

Element–Element Addition to Alkynes Catalyzed by the Group 10 Metals

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I. Introduction

The transition-metal-catalyzed addition of homo- and heteroelement–element compounds to triple bonds in one step opens a synthetic route to functionalized olefins. The replacement of the new carbon–element bonds by C–M, C–Hal, or C–C bonds (in alkylation, vinylation, and arylation via cross-cou-

pling) constitutes a convenient method for the preparation of tri- and tetrasubstituted olefins. When two different elements are used, it is possible to introduce the substituents step by step and thus to prepare olefins with different substituents at the ethylene bond.

A special feature of the addition of an element–element compound is its regio- and stereoselectivity. The reactions proceed in a syn fashion, resulting in products with configurations opposite to those formed by radical processes, other possible routes of element–element addition reactions.

Under which conditions are these reactions possible? First of all, the E–E' bond must be activated by a transition-metal complex to form an E–M–E' complex. Not only the qualities of the E–E' species, but also the nature of the metal and the electronic and steric properties of the ligands bound to the metal are crucial factors governing this process. Moreover, even if an E–M–E' complex is formed, this may not be reactive enough for insertion of the triple bond into either the E–M or the E'–M bond. Again, a variety of conditions must be fulfilled regarding the nature of the complex, including its conformation, geometry, stability, and reactivity as well as the properties of E, E', M, and the groups attached to them.

Little is known about the mechanisms of element–element additions to triple bonds. Several theoretical studies of these reactions have been presented, but their authors have drawn different conclusions when trying to identify the rate-determining step. The relative rates of the individual reaction steps may depend on the nature of the E–E' compounds selected as substrates and on the different theoretical models employed. It is usually unpredictable whether the triple bond will react with the M–E or the M–E' bond.

In this paper we are going to consider (1) the addition of E–E' species to carbon–carbon triple bonds (excluding many interesting reactions that are close to this topic, such as additions to olefins, conjugated dienes, allenes, and enones); (2) the formation of complexes, their stability, reactivity, geometry, and ability to catalyze the addition reactions; and (3) some synthetic applications of the adducts.



Irina Beletskaya received her Diploma in 1955, her Ph.D. in 1958, and her Doctor of Chemistry in 1963 from Moscow State University. The subject for the latter was Electrophilic Substitution at Saturated Carbon. She became a Full Professor in 1970 and in 1974 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 the recipient of the Lomonosov Prize (1979), the Mendeleev Prize (1982), and the Nesmeyanov Prize (1991). She is the author of over 500 articles and 4 monographs. Her current scientific interests are focussed on (i) transition-metal catalysis in organic synthesis; (ii) organic derivatives of lanthanides; and (iii) carbanions and nucleophilic aromatic substitution.



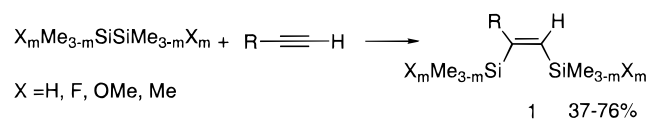
Christina Moberg studied chemistry at Stockholm University (B.Sc., 1970). She then moved to the Royal Institute of Technology (KTH) in Stockholm, where she received her Ph.D. degree in 1975 with Professor M. Nilsson. After a stay with Professor J. Normant at Université Paris 6, she worked for two years with Professor B. Åkermark at KTH, where she then continued independent work. She got a personal research position in organometallic chemistry from the Swedish Natural Science Research Council in 1989 and became Associate Professor in 1994 and Full Professor in 1997.

II. Insertion of Alkynes into Element–Element Bonds

A. Silicon–Silicon

Organosilicon compounds serve as important tools in organic synthesis. They also occur as building blocks in various synthetic materials. The activation of the silicon–silicon bond has been studied extensively, as it creates opportunities for a variety of useful reactions which can be performed catalytically. The reactions reported include additions to unsaturated molecules as well as isomerizations, syntheses

Scheme 1

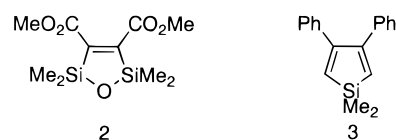


of silylenes, oligomerizations, and polymerizations of disilanes.^{1,2}

Kumada and Sakurai were the first to perform palladium-catalyzed disilylation of acetylenes. Kumada and his group showed that activated disilanes $\text{Me}_n\text{Si}_2\text{X}_{6-n}$ ($n = 2-4$, X = H, F, Cl, or OMe) could add to various alkynes to give products of double silylation (**1**, Scheme 1).^{3,4}

Sakurai and his group have shown that disilylation proceeds smoothly with strained disilanes. The success of these reactions depends on the conditions, the nature of the alkyne, and, in particular, the nature of the catalytic system (metal and ligand).⁵

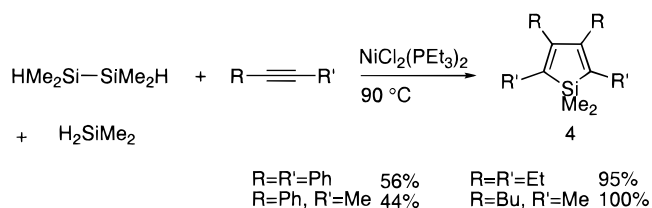
The reaction of an activated disilane, e.g., $\text{HMe}_2\text{-SiSiMe}_2\text{H}$, with dimethyl acetylenedicarboxylate in the presence of $\text{PdCl}_2(\text{PET}_3)_2$ in refluxing benzene gave 40% of the *syn*-adduct and a small amount of a cyclic disiloxane (**2**).



Using $\text{HMe}_2\text{SiSiMe}_3$, a 43% yield of the corresponding product was obtained, whereas $\text{Me}_3\text{SiSiMe}_3$ did not undergo the reaction. Phenylacetylene gave 1,1-dimethyl-3,4-diphenyl-1-sila-2,4-cyclopentadiene (**3**) as the major product (45%), along with doubly silylated styrene (25%).

A nickel complex, $\text{NiCl}_2(\text{PET}_3)_2$, was shown to catalyze the addition of *sym*-tetramethyldisilane to a variety of acetylenes to give silacyclopentadiene derivatives (**4**) in good yields (Scheme 2).⁶

Scheme 2



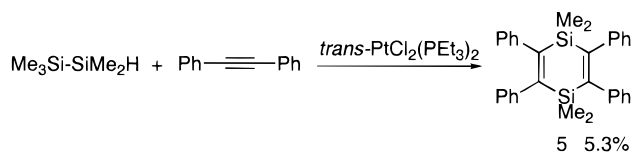
The formation of silacyclopentadiene is a result of disproportionation of bis(dimethylsilicon hydrides) under the action of metal complexes and can be explained by the formation of “ Me_2Si ” (dimethylsilylene) by α -elimination and its trapping by alkynes.

The same type of reaction was observed with diphenylacetylene in a Pt-catalyzed reaction to give a disilacyclohexadiene (**5**, Scheme 3).⁷

Fluorinated disilanes, $\text{F}_m\text{Me}_{3-m}\text{SiSiMe}_{3-m}\text{F}_m$, react with terminal and internal acetylenes in the presence of $\text{Pd}(\text{PPh}_3)_4$ or $\text{PdCl}_2(\text{PPh}_3)_2$ to yield the products **6** (Scheme 4).⁸

Chlorosilanes⁹ ($\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$) and alkoxy silanes⁸ ($\text{Me}_n\text{Si}_2(\text{OMe})_{6-n}$) react with acetylenes at 110 °C in

Scheme 3



Scheme 4

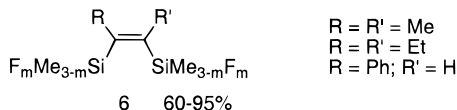


Table 1. Yields of Products Obtained by Addition of Disilanes to Phenylacetylene

disilane	yield (%)
(MeO)Me ₂ SiSiMe ₂ (OMe)	78
(MeO) ₂ MeSiSiMe ₂ (OMe)	75
(MeO) ₂ MeSiSiMe(OMe) ₂	71
(MeO)Me ₂ SiSiMe ₃	18–26
Cl ₂ MeSiSiMeCl ₂	96
Cl ₂ MeSiSiMe ₂ Cl	78
ClMe ₂ SiSiMe ₃	55

Scheme 5

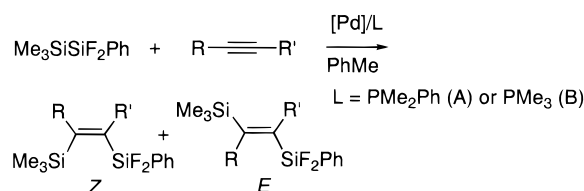


Table 2. Yields of Products Obtained by Addition of Disilanes to Alkynes, Scheme 5

alkyne	temp	catalyst	yield (%)	Z:E
R = R' = Ph	rt	A (B)	95	>99:1
R = R' = Et	60 °C	B	76	99:1
R = Ph, R' = Me	40 °C	B	96	99:1
R = n-C ₆ H ₁₃ , R' = H	rt	A	94	87:13
R = Ph, R' = H	60 °C	A	94	89:11

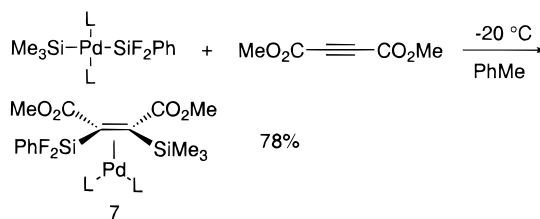
the same manner, forming mainly Z isomers. Reactions with phenylacetylene gave the yields shown in Table 1.

Reactions of alkoxydisilanes (MeO)_nMe_{3-n}SiSiMe_{3-n}(OMe)_n were also performed with several other acetylenes.¹⁰ A high yield of a 1:1 adduct was obtained with butylacetylene (76% using (MeO)Me₂SiSiMe₂(OMe)), whereas lower yields (30–50%) were obtained with (trimethylsilyl)acetylene and unsubstituted acetylene.

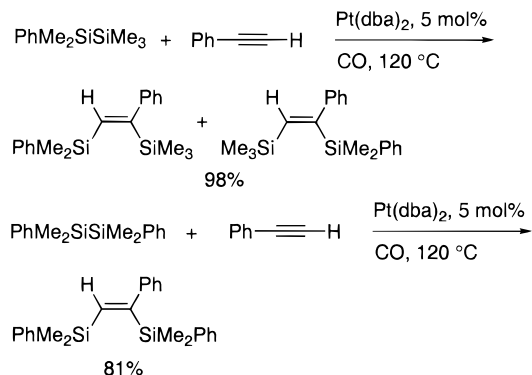
A highly reactive catalytic system, based on the catalyst obtained in situ from [Pd(η³-allyl)Cl]₂ and PMe₂Ph, was employed by Ozawa, Sugawara, and Hayashi for Me₃SiSiF₂Ph disilylation of acetylenes (Scheme 5, Table 2).¹¹

The *trans*-bis(silyl)palladium complexes were isolated in quantitative yields from reactions of L₂Pd-styrene complexes (L = PMe₂Ph, PMe₃) with Me₃SiSiPhF₂ and characterized by ¹H, ¹⁹F, and ³¹P NMR spectroscopy. The complex with L = PMe₂Ph reacted with diphenylacetylene at low temperature to give the bis-silylation product in 82% yield. It also reacted with dimethyl acetylenedicarboxylate to give the novel palladium complex of the product (7), which

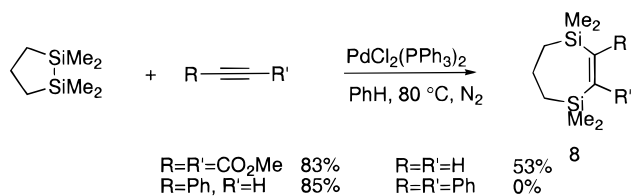
Scheme 6



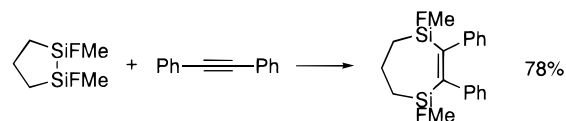
Scheme 7



Scheme 8



Scheme 9



was characterized by X-ray structural analysis (Scheme 6).

Disilanes with phenyl groups showed high activity in the Pt(0)-catalyzed addition of disilanes to 1,3-dienes under CO pressure, while those with, e.g., alkyl, benzyl, vinyl, and allyl groups were unreactive.¹² A similar effect of the phenyl group was observed in the Pt(dba)₂-catalyzed addition of disilanes to acetylenes (Scheme 7). The reason for this was thought to be π-coordination of Pt(0) to the aromatic ring.

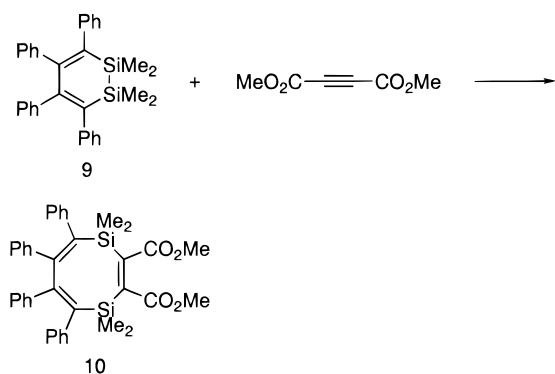
The use of Pd(dba)₂ under the same conditions was shown to lead to the same products.

When PdCl₂(PPh₃)₂ was used as a catalyst precursor, additions of acetylenes to highly strained cyclic molecules containing Si-Si bonds led to cyclic compounds **8** in yields varying from 53% to 85% (Scheme 8).⁵

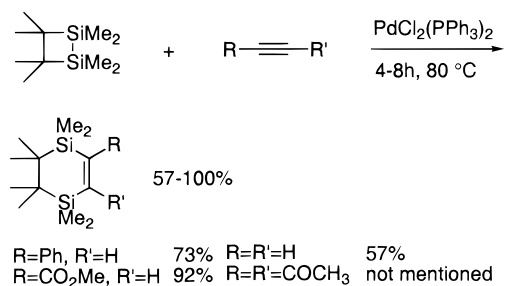
With fluorinated disilanes the yields were high (Scheme 9).

1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,5-cyclohexadiene (**9**) gave an eight-membered ring compound **10** in 73% yield upon reaction with dimethyl acetylenedicarboxylate (Scheme 10).

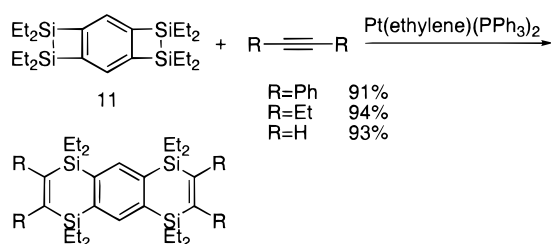
Scheme 10



Scheme 11



Scheme 12



Several other palladium complexes such as $\text{PdCl}_2(\text{MeCN})_2$, $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$, $\text{PdCl}_2(\text{PET}_3)_2$, and $\text{Pd}(\text{PPh}_3)_4$ were shown to be effective, but their use resulted in the formation of byproducts. Unstrained hexaorganodisilanes gave poor results.

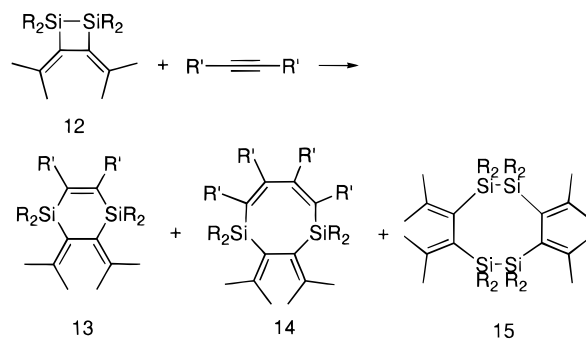
The reaction of a 1,2-disilacyclobutane proceeded only with terminal acetylenes and activated internal acetylenes (Scheme 11).¹³ High yields were obtained only when activated acetylenes were used. Nickel complexes also catalyzed this reaction.

Octaethylbenzobisdisilacyclobutane **11** reacted with terminal as well as internal alkynes in the presence of $\text{Pt}(\text{ethylene})(\text{PPh}_3)_2$ to form high yields of 1:2 adducts (Scheme 12).¹⁴

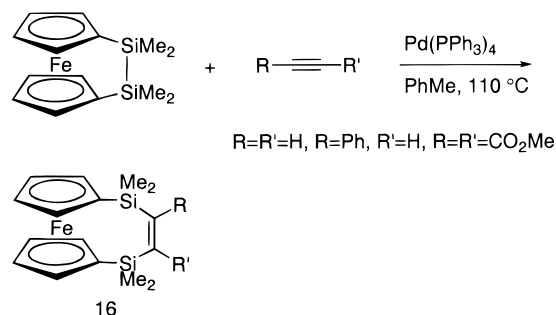
$\text{Pd}(\text{PPh}_3)_4$ was found to be an even more efficient catalyst than the $\text{Pt}(0)$ complex, affording the same products in similar yields but in shorter time. No 1:1 adduct was detected when the reaction was followed by GLC. It was suggested that the metal complex formed by the reductive elimination following the first insertion reaction was not free but interacted with the second Si-Si moiety, forming the final product.

Peralkylated 3,4-bis(alkylidene)-1,2-disilacyclobutanes (**12**), other examples of strained disilanes, reacted with acetylenes in the presence of the palladium or platinum complexes $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{MeCN})_2$, and $\text{Pt}(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)_2$ giving the prod-

Scheme 13



Scheme 14

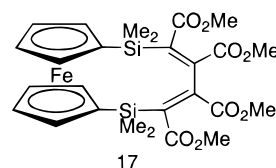


ucts of single insertion (**13**) as well as of double insertion (**14**).¹⁵ Competitive dimerization (to **15**) took place in the presence of $\text{PdCl}_2(\text{PhCN})_2$ (Scheme 13).

The ring-opening polymerization of cyclic compounds containing inorganic or organometallic units affords new macromolecules with novel and potentially useful properties.

Disilylation was used as a route to cyclic organometallic species containing ferrocene moieties together with both organosilicon and unsaturated hydrocarbon units (Scheme 14).¹⁶ The reactions with acetylene and phenylacetylene gave one single product each (**16**); the product obtained with acetylene was characterized by X-ray structural analysis.

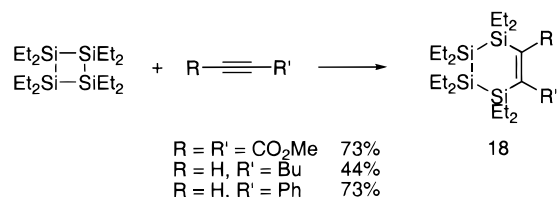
The reaction with the activated alkyne dimethyl acetylenedicarboxylate yielded a mixture of products. The main product was obtained by monoinsertion, but a product (**17**) formed by dimerization of the alkyne was also observed (3–5%).



