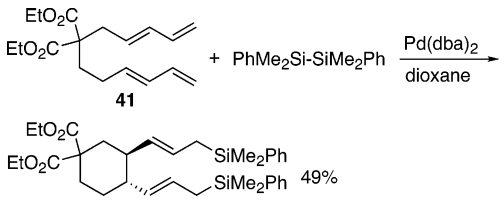
Scheme 70



bisdiene **39** (E = CN) afforded the trans-(*E*),(*Z*)-isomers as the single product.

The homologue **41** also reacted with high stereoselectivity, giving only the 1,2-trans-(*E*),(*E*)-disubstituted isomer (Scheme 71). Other palladium complexes, with or without phosphine

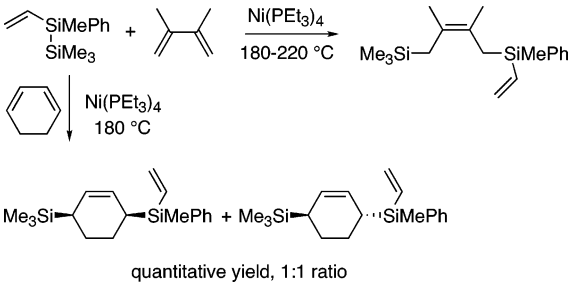
Scheme 71



ligands, such as $Pd(PPh_3)_4$, $PdCl_2(PhCN)_2$, and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ exhibited no catalytic activity in this reaction. The same types of adducts were observed from distannations and silastannations.

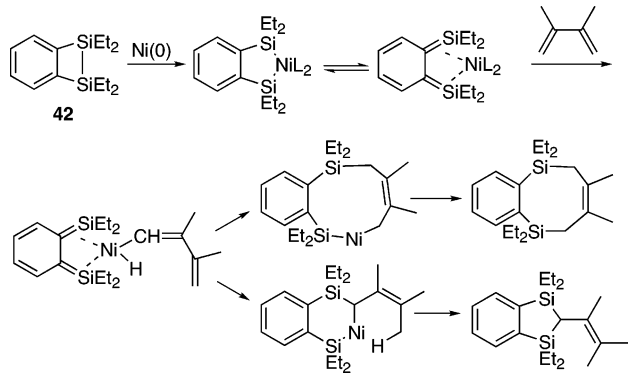
The early work of Kumada[19b] on nickel-catalyzed disilylations of 1,3-dienes was continued in the 1990s. Reaction of 2,3-dimethyl-1,3-butadiene with 1,2,2,2-tetramethylphenylvinyldisilane was shown to afford the (*Z*)-adduct as the single product, whereas from 1,3-cyclohexadiene a mixture of cis- and trans-isomers was obtained (Scheme 72).[124]

Scheme 72



The addition of **42** with a strained Si−Si bond to dienes catalyzed by $Ni(PEt_3)_4$ gave two different products. The authors suggested that the reaction started with sp^2-carbon−hydrogen activation (Scheme 73).[125]

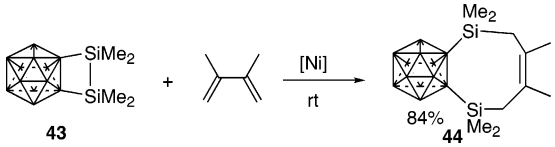
Scheme 73



From 1,3-cyclohexadiene and 1,4-cyclohexadiene, the same product was formed due to isomerization of the 1,4-diene in the first step. The possibility of a tautomeric equilibrium was proposed.

With the strained disilane **43**, 2,3-dimethyl-1,3-butadiene gave 7,8-carboranylene-1,1,6,6-tetramethyl-3,4-dimethyl-1,6-disilacycloocta-3-ene (**44**) in high yield in the presence of $Ni(PEt_3)_4$ at room temperature (Scheme 74).[33b] The reaction,

Scheme 74



like that of **42**, was suggested to proceed via initial activation of a terminal olefinic C−H bond by the intermediate nickel complex obtained from **43** and Ni(0) followed by 1,4-addition across the diene.

The reaction of disilane **43** with 2,3-dimethyl-1,3-butadiene is thus different from that of compound **42**, also with a strained Si−Si bond, which afforded a mixture of two products.[125]

Reactions of 1,3-dienes with disilanes in the presence of acid chlorides and $Pd(dba)_2$ as catalyst did not lead to disilylation but resulted in 1,4-carbosilylation with concomitant decarbonylation.[126] The reactions were highly regio- and stereoselective, providing only the (*E*)-olefins.

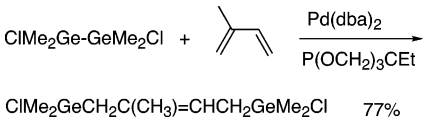
The geometries, bonding nature, and reactivities in C−X (X = Si, Ge, Sn) reductive eliminations of $Pd(XH_3)(\eta^3\text{-}C_3H_5)(PH_3)$ were studied theoretically.[127] In contrast to reductive eliminations involving CH_3 in place of XH_3, moderate activation barriers and moderate reaction energies were found. The moderate activation barriers were explained by the transition state structures, in which the XH_3 group still bound to palladium can interact with the allyl carbon atom as a result of the hypervalency of the elements.

3.2. Ge–Ge

Addition of $ClMe_2Ge-GeMe_2Cl$ to isoprene was achieved by Tanaka using his catalytic system consisting of $Pd(dba)_2$/$P(OCH_2)_3CEt$ (Scheme 75).[44]

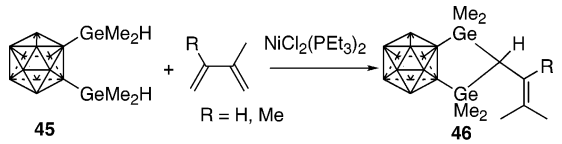
The stoichiometric reaction of the Ni(II) complex of 1,2-bis(dimethylgermyl)carborane **45** with isoprene and 2,3-

Scheme 75



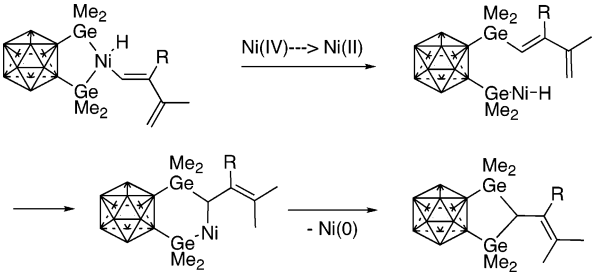
dimethyl-1,3-butadiene afforded five-membered ring compounds **46** with the two germanium atoms attached to the same carbon atom (Scheme 76).[47]

Scheme 76



The mechanism proposed by the authors includes oxidative addition of the terminal olefinic C−H bond to Ni(II), a shift of the diene group from Ni to Ge, with cleavage of the Ni−C and Ni−Ge bonds, 1,4-addition of Ni−H, and reductive elimination to form Ni(0) and the product (Scheme 77).

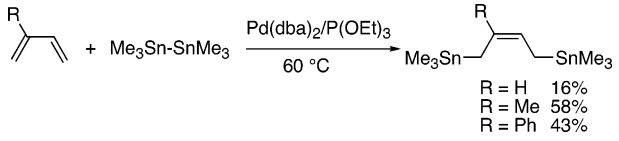
Scheme 77



3.3. Sn–Sn

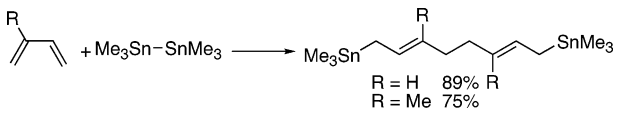
The successful addition of $Me_3Sn-SnMe_3$ to butadiene, isoprene, and 2-phenyl-1,3-butadiene using $Pd(dba)_2$ and trialkyl phosphite as catalyst precursor to obtain 1:1 adducts in modest yields was reported by Mitchell et al. in 1992 (Scheme 78).[128] The same year another publication about

Scheme 78



distannations of dienes appeared, in which Tsuji and Kakehi showed that reaction of hexamethyldistannane catalyzed by $Pd(dba)_2$ led to dimerization−double stannylation in high yield (Scheme 79).[129] No product was obtained employing

Scheme 79

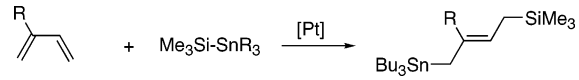


$Pd(PPh_3)_4$, and other phosphine-free palladium complexes such as $Pd(PhCN)_2Cl_2$ or $[Pd(allyl)Cl]_2$ exhibited low or no reactivity. The replacement of hexamethylditin for hexabutylditin led to dramatic changes and resulted in hydrostannation in place of distannation.

3.4. Si–Sn

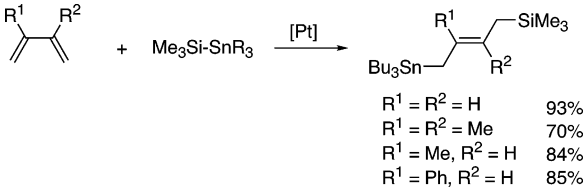
1,4-Silastannation of 1,3-dienes catalyzed by $Pt(CO)(PPh_3)_2$ producing (*E*)-olefins stereoselectively was described by Tsuji and Obora.[130] Other Pt complexes exhibited low or no reactivity, and Pd complexes were essentially unreactive. The reactions with unsymmetrical dienes were highly regioselective, with the products having the tin-containing substituent attached to the most substituted end of the olefin (Scheme 80).

Scheme 80



Only *trans*-1-stannyl-4-silyl-2-butene was formed in the reaction with unsubstituted diene, and only the trans-isomer was obtained in the reaction with 2,3-dimethyl-1,3-butadiene (Scheme 81). The yield decreased sharply when the substituents on silicon were replaced by more bulky groups.

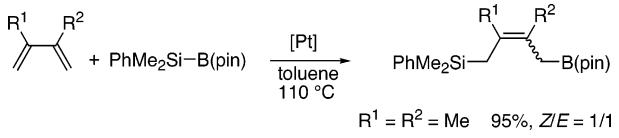
Scheme 81



3.5. B–Si

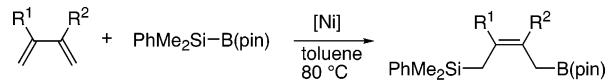
Silaboration of 1,3-dienes in the presence of the platinum−phosphine complex $Pt(CH_2{=}CH_2)(PPh_3)_2$ provided addition products in good yields but with poor stereoselectivity (Scheme 82).[131] Palladium complexes, even $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide, which was the most efficient catalyst for the silaboration of alkynes, did not give any adduct.[132]

Scheme 82



In contrast, stereoselective 1,4-addition to 1,3-dienes to yield (*Z*)-4-boryl-1-silyl-2-alkene derivatives was observed using nickel(0)−phosphine complexes, generated from $Ni(acac)_2$ and diisobutylaluminum hydride, as catalysts. With unsymmetrical dienes, low regioselectivity was observed, however (Scheme 83).[132]

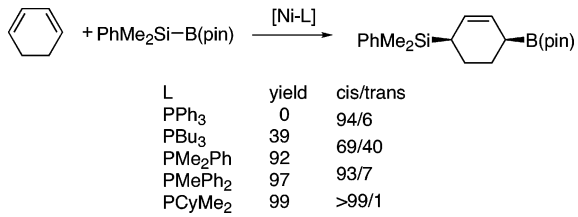
Scheme 83



$R^1 = R^2 = Me$ 90%, *Z*/*E* > 99/1
$R^1 = R^2 = H$ 90%
$R^1 = Me, R^2 = H$ 66% + 26% of regioisomer

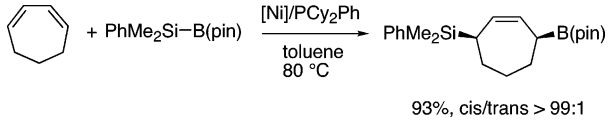
Platinum complexes were reported to be poor catalysts for the silaboration of cyclic dienes, affording merely 21% yield in the reaction with 1,3-cyclohexadiene. In the presence of certain phosphines, nickel(0) catalysts afforded high yields of adducts from 1,3-cyclohexadiene. With cyclohexyldimethylphosphine, an essentially quantitative yield of the cis adduct was obtained (Scheme 84).[132]

Scheme 84



The Ni(0) catalyst with the best phosphine ligand, $PCyPh_2$, catalyzed the reaction of 1,3-cycloheptadiene to give only the cis adduct in high yield (Scheme 85).

