Accounts

Platinum and Palladium Complexes with Metal–Silicon Bonds. New Bonding, Structures, and Chemical Properties

Kohtaro Osakada* and Makoto Tanabe

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

Received January 28, 2005; E-mail: kosakada@res.titech.ac.jp

Studies on the Pt and Pd complexes with Si-containing ligands by the authors are reviewed. *trans*-$[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$, the first Pt(II) complex with two silyl ligands at trans positions, is equilibrated with the thermodynamically more stable *cis* isomer in solution. The reaction of dimethyl acetylenedicarboxylate (Z–C≡C–Z, Z = COOMe) with $[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$ produces 3-sila-1-propenylplatinum complex, *cis*-$[\mathrm{Pt(CZ{=}CZSiHPh_2)(SiHPh_2)(PMe_3)_2}]$, and 4-sila-3-platinacyclobutene, $[\overline{\mathrm{Pt(CZ{=}CZSi}}\mathrm{Ph_2)(PMe_3)_2}]$, depending on the reaction conditions. The former product is turned into the latter, accompanied by elimination of $\mathrm{H_2SiPh_2}$. The spectroscopic data of *cis*-$[\mathrm{Pt(CZ{=}CZSiHPh_2)(SiHPh_2)(PMe_3)_2}]$ as well as the crystallographic structure of the 3-sila-1-propenylplatinum with a chelating bisphosphine, $[\mathrm{Pt(CZ{=}CZSiHPh_2)(SiHPh_2)(dmpe)}]$ (dmpe = 1,2-bis(dimethylphosphino)ethane), indicate intramolecular interaction of the γ-Si–H hydrogen of the ligand with the Pt center. The 4-sila-3-platinacyclobutene reacts with mono-substituted alkynes to produce various 5-sila-2-platina-1,4-cyclohexadienes via insertion of the C≡C bond into the Pt–Si bond of the four-membered ring. $[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$ reacts with nitriles to cause double addition of the Si–H bonds to the C≡N triple bond, yielding $[\overline{\mathrm{Pt\{SiPh_2N(CH_2R)Si}}\mathrm{Ph_2\}(PMe_3)_2}]$ (R = Me and Ph). The reactions of $\mathrm{H_2SiPh_2}$ and $\mathrm{H_2SiPhMe}$ with $[\mathrm{PdEt_2(PMe_3)_2}]$ afford dinuclear Pd complexes with bridging silyl ligands, $[\{\mathrm{Pd(PMe_3)}\}\{\mathrm{Pd(PMe_3)}_n\}(\mu\text{-}\mathrm{HSiPhR})_2]$ (R = Me and Ph; n = 1 and 2). Pd–Pt heterobimetallic complexes with bridging diphenylsilyl ligands, $[\{\mathrm{Pd(PR_3)}\}\{\mathrm{Pt(PR_3)}_n\}(\mu\text{-}\mathrm{HSiPh_2})_2]$ (R = Et and Cy (cyclohexyl); n = 1 and 2), are obtained from the reactions of bis(silyl)platinum(II) complexes with palladium(0)–phosphine complexes. The heterobimetallic complex with $\mathrm{PEt_3}$ ligands reacts with *t*-butyl isocyanide to afford a new disilaplatinacyclopentane, $[\overline{\mathrm{Pt\{SiPh_2CH_2N(\mathit{t}\text{-}Bu)Si}}\mathrm{Ph_2\}(PEt_3)(CN\text{-}\mathit{t}\text{-}Bu)}]$. Heating of $[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$ at 80 °C in solution produces a trinuclear Pt complex with bridging diphenylsilylene ligands, $[\{\mathrm{Pt(PMe_3)}\}_3(\mu\text{-}\mathrm{SiPh_2})_3]$, which was characterized by X-ray crystallography, NMR spectroscopy, and theoretical calculations.

Background

Studies of Pt–Si complexes began with the discovery of bis(silyl)platinum complexes by Chatt and Eaborn in 1966.[1,2] These complexes have attracted attention because they are related to the mechanism of the hydrosilylation of alkenes catalyzed by Pt complexes.[3] Although the active species of hydrosilylation catalysts such as $\mathrm{H_2PtCl_6}$ are considered to be colloidal Pt metals, formed by the reduction of Pt(II) or Pt(IV) compounds of Si–H groups of the substrates,[4–6] the molecular Pt complexes also promote the hydrosilylation of olefins and many other unsaturated compounds.[7–11] Chalk and other researchers proposed two mechanisms for the hydrosilylation of olefins catalyzed by Pt complexes.[12,13] One mechanism involves the initial formation of a hydrido(silyl)platinum(II) intermediate, followed by the insertion of olefin into the Pt–H bond, and the reductive elimination of alkylsilane (Chalk–Harrod mechanism). The insertion of olefin into the Pt–Si bond of the intermediate also leads to the formation of a hydrosilylation product (modified Chalk–Harrod mechanism). Theoretical studies on the pathway of hydrosilylation of ethylene promoted by a Pt(0)–$\mathrm{PH_3}$ complex indicate that the Chalk–Harrod mechanism is more favorable due to a high energy barrier during insertion of ethylene into the Pt–Si bond in the modified Chalk–Harrod mechanism.[14–16] The alkyl(silyl)platinum complexes[17,18] and silylpalladium complexes[19] undergo several important reactions that include the insertion of alkynes into the M–Si bond.

The chemical properties of compounds with M–Si bonds differ from those with M–C bonds. Scheme 1 depicts the fundamental reactions of late transition-metal complexes having M–C and M–Si bonds. Two alkyl or silyl ligands at cis positions of late transition-metal complexes undergo coupling to induce the reductive elimination of the corresponding alkanes or disilanes. Although the high stability of the Pt–C bond prevents the smooth reductive elimination of alkanes from the dialkylplatinum complexes, thermal reactions of diarylplatinum complexes induce the reductive elimination of biaryls.[20] Disilanes cause smooth oxidative addition to low valent transition-metal complexes, leading to cleavage of the Si–Si bond, al-

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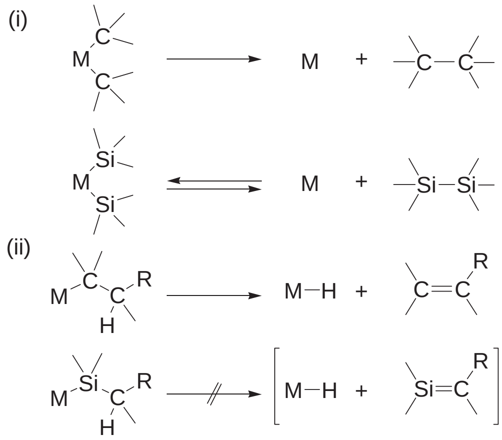


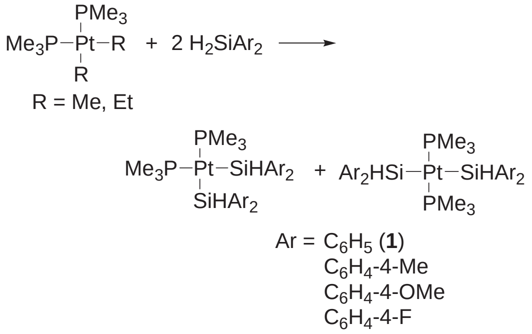
Scheme 1. Fundamental reactions of transition-metal complexes having M–C and M–Si bonds (M = metal center with supporting ligands).

though the oxidative addition of alkanes, accompanied by C–C bond cleavage, occurs only in limited cases (Scheme 1(i)). Many alkyl complexes of transition-metals undergo β-hydrogen elimination to form hydrido complexes and olefins very easily, while the β-hydrogen elimination of the silyl metal complexes does not occur, probably due to instability of the transition state that has a partial C=Si double-bond character (Scheme 1(ii)).

Over the last these few decades, many research groups have reported the chemical properties of new transition-metal complexes with Si-containing ligands, as summarized in the review articles.[21–25] We turned our interest from mono- and di-nuclear Rh complexes with Si-ligands[26] to Pt–Si complexes in 1997. The results obtained over the last decade are described in this article.

