Angewandte Chemie

Silyl Complexes

DOI: 10.1002/ange.201302459

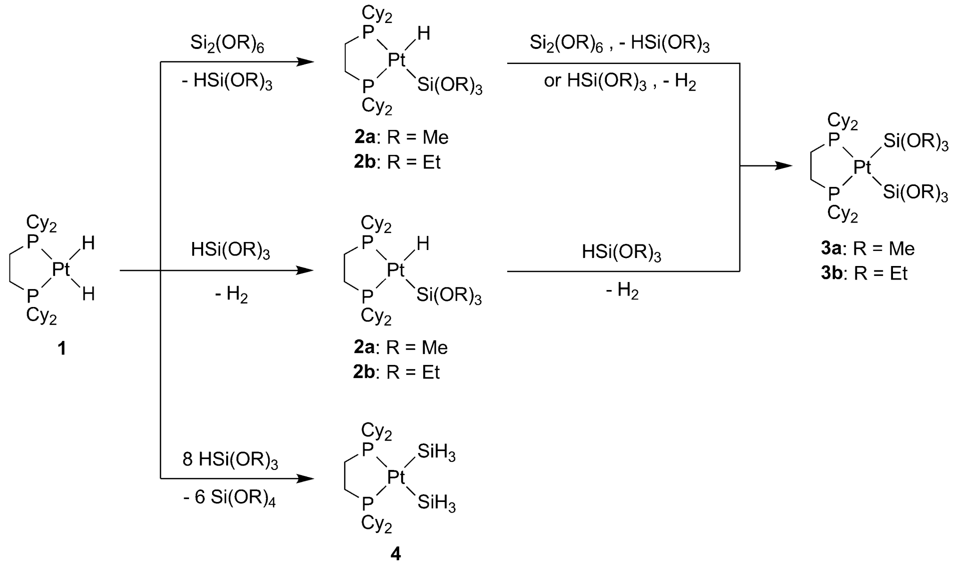
Si–Si and Si–O Bond Activation at Platinum: Stepwise Formation of a SiH_3 Complex**

*Cathérine Mitzenheim and Thomas Braun**

Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

The cleavage of silicon–hydrogen and silicon–silicon bonds has to be considered as an important key step in transition-metal-mediated silylations, like hydrosilylation reactions,[1] bis(silylation) reactions,[2] and the dehydrocoupling of hydrosilanes.[3] With regard to the silylation reactions, the oxidative addition of Si–Si bonds at platinum complexes often leads to the generation of bis(silyl) complexes.[2,4] In contrast, Si_2H_6 as the simplest substrate reacts with $[Pt(H)_2(dcpe)]$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) to form $[Pt_2(\mu\text{-}SiH_2)_2(dcpe)_2]$. The SiH_3 complex $[Pt(SiH_3)_2(dcpe)]$ (**4**) was described to be an intermediate.[5] Studies comprising the generation of complexes that bear SiH_3 ligands, such as **4**, are rare. The complex $[Cp_2Ti(\mu\text{-}HSiH_2)]_2$, which was reported by Harrod et al., was synthesized by reaction of tertiary alkoxysilanes with dimethyltitanocen.[6] The conversion involves a redistribution of the silicon-bound hydrogen atoms and alkoxy groups. Note that zirconium and hafnium complexes are also capable of catalyzing such redistributions.[7] Transition-metal complexes with a non-bridging SiH_3 ligand are accessible by reaction of halogenated silanes with carbonylmetallates.[8] Furthermore, a Cl/H exchange at $SiHCl_2$ ligands with $LiAlH_4$ led to SiH_3 complexes.[9] Moreover, the reaction of the secondary silane $H_2SiMePh$ with $[RuH_2(H_2)(PCy_3)_2]$ results in a redistribution of the silicon-bound groups to give the complexes $[Ru_2H_4(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}SiH_4)(PCy_3)_4]$ and $[RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}HSiPh_3)(PCy_3)_2]$ as well as $HSiMePh_2$ and $HSiMe_2Ph$.[10] Addition of trimethoxysilane to $[Ru_2H_4(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}SiH_4)(PCy_3)_4]$ yields the complex $[Ru_2H_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si(OMe)_2\}_3(PCy_3)_2]$, which displays three bridging alkoxysilane ligands.[10b]

