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Stoichiometric Hydrosilylation of Nitriles with Hydrido(hydrosilylene)tungsten Complexes: Formation of W−Si−N Three-Membered Ring Complexes and Their Unique Thermal Behaviors

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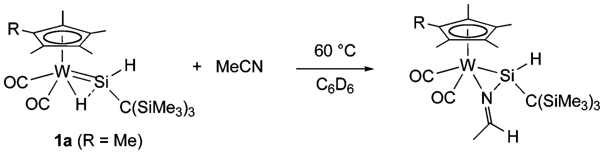
Transition-metal silylene complexes have attracted much attention as hypothetical intermediates in various chemical transformation reactions of organosilicon compounds.[1] Recently, some stoichiometric and catalytic hydrosilylation reactions that really involve silylene complexes have been demonstrated.[2] For example, Tilley et al. reported that cationic base-free silylene iridium complexes underwent hydrosilylation of carbonyl compounds.[2b] They also reported that an in situ generated cationic hydrosilyleneruthenium complex underwent catalytic hydrosilylation of olefin and proposed a new mechanism involving direct addition of a Si−H bond on the silylene ligand to olefins.[2c] However, the number of examples are still limited.

We have recently reported the synthesis and full characterization of neutral base-free silylene complexes, $\mathrm{Cp'(CO)_2(H)W{=}Si(H)[C(SiMe_3)_3]}$ (**1a**, Cp′ = Cp*; **1b**, Cp′ = η^5-$\mathrm{C_5Me_4Et}$), having a Si−H bond and a W−H bond, and an interligand interaction between the hydrido and the silylene ligands.[3] Complex **1a** also reacted with acetone to produce a hydrosilylation product, $\mathrm{Cp^*(CO)_2(H)W{=}Si(O^iPr)[C(SiMe_3)_3]}$ (**2**) as a main product. Here we report stoichiometric hydrosilylation of nitriles, which are usually inactive to hydrosilylation,[4] with **1** to give $\mathrm{Cp'(CO)_2W[\kappa^2(\mathit{N},\mathit{Si})\text{-}Si(H)(N{=}CHR')\{C(SiMe_3)_3\}]}$ (**3**, R′ = Me, **4**, R′ = ^{t}Bu). We also present the thermal conversion of **4** to $\mathrm{Cp'(CO)_2(H)W{=}Si(N{=}CH^tBu)[C(SiMe_3)_3]}$ (**5**), which is structurally closely related to **2**, as well as a possible mechanism for the hydrosilylation of nitrile achieved by the cooperation between the hydrido and silylene ligands of **1**.

Treatment of **1a** with MeCN (6 equiv) in $\mathrm{C_6D_6}$ at 60 °C for 4 h afforded a {κ^2(*N*,*Si*)-ethylideneamino}silyl complex $\mathrm{Cp^*(CO)_2W[\kappa^2(\mathit{N},\mathit{Si})\text{-}Si(H)(N{=}CHMe)\{C(SiMe_3)_3\}]}$ (**3a**) in 69% NMR yield, which was isolated by recrystallization from hexane as yellow crystals in 28% yield (eq 1). Similarly, the η^5-$\mathrm{C_5Me_4Et}$ analogue, **3b**, was isolated in 26% yield. These complexes were fully characterized by the spectral data and elemental analysis,[5,6] and the structure of **3b** was determined by X-ray crystallography.[7]



(1)

1a (R = Me)
1b (R = Et)

3a (R = Me)
3b (R = Et)

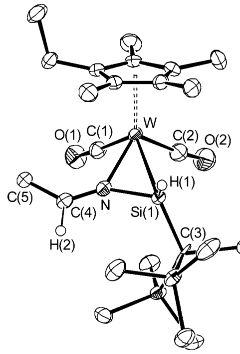
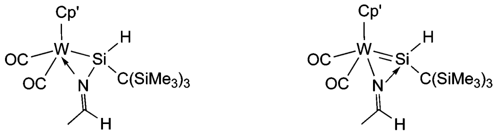


Figure 1. ORTEP drawing of **3b** (50% thermal probability ellipsoids); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): W−Si(1) 2.549(2), W−N 2.184(5), Si(1)−N 1.760(5), N−C(4) 1.286(7), Si(1)−W−N 42.78(13), Si(1)−W−C(2) 89.8(2), W−Si(1)−N 57.5(2), C(1)−W−C(2) 79.4(3).