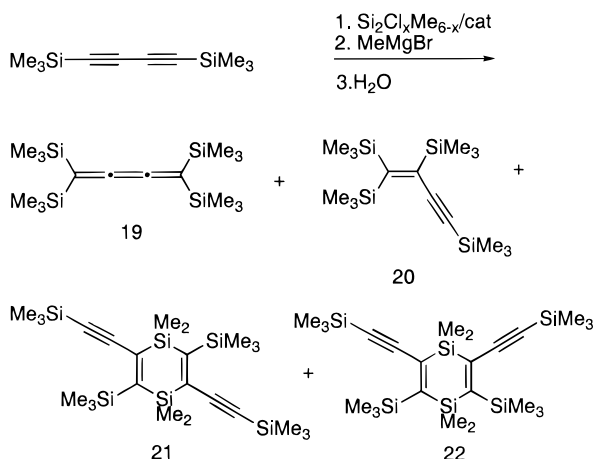
The $\text{Pd}(\text{PPh}_3)_4$ -catalyzed insertion of alkynes into strained cyclotetrasilanes led to 3,4,5,6-tetrasilacyclohexenes (**18**) along with 1,4-disilacyclohexa-2,5-dienes and a small amount of 3,4,5-trisilacyclopentenes (Scheme 15).¹⁷

The double silylation of a conjugated diacetylene, bis(trimethylsilyl)butadiyne, by $\text{Si}_2\text{Cl}_x\text{Me}_{6-x}$ (Scheme 16) as well as by other disilanes in the presence of a palladium catalyst, $\text{PdCl}_2(\text{PET}_3)_2$, was shown after methylation to give a mixture of 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**19**) and 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**20**), along with small

Scheme 15



Scheme 16

Table 3. Yields of **13** and **14** Obtained by Addition of **12** to Alkynes

alkyne	catalyst	yield (%) of 13	yield (%) of 14
R = Ph, R' = CO ₂ Me	Pd(PPh ₃) ₄	68	18
R = Me, R' = CO ₂ Me	PdCl ₂ (PhCN) ₂	30	47
R = Et, R' = CO ₂ Me	Pd(PPh ₃) ₄	77	
R = Et, R' = Ph	Pt(CH ₂ =CH ₂) ₂ (PPh ₃) ₂	71	
R = Me, R' = Ph	Pd(PPh ₃) ₄	87	
R = Ph, R' = H	Pt(CH ₂ =CH ₂) ₂ (PPh ₃) ₂	82	
R = Ph, R' = H	Pd(PPh ₃) ₄	80	

Table 4. Yields of Butatriene and Butenyne from Double Silylation as in Scheme 16

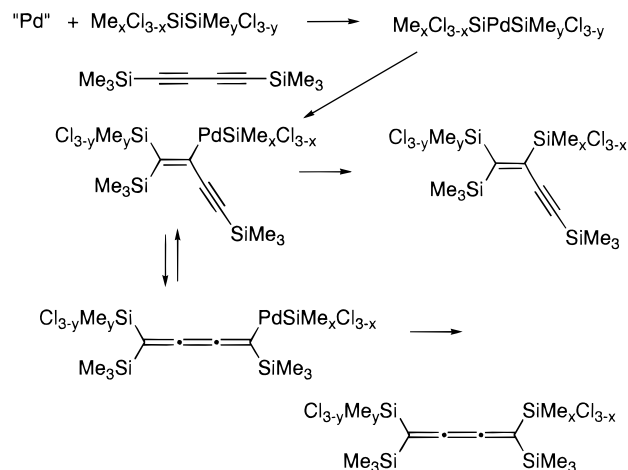
	butatriene (%)	butenyne (%)
Me ₂ ClSiSiClMe ₂	61	<i>E:Z</i> 1:1
Me ₂ FSiSiFMe ₂	86	<i>E:Z</i> not determined
Me ₂ (<i>i</i> PrO)SiSi(<i>i</i> Pr)Me ₂	55	<i>E:Z</i> 1:1
Me ₂ PhSiSiPhMe ₂	13	26 <i>E:Z</i> 1:1

amounts of **21** and **22**. The disilylated products primarily formed were obtained as mixtures of *E* and *Z* isomers (Table 4).¹⁸

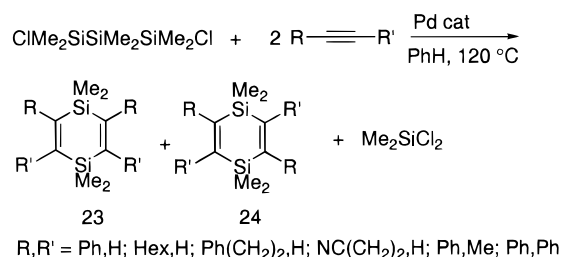
1,1,4,4-Tetrakis(trimethylsilyl)butatriene (**19**) and 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**20**) were the major products, after methylation, with PdCl₂(PET₃)₂, PdCl₂(PMePh₂)₂, and PdCl₂(PMe₂Ph)₂ as catalysts.¹⁹ The ratio between the two products depended on the nature of the silane and of the catalyst. For example, an enyne was obtained as the single product of the reaction of (Me₂Cl)₂Si₂ or Me₂ClSiSiMe₃ catalyzed by PdCl₂(PET₃)₂ or PdCl₂[P(CH₂-Ph)₃]₂. Highly chlorinated disilanes mainly underwent 1,4-disilylation, giving trienes.

The chemical properties of **19** were studied in reactions such as hydrogenations, hydrosilylations, and oxidations.²⁰

Scheme 17



Scheme 18



Many palladium complexes are not active enough to catalyze the disilylation of alkynes. Examples are PdCl₂(PhCN)₂, PdCl₂(dppp), PdCl₂[P(OMe)₃]₂, and Pt-(PMe₃)₄, all of which are totally inactive.

The addition reaction proceeded in a syn manner, but the primary product isomerized into a 1:1 mixture of *E* and *Z* isomers during GLC analysis and upon heating. A mechanism was proposed, which did not involve direct 1,4-addition but isomerization of the palladium complex first obtained by 1,2-addition.¹⁹ This isomerization proceeds better the more chlorinated the disilanes are, since these ligands prevent the reductive elimination step (Scheme 17).

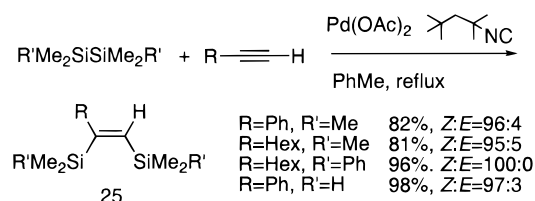
The 1,4-disilacyclohexa-2,5-dienes **23** and **24**, suggested as byproducts in the above reactions,⁷ appeared to be the major products in the reactions of terminal and internal acetylenes with Cl(SiMe₂)₃Cl, catalyzed by PdCl₂L₂ complexes (L = PAr₃ or AsPh₃, Ar = Ph, *o*-Tol, *p*-Tol, *p*-FC₆H₄) (Scheme 18).²¹ Ligands such as trialkylphosphines and bidentate phosphines, including dppe and dppf, or MeCN were shown not to be effective. Nickel and platinum complexes did not catalyze the reaction. Replacement of Cl in the disilane by F or OMe led to low yields of the products.

The palladium-catalyzed reaction of (MeO)Me₂SiSiMe₂(OMe) with cyclopropylacetylene led solely to the product formed by addition to the triple bond.²²

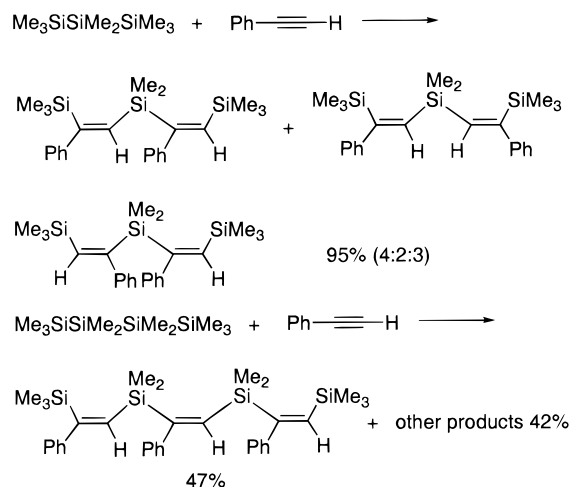
As can be seen, the disilylation of alkynes could be done satisfactorily with disilanes carrying electronegative substituents. Disilylation of hexaalkyl-disilanes gave very low yields.^{18,21}

Several new catalytic systems were suggested to make the reaction possible not only with disilanes with electronegative groups or strained rings but also with ordinary disilanes with nonactivated Si-Si

Scheme 19



Scheme 20



bonds. Ito et al. suggested a new catalyst, $Pd(OAc)_2/1,1,3,3$ -tetramethylbutylisocyanide, which catalyzed intermolecular as well as intramolecular reactions with nonactivated disilanes;²³ additions using mainly this catalyst have been summarized.²⁴ The reactions proceeded in a syn fashion with phenylacetylene and other terminal acetylenes, giving the *Z* isomers **25** in high yields and with high regioselectivity (Scheme 19).

A significant feature and a drawback of the reaction is the fact that the palladium catalyst requires the presence of excess ligand.

The reaction has been applied to polysilanes (Scheme 20).²³

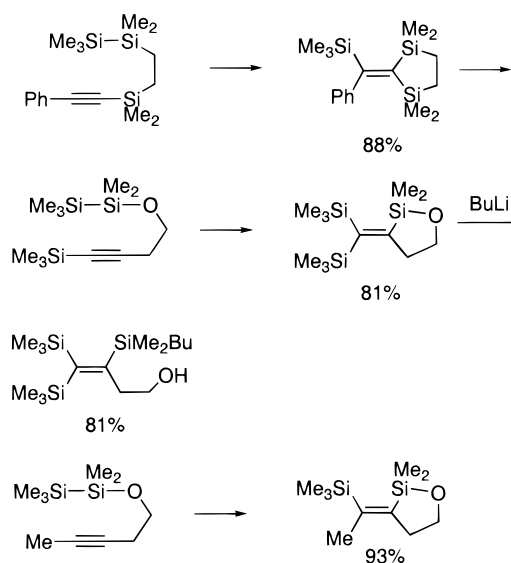
Several intramolecular reactions giving cyclic silicon-containing products have also been carried out (Scheme 21).²³

Due to severe steric hindrance, the reaction proceeded sluggishly with alkynes bearing two silyl groups next to their triple bond.²⁵ However, at high pressure (1.1×10^9 Pa) and 135–140 °C, a new tetrakis(organosilyl)ethene (**26**), in which one olefinic carbon atom was part of a heterocyclic ring, was obtained in 66% yield (Scheme 22). The authors mentioned that the same procedure had been applied by Sakurai et al.²⁶

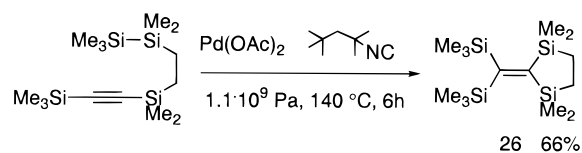
In an X-ray crystallographic investigation, the product, in contrast to the acyclic starting compound, showed neither twisting nor pyramidalization of the sp^2 carbon atom. The study showed that the four silicon atoms were situated essentially in one plane.²⁵

The intramolecular Si–Si addition to propargylic alcohols led to the discovery of a new strategy for making chiral alkenylsilanes. According to NMR data, a reaction of a disilanyl ether gave a product with the Si–O bond in a strained four-membered ring

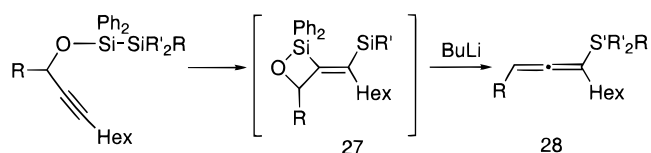
Scheme 21



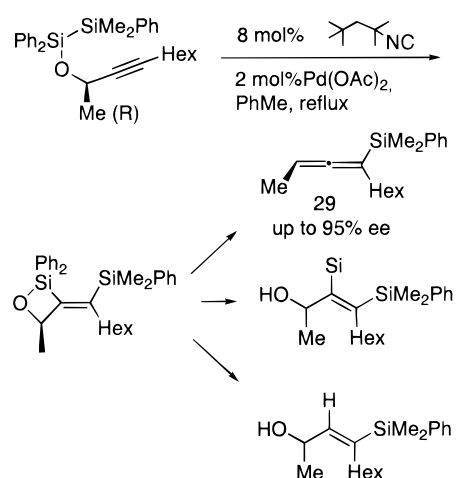
Scheme 22



Scheme 23



Scheme 24

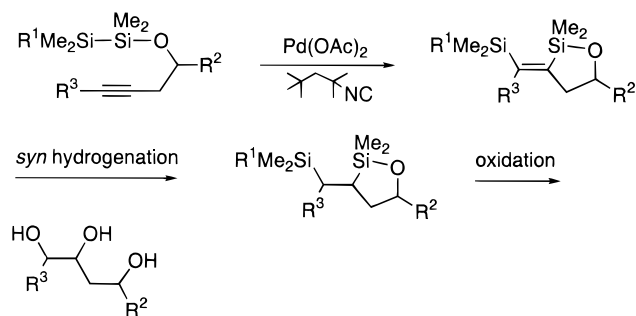


(**27**).²⁷ The product could be converted to an allenylsilane **28** by treatment with butyllithium (Scheme 23).

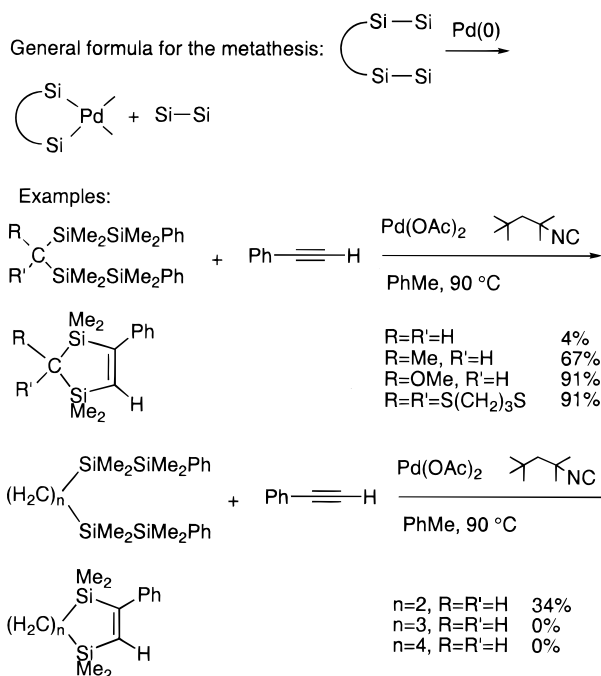
Highly enantioenriched allenylsilanes **29** can be obtained from chiral enantiopure propargylic alcohols, e.g., (*R*)-dec-3-yn-2-ol (Scheme 24).

Stereoselective syntheses of 1,2,4-triols were achieved via intramolecular disilylation of triple bonds (Scheme 25).²⁸ The reaction was performed with a variety of compounds to give high yields of five- and six-membered cyclic oxasilolanes.

Scheme 25



Scheme 26



Bis(disilyl)alkanes react with phenylacetylenes in the presence of catalytic amounts of $\text{Pd}(\text{OAc})_2$ and 1,1,3,3-tetramethylbutylisocyanide (Ito's catalyst²³), giving the disilylation product and disilane (Scheme 26). The process can be considered as a metathesis of the Si-Si bond.

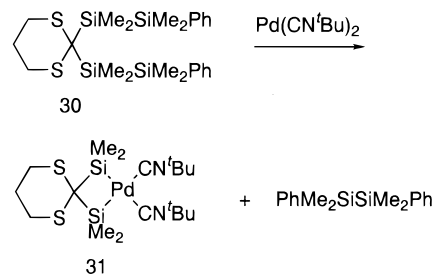
The yield of cyclic disilylation product was low when the nonsubstituted ($\text{R}^1 = \text{R}^2 = \text{H}$) tetrasilane was employed but from good to high with substituted tetrasilanes. Five-membered rings were easily formed, the yield of a six-membered ring product was moderate, and only acyclic products were formed with $n = 3$ and 4.

Stoichiometric reaction of $\text{Pd}(\text{CN}^t\text{Bu})_2$ with **30** gave the palladium complex **31** in 85% yield (Scheme 27).²⁹ The complex was characterized by X-ray structural analysis. It reacted quantitatively with phenylacetylene.

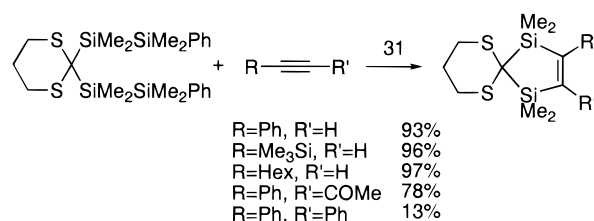
Complex **31** can catalyze the insertion of alkynes into the Si-Si bond as well as the metathesis process following, and it is most likely an intermediate in the addition reaction depicted in Scheme 28.^{29,30}

Tanaka et al. suggested a new and very efficient catalytic system, $\text{Pd}(\text{dba})_2-2\text{P}(\text{OCH}_2)_3\text{CET}$ for the insertion of acetylenes into Si-Si bonds of nonactivated di- and trisilanes as well as polycarbosilanes and poly(dimethylsilylene) (Scheme 29).³¹

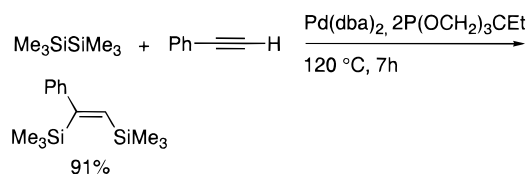
Scheme 27



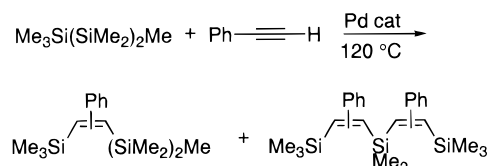
Scheme 28



Scheme 29

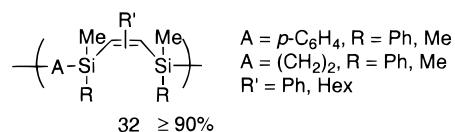


Scheme 30



The new catalytic system, $\text{Pd}(\text{dba})_2 + 2$ equiv $\text{P}(\text{OCH}_2)_3\text{CET}$, was applied to the synthesis of silicon polymers and oligomers (Scheme 30).³²

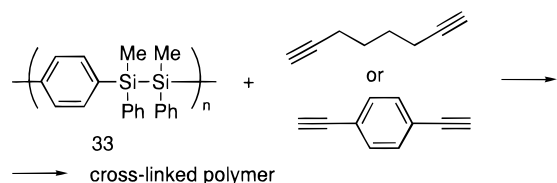
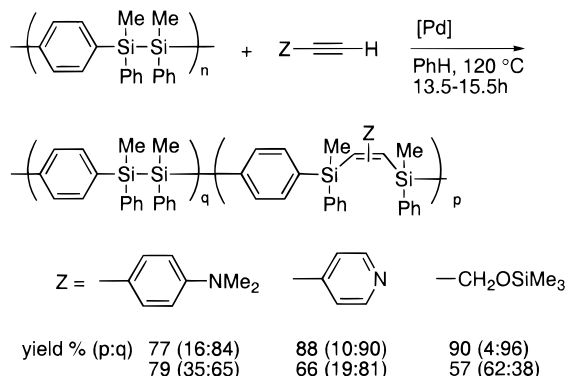
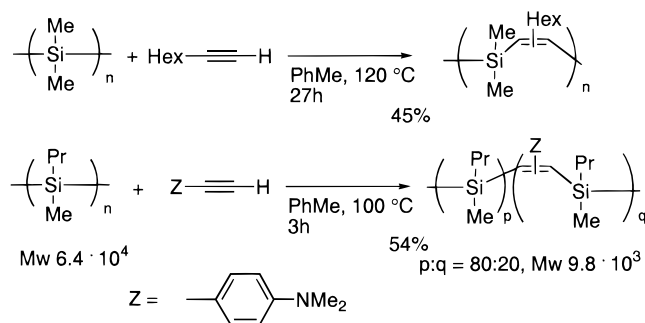
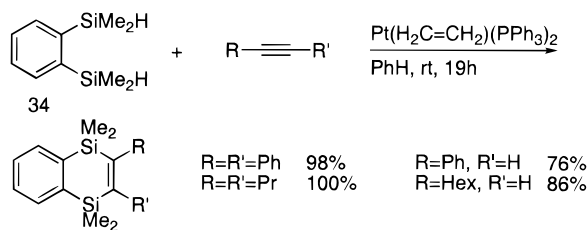
A high yield (>90%) was observed with this catalytic system, whereas the reaction was unselective and the yields were low when $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{PPh}_3)_2$, or $\text{Pd}(\text{dba})_2/2\text{PPh}_3$ was employed as a catalyst. The reaction was applied to various acetylenes RCCH ($\text{R} = 4\text{-Me}_2\text{NC}_6\text{H}_4$, 4-pyridyl, $\text{Me}_3\text{SiOCH}_2$, C_6H_{13}), including some containing functional groups, and polysilanes, the latter affording polymers **32**.