Herein we present the activation of $Si_2(OR)_6$ (R = Me, Et) and $HSi(OR)_3$ at the platinum phosphine complex $[Pt(H)_2(dcpe)]$ (**1**) by Si–Si, Si–H, and Si–O bond cleavage reactions. Reactions with stoichiometric amounts of $Si_2(OR)_6$ or $HSi(OR)_3$ led to the bis(silyl) complexes $[Pt\{Si(OR)_3\}_2(dcpe)]$ (**3a**: R = Me, **3b**: R = Et). Remarkably, treatment of complex **1** with an excess of $HSi(OR)_3$ yielded exclusively the bis(silyl) complex $[Pt(SiH_3)_2(dcpe)]$ (**4**) and $Si(OR)_4$ by repetitive Si–O bond activation, resulting in hydrodealkoxylations.[11] Moreover, intermediates for the formation of **4** were identified by NMR spectroscopy and give an insight into the rearrangement reactions. Complex **4** can act as a source of SiH_4 by protonation.



Scheme 1. Si–Si, Si–H, or Si–O activation reactions at $[Pt(H)_2(dcpe)]$ (**1**).

Treatment of the dihydrido complex **1**[12] with $Si_2(OMe)_6$ or $Si_2(OEt)_6$ yielded the bis(silyl) complexes $[Pt\{Si(OMe)_3\}_2(dcpe)]$ (**3a**) and $[Pt\{Si(OEt)_3\}_2(dcpe)]$ (**3b**), respectively (Scheme 1). NMR spectroscopic investigations revealed the formation of the hydrido silyl complexes $[Pt(H)\{Si(OMe)_3\}(dcpe)]$ (**2a**) and $[Pt(H)\{Si(OEt)_3\}(dcpe)]$ (**2b**) as intermediates. After 4 h, the ratio of **2a** and **3a** is 1:0.9. With hexaethoxydisilane, the ratio of **2b** and **3b** is 1:0.6 after 12 h. The bis(silyl) complexes $[Pt\{Si(OR)_3\}_2(dcpe)]$ (**3a**: R =

---

[*] Dipl.-Chem. C. Mitzenheim, Prof. Dr. T. Braun
Humboldt-Universität zu Berlin, Department of Chemistry
Brook-Taylor-Strasse 2, 12489 Berlin (Gemany)
E-mail: thomas.braun@chemie.hu-berlin.de

[**] We would like to acknowledge the Deutsche Forschungsgesellschaft for financial support. We are grateful to Dr. S. Mebs for the crystallography.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302459.

Me, **3b**: R = Et) show a singlet with ^{195}Pt satellites in the ^{31}P{^{1}H} NMR spectra (**3a**: 76.4 ppm, ^1J(P,Pt) = 1496 Hz; **3b**: 75.3 ppm, ^1J(P,Pt) = 1499 Hz). The ^{29}Si{^{1}H} NMR spectra displays a doublet of doublets with ^{195}Pt satellites (**3a**: 5.52 ppm, ^1J(Si,Pt) = 1902 Hz; **3b**: 2.94 ppm, ^1J(Si,Pt) = 1918 Hz) for the two silyl ligands. The coupling constants to the phosphorus atoms in the *cis* and *trans* position are 14 Hz and 228 Hz.

The NMR data of the hydrido silyl complexes **2a** and **2b** are very similar. The hydrido ligand of **2b** gives rise to a doublet of doublets with ^{195}Pt satellites in the ^{1}H NMR spectrum at $\delta = -1.26$ ppm (^1J(H,Pt) = 968 Hz, ^2J(H,P-trans) = 153 Hz, ^2J(H,P-cis) = 12 Hz). The ^{31}P{^{1}H} NMR spectrum shows two doublets with ^{195}Pt satellites for the two inequivalent phosphorus atoms at $\delta = 84.2$ ppm (^1J(P,Pt) = 1645 Hz, ^2J(P,P) = 2.9 Hz) and at $\delta = 74.2$ ppm (^1J(P,Pt) = 1960 Hz, ^2J(P,P) = 2.9 Hz). Because of the strong *trans* influence of the silyl group,[13] the ^1J(P,Pt) coupling constant for the phosphorus atom in the *trans* position to the silyl ligand (1645 Hz) is smaller than that for the phosphorus atom in the *cis* position (1960 Hz). A selective decoupling experiment revealed a ^2J(P,H-*trans*) coupling constant of 153 Hz for the signal at $\delta = 74.2$ ppm, which can therefore assigned to the phosphorus atom in the *trans* position to the hydrido ligand. The ^{1}H–^{29}Si HMBC NMR spectrum for **2b** displays a resonance at $\delta = 12.9$ ppm in the ^{29}Si domain, which correlates with resonances for the Si(OEt)$_3$ group and for the hydrido ligand.

