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Generation of a Silylene Complex by the 1,2-Migration of Hydrogen from Silicon to Platinum**

Gregory P. Mitchell and T. Don Tilley*

Intramolecular migrations in transition metal silicon compounds have attracted considerable attention in recent years.[1] Many of the catalytic cycles and the most interesting transformations for metal–silicon systems appear to feature such migrations,[1, 2] but discrete examples of these steps have proven difficult to observe and characterize. Silylene complexes of the type $[L_nM{=}SiR_2]$ are commonly featured as key intermediates in mechanistic speculations on 1,2- and 1,3-migrations.[1–3] Silylene complexes have only recently been isolated,[4] but despite great effort the formation of a silylene ligand through an intramolecular migration has not yet been observed. We recently described a reversible 1,2-hydrogen migration which interconverts *cis*-$[(PEt_3)_2Pt(H)Si(StBu)_2][OTf]$ and *cis*-$[(PEt_3)_2Pt(NCMe)SiH(StBu)_2][OTf]$ ($Tf = SO_2CF_3$), probably via an intermediate silylene complex.[5] Here we report the first observation of a facile 1,2-hydride migration which generates an observable platinum silylene complex.

In the search for a 1,2-migration that might produce a silylene ligand, we targeted the synthesis of an alkylsilyl complex of the type $[L_2PtR(SiHR'_2)]$. It was thought that migration of a hydrogen atom to a platinum center to produce the alkyl hydride $[L_2Pt(R)(H)({=}SiR'_2)]$ might result in elimination of alkane[6] to produce a silylene complex of the type $[L_2Pt{=}SiR_2]$. Thus, the reaction of $[(dippe)PtMeCl]$ (dippe = $iPr_2PCH_2CH_2PiPr_2$) with $[(thf)_2LiSiHMes_2]$[7] (Mes = 2,4,6-$Me_3C_6H_2$) in diethyl ether yielded a light brown solution, from which the platinum silyl complex $[(dippe)Pt(Me)SiHMes_2]$ (**1**) was isolated in a 79% yield as colorless crystals that were suitable for an X-ray diffraction study (Figure 1).[8] The Pt–Si distance of 2.388(3) Å is similar to that observed for *cis*-$[(MePh_2P)_2PtMe(SiPh_3)]$ (2.381(2) Å),[9] and the silicon-bound hydrogen atom was located and refined at a distance of 1.36(3) Å from the silicon atom.

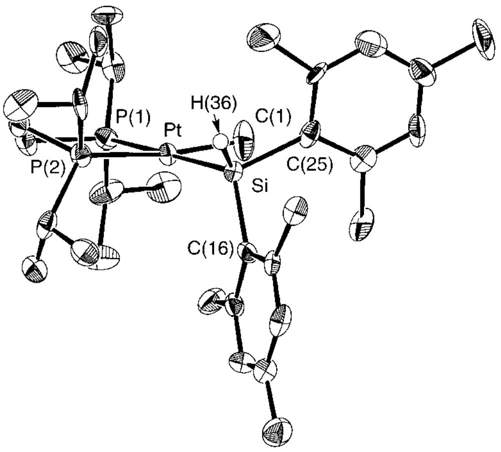
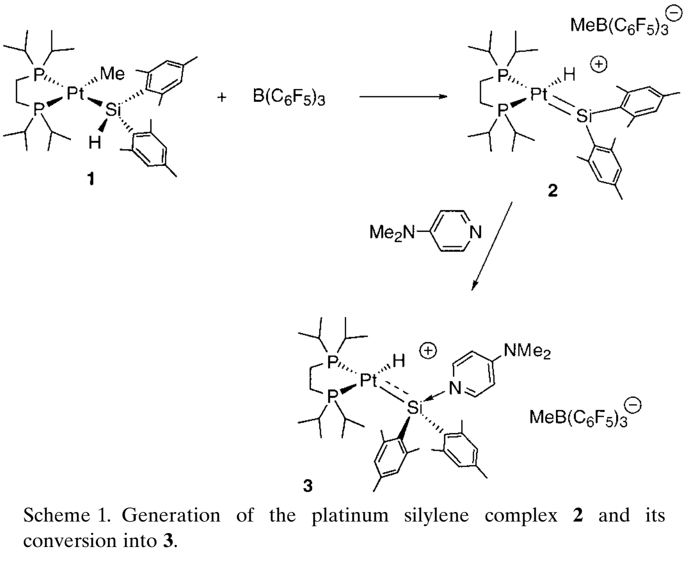


