

II.2.6 Palladium Complexes Containing Metal Ligands

KOICHIRO OSHIMA

A. INTRODUCTION

Transition metal catalyzed addition reactions of metal–hydrogen bonds (Si—H, Sn—H) or metal–metal bonds (Si—Si, Sn—Sn, Si—B, Sn—B) to acetylenes and 1,3-dienes have attracted considerable attention as a general and straightforward route to alkenylmetals or allylmetals, which are extremely useful reagents in organic synthesis. Several Pd-catalyzed addition reactions are described in **Sect. VII.5**. Silyl complexes of palladium have been implicated as important intermediates in a number of Pd-catalyzed transformations of organosilanes, including the hydrosilylation and bis-silylation of organic substrates. In contrast to analogous platinum complexes, palladium silyls are generally considered to be unstable. The few isolated complexes that have been reported to date possess special stabilization from either strongly electron-withdrawing silyl groups or by inclusion of the silyl group in a chelate ring. Since a fundamental knowledge of the reactivity of palladium silyl compounds is essential to understanding their role as catalytic intermediates, the preparation of simple silyl derivatives of palladium has been extensively studied in recent years. Much effort also has been given to prepare and isolate the palladium–stannyl and palladium–boryl complexes in order to get information about the catalytic reaction mechanism.

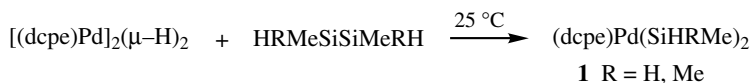
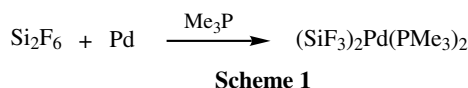
B. Silylpalladium Complexes

Silylpalladium complexes have attracted attention due to their relevance in the mechanism of Pd complex catalyzed reactions such as hydrosilylation of alkenes and dienes, bis-silylation of dienes and alkynes, carbosilylation of alkynes, cross-coupling of organic halides with disilanes, and ring-opening oligomerization and polymerization of cyclic disilanes and polysilanes.

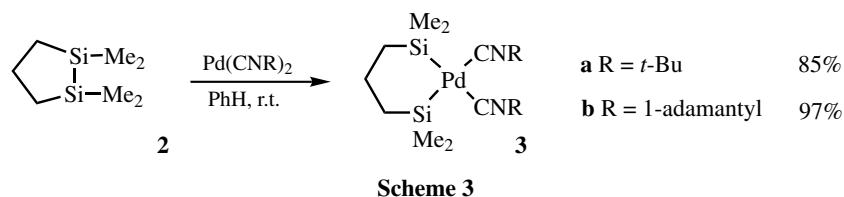
A variety of organosilyl–hydridopalladium complexes have been assumed to be generated *in situ* from hydrosilanes through oxidative addition of the silicon–hydrogen bonds onto palladium complexes. However, few studies have been reported on the isolation and characterization of silyl–hydrido complexes because of their instability.

In contrast, bis(organosilyl)palladium(II) complexes were easily prepared through oxidative addition of the Si—Si bonds onto low-valent palladium complexes.

Bis(trifluorosilyl)bis(trimethylphosphine)palladium was formed by a metal vapor/plasma technique (**Scheme 1**).^[1] Stable *cis*-bis(silyl)palladium complexes were prepared from the direct reaction of either hydrosilanes or 1,2-dihydrodisilanes with the novel dinuclear palladium hydride (**Scheme 2**). A first X-ray crystal structure of the bis(silyl) compound **1** was obtained.^[2]

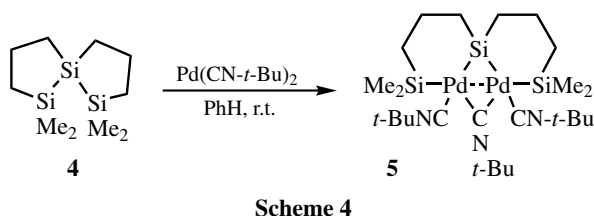


Oxidative addition of the silicon–silicon bond of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **2** onto bis(*tert*-butyl isocyanide)palladium(0) occurred instantaneously to give a six-membered cyclic bis(organosilyl)bis(*tert*-butyl isocyanide)palladium(II) complex **3a** (**Scheme 3**).^[3]

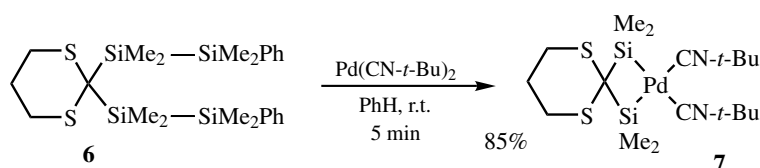


An X-ray analysis of the air-sensitive crystal of the bis(1-adamantyl isocyanide)palladacycle complex **3b** revealed a square planar structure with two coordinated isocyanide ligands on the palladium atom. An addition of phosphine ligands to a solution of **3** induced reductive elimination of the Si—Si bond to give 1,2-disilacyclopentane **2**. Thus, *tert*-alkyl isocyanide ligand plays a critical role to stabilize bis(organosilyl)palladium(II) complexes.