Apparently, the hydrido silyl complexes **2a** and **2b** are generated by reaction of $Si_2(OR)_6$ with the dihydrido complex **1** with a concomitant elimination of the tertiary silane HSi(OR)$_3$. A subsequent reaction of **2a** and **2b** with disilane or with the hydrosilane results in the formation of the bis(silyl) complexes **3a** and **3b** as well as the elimination of HSi(OR)$_3$ or dihydrogen, respectively. Thus, a Si–Si activation of $Si_2(OMe)_6$ and $Si_2(OEt)_6$ could be achieved. The generation of HSi(OR)$_3$ and H_2 was confirmed by NMR spectroscopy and GC/MS meassurements. An independent reaction of **2b** with hexamethoxydisilane yielded the complex **3a**. Note that a hydrogenolysis of disilanes with dihydrogen is rarely investigated; most of the conversions involve rather harsh conditions.[14,15] The hydrogenolysis of $Si_2(OEt)_6$ was described recently at [Pt(PEt$_3$)$_3$]. A reaction in the presence of dihydrogen yielded *cis*-[Pt(H){Si(OEt)$_3$}(PEt$_3$)$_2$] and *trans*-[Pt(H){Si(OEt)$_3$}(PEt$_3$)$_2$] as well as HSi(OEt)$_3$.[16]

Addition of two equivalents of trimethoxysilane or triethoxysilane to [Pt(H)$_2$(dcpe)] (**1**) also afforded the complexes **3a** or **3b**, respectively (Scheme 1). Again, **2a** or **2b** could be detected as intermediates by NMR spectroscopy. Note that Schubert et al. reported the generation of [Pt{Si(OMe)$_3$}$_2${κ^2-(*P*,*N*)-Ph$_2$*P*CH$_2$CH$_2$*N*Me$_2$}] by reaction of [PtMe$_2${κ^2-(*P*,*N*)-Ph$_2$*P*CH$_2$CH$_2$*N*Me$_2$}] with trimethoxysilane.[17] As an intermediate, a methyl silyl complex was identified.

In a remarkable conversion, complex **1** reacts with an excess of HSi(OMe)$_3$ or HSi(OEt)$_3$ to give solely the bis(silyl) complex [Pt(SiH$_3$)$_2$(dcpe)] (**4**) and Si(OR)$_4$ (Scheme 1). This observation is in contrast to activation reactions of Si–H bonds at platinum(0) complexes.[16,18] For instance, treatment of [Pt(PEt$_3$)$_3$] with an excess of HSi(OEt)$_3$ affords the isomeric compounds *cis*-[Pt(H){Si(OEt)$_3$}(PEt$_3$)$_2$] and *trans*-[Pt(H){Si(OEt)$_3$}(PEt$_3$)$_2$].[16] Reaction of an excess of HSiPh$_3$ with [Pt(PCy$_3$)$_2$] yields *cis*-[Pt(H)(SiPh$_3$)(PCy$_3$)$_2$].[18] The generation of Si(OR)$_4$ was confirmed by ^{29}Si{^{1}H} and ^{1}H–^{29}Si HMBC NMR spectroscopy (R = Me: $\delta = -79$ ppm; R = Et: $\delta = -82$ ppm). The ^{31}P{^{1}H} NMR spectrum for **4** shows a singlet with ^{195}Pt satellites at $\delta = 76.8$ ppm (^1J(P,Pt) = 1690 Hz). The SiH$_3$ group gives rise to a virtual triplet in the ^{1}H NMR spectrum at $\delta = 4.12$ ppm (^1J(H,P) = 6.9 Hz) with ^{29}Si satellites and ^{195}Pt satellites. The triplet transforms into a singlet with satellites upon phosphorus decoupling. The hydrogen–platinum coupling constant is 30 Hz and the hydrogen–silicium coupling constant is 166 Hz. The coupling constants are similar to those found for complex [Pt(H)(SiH$_3$)(PCy$_3$)$_2$], which was synthesized by reaction of *trans*-[Pt(H)$_2$(PCy$_3$)$_2$] with SiH$_4$.[19] The ^{29}Si{^{1}H} NMR spectrum for **4** shows a doublet of doublets at $\delta = -72.4$ ppm with ^{195}Pt satellites that are due to couplings to phosphorus atoms in the *cis* and *trans* position. Without hydrogen decoupling, the signal appears as an apparent quintet, which is the result of comparable silicon–hydrogen and silicon–phosphorus coupling constants. These signals are in accordance with the cross-peaks found in the ^{1}H–^{29}Si HMBC NMR spectrum.