The reaction of **33** with compounds containing two triple bonds led to cross-linked polymers (Scheme 31).³²

The reactions of functionalized acetylenes (RCCH , $\text{R} = 4\text{-Me}_2\text{NC}_6\text{H}_4$, 4-pyridyl, $\text{Me}_3\text{SiOCH}_2$) with a poly[*p*-(disilanylene)phenylene] and poly(methylpropyl)silylene gave modified polymers (Scheme 32).³³

The incorporation of vinylene groups with a 4-(*N,N*-dimethylamino)phenyl substituent in the backbone of poly[*p*-(disilanylene)phenylene] allows the conduc-

Scheme 31**Scheme 32****Scheme 33****Scheme 34**

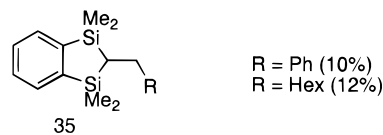
tivity of iodine-doped polymers to be improved (from 3×10^{-4} to 1×10^{-3} S cm⁻¹).³³

The catalyst promoted the insertion of alkynes even into poly(dimethyl)silylene, which is an insoluble and intractable polymer (Scheme 33).

Double silylation of unsaturated hydrocarbons could be achieved not only with compounds containing Si-Si bonds but also with compounds having two vicinal hydrosilane moieties.³⁴ This reaction was named "dehydrogenative double silylation" (Scheme 34).

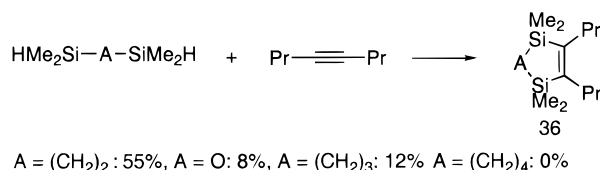
When Pt(ethylene)(PPh₃)₂ was used as a catalyst, the reaction gave high yields with both terminal and internal alkynes; the best results were obtained with internal alkynes, since, with terminal ones, products of bishydrosilylation (**35**) were also formed.

The complexes PtCl₂(PPh₃)₂, Ru₃(CO)₁₂, Pd(dba)₂·2PPh₃, RhCl(PPh₃)₃, PdCl₂(PPh₃)₂, and Pd(PPh₃)₄ all

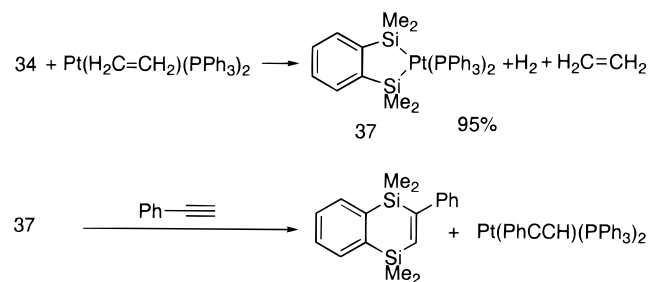


gave poor yields if any. Pt(ethylene)(PPh₃)₂ was thus found to be the best catalyst for this reaction.

The reaction of HMe₂Si(CH₂)₂SiMe₂H with dipropylacetylene under the same conditions gave 55% yield of **36**, the most stable Pt complex with a five-membered ring being formed as an intermediate. In addition, products of hydrosilylation were formed. In all other cases the yields of cyclic products were low (Scheme 35).

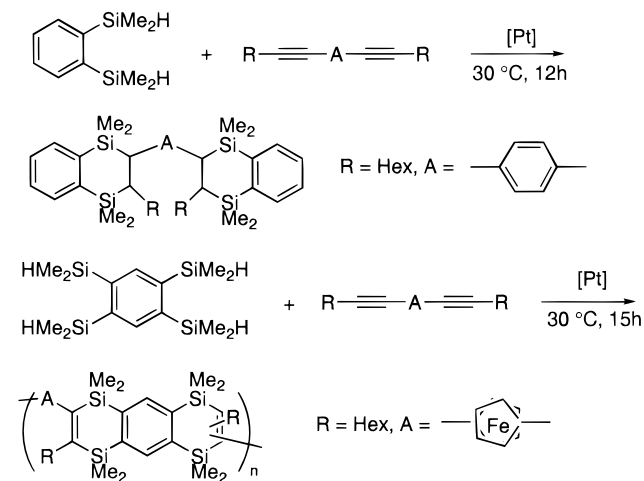
Scheme 35

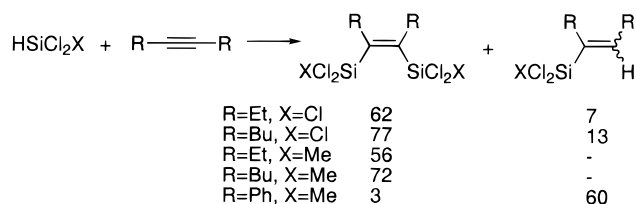
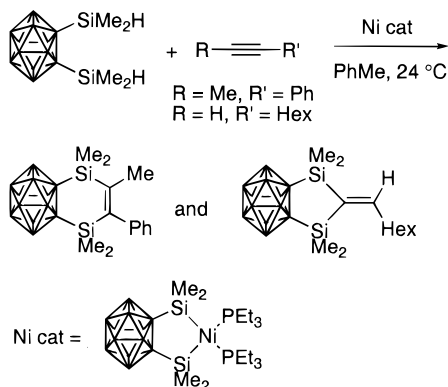
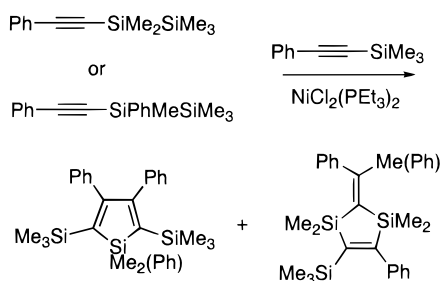
The authors³⁴ confirmed Eaborn's result³⁵ that the interaction of **34** with Pt(ethylene)(PPh₃)₂ led to formation of the Pt complex **37** (Scheme 36). This

Scheme 36

complex reacted with phenylacetylene giving the product in quantitative yield.

Dehydrogenative double silylation catalyzed by Pt(ethylene)(PPh₃)₂ was also applied to the polycondensation of diynes (Scheme 37).³⁶

Scheme 37

Scheme 38**Scheme 39****Scheme 40**

It is interesting to note that dehydrogenative *cis* double silylation of internal alkynes can be brought about even by monosilanes (Scheme 38).³⁷

The application of nickel-containing catalysts for disilylation is rather rare but has been reported. A dehydrogenative disilylation catalyzed by nickel complexes of a carborane was recently performed with *o*-bis(dimethylsilyl)carborane, using two alkynes to yield a new class of heterocyclic compounds (Scheme 39).³⁸ At 70–75 °C the reaction with 1-phenyl-1-propyne also gave a trimer, 1,3,5-trimethyl-2,4,6-triphenylbenzene.

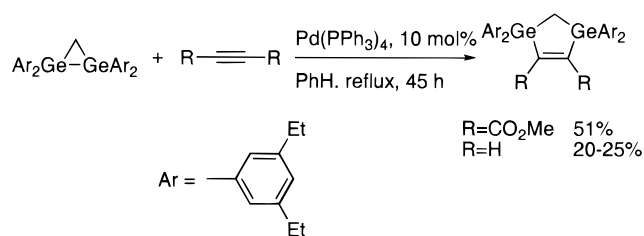
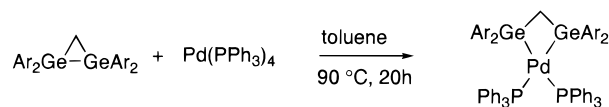
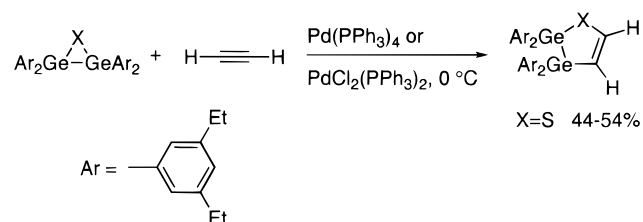
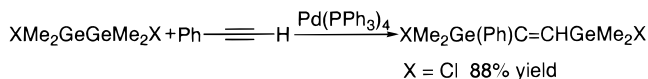
Dimethyl acylenedicarboxylate did not react with the disilylated carborane.

Nickel-catalyzed reactions with acetylenic disilanes led to a mixture of silicon-containing products (Scheme 40).³⁹

B. Germanium-Ge

In contrast to the double silylation of alkynes as well as of other unsaturated carbon compounds, the double germylation is fairly unknown. This is primarily due to the fact that the organogermanium compounds known are rather few as compared with the organosilicon compounds.

The first example of digermylation of alkynes was shown in a reaction of strained digermiranes.⁴⁰

Scheme 41**Scheme 42****Scheme 43****Scheme 44**

This reaction led to the formation of cyclic products under ring expansion (Scheme 41).

The acetylene insertion is also catalyzed by PdCl₂(PPh₃)₂, PdCl₂(MeCN)₂, and NiCl₂(PPh₃)₂. In the stoichiometric reaction of the digermirane with Pd(PPh₃)₄ in toluene, a palladadigermirane was obtained in 48% yield (Scheme 42). This complex reacted with dimethyl acylenedicarboxylate and acetylene, giving the corresponding products in quantitative yields.⁴⁰

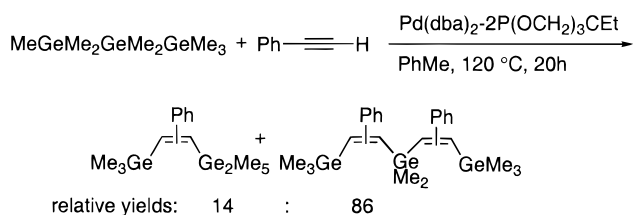
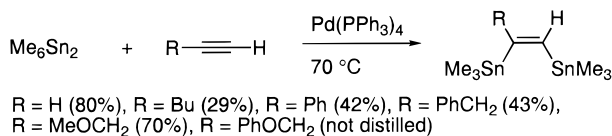
The reactions of sulfur and selenium analogues (sulfa- and selenadigermirane, respectively) with acetylene proceeded to give insertion into the S-Ge and Se-Ge bonds, respectively (Scheme 43).⁴⁰

An analogous azadigermiridine (X = PhN) did not react with alkynes under these conditions. For an explanation of the reaction, the authors⁴⁰ considered a catalytic cycle involving palladacycles.

As in disilylation, the addition of digermanes proceeds easily not only with strained systems but also with activated digermanes (Scheme 44).⁴¹

Low yields were observed with nonactivated digermanes; merely 1.3% of the product of insertion was obtained from Me₃GeGeMe₃.

With unsubstituted acetylene, the yield was only 33% after 12 h (*Z/E* = 17/83) and 45% after 24 h (*Z/E* = 0/100). The best catalyst was Pd(dba)₂·2P(OCH₂)₃CeT (72% after 4 h, *Z/E* = 0/100); Pt(PPh₃)₄ afforded merely 20% (after 12 h, but *Z/E* = 99/1). The predominant formation of products with the *E* configuration in this case, in contrast to the *Z* selectivity in double silylation, is connected with *Z* to *E* isomerization.

Scheme 45**Scheme 46**

The first insertion of alkynes into a nonactivated germanium–germanium bond was carried out using the catalytic system Pd(dba)₂·2P(OCH₂)₃CEt suggested by Tanaka et al.⁴² Complexes such as Pd(PPh₃)₄, PdCl₂(PPh₃)₂, Pd(dba)₂·2PPh₃, Pd(dba)₂·2P(OPh)₃ were not effective. The authors suggested that the success of P(OCH₂)₃CEt was due to its basicity and to steric factors.

The same system was applied to oligogermanes such as octamethyltrigermane and decamethyltetragermane (Scheme 45).

The same reaction can be carried out with (PhMe₂-Ge)₂GeMe₂ (single insertion 8%, double insertion 61%).

All other acetylenes investigated, including 1-hexyne, (trimethylsilyl)acetylene and 1-phenyl-1-propyne, gave poor results or did not react at all, the only exception being dimethyl acetylenedicarboxylate, which gave the product of double insertion in 54% yield.

The reaction of Me(Me₂Ge)₄Me with phenylacetylene gave products of single (two isomers) and double insertion, but the total yield was not higher than 69%, due to the formation of unidentified byproducts.

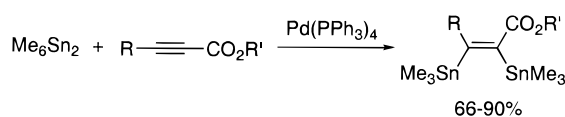
C. Tin–Tin

The distannylation of terminal alkynes, as catalyzed by the palladium complex Pd(PPh₃)₄, has been known since 1983. Mitchell et al.⁴³ showed that terminal acetylenes (without solvent) reacted with hexamethyldistannane in a syn fashion, giving products with *Z* configuration in modest to good yields (Scheme 46). Under the reaction conditions the addition product isomerized to the *E* isomer. The reaction with phenyl propargyl ether was complicated by decomposition of the product. The reactions could be carried out via a radical pathway in a nonstereoselective manner.

α,β-Acetylenic esters and amides react analogously to give *Z* isomers. Products with *Z* configuration are initially formed from the acetylenic esters, but the products undergo rearrangement to the *E* isomers at 75–95 °C (Scheme 47).^{44,45}

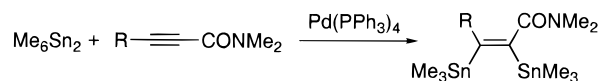
The reactions with α,β-acetylenic amides were slower and not as efficient as those of the esters. The *Z*-amides initially formed are not as stable as the *Z*-esters (Scheme 48).

The products from acetylenes where R is an ω-halogenoalkyl group are precursors of 2-trimethylstan-

Scheme 47

→ *E*-isomer

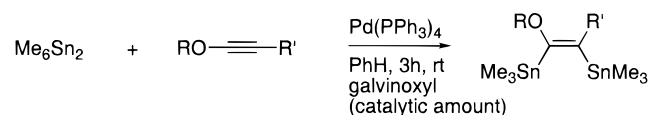
R = Me, ^tPr, cyclopropyl, cyclohex-3-enylmethyl, 2-cyclopent-2-enylethyl, ^tBuMe₂SiOCH₂, ^tBuMe₂SiO(CH₂)₄, THPO(CH₂)₃, Cl(CH₂)₃, Br(CH₂)₅, Br(CH₂)₃, Br(CH₂)₂; R₂ = Et, Me

Scheme 48

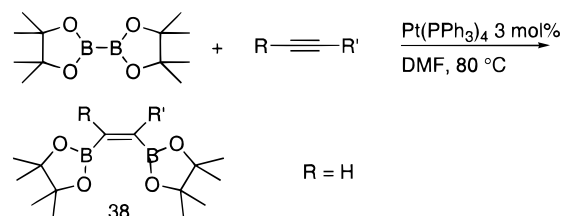
→ *E*-isomer

48–75%

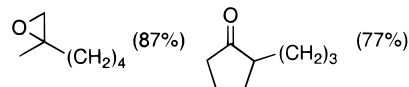
R = Me, Et, ^tBuMe₂SiO(CH₂)₃, Br(CH₂)₃

Scheme 49

RO	R'	yield, %	RO	R'	yield, %
	Me	71		Bu	72
	C ₆ H ₁₃	88		Bu	26

Scheme 50

R' = C₆H₁₃ (82%), C₈H₁₇ (86%), c-C₆H₁₁ (78%), Ph (79% at 120 °C), Cl(CH₂)₃ (83%), CH₃CO(CH₂)₄ (89%), NC(CH₂)₃ (79%)



R = R' = Pr (86%), Ph (79%)

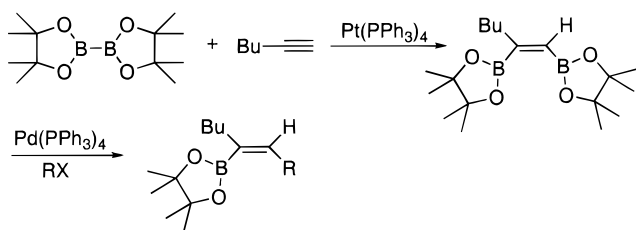
nylcyclo-1-enecarboxylic acid derivatives. The product of distannylation of THPOCH₂C≡CCO₂Me was obtained in 75% yield. It gave a lactone which could be converted into a 3,4-disubstituted 2(5*H*)-furanone.⁴⁶

1-Alkoxy-1-alkynes and 1-phenylthio-1-alkynes react with hexamethyldistannane in a palladium-catalyzed reaction in benzene, giving the product of stannylation–stannylation in modest to high yield (Scheme 49).⁴⁷

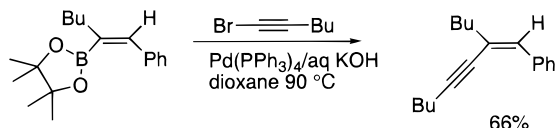
D. Boron–Boron

A pinacol ester derivative was added to terminal as well as internal acetylenes in DMF at 80 °C with Pt(PMe₃)₄ or Pt(CO)₂(PPh₃)₂ as catalyst to give *cis*-bis(boryl)alkenes **38** (Scheme 50). Palladium complexes did not catalyze the process.⁴⁸ The reaction with phenylacetylene was slow at 80 °C but gave 70% yield at 120 °C. Terminal and internal acetylenes exhibited similar reactivities. Polar solvents accelerated the reaction.