Noteworthy is that the spirocyclic trisilane **4**, in which both the five-membered rings contain an Si—Si bond, reacted with Pd(CN-*t*-Bu)₂ to give the dinuclear palladium(II) complex **5** having μ -silylene and μ -isocyanide ligands coordinated to the two palladium atoms (**Scheme 4**).^[4] Interestingly, an X-ray analysis showed that the two palladium atoms are separated by 2.75 Å, which is the same as the shortest metal–metal contact in metallic palladium.

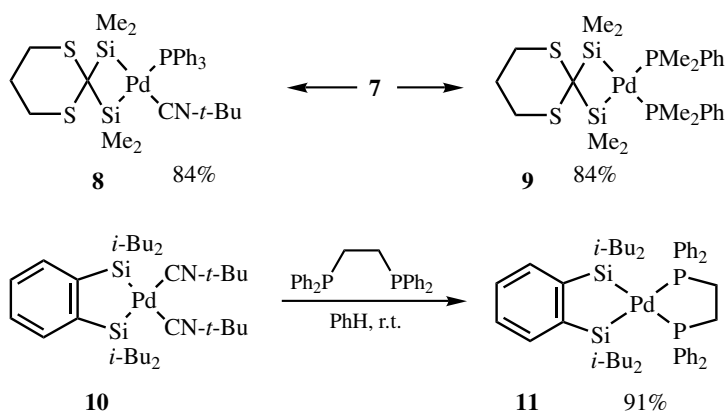


Reaction of bis(disilanyl)dithiane **6** with an equimolar amount of $\text{Pd}(\text{CN-}t\text{-Bu})_2$ in benzene was examined at room temperature. The reaction was completed within 5 min, affording 1,1,2,2-tetramethyl-1,2-diphenyldisilane and a four-membered cyclic bis-(organosilyl) complex **7** in 85% yield after isolation by crystallization with pentane (**Scheme 5**).^[5] A crystal structure of **7** exhibited a distorted square planar structure, in which the two silicon atoms in the ring are separated only by 2.61 Å. Presumably, the formation of **7** may have arisen from the simultaneous activation of the two Si—Si bonds on palladium, which led to intramolecular metathesis (disproportionation).



Scheme 5

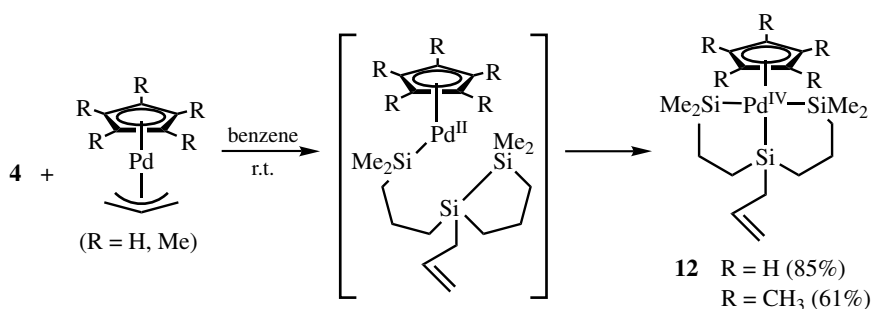
The isocyanide ligands in the four-membered complex **7** were replaced by phosphine ligands. Thus, addition of an equimolar amount of triphenylphosphine gave the corresponding mono(isocyanide)mono(phosphine)palladium(II) complex **8** in high yield (**Scheme 6**). A less bulky phosphine, dimethylphenylphosphine, could replace both isocyanide ligands to afford the bis(phosphine)palladium(II) complex **9**. Use of the bidentate ligand, bis(diphenylphosphino)ethane (dppe) and the five-membered palladium complex **10** gave the corresponding dppe complex **11**, whose structure was determined by a single-crystal X-ray analysis.^[6] As already mentioned, addition of dppe to the six-membered ring complex **3** resulted in reductive elimination to give disilane **2** along with an unidentified palladium complex having dppe ligands.