The molecular structure of **4** was determined by X-ray diffraction analyses (Figure 1).[20] Suitable crystals were obtained from a toluene/pentane solution at 278 K. Complex **4** shows a distorted square-planar arrangement of the chelating phosphine ligand and the two silyl ligands at the platinum center. The silicon-bound hydrogen atoms were located in the difference Fourier map and were refined isotropically. The Pt–Si bond lengths of 2.3500(7) Å and 2.3408(6) Å are slightly shorter than that in the platinum complex *trans*-[Pt(H)(SiH$_3$)(PCy$_3$)$_2$] (2.382(3) Å).[19] The platinum–phosphorus bond is slightly longer (2.3045(5) Å and 2.3075(6) Å) compared to the distances in *trans*-[Pt(H)(SiH$_3$)(PCy$_3$)$_2$] (2.280(2) Å and 2.283(2) Å).[19]

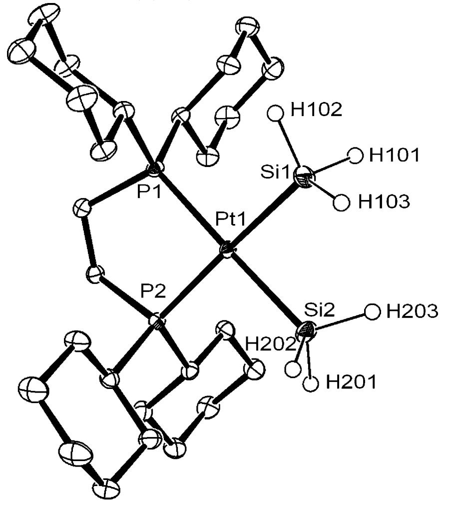
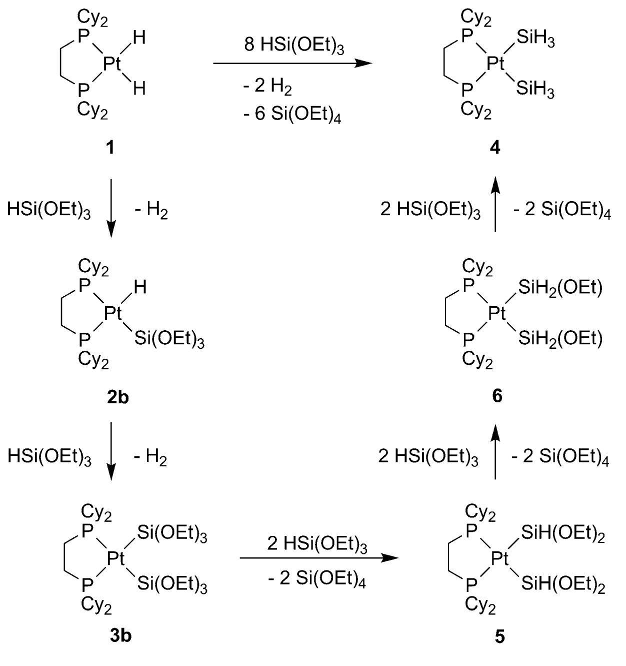


Figure 1. An ORTEP diagram of **4**. Ellipsoids are set at 50% probability; hydrogen atoms at the dcpe ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Pt1 2.3500(7), Si2–Pt1 2.3408(6), P1–Pt1 2.3045(5), P2–Pt1 2.3075(6); P1-Pt1-P2 86.992(19), P1-Pt1-Si1 95.38(2), P1-Pt1-Si2 178.45(2), P2-Pt1-Si1 176.31(2), P2-Pt1-Si2 94.54(2), Si2-Pt1-Si1 83.10(2).