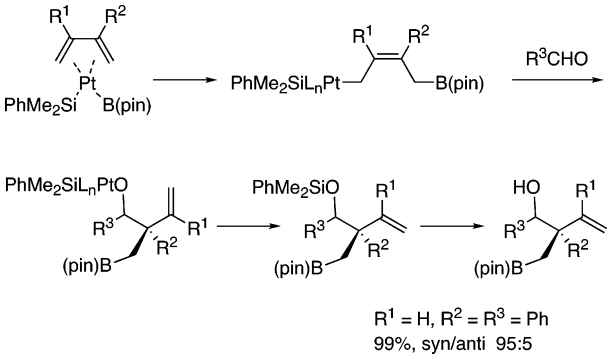
Scheme 85



Later, it was found that platinum complexes with a variety of phosphorus ligands catalyzed silaborations of 1,3-cyclohexadiene, although at higher temperatures, 110 °C in place of 80 °C, than required for the Ni complexes.[133] Catalysts generated from $Pt(acac)_2$, DIBALH, and chiral phosphoramidites led to enantioenriched 1,4-addition products (up to 70% ee).

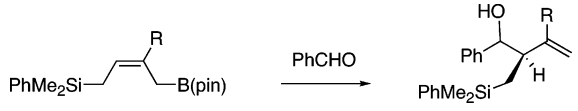
The silaboration of 2,3-dimethyl-1,3-butadiene, catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$, was performed in the presence of aldehydes to yield a product with a new C−C bond at the less substituted position, showing that insertion of 1,3-dienes takes place into the platinum−boron bond (Scheme 86).[131]

Scheme 86



The product was different from that obtained by subsequent reaction of an aldehyde with the product from silaboration of the diene (Scheme 87), showing that, when aldehyde is present, the platinum complex is trapped by the aldehyde prior to reductive elimination.[10]

Scheme 87

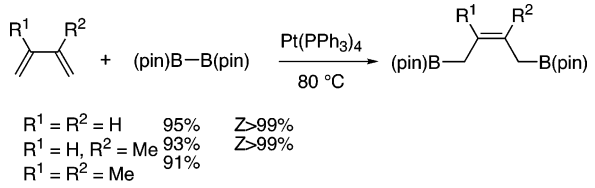


Oxidative additions of $(HO)B_2-XH_3$ (X = Si, Ge, Sn) bonds to $Pd(PH_3)_2$ and $Pt(PH_3)_2$ were investigated theoretically.[127b,134] Low activation energies were observed. Additions to Pt(0) were highly exothermic, while those to Pd(0) were less exothermic due to weaker M−X and M−B bonds. π-Back-donation from a filled metal d orbital to the empty p orbital on boron accounts for the strong B−M bonds. This charge-transfer interaction stabilizes the transition states and thus explains the observed high reactivity of the interelement compounds. The trans influence of the boryl group was found to be stronger than that of the silyl group.

3.6. B–B

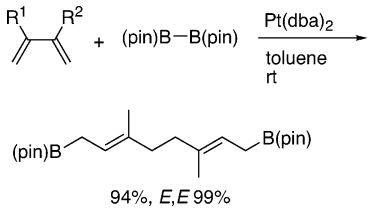
Miyaura and co-workers were the first to report Pt-catalyzed diboration of 1,3-dienes.[135] With butadiene, isoprene, and 2,3-dimethylbutadiene, the reaction proceeded smoothly, affording the 1,4-syn addition products in high yields and with high stereoselectivity in the presence of Pt-$(PPh_3)_4$ (Scheme 88).

Scheme 88



Exchanging $Pt(PPh_3)_4$ for $Pt(dba)_2$ allowed the reaction to be performed at room temperature, but dimerization−addition was observed in place of simple 1,4-addition (Scheme 89). The dimers were thought to result from diene

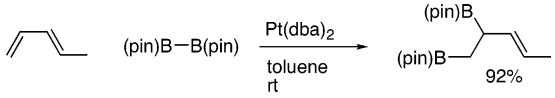
Scheme 89



insertion into the platinum−carbon bond.

With $Pt(dba)_2$, 1,2-addition to 1,3-pentadiene was observed, demonstrating that small changes in substrate and catalyst structure lead to major changes in product formation (Scheme 90).[136]

Scheme 90



The catalytic cycle for the 1,4-addition was suggested to include oxidative addition, formation of a π-allyl platinum intermediate, and reductive elimination (Scheme 91).[135] The procedure has been employed in synthetic applications.[12]

Several chiral diboranes (**47**−**50**) and their complexes with Pt were prepared (Chart 2). The structure of **47** was determined by X-ray crystallography. The diboranes reacted with $Pt(CH_2{=}CH_2)(PPh_3)_2$ to yield cis-platinum complexes quantitatively.[137]

Scheme 91

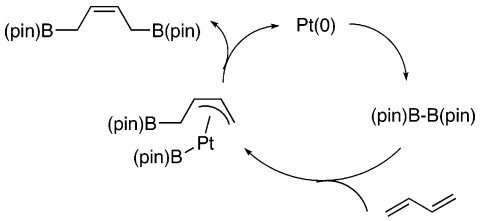
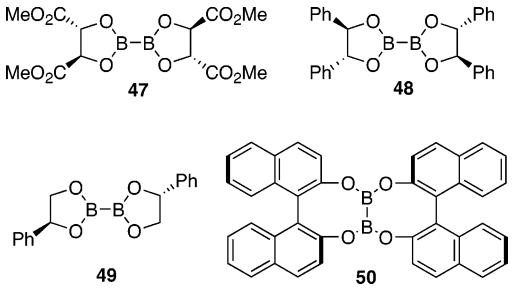


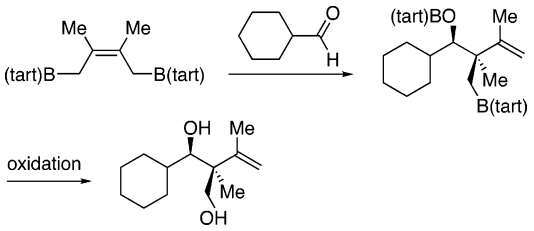
Chart 2



In diboration of dienes, chirality transfer from the diborane diolate groups was inefficient. From (*E*)-1,3-pentadiene, approximately eqaual amounts of the two diastereomers were formed, with the highest de observed amounting to 20%. Diboration of 1,3-cyclohexadiene proceeded faster than that of acyclic dienes and afforded, according to ^{1}H NMR spectroscopy, one single diastereomer formed by syn addition.

The product obtained by diboration of a 2,3-dimethyl-1,3-butadiene using bis(diethyl-L-tartrateglycolato)diboron was trapped by aldehydes, to form enantioenriched (up to 74% ee) allylated product via chirality transfer from the boronate groups to the new stereogenic center (Scheme 92).[138]

Scheme 92



Diboration of 1,3-dienes, employing Ni(cod)$_2$ and tris(2-furyl)phosphine, followed by sequential intramolecular and intermolecular allylation of two aldehyde groups, afforded systems with four stereogenic centers with high diastereoselectivity (Scheme 93).[139] Products with six membered rings could be prepared using the same method.

3.7. B–Sn

Regio- and stereoselective 1,4-stannaboration of 1,3-dienes was shown to proceed smoothly in the presence of catalytic amounts of Pd$_2$(dba)$_3$ and P(OCH$_2$)$_3$CEt to give high yields of (*Z*)-1-boryl-4-stannyl-2-butenes (Scheme 94).[140] The product obtained (R^1 = Me; R^2 = H) was employed in allylations of aldehydes. No stannaboration was observed with 1,3-cyclohexadiene even at 110 °C.

3.8. Comments on Additions to 1,3-Dienes

(1) Homo- and hetero-interelement compounds usually add in a 1,4-fashion to 1,3-dienes. The reactions are often complicated by dimerization of the diene. As usual, the outcome of the reaction is determined by the nature of the catalyst, and even by the ligand.

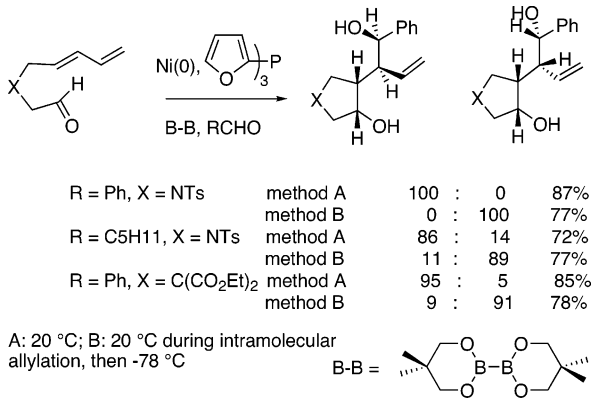
(2) Pt complexes are often more efficient as catalysts than Pd complexes, not only for additions of B−B and B−Si bonds, but also for additions of Si−Sn bonds.

(3) The regioselectivity is high since it is determined by the nature of the bond into which insertion proceeds. The insertion results in unavoidable formation of a π-allyl complex.

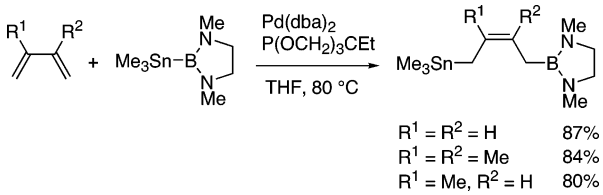
(4) The stereoselectivity depends on the nature of the interelement compound. Cis products are usually formed from additions of Si−Si and B−B bonds, whereas trans products result from additions of Si−Sn bonds. The stereoselectivity of B−Si additions is often poor.

(5) Ligandless palladium can be used for carbocyclizations involving Si−Si, Sn−Sn, and Si−Sn bonds.

Scheme 93



Scheme 94



4. Additions to 1,2-Dienes

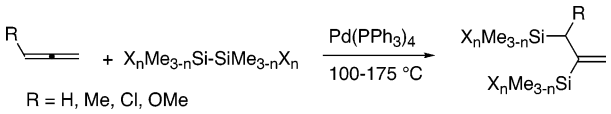
Studies of transition metal-catalyzed additions of interelement compounds to 1,2-dienes have been rather limited. Through the additions, compounds having vinyl as well as allyl metal moieties are accessible in one step. The products have large potential for a wide variety of subsequent synthetic transformations.

4.1. Si–Si

Disilylations of allene and 1,2-butadiene catalyzed by Pd(PPh$_3$)$_4$ were first described by Watanabe and co-workers in 1981.[141] In the reaction of chloromethyl- and methoxymethyldisilanes as well as hexamethyldisilane to 1,2-butadiene, only one regioisomer, formed by addition to the internal double bond, i.e., 2,3-addition, was observed. With unsymmetrical disilanes, the most electron deficient silyl group added to the allylic position (Scheme 95).

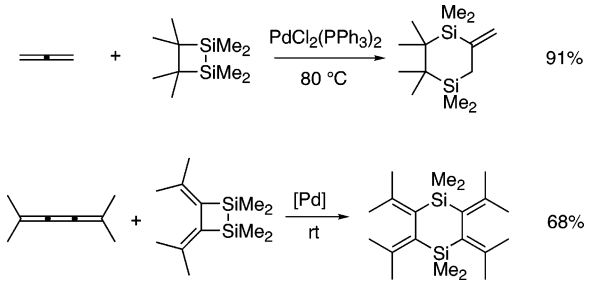
Cyclic disilanes with strained Si−Si bonds were shown to react under milder conditions. Thus, addition of octamethyl-1,2-disilacyclobutadiene to allene took place at 80

Scheme 95



°C,[21] and some additions occurred even at room temperature (Scheme 96).[142]

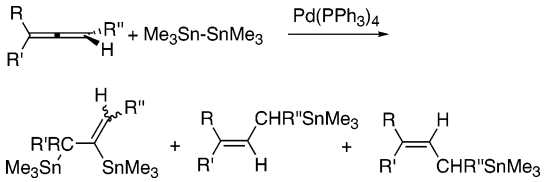
Scheme 96



4.2. Sn–Sn

Mitchell and co-workers showed that hexamethylditin adds to 1,2-dienes in the presence of $Pd(PPh_3)_4$ (Scheme 97). At

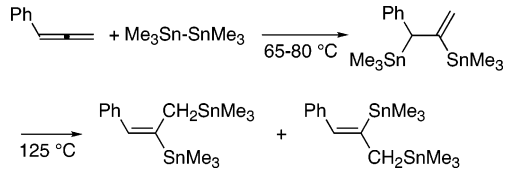
Scheme 97



lower temperatures, reversible formation of the kinetically favored product occurred, while at higher temperatures the thermodynamically stable products were obtained.[143] Other hexaalkylditin compounds reacted analogously.[144] The distribution of products was dependent on the reaction conditions as well as on the structure of the allene and the distannane.