Scheme 6

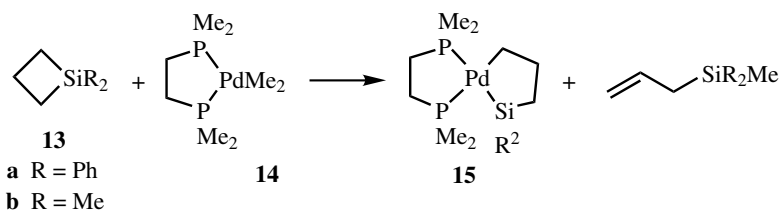
One exceptional reaction involving oxidative addition onto divalent palladium complexes has been reported. The spiro trisilane **4** is reacted with $(\eta^3\text{-allyl})\text{CpPd}(\text{II})$ complexes at room temperature to afford tris(organosilyl) $\text{CpPd}(\text{IV})$ complexes **12** in good

yields (**Scheme 7**).^[4] The reaction may be rationalized by oxidative addition of one of the two Si—Si bonds of **4**, subsequent reductive elimination with formation of the Silicon—allyl bond giving mono(silyl)CpPd(II) complexes, and then oxidative addition of another Si—Si bond in the molecule onto the Pd(II).



Scheme 7

Although silicon—carbon bonds usually are unreactive toward transition metal complexes, those of silacyclobutanes (**13**) are exceptions. They are reactive due to their ring strain. Quite a few reactions of **13** that are catalyzed by transition metal complexes have been reported, such as ring-opening polymerization, dimerization, cross-dimerization with disilanes, and cycloaddition reactions^{[7],[8]} with acetylenes and allenes. 1-Metalla-2-silacyclopentanes are believed to be involved as intermediates in these catalytic reactions. Indeed, 1-pallada-2-silacyclopentane complexes have been isolated. 1,1-Diphenyl- and 1,1-dimethylsilacyclobutanes **13** have reacted with Me₂Pd(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) or Pd(PhCH=CH₂)(dmpe) to give 2,2-diphenyl- and 2,2-dimethyl-1-pallada-2-silacyclopentane complexes, the diphenyl complex **15a** being characterized by X-ray analysis (**Scheme 8**).^[9]

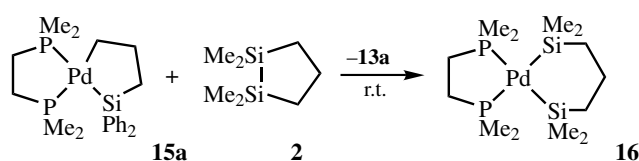


Scheme 8

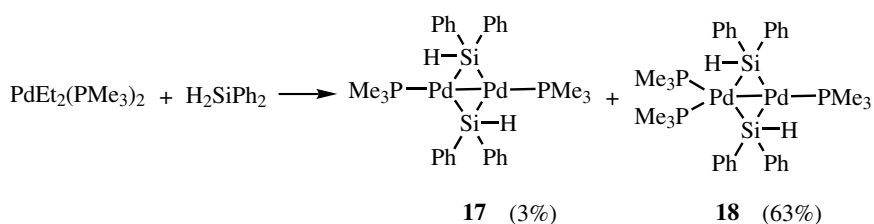
When 1,1,2,2-tetramethyl-1,2-disilacyclopentane **2** was added to **15a** in C₆D₆ in a sealed NMR tube, nearly quantitative formation of a bis(silyl)complex **16** was observed after 24 h at room temperature, together with **13a** (97%) arising from reductive elimination (**Scheme 9**).

Dipalladium complexes with bridging diorganosilyl ligands have been prepared. The complexes *trans*-PdEt₂L₂ (L = PMe₃, PEt₃, or PMePh₂) reacted with equimolar or twofold molar amounts of H₂SiPh₂ to produce various bimetallic palladium(II) complexes with bridging diphenylsilyl ligands, [(Me₃P)Pd(μ-SiHPh₂)]₂ **17**, (Me₃P)Pd(μ-SiHPh₂)Pd(PMe₃)₂

18, and $[\text{LPd}(\mu\text{-SiHPh}_2)]_2$ ($\text{L} = \text{PEt}_3$ **19** or PMePh_2 **20**), in moderate to good yields (**Scheme 10**).^[10] Similar reactions using H_2SiMePh afforded the complexes $[\text{LPd}(\mu\text{-SiHMePh})]_2$ ($\text{L} = \text{PMe}_3$ **21a** or PEt_3 **21b**). The isolated complexes were characterized by NMR spectroscopy and elemental analyses. Molecular structures of **19** and **21a** have been determined by X-ray crystallography and suggest an agostic interaction between the $\mu\text{-SiHPh}_2$ or $\mu\text{-SiHMePh}$ group and the Pd. The NMR study of the complexes revealed the bridging coordination of the silyl ligand with the Si—H—Pd three-center, two-electron bond in solution similar to that in the solid state. Complex **18** undergoes exchange of the PMe_3 ligands on the NMR timescale. The reactions of **18** with CO and HSPH afforded **17** and $\text{Pd}(\text{SPh})_2(\text{PMe}_3)_2$, respectively.