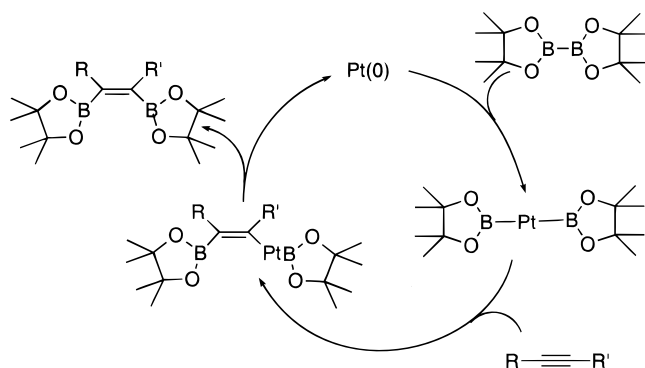
Scheme 51



Scheme 52



Scheme 53



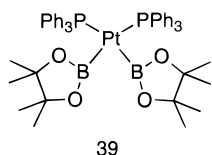
The reaction could be performed in the presence of various functional groups. It did not proceed with alkenes, and only the triple bond in enynes underwent the reaction.

Bis(boryl)alkenes can be used in a variety of cross-coupling reactions. Thus, 1,2-bis(boryl)-1-hexene has been introduced in Pd-catalyzed cross-couplings with aryl, alkenyl, benzyl, and allyl halides, providing *E*-(1-butyl-1-alkenyl)boronates in good yields (Scheme 51).⁴⁹

The reaction rate was affected by the nature of the base. The substitution of both boryl groups afforded trisubstituted olefins (Scheme 52).

The mechanism of diboration includes B–B bond activation by oxidative addition of diboron to $\text{Pt}(0)$ to form a bis(boryl)platinum intermediate, followed by alkyne insertion into the B–Pt bond and reductive elimination (Scheme 53).⁵⁰

The formation of a *cis*-coordinated complex with B–Pt–B bonds was supported by NMR data and X-ray analysis of crystals of complex **39** obtained in 82% yield by reaction of $\text{Pt}(\text{PPh}_3)_4$ with 20 equiv of the tetraalkoxydiboron compound. A distorted square

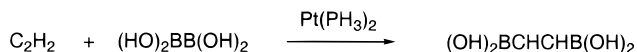


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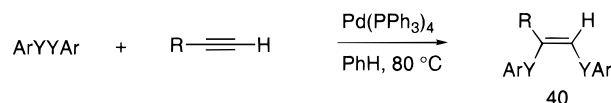
planar structure was found ($\angle\text{P-Pt-P} = 102.65^\circ$, $\angle\text{B-Pt-B} = 75.3^\circ$).

This complex reacted with alkynes, for example with octyne (87% yield at 50°C in C_6D_6) and phenyl-

Scheme 54



Scheme 55



$\text{Y} = \text{S}$ $\text{Ar} = \text{Ph}$

$\text{R} = (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2$, $(\text{CH}_3)_2\text{C}(\text{OH})$, $\text{CH}_3\text{CH}(\text{OH})$, $\text{CH}_2(\text{OH})$, HOCH_2CH_2 , H_2NCH_2 , Ph , $(\text{CH}_3)_3\text{Si}$, $\text{CH}_2=\text{CHCH}_2$, $(\text{CH}_3)_2\text{CH}$

$\text{Y} = \text{Se}$ $\text{Ar} = \text{Ph}$

$\text{R} = (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2$, $(\text{CH}_3)_2\text{C}(\text{OH})$, $(\text{CH}_3)_3\text{Si}$, H_2NCH_2 , Ph , BrCH_2 , $\text{CH}_2=\text{CHCH}_2\text{OCH}_2$

$\text{Ar} = p\text{-Tol}$ $\text{R} = \text{Ph}$ (*E/Z* = 15/85)

$\text{Y} = \text{Se}$ $\text{Ar} = \text{Ph}, p\text{-Tol}, p\text{-CF}_3\text{C}_6\text{H}_4$ $\text{R} = \text{C}_6\text{H}_{13}$

acetylene (74% at 50°C), though in the catalytic reaction, phenylacetylene retarded the formation of unsaturated species.

The complex did not react with alkenes.⁵⁰ However, bis-catecholborane reacted with 4-methoxystyrene in the presence of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, giving a mixture with 10% of a diborylated product. With ionic $\text{Rh}(\text{dppb})\text{-}[\eta^6\text{-(cat)B}(\text{cat})]$ as a catalyst, the yield was 44%.⁵¹ In the reaction of bis(catecholborane) with *p*-(trifluoromethyl)styrene catalyzed by a gold complex, generated from $\text{AuCl}(\text{PET}_3)_4$ and bis(dicyclohexylphosphino)ethane, 1,2-bisboronate esters were formed exclusively.⁵²

A theoretical study of the mechanism of alkyne diboration catalyzed by $\text{Pt}(0)$ was recently made, employing $(\text{HO})_2\text{BB}(\text{OH})_2$ as a model compound.⁵³ It was shown for large alkynes that a mechanism involving oxidative addition of B–B to $\text{Pt}(0)$ (hydride way) was favored over initial coordination of the alkyne (olefin way). The mechanism was shown to include dissociation of the phosphine ligand before coordination of the alkyne (or alkene), migratory insertion of the alkyne into the Pt–B bond, migration of the $\text{CH}=\text{CH}-\text{B}(\text{OH})_2$ group to become *cis* to $\text{B}(\text{OH})_2$, recoordination of the phosphine, and reductive elimination to give the product. The rate-determining step was found to be the dissociation of the phosphine ligand (Scheme 54).

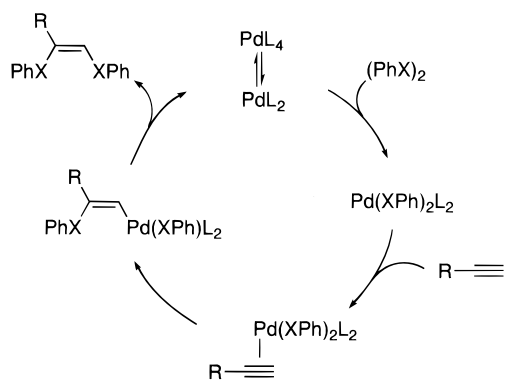
That phosphine dissociation is a crucial step in the catalytic pathway was also demonstrated in experimental mechanistic studies.^{54,55}

E. Sulfur–Sulfur, Selenium–Selenium

Aromatic disulfides and diselenides add stereoselectively to terminal acetylenes in palladium-catalyzed reactions to give *Z*-1,2-bis(aryltio)-1-alkenes (**40**, $\text{X} = \text{S}$) and *Z*-1,2-bis(arylseleno)-1-alkenes (**40**, $\text{X} = \text{Se}$), respectively, in high yields (Scheme 55).⁵⁶ The reaction was performed with a variety of acetylenes, including several carrying functional groups.

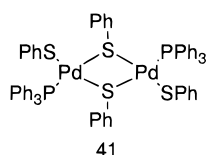
The dialkyldiselenides reacted sluggishly, the addition of dibutylselenide and dibenzylselenide to 1-octyne affording the product in 24, and 0% yield, respectively. Complexes with $\text{Pd}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Ru}(\text{II})$ were not efficient as catalysts. With $\text{RhCl}(\text{PPh}_3)_3$

Scheme 56



and $\text{Pt}(\text{PPh}_3)_4$ the yield of the product of addition of diphenyl disulfide to 1-octyne was about 20%. The reaction did not proceed with internal alkynes. With substrates containing both double and triple bonds, only addition to the triple bond took place. The noncatalytic reaction could be performed under irradiation, yielding either the *E* isomer alone or a mixture of the *E* and *Z* isomers.

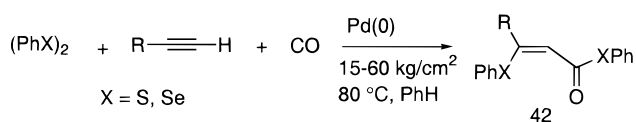
The following catalytic cycle was suggested for the reaction (Scheme 56).⁵⁶ The mechanism suggested was shown to be in accordance with the observation that the palladium complex **41**, obtained by Graziani,⁵⁷ reacts with 1-octyne to give the same product as that formed in the catalytic reaction depicted in Scheme 56 (65% at 65 °C).



No reaction took place when diphenylditelluride was used in place of a diselenide, although the addition of diaryl ditellurides to Pd(0) proceeds readily.⁵⁸

In the presence of CO, the reactions of disulfides and diselenides with alkynes were shown to give products (**42**) of carbonylative addition^{56,59} (which resembles the carbonylative hydrosilylation, Scheme 57). The insertion of CO resulted in CO–Pd bond

Scheme 57



formation.

Bis(triisopropylsilyl)disulfide was shown to undergo $\text{Pd}(\text{PPh}_3)_4$ -catalyzed *syn*-addition to terminal acetylenes in benzene at 80 °C to give insertion products in modest to excellent yields.⁶⁰

F. Silicon–Tin

A silyl-stannation of terminal acetylenes was first performed in the presence of $\text{Pd}(\text{PPh}_3)_4$ in THF at 65 °C.⁶¹ The reaction proceeded regio- and stereoselec-

Scheme 58

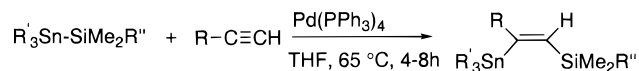
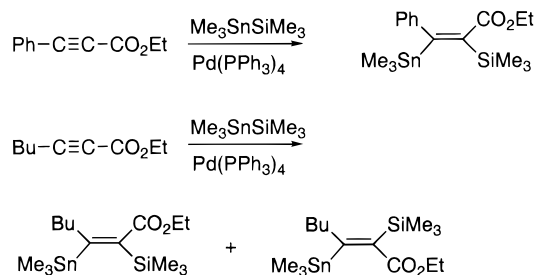


Table 5. Yields of Silyl-stannylated of Alkyne (Scheme 58)

silyl-stannane	R	yield (%) ⁶¹
R' = Me, R'' = <i>t</i> Bu	Ph	93
R' = Me, R'' = <i>t</i> Bu	CH ₃ (CH ₂) ₃	74
R' = Me, R'' = <i>t</i> Bu	<i>i</i> Pr	67
R' = Me, R'' = <i>t</i> Bu	<i>t</i> Bu	10
R' = Me, R'' = <i>t</i> Bu	NC(CH ₂) ₃	90
R' = Bu, R'' = Me	Ph	91
R' = Bu, R'' = Me	NC(CH ₂) ₃	90
R' = Bu, R'' = Me	Me ₃ Si	85
R' = Bu, R'' = Me	HO(CH ₂) ₃	87
R' = Bu, R'' = Me	THPO(CH ₂) ₂	92
R' = Ph, R'' = <i>t</i> Bu	H	85 ⁶⁴
Me ₃ SnSiBuMe ₂	Cl(CH ₂) ₃	87 ⁶⁴

Scheme 59



tively to yield products with Sn in the internal position (Scheme 58, Table 5).

The regioselectivity does not change with the bulkiness of the substituent on the tin atom (from Me to Ph and *t*Bu). The reaction tolerates functional groups in the acetylene.

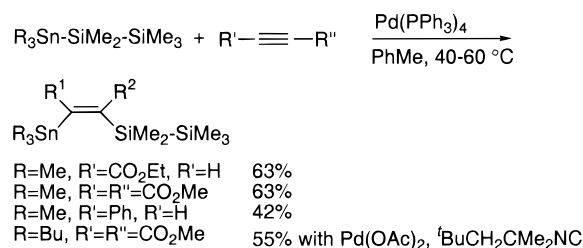
Mitchell et al.^{62,63} carried out the reaction with 22 terminal acetylenes carrying a variety of substituents, such as R = Bu, *t*Bu, Ph, Bn, Me₂NCH₂, MeOCH₂, HOCH₂, HOCHMe, HOCMe₂, HOCH₂CH₂, PhOCH₂, MeCOCH₂, O(CH₂CH₂)₂NCH₂, EtCO₂, and Me₃SiSnMe₃, without solvent in THF or DME at 60–80 °C. The yields varied between 44% and 89%. With propargylic derivatives the results were poor. No adducts were observed with R = CH₂Br and R = CMe₂ (OAc).⁶⁴

Several derivatizations, including some Pd-catalyzed cross-coupling reactions involving exchange of Sn for Hal, Li, COR, Bu, allyl, and Bn and retention of the Si moiety, were carried out with the adducts obtained.⁶³

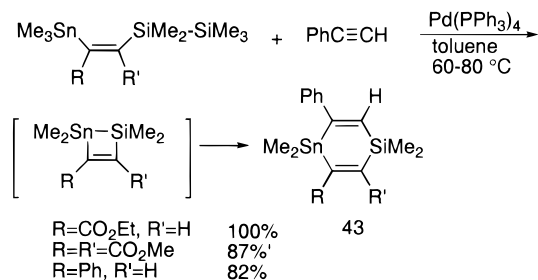
A more complicated picture was observed in the reactions of internal acetylenes. The authors⁶⁵ showed that some internal alkynes (R–CC–R', R = R' = MeOCH₂ or EtOOC) reacted with Me₃SnSiMe₃ or Bu₃SnSiMe₃ to give poor or modest yields of products (14–48%), whereas another one (R = Ph, R' = CO₂Et) afforded the product regio- and stereoselectively in a yield of 84%. With R = Bu, R' = CO₂Et, a mixture of the *Z* and *E* isomers was obtained but the reaction was regioselective (Scheme 59).

The symmetrical alkynes with R = HOCH₂, HOCHMe, MeOCHMe, and MeOCMe₂ did not react under these conditions.

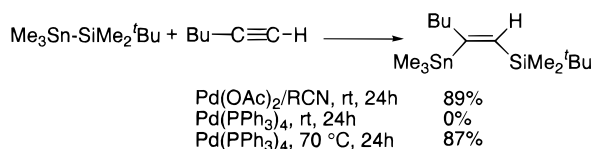
Scheme 60



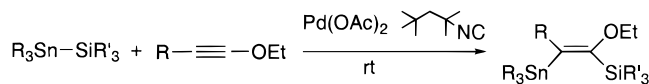
Scheme 61



Scheme 62



Scheme 63



Propynoate $THPOCH_2C\equiv CCO_2Me$ reacted with $Bu_3SnSiMe_3$ in the presence of $PdCl_2L_2$ in THF at room temperature to give a 1:1 mixture of regioisomers in 66% yield after 144 h.⁴⁶ In the $Pd(PPh_3)_4$ -catalyzed reaction of disilanylstannanes with alkynes, insertion was observed only into the Si-Sn bond (Scheme 60).⁶⁵

Only the products of *cis*-addition were observed. With terminal acetylenes, the stannyl group entered into the internal position, as expected. Aliphatic alkynes did not react under the conditions normally used for the reaction in Scheme 60.

The palladium-catalyzed reaction of the adducts with phenylacetylene gave 1-sila-4-stannacyclohexa-2,5-dienes (**43**) as a result of Me_4Si elimination (Scheme 61).

Ito's catalyst⁶⁶ allowed silastannylation of 1-hexyne to be done at room temperature rather than with $Pd(PPh_3)_4$ at about 70 °C (Scheme 62).

Alkenes and ordinary internal alkynes failed to react even with this catalyst, however. In the reaction with alkoxyacetylenes, high yields were obtained with both terminal and internal triple bonds (Scheme 63, Table 6).

High regioselectivity of the acetylene addition was observed (Si in α -position to the OEt group), except for $Me_3Sn-SiMe_3$; the reason for the nonselective reaction of the latter is not clear.

The adduct obtained in the above reaction (Scheme 63) was subjected to a variety of cross-coupling reactions with allyl bromide, iodobenzene, benzyl

Table 6. Silylstannylation of Ethoxyalkynes, Scheme 63

Sn-Si	R	yield (%)
$Me_3Sn-SiMe_2^tBu$	H	92 (>95:5)
$Me_3Sn-SiMe_2^tBu$	Me	99 (>95:5)
$Bu_3Sn-SiMe_3$	H	75 (>95:5)
$Me_3Sn-SiMe_3$	H	99 (\approx 55:45)

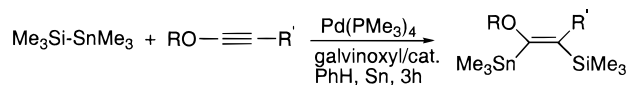
bromide, vinyl bromide, and benzoyl chloride, giving high yields of products. For example, **44** was obtained in 89% yield. The reaction of **45** with trifluoroacetic



acid in water-THF gave the acylsilane $RCOSiMe_2-tBu$.

Contrary to the observation by Ito, the silylstannylation of alkoxyacetylenes with $Pd(PPh_3)_4$ (under the same conditions as distannylation) led to syn addition products with Sn in the α -position to the heteroatom (Scheme 64, Table 7).⁶⁷

Scheme 64



The cross-coupling reaction of (*Z*)-1-ethoxy-1-(trimethylstannyl)-2-(trimethylsilyl)-1-octene with 2-iodothiophene afforded only a modest yield of the cross-coupling product (Scheme 65).

Mori et al.⁶⁸ showed that the reaction of $Bu_3Sn-SiMe_3$ with MeO_2CCCH , catalyzed by a palladium complex in the presence of $BnEt_3NCl$ (or CsF) in DMF, led to a doubly stannylated product ($Bu_3Sn-Sn_2CHCH_2CO_2Me$).

Like in the disilylation by disilanes containing Si-H bonds, the reaction of (trialkylstannyl)dimethylsilane with terminal acetylenes, catalyzed by a triphenylphosphine palladium complex at 25 °C, led to the formation of 1-silacyclopentadiene derivatives **46** as the major products (Scheme 66).⁶⁹

The observations made by the authors indicated the formation of a palladium-dimethylsilylene species, $L_2Pd=SiMe_2$, in this reaction.