From monosubstituted allenes, quite high yields of adducts were obtained, whereas for 1,1-disubstituted compounds, yields were considerably lower, although conversions were high, and, for trisubstituted allenes, even conversions were low (Scheme 98).[143]

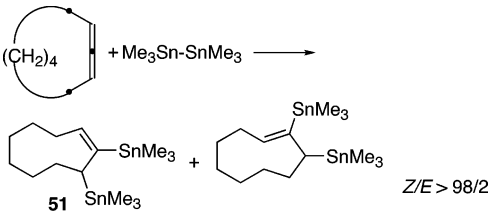
Scheme 98



$Me_3Sn-SnMe_3$ was shown to undergo palladium-catalyzed addition to medium-sized cyclic 1,2-dienes. Cyclonona-1,2-diene, the smallest cyclic allene, gave mainly one isomer (**51**, Scheme 99), whereas a mixture of isomers was obtained from cyclodeca-1,2-diene and cycloundeca-1,2-diene.[145] The reactions were suggested to proceed via formation of an anti-anti-π-allyl palladium complex.

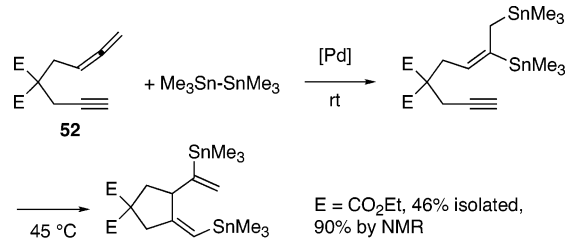
Allenynes **52** were subjected to palladium-catalyzed distannation. At room temperature, only 1,2-addition to the allenic moiety was observed, but at elevated temperatures,

Scheme 99



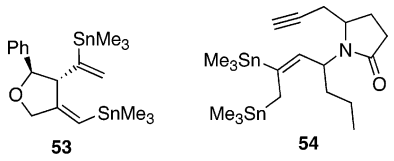
cyclization occurred as a result of interaction of the allyltin function with the triple bond (Scheme 100). According to

Scheme 100



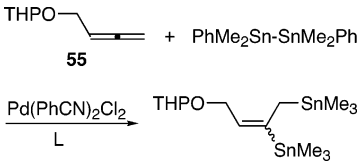
NMR spectroscopy, the yields of cyclized products were high, but the products were not stable and therefore were difficult to isolate. For this reason, distannation was not recommended for this type of carbocyclizations.[146]

Compound **53** was obtained in 42% yield but not isolated due to decomposition during chromatography. An example of a product from 1,2-addition to the allenic part of the substrate, with the triple bond untouched, is provided by **54**.



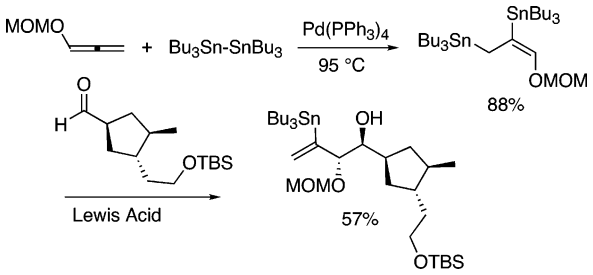
The THP-substituted allene **55** was shown to react with 1,1,2,2-tetramethyl-1,2-phenylditin to give a product from 1,2-addition to the terminal allenic bond (Scheme 101).[146b]

Scheme 101



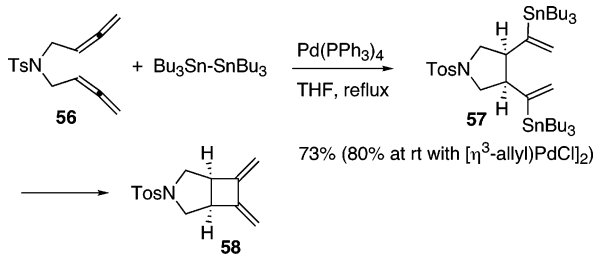
A single olefin isomer was obtained from distannation of 1-(methoxy)methoxyallene. Subsequent treatment with chiral nonracemic aldehydes provided product alcohols as single diastereomers (Scheme 102).[147]

Scheme 102



Treatment of bisallene **56** with $Bu_3Sn-SnBu_3$ in the presence of Pd catalysts resulted in cyclization–distannation to afford cis-fused product **57**, which upon prolonged reaction underwent intramolecular homocoupling to yield **58** (Scheme 103).[148]

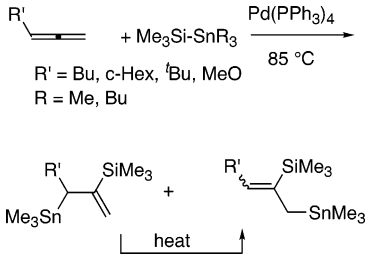
Scheme 103



4.3. Si–Sn

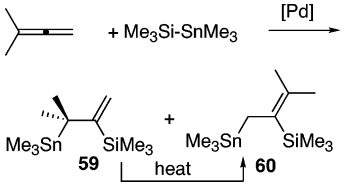
The most extensively studied additions of interelement compounds to allenes are those involving Si–Sn bonds. These reactions have some advantages compared to those involving Sn–Sn or Sn–B compounds, as the silylstannanes are easy to handle and the products are easy to isolate. Mitchell found in 1985 that products with the silyl group attached to the central carbon atom were exclusively formed (Scheme 104).[149] The position of the tin-containing substituent was shown to depend on the substituents on the allene, with bulky groups favoring addition to the terminal position.[144,150]

Scheme 104



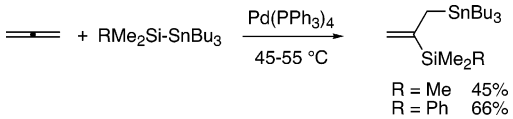
Addition of (trimethylsilyl)trimethylstannane to 1,1-dimethylallene in the presence of $Pd(PPh_3)_4$ afforded a 1:1 mixture of **59** and **60**. By treating the product mixture with additional $Pd(PPh_3)_4$ under heating, 80% of **60** was obtained (Scheme 105).[149]

Scheme 105



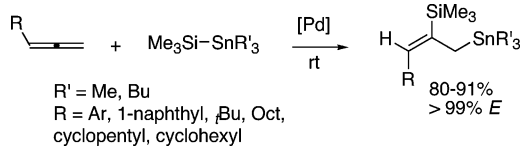
Reactions of $Me_3Si-SnBu_3$ and $PhMe_2Si-SnBu_3$ with unsubstituted allene afforded the addition products in high yields under mild conditions (Scheme 106).[151]

Scheme 106



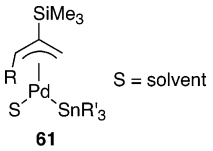
Both the regioselectivity and the stereoselecivity were greatly improved by the use of the phosphine-free palladium complex $Pd_2(dba)_3$·dba.[152] Only one product, with *E*-configuration, having the silyl group at the central position and the stannyl group at the unsubstituted terminal carbon atom was obtained, independent of the electronic and steric factors in the allene (Scheme 107). The reaction proceeded smoothly

Scheme 107



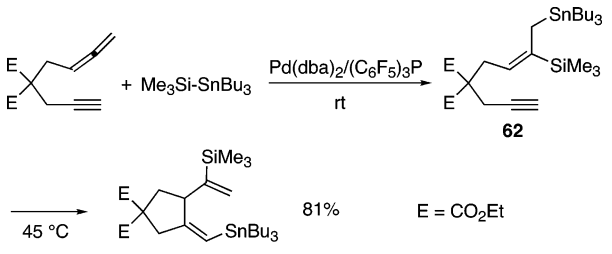
in toluene at room temperature or at 80 °C to give high yields of products.

The absence of the kinetic product even at room temperature using the phosphine-free catalyst was explained by the formation of a π-allyl palladium complex (**61**) with the R group anti to the silyl group. Reductive elimination from this intermediate led to the observed isomer.



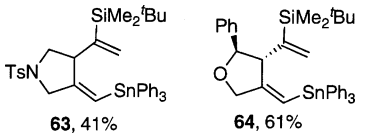
Modified conditions for silastannation of 1,2-dienes affording higher regio- and stereoselectivities were recently presented by RajanBabu and co-workers.[146] Using $Pd_2(dba)_3-P(C_6F_5)_3$ or $Pd(PhCN)_2Cl_2-P(C_6F_5)_3$ as catalyst precursor, they synthesized a variety of interesting allylic tin derivatives via palladium-catalyzed silastannation of functionalized allenes. The examples provided demonstrate the functional group tolerance of the process. Of five selected phosphine ligands, $P(C_6F_5)_3$, $P(3,5\text{-}Me_2C_6H_5)_3$, PPh_3, PBu_3, and P^tBu_3, the first two showed the best results. The rate of reaction was also dependent on the palladium precursor; with $P(C_6F_5)_3$ as ligand, rates decreased in the order $Pd(PhCN)_2Cl_2$ > [Pd(allyl)Cl]$_2$/AgOTf ≈ $Pd_2(dba)_3$·$CHCl_3$ ≫ $Pd(PPh_3)_2Cl_2$ ≈ $Pd(PPh_3)_4$. As in the case of α,ω-enynes,[70] the combination of (trialkylsilyl)trialkylstannanes and the catalytic system turned out to be very efficient for cyclizations of 1,2-diene-8-ynes. However, in the former case, initial addition to the alkyne system occurred, whereas, in the latter, the allene function reacted first. Reactions with less reactive silylstannanes such as $Me_3Si-SnBu_3$ permitted the isolation of **62**, which was converted to the cyclic product (Scheme 108). In contrast, with the more reactive reagent $^tBuMe_2Si-SnPh_3$, only the cyclic product was observed.

Scheme 108



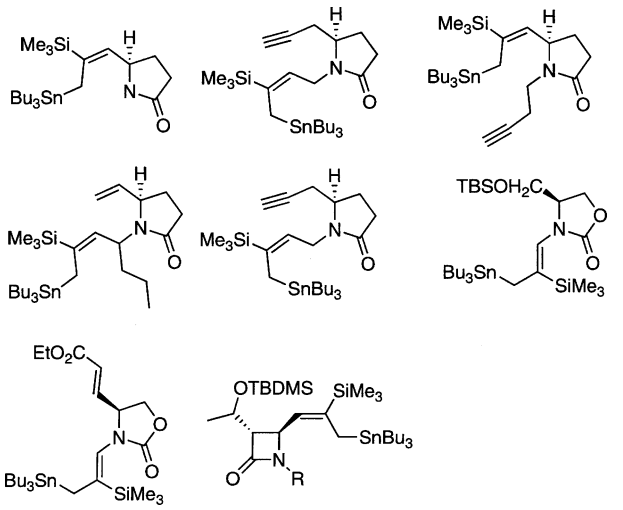
Heterocyclic compounds, such as **63** and **64**, were obtained using the same procedure. High yields were obtained

according to NMR spectroscopy, but the yields of isolated products were lower.



The use of this approach for the synthesis of highly functionalized carbocyclic and heterocyclic compounds, including the syntheses of pyrrolidines and indolizidines, was recently beautifully demonstrated (Chart 3).[146] The reaction

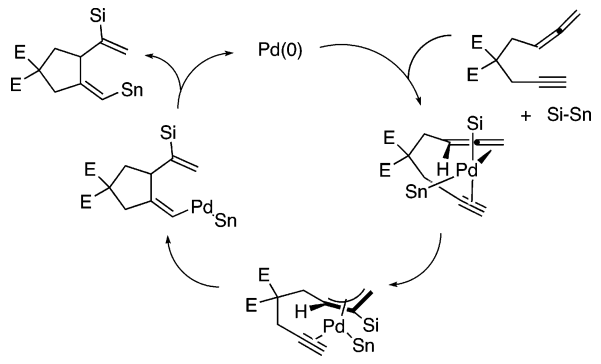
Chart 3



was limited to terminal acetylenes; only addition to the allenic bond was observed in compounds containing an internal triple bond. Along with the cyclized products, many interesting highly functionalized compounds were obtained from 1,2-addition to the allenic function.

