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Diplatinum Complexes with Bridging Silyl Ligands. Si−H Bond Activation of μ-Silyl Ligand Leading to a New Platinum Complex with Bridging Silylene and Silane Ligands

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Summary: A diplatinum complex with bridging diethylsilyl ligands, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiEt_2)_2]$ (**1**)*, reacted with an excess of* H_2SiPh_2 *to yield* $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiPh_2)_2]$ (**2**) *via exchange of the bridging* $SiHEt_2$ *ligands with* $SiHPh_2$ *groups. An equimolar reaction of* H_2SiPh_2 *with* **1** *afforded a mixture of the dinuclear complexes* $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiEt_2)(\mu\text{-}\eta^2\text{-}HSiPh_2)]$ (**3**) *and* $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SiEt_2)(\mu\text{-}SiPh_2)]$ (**4**)*. X-ray crystallographic structure determination of* **4** *showed bridging coordination of the* H_2SiEt_2 *ligand to two Pt centers via two Pt−H−Si three-center two-electron bonds (Pt−Si = 2.375(8) and 2.39(1) Å).*

Bridging primary ($RSiH_2$) or secondary (R_2SiH) organosilyl ligands in dinuclear transition metal complexes are bonded to one metal via an M−Si σ-bond and to the other via an M−H−Si three-center two-electron bond.[1] Diplatinum,[2−4] dipalladium,[5] and Pd−Pt heterobimetallic complexes[6] with two bridging silyl ligands, formulated as $[\{M(PR_3)\}_2(\mu\text{-}\eta^2\text{-}HSiR_2)_2]$ (M = Pd and/or Pt), have a four-membered M_2Si_2 core, which contains the M−Si and M−H−Si bonds as well as a bond between the two d^9 metal centers. A theoretical study of the complexes revealed a partial character of μ-silane and hydride ligands bonded to two metal centers caused by Si−H bond activation.[7] Dinuclear Rh complexes with μ-silylene and hydride ligands were reported to undergo intramolecular hydrogen exchange via an intermediate complex with a silyl ligand bonded to two Rh atoms via Rh−Si and Rh−H−Si bonds.[8,9] Dinuclear transition metal complexes with bridging silane ligands are much less common

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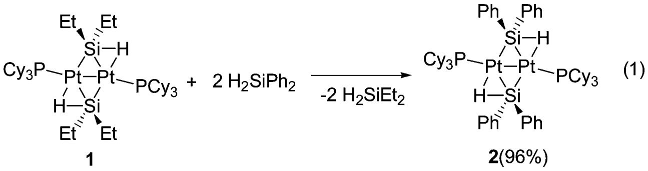
than those with bridging silyl or silylene ligands. Graham, Carreño, Suzuki, Kira, and their respective co-workers reported dinuclear Re, Mn, and Ru complexes in which the secondary silane coordinated to the metal centers via two M−H−Si bonds.[10−12] Small $J_{\mathrm{H-Si}}$ values (36 Hz) of the bridging HSi($C_6H_4Me)_2$ ligand in the Ru complexes suggest partial activation of the Si−H bond involved in the three-center two-electron bonds.[12] Herein, we report the reactions of H_2SiPh_2 with a diplatinum complex that contains two dialkylsilyl ligands, which results in formation of a new diplatinum complex with bridging silane and silylene ligands via migration of a hydrogen atom of the bridging diphenylsilyl ligands.

A diplatinum complex with bridging diethylsilyl ligands, [{Pt(PCy_3)}$_2$(μ-η^2-HSiEt$_2$)$_2$] (**1**), reacted with an excess of H_2SiPh_2 (Pt:Si = 1:3.7) at room temperature to produce [{Pt(PCy_3)}$_2$(μ-η^2-HSiPh$_2$)$_2$] (**2**) in 96% yield, as shown in eq 1. Complex



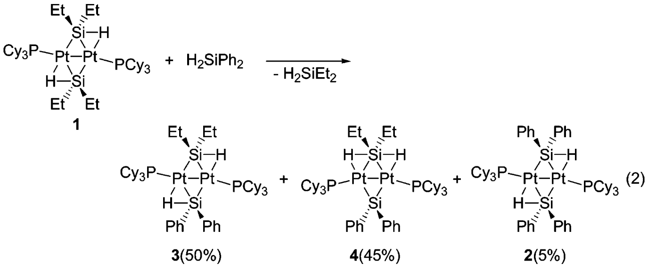
1

2(96%)