Mononuclear Silylplatinum Complexes

Previous studies of the silyl complexes of Pt(II), formulated as $[\mathrm{Pt(SiR_3)_2(PR'_3)_2}]$ and $[\mathrm{PtH(SiR_3)(PR'_3)_2}]$ by X-ray crystallography and NMR spectroscopy, indicate that these complexes have a strong tendency to form a cis structure.[27–31] The hydrido and silyl ligands exhibit larger trans influence than alkyl and many other ligands, as shown in the bond parameters and the NMR coupling constants of the complexes. The exclusive formation of the *cis* isomer of the above complexes was attributed to a large trans effect of the ligands. The 2:1 reaction of $\mathrm{H_2SiPh_2}$ with *cis*-$[\mathrm{PtR_2(PMe_3)_2}]$ (R = Me and Et) affords $[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$ (**1**) as a mixture of the *trans* and *cis* isomers, as shown in Eq. 1.[32] The recrystallization of the products results in isolation of *trans*-$[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$ (***trans*-1**) as the first Pt complex having two silyl ligands at trans positions. X-ray crystallography indicates the trans geometry with a long Pt–Si bond distance (2.407(2) Å). Dissolution of ***trans*-1** readily regenerates a mixture of the *cis* and *trans* isomers. The NMR studies in the solution indicate the presence of equilibrium between the *cis* and *trans* isomers. The *trans* isomer is more stable than the *cis*, with thermodynamic parameters: $\Delta H^\circ = 5.7(3)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ = 6.7(7)\,\mathrm{J\,mol^{-1}\,deg^{-1}}$ in $\mathrm{CD_2Cl_2}$, and $\Delta H^\circ = 3.8(2)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ = 3.5(6)\,\mathrm{J\,mol^{-1}\,deg^{-1}}$ in THF-d_8. Analogous complexes with $\mathrm{SiHAr_2}$ ligands (Ar = $\mathrm{C_6H_4}$-4-Me, $\mathrm{C_6H_4}$-4-OMe, and $\mathrm{C_6H_4}$-4-F) and with $\mathrm{PEt_3}$ also exist as mixtures of the *cis* and *trans* isomers in solution.

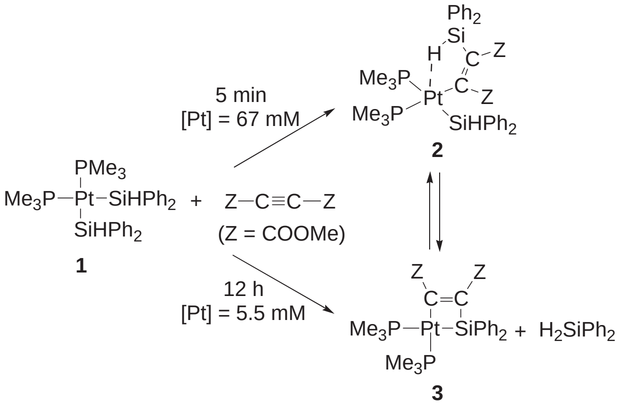


(1)

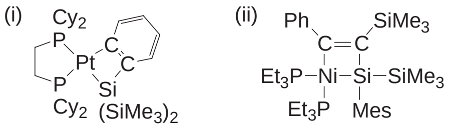
Very recently, Perutz et al. reported the preparation of *trans*-$[\mathrm{PtH(SiMe_{3-\mathit{n}}Cl_{\mathit{n}})(PCy_3)_2}]$ (n = 1–3) from chloro(methyl)silanes and $[\mathrm{Pt(PCy_3)_2}]$ (Cy = cyclohexyl).[33] The reaction at −78 °C forms *cis*-hydrido(silyl)platinum complexes, which have the reasonable configuration as the product of concerted oxidative addition of the Si–H bond to platinum. *cis* Isomer is easily converted into the *trans* isomer at 20 °C, indicating that the latter is thermodynamically more stable than the former. X-ray crystallography of *cis*-$[\mathrm{PtH(SiHPh_2)(PCy_3)_2}]$ shows a highly distorted square-planar structure due to severe steric repulsion between the bulky phosphine ligands, which is probably related to the stability of the *trans* complex being higher than that of the *cis*. Kang and his co-workers reported another example of the Pt complex with two silyl ligands at trans positions. Both the *trans* and *cis* isomers of the Pt complex were obtained by employing P–Si chelating ligands with bridging carboranediyl groups.[34,35] There seems to be no steric reason to stabilize the *trans* isomer because stereochemical circumstances around the P atom and Si atom of the ligands are similar to each other. Their DFT studies of the complex support the higher thermodynamic stability of the *trans* isomer compared to that of the *cis*.

Several research groups investigated stoichiometric reactions of alkynes with silylplatinum complexes and discussed the insertion of alkynes into the Pt–Si bond in detail.[36–40] The reaction of dimethyl acetylenedicarboxylate (Z–C≡C–Z, Z = COOMe) with **1** produces two complexes depending on the reaction conditions, as shown in Scheme 2.[41,42] The equimolar reaction with [Pt] = 67 mM for 5 min and the quick isolation of the products afford a 3-sila-1-propenylplatinum complex, *cis*-$[\mathrm{Pt(CZ{=}CZSiHPh_2)(SiHPh_2)(PMe_3)_2}]$ (**2**), via insertion of the alkyne into the Pt–Si bond. The reaction with [Pt] = 5.5 mM for 12 h produces a four-membered silaplatinacyclobutene, $[\overline{\mathrm{Pt(CZ{=}CZSi}}\mathrm{Ph_2)(PMe_3)_2}]$ (**3**). Dissolution of **2** converts it into **3**, suggesting that the formation of **3** in Scheme 2 involves **2** as the intermediate. Since addition of $\mathrm{H_2SiPh_2}$ to the solution of **3** regenerates **2**, complexes **2** and **3** are in equilibrium in the above reaction mixture. Formation of the silaplatinacyclobutene is favored at low concentration of these complexes and at high temperature.

Complex **3** is the first isolated silacyclobutene containing a transition-metal atom in the four-membered ring. The existence of such complexes was predicted as a reasonable intermediate of the synthetic organic reactions using Si-containing

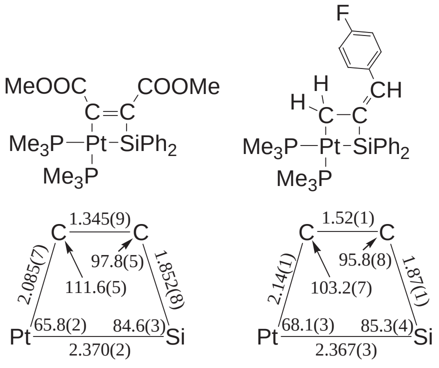


Scheme 2.

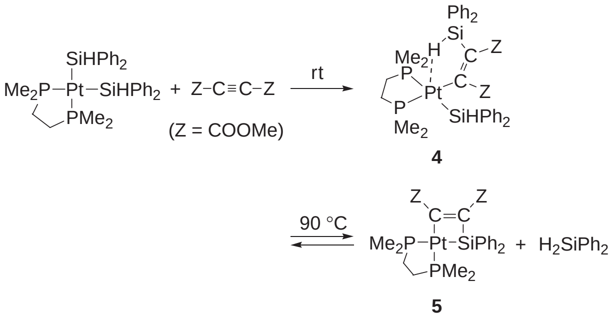


Scheme 3. Silametallacyclobutenes characterized with spectroscopy.