The addition thus proceeds in two steps: 1,2-addition to the allenic moiety and reaction of the allyltin function with the triple bond, with the latter step being well-known in the literature (Scheme 109).[153]

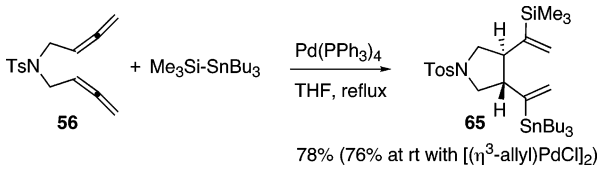
Scheme 109



Silastannation−aldehyde cyclization was recently used as a key step in the synthesis of indolizidine alkaloids.[154]

In contrast to distannation, the palladium-catalyzed carbocyclization−silastannation of bis(allenes) provided trans-fused cyclized products (compare Scheme 103).[118] Thus, reaction of $Me_3Si-SnBu_3$ with bis(allene) **56** gave **65** (Scheme 110). The striking reversal of stereoselectivity was explained by larger steric hindrance provided by the $SiMe_3$

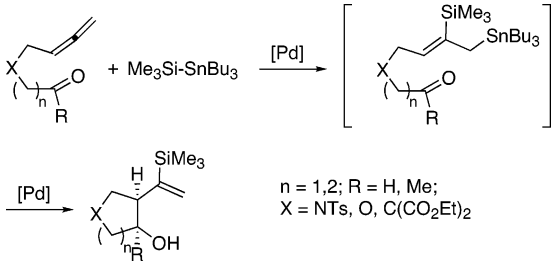
Scheme 110



group compared to $SnBu_3$, with the former having a larger effective size due to the short C−Si bond. Carbocyclic analogues, with cis or trans substitution depending on the distannane used, were obtained using the same procedure.

Recently, Kang and co-workers presented tandem silastannation−allylstannane carbonyl addition, thereby achieving stereoselective formation of cis-cyclopentanols in high yields from allene aldehydes and allene ketones (Scheme 111).[155] The stereochemistry observed was explained by the

Scheme 111

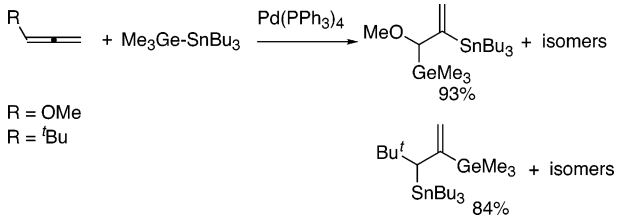


higher stability of the intermediate leading to the cis-isomer. The best catalyst for the transformation was found to be bis(π-allylpalladium chloride), which allowed the reaction to be performed at room temperature.

4.4. Ge–Sn

In connection to studies of disilylations and distannations, Mitchell investigated palladium-catalyzed additions of tin−germanium bonds to allenes.[156] The regioselectivity was shown to be dependent on the substituents on the allene, demonstrating that the reaction can proceed via insertion into the Pd−Sn bond as well as into the Pd−Ge bond (Scheme 112).

Scheme 112



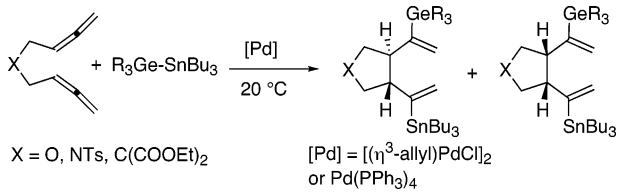
A study of carbocyclizations of bis(allenes) leading to five-membered carbo- and heterocycles which was mediated by germylstannanes ($Ph_3GeSnBu_3$ and $Bu_3GeSnBu_3$) and catalyzed by palladium complexes revealed that the stereoselectivity was highly dependent on the structure of the reagent and the reaction conditions (Scheme 113).[157]

Depending on the R group and the nature of the catalyst, either trans- or cis-fused product was obtained, the latter along with bicyclic dienes, as a result of the equilibrium shown in Scheme 114.[148]

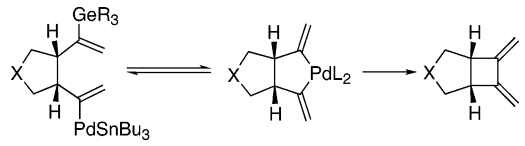
4.5. B–B

Additions of bis(pinacolato)diboron to allenes were performed in the presence of $Pt(PPh_3)_4$ or $Pt(dba)_2$ and a

Scheme 113

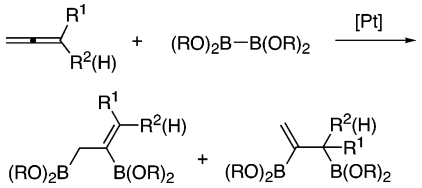


Scheme 114



phosphine, with the latter catalytic system even at room temperature (Scheme 115).[158] Low yields were observed due

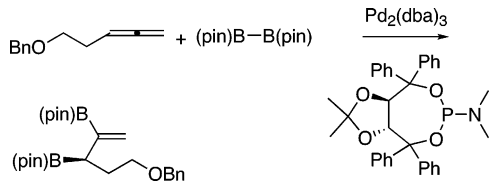
Scheme 115



to decomposition of the catalyst. The inefficiency of catalysts based on palladium to catalyze the reaction was believed to be due to unfavorable oxidative addition of the diborane to Pd(0). With substituted allenes, addition to the internal olefinic bond was preferred, although, with 1,1-disubstituted allenes, the opposite regiochemistry was observed. Heterosubstituents retarded the reaction due to slow insertion of the electron-rich double bond. The stoichiometric reaction between 1,2-heptadiene and *cis*-Pt($BO_2C_2Me_4$)$_2$(PPh_3)$_2$ afforded the same product as the catalytic reaction, but with a different isomeric ratio. The ratio of the two isomers was shown to depend on the nature of the platinum complex and the temperature ($Pt(PPh_3)_4$ at 80 °C or $Pt(dba)_2/PCy_3$ at 50 °C).

In the presence of chiral enantiopure phosphoramidites, highly enantioenriched adducts were obtained (Scheme 116).[159] Binaphthol-based phosphoramidites provided poor

Scheme 116

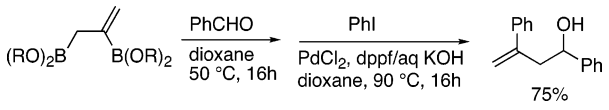


enantioselectivity, whereas those based on taddol afforded up to 91% ee. Modification of the ligand structure, achieved by replacing the phenyl substituents by 3,5-dimethylaryl groups, resulted in improved enantioselectivities (up to 98% ee).[160]

The product from diboration of allene was used for the synthesis of a homoallylic alcohol via reaction of the allylic boronate with benzaldehyde, followed by cross-coupling with iodobenzene (Scheme 117).[158]

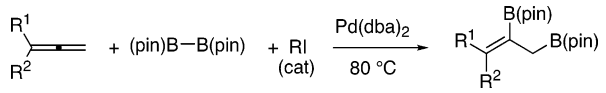
Single pot diboration/allylboration/oxidation afforded β-hydroxyketones with good levels of enantiocontrol.[160]

Scheme 117



Theoretical considerations[87] have suggested that the oxidative addition of B−B bonds to Pd(0) is an unfavored process and that palladium complexes therefore fail to catalyze diborations of unsaturated carbon−carbon bonds. However, it has been shown that it is possible to modify the reaction by employing a different approach. Cheng and co-workers showed that palladium-catalyzed diboration of allenes proceeds smoothly to give high yields of products with high regio- and stereoselectivities in the presence of a catalytic amount of an aryl or alkenyl iodide or iodine (Scheme 118).[161] The regioselectivity observed was different from that

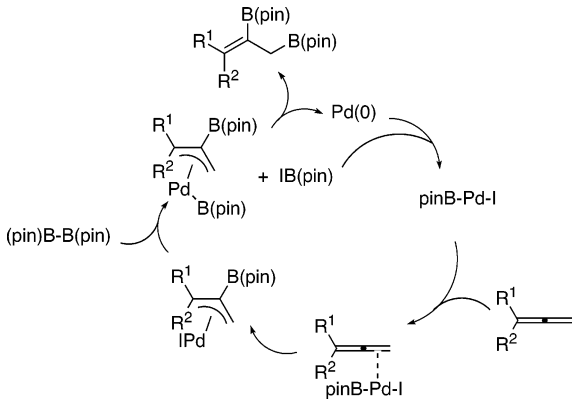
Scheme 118



of normal diborations; whereas one boryl group added to the central allenic carbon atom, the second boryl group added to the terminal unsaturated position of the allene.

The authors suggested that iodo(pinacolato)boron was generated and started the catalytic process by oxidative addition to Pd(0). The iodoboron intermediate is regenerated in the catalytic cycle, and therefore, only a catalytic amount of the iodide is required (Scheme 119). $Pt(PPh_3)_4$ did not

Scheme 119



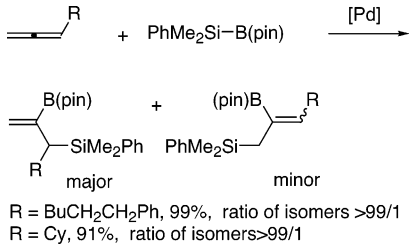
catalyze the reaction in the presence of organic iodides. The *Z*-stereoselectivity (93−95% *Z*-isomer) is a result of face selective coordination of Pd to the allene, leading to a syn-π-allyl palladium complex.

Other phosphine-free palladium complexes, such as Pd$(OAc)_2$, $PdCl_2(MeCN)_2$, and $PdCl_2(PhCN)_2$, also served as active catalysts for the process, whereas [PdCl(π-allyl)]$_2$ was less active and resulted in lower yield. The addition of phosphines inhibited the reaction.

4.6. B–Si

Silaborations of allenes catalyzed by palladium complexes with 2,6-xylyl isocyanide were shown by Ito and co-workers to proceed regioselectively with addition of the boron containing substituent to the central carbon atom of the 1,2-diene (Scheme 120).[162] With substituted allenes, reaction

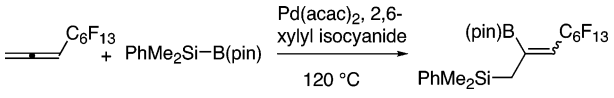
Scheme 120



occurred at the internal double bond, in analogy to the addition of disilanes.[141]

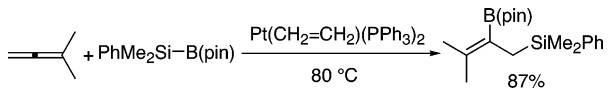
From an allene substituted with a perfluoroalkyl group, Ito obtained only the product from addition to the terminal double bond (Scheme 121).

Scheme 121



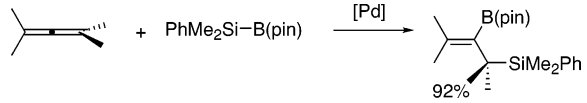
Tanaka and co-workers observed the same regiochemistry in additions using their Pd/etpo catalytic system.[163] However, in contrast to the situation with Pd, the reaction of 1,1-dimethylallene catalyzed by platinum complexes gave only the product formed by addition to the unsubstituted olefinic bond (Scheme 122).

Scheme 122



With the Pd/etpo catalytic system, even tetrasubstituted allenes afforded high yields of products (Scheme 123).

Scheme 123

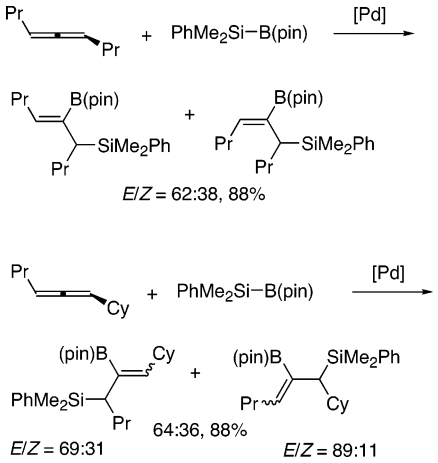


The regioselectivity of the silaboration of 1,2-dienes was considered in detail by Suginome and Ito.[164] For monosubstituted, 1,1-disubstituted, and 1,3-disubstituted allenes, the regioselectivity was dependent on the nature of the substituents and the nature of the catalyst as well as on the reaction conditions. The regioselectivity was usually very high. For unsymmetrical 1,3-disubstituted allenes, the regioselectivity and the *E*/*Z* selectivity were low, however (Scheme 124).

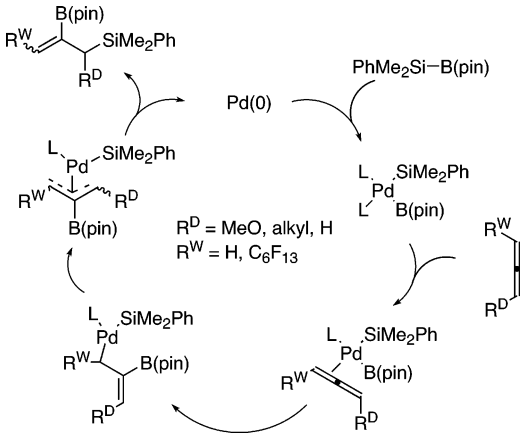
After oxidative addition of the borylsilane to Pd(0), coordination and insertion of the more electron deficient olefinic bond into the Pt−B bond occurred. Formation of π-allyl complex and reductive elimination gave the product (Scheme 125).