The ORTEP drawing of **3b** (Figure 1) clearly reveals that **3b** has a W−Si−N three-membered ring structure. The incoming MeCN is hydrosilylated through *cis* addition, and the resulting (ethylideneamino)silyl ligand is coordinated to the W atom. The W atom in **3b** adopts a distorted four-legged piano-stool structure. The W−Si(1) bond length (2.549(2) Å) is significantly longer than that of silylene complex **1b** (2.3703(11) Å)[3] and within those of known silyltungsten complexes (2.47−2.63 Å).[8] The Si(1)−N bond lengths (1.760(5) Å) are within the range for a normal Si−N single bond of aminosilyl complexes (1.70−1.78 Å).[8] Therefore, the contribution of a possible canonical structure **B** shown in Chart 1 seems to be smaller than **A**. In addition, a dinuclear ruthenium complex having a similar μ-(ethylideneamino)silyl ligand has been reported before,[9] but no related mononuclear complex is known.

Chart 1



A **B**

The NMR data[5,6] of **3b** are consistent with the X-ray crystal structure. Thus, the ^{1}H NMR spectrum at 250 K[10] indicates a singlet signal for SiH and a quartet signal for N═C*H*Me at 3.88 and 8.67 ppm, respectively. Because the tungsten center is chiral, four singlets of the methyl groups of $\mathrm{C_5Me_4Et}$ and two singlets of CO ligands are observed in the ^{1}H and ^{13}C NMR spectra, respectively. The ^{29}Si NMR spectrum of **3b** at 250 K exhibits two signals for aminosilyl and silyl ligands at −48.3 ($^1J_{\mathrm{WSi}}$ = 51.8 Hz) and 0.0 ppm, respectively. The high-field shift of the former is attributed to the W−Si−N three-membered ring structure.[11] All NMR data except those of Cp* of **3a** resemble those of **3b**.[5,6]

Complex **1a** also reacted with ^{t}BuCN (6 equiv) in $\mathrm{C_6D_6}$ at 60 °C within 2.5 h to give a mixture of $\mathrm{Cp^*(CO)_2W[\kappa^2(\mathit{N},\mathit{Si})\text{-}Si(H)(N{=}CH^tBu)\{C(SiMe_3)_3\}]}$ (**4a**) and $\mathrm{Cp^*(CO)_2(H)W{=}Si{-}(N{=}CH^tBu)[C(SiMe_3)_3]}$ (**5a**) in 81 and 11% NMR yields, respectively (eq 2). The NMR data[12] of **4a** and **5a** indicate that **4a** is an

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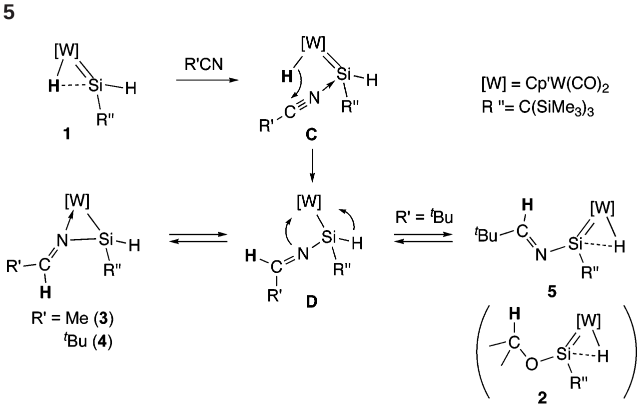
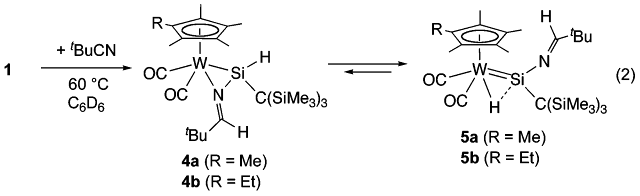
Scheme 1. A Possible Mechanism for the Formation of **3**, **4**, and **5**