substrates catalyzed by Pt, Pd, and Ni complexes. Sakurai and Seyferth independently reported the ring expansion reactions of silacyclopropenes with alkynes catalyzed by Pd complexes and proposed the silapalladacyclobutene intermediates in their reactions.[43–46] Ni-catalyzed reactions of silacyclopropenes[47–49] and Pd-catalyzed reactions of silacyclopropanes[50,51] with alkynes afforded a variety of four-, five-, and six-membered cyclic compounds containing Si atoms. Formations of the silametallacyclobutene intermediates via insertion of a metal center into the three-membered ring molecules and their further reactions with unsaturated compounds account for the products of the catalytic reactions. Pt-catalyzed cyclization of disilane with alkynes was reported by Kumada at first[52] and investigated in detail by Tanaka, who proposed the silylene–platinum intermediates and 4-sila-3-platinacyclobutenes.[53] In spite of these early reports, isolation of 4-sila-3-metallacyclobutene has not been successful to date. Fink reported preparation of benzocyclobutene containing Pt and Si atoms (Scheme 3(i)).[54] This complex is extremely sensitive to H_2O, and undergoes hydrolysis very easily. Ohshita and Ishikawa prepared a silanickelacyclobutene, which was characterized by NMR spectroscopy in the solution (Scheme 3(ii)).[55,56] Although the Si atom bonded to the metal center of these complexes was protected by bulky $SiMe_3$ substituents, the high reactivity prevented the isolation and determination of the structures by X-ray crystallography. Scheme 4 depicts the bond parameters of **3** and a related silaplatinacyclobutane formed by the reaction of 4-fluorophenylallene with **1** (vide infra).[57] The four-membered rings are planar trapezoids composed of Pt, Si, and two C atoms. The bond distances in these metallacycles are quite different due to covalent radii of the elements, Pt–Si > Pt–C > Si–C > C=C. The C–C bond distance of **3** (1.345(9) Å) is reasonable as the common C=C double bond, while the C–C bond of the silaplatinacyclobutane (1.52(1) Å) shows a single C–C bond character.



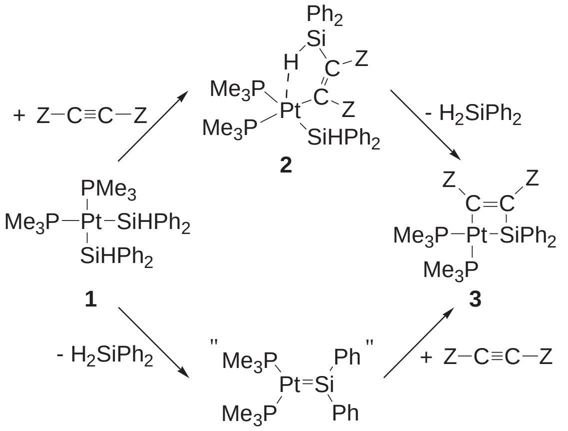
Scheme 4. Bond parameters of silaplatinacyclobutene and silaplatinacyclobutane.



Scheme 5.

A reaction of dimethyl acetylenedicarboxylate with $[\text{Pt}(\text{SiHPh}_2)_2(\text{dmpe})]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) also yields the two complexes via insertion of the alkyne into the Pt–Si bond, as shown in Scheme 5. The reaction at room temperature gives a 3-sila-1-propenylplatinum complex, $[\text{Pt}(\text{CZ=CZSiHPh}_2)(\text{SiHPh}_2)(\text{dmpe})]$ (**4**). Heating a solution of **4** results in partial conversion of it into 4-sila-3-platinacyclobutene, $[\overline{\text{Pt}(\text{CZ=CZSi}}\text{Ph}_2)(\text{dmpe})]$ (**5**). The reaction at 90 °C forms a mixture of **4** and **5** in approximately 30:70 ratio. This behavior is contrasted with the more facile conversion of **2** into **3** at room temperature. X-ray crystallographic results of **4** indicate an intramolecular close contact of the Si–H group of the 3-sila-1-propenyl ligand with the Pt center. The Pt···H distance between the hydrogen positioned at the ideal geometry in the crystal structure and the Pt center is 2.40 Å, which is within the sum of the van der Waals radii of these elements.[58] The first review article of the C–H···M interaction[59] cited the Pd(II) complex as having such interaction of the hydrogen with the apical coordination site of square-planar d^8 metal center.[60]

The following IR and NMR data of **2** and **4** suggest the presence of Si–H···Pt interaction in the solid state and in solution. The 3-sila-1-propenylplatinum complexes show lower wavenumbers of the ν(Si–H) vibration (2098 and 2116 cm^{-1}) in IR spectra (KBr) and smaller J(Si–H) values of γ-Si–H bonds in the ^{1}H NMR spectra (197 and 196 Hz) compared with those of diphenyl(vinyl)silane (2124 cm^{-1} and 206 Hz). Recent reports on the complexes of d^8 transition-metals, Pt(II), Pd(II), and Rh(I), indicated existence of the three-center-four-electron bond between C–H bonds of the ligand and the filled d_{z^2} orbital of the metal center.[61–67] These complexes also show slight

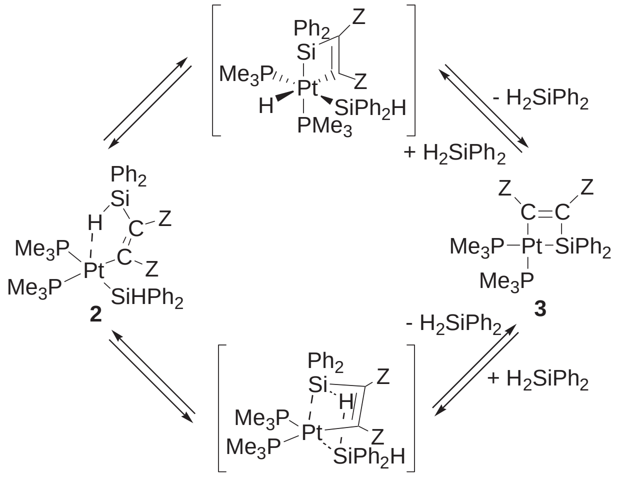


Scheme 6. Possible mechanisms for formation of silaplatinacyclobutene.

decreases of ν(C–H) wavenumber and J(C–H) coupling constants. This tendency is differentiated from the C–H···M three-center-two-electron interaction that causes significant change of the IR and NMR parameters.[21–23]

The formation of 4-sila-3-platinacyclobutene in our study involves initial insertion of alkyne into a Pt–Si bond of the bis(silyl)platinum complex, as shown in the upper route of Scheme 6. It is closely related to the Ni complex-catalyzed cyclizative addition of diorganosilanes to alkynes, giving 1-silacyclopentadienes.[68,69] It may involve the 4-sila-3-metallacyclobutene intermediates which react with alkyne to form the products with a five-membered ring via extrusion of the metal atom. The activation of the γ-Si–H bond of the 3-sila-1-propenyl ligand of **2** by the Pt center is geometrically favorable and would cause the subsequent formation of silaplatinacyclobutene **3**, accompanied by the easy elimination of H_2SiPh_2. Another pathway to silaplatinacyclobutene involves the initial formation of a silylene–platinum intermediate, followed by [2 + 2] cycloaddition of the Si=Pt double bond to the C≡C triple bond of alkyne, as shown in the lower route of Scheme 6. Several research groups have proposed this mechanism to account for C–Si bond-forming reactions catalyzed by Pt complexes. One of the grounds for this pathway is that the Pt complexes catalyze not only coupling of alkyne with organosilanes[52] but also conversion of the organosilanes into oligosilanes via polymerization of SiR_2 fragments.[70] The isolation and full characterization of silylene-coordinated Pt complexes was achieved by Tilley et al.[71–74] They prepared both the three-coordinated neutral Pt(0) silylene complexes and the cationic Pt(II) silylene complexes with non-coordinating borate anion. Bulky substituents at the Si atom bonded to the Pt center serve to stabilize the Pt=Si bond. The isolated Pt–silylene complexes undergo addition of H_2 to the $Pt{=}SiR_2$ bond to give the Pt–silyl complexes with hydrido and secondary silyl ligands. Although the lower reaction pathway in Scheme 6 may still be possible for the reactions of organosilanes with alkynes other than dimethyl acetylenedicarboxylate, the results of our study indicate the reaction pathway that involves an initial insertion of dimethyl acetylenedicarboxylate, followed by a γ-Si–H bond activation to release the organosilane.