Recently, it was reported that Cp(allyl)Pd/PPh_3 serves as a very efficient catalytic system for silaborations of allenes, allowing the reactions to be performed at room temperature.[165] This catalyst was employed in an asymmetric version of the reaction, using chiral silylboranes (**66**−**68**) as well as chiral phosphorus ligands (**69**−**71**, Scheme 126). With

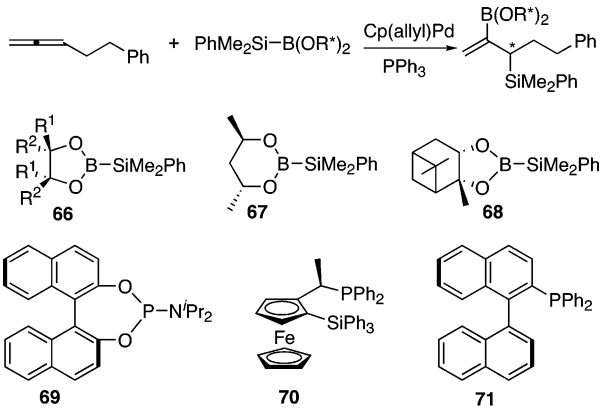
Scheme 124



Scheme 125



Scheme 126



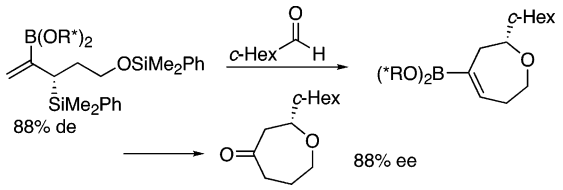
68/69: 24% de; **68/70**: 81% de; **68/71**: 89% de

boranes as the only source of chirality, low diastereoselectivity was observed, but in combination with chiral ligands, high selectivity was achieved.

It is interesting to note that the application of the catalyst containing ligand **71** to achiral silylborane led to a moderate enantioselectivity (68% ee), indicating that the chiral group on boron plays an important role in the enantioface discrimination. An enantioenriched allylsilane was subjected to Markó-type cyclization to afford a cyclic alkenylborane, which was oxidized to a ketone (Scheme 127).

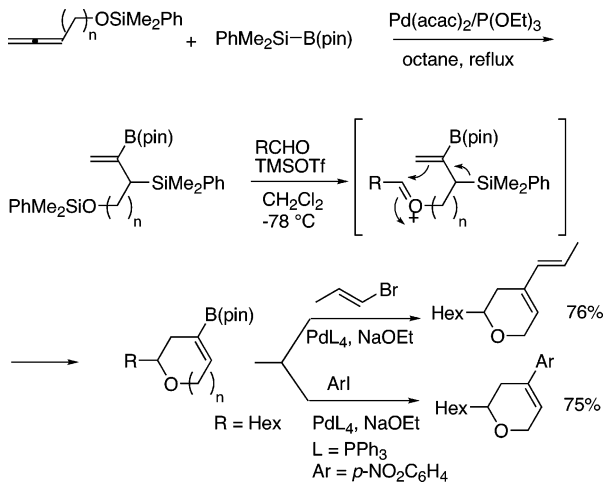
Since silaborations of allenes are highly regioselective, the products can be used for the preparation of functionalized

Scheme 127



alkenylboranes, by taking advantage of the reactivity of the allylsilane moiety (Scheme 128).[166]

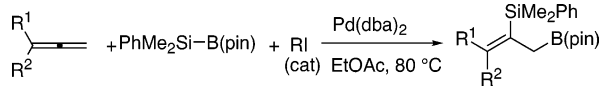
Scheme 128



A cascade cyclization giving *trans*-1,2-benzodecaline skeletons via sequential reaction of α-phenethyl-*β*-boryl-allylsilane with aldehydes was reported.[167]

The same methodology as for palladium-catalyzed diborations of allenes was used by Cheng and co-workers to perform palladium-catalyzed silaboration of allenes.[168] The authors showed that the addition of a catalytic amount of an organic iodide, iodine, or a silyl iodide initiated the reaction of silylboranes with allenes in the presence of phosphine-free palladium complexes (Scheme 129). The reaction

Scheme 129



proceeded with high regio- and stereoselectivities and produced high yields of products having the silyl substituent at the central carbon atom and the boryl group at the terminal unsubstituted carbon atom, i.e., as in the case of the diboration.

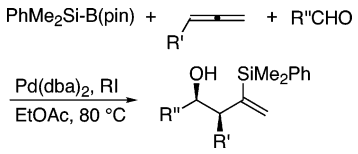
The regiochemistry was thus opposite to that observed under the conditions of Ito[162] and Tanaka.[163] The explanation for this difference was based, as for the analogous diboration,[161] on the formation of $PhMe_2SiI$ and its participation in the catalytic cycle.

As an application of the methodology, the authors showed that homoallylic alcohols could be obtained in high yields with excellent syn selectivity (>99%) using a one pot procedure with added aldehyde (Scheme 130). Desilylation with preserved stereochemistry was achieved by treatment with fluoride.

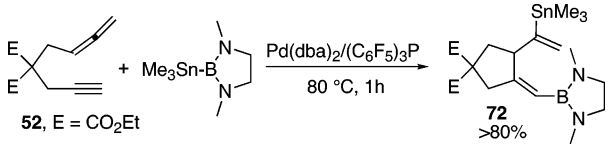
4.7. B–Sn

Stannaboration of allenyne **52** was shown by RajanBabu to lead to cyclized product **72** (Scheme 131).[146] Although

Scheme 130



Scheme 131

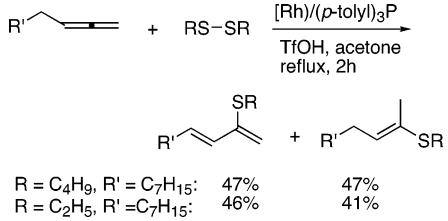


the reaction proceeded well by NMR, the product was isolated in a yield of merely 50%.

4.8. Se–Se and S–S

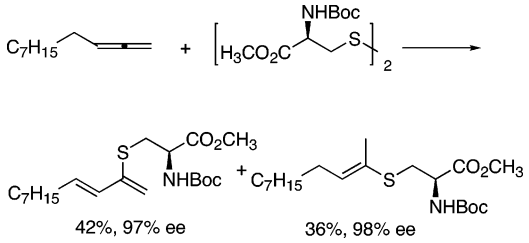
The addition of dialkyl disulfides to 1,2-dienes catalyzed by $RhH(PPh_3)_4$ was shown to lead to mixtures of monosubstituted dienes and alkenes (Scheme 132).[169]

Scheme 132



A cysteine derivative gave adducts without racemization (Scheme 133).

Scheme 133

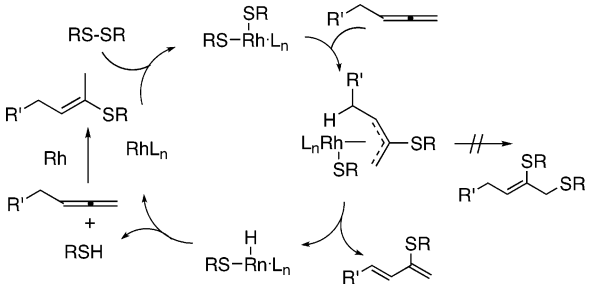


The same reaction proceeded with dialkyl diselenides, although low yields were obtained. In the additions of S−S and Se−Se bonds, the yields and the distribution of isomers were dependent on the nature of the phosphine ligand, but the influence was different for the two types of reactions.

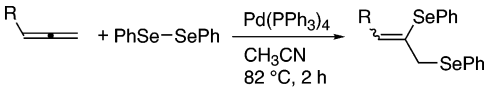
The mechanism was suggested to include oxidative addition of the disulfide followed by insertion of the allene to form a *π*-allyl complex. *β*-Elimination, being more rapid than reductive elimination, led to one product and a rhodium hydride. Reductive elimination and Rh-catalyzed reaction of allene with the thiol obtained explains the formation of the second product (Scheme 134).

Ogawa recently showed that diselenation of allenes is catalyzed by $Pd(PPh_3)_4$ (Scheme 135).[170] Use of polar solvents, in particular acetonitrile, afforded high yields of products obtained as mixtures of *E*- and *Z*-isomers by addition to the unsubstituted double bond; in contrast to the analogous reaction with alkynes,[96] low yields were obtained when the reactions were run in benzene. Divalent palladium complexes were inefficient as catalyst precursors. The

Scheme 134



Scheme 135



R = ^{n}Hex: 72% *E*/*Z* 49:51; R = ^{c}Hex: 96% *E*/*Z* 93:7;
R = Ph: 67% *E*/*Z* 49:51; R = ^{t}Bu: no reaction

reaction was suggested to proceed by oxidative addition of the diselenide to Pd(0) followed by insertion of the allene to form a vinylpalladium species. That an allylpalladium complex was not formed was shown by carbonylation of the intermediate palladium complex.

4.9. Comments on Additions to 1,2-Dienes

(1) Palladium-catalyzed additions of interelement compounds to 1,2-dienes are highly stereo- and regioselective, resulting in the attachment of one element to the central carbon atom and the other, linked to Pd, to the substituted terminal allenic carbon atom.

(2) Many exceptions to this "classical" (electronically controlled) pattern have been observed, particularly for distannations. These processes are reversible and lead to different isomers depending on whether the reaction occurs under kinetic or thermodynamic control.

(3) In silastannations, Si becomes attached to the central position as a result of insertion of the unsaturated moiety into the Pd−Si bond.

(4) As with diynes and enynes, synthetically versatile carbocyclizations take place with α,ω-bis(1,2-dienes).

(5) With monosubstituted 1,2-dienes, highly enantioselective diborations can be carried out.

(6) Diborations and silaborations of allenes with electron-withdrawing or sterically bulky substituents may lead to the formation of two isomers having B at the central position and the second element at the unsubstituted terminal position. This is particularly true for Pt-catalyzed reactions. Simple 1,2-addition provides an alternative explanation for the formation of such regioisomers.

(7) Diborations and silaborations of allenes are promoted by organic iodides and iodine.

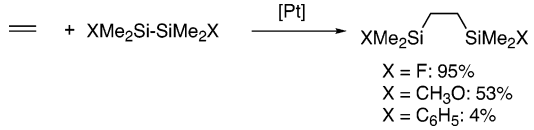
(8) Other E−E additions are not well studied or studied at all.

5. Additions to Alkenes

5.1. Si–Si

In comparison with additions to alkynes, 1,3-dienes, and 1,2-dienes, additions to olefins is a relatively new field. The first example was the disilylation of ethene, catalyzed by $Pt(PPh_3)_4$, published by Tanaka and co-workers in 1990 (Scheme 136).[171] High yields were observed only for 1,2-

Scheme 136



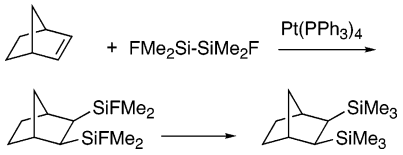
X = F: 95%
X = CH_3O: 53%
X = C_6H_5: 4%

difluoro-1,1,2,2-tetramethyldisilane, whereas disilanes with less electronegative substituents, such as 1,2-dimethoxy-1,1,2,2-tetramethyldisilane, resulted in moderate yields. Poor results obtained using 1,2-diphenyl-substituted disilane were thought to be due to the increased steric demand of the phenyl substituents.

The structure of the phosphine ligand proved to be important for the outcome of the reaction. Improved results were obtained with more electron donating and sterically less demanding phosphines. $Pd(PPh_3)_4$ and $PdCl_2(PhCN)_2$, which are known to catalyze disilylations of alkynes and dienes, were inactive in the present reaction.

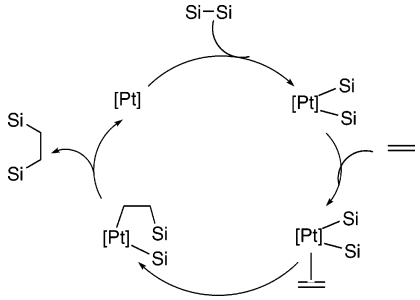
Using norbornene as the substrate, addition of the disilane was shown to be a cis process (Scheme 137).

Scheme 137



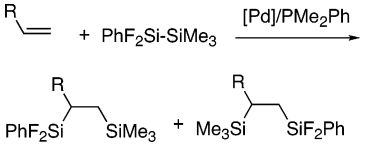
From model stoichiometric studies, a mechanism involving oxidative addition of the disilane to Pt(0) followed by insertion of ethylene into a Pt−Si bond and final reductive elimination was suggested (Scheme 138). Nevertheless, a

Scheme 138



palladium complex generated in situ from bis(π-allylpalladium chloride) and dimethylphenylphosphine was later shown to exhibit high reactivity as a catalyst for the disilylation of olefins using 1,1-difluoro-2,2,2-trimethyl-1-phenyldisilane (Scheme 139).[23] Modest regioselectivity was

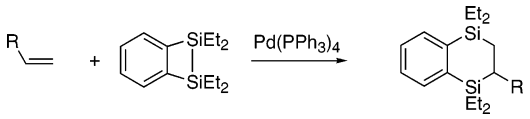
Scheme 139



observed in additions to unsymmetric olefins.