The conversion of **1** into **4** with trimethoxysilane is complete within 30 min, whereas with triethoxysilane the process needs 16 h to be completed. Thus, for the latter case it was possible to detect the four intermediates **2b**, **3b**, $[Pt\{SiH(OEt)_2\}_3(dcpe)]$ (**5**), and $[Pt\{SiH_2(OEt)\}_2(dcpe)]$ (**6**) by monitoring the reaction by NMR spectroscopy (Scheme 2).

The $^{31}P\{^1H\}$ NMR spectrum for **5** shows a singlet with ^{195}Pt satellites at $\delta = 79.1$ ppm ($^1J(P,Pt) = 1602$ Hz). The resonances for the $SiH(OEt)_2$ ligands appear as a doublet of doublets in the ^1H NMR spectrum at $\delta = 6.40$ ppm ($^3J(H,P\text{-}trans) = 13$ Hz, $^3J(H,P\text{-}cis) = 5$ Hz) for the silicon-bound hydrogen atom. The $^{29}Si\{^1H\}$ NMR spectrum shows a doublet of doublets with ^{195}Pt satellites at $\delta = 17.8$ ppm ($^1J(Si,Pt) = 1254$ Hz, $^2J(Si,P\text{-}trans) = 128$ Hz, $^2J(Si,P\text{-}cis) = 5.4$ Hz). The $^{31}P\{^1H\}$ NMR spectrum for **6** displays a singlet with ^{195}Pt satellites at $\delta = 35.8$ ppm ($^1J(P,Pt) = 1600$ Hz). A triplet in the ^1H NMR spectrum at $\delta = 5.60$ ppm ($^1J(H,Pt) = 66$ Hz, $^2J(H,Si) = 168$ Hz, $^3J(H,P) = 6.4$ Hz) can again be assigned to the SiH hydrogen atom at the $SiH_2(OEt)$ moiety. The $^{29}Si\{^1H\}$ NMR spectrum shows a virtual triplet at $\delta = 8.8$ ppm ($^1J(Si,Pt) = 1140$ Hz; apparent $^2J(Si,P) = 33$ Hz). The NMR data of **6** are comparable to these of complex *cis*-$[Pt\{SiH_2(p\text{-}Tol)\}(PPh_3)_3]$ ($p\text{-}Tol = C_7H_7$), which was reported by Braddock-Wiking et al.[21]

Based on these observations, the following reaction pathway can be elucidated (Scheme 2). First, the hydrido silyl complex **2b** is formed by oxidative addition of the Si–H bond of triethoxysilane. A second addition of triethoxysilane yields the bis(silyl) complex **3b** and leads to the release of dihydrogen. Further addition of the silane and rearrangement of the substituents at the silyl groups give two equivalents of tetraethoxysilane and the complex $[Pt\{SiH(OEt)_2\}_3(dcpe)]$ (**5**). The complexes $[Pt\{SiH_2(OEt)\}_3(dcpe)]$ (**6**) and **4** are generated in the same way by a consecutive exchange of the ethoxy moiety to silicon-bounded hydrogen atoms and a simultaneous formation of tetraethoxysilane. In accordance with this hydrodealkoxylations, an independent reaction revealed that treatment of complex **3b** with excess $HSi(OEt)_3$ also yields the complex **4**.