A theoretical study of the silastannylation of acetylene was carried out using a model reaction (Scheme 67).⁷⁰

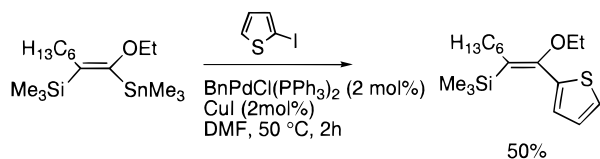
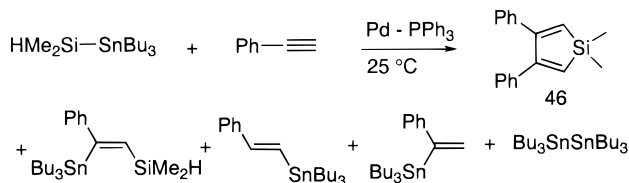
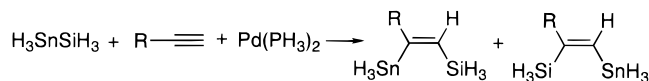
It showed that the rate-determining step was the insertion of acetylene into the Pd-Sn or Pd-Si bond of the complex. The authors explained the different results in the regioselectivity described above by consideration of electronic and steric factors including steric effects of the ligand.

G. Germanium-Tin

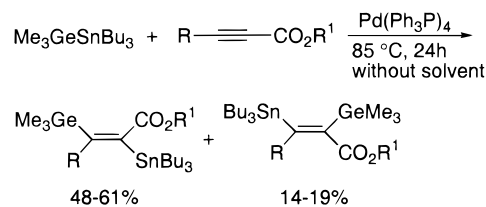
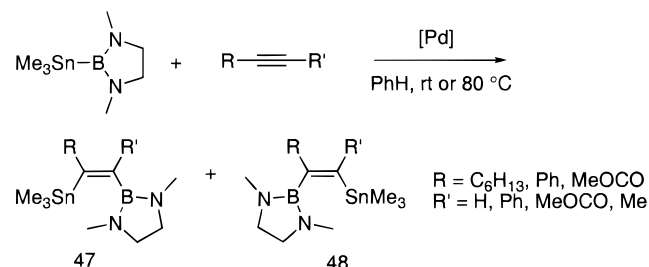
In contrast to silylstannylation, germylstannylation has been carried out only with α,β -acetylenic esters and led to two isomers. The reaction was not regioselective (Scheme 68).⁷¹

Table 7. Silylstannylation of Alkoxyalkynes, Scheme 64

RO	R'	yield (%)
BnOCH ₂ O	Bu	58
EtO	C ₆ H ₁₃	90
	Me	32
	Me	91
	Me	77
	Me	90
	Me	69
	H	61

Scheme 65**Scheme 66****Scheme 67**

The product was transformed to a variety of germyl-containing 1,4-dienes using Sn–Li transmetalation and reactions with allyl moieties.

Scheme 68**Scheme 69****Table 8. Borylstannation of Alkynes, Scheme 69**

R	R'	yield (%) (temp)	ratio 47:48
C ₆ H ₁₃	H	98 (rt)	>99:1
Ph	H	97 (rt)	>99:1
Ph	Ph	97 (80 °C)	
MeOCO	MeOCO	91 (80 °C)	
Ph	Me	97 (80 °C)	85:15

H. Silicon–Boron, Tin–Boron⁷²

Highly stereo- and regioselective palladium-catalyzed borylstannation of alkynes, to afford regioisomers **47** and **48**, was observed by Tanaka et al. using Me₃SnB[MeN(CH₂CH₂)NMe] and Me₃SnB(NEt₂)₂ and palladium complexes such as Pd(PPh₃)₄, Pd(dba)₂, PdCl₂(PPh₃)₂, and [Me₂P(CH₂CH₂)PMe₂]PdMe₂ (Scheme 69). The last catalyst was inactive at room temperature but efficient at 80 °C.⁷³ Pt(PPh₃)₄ did not catalyze the process.

The yields were essentially quantitative both with terminal and internal acetylenes.

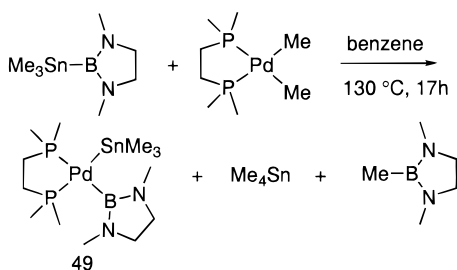
Products with tin at the internal position (**47**) were formed from terminal acetylenes (Table 8).

The products of addition of Me₃SnB(NEt₂)₂ to alkynes were not stable. Oxidative addition of Sn–B to Pd(0) was shown to occur in the reaction with Me₂Pd(dmpc) at 130 °C; the product **49** was formed along with Me₄Sn and MeB[MeN(CH₂CH₂)NMe]. The boryl(stannyl)palladium complex formed had the BSn–PdP₂ atoms in one plane, and the diazaborolane ring was nearly perpendicular to that plane. The complex could be considered as an intermediate in the corresponding reaction (Scheme 70).

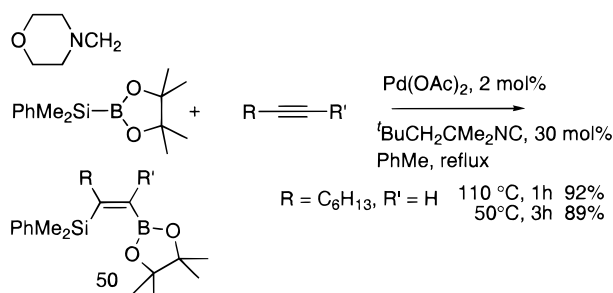
The complex (**49**) was shown to react with alkynes and to catalyze the addition of Me₃SnB[MeN(CH₂CH₂)NMe] to alkynes; it is unknown whether insertion of the alkyne into the Pd–Sn or the Pd–B bond occurs. It is interesting to note that the noncatalyzed reaction gave 36% yield whereas the catalytic one afforded 90% yield.⁷³

Ito et al. found that a palladium(II) *tert*-alkyl isocyanide complex catalyzed the stereo- and regioselective addition of a silylborane to oct-1-yne to yield a product with boron at the nonsubstituted carbon.⁷⁴

Scheme 70

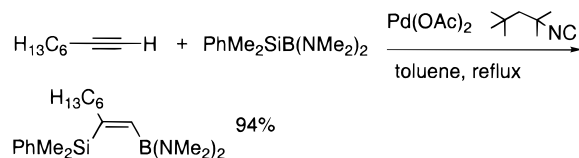


Scheme 71



R = H, R' = Ph (82%), THPO(CH₂)₂ (88%), MEMO(CH₂)₃ (85%), c-Hex-1-enyl (82%), Me₃Si (73%, mixture of regioisomers 94:6)
R = R' = Ph (74%), Bu (24%)

Scheme 72



Pd(PPh₃)₄ was a poor catalyst, whereas Pt(PPh₃)₄ was efficient (80% yield after 1 h at 100 °C, with a regioselectivity of 90:10). A product, **50**, with the silyl group at the internal position, was obtained from terminal acetylenes (Scheme 71). No reaction took place in the presence of Rh(PPh₃)₃Cl.

The reaction can be applied to alkynes with functional groups and also to internal alkynes; the yield remains high for diphenylacetylene but drops to 24% for dibutylacetylene.

Silaboration of 1-octyne with the diamino derivative PhMe₂SiB(NMe₂)₂ proceeded in the same manner (Scheme 72).

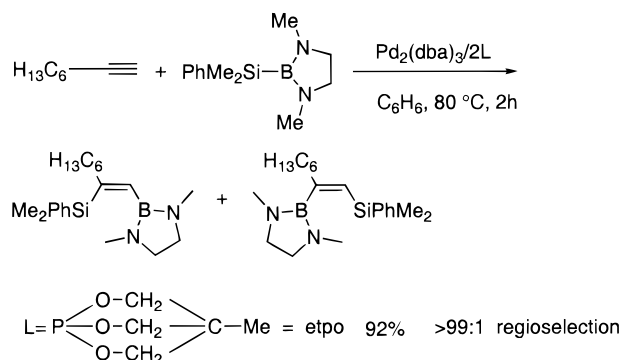
The addition of a diamino borane to terminal acetylenes was performed using a palladium phosphite complex (Tanaka's catalyst) (Scheme 73).⁷⁵

Pd-PPh₃ complexes, efficient as catalysts for borylstannation, were not efficient for silaboration. However, use of a Pd-PMe₃ complex resulted in 70% yield and the same selectivity as that observed using the Pd-etpo complex. A decreasing trend of performance etpo > PMe₃ > PPh₃ was observed among the ligands used. Reaction with phenylacetylene required a temperature of 110 °C but gave the product in 97% yield.

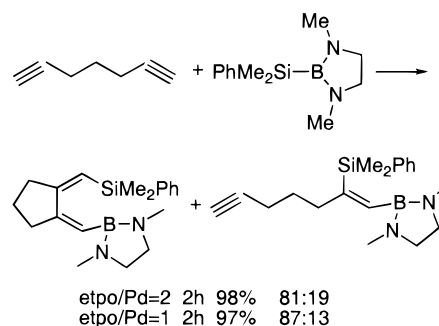
Silaboration of 1,6-diynes led to borylsilylative carbocyclization along with monosubstitution (Scheme 74).

The reaction also proceeds with Pd-PMe₃ and Pd-PPh₃ complexes (L/Pd = 2), albeit with low selectivity (84%, 30:70 after 2 h, and 98%, 26:74 after 7 h).

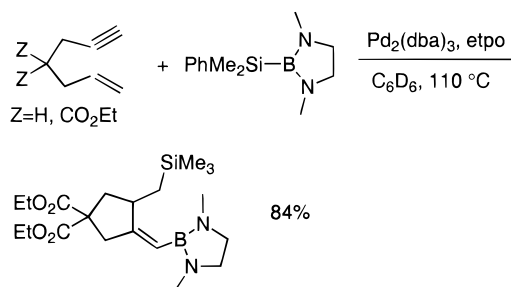
Scheme 73



Scheme 74



Scheme 75



The analogous reaction with 1,7-diynes resulted in a low yield (17%) of cyclized product, the major product being that obtained by monosubstitution. Simultaneous coordination of Pd to the two triple bonds, which is a prerequisite for cyclization, is less favored with 1,7-diynes than with 1,6-diynes.

The reaction is also applicable to enynes, as demonstrated in the reaction with 4,4-bis(ethoxycarbonyl)hept-6-en-1-yne (Scheme 75).⁷⁵

The formation of the product with boron linked to an alkene group supports the assumption that the reaction proceeds via the insertion of the alkyne group into the Pd-B bond.

The same carbocyclization of diynes and enynes involving borylstannanes in place of borylsilanes was also performed (borylstannylative carbocyclization).⁷⁶ With PdCl₂(PMe₃)₂, which was inefficient for the addition of borylsilanes, the carbocyclization reaction resulted in a high yield of product at room temperature (Scheme 76).

The reaction was applied to various alkyne substrates, including 1,7-octadiyne, 1,5-hexadiyne, and nitrogen- and oxygen-containing substrates (Table 9). The reaction with 1,5-hexadiyne resulted in the formation of a strained four-membered ring. In a

Scheme 76

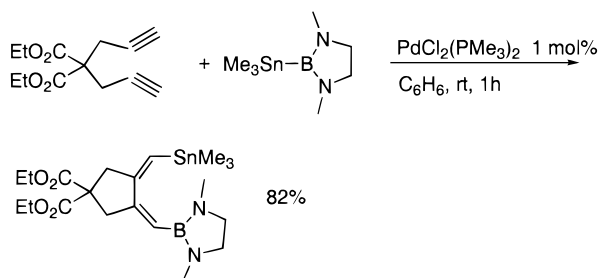
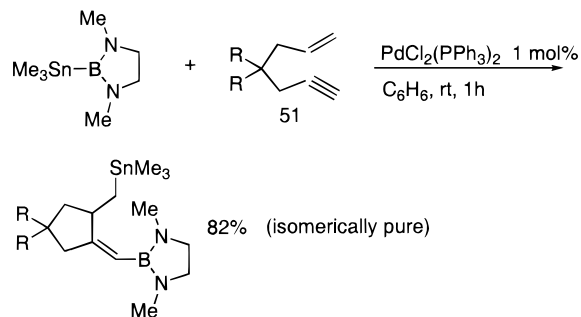


Table 9. Borylstannylation of Alkynes

alkyne	product	yield (%; values in brackets as determined by GLC)
		79(92)
		74(84)
		64(97)
		82
		83(93)
		86

Scheme 77



reaction with an unsymmetrical diyne, the boryl residue was selectively attached to the terminal acetylenic bond and tin to the substituted alkyne group. The fact that products with *Z,Z* configuration were obtained was confirmed by X-ray structural determination of the product of reaction with TsN-(CH₂CCH)₂.

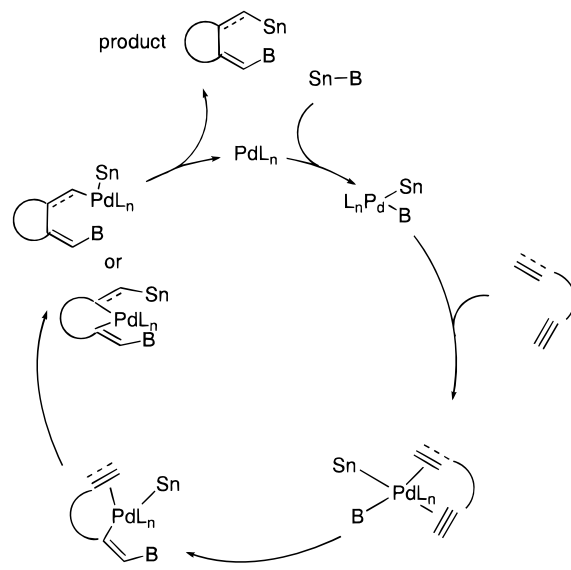
Other Pd complexes, such as PdCl₂[P(*o*-tolyl)]₂, Pd(PPh₃)₄, and Pd(dba)₂, were also found to catalyze the reaction.

The hept-6-en-1-yne derivatives **51** also underwent borylstannylation in a completely regioselective manner, the boryl group being introduced exclusively at the acetylenic bond (Scheme 77).

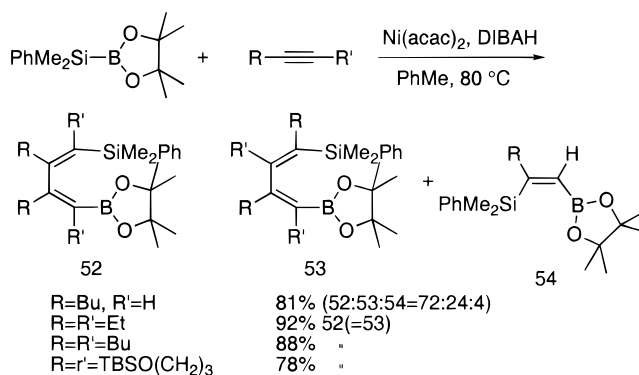
The authors⁷⁶ considered two possible routes of the reaction, one of which included the formation of a palladacycle (Scheme 78). Both routes involved insertion of the triple bond into the Pd–B bond.

Unprecedented silaborative dimerization of terminal alkynes to yield products **52** and **53** along with the 1:1 adduct **54** took place in the presence of a Ni-

Scheme 78



Scheme 79



(0) catalyst (Scheme 79).⁷⁷ The boryl group was exclusively introduced to the terminal alkynyl carbon atom. Internal alkynes afforded dimerization products with *Z,Z* configuration. 1,7-Octadiyne reacted analogously to give a dimethylenecyclohexane derivative. Diphenylacetylene did not undergo the reaction.

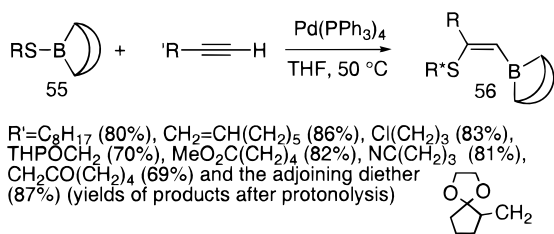
The mechanism was thought to involve oxidative addition of Si–B to Ni(0) and regioselective insertion of the alkyne into the Ni–B bond, followed by insertion of a second molecule of alkyne into the Si–Ni bond. The second insertion proceeded faster than reductive elimination, thus preventing the formation of the product of monoaddition, and it showed lower regioselectivity than the first one.

Products of the same type were formed upon germlyboration of 1-hexyne.

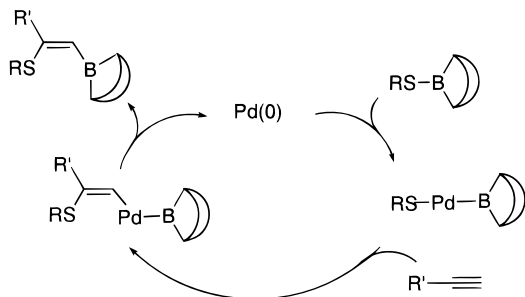
I. Sulfur–Boron

The addition of boron–heteroatom bonds to alkynes is an attractive route to functionalized 1-alkeneboron compounds. It has been shown that 9-(alkylthio)-9-borabicyclo[3.3.1]nonanes (**55**) react with terminal alkynes in the presence of Pd(PPh₃)₄ to give 9-[(*Z*)-2-(alkylthio)-1-alkenyl]-9-borabicyclo[3.3.1]nonanes (**56**) in high yields in a regio- and stereoselective manner (Scheme 80).⁷⁸

Scheme 80



Scheme 81



Scheme 82

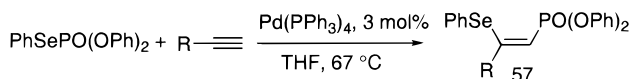


Table 10. Selenophosphorylation of Alkynes, Scheme 82

Alkyne	Yield of addition product (isolated, %)
$\text{C}_6\text{H}_{13}\text{-C}\equiv\text{C-H}$	95
$\text{H-C}\equiv\text{C-H}$	68
$\text{MeOCH}_2\text{-C}\equiv\text{C-H}$	87
$\text{NC}(\text{CH}_2)_2\text{-C}\equiv\text{C-H}$	91
$\text{C}\equiv\text{C}-(\text{CH}_2)_5\text{-C}\equiv\text{C-H}$	97
$\text{Ph-C}\equiv\text{C-H}$	65
$p\text{-MeC}_6\text{H}_4\text{-C}\equiv\text{C-H}$	87
	79

No reaction was observed when $\text{PdCl}_2(\text{PPh}_3)_2$ was tried as a catalyst. The authors⁷⁸ suggested a mechanism involving the oxidative addition of a boron-sulfur bond to $\text{Pd}(0)$ to form a $\text{Pd}(\text{II})$ species, followed by insertion of the alkyne group into the S-Pd bond (as in the thiol addition) to give the Markovnikov adduct. Attempts to detect an intermediate by ^{11}B or ^{31}P NMR spectroscopy were unsuccessful, probably due to preferential B-S bond formation (Scheme 81).

