J. Am. Chem. Soc. **1998,** *120,* 7635−7636

Communications to the Editor

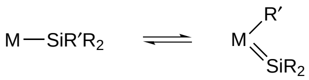
Reversible 1,2-Migration of Hydrogen between Platinum and Silicon via Intermediate Silylene Complexes

Gregory P. Mitchell and T. Don Tilley*

Department of Chemistry
University of California at Berkeley
Berkeley, California 94720-1460

Received March 13, 1998

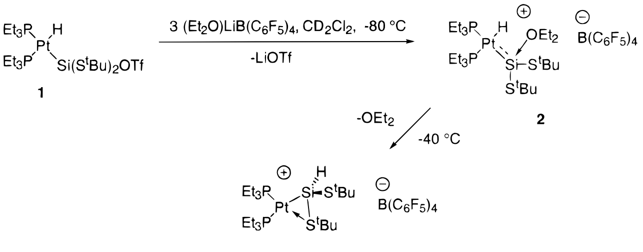
A number of transition metal-catalyzed reactions involving organosilanes are thought to involve silylene complexes as intermediates.[1] In addition, given the many and varied roles that carbene complexes play in useful chemical transformations,[2] it seems that analogous silicon compounds of the type $L_nM{=}SiR_2$ might provide powerful synthetic intermediates. As a result of these interests, synthetic routes to silylene complexes have recently been developed,[3] and their characteristic reactivity patterns are beginning to emerge.[4] In related work, it is becoming increasingly clear that intramolecular migrations in metal silyl complexes may involve intermediate silylene ligands, which might arise via 1,2-migrations between silicon and the metal center (eq 1).[5,6] However, this kind of migration reaction has never been



$$M{-}SiR'R_2 \rightleftharpoons M(R'){=}SiR_2 \qquad (1)$$

directly observed. Clearly, a better understanding of transition metal−silicon chemistry will result from experimental studies on such migrations, which seem like the most likely pathway for generation of a silylene complex in a catalytic cycle. Here we report the formation of a platinum hydrido(silylene) complex, which reacts via reversible 1,2-migration of hydrogen between platinum and silicon.

Scheme 1



We have previously demonstrated that cationic silylene complexes may be formed by exchange of the triflate in $L_nM{-}SiR_2(OTf)$ complexes with BPh_4^- or $B(C_6F_5)_4^-$.[3c,d] Following this approach, we obtained the triflato−silyl complex *cis*-$(PEt_3)_2Pt(H)Si(S^tBu)_2OTf$ (**1**) in 58% yield by reaction of Me_3SiOTf with *cis*-$(PEt_3)_2Pt(H)Si(S^tBu)_3$ in dichloromethane. The ^{29}Si NMR spectrum of **1** consists of a resonance at δ 52.22, which is somewhat downfield shifted from that for *cis*-$(PEt_3)_2Pt(H)Si(S^tBu)_3$ (δ 16.26). This value is consistent with the presence of a covalently bound triflate group, since transition metal silylene complexes typically possess ^{29}Si NMR chemical shifts near 300 ppm.[3]

In an attempt to generate and observe the silylene complex [*cis*-$(PEt_3)_2(H)Pt{=}Si(S^tBu)_2$][$B(C_6F_5)_4$], we monitored the reaction of **1** with excess (3 equiv) $(Et_2O)LiB(C_6F_5)_4$ in dichloromethane-d_2 at −80 °C, by ^1H and ^{31}P NMR spectroscopy. At this temperature, formation of an intermediate (**2**) is indicated by appearance of a new hydride resonance in the ^1H NMR spectrum at δ −5.35, which displays coupling to inequivalent phosphorus atoms. The $^{29}Si\{^1H\}$ NMR resonance for this species (δ 88.62) is too far upfield to be consistent with a base-free silylene complex, but does lie in the region expected for a base-stabilized silylene complex (Scheme 1).[3] Further evidence for the characterization of this species as an ether adduct is seen in the ^1H NMR spectrum, which contains two resonances (at δ 3.41 and 4.55) for $-OCH_2-$ groups, assigned to bound and free (or lithium-bound) diethyl ether, respectively. Variable-temperature spectra revealed a coalescence of these resonances at −50 °C, which corresponds to a barrier for exchange of 10.0 ± 0.3 kcal mol^{-1}.

