Synthesis, Structure, and Silylene Exchange Reaction of Base-Stabilized Hydrido(silylene)tungsten Complexes and Rearrangement of Hydrosilyl(pyridine)tungsten Complexes to the Base-Stabilized Hydrido(silylene) Complexes via 1,2-Hydrogen Migration

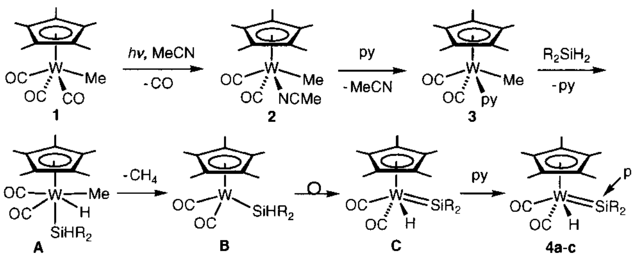
Hiroyuki Sakaba,* Masanori Tsukamoto, Takeshi Hirata, Chizuko Kabuto, and Hiroshi Horino*

Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578, Japan

Received September 9, 1999

There has been considerable recent interest in migration reactions of transition-metal silyl and silylene complexes. 1,2-Silyl migration in coordinatively unsaturated disilanyl complexes has been shown to generate intermediate silyl(silylene) complexes,[1−5] and in some cases they are isolated as base-stabilized silyl(silylene) or bis(silylene) complexes in the presence of external or intramolecular bases.[2b−d,5] 1,3-Substituent migration in the silyl(silylene) intermediates has been proposed in a variety of reactions.[1,2,4−6] Compared to the recent extensive studies on these migrations, however, investigations focused on 1,2-hydrogen migration converting a hydrosilyl complex to a hydrido(silylene) complex are relatively limited,[7−9] despite the facts that this migration process has been postulated as a key step in several reactions of transition-metal complexes with organosilicon compounds,[10] and that the corresponding migration has been established in the chemistry of carbene complexes.[11] Quite recently reversible 1,2-hydrogen migration has been shown to occur in a hydrosilylplatinum complex via an intermediate hydrido(silylene) complex by low-temperature NMR studies.[8a,12] Here we report the synthesis and structure of base-stabilized hydrido(silylene)tungsten complexes via Si−H bond activation of secondary silanes, the reactivity of hydrosilyl(pyridine)tungsten complexes to rearrange to the hydrido(silylene) complexes via 1,2-hydrogen migration, and a novel silylene exchange reaction for the hydrido(silylene) complexes.

Scheme 1



We have recently reported the synthesis of *cis*-Cp*(CO)$_2$(MeCN)WMe (**2**) by the photolysis of Cp*(CO)$_3$WMe (**1**) in MeCN and its reactivity to substitution and oxidative addition reactions.[13] The corresponding pyridine complex *cis*-Cp*(CO)$_2$(py)WMe (**3**), which was conveniently obtained by dissolving **2** in pyridine, reacted immediately with Ph$_2$SiH$_2$ (3 equiv) in C$_6$D$_6$ at room temperature to give exclusively the base-stabilized hydrido(silylene) complex *cis*-Cp*(CO)$_2$(H)W=SiPh$_2$·py (**4a**) accompanied by generation of methane (0.16 ppm) (Scheme 1). In a preparative scale reaction in toluene, **4a** was isolated as air-sensitive orange crystals in 78% yield based on **1**, and similar reactions using Et$_2$SiH$_2$ and MePhSiH$_2$ gave *cis*-Cp*(CO)$_2$(H)W=SiEt$_2$·py (**4b**) and *cis*-Cp*(CO)$_2$(H)W=SiMePh·py (**4c**) in 72 and 85% yields, respectively. A possible mechanism for the formation of **4a**−**c** is shown in Scheme 1. (i) Oxidative addition of the secondary silane to the coordinatively unsaturated intermediate generated by dissociation of the pyridine ligand from **3** produces the hydrido(methyl)silyl intermediate **A**. (ii) Reductive elimination of methane forms the unsaturated intermediate **B**. (iii) 1,2-Hydrogen migration from the silicon to the tungsten gives the hydrido(silylene) complex **C**, which is subsequently coordinated by pyridine to give the stabilized product **4a**−**c**.