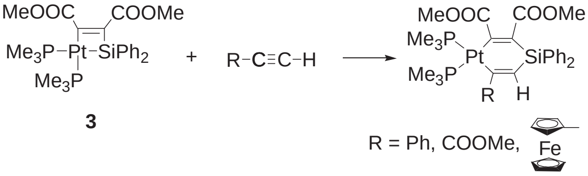
Scheme 7 depicts plausible pathways for the reversible conversion between **2** and **3** in the presence of H_2SiPh_2. The upper



Scheme 7.

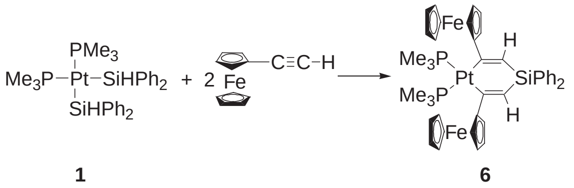
pathway involves a hexa-coordinated (hydrido)bis(silyl)platinum(IV) intermediate, formed via intramolecular γ-Si–H bond activation by Pt(II) center of **2** or oxidative addition of H_2SiPh_2 to **3**. The 3-sila-4-platinacyclobutene **3** is formed smoothly from coupling of the hydrido and diphenylsilyl ligands at the cis positions. Recently, Shimada and Tanaka reported that the Pt(IV) and Pd(IV) complexes with organosilyl ligands.[75,76] The lower pathway in Scheme 7 shows concerted hydrogen migration between two Si atoms of **2**, which also forms the 4-sila-3-platinacyclobutene and H_2SiPh_2. We do not have the experimental results to compare plausibility of the two reaction pathways in Scheme 7. The lower pathway, involving σ-bond metathesis, appears to be more probable than the upper one because oxidative addition of the Si–H bond to Pt(II) centers of **2** and **3** would require distortion of the four-membered ring during the formation of the hexa-coordinated intermediate. The chelating dmpe ligand of **4** and **5** (Scheme 5) also renders the formation of a hexa-coordinated intermediate less kinetically favorable than that of the intermediate in lower pathway of Scheme 7. Ozawa proposed similar two reaction pathways, involving σ-bond metathesis and oxidative addition of the Si–H bond, to account for the result of the reactions of alkyl(silyl)platinum with organosilanes.[17]

Complex **3** reacts with mono-substituted alkynes such as PhC≡CH, MeOOCC≡CH, and FcC≡CH (Fc = ferrocenyl) to afford the six-membered cyclic compounds, $[Pt\{CR{=}CHSiPh_2C(COOMe){=}C(COOMe)\}(PMe_3)_2]$ (R = Ph, MeOOC, and Fc) (Eq. 2).



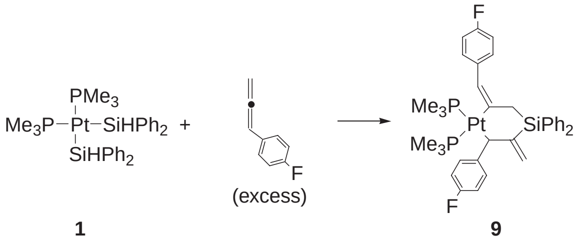
(2)

These products are composed of a single regioisomer with the substituents at α-position of the metallacycles. The regioselectivity is consistent with insertion of alkyne into the metal–carbon bond.[77,78] The silaplatinacyclohexadiene having two ferrocenyl groups, $[Pt(CFc{=}CHSiPh_2CH{=}CFc)(PMe_3)_2]$ (**6**), was obtained from the reaction of **1** with excess ethynylferrocene (Eq. 3). The reaction probably takes place via the stepwise formation of the silaplatinacyclobutene, $[Pt(CFc{=}CHSiPh_2)(PMe_3)_2]$, and the insertion of another alkyne into the Pt–Si bond. The pendent ferrocenyl groups in **6** show some electrochemical communication at −40 °C.[79] Two reversible redox peaks are observed at $E_{1/2} = -0.08$ and 0.07 V (vs Ag^+/Ag). They are assigned to the oxidation of the first and second ferrocenyl groups, indicating the presence of a mixed-valence state.



(3)

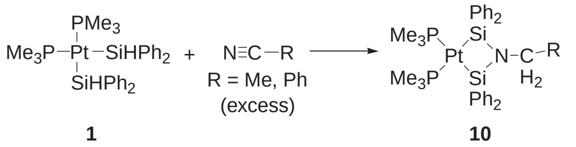
A C=C double bond of 4-fluorophenylallene inserts into a Pt–Si bond to yield a 2-sila-1-platinacyclobutane, $[Pt(CH_2C({=}CHC_6H_4\text{-}4\text{-}F)SiPh_2)(PMe_3)_2]$ (**7**), accompanied by reductive elimination of diorganosilane, as shown in Scheme 8.[57] The bond parameters of the complex are shown in Scheme 4. Heating of **7** at 50 °C in the presence of H_2SiPh_2 produces the disilaplatinacycle with a five-membered ring, $Pt(SiPh_2C({=}CHC_6H_4\text{-}4\text{-}F)CH_2SiPh_2)(PMe_3)_2$ (**8**). The reaction of **1** with excess arylallene affords a 4-sila-1-platinacyclohexane, $Pt(C({=}CHC_6H_4\text{-}4\text{-}F)CH_2SiPh_2C({=}CH_2)CC_6H_4\text{-}4\text{-}F)(PMe_3)_2$ (**9**), as shown in Eq. 4.



(4)

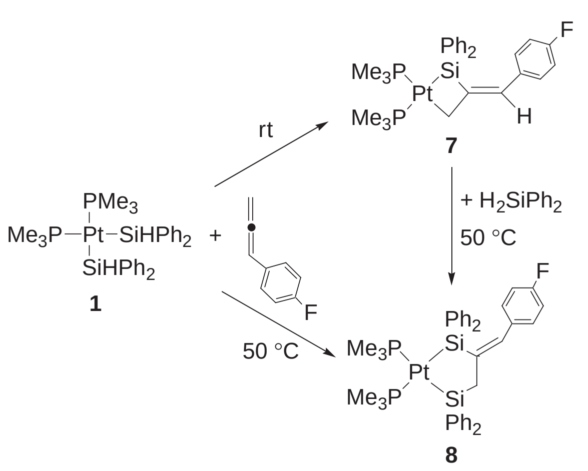
The reaction does not involve initial formation of the four- and five-membered complexes, because orientation of the substituents of **9** is different from that of **7** and **8**.

The reactions of acetonitrile and benzonitrile with **1** produce unexpected 3-aza-2,4-disilaplatinacyclobutane, $Pt(SiPh_2N(CH_2R)SiPh_2)(PMe_3)_2$ (**10**), (R = Me and Ph) via double addition of the Si–H bonds to a C≡N triple bond (Eq. 5).[80]



(5)

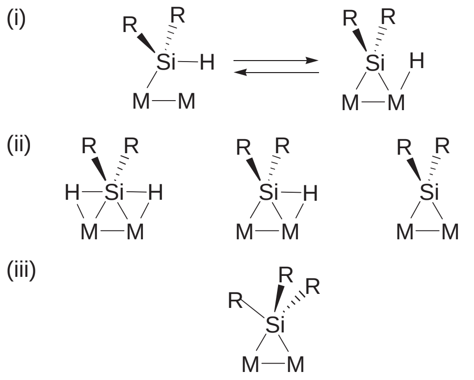
The reaction mixture does not contain any other products formed via insertion of nitrile into the Pt–Si bond. The metal-catalyzed hydrosilylations of the C≡N bonds are much less common compared with those of C≡C bonds. Corriu and Kira independently reported the Si–N bond formation by the reaction of the silyl ligand bonded to transition-metals (Fe and Ru) with nitriles.[81,82] The reaction of *t*-butyl isocyanide with **1** causes displacement of one phosphine ligand, but does not cause insertion of the triple bond into the Pt–Si bond nor into the Si–H bond.[83] This results indicate that isonitriles undergo facile insertion into metal–carbon bond.