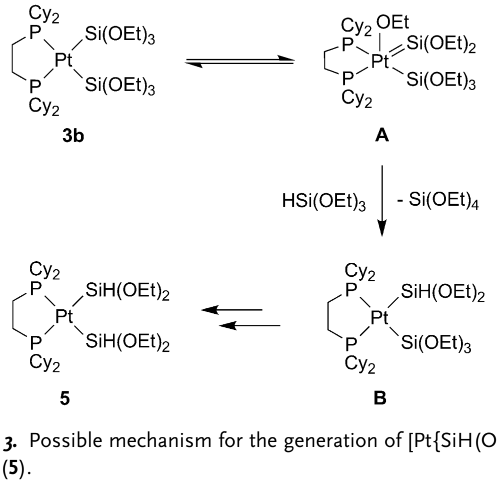


Scheme 2. Intermediates during the formation of $[Pt(SiH_3)_2(dcpe)]$ (**4**).

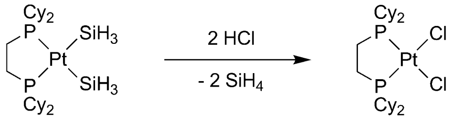
For the hydrodealkoxylation steps, we suggest tentatively that a dissociation of OEt^- from an ethoxysilyl ligand of **3b** could lead to the cationic silyl(silylene)platinum intermediate $[Pt\{Si(OEt)_3\}\{{=}Si(OEt)_2\}(dcpe)]OEt$, or an OEt^- group might migrate to the platinum center to furnish the silylene complex **A** (Scheme 3). Because the silicon atom is strongly oxophilic, the latter reaction pathway seems to be more likely. In the next step, another molecule of triethoxysilane can add to the silylene ligand to form the Si–H bond in complex **B** and tetraethoxysilane. Iteration of these steps gives complex **5**. Note that $^{31}P\{^1H\}$ NMR spectra display signals for small amounts of additional compounds, which might be mixed species, such as **B**, or even Pt^{IV} compounds.

Comparable reaction steps for rearrangement reactions which involve silyl ligands were suggested by Berry et al.[22] For instance, for the redistribution of methyl groups and X^- in the complexes $[Cp_2W(SiMe_3)(SiR_2X)]$ ($R = i$Pr, CH_3, CD_3; $X = Cl$, OSO_2CF_3), a dissociation of X^- and the formation of a cationic silyl(silylene)tungsten intermediate was proposed.[22] Migration of the methyl group to the electrophilic silicon atom at the silylene center and reassociation of X^- to the other silicon atom complete the process. The cleavage of a Si–O bond at a silyl ligand to form a silyl(silylene) complex was also proposed by Tilley et al.[23] The reaction of *cis*-$[Pt(H)\{Si(StBu)_2OTf\}(PEt_3)_2]$ with MeCN to generate *cis*-$[Pt\{SiH(StBu)_2\}(NCMe)(PEt_3)_2]OTf$ is supposed to proceed by a dissociation of a triflate ion to form the silylene complex *cis*-$[Pt(H)\{{=}Si(StBu)_2\}(PEt_3)_2]OTf$ as an intermediate. Note that a silylene ligand might also be stabilized by an intramolecular interaction from an alkoxy group of the neighboring silyl ligand with the silylene silicon atom.[24]

Treatment of complex **4** with hydrochloric acid gave SiH_4 and $[Pt(Cl)_2(dcpe)]$ (**7**) (Scheme 4). This conversion completes a cyclic process for the formation of SiH_4 from $HSi(OMe)_3$ or $HSi(OEt)_3$, because **1** can again be synthesized by treatment of **7** with lithium triethylborohydride.[12] Complex **7** was identified by comparison of the NMR data with



Scheme 3. Possible mechanism for the generation of $[Pt\{SiH(OEt)_2\}_3(dcpe)]$ (**5**).



4 **7**

Scheme 4. Generation of SiH_4.

literature.[25] The ^1H NMR spectrum of the reaction solution displays a singlet with ^{29}Si satellites at $\delta = 3.1$ ppm (^1J(H,Si) = 203 Hz) for the generated SiH_4. The $^{29}Si\{^1H\}$ NMR spectrum shows a singlet at $\delta = -95.66$ ppm, which is accordance with the literature.[26]