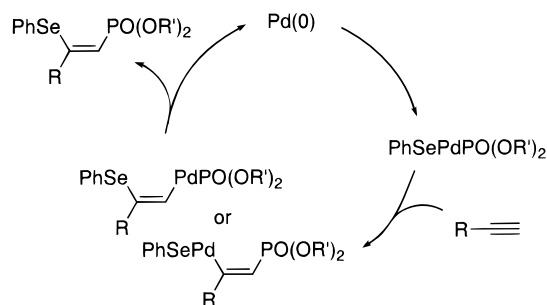
J. Selenium-Phosphorus

Selenophosphonates undergo palladium-catalyzed addition to terminal alkynes to give high yields of syn addition products **57** regioselectively, with the selenium atom at the internal position (Scheme 82).⁷⁹

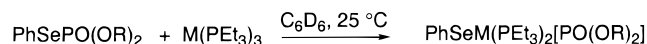
The reaction can be applied to acetylene itself as well as to various kinds of alkynes containing further alkyl as well as aryl groups (Table 10).

Two equivalents of the selenophosphonate react with diynes to give the product resulting from double

Scheme 83



Scheme 84



addition (Table 10). No reaction with the double bonds occurs. The reaction can also be performed in benzene or toluene but not above 67°C .

The rate of reaction is strongly dependent on the nature of the R group and on the structure of the selenophosphonate; PhSePO(OEt)_2 reacts more slowly than PhSePO(OPh)_2 . The catalytic cycle probably involves oxidative addition of the P-Se bond to $\text{Pd}(0)$, insertion of the alkyne into the Se-Pd or P-Pd bond, and reductive elimination (Scheme 83). The authors mention that it is unknown whether selenopalladation or phosphinopalladation occurs.

When more electron-rich ligands than PPh_3 were employed, the authors succeeded in isolating complexes with Se-Pd-P and Se-Pt-P bonds, formed by oxidative addition of selenophosphonates to $\text{Pd}(0)$ and $\text{Pt}(0)$ (Scheme 84). An X-ray crystallographic analysis of orange crystals of the Pt complex, which did not catalyze the addition, showed that the complex had a distorted square planar structure with *trans*-configuration.

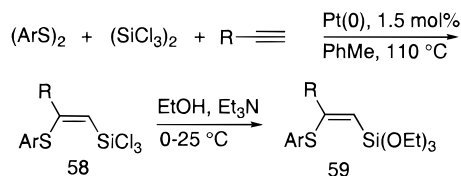
K. Silicon-Sulfur

The information about addition of E-E' bonds, where $\text{E} = \text{S, Se, or Te}$ and $\text{E}' = \text{Sn or Si}$, to alkynes is quite limited, although complexes with Se(Te)-Pt-Sn(Si) bonds have been obtained by oxidative addition of Se-Sn(Si) and Te-Sn(Si) to $\text{Pt}(0)$ and are well characterized.⁸⁰ It was shown that the formation rates of the products decreased in the order $\text{Ph-SeSnMe}_3 > \text{Ph-SeSiMe}_3$; $\text{Ph-TeSnMe}_3 > \text{Ph-TeSiMe}_3$. No reaction was observed with MeSSiMe_3 .

Tanaka et al.⁸¹ recently showed that mixtures of ArSSAr and $\text{Cl}_3\text{SiSiCl}_3$ reacted with terminal acetylenes under heating in the presence of a platinum complex to afford (*Z*)-1-silyl-2-thio-1-alkenes **58** (**59** after ethanolic workup) in good yields. The reaction proceeded in a regio- and stereoselective manner to give the product with the sulfur atom at the internal position (Scheme 85). Alkenes did not react.

The first step of the reaction with alkynes (Scheme 85) was the formation of the unsymmetrical product ArSSiCl_3 . Other disilanes than $(\text{Cl}_3\text{Si})_2$, e.g., $(\text{Me}_3\text{Si})_2$, did not disproportionate under these conditions. The highly air- and moisture-sensitive PhSSiCl_3 isolated (obtained by reaction of PhSLi with a large excess of SiCl_4 in ca. 7% yield) reacted with alkynes in the presence of $\text{Pt}(0)$ and underwent oxidative addition

Scheme 85



Pt(0) = Pt(CH₂=CH₂)PPh₃)₂

Ar = Ph, *p*-Tol, *p*-ClC₆H₄, R = C₆H₁₃

Ar = *p*-ClC₆H₄, R = C₆H₁₃ (83%), Bn (76%), Ph (62%), *p*-ClC₆H₄ (65%),
p-Tol (60%), Cl(CH₂)₃ (79%), NC(CH₂)₃ (81%), TBDMSO(CH₂)₄ (72%),
^tBuCO₂(CH₂)₂ (87%), CHC(CH₂)₅ (double addition, 69%),
 cyclohexen-1-yl (51%)

to Pt(PET₃)₃ at room temperature. This could be considered as evidence for a mechanism with participation of (PhS)Pt(SiCl₃)(PET₃)₂ as an intermediate in the addition reaction.

However, the equilibrium between (PhS)₂Pt(PET₃)₂ and (PhS)Pt(SiCl₃)(PET₃)₂ was found to be shifted strongly to the left. The reactivity of the latter complex, present in negligible concentration, in the insertion reaction was thus much higher than that of (PhS)₂Pt(PET₃)₂. The authors⁸¹ tentatively proposed that the insertion of the alkyne proceeded into the Pt–S bond of (PhS)Pt(SiCl₃)(PET₃)₂.

III. Oxidative Addition of E–E' to M(0)

Two key factors determine the possibilities of element–element additions to triple bonds through catalysis by transition-metal complexes. The first is the formation of complexes with E–M–E' bonds as a result of oxidative addition of E–E' to the metal. This problem has been addressed in several theoretical studies.^{82–85} The second factor is the possibility of insertion of the alkyne into the M–E or M–E' bond. Both factors are equally important for this reaction.

As one can see from the above discussion of these reactions, many complexes obtained by oxidative addition were isolated or identified as intermediates and their participation in the reaction as reagents or catalysts was demonstrated. We have also mentioned that these complexes can be obtained in other ways than by oxidative addition and then react with alkynes.

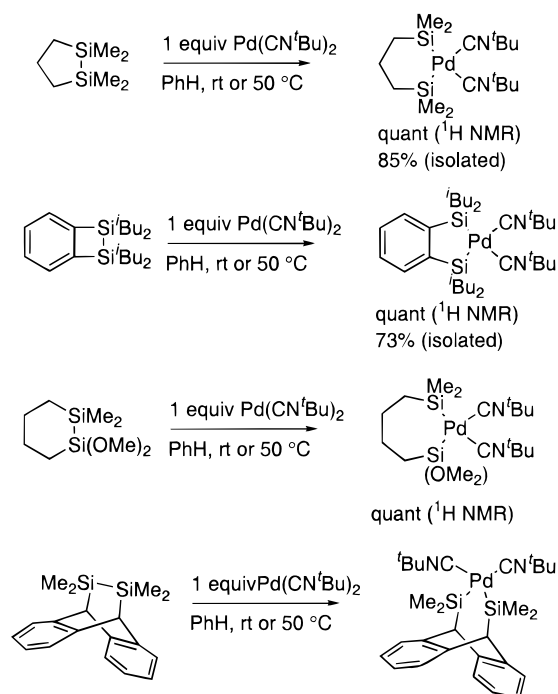
Finally, it is important to analyze those reactions in which the complexes exist but the insertion does not take place. Here we shall consider the formation of these complexes, their structure, and their reactivity toward alkynes (stabilities and reactivities strongly depend on the nature of metals and ligands).

A. Pd Complexes with Si–Si

Oxidative addition of disilanes to low-valent transition metals proceeds easily with disilanes having electronegative groups and also with strained cyclic disilanes.

Several Pd complexes obtained in the reaction of L₂Pd(styrene) with Me₃Si–SiF₂Ph or PhF₂SiSiF₂Ph, where L = PMe₃ and PMe₂Ph, were characterized, and reactions of the products with dimethyl acetyl-

Scheme 86

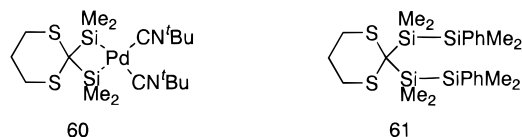


enedicarboxylate were performed. However, no oxidative addition occurred with Me₃SiSiMe₃.⁸⁶

Eaborn et al. showed that hexachlorodisilane reacted with Pd(PPh₃)₄ at room temperature to give the moisture-sensitive solid complex Pd(SiCl₃)₂(PPh₃)₂. No reaction was observed with hexamethyldisilane.⁸⁷

Several Pd complexes bearing two silyl ligands were isolated in reactions of cyclic disilanes with the Pd(0) complex Pd(CN^tBu)₂ (Scheme 86).²⁹

A palladium complex **60** was obtained in 85% yield from the reaction of disilane **61** with Pd(CN^tBu)₂. The



complex was characterized by X-ray structural analysis.

Palladacycles containing Si–Pd–Si bonds were also obtained in a new intramolecular metathesis process of two Si–Si bonds (Scheme 87).²⁹

The reaction was reversible, as demonstrated by the exchange of ligands to yield the most stable complex (Scheme 88).

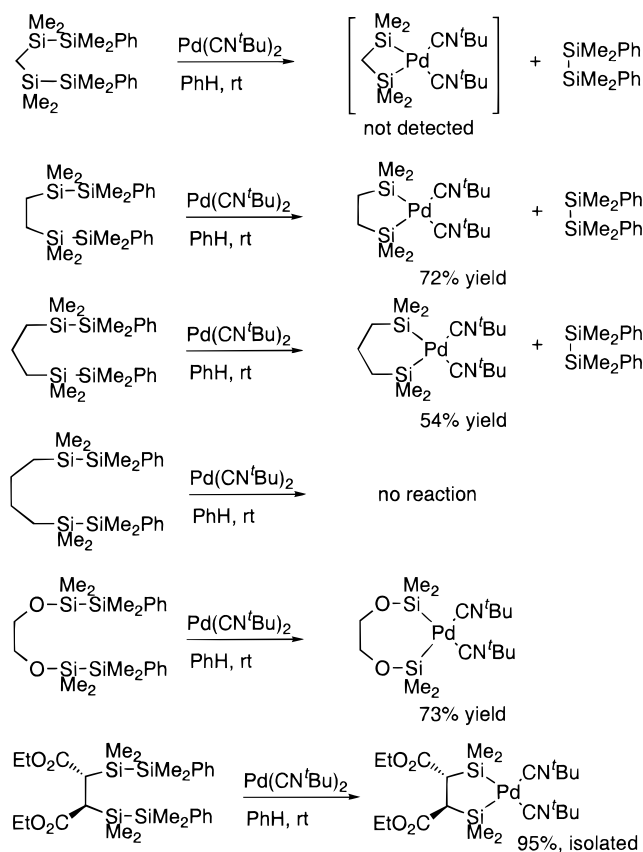
The equilibrium was shifted toward the five-membered ring compounds in the reaction between a disilacyclobutane and a six-membered palladacycle (Scheme 89).

Due to the reversibility, intramolecular metathesis could proceed in the presence of a complex (Scheme 90). Accordingly, it has been shown that metathesis occurs in polydisilanes.

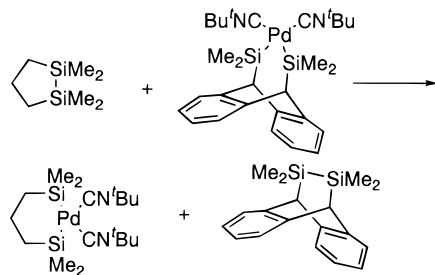
The insertion of acetylenes into the Si–Pd bonds in palladacycles proceeded with close to quantitative yield of the addition product (Scheme 91).

The reaction of a disilacyclobutane with 1 equiv of PdCl₂L₂ gave a palladacycle in 73% yield along with

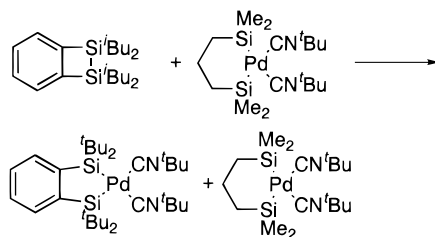
Scheme 87



Scheme 88



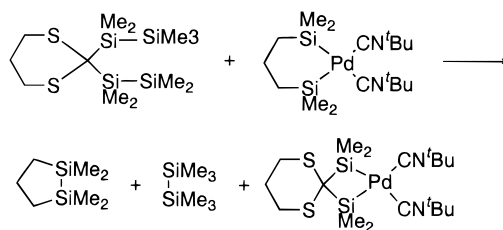
Scheme 89



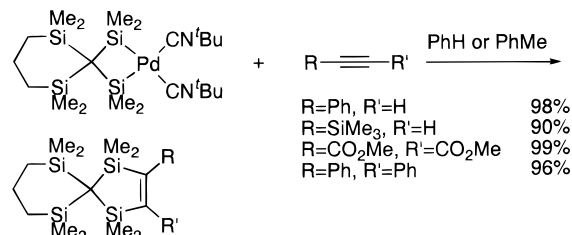
$\text{ClSiMe}_2\text{CMe}_2\text{CMe}_2\text{SiMe}_2\text{Cl}$ (80%). The structure (**62**) suggested for the palladacycle was tentative, as the complex was almost insoluble and thus inaccessible to NMR studies. The complex reacted with phenylacetylene to give the same product as the catalytic reaction in 80% yield (Scheme 92).

A disilane (**63**) containing two tethers, each ending in a diphenylphosphine group, was designed to stabilize the (bissilyl)palladium complex **64** (Scheme 93).⁸⁸ The complex was obtained by dehydrogenative reaction of $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SiMe}_2\text{H}$ with L_2PdMe_2 . Bis(silyl)palladium complexes of the *cis*-(MePh_2P)₂Pd-

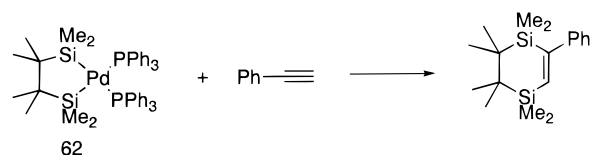
Scheme 90



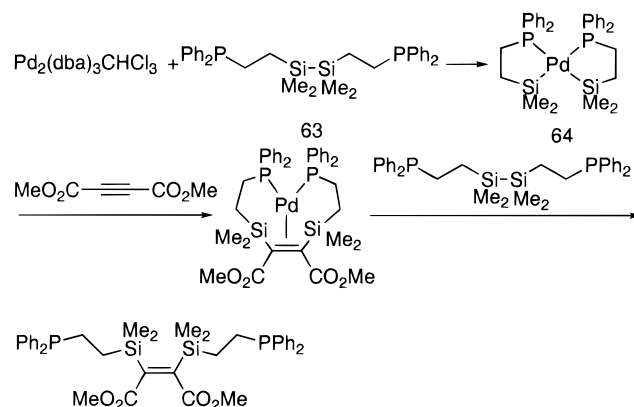
Scheme 91



Scheme 92



Scheme 93

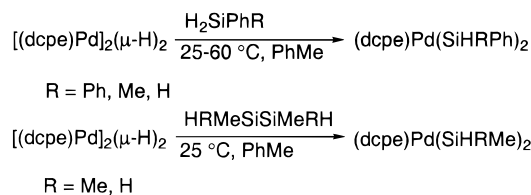
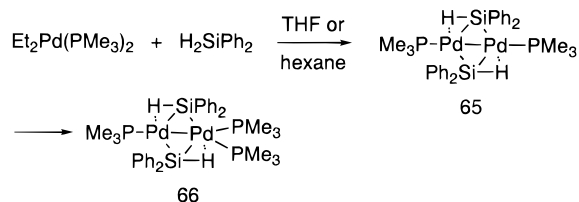
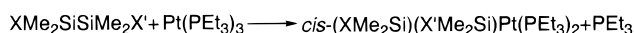


(SiHR_2)₂ type and obtained in the same way were not stable but decomposed to give $\text{H}_2\text{Si}_2\text{R}_4$. The authors⁸⁸ synthesized $\text{L}_2\text{Pd}(\text{SiCl}_3)_2$ using a novel reaction of L_2PdCl_2 and HSiCl_3 in the presence of KH . Ito et al. obtained the same complex by oxidative addition of a disilane to $\text{Pd}(0)$ (vide infra).

Complex **64** was stable in air. An X-ray structural determination showed that it had a square planar geometry with a *cis*-arrangement of the two silicon atoms. Dimethyl acetylenedicarboxylate reacted with **64** in benzene at room temperature to give a crystalline $\text{Pd}(0)$ complex (57%), which was characterized by X-ray analysis and by NMR. This $\text{Pd}(0)$ complex showed even higher stability than the $\text{Pd}(II)$ complex (**64**).⁸⁸

Very stable bis(silyl)palladium complexes were prepared in good yields (50–70%, Scheme 94) by reaction of a dinuclear palladium(I)hydride with hydrosilanes or disilanes.⁸⁹

These complexes were the first *cis*-bis(silyl)palladium complexes isolated having simple organic sub-

Scheme 94**Scheme 95****Scheme 96**

stituents and hydrogen on silicon. The structure of the complex $(dcpe)Pd(SiHMe_2)_2$ was determined by X-ray analysis. The complex reacted with dimethyl acetylenedicarboxylate at room temperature to give *cis*-maleate only.⁸⁹

Complexes of this type but with less basic phosphine ligands cannot be isolated due to rapid reductive elimination of disilanes. For this reason, they can be characterized only in solution.

Binuclear palladium complexes with bridging diphenylsilyl ligands (**65** and **66**) were recently obtained via reaction of $PdEt_2(PMe_3)_2$ with diphenylsilane (Scheme 95).⁹⁰ By fractional crystallization, the complexes were isolated in yields of 3% and 63%, respectively. Complex **65** was characterized by X-ray analysis.

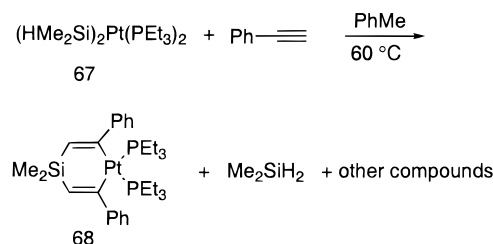
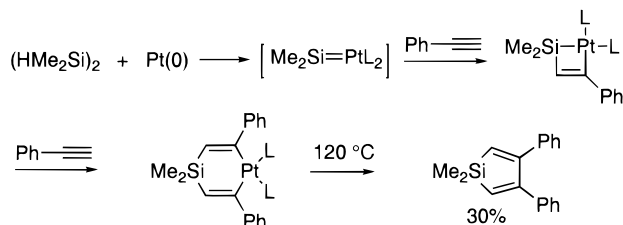
B. Pt Complexes with Si-Si

Pt complexes with E-Pt-E' bonds are more stable than their Pd analogues and easy to obtain. It is not surprising, then, that a large number of such complexes are known and well characterized. First of all they are the complexes of halodisilanes. The complex $Pt(SiCl_3)_2(PPh_3)_2$ was obtained by oxidative addition of Si_2Cl_6 to $Pt(PPh_3)_4$.^{91,92}

Many of them were obtained in reactions of $X-Me_2Si-SiMe_2X'$ with $Pt(PEt_3)_3$: X = X' = F; X = X' = Cl; X = Cl, X' = Me; X = Br, X' = Me. According to NMR these complexes have *cis*-configurations (Scheme 96).⁹³

The complex $FMe_2SiSiMe_2F$ reacted with diphenylacetylene to give the *Z*-addition product in 93% yield. Disilanes with at least one halogen atom placed on silicon reacted with $Pt(PEt_3)_3$ at room temperature. The reactivity order was $(FMe_2Si)_2 > (ClMe_2Si)_2 > ClMe_2SiSiMe_3 > BrMe_2SiSiMe_3 \gg (PhMe_2Si)_2 \gg (Me_3Si)_2$.