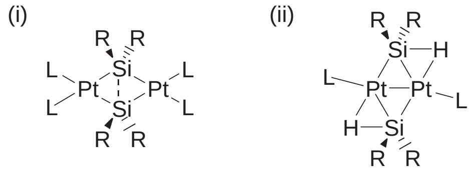
Scheme 8. Reactions of arylallene with a bis(silyl)platinum complex.

Dinuclear and Trinuclear Complexes

There have been many reports on the dinuclear transition-metal complexes with the bridging Si-ligands.[22–25] The substituted silylene (SiR_2) groups coordinate to two metal centers via two M–Si single bonds. The bridging coordination is much more stable than that of the silylene ligands in the mononuclear transition-metal complexes. The silyl groups with Si–H bonds (SiR_2H or $SiRH_2$) also form a stable bridging coordination with two metal centers via the M–Si single bond and the M–H–Si three-center-two-electron bond. The transition-metal complexes with bridging silyl ligands are thermally stable, but they exhibit high fluxionality due to the facile cleavage and formation of the Si–H bond promoted by the metal centers. Eisenberg and Fryzuk independently reported structures of the dinuclear Rh complexes with bridging Si-ligands and proposed reversible exchange between the bridging silyl ligand and the silylene and hydrido ligands.[84–88] This process accompanies rapid cleavage and formation of the Si–H bond by a Rh center, as shown in Scheme 9(i). Suzuki prepared a series of the dinuclear Ru complexes having different coordination modes of the bridging ligands such as the silane ligand with two Ru–H–Si bonds, the silyl ligand with one Ru–Si bond and one Ru–H–Si bond, and the silylene ligand with two Ru–Si single bonds, using the same Cp*–Ru–Ru–Cp* framework



Scheme 9.

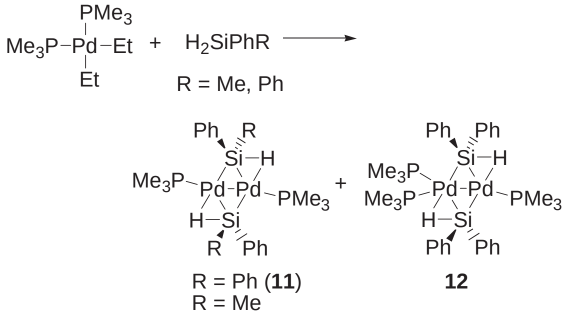


Scheme 10.

(Scheme 9(ii)).[89,90] The formation of these Rh and Ru complexes involves coordination and activation of the Si–H bonds of organosilane by the transition-metal centers. Bridging coordination of a tertiary silyl group (SiR_3) is much less common than that of $SiHR_2$ and SiR_2 groups. The Rh complexes with a bridging triarylsilyl ligand, having a hypervalent Si center, are isolated and fully characterized (Scheme 9(iii)).[91,92] The complexes are regarded as the intermediates for the migration of the tertiary silyl ligand from one metal to the other in the dinuclear transition-metal complexes.[93–96]

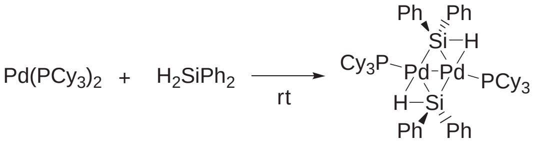
Most of the dinuclear Pt complexes reported so far contain Pt_2Si_2 four-membered rings. Scheme 10(i) shows a typical structure which includes two bridging silylene ligands. The reactions of H_3SiR having bulky organosilyl substituents with $[PtMe_2(PMe_nPh_{3-n})_2]$ ($n = 1$–3) form the silylene-bridged dinuclear Pt complexes.[97] The two metals are somewhat separated from each other (3.96–4.05 Å) and do not have metal–metal bonds.[75,97–100] Contrastively, the two Si atoms of the complexes show close contact (2.55–2.72 Å). The Si–Pt–Si bond angles of the above complexes are acute (64.4–68.9°) due to access of the two Si atoms. Such a close contact of the two Si atoms of the Si–X–Si group is not unique to the dinuclear complexes and is observed in the mononuclear complexes with chelating Si–O–Si[101] and Si–N–Si[80] ligands also. The reactions of primary silanes with Pt(0)–PPh_3 complexes, however, yield the diplatinum complexes whose two metal centers are bridged by $SiHR_2$ ligands, as shown in Scheme 10(ii). Short Pt–Pt distances (2.68–2.72 Å) suggest the presence of a metal–metal bond between two Pt(I) centers with d^9 configuration. One of the two Pt–Si bonds of the bridging silyl ligands is elongated by the Pt–H–Si three-center-two-electron bond. The reaction of 2-isopropyl-6-methylphenylsilane with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ produces the dinuclear Pt complexes $[\{Pt(PPh_3)\}_2(\mu\text{-}SiH_2Ar)_2]$ (Ar = 2-isopropyl-6-methylphenyl) whose bridging silyl ligands are coordinated to one Pt via the Pt–Si bond and to the other Pt via the Pt–H–Si bond.[102] The exchange from a PPh_3 ligand to a more basic PMe_2Ph leads to the formation of the diplatinum species with bridging silylene ligands, $[\{Pt(PMe_2Ph)\}_2(\mu\text{-}SiHAr)_2]$, accompanied by the elimination of H_2.[103] Hexylsilane reacts with $[Pt(PEt_3)_3]$ to yield a mixture of the dinuclear Pt complexes with bridging silylene ligands, $[\{Pt(PEt_3)\}_2(\mu\text{-}SiHhex)_2]$, and with bridging silyl ligands, $[\{Pt(PEt_3)\}_2[\mu\text{-}SiHhex\{PtH(PEt_3)_2\}]_2]$.[104] The Si atoms of the latter complex are stabilized by coordination to three Pt centers.

The dinuclear Pd complexes with the above structures were known only by using *N*-substituted silylene ligands.[105,106] The crystal structures of the complexes did not show close contact between the Si atoms. We conducted the reactions of H_2SiPh_2 and $H_2SiPhMe$ with $[PdEt_2(PMe_3)_2]$ and obtained the dinuclear Pd complexes, $[\{Pd(PMe_3)\}_2(\mu\text{-}HSiPh_2)_2]$ (**11**), with the bridging diarylsilyl ligands bonded to one Pd center by a Pd–Si single bond and to the other by a Pd–H–Si bond, as shown in Eq. 6.[107,108]



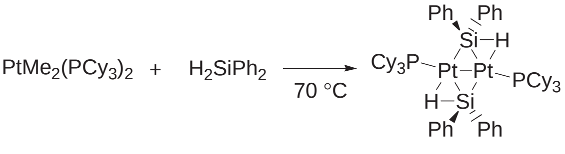
(6)

$[\{Pd(PMe_3)\}\{Pd(PMe_3)_2\}(\mu\text{-}HSiPh_2)_2]$ (**12**) was also obtained by fractional recrystallization of the crude products. Complex **12** contains two PMe_3 ligands at one Pd center and one PMe_3 ligand at the other in the solid state. An analogous Pt complex with unsymmetrical coordination of three PPh_3 ligands was prepared and characterized by detailed NMR analysis by Braddock-Wilking.[109] The reaction of diarylsilane with Pd(0) complex, $[Pd(CH_2{=}CHPh)(PMe_3)_2]$, prepared in situ from the reaction of styrene with $[PdEt_2(PMe_3)_2]$, also produces the same complexes, indicating that the reaction in Eq. 6 proceeds via the initial formation of the Pd(0) complex by the elimination of ethylene and ethane, followed by the oxidative addition of the diarylsilanes. Complex **12** shows a single broad ^{31}P NMR signal at room temperature due to exchange of the phosphine ligands and two signals with P–P coupling at −40 °C. The dinuclear Pd complex with two bulky PCy_3 ligands, $[\{Pd(PCy_3)\}_2(\mu\text{-}HSiPh_2)_2]$ (**13**), is prepared by the reaction of diarylsilanes with Pd(0) complex, as shown in Eq. 7.[110] The reaction takes place under milder conditions (room temperature) than the formation of the diplatinum complex, $[\{Pt(PCy_3)\}_2(\mu\text{-}HSiPh_2)_2]$ (**14**), from the reaction of excess H_2SiPh_2 with $[PtMe_2(PCy_3)_2]$ at 70 °C (Eq. 8).[111]