Figure 1. Molecular structure of **2**. Selected interatomic distances [Å] and angles [°]: Pt–Si 2.388 (3), Pt–P(1) 2.329 (3), Pt–P(2) 2.285 (3), Pt–C(1) 2.09 (1), Si–H(36) 1.46 (3), Si–C(16) 1.93 (1), Si–C(25) 1.91 (1); P(1)-Pt-P(2) 86.1 (1), P(1)-Pt-Si 177.7 (1), P(1)-Pt-C(1) 91.0 (4), P(2)-Pt-Si 96.1 (1), P(2)-Pt-C(1) 172.0 (4), Si-Pt-C(1) 86.8 (4), Pt-Si-C(16) 119.3 (4), Pt-Si-C(25) 117.7(4).

Compound **1** is remarkably stable. Heating a solution of **1** in [D$_8$]toluene at 110 °C for two weeks resulted in no detectable decomposition (^{1}H and ^{31}P NMR spectroscopy). Also, no reaction was observed between **1** and diphenylacetylene or 2-butyne after heating at 100 °C in [D$_8$]toluene for three days. However, **1** does react with H_2 at 110 °C over a period of one month to give $MeSi(H)Mes_2$[7] (GC/MS and ^{1}H NMR spectroscopy), presumably by reductive elimination and formation of a Si–C bond. These results suggest that a 1,2-hydrogen migration from the silicon atom to produce a five-coordinate platinum silylene species might be disfavored.

The reaction of **1** with $B(C_6F_5)_3$ in [D$_2$]dichloromethane resulted in the rapid generation of a clear yellow solution and formation of primarily (>95%) one new compound (^{1}H and ^{31}P NMR spectroscopy). The Si–H resonance of **1** ($\delta = 6.21$) was replaced by a Pt–H signal at $\delta = -1.50$ ($^1J(H,Pt) = 743$ Hz), suggesting that a 1,2-hydride shift had taken place to generate the silylene complex $[(dippe)(H)Pt{=}SiMes_2][MeB(C_6F_5)_3]$ (**2**, Scheme 1). This was confirmed by observa-



Scheme 1. Generation of the platinum silylene complex **2** and its conversion into **3**.

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[*] Prof. Dr. T. D. Tilley, G. P. Mitchell
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-642-8940
E-mail: tdtilley@socrates.berkeley.edu

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tion of the ^{29}Si NMR chemical shift at $\delta = 338.5$ (Figure 2), which is indicative of the presence of a three-coordinate silicon atom,[4c,d] and by the ^{19}F NMR spectrum, which is consistent with formation of $[MeB(C_6F_5)_3]^-$.[10] The ^{1}H NMR spectrum of **2** also contains a broad signal at $\delta = 1.37$, which is assigned to the BCH_3 group. This ^{1}H NMR chemical shift is noticably downfield from that of free $[MeB(C_6F_5)_3]^-$ ($\delta \approx 0.5$ (br) in [D$_2$]dichloromethane[10, 11]), and may therefore indicate the presence of a tight ion pair. A similar downfield chemical shift ($\delta = 1.67$) for $[MeB(C_6F_5)_3]^-$, was observed by Jordan and Coles for an aluminum amidinate system and was attributed to an $Al \cdots MeB(C_6F_5)_3$ interaction.[12] However, the exceptional downfield-shifted ^{29}Si NMR resonance for **2** strongly indicates that any $Si \cdots MeB(C_6F_5)_3$ interaction must be extremely weak or nonexistent. The value of ^1J(Si,Pt) for **2** (1305 Hz) is moderately smaller than the analogous value for **1** (1315 Hz), possibly reflecting the weaker σ donating ability of the :SiMes$_2$ ligand relative to $-$SiHMes$_2$. However, a much larger drop in the value of ^1J(Si,Pt) was observed when *trans*-$[(Cy_3P)_2(H)PtSi(SEt)_2][OTf]$ (1825 Hz) was converted into *trans*-$[(Cy_3P)_2(H)PtSi(SEt)_2][BPh_4]$ (1558 Hz).[4c] Initial attempts to isolate **2** indicate that it is an oil at room temperature. It is somewhat thermally sensitive, and decomposes at room temperature with a half-life of approximately 12 h in [D$_2$]dichloromethane.