In conclusion, we have synthesized the bis(silyl) complexes $[Pt\{Si(OR)_3\}_2(dcpe)]$ (**3a**: R = Me, **3b**: R = Et) by Si–Si activation of $Si_2(OR)_6$ at $[Pt(H)_2(dcpe)]$ (**1**) at room temperature. Hydrido silyl complexes $[Pt(H)\{Si(OR)_3\}(dcpe)]$ (**2a**: R = Me, **2b**: R = Et) were shown to be intermediates. Treatment of **1** with an excess of $HSi(OR)_3$ leads in a remarkable reaction to hydrodealkoxylation reactions and the formation of $[Pt(SiH_3)_2(dcpe)]$ (**4**) and $Si(OR)_4$. The identification of four intermediate complexes by NMR spectroscopy and the stepwise formation of the SiH_3 ligands from $HSi(OR)_3$ by a repetitive activation of Si–O bonds is unprecedented. Furthermore, the bis(silyl) complex $[Pt(SiH_3)_2(dcpe)]$ (**4**) reacts with HCl to give the silane SiH_4. We believe that in future studies, the SiH_3 ligand can be used as a building block in Si–C coupling reactions.

Received: March 24, 2013

Keywords: platinum · silanes · silyl ligands · Si–O bond activation · Si–Si bond activation