(1)

2 was characterized by comparison of its NMR data with those in the previous report.[2] Recently, Braddock-Wilking reported that a diplatinum complex with bridging silafluorenyl groups, [{Pt($PPh_3)_2$(H)}{Pt(PPh_3)}(μ-SiC$_{20}$H$_{24}$)(μ-η^2-HSiC$_{20}$H$_{24}$)], undergoes exchange of the Si ligands with bridging HGePh$_2$ groups to produce [{Pt(PPh_3)}$_2$(μ-η^2-HGePh$_2$)$_2$] caused by addition of H_2GePh_2.[13] Mononuclear Pt complexes containing a Pt−Ge bond were reported to be thermodynamically more stable than that of the silyl ligand of the Pt complexes.[14] Fink reported higher stability of M−Si (M = Pd, Pt) bonds of the complexes with aryl-substituted silyl ligands than those with alkylsilyl ligands.[15]

An equimolar reaction of H_2SiPh_2 with **1** formed a mixture of a diplatinum complex with two different bridging secondary silyl ligands, [{Pt(PCy_3)}$_2$(μ-η^2-HSiPh$_2$)(μ-η^2-HSiEt$_2$)] (**3**; 50%), and the complex with bridging diethylsilane and diphenylsilylene ligands, [{Pt(PCy_3)}$_2$(μ-η^2:η^2-H$_2$SiEt$_2$)(μ-SiPh$_2$)] (**4**; 45%), together with a small amount of **2** (5%) (eq 2). Recrystallization of the products formed a mixture of **3** and **4** in 55:45 molar ratio, which was determined by integration of C_6H_5-*ortho* hydrogen signals in the ^{1}H NMR spectrum. Addition of H_2SiPh_2 to the mixture of **3** and **4** (Pt:Si = 1:3) at room temperature formed complex **2** in 67% yield as the sole product. This result indicates that the displacement of bridging silyl ligands proceeds via formation of intermediates **3** and **4**, and then further reaction with H_2SiPh_2 produces **2**.



1

3(50%) **4**(45%) **2**(5%)

(2)

Repeated recrystallization of the products of reaction 2 from toluene−hexane (1:7) at −20 °C yielded a solid composed of **3** and **4** in 6:94 molar ratio. Single crystals of **3** and **4** suitable for X-ray crystallography were obtained by carefully choosing the crystals from the mixtures. Isolation of pure samples of **3** or **4** was not feasible partly due to mutual isomerization of the complexes in solution (vide infra). Figure 1 shows molecular structures of **3** and **4**.[16] Distances between the two Pt centers of **3** (2.6591(7) Å) and **4** (2.708(1) Å) are within the range of Pt−Pt bonds in diplatinum(I) complexes.[2,3,4a,d,f] The Pt1−Si1 (2.402(4) Å) and Pt2−Si2 (2.388(3) Å) bonds of **3** are significantly longer than two other bonds (Pt1−Si2 = 2.318(3) Å, Pt2−Si1 = 2.306(4) Å). The longer Pt−Si bonds are assigned to those involved in the Pt−H−Si interaction, although positions of the Pt−H−Si hydrogens were not determined by difference Fourier synthesis. The complex, [{Pt(PCy_3)}$_2$(μ-η^2-HSiMe$_2$)$_2$], was also reported to have the Pt_2Si_2 core with a distorted rectangular structure (Pt−Si = 2.324(2), 2.420(2) Å).[2] The Pt−H−Si bonds of **3** are assigned at opposite positions of the Pt_2Si_2 core, which is formed by two Pt centers and the bridging diphenylsilyl and diethylsilyl ligands. The Pt_2Si_2 core of **4** contains two longer Pt−Si bonds on the same side of the Pt−Pt bond (Pt1−Si1 = 2.375(8) Å, Pt2−Si1 = 2.39(1) Å) and two other Pt−Si bonds that are shorter (Pt1−Si2 = 2.314(8) Å, Pt2−Si2 = 2.304(7) Å). The two former bonds are assigned to those involved in the Pt−H−Si interactions, while the latter bonds are due to Pt−Si bonds, indicating a structure with bridging H_2SiEt_2 and $SiPh_2$ ligands. The torsion angle for the P2−Pt2−Pt1−P1 unit of **4** (160.9(3)°) indicates an *syn*-orientation of the Pt−P bonds with respect to the Pt−Pt bond, while the corresponding angle of **3** is smaller (113.9(6)°).