Complexes **4a**−**c** exhibit the characteristic high-field ^{1}H resonances due to the tungsten hydrides and low-field ^{29}Si resonances with large coupling constants between Si and ^{183}W. For instance, **4a** gives the hydride signal at −7.70 ppm ($^1J_{\mathrm{WH}} = 65$ Hz) and the ^{29}Si resonance at 94.0 ppm ($^1J_{\mathrm{WSi}} = 111$ Hz). A similar observation for the ^{29}Si resonance has been reported for the base-stabilized silyl(silylene)tungsten complex *trans*-Cp(CO)$_2$(Me$_3$Si)W=SiMe$_2$·HMPA, which shows the ^{29}Si resonances of the silylene and silyl ligands at 92.5 ppm ($^1J_{\mathrm{WSi}} = 121$ Hz) and 18.6 ppm ($^1J_{\mathrm{WSi}} = 59$ Hz), respectively, and the significant low-field shift and largely increased coupling constants observed for the silylene ligand have been recognized as consequences of the partial double-bond character of the tungsten-silylene bond.[2c]

In contrast with the reaction of **3** with of Ph$_2$SiH$_2$ in C$_6$D$_6$, the reaction of *cis*-Cp*(CO)$_2$(py-*d*$_5$)WMe (**3-*d*$_5$**) with a large excess of Ph$_2$SiH$_2$ (51 equiv) in pyridine-*d*$_5$ proceeded slowly to give two new products **5-*d*$_5$** and **6-*d*$_5$** in addition to the expected product **4a-*d*$_5$** (**4a-*d*$_5$**:**5-*d*$_5$**:**6-*d*$_5$** = 15:52:33 at ∼96% conversion after 2 h) (Scheme 2). Complex **6-*d*$_5$** was gradually converted to **5-*d*$_5$** with a slight increment of **4a-*d*$_5$** (**4a-*d*$_5$**:**5-*d*$_5$**:**6-*d*$_5$** = 17:79:4 at complete conversion after 8.5 h). The undeuterated complex **5** was isolated in 34% from the reaction of **3** with the silane in pyridine and fully characterized as *trans*-Cp*(CO)$_2$(py)WSiHPh$_2$, which showed a SiH signal (5.96 ppm, $^1J_{\mathrm{SiH}} = 176$ Hz), a single CO signal (241.3 ppm), and a ^{29}Si signal (22.4 ppm, $^1J_{\mathrm{WSi}} = 38$ Hz) in the NMR spectra in C$_6$D$_6$. Complex **6** was unable to be isolated, but characterized as *cis*-Cp*(CO)$_2$(py)WSiHPh$_2$ on the

---

(1) (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (b) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (c) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315 and references therein.

(2) (a) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138. (d) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2844 and references therein.

(3) 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.

(4) (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.

(5) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861.

(6) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173.

(7) (a) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1996**, 477. (b) Okazaki, M.; Tobita, H.; Kawano, Y.; Inomata, S.; Ogino, H. *J. Organomet. Chem.* **1998**, *553*, 1.

(8) (a) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635. (b) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524.

(9) Fickert, C.; Nagel, V.; Kiefer, W.; Möller, S.; Jehle, H.; Malisch, W.; Stowasser, R.; Bringmann, G. *J. Organomet. Chem.* **1998**, *566*, 225.

(10) (a) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (b) Esteruelas, M. A.; Nürnberg, O.; Oliván, M.; Oro, L. A.; Werner, H. *Organometallics* **1993**, *12*, 3264. (c) Chen, W.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oro, L. A. *Organometallics* **1996**, *15*, 2185. (d) Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403 and references therein.

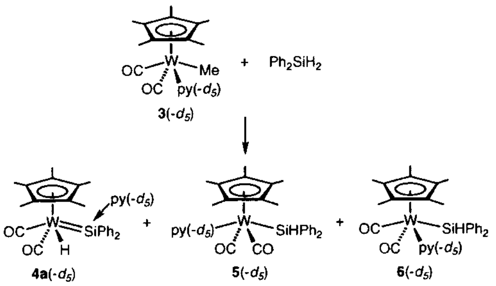
(11) For reversible 1,2-hydrogen migration in carbene complexes, see: Winter, M. J. *Polyhedron*, **1989**, *8*, 1583 and references therein.

(12) After this paper was submitted for publication, the following reports concerning Si−H activation and 1,2-hydrogen migration to form iridium silylene complexes have appeared: (a) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (b) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

(13) (a) Sakaba, H.; Ishida, K.; Horino H. *Chem. Lett.* **1995**, 1145. (b) Sakaba, H.; Ishida, K.; Horino H. *Chem. Lett.* **1998**, 149.