Intermediate **2** is thermally unstable, and above −40 °C it is observed to convert quantitatively to a new compound (**3**), as indicated by replacement of the hydride resonance of **2** (with $J_{PtH} = 750$ Hz) by an Si−H signal at δ 5.39 ($J_{PtH} = 110$ Hz; $J_{SiH} = 252$ Hz). The ^{31}P NMR spectrum of **3** exhibits peaks for inequivalent phosphorus atoms (δ 21.66, 22.17) and a low $^2J_{PP}$ coupling constant of 5.7 Hz. Variable-temperature ^1H NMR studies indicate the presence of inequivalent and interconverting $-S^tBu$ groups ($T_c \approx 10$ °C), and the latter process is also manifested in coalescence of the ^{31}P resonances at 40 °C ($\Delta G^\ddagger = 15.4 \pm 0.4$ kcal mol^{-1}). This dynamic process might seem to be associated with hindered rotation about the Pt−Si bond, but a purely steric basis for this is not reasonable considering the fact that restricted rotation in *cis*-$(PEt_3)_2Pt(H)Si(S^tBu)_3$ is not observed. We attribute these observations to the presence of a dative S→Pt interaction in the migrated product **3**, as indicated by the structure

---

[1] (a) Tilley, T. D. In *The Silicon-Heteroatom Bond;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245 and 309. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10,* 37. (d) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271. (e) Corey, J. In *Advances in Silicon Chemistry;* Larson, G., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 327. (f) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95,* 1351. (g) Zybill, C. *Top. Curr. Chem.* **1991**, *160,* 1.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987, Chapter 16.

[3] Silylene complexes with sp^2 silicon atoms: (a) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112,* 7801. (b) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115,* 358. (c) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115,* 7884. (d) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116,* 5495. (e) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

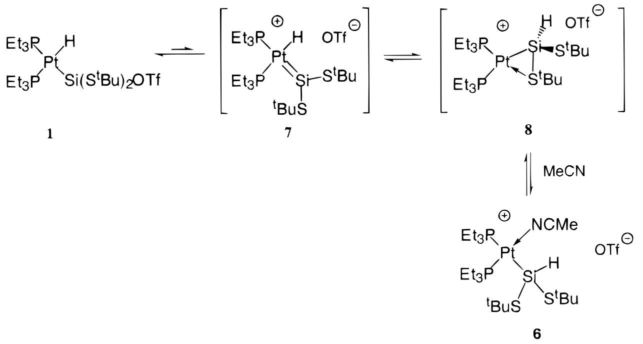
[4] (a) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119,* 11236. (b) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14,* 127. (c) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116,* 6951.

[5] (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14,* 5472. (b) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15,* 3477.

[6] (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5,* 1056. (b) Pannell, K. H.; Rozell, J. M, Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111,* 4482. (c) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8,* 550. (d) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10,* 954. (e) Tobita, H.; Ueno, K.; Ogino, H. *Bull Chem. Soc. Jpn.* **1988**, *61,* 2797. (f) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (g) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113,* 2011. (h) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35,* 186. (i) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13,* 4173. (j) Sekiguchi, A.; Sato, T.; Ando, W. *Organometallics* **1987**, *6,* 2337.

S0002-7863(98)00834-8 CCC: $15.00

Scheme 2



in Scheme 1. This structure has precedent in the cationic alkyl analogue *cis*-$[(PPh_3)_2PtC(H)SCH_2CH_2S]BF_4$, which also features donation from sulfur to platinum (as determined by X-ray crystallography).[7] Interestingly, the latter complex formed via a 1,2-hydrogen migration from platinum to the carbene carbon atom.

Compound **3** could not be isolated, since it is thermally unstable and decomposes at room temperature in dichloromethane-d_2 to a number of products ($t_{1/2} \approx 1$ h). However, simple derivatives of **3** have been isolated and completely characterized. Thus, reaction of **3** with MeMgBr in diethyl ether produced the platinum methyl complex *trans*-$(PEt_3)_2Pt(Me)SiH(S^tBu)_2$ (**4**), isolated in 45% yield. In addition, reaction of **3** with Bu_4NBr in diethyl ether gave *cis*-$(PEt_3)_2Pt(Br)SiH(S^tBu)_2$ (**5**), isolated in 85% yield.

Interestingly, addition of 2 equiv of $[Bu_4N][OTf]$ to a solution of **3** does not form a complex analogous to **5**, but results instead in complete regeneration of **1**, demonstrating facile reversibility of this hydride migration. This reversibility is also indicated by the reaction of **1** with a large excess of MeCN (ca. 300 equiv; dichloromethane-d_2), which induced quantitative hydride migration from Pt to Si to form the migrated complex [*cis*-$(PEt_3)_2Pt(NCMe)SiH(S^tBu)_2$][OTf] (**6**, Scheme 2), characterized in solution by NMR spectroscopy. Like **3**, **6** displays fluxional behavior, as observed by ^{31}P NMR spectroscopy. At −20 °C, fully resolved signals were observed for the inequivalent PEt_3 ligands, and the barrier to phosphine interconversion (15.0 ± 0.5 kcal mol^{-1}) is similar to that for the analogous complex **3**. Attempts to isolate **6** were unsuccessful, presumably due to the lability of the MeCN ligand.