The multinuclear NMR (^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR) spectra were obtained from a mixture of **3** and **4** in 6:94 molar ratio, while NMR data of **3** were obtained from the mixture in 55:45 molar ratio. The ^{31}P{^{1}H} NMR spectrum of **4** displays a single signal at δ 51.8 as part of an AA′XX′ spin system ($J_{\mathrm{Pt-P}}$ = 3849, 362 Hz, $^3J_{\mathrm{P-P}}$ = 55 Hz). Complex **3** exhibits two ^{31}P{^{1}H} NMR signals at δ 53.2 and 53.5 ($^3J_{\mathrm{P-P}}$ = 59 Hz), which is consistent with the unsymmetrical structure shown in eq 2. Two ^{29}Si resonances of **4** are observed at δ 230.1

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(16) Crystallographic data for **3**: $C_{52}H_{88}P_2Si_2Pt_2$, fw = 1221.57, triclinic, space group $P\bar{1}$, a = 13.792(3) Å, b = 14.357(2) Å, c = 14.581(3) Å, α = 63.636(5)°, β = 88.025(8)°, γ = 84.744(8)°, V = 2575.8(8) Å^3, Z = 2, T = 133 K, ρ_{calcd} = 1.575 g cm^{-3}, μ = 5.5449 mm^{-1}, F(000) = 1228, Rigaku Saturn-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), yellow crystal (0.20 × 0.32 × 0.45 mm). Of 19314 reflections collected, 10 980 were independent (R_{int} = 0.024); 609 variables refined with 8459 reflections to final R indices R1($I > 2\sigma(I)$) = 0.0644, wR2($I > 2\sigma(I)$) = 0.1383, GOF = 1.088. Crystallographic data for **4**: $C_{52}H_{88}P_2Si_2Pt_2$, fw = 1221.57, triclinic, space group $P1$, a = 13.897(3) Å, b = 13.971(4) Å, c = 14.889(3) Å, α = 86.84(2)°, β = 69.18(1)°, γ = 79.58(1)°, V = 2657(1) Å^3, Z = 2, T = 133 K, ρ_{calcd} = 1.527 g cm^{-3}, μ = 5.3752 mm^{-1}, F(000) = 1228, Rigaku Saturn-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), yellow crystal (0.30 × 0.20 × 0.20 mm). Of 19 998 reflections collected, 11296 were independent (R_{int} = 0.061); 604 variables refined with 5788 reflections to final R indices R1($I > 2\sigma(I)$) = 0.1149, wR2($I > 2\sigma(I)$) = 0.3341, GOF = 1.118.

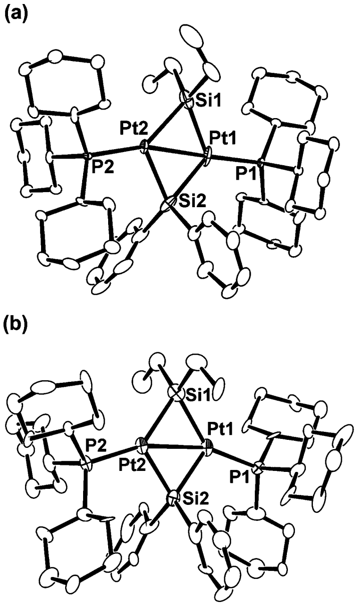


Figure 1. ORTEP drawings of (a) **3** and (b) **4** at 30% ellipsoidal level. Hydrogens except for bridging hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **3**: Pt1−Pt2 2.6951(7), Pt1−P1 2.270(2), Pt1−Si1 2.402(4), Pt1−Si2 2.318(3), Pt2−P2 2.266(2), Pt2−Si1 2.306(4), Pt2−Si2 2.388(3), Pt2−Pt1−P1 163.74(5), P1−Pt1−Si1 142.7(1), P1−Pt1−Si2 107.7(1), Si1−Pt1−Si2 109.5(2), Pt1−Pt2−P2 174.08(6), P2−Pt2−Si1 121.2(1), P2−Pt2−Si2 127.2(1), Si1−Pt2−Si2 110.4(2), Pt1−Si1−Pt2 69.8(1), Pt1−Si2−Pt2 69.86(9). Selected bond distances (Å) and angles (deg) for **4**: Pt1−Pt2 2.708(1), Pt1−P1 2.264(5), Pt1−Si1 2.375(8), Pt1−Si2 2.314(8), Pt2−P2 2.262(5), Pt2−Si1 2.39(1), Pt2−Si2 2.304(7), Pt2−Pt1−P1 162.4(2), P1−Pt1−Si1 141.8(3), P1−Pt1−Si2 108.6(2), Si1−Pt1−Si2 109.6(2), Pt1−Pt2−P2 161.4(2), P2−Pt2−Si1 142.8(2), P2−Pt2−Si2 107.5(2), Si1−Pt2−Si2 109.4(2), Pt1−Si1−Pt2 69.3(2), Pt1−Si2−Pt2 71.8(2).