The reaction of $Me_3SiSiMe_2I$ with $Pt(PEt_3)_2$ resulted in the insertion of Pt into the Si-I bond to give *trans*- $(Me_3Si-SiMe_2)PtI(PEt_3)$, resembling the addition of Me_3SiBr to PtL_3 , where $Me_3SiPtBrL_2$ is formed.⁹⁴ The disilanes $Me_3SiSiMe_3$ and $Ph_3SiSiPh_3$

Scheme 97**Scheme 98**

do not react with $Pt(PEt_3)_3$ at room temperature or even at 120 °C.

However, $Me_2PhSiSiPhMe_2$ reacted even better than $FMe_2SiSiMe_2F$ with $Pt(PEt_3)_3$ (the authors⁹³ suggest that the F atoms destabilize Si-Pt bonds). We have already mentioned the effect of the Ph group.

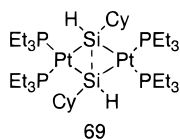
The Pt complex with $(Me_2PhSi)_2$, *cis*- $(Me_2PhSi)_2Pt(PMePh_2)_2$, was shown to react with diphenylacetylene at room temperature to give the syn product in 79% isolated yield after 15 min. The product of reaction with phenylacetylene was isolated in 86% yield after 30 min.⁹⁵

cis- $(HMe_2Si)_2Pt(PEt_3)_2$ was obtained in nearly quantitative yield from the reaction of $HMe_2Si-SiMe_2H$ with $Pt(PEt_3)_3$.⁹⁶ The authors suggested, in agreement with MO calculations,⁹⁷ that insertion of Pt(0) into the H-Si bond proceeds but that the hydrido-disilanylplatinum complex primarily formed somehow rearranges into the thermodynamically more stable bis(silyl) platinum complex (**67**). The complex reacts with phenylacetylene to give another platinum complex (**68**) in 46% yield (Scheme 97).

The complex was characterized by X-ray structural analysis. Heating of the complex caused reductive elimination. A possible mechanism for the formation of **68** may involve the formation of $Me_2Si=PtL_2$ (Scheme 98).

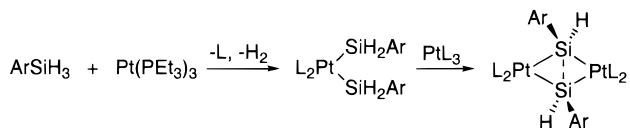
Like Pd complexes, Pt complexes with Si-Pt-Si bonds can be obtained in other reactions than the oxidative addition of a Si-Si bond to Pt(0), as, for example, in dehydrogenation reactions with hydridosilanes. Platinum complexes of the $Pt(SiCl_3)_2L_2$ type can be obtained via dehydrogenation of silanes under the action of $Pt(PPh_3)_4$.⁹⁸⁻¹⁰⁰

Hydrosilylation of olefins with $MeCl_2SiH$, using $Pt(ethylene)(PMe_3)_2$ as a catalyst, gave the complexes $PtH(SiMeCl_2)(PPh_3)_2$ and $Pt(SiMeCl_2)_2(PPh_3)_2$ along with the hydrosilylation products. Only the complex $Pt(SiCl_3)_2(PPh_3)_2$ was formed under the same conditions independently of the presence of an olefin. The first nonplanar four-membered Pt-Si ring complex $[(Et_3P)_2Pt(SiCyH)]_2$ (**69**) was obtained and found to have a very short Si-Si distance.¹⁰¹



Many Pt complexes with silene bridges were obtained in the reactions of Pt(0) complexes with ArSiH_3 (Scheme 99).¹⁰²

Scheme 99

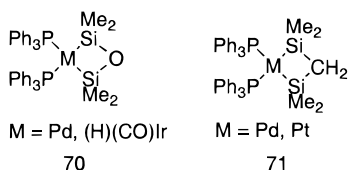


Ar = Ph, Tol, Mes
L = PEt_3 , $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$
and other bidentated phosphines

square pyramidal coordination
geometry of the Pt atom

Bis(hydrosilanes) with various bridges between the silane atoms can also react with Pt(0) to give Si-Pt-Si bonds.

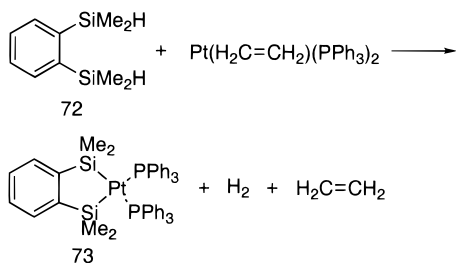
Several small metallacycles—cyclometalladisiloxanes (**70**) and disilametallacyclobutanes (**71**)—were synthesized from $(\text{Me}_2\text{HSi})_2\text{X}$, X = O, CH_2 , for palladium, platinum, and iridium.¹⁰³



Analogously, the complex (**70**, M = Pt) with an Si-O-Si bond was obtained from $\text{O}(\text{SiMe}_2\text{H})_2$ and $\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PPh}_3)_2$.¹⁰⁴

Eaborn found that the reaction of the bis(hydrosilane) **72** with $\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PPh}_3)_2$ gave complex **73** by oxidative addition (Scheme 100).¹⁰⁵

Scheme 100

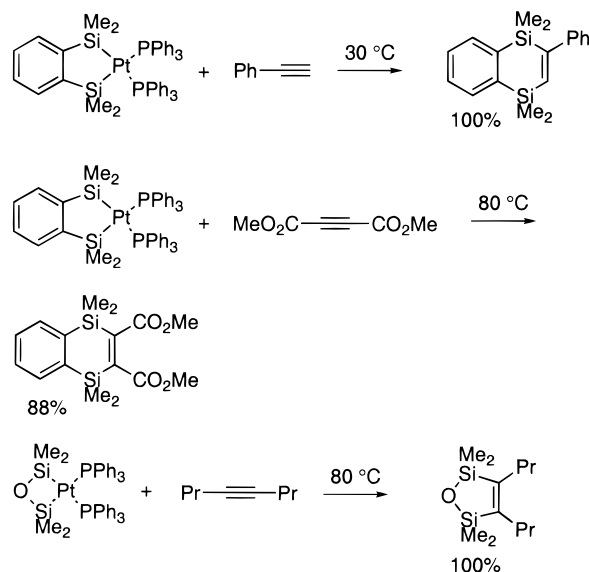


The same type of reaction led to the formation of the Pt complexes $\text{cis-Pt}(\text{SiMePh}_2)_2(\text{PMe}_2\text{Ph})_2$ and $\text{cis-Pt}(\text{SiMe}_2\text{Cl})_2(\text{PMe}_2\text{Ph})_2$. The reaction of phenylacetylene with the former complex led to a complex containing phenylacetylene as a ligand.^{106,107}

Complexes **70** and **73** reacted with alkynes to give addition products in quantitative yields (Scheme 101).

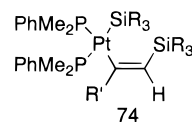
Several complexes of the type $\text{cis}-(\text{Me}_2\text{PhSi})_2\text{PtL}_2$ with L = PPh_2Me , PEt_3 , PPhMe_2 , or PMe_3 ¹⁰⁸ and $\text{cis}-(\text{R}_3\text{Si})_2\text{Pt}(\text{PMe}_2\text{Ph})_2$ with $\text{R}_3\text{Si} = \text{SiMe}_2\text{Ph}$, SiMePh_2 ,

Scheme 101



SiPh_3 , and SiFPh_2 ¹⁰⁹ were obtained by metathesis of the corresponding $\text{cis-Cl}_2\text{Pt}(\text{PR}_3)_2$ complex with $\text{PhMe}_2\text{-SiLi}$ in THF. The complex with L = PPh_3 was not formed due to thermodynamic instability. The authors studied the thermolysis of these complexes and showed that the reactions gave mixtures of products, including disilanes obtained by reductive elimination.¹⁰⁸ The yield of the latter depended on the nature of the ligand and decreased in the order $\text{PPh}_2\text{Me} > \text{PEt}_3 > \text{PPhMe}_2 > \text{PMe}_3$. The yield increased sharply in the presence of a free phosphine ligand.¹⁰⁸

In the reaction of $\text{cis}-(\text{R}_3\text{Si})_2\text{Pt}(\text{PMe}_2\text{Ph})_2$ with alkynes, the authors could isolate the products of insertion of the alkyne into the Pt-Si bond (**74**).¹⁰⁹



The complex obtained from acetylene (**74**, R = Ph, R' = H) was characterized by X-ray analysis.

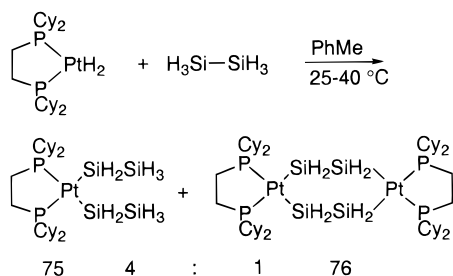
The kinetics of the insertion process were studied and found to be consistent with a mechanism involving dissociation of a phosphine ligand from $\text{cis}-(\text{R}_3\text{-Si})_2\text{Pt}(\text{PMe}_2\text{Ph})_2$, cis addition of Pt-Si to the alkyne via prior coordination of the alkyne to the vacant site at the metal, trans to cis isomerization, and final coordination of a phosphine molecule.

Reaction of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiHRR}'$ with $\text{Pt}(\text{cod})_2$ afforded ca. 90% yields of complexes stabilized by chelation. The complexes were shown to have cis-configurations by an NMR study and for $(\text{Me}_2\text{SiCH}_2\text{-CH}_2\text{PMe}_2)_2\text{Pt}$ by an X-ray crystallographic study.¹¹⁰

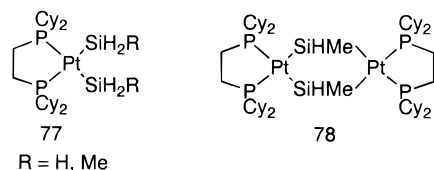
The reaction of $\text{cis}-(\text{dcpe})\text{PtH}_2$ with disilanes containing SiH_3 moieties was shown to lead to new Pt complexes (**75** and **76**, Scheme 102). $(\text{SiH}_2\text{Me})_2$ gave the tetramethyl analogues.

Complex **76** was more stable than **75** and was characterized by X-ray analysis. Other complexes (**77** and **78**), resulting from Si-Si bond cleavage, were

Scheme 102

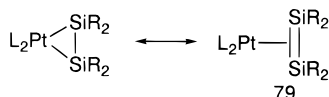


obtained by changing the rate of addition of the disilane to *cis*-(dcpe) PtH_2 .¹¹¹



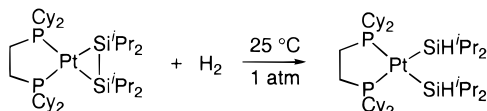
Pt complexes with Si-Pt-Si bonds could be obtained by reduction of platinum η^2 -disilene complexes (**79**, Scheme 103).¹¹²

Scheme 103



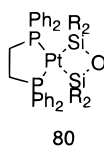
In the presence of chelating phosphines, the Si-Si but not the Si-Pt bond was found to undergo hydrogenolysis (Scheme 104); the X-ray crystal structure of the complex obtained was determined.¹¹³

Scheme 104



ture of the complex obtained was determined.¹¹³

Oxidation of the disilene complexes led to novel complexes **80** (compare complex **70**), which were characterized by ^1H and ^{29}Si NMR and, one of them ($\text{R} = \text{Me}$), by X-ray structural analysis.¹¹²

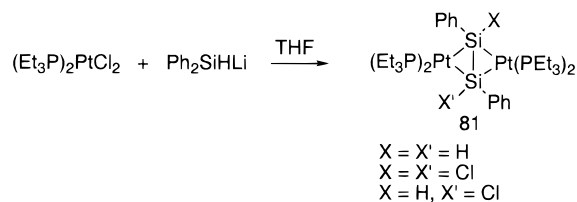


Metathesis of the Pt-Cl and Li-Si bonds in the reaction of L_2PtCl_2 with Ph_2SiHLi or with PhSiH_3 and Na gave dimers (**81**) with unusually short crossing SiSi distances. All of the complexes were characterized by X-ray analyses (Scheme 105).¹¹⁴

C. Ni Complexes with Si-Si

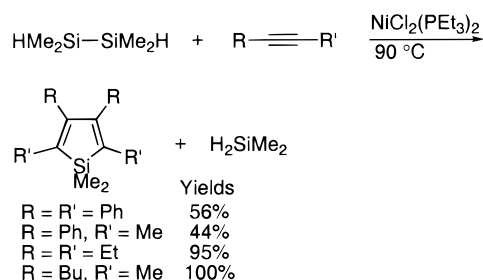
The formation of Ni complexes with Si-Ni-Si bonds as intermediates in disilylation reactions has been suggested in many cases, for example, in the NiL_4 -catalyzed reactions of disilanes with vinylsilane or dienes.¹¹⁵

Scheme 105



Ni complexes were shown to catalyze the reaction of *sym*-tetramethyldisilane with a variety of acetylenes, albeit not with dimethyl acetylenedicarboxylate, to give 1-silacyclopentadiene derivatives in good yields (based on the acetylene). The authors suggested that the reaction involved an α -elimination of the methylsilyl hydride with loss of "dimethylsilylene" (Scheme 106). The use of a Pt complex in

Scheme 106



place of the Ni complex in the reaction with diphenylacetylene gave the product ($\text{R} = \text{R}' = \text{Ph}$) in merely 5% yield.¹¹⁶

A stable Ni complex with an Si-Si bond was isolated and characterized (see Scheme 39).³⁸ Ni complexes with Si-Ni-Si bonds were obtained or suggested in many transformation of Si-containing compounds¹¹⁷⁻¹¹⁹ as, for example, in the reaction of $\text{Ni}(\text{PETe}_3)_4$ with $\text{PhC}\equiv\text{CSi}(\text{SiMe}_3)_3$.¹²⁰

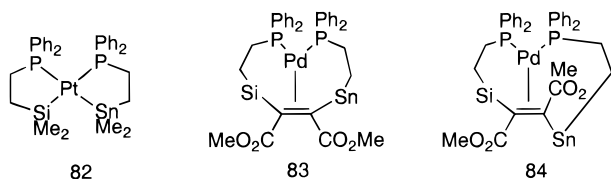
D. Pt Complexes with Ge-Ge

The reaction of the digermane $\text{ClMe}_2\text{GeGeMe}_2\text{Cl}$ with $\text{Pt}(\text{PETe}_3)_3$ gave *cis*- and *trans*-(ClMe_2Ge) $_2\text{Pt}(\text{PETe}_3)_2$. The structure of the *cis*-isomer was confirmed by X-ray crystallography. It is interesting to note that the analogous complex (ClMe_2Si) $_2\text{Pt}(\text{PETe}_3)_2$ was obtained only in the *cis* form in the similar reaction of (ClMe_2Si) $_2$. The reaction of (Me_3Ge) $_2$ with $\text{Pt}(\text{PETe}_3)_3$ did not proceed even at 60°C , the reactivity of the digermane thus resembling that of disilanes.¹²¹

E. Pd Complexes with Si-Sn

Oxidative additions of $t\text{BuMe}_2\text{SiSnMe}_3$ and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SiMe}_2\text{SnMe}_3$ to $\text{Pd}_2(\text{dba})_3(\text{CHCl}_3)_{0.5}$ did not give stable complexes but only disproportionation products. However, a complex (**82**) was obtained from $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SiSn}(\text{CH}_2)_2\text{PPh}_2$, due to stabilization by intramolecular coordination. The complex was characterized by X-ray structural analysis.¹²²

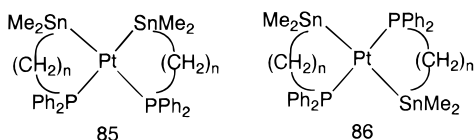
It was shown that the complex reacted with acetylenedicarboxylate at room temperature, giving a silylstannylated palladium(0) complex as a mixture of *cis* (**83**) and *trans* (**84**) isomers ($\sim 10:1$ based on ^{31}P NMR). Both complexes were characterized by



X-ray diffraction. The explanation of the formation of the *trans* isomer was found in the isomerization into a zwitterionic carbene Pd complex.

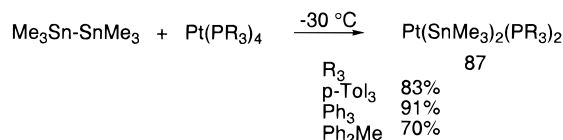
F. Pt Complexes with Sn-Sn

The first oxidative addition of the organodistannane $\text{Me}_3\text{SnSnMe}_3$ to $\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)(\text{PPh}_3)_2$ or to $\text{Pt}(\text{PPh}_3)_4$ was described by Clark et al.¹²³ According to IR and NMR, they obtained *trans*- $(\text{Me}_3\text{Sn})_2\text{Pt}(\text{PPh}_3)_2$ and studied its reactions with H_2 , Br_2 , and HCl . The oxidative addition of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{Me}_2\text{Sn}-\text{SnMe}_2(\text{CH}_2)_n\text{PPh}_2$ ($n = 2$ or 3) to $\text{Pt}(\text{PPh}_3)_4$ gave mixtures of *cis* (**85**) and *trans* (**86**) isomers. The same products were obtained in the reaction of $\text{Me}_2\text{Sn}(\text{Cl})(\text{CH}_2)_n\text{PPh}_2$ with Na and PdL_4 .¹²⁴



The complexes were recrystallized and their structures confirmed by ^{31}P , ^{119}Sn , and ^1H NMR. An X-ray crystallographic analysis of the product of oxidative addition of $\text{Me}_3\text{SnSnMe}_3$ to $\text{Pt}[\text{P}(p\text{-Tol})_3]_4$ (**87**, $\text{R} = p\text{-Tol}$) showed that the complex has a twisted square planar structure with *cis*-orientation of the ligands (Scheme 107).¹²⁵ This is in contrast to the *trans*

Scheme 107

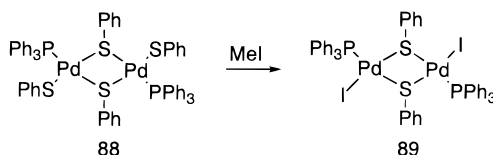


structure demonstrated by Clark.¹²³ The complex showed unique fluxional behavior. It was studied by multinuclear (including solid ^{31}P) NMR, X-ray crystallographic analysis, and ab initio MO calculations.