13

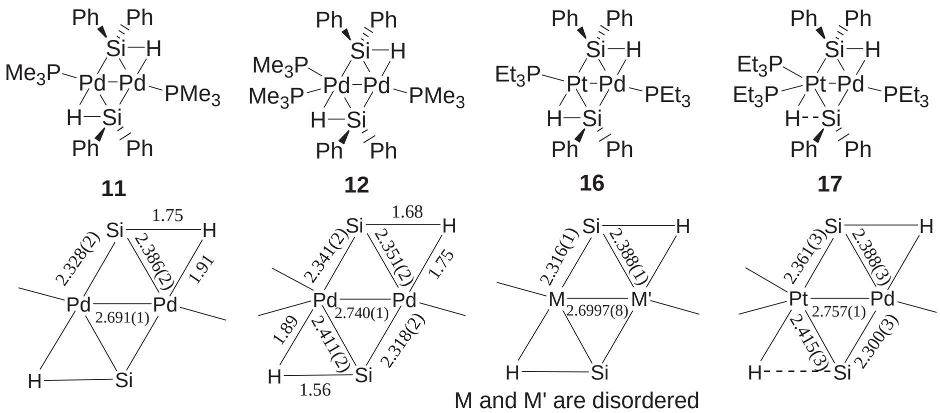
(7)



14

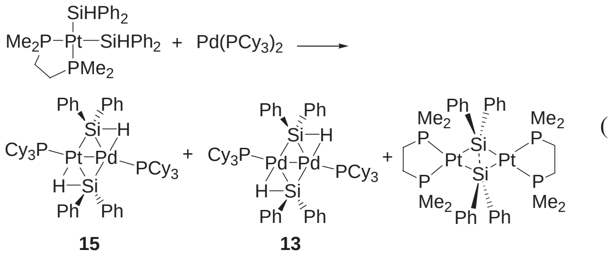
(8)

Since the reactivity of the Pd complexes and the Pt complexes is different, the reaction of organosilanes with low valent complexes of these metals cannot be directly applied to the synthesis of the Pt–Pd heterobimetallic complex with bridging diarylsilyl ligands. The reaction of $[Pt(SiHPh_2)_2(dmpe)]$ with $[Pd(PCy_3)_2]$ results in the successful formation of the Pt–Pd dinuclear complex, $[\{Pd(PCy_3)\}\{Pt(PCy_3)\}(\mu\text{-}HSiPh_2)_2]$ (**15**), as shown in Eq. 9.[110]



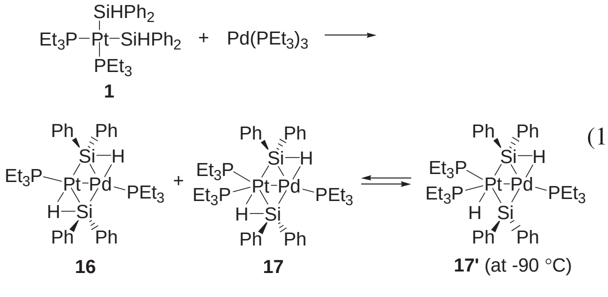
M and M' are disordered in the crystal structure.

Scheme 11.



(9)

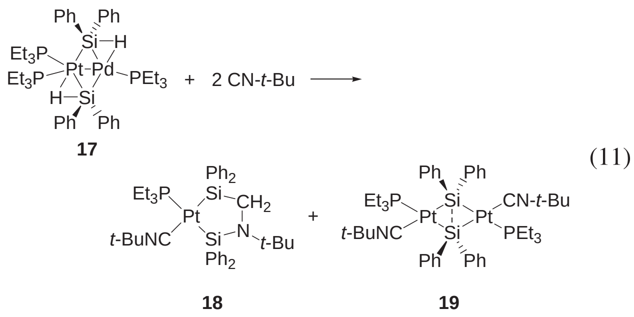
The bridging coordination of the two $SiHPh_2$ ligands of the Pt(II) complex to Pd(0) and the replacement of dmpe with PCy_3 lead to the heterobimetallic product, which is isolated and fully characterized. The ^1H NMR spectrum of **15** shows two peaks of the Si–H hydrogens at δ 1.70 and 2.49. The former signal is assigned to the hydrogen contained in the Pt–H–Si bond because it shows a much larger J(HPt) value (601 Hz) than the latter signal ($J(HPt) = 73$ Hz). These data indicate the structure for **15** rather than the other structures having two Pd–H–Si bonds or two Pt–H–Si bonds. The formation of the dinuclear Pd complex with bridging $SiHPh_2$ ligands suggests a transfer of the silyl ligand from Pt to Pd during the reaction. The choice of the starting complexes is important because the reaction of $[Pd(SiHPh_2)_2(dmpe)]$ with $[Pt(PCy_3)_2]$ does not produce the heterobimetallic complex at all. The reaction of $[Pt(SiHPh_2)_2(PEt_3)_2]$ with $[Pd(PEt_3)_3]$ also produces heterodinuclear complexes with bridging silyl ligands, $[\{Pd(PEt_3)\}\{Pt(PEt_3)\}(\mu\text{-}HSiPh_2)_2]$ (**16**) and $[\{Pd(PEt_3)\}\{Pt(PEt_3)_2\}(\mu\text{-}HSiPh_2)_2]$ (**17**), as shown in Eq. 10.[112]



(10)

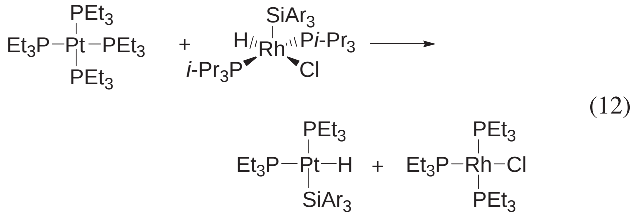
The $^{31}P\{^1H\}$ NMR spectrum of **17** at -90 °C indicates two PEt_3 ligands at Pt and one PEt_3 ligand at Pd. The ^1H NMR spectrum of **17** at -90 °C exhibits the signal at δ -8.61, which is ascribed to the structure **17′** having a hydrido ligand bonded to Pt. Since the signal is shifted to δ 0.41 at 25 °C (^2H NMR signal of the isotope labeled complex), we conclude that the structures **17** and **17′** are in rapid equilibrium in solution.

Scheme 11 summarizes the bond distances of the four-membered cyclic core of the Pd–Pd and Pd–Pt complexes with bridging silyl groups obtained from the X-ray crystallographic results. Hydrogen positions of the Pd–Pd dinuclear complexes **11** and **12** are determined unequivocally. Complex **11** shows elongation of one of the two crystallographically independent Pd–Si bonds (2.386(2) and 2.328(2) Å) owing to the presence of Pd–H–Si three-center-two-electron bonds. The Pd–Si single bond of the Pd with two PMe_3 ligands of **12** (2.341(2) Å) is shorter than the Pd–Si distance of the Pd–H–Si bonds (2.411(2) Å) at the same metal. These Pd–Si distances are longer than the corresponding distances of the bonds at the Pd with one PMe_3 ligand (2.318(2) and 2.351(2) Å, respectively). The molecular structure of the Pt–Pd dinuclear complex **16** determined by X-ray crystallography contains the two metal centers at disordered positions. The averaged structure of the two disordered molecules suggests that the M–Si bonds in M–H–Si coordination (M = Pd or Pt) are longer than the M–Si single bonds. Crystallographic results of **17** indicated the coordination of P and Si atoms to the metal centers shown in Eq. 10, although the results were not precise enough for us to determine the hydrogen positions. One Pt–Si distance (2.415(3) Å) is longer than the other (2.361(3) Å) due to a Pt–H–Si bond or the presence of a hydrido ligand close to the Si atom. The two Pt–Si distances are significantly longer than the Pd–Si distances. Complex **17** reacts with t-butyl isocyanide to form a five-membered platinacycle containing Pt, Si, N, and C atoms, $[\overline{Pt\{SiPh_2CH_2N(t\text{-}Bu)Si}Ph_2\}(PEt_3)(CN\text{-}t\text{-}Bu)]$ (**18**), and a diplatinum complex with bridging silylene ligands, $[\{Pt(PEt_3)(CN\text{-}t\text{-}Bu)\}_2(\mu\text{-}SiPh_2)_2]$ (**19**), as shown in Eq. 11.[112] A plausible mechanism for the formation of the five-membered ring of **18** involves insertion of isonitrile into a Pd–Si bond, followed by formation of the Si–N bond via insertion of the C=N double bond into the Si–H bond of the other silyl ligands. The reaction of the same isocyanide with diplatinum complex **14** produced a corresponding dinuclear complex, $[\{Pt(PCy_3)(CN\text{-}t\text{-}Bu)\}_2(\mu\text{-}SiPh_2)_2]$, exclusively. No insertion of isonitrile into the Pt–Si bond was observed.