10.1021/ja993279w CCC: $19.00

Scheme 2



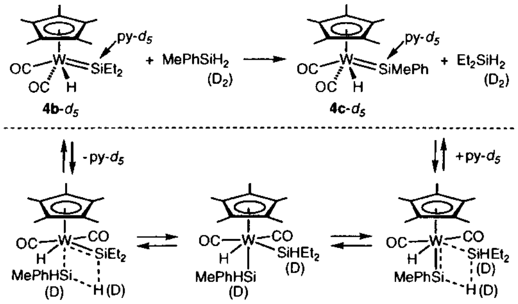
basis of the following characteristic NMR data for **6-*d*$_5$**; a SiH signal (6.79 ppm, $^1J_{SiH} = 177$ Hz), two CO signals (237.5 and 238.7 ppm at −35 °C), and a ^{29}Si signal (100.0 ppm, $^1J_{WSi} = 81$ Hz at −35 °C) in the spectra of the reaction mixture containing **4a-*d*$_5$**, **5-*d*$_5$**, and **6-*d*$_5$** in pyridine-*d*$_5$.[14] The existence of the pyridine ligand in **6** was confirmed by the detection of two (5.92 and 6.31 ppm) of the three expected signals in the ^{1}H NMR spectrum of the mixture of **4a**, **5**, and **6** in C_6D_6, which was prepared by the reaction of **3** with Ph_2SiH_2 in pyridine followed by replacing the solvent with C_6D_6.

X-ray analyses of **4a** and **5** clearly demonstrate the partial double bond character in the W−Si bond of **4a** (see Supporting Information for details). The W−Si bond length (2.445(2) Å) in **4a** is considerably shorter than those (2.570(4) Å in molecule A, 2.582(4) Å in molecule B, and 2.576 Å for the averaged length) in **5**, whose crystal contains two independent molecules. The latter are comparable with the W−Si bond lengths (2.533−2.633 Å) in the structurally related silyltungsten complexes *trans*-Cp$^{(*)}$-$(CO)_2(PR_3)WSiR'_3$.[15] Recent X-ray structure determination of *trans*-$Cp(CO)_2(Me_3Si)W{=}SiMe_2{\cdot}HMPA$ has shown 2.481 Å for the tungsten-silylene bond and 2.553 Å for the tungsten-silyl bond.[2c]

When the ^{1}H NMR spectrum of the mixture of **4a**, **5**, and **6** in C_6D_6 described above was monitored, surprisingly fast rearrangement of **6** to **4a** was observed (first order in **6**, $k_{obs} = 9.1 \times 10^{-4}$ s^{-1}, $t_{1/2} = 13$ min at 26 °C), but no isomerization of **6** to **5** was detected. Addition of pyridine (∼55 equiv to **6**) to a C_6D_6 solution containing **4a**, **5**, and **6** caused decrease in the rate of the rearrangement of **6** to **4a** ($k_r = 2.4 \times 10^{-4}$ s^{-1}) and concurrent occurrence of the isomerization of **6** to **5** ($k_i = 1.5 \times 10^{-4}$ s^{-1}). Accompanied by significantly higher stability of **6-*d*$_5$** against the rearrangement to **4a-*d*$_5$** in pyridine-*d*$_5$ (vide supra), these results indicate the presence of a dissociative path via the unsaturated intermediate **B** in the rearrangement of **6** to **4a**.

Complex **5** is stable in C_6D_6 at room temperature in contrast with **6**, but heating to 60 °C led to clean conversion of **5** to **4a** (first order in **5**, $k_{obs} = 1.7 \times 10^{-4}$ s^{-1}, $t_{1/2} = 69$ min at 60 °C). Addition of pyridine-*d*$_5$ (∼55 equiv to **5**) did not affect the conversion rate of **5** to **4a**−***d*$_5$**, and the relative intensities of the coordinated-pyridine signals to the Cp* signal for **5** were not decreased throughout the reaction (at least up to 3 half-lives). These observations indicate that the exchange between the coordinated pyridine and free pyridine-*d*$_5$ does not occur in **5**, and that the 1,2-hydrogen migration in **5** might occur concertedly with the dissociation of the pyridine, not passing through the unsaturated intermediate. Thus, the isomeric hydrosilyl(pyridine) complexes **5** and **6** have been found to rearrange thermally to the hydrido(silylene) complex **4a** via 1,2-hydrogen migration, showing quite interesting reactivity differences.