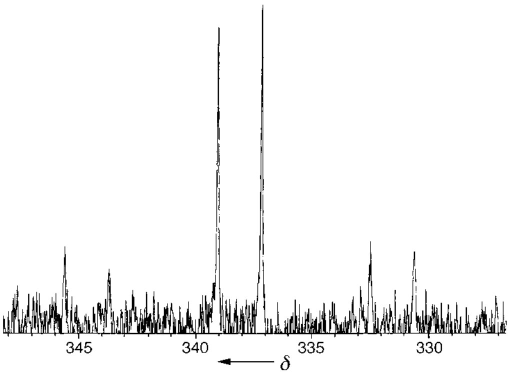

Figure 2. ^{29}Si{^{1}H} NMR spectrum of **2** (99.3 MHz): $\delta = 338.1$ (^1J(Si,Pt) = 1305, $^2J(\text{Si,Pt})_{trans} = 187.8$ Hz; $^2J(\text{Si,P})_{cis}$ coupling was not observed).

As with a similar silylene complex,[4c] the reaction of **2** with *p*-dimethylaminopyridine (DMAP) generates the base-stabilized silylene complex $[(dippe)(H)PtSiMes_2(DMAP)][MeB(C_6F_5)_3]$ (**3**), which was isolated in a 47% yield as a light yellow solid (Scheme 1). The ^{1}H NMR chemical shift of $\delta = 0.47$ ([D$_2$]dichloromethane) for $[MeB(C_6F_5)_3]^-$ is consistent with formation of the free anion, which has presumably been completely displaced from the complex by the much more basic DMAP ligand. Not surprisingly, compound **3** is considerably more stable than **2**, and undergoes less than 10% decomposition over one week in [D$_2$]dichloromethane at room temperature.

Monitoring the formation of **2** at -70 °C by ^{31}P NMR spectroscopy provided no evidence of reaction intermediates, such as the three-coordinate platinum species $[(dippe)PtSiHMes_2][MeB(C_6F_5)_3]$. Addition of H_2SiPh_2 and $HClSiPh_2$ to **2** resulted in the rapid formation of H_2SiMes_2 (^{1}H NMR spectroscopy) and multiple platinum-containing products, but no products with silicon–silicon bonds were observed. Similarly, treatment of **2** with H_2 generated H_2SiMes_2 as the major species containing a mesityl group as well as several uncharacterized platinum products.

This work represents the first direct detection of a 1,2-migration from silicon to a metal atom to generate an observable transition metal silylene complex. Of particular interest is the fact that the four-coordinate platinum complex **1** is remarkably inert, while facile migration occurs when a coordination site on the metal is vacated. In reactions of square planar, four-coordinate platinum silyl complexes, therefore, it seems that α-hydrogen migration (without prior ligand dissociation) is an unlikely mechanistic step. Thus, for example, the previously observed elimination of $MesSiH_3$ from $[(dmpe)Pt(SiH_2Mes)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), to form the "dimerized" platinum silylene complex $[(dmpe)Pt(\mu\text{-}SiHMes)_2Pt(dmpe)]$, probably proceeds through oxidative addition/reductive elimination cycles rather than via the silylene intermediates $[(dmpe)Pt({=}SiHMes)(H)(SiH_2Mes)]$ and $[(dmpe)Pt{=}SiHMes]$.[13]

Despite abundant circumstantial evidence, the relevance of intramolecular 1,2- and 1,3-migrations in silane polymerization, hydrosilation, and silane redistribution mechanisms is still largely a matter of speculation. Nevertheless, such migrations are viable and may even be prevalent in transformations of transition metal silicon complexes.

Experimental Section

General procedures: All reactions were carried out under nitrogen using standard Schlenk techniques. Benzene, pentane, and diethyl ether were distilled from Na/benzophenone prior to use and stored under nitrogen. Dichloromethane was distilled from CaH_2 and degassed with two freeze-pump-thaw cycles prior to use. The compounds [(cod)PtMeCl] (cod = 1,5-cyclooctadiene),[14] dippe,[15] $[(thf)_2LiSiHMes_2]$,[7] and $B(C_6F_5)_3$[16] were prepared according to known prodedures. NMR spectra were recorded in [D$_6$]benzene at room temperature unless otherwise noted. Elemental analyses were performed by the microanalytical facility at the University of California, Berkeley. All IR samples were prepared as KBr pellets.