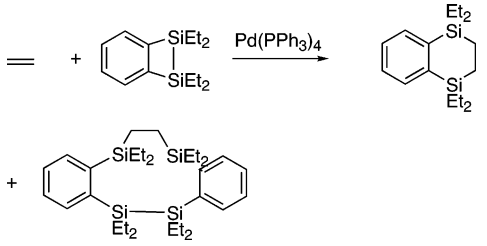
With a cyclic, strained disilane, additions to ethene, 1-hexene, and styrene took place even at room temperature using $Pd(PPh_3)_4$ as catalyst (Scheme 140).[32b]

Scheme 140



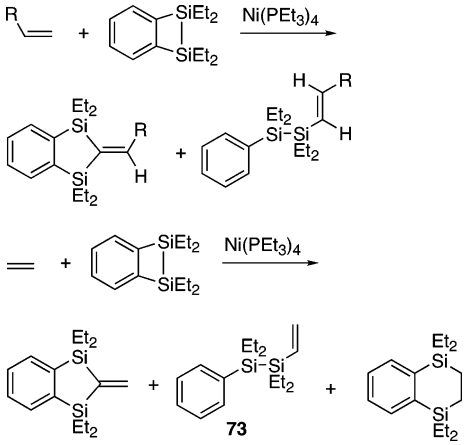
Ethene reacted in a different fashion from that of 1-hexene and styrene, producing two products (Scheme 141).

Scheme 141



Unlike the palladium-catalyzed addition of 3,4-dibenzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene to olefins,[32b] the nickel-catalyzed process did not result in simple 1,2-addition to the double bond.[125] Instead, products analogous to those obtained by reaction with dienes,[123] formed as a result of insertion of Ni into the sp^2-carbon−hydrogen bond, were obtained (Scheme 142). Of special interest is the formation

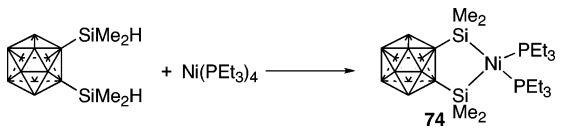
Scheme 142



of **73**, formed via cleavage of a C_{Ar}−Si bond. A product from 1,2-addition to the alkene was observed only in the case of ethene.

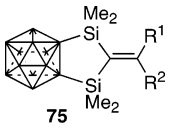
1,2-Bisdimethylsilylcarborane underwent the same type of additions to olefins catalyzed by $Ni(PEt_3)_4$.[15] The reaction involved Ni complex **74** (Scheme 143), which was able to

Scheme 143



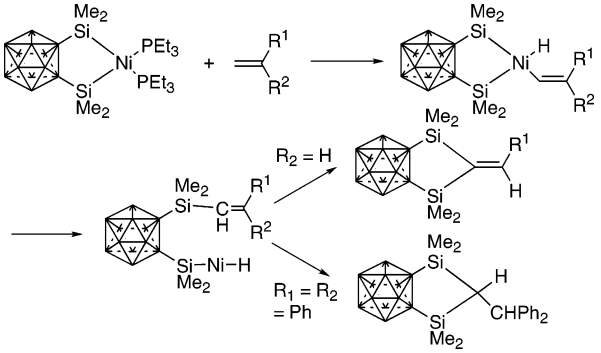
catalyze the reaction of the disilane with olefins such as 1-octene, but not the disilylation of styrene. However, the stoichiometric reaction of **74** with styrene afforded the disilylated product.

All reactions led to the same type of five-membered ring disilylene compounds **75**. The reaction was suggested to



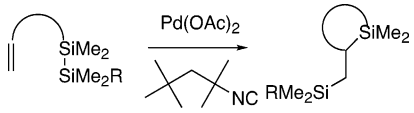
proceed as shown in Scheme 144.

Scheme 144



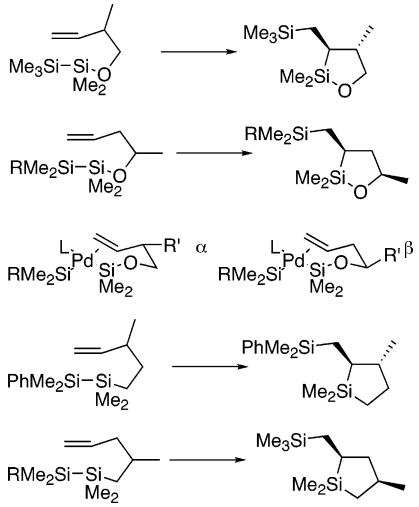
Ito and co-workers have also studied intramolecular disilylations.[172] In contrast to the situation with analogous intermolecular reactions,[171] disilanes lacking electron withdrawing groups reacted readily (Scheme 145).

Scheme 145



Disilanes tethered to the olefinic group by three atoms underwent stereo- and regioselective exo ring closure to afford five-membered ring products (Scheme 146). Alkenes

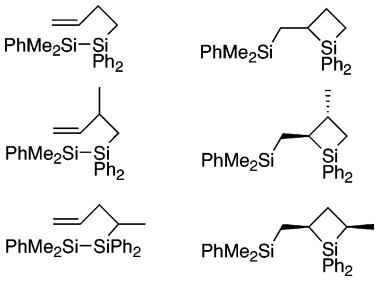
Scheme 146



with an allylic substituent gave trans-3,4-disubstituted products, whereas, from β-substituted alkenes, cis-3,5-disubstituted isomers were favored. The high diastereoselectivity observed was suggested to be due to a preference for a chairlike transition state over a boatlike one, with the α- and β-substituents occupying equatorial positions. Poor stereoselectivity was observed with γ-substituted substrates.

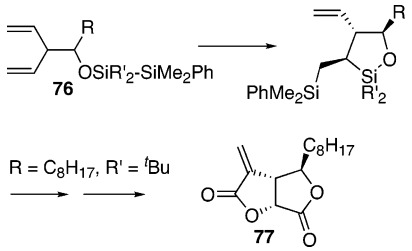
Disilanes tethered to the olefinic group by a two-carbon-atom tether reacted analogously to afford four-membered rings with high diastereoselectivity (Scheme 147).

Scheme 147



Intramolecular disilylation of dienol **76** was shown to proceed with high diastereofacial selectivity and moderate to high diastereotopic selectivity, affording the (*RS*,*RS*,*RS*)- and (*RS*,*SR*,*RS*)-isomers as the main products, with the ratio depending on the substituents on the dienol part as well as on the disilanyl part of the substrate (Scheme 148).[173] The

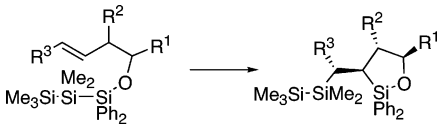
Scheme 148



protocol was used for the highly stereoselective synthesis of (−)-avenaciolide (**77**).

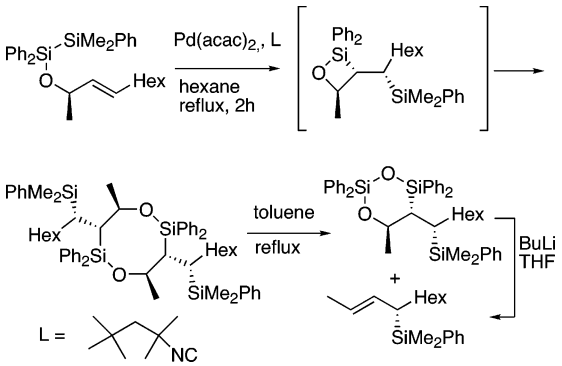
Intramolecular cyclization of trisilyl ethers of homoallylic alcohols also proceeded regio- and stereoselectively (Scheme 149).[174]

Scheme 149



Use of disilanes derived from enantiopure allylic alcohols afforded highly enriched allylsilanes.[175] In a recent study, it was shown that the initially formed 1,2-oxasiletanes dimerize to stereoselectively give 1,5-dioxa-2,6-disilacyclooctanes (Scheme 150).[176] The latter compounds underwent thermal

Scheme 150



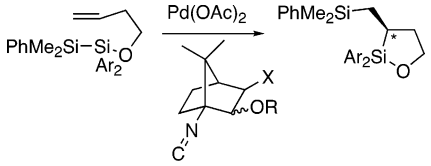
extrusion of (*E*)-allylsilanes along with 1,3-dioxa-2,5-disilacyclohexanes, which in turn underwent Peterson-type elimination by treatment with BuLi or PhLi to give (*E*)-allylsilanes. Excellent 1,3-chirality transfer was observed in the reactions. Enantioenriched allylsilanes were obtained from allylic alcohols of lower enantiomeric purity via separation of diastereomeric dimers.

The same protocol was applied to the synthesis of enantioenriched allylsilanes using polymer-bound disilanes.[177]

The stereodifferentiation in disubstituted olefinic disilanes is more complicated, but products having a cis relationship between the 3- and 5-substituents were favored.

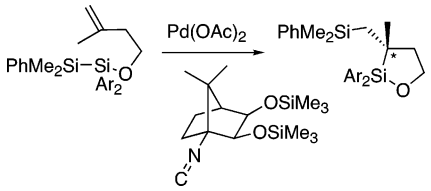
The use of chiral isocyanide, prepared from (+)-ketopinic acid, as ligand allowed the realization of an enantioselective intramolecular disilylation (Scheme 151).[178] The best results

Scheme 151



were obtained with disilanes derived from 3-buten-1-ol (87% yield, 64% ee) and 3-methyl-3-buten-1-ol (59% yield, 78% ee, Scheme 152).

Scheme 152

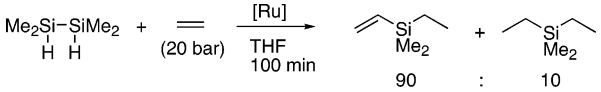


The enantioenriched allylsilanes were used in synthetic applications.[179]

An important application of this type of process is the synthesis of polyols. The authors demonstrated that the 1,2-oxasilolanes obtained were oxidized, with cleavage of the Si−O bond, to 1,2,4-triols with retention of configuration.[172] Using the same procedure, pentaols were also obtained. The intramolecular disilylation of the corresponding silylamides followed by oxidation, after removal of the catalyst, led to stereoselective formation of 4-acetamido-1,2-diols. The cyclic products obtained from disilanes derived from allylic alcohols were difficult to isolate but underwent oxidation to yield products with the expected stereochemistry.

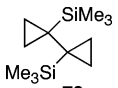
Both $RuH_2(H_2)_2(PCy_3)_2$ and the complex obtained by reaction with ethene, $RuH(C_2H_4)[P(\eta_3\text{-}C_6H_8)Cy_2]_3(PCy_3)$, catalyzed the reaction of ethene with $HMe_2Si-SiMe_2H$ to yield monosilanes, formed via cleavage of the Si−Si bond and functionalization of the Si−H bonds (Scheme 153).[180]

Scheme 153



The palladium-catalyzed additions of interelement bonds to bicyclopropylidene can hardly be considered as a simple addition to a double bond, as the substrate has features resembling those of cumulenes. However, to provide a clear classification, these substrates are included here together with

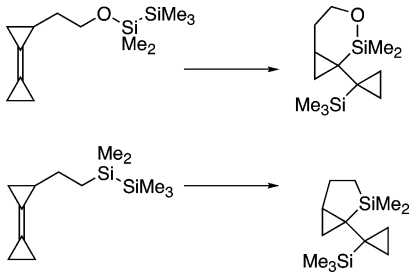
other cyclopropane derivatives. Using Ito's catalyst, $Pd(OAc)_2$−1,1,3,3-tetramethylbutyl isocyanide, high yields of products (**78** from bicyclopropylidene) were obtained.[181]



78

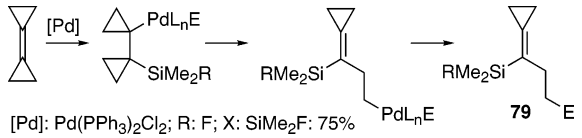
The intramolecular version of the reaction led to products with retention of both cyclopropane rings (Scheme 154).