---

[1] a) J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175–292; b) J. Y. Corey, *Chem. Rev.* **2011**, *111*, 863–1071.
[2] H. K. Sharma, K. H. Pannell, *Chem. Rev.* **1995**, *95*, 1351–1374.
[3] J. Y. Corey, *Adv. Organomet. Chem.* **2004**, *51*, 1–52.
[4] A. Roscher, A. Bockholt, T. Braun, *Dalton Trans.* **2009**, 1378–1382.
[5] M. J. Michalczyk, C. A. Recatto, J. C. Calabrese, M. J. Fink, *J. Am. Chem. Soc.* **1992**, *114*, 7955–7957.
[6] a) L. Hao, A.-M. Lebuis, J. F. Harrod, E. Samuel, *Chem. Commun.* **1997**, 2193–2194; b) L. Hao, A.-M. Lebuis, J. F. Harrod, *Chem. Commun.* **1998**, 1089–1090; c) J. F. Harrod, *Coord. Chem. Rev.* **2000**, *206–207*, 493–531.
[7] H.-G. Woo, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 5698–5707.
[8] a) B. J. Aylett, J. M. Campbell, *J. Chem. Soc. A* **1969**, 1910–1916; b) B. J. Aylett, J. M. Campbell, A. Walton, *J. Chem. Soc. A* **1969**, 2110–2113; c) A. P. Hagen, C. R. Higgins, P. J. Russo, *Inorg. Chem.* **1971**, *10*, 1657–1660; d) J. S. Allinson, B. J. Aylett, H. M. Colquhoun, *J. Organomet. Chem.* **1976**, *112*, C7–C8.
[9] a) S. Schmitzer, U. Weis, H. Kab, W. Buchner, W. Malisch, T. Polzer, U. Posset, W. Kiefer, *Inorg. Chem.* **1993**, *32*, 303–309; b) W. Malisch, S. Moller, O. Fey, H.-U. Wekel, R. Pikl, U. Posset, W. Kiefer, *J. Organomet. Chem.* **1996**, *507*, 117–124.
[10] a) I. Atheaux, B. Donnadieu, V. Rodriguez, S. Sabo-Etienne, B. Chaudret, K. Hussein, J.-C. Barthelat, *J. Am. Chem. Soc.* **2000**, *122*, 5664–5665; b) R. B. Said, K. Hussein, J.-C. Barthelat, I. Atheaux, S. Sabo-Etienne, M. Grellier, B. Donnadieu, B. Chaudret, *Dalton Trans.* **2003**, 4139–4146; c) see also: M. C. Lipke, T. D. Tilley, *Angew. Chem.* **2012**, *124*, 11277–11283; *Angew. Chem. Int. Ed.* **2012**, *51*, 11115–11121.
[11] J.-P. Djukic, F. Rose-Munch, E. Rose, F. Simon, *Organometallics* **1995**, *14*, 2027–2038.
[12] Note that **1** was generated in situ by reaction of $[Pt(Cl)_2(dcpe)]$ with lithium triethylborohydride: a) C. A. Jaska, A. J. Lough, I. Manners, *Dalton Trans.* **2005**, 326–331; b) D. J. Schwartz, R. A. Andersen, *J. Am. Chem. Soc.* **1995**, *117*, 4014–4025.
[13] B. J. Coe, S. J. Glenwright, *Coord. Chem. Rev.* **2000**, *203*, 5–80.
[14] Union Carbide Co., US Pat., 2 606 811, **1952**; Dow Corning Co., US Pat., 3 639 105, **1972**; Dow Corning Co., US Pat., 6 013 235, **2000**.
[15] a) J. Voigt, M. A. Chilleck, T. Braun, *Dalton Trans.* **2013**, *42*, 4052–4058; b) for a catalytic reaction at rhodium see: L. Rosenberg, C. W. Davis, J. Yao, *J. Am. Chem. Soc.* **2001**, *123*, 5120–5121.
[16] J. Voigt, T. Braun, *Dalton Trans.* **2011**, *40*, 12699–12704.
[17] J. Pfeiffer, U. Schubert, *Organometallics* **1999**, *18*, 3245–3248.
[18] D. Chan, S. B. Duckett, S. L. Heath, I. G. Khazal, R. N. Perutz, S. Sabo-Etienne, P. L. Timmins, *Organometallics* **2004**, *23*, 5744–5756.
[19] E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed, R. O. Gould, *J. Chem. Soc. Dalton Trans.* **1978**, 1167–1170.
[20] X-ray structure analysis of **4**: $C_{32}H_{60}P_2PtSi_2$, $M_r = 758.01$, crystal dimensions $0.29 \times 0.28 \times 0.27\ mm^3$; monoclinic; $P2_1/c$; $a = 12.1816(2)$, $b = 17.9500(3)$, $c = 16.6358(3)$ Å, $\beta = 101.302(2)°$, $Z = 4$, $V = 3567.04(11)$ Å^3, $\rho_{calcd} = 1.411\ mg\,m^{-3}$; $2\theta_{max} = 28.45°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$), $T = 100(2)$ K, 57814 reflections collected, 8975 were unique ($R_{int} = 0.0694$); STOE IPDS 2Θ diffractometer; multiscan absorption correction (min./max transmission 0.3587/0.4424), $\mu = 4.109\ mm^{-1}$. The structure was solved by direct methods and was refined with full-matrix least-squares methods on F^2 (SHELX-97).[27] Final R_1, wR_2 values on all data: 0.0277, 0.0351; R_1, wR_2 values for 8975 reflections with $I_0 > 2\sigma(I_0)$: 0.0171, 0.0343; residual electron density +0.654/−0.986 e Å^3. Hydrogen atoms were placed at calculated positions and refined using a riding model. The hydrogen atoms on the silicon were located on the difference Fourier map and refined isotropically. CCDC 930069 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[21] J. Braddock-Wilking, Y. Levchinsky, N. P. Rath, *Organometallics* **2000**, *19*, 5500–5510.
[22] D. C. Pestana, T. S. Koloski, D. H. Berry, *Organometallics* **1994**, *13*, 4173–4175.
[23] G. P. Mitchell, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 7635–7636.
[24] a) H. Tobita, K. Ueno, M. Shimoi, H. Ogino, *J. Am. Chem. Soc.* **1990**, *112*, 3415–3420; b) T. Takeuchi, H. Tobita, H. Ogino, *Organometallics* **1991**, *10*, 835–836; c) H. Ogino, *Chem. Rec.* **2002**, *2*, 291–306; d) M. Besora, F. Maseras, A. Lledós, O. Eisenstein, *Inorg. Chem.* **2002**, *41*, 7105–7112; e) S. Park, B. G. Kim, I. Göttker-Schnetmann, M. Brookhart, *ACS Catal.* **2012**, *2*, 307–316.
[25] M. Hackett, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 1449–1462.
[26] a) K. Thorshaug, O. Swang, I. M. Dahl, A. Olafsen, *J. Phys. Chem. A* **2006**, *110*, 9801–9804; b) E. A. V. Ebsworth, J. J. Turner, *J. Chem. Phys.* **1962**, *36*, 2628–2634.
[27] a) SHELX-97, G. M. Sheldrick, program for crystal structure refinement, University of Göttingen, **1997**; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.