[(dippe)PtMeCl]: A procedure analogous to the preparation of [(dppe)PtMeCl] (dppe = 1,2-bis(diphenylphosphanyl)ethane) was used,[17] but starting from [(cod)PtMeCl] and dippe in benzene. Thus, [(dippe)PtMeCl] was crystallized from dichloromethane at -40 °C. ^{1}H NMR (400 MHz): δ = 0.66 (dd, ^3J(H,H) = 7.2, ^3J(H,P) = 14.4 Hz, 6H, *i*Pr), 0.70 (m, PtMe), 0.81 (dd, ^3J(H,H) = 7.2, ^3J(H,P) = 13.6 Hz, 6H, *i*Pr), 0.92 (dd, ^3J(H,H) = 7.2, ^3J(H,P) = 16.4 Hz, 6H, *i*Pr), 1.17 (m, CH$_2$), 1.28 (dd, ^3J(H,H) = 7.2, ^3J(H,P) = 15.6 Hz, 6H, *i*Pr), 1.83 (m, 2H, ^{i}Pr), 2.25 (m, 2H, *i*Pr); ^{31}P{^{1}H} NMR (161.98 MHz): δ = 63.19 (s with ^{195}Pt satellites, ^1J(P,Pt) = 4013 Hz), 72.49 (s with ^{195}Pt satellites, ^1J(P,Pt) = 1760 Hz).

1: Et$_2$O (15 mL) was added to a mixture of [(dippe)PtMeCl] (0.411 g, 0.810 mmol) and $[(thf)_2LiSiHMes_2]$ (0.339 g, 0.810 mmol). The mixture was stirred for 12 hours, and then the volatile compounds were removed under reduced pressure. Extraction of the residue with pentane (5 × 20 mL), followed by concentration to approximately half its volume and cooling to -78 °C, resulted in crystallization of pure **1**. Yield 79% (0.473 g). Elemental analysis calcd for $C_{33}H_{58}P_2PtSi$: C 53.57, H 7.90; found: C 53.23, H 8.12; m.p. 195-198 °C (decomp); ^{1}H NMR (400 MHz): δ = 0.76 (m, 12H, *i*Pr), 0.91 (m, 12H, *i*Pr), 1.05 (dd, ^3J(Si,P) = 9.6, ^3J(H,P) = 6.4 Hz, PtMe), 1.13 (m, CH$_2$ and *i*Pr), 1.96 (m, 2H, CH$_2$), 2.23 (s, 6H, *p*-Me), 2.78 (s, 12H, *o*-Me), 6.21 (m, 1H, SiH), 6.93 (s, 4H, ArH); ^{13}C{^{1}H} NMR (100 MHz): δ = 5.6 (m, *i*Pr), 8.6 (m, *i*Pr), 13.1 (m, PtMe), 16.4 (s, Mes), 18.2 (s, Mes), 17.1 (m, CH$_2$), 18.2 (m, CH$_2$), 25.2 (m, *i*Pr), 27.4 (m, *i*Pr), 118.8 (s, Ar), 122.1 (s, Ar), 125.3 (s, Ar), 131.1 (s, Ar), 132.3 (s, Ar), 138.8 (s, Ar); ^{31}P{^{1}H} NMR (161.98 MHz): δ = 66.54 (s with ^{195}Pt satellites, ^1J(P,Pt) =

1784 Hz), 76.00 (s with ^{195}Pt satellites, ^{1}J(P,Pt) = 1378 Hz); ^{29}Si{^{1}H} NMR (99.3 MHz): $\delta = -28.70$ (dd with ^{195}Pt satellites, ^{1}J(P,Pt) = 1315, $^{2}J(\mathrm{Si,Pt})_{trans} = 192$, $^{2}J(\mathrm{Si,P})_{cis} = 13.3$ Hz); IR: 2956 s, 2913 s, 2051 m (SiH), 1600 w, 1542 w, 1459 s, 1405 m 1384 w, 1253 w, 1226 w, 1035 m, 836 s, 698 m, 657 m, 632 m, 594 m, 549 w, 424 cm^{-1} m.

2: A mixture of **1** (0.050 g, 0.067 mmol) and $B(C_6F_5)_3$ (0.035 g, 0.068 mmol) was dissolved in [D_2]dichloromethane (0.700 mL), generating a bright yellow solution of **2**. ^{1}H NMR (400 MHz): $\delta = -1.50$ (dd, $^{2}J(\mathrm{H,P})_{cis} = 7.1$, $^{2}J(\mathrm{H,P})_{trans} = 105$, ^{1}J(H,Pt) = 743 Hz, 1 H, PtH), 0.63 (m, 12 H, *i*Pr), 0.85 (m, 12 H, *i*Pr), 1.25 (m, CH_2 and *i*Pr), 1.36 (br s, 3 H, $MeB(C_6F_5)_3$), 1.62 (m, 2 H, CH_2), 2.00(s, 6 H, *p*-Me), 2.23 (s, 12 H, *o*-Me), 6.62 (s, 4 H, ArH); ^{31}P{^{1}H} NMR (161.98 MHz): $\delta = 77.2$ (s with ^{195}Pt satellites, ^{1}J(P,Pt) = 1726 Hz), 81.4 (s with ^{195}Pt satellites, ^{1}J(P,Pt) = 2523 Hz); ^{19}F NMR (376.4 MHz): $\delta = -132.2$ (br s, 2 F), -165.1 (br s, 1 F), -167.2 (br s, 2 F); ^{29}Si{^{1}H} NMR (99.38 Mhz): $\delta = 338.1$ (d with ^{195}Pt satellites, ^{2}J(Si,P) = 187.8, ^{1}J(Si,Pt) = 1305 Hz).