Scheme 154



The presence of electron withdrawing groups at silicon did not result in simple disilylation of the olefinic bond, but afforded **79**, formed via cyclopropylmethyl to homoallyl rearrangement (Scheme 155). The reactivity and the type of

Scheme 155

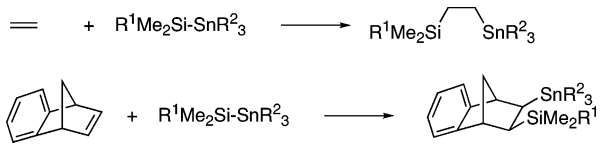


product formed in each case were dependent on the nature of the element attached to silicon, the nature of the ligand, and the source of palladium.

5.2. Si–Sn and Sn–Sn

Shortly after Tanaka's study of disilylations of olefins, Tsuji and co-workers showed that ethene and norbornene can be inserted into Si−Sn bonds using Pd complexes with trialkylphosphine ligands as catalysts (Scheme 156).[182] Rather

Scheme 156



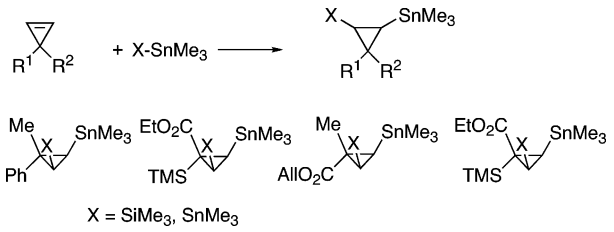
harsh conditions were required for the reaction to proceed, but the yields obtained were high. Silastannation of benzonorbornene resulted in a moderate yield, and 1-hexene, styrene, cyclohexene, and cyclopentene were unreactive.

The addition of Sn−Sn and Sn−Si bonds to 1,1-disubstituted cyclopropenes catalyzed by $Pd(OAc)_2$−*tert*-isooctyl isocyanide was shown to proceed easily at room temperature, providing high yields of tetrasubstituted cyclopropanes (Scheme 157).[183] The reactions proceeded with high facial selectivity to yield syn addition products, as controlled by steric factors.

5.3. B–B

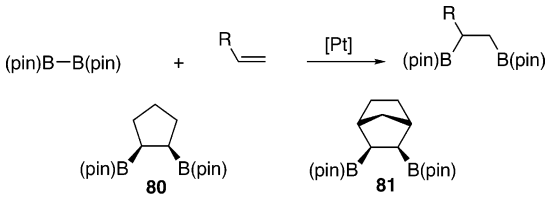
Diboration of vinylarenes was shown to be catalyzed by Rh(I) complexes with chelating phosphines.[184] Products

Scheme 157



resulting from β-elimination were obtained, but could be avoided using an Au(I) catalyst. Diborations of alkenes, catalyzed by Pt complexes, were reported by Miyaura and co-workers.[136] Terminal alkenes or cyclic alkenes with strained double bonds reacted with bis(pinacolato)diboron in the presence of $Pt(dba)_2$ under rather mild conditions to give diborylated products in high yields (Scheme 158). The

Scheme 158

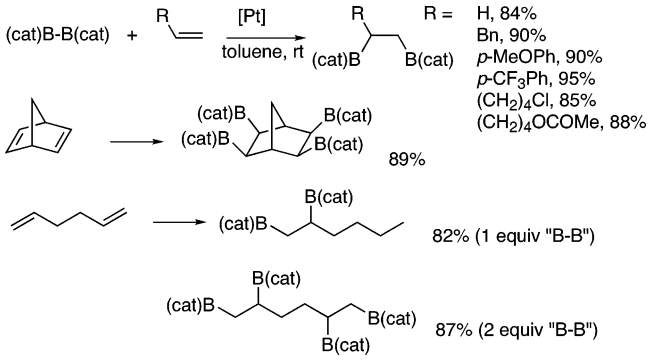


addition of ligands such as PPh_3, $AsPh_3$, or PCy_3 provided no advantages. The additions to cycloalkenes showed that the additions are stereoselective, proceeding in a syn manner (affording **80** and **81** from cyclopentene and norbornene, respectively). With cyclooctene, the yield was low, and terminal alkenes were unreactive.

Asymmetric diboration was achieved using chiral diboranes. Addition of the diborane derived from 1,2-diphenylethanediol (**48**, Chart 2) to arylalkenes catalyzed by phosphine-free Pt complexes afforded, in analogy to the addition of bis(pinacolato)diboron, moderate to high yields of the diborylated product with modest diastereoselectivity.[185] The selectivity was even lower using tartrate derivative **47**. The best results (80% yield, 60% de) were observed with *p*-methoxyphenylethene.

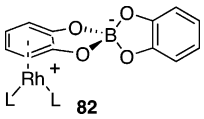
Iverson and Smith studied the addition of bis(catecholato)diboron using $Pt(cod)_2$ as a catalyst precursor and also found that the reaction led to high yields of products (Scheme 159).[186] The catalyst tolerated various functional groups.

Scheme 159



Internal olefins, with the exception of norbornene and norbornadiene, gave complex mixtures of products due to β-hydrogen elimination.

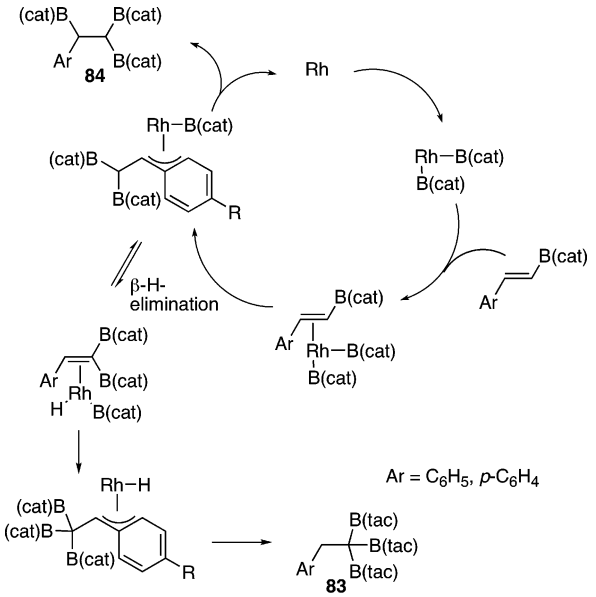
A zwitterionic Rh complex (**82**) was later shown to serve as an excellent catalyst for the diboration of alkenes, including norbornene and internal olefins, under mild conditions.[187]



82

Diboration of alkenes is a very complicated process due to the possibility of β-elimination with subsequent hydroboration, resulting in complex mixtures of products. Marder recently showed that Rh(I)-catalyzed diboration of (*E*)-styrylboronate esters gave predominantly either **83** or **84**, both containing three boryl groups, depending on the catalyst employed; the first type of product was formed by using Wilkinson's catalyst, and the second was formed by using $[Rh(COE)_2(\mu\text{-Cl})]_2$.[188] The catalytic cycle in Scheme 160 was

Scheme 160



suggested to explain the influence of the rhodium catalyst.

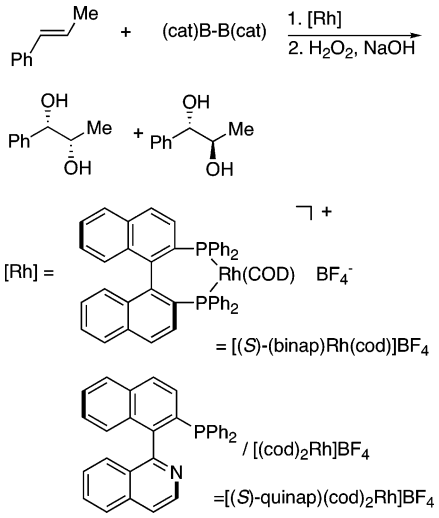
Diboration of simple alkenes using chiral Rh catalysts allowed Morken and co-workers to prepare highly enantioenriched 1,2-diols via oxidation of the primarily obtained diboranes (Scheme 161).[189] Higher syn/anti selectivity and enantioselectivity were observed with (*S*)-quinap/$[(cod)_2Rh]BF_4$ than with [(*S*)-(binap)Rh(cod)]BF_4, and replacement of 1,5-cyclooctadiene for norbornadiene resulted in improved results. The reaction appeared to be general for trans alkenes, whereas diboration of cis alkenes was less general.

Surprisingly, dihydronaphthalene and *cis*-β-methylstyrene gave products with opposite absolute configuration relative to indene. Monosubstituted and 1,1-disubstituted alkenes reacted with lower selectivity (Scheme 162).

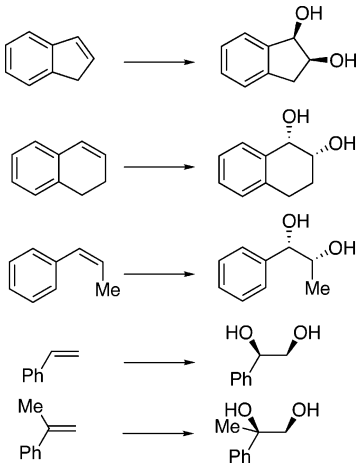
Diboration of *trans*-5-decene was achieved on a 1 g scale using merely 0.5 mol % of catalyst.[189] A variety of 1-alkenes were subjected to one-pot diboration−Suzuki cross-coupling, resulting in highly enantioselective formation of carbohydroxylated products (Scheme 163).[190]

In situ regioselective homologation of the 1,2-bis(catecholboronates) using $TMSCHN_2$ was also recently accomplished.[191]

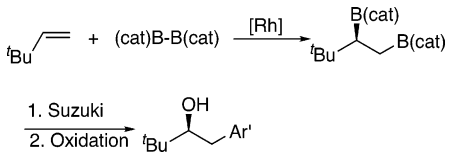
Scheme 161



Scheme 162



Scheme 163



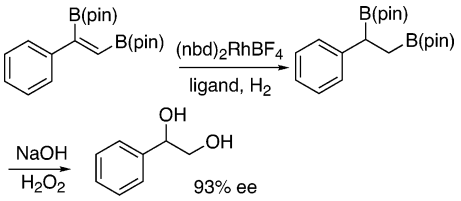
Silver(I) *N*-heterocyclic carbene complexes were recently employed as catalysts for the diboration of internal and terminal alkenes.[192] No chiral induction was observed when a carbene complex derived from menthol was used.

The influence of the nature of the catalyst and the electronic properties of the substrate on the competing β-elimination, affording mono(boronate)esters, in Rh-catalyzed diborations of vinylarenes was recently studied.[193]

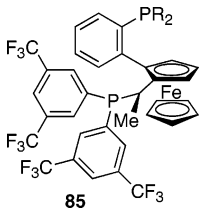
An alternative route to enantioenriched 1,2-diboronates consists of enantioselective rhodium-catalyzed hydrogenation of the products obtained by diboration of alkynes.[194] This strategy provides access to chiral diols, which were obtained with low enantioselectivity from diboration of monosubstituted olefins[189] (Scheme 164).

The solvent had a strong influence on the selectivity. The best results were obtained employing Walphos-W001 (**85**, R = Ph) and Walphos-W008 (**85**, R = Cy) as ligands. An excess of ligand was required for high enantioselectivity. Surprisingly, ligand-to-metal ratios below 1:1 afforded the

Scheme 164



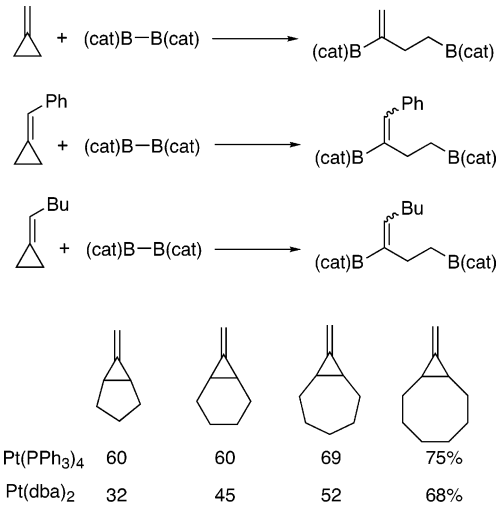
product with opposite absolute configuration, although with low enantioselectivity.



85

Many examples of diboration of methylenecyclopropanes to provide 2,4-bis(boryl)-1-butene derivatives were presented (Scheme 165).[195] The reactions were catalyzed by $Pt(PPh_3)_4$

Scheme 165

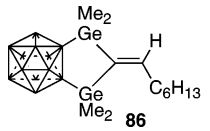


and $Pt(dba)_2$; the latter exhibited higher reactivity but sometimes resulted in lower yields due to decompostion of the ligand-free complex. The rate of reaction decreased with increased sterical hindrance in the substrate. Diboration of bicyclic substrates demonstrated that the reaction proceeded with retention of configuration at the stereogenic center to provide the cis-isomer as the sole product.