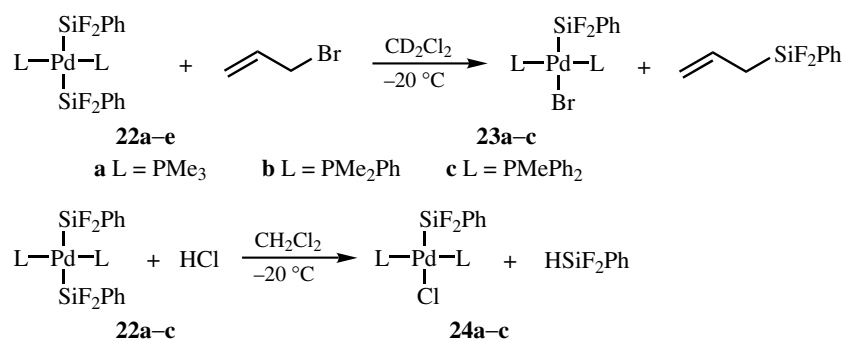


Scheme 9



Scheme 10

Reactions of $\text{trans-Pd}(\text{SiF}_2\text{Ph})_2\text{L}_2$ [$\text{L} = \text{PMe}_3$ (**22a**), PMe_2Ph (**22b**), PMePh_2 (**22c**)] with allyl bromide readily proceeded in CH_2Cl_2 at -20°C to form $\text{CH}_2=\text{CHCH}_2\text{SiF}_2\text{Ph}$ and the corresponding bromo(silyl)palladium complexes, $\text{trans-PdBr}(\text{SiF}_2\text{Ph})\text{L}_2$ (**23a–23c**) in high selectivities. Treatment of **22a–22c** with dry HCl in CH_2Cl_2 at -20°C gave silyl chloride complexes, $\text{trans-PdCl}(\text{SiF}_2\text{Ph})\text{L}_2$ (**24a–24c**), respectively (**Scheme 11**). Complexes **23a–23c** and **24a–24c** were isolated and characterized by NMR spectroscopy



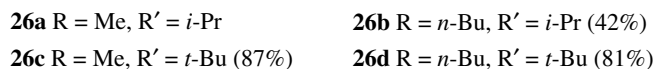
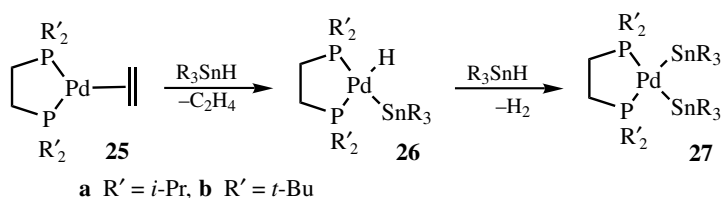
Scheme 11

and/or elemental analysis. One of the complexes, *trans*-PdCl(SiF₂Ph)(PMe₂Ph)₂ (**24b**), was identified also by X-ray diffraction study. Relevance of bis-silyl complexes to catalytic silylation of allylic compounds with disilanes has been discussed.^[11]

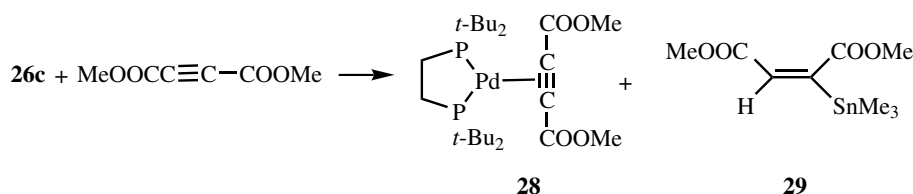
C. STANNYLPALLADIUM COMPLEXES

Palladium-catalyzed hydrostannation of alkynes proceeds regio- and stereospecifically to afford the synthetically useful (*E*)-vinylstannanes. This reaction implies oxidative addition of R₃Sn—H to Pd(0) to generate a Pd(II) hydrido stannyl intermediate, which then undergoes *cis* addition of the Pd—Sn bond to the alkyne bond, followed by reductive elimination of the (*E*)-vinylstannane.^[12] The supposed *cis*-Pd(II) hydrido trialkylstannyl intermediates had so far remained elusive. Very recently, *cis*-Pd(II) hydrido trialkylstannyl complexes have been synthesized for the first time.^[13]