3: Dichloromethane (10 mL) was added to a mixture of **1** (0.300 g, 0.405 mmol) and $B(C_6F_5)_3$ (0.207 g, 0.405 mmol) to generate **2**. After all of the reactants had dissolved, a solution of DMAP (0.049 g, 0.405 mmol) in dichloromethane (5 mL) was added by cannula. This resulted in the immediate formation of a colorless solution. Removal of the volatile material under reduced pressure gave a light yellow oil, to which Et_2O (5 mL) was added. Cooling the mixture to −78 °C for 12 h resulted in precipitation of **3** as a light yellow powder. Yield 47 % (0.225 g). Elemental analysis calcd for $C_{58}H_{68}BF_{15}N_2P_2PtSi$: C 58.83, H 5.79; found: C 58.53, H 5.56; m.p. 105–107 °C (dec). ^{1}H NMR (400 MHz, [D_2]dichloromethane): $\delta = -3.57$ (dd with ^{195}Pt satellites, $^{2}J(\mathrm{H,P})_{cis} =$, $^{2}J(\mathrm{H,P})_{trans} = 148$, ^{1}J(H,Pt) = 918 Hz, 1 H, PtH), 0.47 (br s, $MeB(C_6F_5)_3$), 0.65 (m, 12 H, *i*Pr), 0.94 (m, 12 H, *i*Pr), 1.13 (m, CH_2 and *i*Pr), 1.96 (m, 2 H, CH_2), 2.32 (s, 6 H, *p*-Me), 2.36 (s, 12 H, *o*-Me), 3.09 (s, 6 H, NMe_2), 6.56 (d, ^{3}J(HH) = 7.6 Hz), 6.81 (s, 1 H, ArH), 8.32 (d); ^{13}C{^{1}H} NMR (100 MHz, [D_2]dichloromethane): $\delta = 7.1$ (m, *i*Pr), 8.2 (m, *i*Pr), 10.1 (br s, $MeBAr_3$), 19.1 (s, Mes), 19.9 (s, Mes), 23.3 (m, CH_2), 28.4 (m, CH_2), 32.1 (s, NMe_2), 117.5 (s, Ar), 119.1 (s, Ar), 121.3 (s, Ar), 124.1 (s, Ar), 127.1 (s, Ar), 130.1 (s, Ar), 131.6 (s, Ar), not all of the aryl carbon atoms were observed; ^{31}P{^{1}H} NMR (161.98 MHz, [D_2]dichloromethane): $\delta = 71.87$ (d with ^{195}Pt satellites, ^{2}J(P,P) = 3.4, ^{1}J(P,Pt) = 2075 Hz), 92.37 (d with ^{195}Pt satellites, ^{1}J(P,Pt) = 1636 Hz); IR: 2971 s, 2916 s, 2072 m (PtH), 1572 w, 1489 s, 1426 m 1401 w, 1319 w, 1251 w, 1092 m, 913 s, 852 m, 741 m, 695 m, 525 cm^{-1} m.

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[8] Crystal data for **1**: $C_{33}H_{57}PtP_2Si$, 0.10 × 0.15 × 0.10 mm, tetragonal, space group $P2_1c$, $a = 22.0264$ (3), $c = 14.2660$ (2) Å, $V = 6947.3$ (1) Å^{3}, $Z = 8$; $\mu(\mathrm{Mo}_{K\alpha}) = 41.69$ cm^{-1}, $T = 158$ K. Of 28993 data collected ($2\theta < 46.5°$), 3551 were independent and used in the refinement of 334 variables. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were treated as idealized contributions, except H(36), which was located and refined isotropically . $R(F) = 0.029$; $R(wF) = 0.029$. Max./min. peaks in final difference map: 0.55/−0.57 e^{-} Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102839. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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