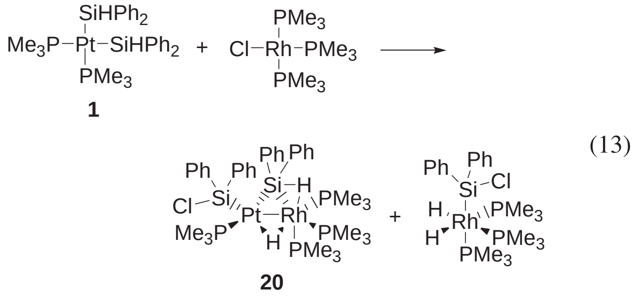
(11)

Heterobimetallic complexes with bridging silyl ligands are involved in transfer of the silyl ligands between different metal centers (transmetallation). The reaction of $[RhCl(H)(SiAr_3)\{P(i\text{-}Pr)_3\}_2]$ with $[Pt(PEt_3)_4]$ produces *cis*-$[PtH(SiAr_3)(PEt_3)_2]$ via intermolecular transfer of the silyl ligand, as shown in Eq. 12.[113]



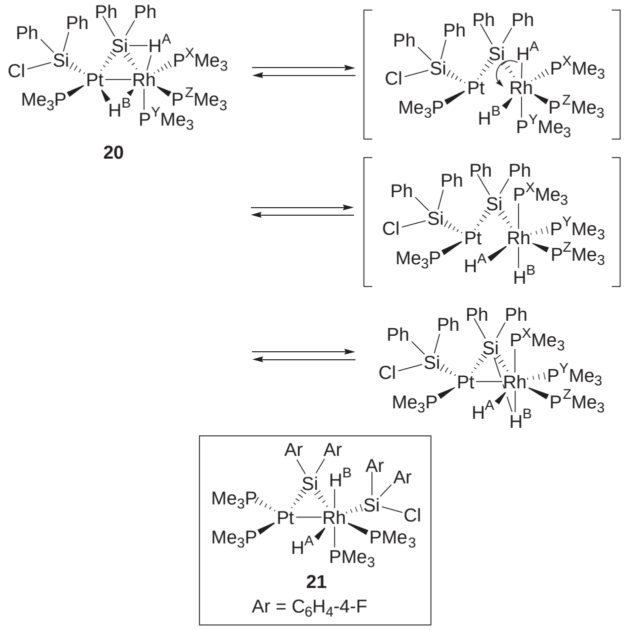
(12)

The reaction of bis(silyl)platinum complex **1** with $[RhCl(PMe_3)_3]$ forms a mixture of the Pt–Rh heterobimetallic complexes, $[\{Pt(SiClPh_2)(PMe_3)\}\{Rh(PMe_3)_3\}(\mu\text{-}H)(\mu\text{-}HSiPh_2)]$ (**20**) and *mer*-$[RhH_2(SiClPh_2)(PMe_3)_3]$, as shown in Eq. 13.[114,115]



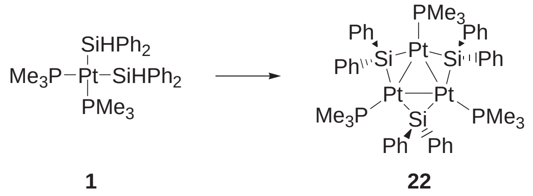
(13)

The latter product is attributed to initial formation of *mer*-$[RhCl(H)(SiHPh_2)(PMe_3)_3]$ via silyl ligand transfer from Pt to Rh and subsequent migration of the Cl ligand from Rh to Si.[116] Variable temperature NMR spectra of **20** indicate fluxional behavior of the molecule caused by exchange of two hydrido ligands and three PMe_3 ligands bonded to Rh on the NMR time scale. Scheme 12 displays one possible mechanism to account for change of the NMR spectra. Cleavage of the Pt–H and Si–H bond of **20** forms an intermediate complex with a three-coordinated Pt center and a Rh center with two non-bridged hydrido ligands. The Rh–Si single bond between the bridging silylene ligand and Rh rotates freely to cause the exchange of the relative positions of the two hydrido and two phosphine ligands. The formation of the Pt–H and Si–H bonds with the pairs different from those in the original complex results in an exchange of the hydrido and PMe_3 ligands. A dinuclear complex with three-coordinated Pt center, $\{Pt(PMe_3)_2\}\{RhH_2(SiAr_2Cl)(PMe_3)_2\}(\mu\text{-}SiAr_2)$ (**21**: Ar = C_6H_4-4-F), which has a similar structure to the above intermediate, was isolated independently and characterized by X-ray crystallography.



Scheme 12.

Heating complex **1** at 100 °C affords a trinuclear Pt complex, $[\{Pt(PMe_3)\}_3(\mu\text{-}SiPh_2)_3]$ (**22**), with bridging diphenylsilyl ligands, as shown in Eq. 14.[117]

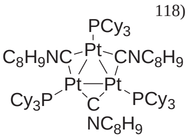
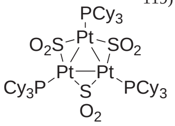
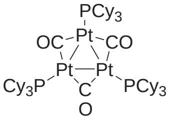
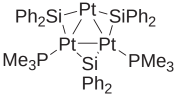


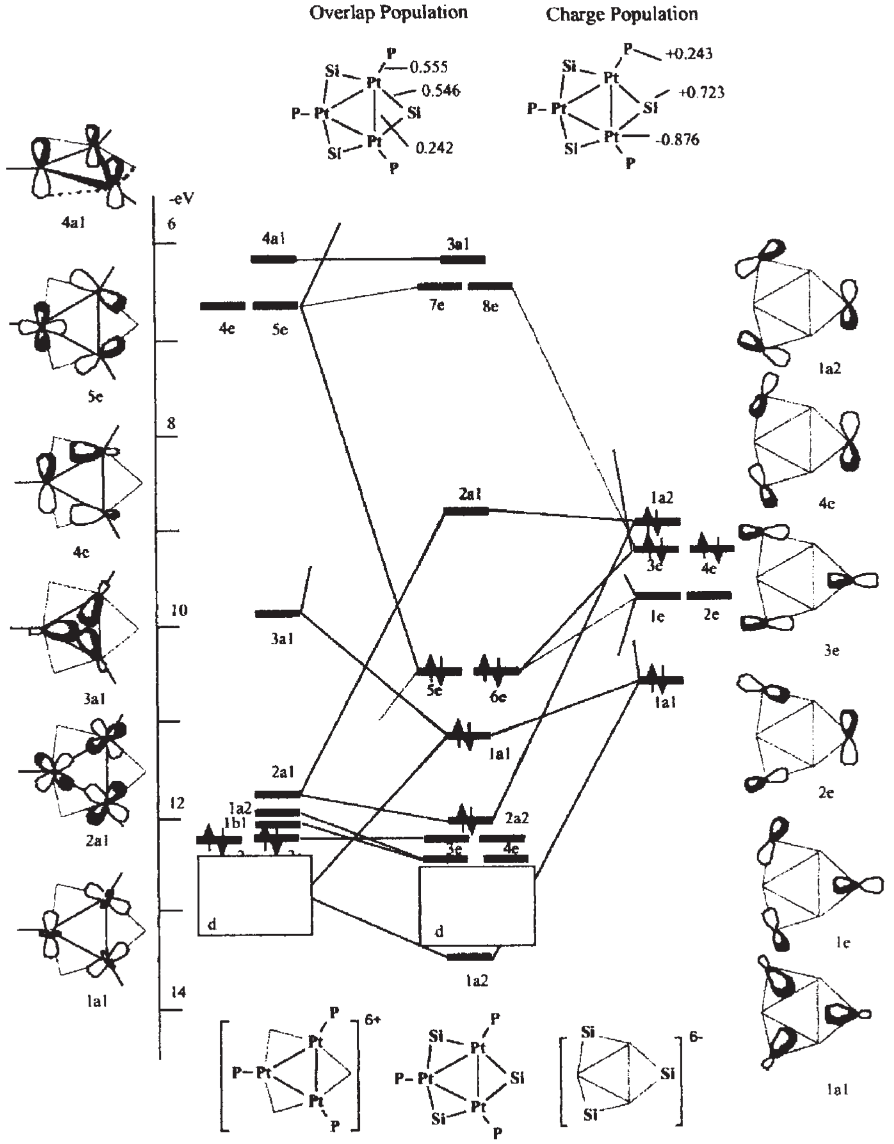
(14)