The complexes (R'₂PC₂H₄PR'₂)Pd(C₂H₄) (**25a**: R' = *i*-Pr, **25b**: R' = *t*-Bu) react with R₃SnH (R = Me, *n*-Bu) by displacement of the ethene ligand and oxidative addition of the Sn—H bond to generate the chelating phosphane stabilized *cis*-Pd(II) hydrido stannyl complexes (R'₂PC₂H₄PR'₂)PdH(SnR₃) (R' = *i*-Pr, *t*-Bu) (**Scheme 12**). Complex **26a** (R' = *i*-Pr, R = Me), containing the smallest substituents, is only transiently formed but has been detected at −80 °C by NMR spectroscopy. In contrast, the isolated (d-*i*-ppe)PdH(Sn-*n*-Bu₃) (**26b**) is briefly stable at ambient temperature, whereas the sterically encumbered species (d-*t*-bpe)PdH(SnR₃) [R = Me (**26c**), *n*-Bu (**26d**)] are stable well above 100 °C. The molecular structure of **26c** has been determined by X-ray crystallography. Complex **26c** reacts with 2 equiv of C₂R''₂ [R'' = CO₂Me] to give (d-*t*-bpe)Pd(C₂R''₂) (**28**) and predominantly the corresponding (*E*)-vinylstannane (*E*)-(R'')(H)C=C(SnMe₃)(R'') (**29**) (**Scheme 13**). Since **26c** also catalyzes the hydrostannation of the alkyne, the *cis*-Pd(II) hydrido stannyl complexes **26a**, **26b**, **26c**, and **26d** represent trapped intermediates in the Pd-catalyzed hydrostannation of alkynes.



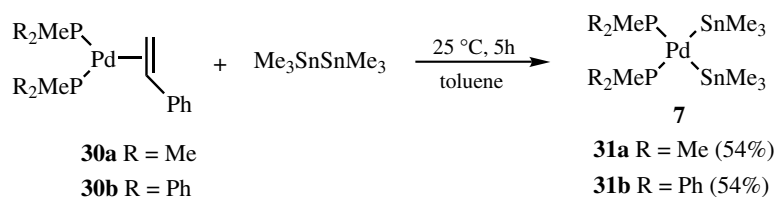
Scheme 12



Scheme 13

The complex **26a** reacts further with Me_3SnH to yield $(d\text{-}i\text{-ppe})\text{Pd}(\text{SnMe}_3)_2$ (**27a**) and hydrogen. The reaction probably proceeds through an octahedral $[(d\text{-}i\text{-ppe})\text{Pd}(\text{H})_2(\text{SnMe}_3)_2]$ intermediate, which reductively eliminates the hydrogen.

Oxidative addition of $\text{Me}_3\text{SnSnMe}_3$ to the corresponding $\text{Pd}(0)$ complexes is an alternative procedure for the preparation of *cis*-bis(stannyl)bis(phosphine)palladium complexes.^[14] An addition of $\text{Me}_3\text{SnSnMe}_3$ to $\text{Pd}(\text{styrene})(\text{PR}_2\text{Me})_2$ **30a** provided the bis(stannyl) complexes **31a**, which were often employed as a catalyst precursor in bis(stannylation) reactions using organodistannanes (**Scheme 14**). X-ray analysis showed that the complex has a twisted square-planar structure; the dihedral angle between the PdP_2 and the PdSn_2 plane is 16.8° .