Scheme 3



An intriguing reactivity of the base-stabilized hydrido(silylene) complexes was revealed in the reaction of **4b-*d*$_5$** with a large excess of $MePhSiH_2$ (36 equiv) in pyridine-*d*$_5$ in an evacuated sealed NMR tube. The silylene exchange product **4c-*d*$_5$** was formed in a quantitative yield based on 90% conversion of **4b-*d*$_5$** along with Et_2SiH_2 (71%) after 4 days at room temperature (Scheme 3). Quite interestingly, a similar reaction using **4b-*d*$_5$** with $MePhSiD_2$ (99% D) led to the highly selective formation of **4c-*d*$_5$** and Et_2SiD_2 (>97% D). The relative intensity of the WH signal to the Cp* signal for **4b-*d*$_5$** was 1.0:15 at the beginning of the reaction and the exactly same ratio was observed for that for **4c-*d*$_5$** at 93% conversion after 5 days, indicating no deuterium incorporation into the WH position. The selective formation of Et_2SiD_2 was shown by the observations that SiH signals assignable to Et_2SiHD and Et_2SiH_2 were not detected by ^{1}H NMR and that, in a separate experiment using **4b**, $MePhSiD_2$, and pyridine as a solvent, a single new signal assigned to Et_2SiD_2 was found at 3.73 ppm in addition to excess $MePhSiD_2$ (4.40 ppm) by ^{2}H NMR. No deuterium signal was observed in the hydrido region. A possible explanation for these results is shown in Scheme 3, where the reaction proceeds via a four-center transition state formed by the interaction between the Si−H bond of the silane and the formal polarized double bond of **4b-*d*$_5$** or the base-free silylene complex generated from **4b-*d*$_5$**. Another possibility, oxidative addition/reductive elimination mechanism of the silane initiated by the dissociation of the pyridine and subsequent 1,2-hydrogen migration from the tungsten to the silicon in **4b-*d*$_5$** is ruled out, since the formation of *cis*-Cp*$(CO)_2(D)W{=}SiMePh{\cdot}$py-*d*$_5$ and Et_2SiHD would be expected in this mechanism.[16]

Although the formation of silanes derived from silylene ligands has been observed in several reactions of silylene complexes with hydrosilanes, the reactions are generally complex and silicon-containing complexes have been rarely characterized.[8b,17] To our knowledge, the above reaction is the first example of a silylene exchange reaction for base-free and -stabilized silylene complexes. Further efforts to explore reactivity of the base-stabilized hydrido(silylene) complexes are in progress.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Grant No. 10640536) from Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: Experimental details and spectroscopic data for compounds **3**, **4a**−**c**, **5**, and **6** and crystallographic data for **4a**·CH_3CN and **5** (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA993279W

---

[14] The structurally related silyltungsten complexes *trans*-Cp*$(CO)_2$-$(PMe_3)WSiR_3$ ($SiR_3 = SiH_2Me$, $SiHMe_2$, $SiHPh_2$) have been shown to give the ^{29}Si resonances in the range of 7.4−18.5 ppm ($^1J_{WSi} = 42−53$ Hz),[15b,c] but the data for their *cis* isomers are not available. The ^{29}Si chemical shift (22.4 ppm) for the *trans* isomer **5** is very close to this range, while that (100.0 ppm) for the *cis* isomer **6-*d*$_5$** is far away from it. The reason for the unusual chemical shift for **6-*d*$_5$** is not clear at present, though it might reflect a decrease in an average excitation energy in the paramagnetic term contributing largely to ^{29}Si chemical shifts.

[15] (a) Sharma, S.; Kapoor, R. N.; Cervantes-Lee, F.; Pannell, K. H. *Polyhedron* **1991**, *10*, 1177. (b) Schmitzer, S.; Weis, U.; Käb, H.; Buchner, W.; Malisch, W.; Polzer, T.; Posset, U.; Kiefer, W. *Inorg. Chem.* **1993**, *32*, 303. (c) Malisch, W.; Schmitzer, S.; Lankat, R.; Neumayer, M.; Prechtl, F.; Adam, W. *Chem. Ber.* **1995**, *128*, 1251.

[16] It has been shown that the raction of the hydrido alkylidene complex Cp*$_2$(H)Ta=CH$_2$ with SiH$_4$ affords Cp*$_2$Ta(SiH$_3$)(CH$_3$)H by oxidative addition of the silane to Cp*$_2$TaCH$_3$ equilibrated with the alkylidene complex via 1,2-hydrogen migration: Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

[17] Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D. *Organometallics* **1998**, *17*, 5607.