Interestingly, compounds **1** and **6** exist in equilibrium, as demonstrated by monitoring the [**6**]/[**1**] ratio as a function of [MeCN]. This equilibrium is unaffected by the presence of $[Bu_4N][OTf]$, suggesting that **6** is best described as a contact ion-pair.[8] Thus, the equilibrium constant expression, [**6**]/[**1**][CH_3CN], was determined to have a value of 6.0 ± 0.1 M^{-1} at 298 K. Note that in nonpolar solvents such as benzene and toluene, **1** is stable toward migration even in the presence of excess acetonitrile (5−12 equiv).

The rate of reaction between **1** and CH_3CN is slow enough at 10 °C to be monitored easily by ^1H NMR spectroscopy. The initial rates of formation of **6** (<10% reaction, ca. 30 min) were found to be independent of [CH_3CN] (0.08−1.56 M). To assess the kinetic role of hydrogen migration in this equilibrium, we prepared the deuteride *cis*-$(PEt_3)_2Pt(D)Si(S^tBu)_2OTf$ (**1**-*d*)[9,10] and monitored its conversion to **6**-*d* to obtain a kinetic isotope effect (k_H/k_D) of 1.3 ± 0.1. This relatively small KIE suggests that hydride migration does not feature prominently in the rate-limiting step; however, it is difficult at this point to predict what the magnitude of a primary effect for such a migration would be. Since the thermodynamic isotope effect is also small ($K_{eq(H)}/K_{eq(D)} = 1.1 \pm 0.1$), the KIE for the reverse reaction (**6** to **1**) must be small as well. We therefore propose that the rate-determining step in the formation of **6** from **1** is dissociation of triflate to form the silylene species [*cis*-$(PEt_3)_2(H)Pt{=}Si(S^tBu)_2$][OTf] (**7**) (Scheme 2). This silylene intermediate is probably also best viewed as a contact ion-pair, since the initial rate of reaction is not inhibited by added $[Bu_4N][OTf]$, with $[Bu_4N][B(C_6F_5)_4]$ present to maintain conditions of constant ionic strength.[8] Intermediate **7** is proposed to undergo rapid hydride migration to generate **8** (analogous to **3**), which is then trapped by acetonitrile to form the observed product **6**. It therefore appears that in dichloromethane, **1** is in equilibrium with minute quantities of **7** and **8**. It is also possible that in the presence of acetonitrile, **7** is trapped to a small, undetectable degree as a base-stabilized silylene complex.

In conclusion, we have observed the facile and clean migration of hydrogen from platinum to silicon, via the putative silylene hydride intermediate $[(PEt_3)_2(H)Pt{=}Si(S^tBu)_2]^+$.[11] In the presence of the noncoordinating counteranion $B(C_6F_5)_4^-$, this migration is rapid and irreversible. However, with a triflate counteranion the migration is slow (requiring triflate dissociation from silicon) and reversible. Acetonitrile traps the migrated product but in the resulting $-SiH(S^tBu)_2$ derivative (**6**), hydrogen reversibly migrates between silicon and platinum. These initial results on 1,2-migration between a metal and silicon suggest that such processes may be facile, and highly sensitive to reaction conditions and substituent effects.

Acknowledgment is made to the National Science Foundation for their generous support of this work. We also thank Professors Robert Bergman and Andrew Streitwieser for valuable discussions on isotope effects.

Supporting Information Available: Synthetic details and characterization data for the compounds and kinetic plots (19 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9808346

---

[7] Michelin, R. A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Organometallics* **1993**, *12*, 2372.

[8] *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, NY, 1972−1974; Vols. 1−2.

[9] $DSiCl_3$, which was used to synthesize $DSi(S^tBu)_3$, was prepared in situ via reduction of $SiCl_4$ with Bu_3SnD by using a modified procedure: Pätzold, U.; Roewer, G.; Herzog, U. *J. Organomet. Chem.* **1996**, *508*, 147.

[10] Selected data for *cis*-$(PEt_3)_2Pt(D)Si(S^tBu)_3$: $^{31}P\{^1H\}$ NMR (dichloromethane-d_2, 161.98 MHz): δ 14.44 (dt with ^{195}Pt satellites, $^2J_{PP} = 17.00$ Hz, $^2J_{PD} = 23.00$ Hz, $^1J_{PPt} = 2219$ Hz), 18.22 (d with ^{195}Pt satellites, $^1J_{PPt} = 1749$ Hz). IR (KBr pellet): 1508 s (PtD). **1**-*d*: $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 14.37 (q with ^{195}Pt satellites, $^2J_{PP} = 19.4$ Hz, $^2J_{PD} = 19.4$ Hz, $^1J_{PPt} = 2260$ Hz), 19.85 (d with ^{195}Pt satellites, $^1J_{PPt} = 1959$ Hz). IR (KBr pellet): 1483 m (PtD).

[11] A related migration involving Pt and Ge may occur, see: (a) Litz, K. E.; Henderson, K.; Gourley, R. W.; Banaszak Holl, M. M. *Organometallics* **1995**, *14*, 5008. (b) Litz, K. E.; Bender, J. E., IV; Kampf, J. W.; Banaszak Holl, M. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 496.