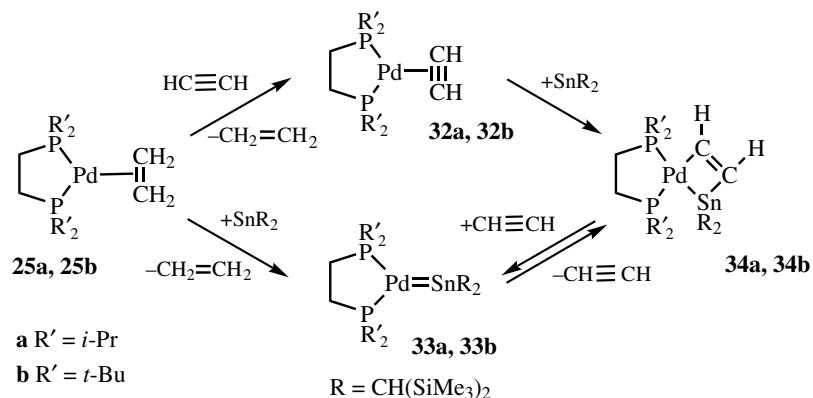
Scheme 14

The mechanistic study on a Pd-catalyzed $(2 + 2 + 1)$ cycloaddition reaction of two ethenes and one stannylene $[\text{SnR}_2, \text{R} = \text{CH}(\text{SiMe}_3)_2]$ to form stannoles ($\text{C}_4\text{H}_4\text{SnR}_2$) led to an isolation of $\text{Pd}(0)\text{--Sn(II)}$ adducts.^[15] The ethene ligands in $(i\text{-Pr}_2\text{PC}_2\text{H}_4\text{P-}i\text{-Pr}_2)\text{Pd}(\text{C}_2\text{H}_4)$ (**25a**) and $(t\text{-Bu}_2\text{PC}_2\text{H}_4\text{P-}t\text{-Bu}_2)\text{Pd}(\text{C}_2\text{H}_4)$ (**25b**) are readily displaced by ethyne at $-78/-30^\circ\text{C}$ to yield the corresponding $\text{Pd}(0)\text{--ethyne}$ complexes $(i\text{-Pr}_2\text{PC}_2\text{H}_4\text{P-}i\text{-Pr}_2)\text{Pd}(\text{C}_2\text{H}_2)$ (**32a**) and $(t\text{-Bu}_2\text{PC}_2\text{H}_4\text{P-}t\text{-Bu}_2)\text{Pd}(\text{C}_2\text{H}_2)$ (**32b**) (**Scheme 15**). In addition, the ethene ligands are just as readily displaced by stannylenes. Thus, when pentane solutions of **25a** and **25b** are combined with the magenta ethereal solution of SnR_2 at 0°C , the color turns red and at $-30/-78^\circ\text{C}$ large dark red cubes of the $\text{Pd}(0)\text{--stannylene}$ complexes **33a** (90%) and **33b** (84%), respectively, separate. Complexes **33a** (mp 171°C) and **33b** (mp 214°C) are thermally stable and are very soluble in ether or hydrocarbons. In the EI mass spectra (70 eV; $120\text{--}150^\circ\text{C}$), the molecular ions of **33a** (806) and **33b** (862) are detected, which fragment with stepwise destruction of the stannylene ligand to form the ions $[(d\text{-}i\text{-ppe})\text{Pd}]^+$ and $[(d\text{-}t\text{-bpe})\text{Pd}]^+$, respectively. Complexes **33a** and **33b** represent adducts of stannylene with $(\text{R}'_2\text{PC}_2\text{H}_4\text{PR}'_2)\text{Pd}(0)$ fragments in which both metal atoms are trigonal-planar (*TP*-3) coordinated.

When the colorless ethereal solution of the $\text{Pd}(0)\text{--ethyne}$ complex **32** and the magenta solution of SnR_2 are mixed at -30°C , orange crystals of the 1,2-palladastannete complex **34a** separate in 94% yield. The reaction proceeds virtually instantaneously at -30°C and is also fast at -100 to -78°C . Correspondingly, the pentane suspension of **32b** reacts with SnR_2 at -78°C to produce the orange precipitate of **34b** in 74% yield (**Scheme 15**). By reacting the deuterated ethyne complex $(i\text{-Pr}_2\text{PC}_2\text{H}_4\text{P-}i\text{-Pr}_2)\text{Pd}(\text{C}_2\text{D}_2)$ (**32a**) with SnR_2 , the ring deuterated derivative $(i\text{-Pr}_2\text{PC}_2\text{H}_4\text{P-}i\text{-Pr}_2)\text{Pd}(\text{CD}=\text{CD})\text{SnR}_2$ (**34a**) can be synthesized.

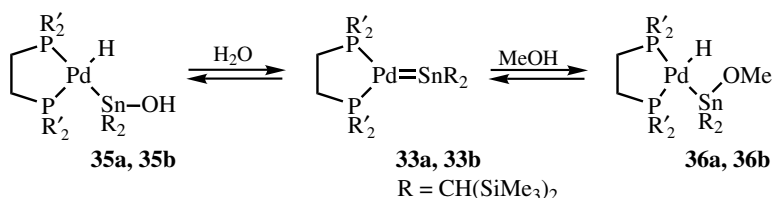
The 1,2-palladastannete complexes **34a** and **34b** are also obtained by treating the $\text{Pd}(0)\text{--stannylene}$ complexes **33a** and **33b** with ethyne. When the red ethereal or pentane solutions of **33a** and **33b** are exposed to ethyne at -78°C , the color lightens immediately and soon after complexes **34a** (93%) and **34b** (60%) precipitate (**Scheme 15**). It is

important that the syntheses are carried out at low temperatures (**34a**, $-30\text{ }^{\circ}\text{C}$ or below; **34b**, $-78\text{ }^{\circ}\text{C}$) and that **34b** quickly precipitates from the solution (pentane) to avoid the ring degradation reaction.