Braddock-Wilking and co-workers also reported the preparation of the similar triplatinum complex, $[\{Pt(PPh_3)\}_3(\mu\text{-}SiC_{12}H_8)_3]$, from the reaction of $H_2SiC_{12}H_8$ with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$.[109] The cyclic triplatinum complexes reported so far were stabilized by strong π-acceptor ligands such as CO and CNR. The organosilyl groups with a strong σ-donor character may be mismatched with electron-rich low valent cyclic Pt_3 centers. Complex **22**, however, is isolated as crystals and exhibits high thermal stability in solution. Crystallographic study of **22** shows a C_{3v} triangular structure with bridging μ-$SiPh_2$ ligands and terminal PMe_3 ligands on each Pt atom. The phenyl planes are almost perpendicular to the plane which is composed of the Pt, Si, and P atoms. $[\{Pt(PPh_3)\}_3(\mu\text{-}SiC_{12}H_8)_3]$ shows a bending structure of a Pt–Si–Pt group from the Pt_3 plane.[109]

Table 1 summarizes the bond and spectroscopic parameters for triplatinum complexes, $[\{Pt(PR_3)\}_3(\mu\text{-}L)_3]$, with various bridging ligands. The average Pt–Pt bond distances (2.708(1) Å) of **22** is in the range for those of trinuclear Pt complexes, $[\{Pt(PCy_3)\}_3(\mu\text{-}SO_2)_3]$ (average 2.814(1) Å), $[\{Pt(PCy_3)\}_3(\mu\text{-}CNC_8H_9)_3]$ (average 2.6855(6) Å), and $[\{Pt(PCy_3)\}_3(\mu\text{-}CO_2)_3]$ (average 2.655(2) Å), indicating the presence of Pt–Pt bonds in **22**. The *J*(PtPt) of **22** (2950 Hz) is much larger

Table 1. Bond and Spectroscopic Parameters of the Triangular Triplatinum Complexes $[\{Pt(PR_3)\}_3(\mu\text{-}L)_3]$

	 [118]	 [119]	 [120,121]	 [117]
X-ray				
Pt–Pt/Å	2.6855(6)	2.814(1)	2.655(2)	2.708(1)
Pt–P/Å	2.289(3)	2.287(6)	2.549(8)	2.240(5)
Pt–Pt–Pt/deg	60.00(1)	60.00(3)	60.0(1)	60.00(3)
NMR				
J(PtPt)/Hz	—	700	1560	2950
J(PPt)/Hz	4693	3760	4410	2959
^2J(PPt)/Hz	418	330	426	418
^3J(PP)/Hz	52	49	60	86



Scheme 13.

than those of the complexes with bridging CO and SO_2 ligands (1560 and 700 Hz), while the J(PPt) value of **22** (2959 Hz) is the smallest among the complexes in Table 1. The $^{29}Si\{^1H\}$ NMR spectrum of **22** exhibits one signal in low field magnetic field with the coupling constant of ^{195}Pt nucleus (δ 279, $J(\mathrm{SiPt}) = 922$ Hz). The silylene-coordinated Pt complexes $[Pt{=}SiMes_2(PR_3)_2]$ (R = Cy and *i*-Pr) show their signals at extremely low field positions (δ 358 and 367) in the $^{29}Si\{^1H\}$ NMR spectrum.[72,74]

Triplatinum complex **22**, which contains both strong electron-donating $SiPh_2$ and PMe_3 ligands, is expected to possess a unique electronic state. Scheme 13 shows the diagram of a C_{3v} model compound, $[\{Pt(PH_3)\}_3(\mu\text{-}SiH_2)_3]$ (**23**), as obtained from extended Hückel molecular orbital (EHMO) calculations. The electronic structure is consistent with 42-electron clusters in three platinum centers with metal–metal bonds. The frontier orbitals of the organosilyl groups are located at higher energy levels than those of the complexes with π-acceptor bridging ligands. These orbitals of Si atom cause an increase of the HOMO–LUMO band energy gap.

Conclusion

Although platinum(II) complexes with Si-ligands have been known for almost a half century, studies conducted by several distinguished research groups in the last decade have revealed novel and exciting chemical properties of these complexes. Our contribution to the progress of this field is shown in this account. The study of classical bis(silyl)platinum complexes has provided a solution to long-standing problems, such as isolation of the silametallacyclobutene and elucidation of its formation mechanism. Intramolecular activation of the γ-Si–H group plays an important role in the formation of the four-membered metallacycles from alkynes and the silyl group bonded to Pt. The Si-ligands bridging the two metal centers were employed to prepare new homo- and hetero-bimetallic complexes of Pd and Pt. The facile formation of the dinuclear and cyclic trinuclear complexes from the mononuclear complexes of Pt, Pd, and Rh suggests their potential roles as the precursors of multimetallic complexes with the bridging Si-ligands. A study of new transition-metal clusters composed of many metal–silicon bonds is now in progress.

We are grateful to Prof. Takakazu Yamamoto of our Institute and Prof. Tomoaki Tanase of Nara Women's University for stimulating discussion during this study. Names of the students who devoted themselves to the research work are raised in the references from our group. We would like to show our respect to the authors of the early reports (1970's) because of their pioneering works in this filed. The studies cited here were financially supported by Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan and from the Japan Society for the Promotion of Science and by the 21st Century COE Program "Creation of Molecular Diversity and Development of Functionalities" (Tokyo Institute of Technology).

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Kohtaro Osakada was born in Okayama in 1955. He received his Bachelor degree in 1977 and his Doctor of Engineering degree in 1982 from Tokyo University under the direction of Prof. Sadao Yoshikawa. He joined the Research Laboratory of Resources Utilization (the former name of Chemical Resources Laboratory) of the Tokyo Institute of Technology as an assistant professor in the group of Prof. Takakazu Yamamoto and Prof. Akio Yamamoto in 1982. He was appointed as professor of Chemical Research Laboratory in 1999. His current research covers the structure and chemical properties of new organotransition-metal complexes, the synthesis of polymers using metal-catalyzed C–C bond-forming reactions, and interlocked molecular assembly composed of organometallic molecules.

Makoto Tanabe was born in Tokyo in 1974. He received his Bachelor degree in Chemistry in 1998 from Rikkyo University and his Ph.D. degree in 2003 from the Tokyo Institute of Technology under the supervision of Prof. Kohtaro Osakada. He worked in the field of metal-containing polymer chemistry with Prof. Ian Manners at the University of Toronto in Canada. He joined Chemical Resources Laboratory of the Tokyo Institute of Technology in 2004 as an assistant professor in the group led by Prof. Kohtaro Osakada. His research interest focuses on the synthesis, properties, and applications of transition-metal multinuclear complexes and the photochemistry of organotransition-metal compounds.