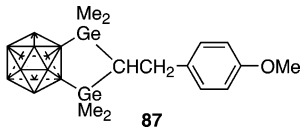
The suggested mechanism includes the addition of the diborane to the double bond and homoallylic rearrangement with cleavage of the less hindered proximal cyclopropane C–C bond.

5.4. Ge–Ge

Bisgermylation of octene, catalyzed by $Ni(PEt_3)_4$, using *o*-bis(dimethylgermyl)carborane proceeded in the same way as the analogous bissilylation, affording **86**.[15] When 4-vinylanisole was used as a substrate, the first step, the activation of the sp^2-carbon–hydrogen bond, was similar to that of the bissilylation, but then it proceeded in a different way to give **87**.[46] With 1,1-diphenylethene, a product analogous to that obtained from the disilylation was obtained.



86

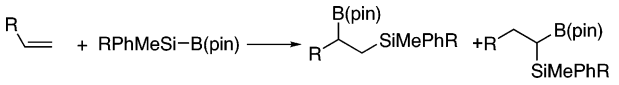


87

5.5. B–Si

The first example of heterometalation of an olefinic bond was the silaboration of double bonds by Ito and coworkers.[196] The reactions of $PhMe_2Si$–B(pin) and Ph_2MeSi–B(pin) with a variety of alkenes catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ exhibited good regioselectivity but resulted in modest yields of products (Scheme 166). $Pd(OAc)_2$–1,1,3,3-

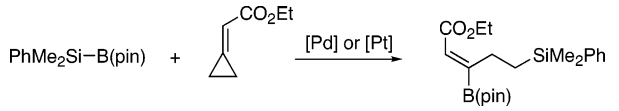
Scheme 166



tetramethylbutyl isocyanide did not catalyze the reaction. A catalytic cycle including oxidative addition of the borylsilane to Pt(0) and coordination, followed by migratory insertion of the olefin into the Pt–B bond and reductive elimination was proposed. The isolation of a small amount of α-boryl-4-methoxystyrene corroborates the suggested mechanism, since this compound may be formed by β-hydride elimination from the Pt alkyl intermediate. The formation of the minor regioisomer was explained by regioisomeric insertion of the double bond into the Pt–B bond, β-hydride elimination, reinsertion of the resulting alkenylborane into the Pt–H bond, and reductive elimination.

Recently, the addition of $PhMe_2Si$–B(pin) to highly strained methylenecyclopropanes was reported.[197] The reaction was found to be catalyzed by Pt and Pd complexes. Both types of reactions proceeded with ring opening with the same regioselectivity, affording products with the boron substituent in the vinylic position and with a homoallylic silyl group (Scheme 167). In the reactions of benzylidenecyclopropane,

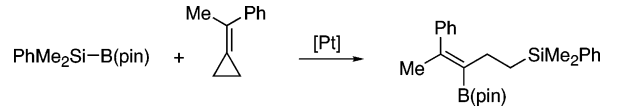
Scheme 167



different stereoisomers were formed using the two types of catalysts, however.

The influence of steric effects is evident from reaction with 1-methyl-1-phenylmethylenecyclopropane, where only one isomer was formed due to selective cleavage of the less sterically hindered proximal C–C bond (Scheme 168).

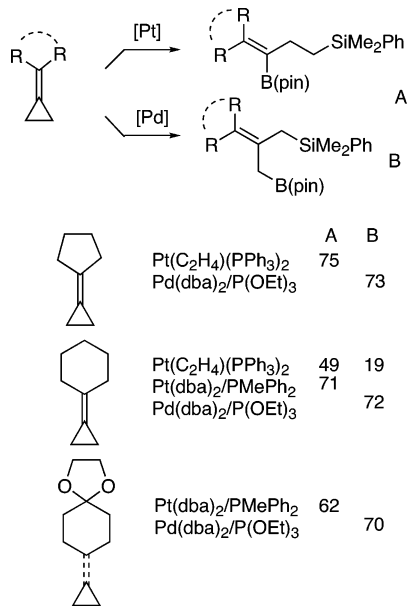
Scheme 168



For cycloalkylidenecyclopropanes, cleavage of proximal (A, Scheme 169) as well as distal (B) C–C bonds was observed, with the product obtained being dependent on the structure of the substrate and the nature of the catalyst.

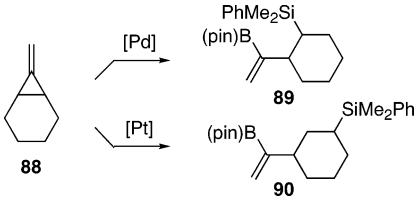
With methylenecyclopropane **88**, having substituents in the cyclopropane ring, an opposite situation was encountered, in that the Pd catalyst induced proximal bond cleavage affording **89**, whereas the Pt catalyst provided **90**, which may

Scheme 169



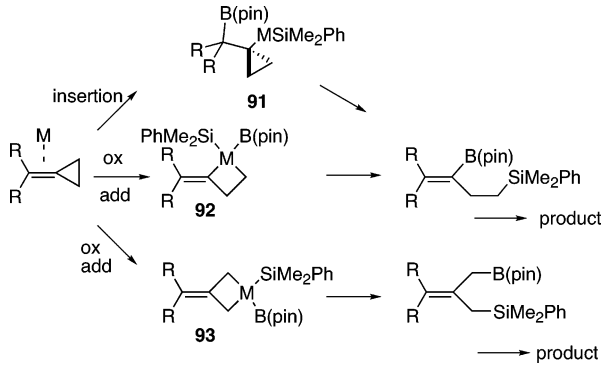
also be derived via the proximal C−C bond cleavage (Scheme 170).[197]

Scheme 170



Three types of intermediates (**90**, **91**, and **92**; Scheme 171)

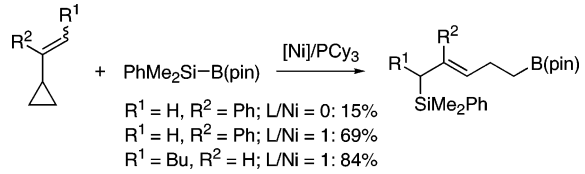
Scheme 171



can be considered.

Silaboration of vinylcyclopropanes catalyzed by a Ni(0) catalyst generated from $Ni(acac)_2$/DIBALH/PCy_3 was also studied by Suginome, Ito, and co-workers (Scheme 172).[10,198]

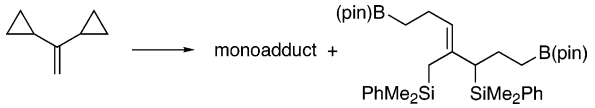
Scheme 172



The reaction proceeded regio- and stereoselectively with cleavage of the proximal C−C bond in the cyclopropane ring and formation of (*E*)-allylsilanes containing an *ω*-boronyl group.

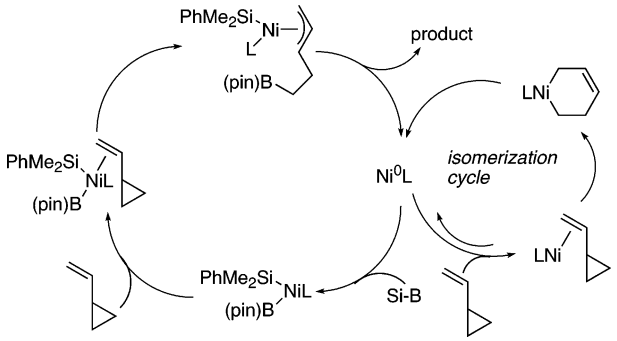
Double addition was observed for bis(cyclopropyl)ethene (Scheme 173).

Scheme 173



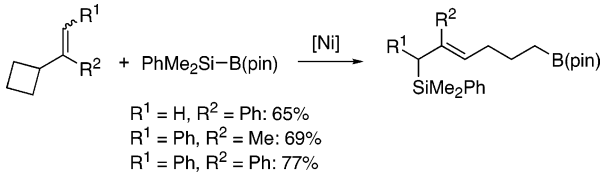
The mechanism was suggested to involve formation of a *π*-allyl nickel complex (Scheme 174).

Scheme 174



The reaction of vinylcyclobutanes proceeded analogously, with formation of different side products, however (Scheme 175).

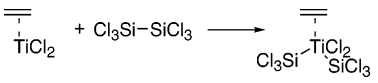
Scheme 175



5.6. Other Catalysts

We have so far considered transition metal complexes with Pt, Pd, Ni, and Rh as catalysts for interelement additions to double bonds, with their activities being dependent on the nature of the interelement compound. It is interesting to note that, according to a theoretical study, bissilylation of ethene also can be catalyzed by titanium dichloride (Scheme 176).[199]

Scheme 176



Reaction of gem-aryl-disubstituted methylenecyclopropanes with diaryl diselenide produced 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-enes in the presence of iodosobenzene diacetate in moderate to good yields.[200]

5.7. Comments on Additions to Alkenes

(1) Despite difficulties to achieve transition metal-catalyzed additions of element−element bonds to double bonds, some examples of this process are known, particularly additions of activated disilanes. Nonactivated disilanes are involved in intramolecular processes leading to diastereo-

selective formation of silacycles. Enantioselective cyclizations are possible in the presence of a chiral ligand.

(2) Diboration can be performed using Pt, Au, or Rh complexes as catalysts. Enantioselective diborations have been performed.

(3) Reactions of cyclic alkenes with Si−Si and B−B bonds have shown that the reactions are syn additions.

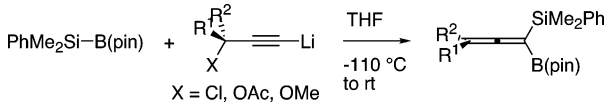
(4) The regiochemistry of silaborations catalyzed by Pd showed that insertion proceeds into the Pd−B bond, with formation of the Markovnikov product.

6. Miscellaneous

The same type of compounds as well as compounds with similar structures to those obtained from element−element additions may be obtained by alternative routes. Thus, disulfides were shown to react with alkynes and alkenes in the presence of gallium trichloride to provide good to high yields of 1,2-adducts, mainly with *E*-configuration, probably via a thiirenium ion which undergoes nucleophilic attack by sulfide.[201] Radical processes are known to yield mixtures of *E*- and *Z*-isomers.[202] Regio- and (*E*)-stereoselective distannation by $Me_3SnCuSMeLiBr$ of an unsymmetrically substituted alkyne was observed.[203]

Geminal functionalizations have also been achieved. Alkylidene-type lithium carbenoids were shown to react with diboranes and silylboranes to afford gem-dimetallic compounds.[204] Geminal silaboration with formation of 1-boryl-1-silylallenes was achieved by reaction of 3-chloro- or 3-alkoxyalkyn-1-yllithiums with (dimethylphenylsilyl)(pinacolato)boron (Scheme 177).[205]

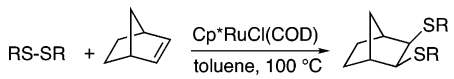
Scheme 177



Tri- and tetrametalated methanes, substituted with, e.g., S, Si, Ge, and Sn, were obtained via silaboration of halomethyllithiums with silylboranes.[206] During studies of dehydrogenative borylation of alkenes, conditions affording 1,1-diboration were found.[207]

Electrophilic addition of disulfides to alkenes catalyzed by Lewis acids was shown to lead to formation of dithioethers. The only known reaction of disulfides with alkenes catalyzed by transition metals is the reaction using ruthenium complexes (Scheme 178).[208]

Scheme 178



Palladium pincer complexes were shown to catalyze substitution of propargylic substrates by hexamethyldistannane, affording propargylstannanes and allenylstannanes in place of the commonly formed addition products.[209] The ratio of the two types of products was dependent on the nature of the substituents on the unsaturated compound. In the analogous process with silylstannes, exclusive silyl transfer to palladium took place, leading to allenylsilanes.[210]

The fact that insertion of alkynes and other unsaturated bonds takes place into a particular bond can sometimes be predicted from the dissociation energies of the bonds. The energies decrease in the following order: $Pt-SiMe_3$ (55.6) > $PtGeMe_3$ (43.4) > $Pt-SnMe_3$ (41.0). The energies of formation are as follows: Me−Si (75.7) > Me−Ge (63.2) > Me−Sn (53.9). Thus, insertion into the metal−Si bond is favored, in particular for Pd.

7. Conclusions and Outlook

Additions of interelement compounds to unsaturated carbon−carbon bonds constitute versatile synthetic procedures. Fundamental studies of oxidative additions of interelement compounds to low valent transition metal complexes and insertion of different types of unsaturated hydrocarbons have resulted in deep insight into mechanistic aspects as well as important synthetic methodology. However, for wider synthetic applications, many aspects remain to be elucidated. Higher chemoselectivity, regioselectivity, and enantioselectivity are needed for many processes. With this achieved, the reactions will serve as invaluable constituents of the synthetic tool box, and wide synthetic applications are to be expected.

8. Acknowledgments

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