Scheme 15

The adducts $\text{L}_2\text{Pd}(0)=\text{SnR}_2$ (L_2 = chelating bidentate phosphane) undergo reversible oxidative addition of water and methanol.^[16] When deoxygenated water is added at $20\text{ }^{\circ}\text{C}$ to the red THF solutions of the complexes $(\text{R}'_2\text{PC}_2\text{H}_4\text{PR}'_2)\text{Pd}=\text{SnR}_2$ [$\text{R}' = i\text{-Pr}$ (**33a**), $t\text{-Bu}$ (**33b**)], the color fades immediately. After evaporation of the solvent and recrystallization (pentane), colorless crystals of the bimetallic hydrido–hydroxy complexes $(\text{R}'_2\text{PC}_2\text{H}_4\text{PR}'_2)\text{Pd}(\text{H})\text{Sn}(\text{OH})\text{R}_2$ [$\text{R}' = i\text{-Pr}$ (**35a**), $t\text{-Bu}$ (**35b**)] are isolated. Similarly, complexes $(\text{R}'_2\text{PC}_2\text{H}_4\text{PR}'_2)\text{Pd}(\text{H})\text{Sn}(\text{OCH}_3)\text{R}_2$ [$\text{R}' = i\text{-Pr}$ (**36a**), $t\text{-Bu}$ (**36b**)] are obtained by an addition of methanol (Scheme 16).

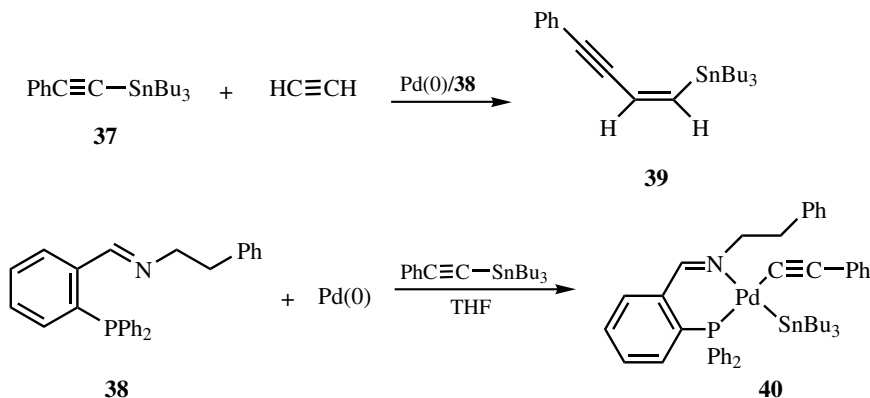


Scheme 16

When **35a** ($100\text{ }^{\circ}\text{C}$) and **36a** ($70\text{ }^{\circ}\text{C}$) are heated under vacuum, they slowly eliminate water and methanol, respectively, to form **33a** (ca. 35% conversion of **35a** in 1 h). Thus, the oxidative addition of water or methanol to **33a** and **33b** to afford **35a**, **35b**, **36a**, and **36b** is reversible and methanol elimination proceeds more readily than water elimination.

Carbostannylation of alkynes generates *cis*-substituted alkenylstannanes and is one of the most useful reactions for stereoselective olefin synthesis. Treatment of tributyl-(phenylethynyl)tin **37** with a 1:2 mixture of $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ -*N*-(2-diphenylphosphino benzylidene)-2-phenylethylamine (**38**) under an acetylene atmosphere in THF at

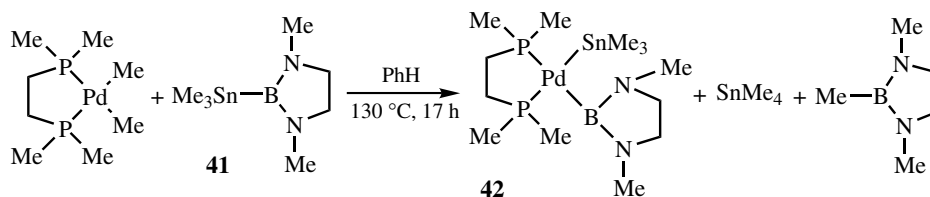
50 °C gave tributyl[(*Z*)-2-(phenylethynyl)ethenyl]tin **39** in good yield. The palladium–stannane complex (**40**), which could be generated by oxidative addition of Pd(0) coordinated by **38** onto C—Ph bond of phenylethyne, is assumed to involve the catalytic cycle (Scheme 17).^{[17],[18]}