and 141.3. The signals are assigned to the Si nuclei of the $SiPh_2$ ligand and of H_2SiEt_2, respectively, based on their peak positions. The difference of the ^{29}Si NMR peak positions between the μ-$HSiEt_2$ and μ-$HSiPh_2$ ligands of **3** (δ 195.5 and 163.7) is much smaller than that of the two Si signals of **4**. The ^{29}Si{^{1}H} NMR spectrum of $[Ru_2(CO)_6\{\mu\text{-}Si(C_6H_4Me)_2\}(\mu\text{-}PPh_2CH_2PPh_2)]$ exhibited a signal due to the μ-silylene ligand at δ 172.6, which was at lower magnetic field position than the signal of $[Ru_2(CO)_4\{SiH(C_6H_4Me)_2\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si(C_6H_4Me)_2\}(\mu\text{-}PPh_2CH_2PPh_2)]$ (δ 154.8).[12] The ^{29}Si NMR signal of the H_2SiEt_2 ligand of **4** shows a larger coupling constant ($^2J_{P-Si} = 72$ Hz) than the signal of the $SiPh_2$ ligand ($^2J_{P-Si} = 3.5$ Hz). Two $^2J_{P-Si}$ values observed with the Si signal of **3** (60 and 11 Hz) are assigned to an interaction through the Pt−H−Si bond and to that through the Pt−Si bond, respectively, on the basis of comparison of the values with **4**.

The ^{1}H NMR signals due to Pt−H−Si hydrogens of **3** and **4** are overlapped severely by the signals of the PCy_3 hydrogens. Preparation of a partially deuterated complex by the reaction of D_2SiPh_2 with **1** and ^{2}H{^{1}H} NMR measurement of the products enabled determination of the peak positions. Figure 2a displays the ^{2}H{^{1}H} NMR spectrum of $[\{Pt(PCy_3)\}_2(\mu\text{-}SiPh_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}DHSiEt_2)]$ (**4**-*d*) obtained by repeated recrystallization of the products. A single signal at δ 1.01 flanked by ^{195}Pt satellites ($J_{Pt-D} = 99$ Hz) is assigned to the deuterium coordinated to the diethylsilane ligand. Figure 2b shows the spectrum of the products before recrystallization. Two signals with equal intensity are observed at δ 2.43 and 1.44, which are assigned to deuterium nuclei of two isotopomers of **3**, $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}DSiPh_2)(\mu\text{-}\eta^2\text{-}HSiEt_2)]$ (**3**-$DSiPh_2$) and $[\{Pt(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}\eta^2\text{-}DSiEt_2)]$ (**3**-$DSiEt_2$). The assigned signal for **3**-$DSiPh_2$ is at a similar position (δ 2.43) to the ^{1}H NMR peak position for the Pt−H−$SiPh_2$ hydrogen of **2** (δ 2.45).[6a] Formation of **3**-$DSiEt_2$ indicates intramolecular exchange of Si−H hydrogen atoms between the diethylsilyl and diphenylsilyl ligands.