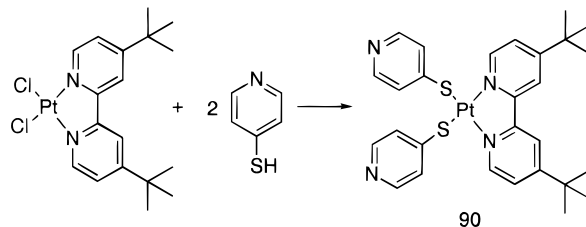
G. Pd and Pt Complexes with S-S

Oxidative addition of disulfides RSSR ($\text{R} = \text{Ph}$, o - and m - $\text{O}_2\text{NC}_6\text{H}_4$, $t\text{Bu}$, CN) to $\text{Pd}(\text{PPh}_3)_4$ was shown to lead to complexes containing S-Pd-S linkages.⁵⁷ These complexes could be dimeric or monomeric depending on the nature of the organic group. Dimer **88** was obtained with PhSSPh . Its reaction with MeI gave methylphenylsulfide and a mixed dimeric complex (**89**, Scheme 108). The complex formed with $(p\text{-O}_2\text{NC}_6\text{H}_4\text{S})_2$ was monomeric. All platinum complexes were monomeric, e.g., $(\text{RS})_2\text{Pt}(\text{PPh}_3)_2$. Complexes *cis*- $\text{M}(\text{PPh}_3)_2(\text{NCS})_2$, with the thiocyanogen ligand bound to the metal via the nitrogen atom, were easily formed from thiocyanogen, $(\text{SCN})_2$, and $\text{Pd}(0)$ or $\text{Pt}(0)$.

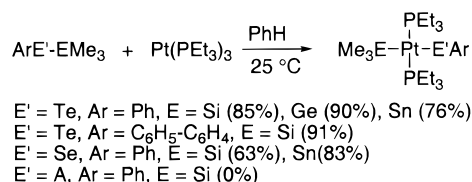
Scheme 108



Scheme 109



Scheme 110



The metathesis of Pt-Cl and H-S bonds was used for preparing a Pt complex (**90**) with an S-Pt-S moiety (Scheme 109). The complex was characterized by X-ray structural analysis.

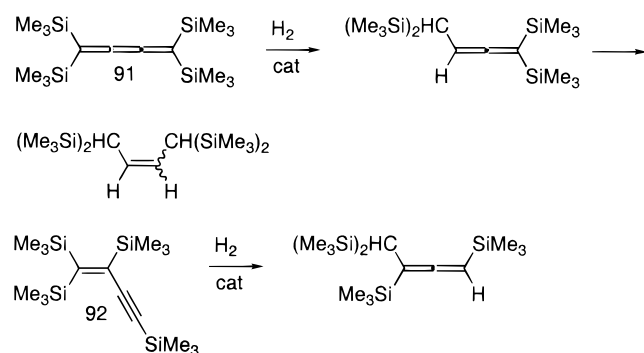
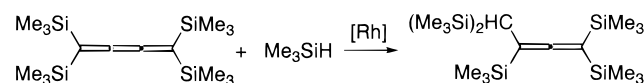
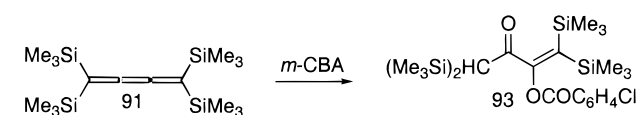
H. Pd and Pt Complexes with Sn(Si,Ge)-Se(Te)

All tellurides PhTeEMe_3 of the 14th group of elements ($\text{E} = \text{Si}$, Ge , Sn) add to $\text{Pt}(\text{PEt}_3)_n$, $n = 3, 4$, to give complexes with Te-Pt-E bonds. The ability of $\text{Pd}(\text{PEt}_3)_4$ to form analogous complexes is the same. A biphenyl analogue was characterized by X-ray crystallographic analysis and proved to have a *trans* square planar structure. The alkyltelluride complex $\text{BuTePt}(\text{PEt}_3)_2\text{SiMe}_3$ was formed quantitatively, according to NMR spectroscopy. The complexes with E-Te-Pt-E bonds ($\text{E} = \text{Si}$, Sn) were obtained from $(\text{Me}_3\text{Si})_2\text{Te}$ and $(\text{Me}_3\text{Sn})_2\text{Te}$ in 74% and 88% yield, respectively. The yields with ArTeSiMe_3 and ArTe-SnMe_3 were also high. Despite the possibility of oxidative addition via the C-Te bond,¹²⁶ only one product from oxidative addition, via the Te-M bond, was observed.⁵⁸

The reaction of PhSeSiMe_3 proceeded slowly at room temperature, but the complex *trans*- $\text{PhSePt}(\text{PEt}_3)_2\text{SiMe}_3$ could be obtained in good yield (24% after 0.5 h and 63% after 1 day). PhSeSnMe_3 was more reactive, affording the product from oxidative addition in 84% yield in less than 10 min. The sulfur derivatives PhSSiMe_3 and MeSSiMe_3 did not undergo oxidative addition even at elevated temperature. The complex $\text{PhTePt}(\text{PEt}_3)_2\text{SiMe}_3$ was stable in the solid state under argon but gradually decomposed in benzene even at room temperature, affording $\text{PhTePt}(\text{PEt}_3)_2\text{Ph}$, $\text{PhPt}(\text{PEt}_3)_2\text{TeSiMe}_3$, PhSiMe_3 , and $(\text{Me}_3\text{-Si})_2\text{Te}$ (Scheme 110).

IV. Synthetic Applications

Regio- and stereoselective addition of element-element bonds to triple bonds leads to a variety of

Scheme 111**Scheme 112****Scheme 113**

cis-substituted olefins which can be converted to many functionalized olefins and thus have a great potential synthetic value. We have already mentioned several reactions where C–E bonds are transformed into carbon–carbon bonds or carbon–heteroatom bonds. Further examples of such processes are described below.

A. Si–Si

Hydrogenation of silylated butatriene **91** and butenyne **92** using Rh/C, Pd/C, or Pt/C proceeds stepwise with formation of tetra(trimethylsilyl)-2-butene and tetra(trimethylsilyl)allene, respectively (Scheme 111).

Hydrosilylation of the triene, catalyzed by RhCl(PPh₃)₃, using Me₃SiH afforded a pentasilylated allene (Scheme 112).¹⁹

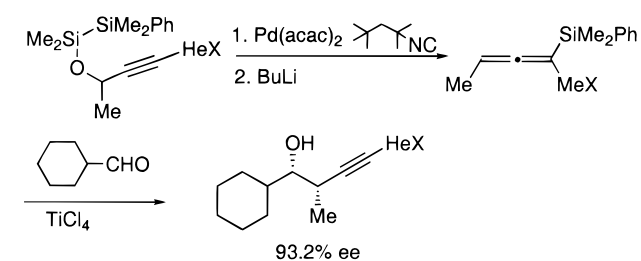
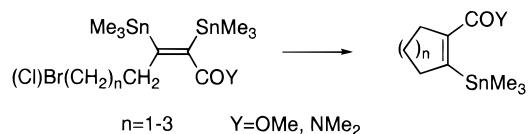
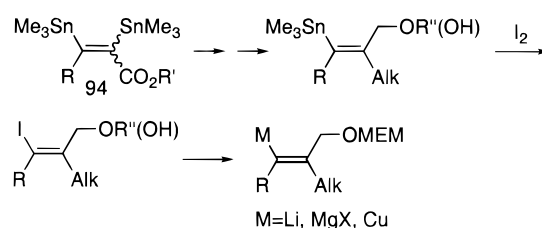
Other silanes, such as Et₃SiH, PhMe₂SiH, and Me₂ClSiH, did not react due to steric hindrance. The butenyne **92** did not undergo hydrosilylation.

Oxidation of the triene **91** by *m*-chlorobenzoic acid led to the formation of **93** (Scheme 113).²⁰

As mentioned previously, the *cis*-addition of disilanes to carbon–carbon triple bonds followed by Peterson syn elimination constituted the stereospecific synthesis of highly enantioenriched allenesilanes. A Lewis-acid-promoted reaction of these allenes with cyclohexanecarboxaldehyde proceeded stereoselectively to give homopropargylic alcohols with high enantiopurity (Scheme 114).²⁷

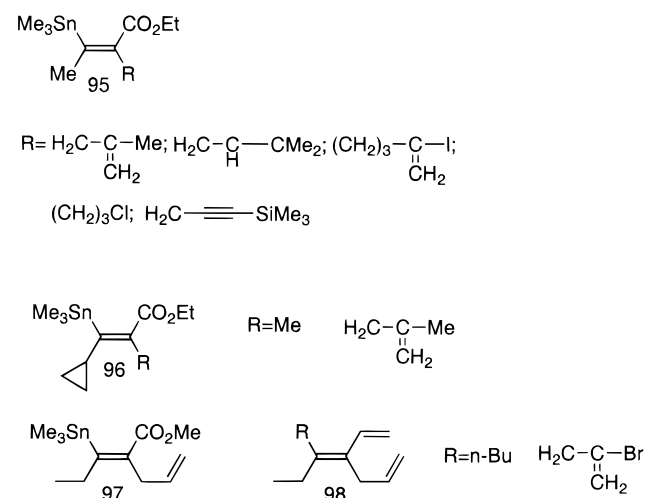
B. Sn–Sn

As mentioned above, the products formed in the Pd-catalyzed addition of ditin derivatives to α,β -acetylenic esters or amides bearing ω -alkyl groups serve as precursors of 2-(trimethylstannyl)cycloalk-1-ene carboxylic acid derivatives (Scheme 115).⁴⁴ Yields up to 70% after treatment with MeLi were observed.

Scheme 114**Scheme 115****Scheme 116**

The addition products, (*E*)- or (*Z*)-2,3-bis(trimethylstannyl)-2-alkenoates (**94**), were used for the synthesis of functionalized tetrasubstituted alkenes (Sn → Li → E). Reduction of the carboxylic group led to allylic alcohols (Scheme 116).¹²⁷

Compounds **95–98** are examples of compounds prepared in this manner.

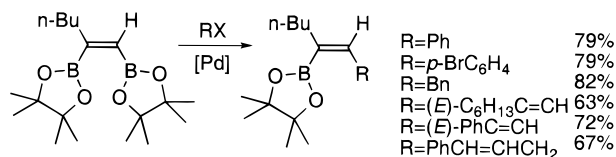
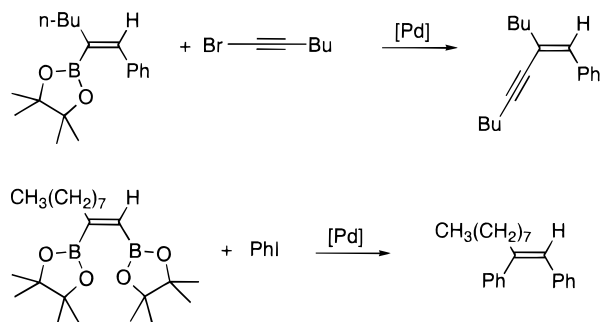
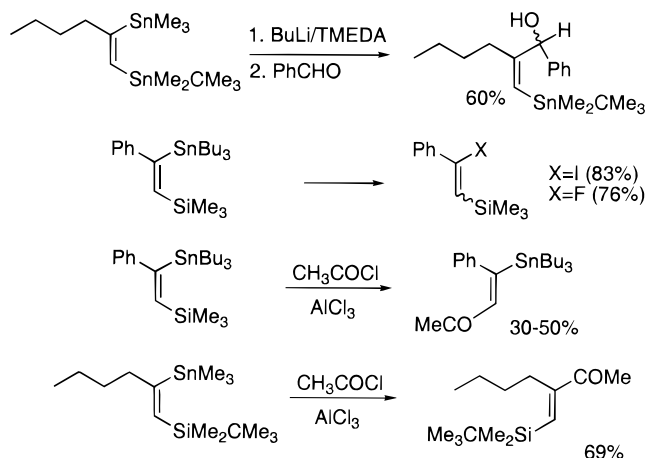
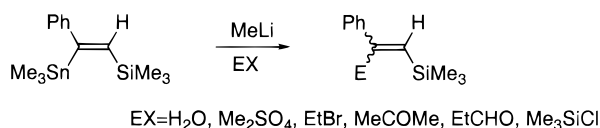


Reactions of (*Z*)-1,2-bis(trimethylstannyl)-1-alkenes with a variety of electrophiles have been reported.¹²⁸

C. B–B

The products obtained via diboration have been employed in a variety of Pd-catalyzed cross-coupling reactions (Scheme 117).⁴⁹

The diboranes, which are easily available from terminal acetylenes, can be treated with organic halides to afford trisubstituted alkenes (Scheme 118).⁵⁰

Scheme 117**Scheme 118****Scheme 119****Scheme 120****D. Si-Sn**

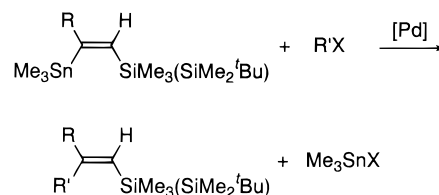
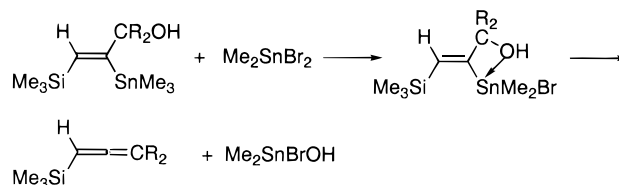
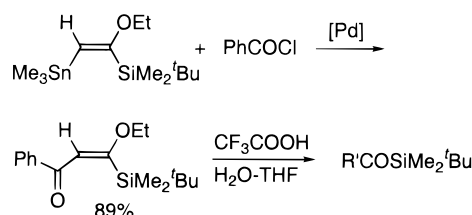
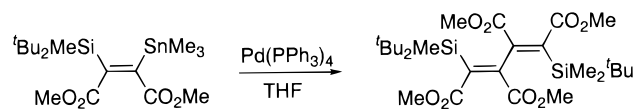
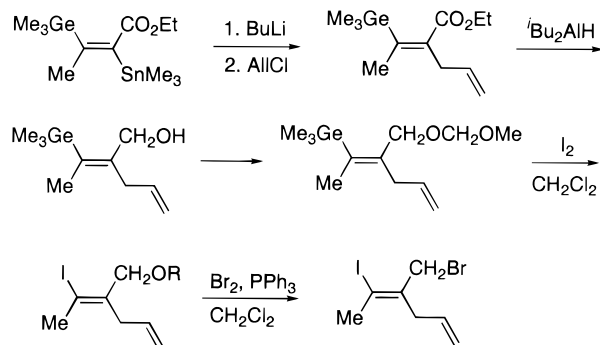
The products obtained by silylstannylation have a large synthetic potential in that they contain two reaction centers with different reactivity. The carbon-tin bond allows tin-lithium exchange, halogenation, and Lewis-acid-catalyzed acylation (Scheme 119).⁶⁴

The lithiated product reacts with a variety of electrophiles, such as aldehydes and, in the presence of Lewis acids, acid chlorides (Scheme 120).

The carbon-tin bond undergoes palladium-catalyzed reactions with allyl bromide, aryl halides, vinyl bromide, benzyl bromide, and acid chlorides (Scheme 121).⁶³

Treatment of the product with Me₂SnBr₂ led to allenasilanes (Scheme 122).⁶³

The product obtained by silylstannylation of ethoxyacetylene undergoes palladium-catalyzed cross-coupling reactions with iodobenzene, benzyl bromide,

Scheme 121**Scheme 122****Scheme 123****Scheme 124****Scheme 125**

allyl bromide, vinyl bromide, and acid chlorides to give products in high yields (Scheme 123).⁶⁶

The product from a silylstannylation has been transformed to a disilylated diene in a palladium-catalyzed reaction (Scheme 124).¹²²

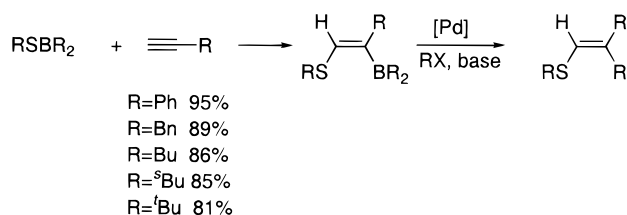
E. Ge-Sn

Germylstannylated α,β -acetylenic esters can be used in a variety of transformations. Treatment with butyllithium followed by alkylation gave an ester. Examples of other transformations are shown in Scheme 125.⁷¹

F. B-S

Thioboration of terminal alkynes leads to alkenes with boron at the terminal position. The borane

Scheme 126



derivatives undergo palladium-catalyzed cross-coupling reactions in the presence of base (Scheme 126). The reactions can be performed as one-pot procedures.⁷⁸

V. Conclusions

This review summarizes and discusses the literature on the formation of complexes containing E–M–E' bonds and the use of these complexes as reagents or catalysts in additions to alkynes. This type of regio- and stereoselective synthesis of functionalized olefins illustrates the power of transition-metal catalysis. Despite the great success of the synthetic methodology presented here, however, a lot of questions remain to be answered. It is still not clear what kinds of E–E' bonds can be added to a transition metal and what kind of metal (and ligand) is needed for this addition. Lots of efforts, including theoretical calculations and mechanistic studies, remain to be made before a clear picture of these reactions will emerge and their outcome will be predictable.

VI. Acknowledgment

A grant from the Swedish Research Council of Engineering Sciences covering the stay of I.B. in Stockholm made this review possible. We are grateful to Dr. Gunhild Aulin-Erdtman for valuable comments. The figures were drawn by Mr. Henry Challis.

VII. Note Added in Proof

After the completion of this review, a few additional articles related to the subject have appeared. *Silicon–Silicon*: Naka, A.; Lee, K. K.; Yoshizawa, K.; Yamabe, T.; Ishikawa, M. *J. Organomet. Chem.* **1999**, *587*, 1–8. Ito, Y. *J. Organomet. Chem.* **1999**, *576*, 300–304. *Tin–Tin*: Herberhold, M.; Steffl, U.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *577*, 76–81. *Silicon–Tin*: Bleckmann, P.; Englich, U.; Hermann, U.; Prass, I.; Ruhlandt-Senge, K.; Schürmann, M.; Schwittek, C.; Uhlig, F. *Z. Naturforsch. B* **1999**, *54*, 1188–1196. *Silicon–Boron*: Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787–8800. *Sulfur–Phosphorus*: Han, L. B.; Tanaka, M. *Chem. Lett.* **1999**, 863–864.

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