Scheme 17

D. BORYLPALLADIUM COMPLEXES

cis-Addition of the borylstannanes $\text{Me}_3\text{SnB}[\text{NMe}(\text{CH}_2\text{CH}_2)\text{NMe}]$ (**41**) across alkynes was efficiently catalyzed at room temperature or 80 °C by $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{dba})_2$, $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, or $\text{Me}_2\text{Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ to give (β -stannylalkenyl)boranes in high yields. Treatments of **41** with $\text{Me}_2\text{Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ (**14**) and gave $[\{\text{MeN}(\text{CH}_2\text{CH}_2)\text{MeN}\}\text{B}](\text{Me}_3\text{Sn})\text{Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ (**42**), which was characterized by X-ray analysis (Scheme 18). Complex **42**, when treated with 1-octyne, formed the corresponding (β -stannyl-1-octen-1-yl)borane and could catalyze the addition reaction of **41** with 1-octyne.^[19]



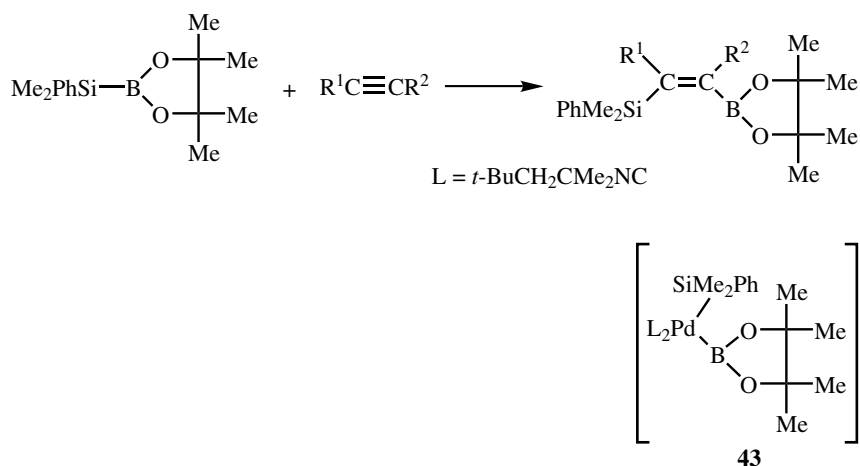
Scheme 18

Addition of the silicon–boron bond across carbon–carbon triple bonds (i.e., silaboration) is most effectively catalyzed by a palladium(0)-*tert*-alkyl isocyanide complex to give (*Z*)-1-boryl-2-silyl alkenes with high regio- and stereoselectivity, which are useful for synthesis of stereodefined alkenylsilanes.

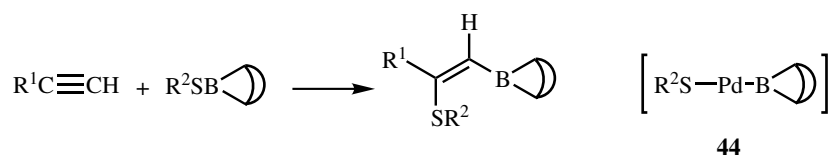
The (boryl)(silyl)palladium intermediate **43**, which is formed by oxidative addition of silylborane onto palladium, would play a critical role for the reaction (Scheme 19).^{[20],[21]}

The thioboration of alkynes with 9-(alkylthio)-9-borabicyclo[3.3.1]nonane also proceeds with high regio- and stereoselectivity in the presence of Pd(0) catalyst. Like other

related reactions catalyzed by transition metals, especially the catalytic hydroboration and the addition of thiols or disulfides to alkynes, the present thio-boration reaction may involve an oxidative addition of the B—S bond to the palladium(0) complex. Although the complex (44) might be postulated as a reactive catalyst, no direct evidence has been provided (Scheme 20).^[22]



Scheme 19



Scheme 20

E. SUMMARY

1. The chemistry of metal–palladium complexes has received particular attention in relation to the mechanism of Pd-catalyzed reactions such as hydrosilylation, bis-silylation, or hydrostannation.

2. Reports on palladium complexes with organosilyl ligands are fewer in number than those on silylplatinum complexes because of their instability. Very recently, bis(silyl)palladium complexes have been isolated and characterized by X-ray analysis.

3. Hydridostannyl–palladium complexes have been prepared by an addition of R_3SnH to palladium–ethylene complex. The use of distannane in place of hydrostannane affords distannyl–palladium complex by oxidative addition of distannane onto Pd(0) species.

4. The borylstannyl–palladium complex has been also isolated from the reaction of borylstannanes with low-valent palladium complex. The borylsilyl–palladium complex might be also postulated as a reactive catalyst. However, no direct evidence has been provided.

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