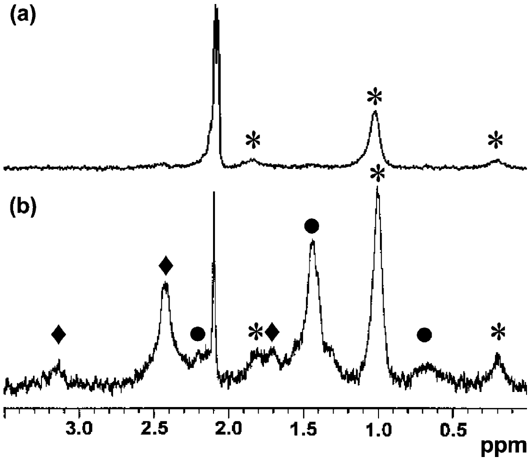


Figure 2. ^{2}H{^{1}H} NMR spectra (toluene, 40 °C) of the products obtained from an equimolar reaction of D_2SiPh_2 with **1** (a) after purification and (b) before purification. Peaks with ◆, ●, and * are due to **3**-$DSiPh_2$, **3**-$DSiEt_2$, and **4**-*d*, respectively.

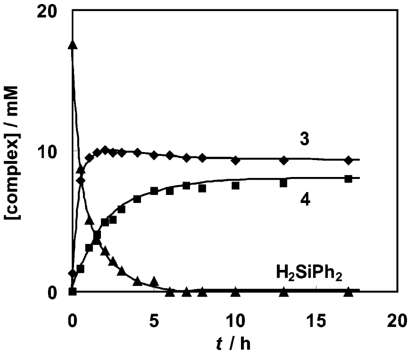
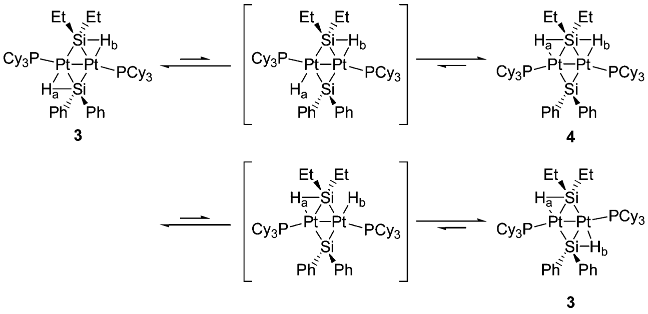


Figure 3. Change in amounts of H_2SiPh_2, **3**, and **4** during the equimolar reaction of H_2SiPh_2 with **1** at 25 °C. [**1**] = 18 mM in toluene-d_8. Dibenzyl was used as an internal standard (18 mM).

Figure 3 plots the change in the amount of the complexes during the reaction of H_2SiPh_2 with **1**, as determined by ^{1}H NMR spectroscopy. The increase in the formation of **3** is much faster than that of **4** at the initial stage of the reaction, while gradual isomerization of **3** and **4** is observed after about 2 h. After 10 h a mixture of the complexes **3** and **4** is observed in a 55:45 molar ratio. The isomerization of the complexes starting from a mixture of **3** and **4** in a 6:94 ratio in the presence of added PCy_3 (Pt:PCy_3 = 1:0.6) eventually gives a new ratio of **3** to **4** of close to 55:45 after 25 h, but it occurs more slowly in the absence of PCy_3 and requires 2 weeks to attain equilibrium. Scheme 1 illustrates a possible mechanistic pathway that accounts for hydrogen migration between the Si ligands. Transformation of an Si−H bond (Ha) in the bis(μ-silyl)platinum complex **3** and formation of a new bond between the resulting hydride ligand in the intermediate species and the Si atom of the other silyl ligand ($SiEt_2$) yield the bridging silane ligand in **4**. Intramolecular transfer of a hydrogen from the silane ligand in **4** to the silylene ligand regenerates the complex with two bridging silyl ligands in **3**. Repetition of the transformation

Scheme 1



process in Scheme 1 results in hydrogen exchange between the two silyl ligands of **3**.

Activation of the Si−H bond to form an intermediate complex with hydride and μ-silylene ligands may be facilitated by the coordination of an additional phosphine ligand, because Pd−Pt and Pt−Pt complexes with hydride and μ-silylene ligands, $[\{M(H)(PR_3)_2\}\{M(PR_3)\}(\mu\text{-}SiR_2)(\mu\text{-}\eta^2\text{-}HSiR_2)]$, were reported to be formed by addition of the phosphine ligand to the dinuclear complexes with two bridging silyl ligands.[4c,f,6b]

In summary, we observed stepwise displacement of the two bridging diethylsilyl ligands caused by addition of diphenylsilane. One of the two intermediates has a new structure composed of two Pt centers bridged by H_2SiEt_2 and $SiPh_2$ ligands.

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Supporting Information Available: Experimental procedures for the synthesis of complexes **1**−**4** and crystallographic data of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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