(alkylideneamino)silyl complex analogous to **3**, while **5a** is a hydrido(silylene) complex analogous to **2**. Thus, the ^{29}Si signal of the aminosilyl ligand of **4a** appears at -50.5 ppm, which is close to that of **3a** (-47.8 ppm), indicating the three-membered ring structure. The ^{1}H signals for SiH and N$=$CH^tBu of **4a** are observed at 3.82 and 9.00 ppm, respectively. Complex **5a** shows the ^{29}Si signal for the silylene ligand at 188.3 ppm, which is comparable with that of **2** (229.2 ppm). The large $^1J_{\mathrm{WSi}}$ value (130.8 Hz) also agrees with the W$-$Si double bond character.[13] The hydrido signal of **5a** appears at -6.07 ppm with two satellites ($^1J_{\mathrm{WH}} = 55.4$ Hz, $^2J_{\mathrm{SiH}} = 32.4$ Hz). The $^2J_{\mathrm{SiH}}$ value implies the existence of a weak interaction between the hydrido and silylene ligands as observed for **1**, **2**,[3] and the related complexes.[14] The η^5-C_5Me_4Et analogues **4b** and **5b** were also obtained in a 6:1 ratio by heating **1b** and ^{t}BuCN at 70 °C after 4.5 h (eq 2).[6]



Further heating of the above reaction mixture containing **4** and **5** at 70 °C caused the thermal rearrangement of **4** to **5** (eq 2). The molar ratio of **4a** to **5a** decreased, and the equilibrium between **4a** and **5a** was attained with $K = [\mathbf{5a}]/[\mathbf{4a}] = 3.0$ after 30 h. Similarly, **4b** and **5b** also reached equilibrium with $K = [\mathbf{5b}]/[\mathbf{4b}] = 3.5$ in C_6D_6 at 70 °C after 80 h. These thermal rearrangement and equilibrium constants reveal that **4** is a kinetically controlled product, while **5** is a thermodynamically controlled product. Importantly, the observation of the initial formation of aminosilyl complex **4**, which has no W$-$H bond, suggests that the hydrido ligand on the tungsten migrates to the nitrile carbon.

A possible mechanism for the formation of **3**, **4**, and **5** is described in Scheme 1. First, a nitrile is coordinated to the electrophilic Si atom of the silylene ligand of **1** to form the base-stabilized silylene intermediate **C**. Subsequently, H-migration from W to the nitrile carbon in **C** occurs to generate 16e species **D**. To saturate the W center in **D**, two routes, namely, (1) coordination of the lone pair on the N atom of the resulting aminosilyl group and (2) 1,2-H migration from Si to W, are possible, but the former is kinetically preferred to give complexes **3** and **4** primarily. In the case of ^{t}BuCN, because of the steric repulsion between the bulky ^{t}Bu group and the Cp* ligand in **4**, **4** is thermodynamically destabilized and converts to more stable **5** via **D** on which 1,2-H migration from Si to W proceeds. These results imply that the previously reported hydrosilylation product **2** is also formed via a mechanism analogous to the formation of **5** (Scheme 1).

As there are examples of acetonitrile-coordinated silylene complexes,[15] it is likely that a nitrile-coordinated silylene intermediate **C** forms at the initial stage of the reaction of **1** with nitrile. Although we cannot observe the acetonitrile adduct of **1**, addition of 4-(dimethylamino)pyridine (DMAP), a much stronger Lewis base, to **1a** afforded a DMAP-coordinated silylene complex, Cp*(CO)$_2$(H)W$=$Si(H)[C(SiMe$_3$)$_3$]·(DMAP) (**6**), which was fully characterized by spectroscopic and structural analyses.[6] The formation of **6** strongly supports the generation of the intermediate **C** in Scheme 1.

Further research on the reactivity of **1** toward small molecules is in progress.

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Supporting Information Available: Experimental procedures and characterization data (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 24. (b) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Chapter 35. (c) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (d) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493.

(2) (a) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065. (b) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4648. (c) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640.

(3) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218.

(4) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Chapter 29.

(5) **3a**: ^{1}H NMR (300 MHz, toluene-d_8, 250 K, δ): 0.44 (s, 27H, SiMe), 1.70 (d, $^3J_{\mathrm{HH}} = 4.9$ Hz, 3H, N$=$CH*Me*), 1.72 (s, 15H, C_5Me_5), 3.85 (s, 1H, SiH, $^1J_{\mathrm{SiH}} = 189.9$ Hz), 8.68 (q, $^3J_{\mathrm{HH}} = 4.9$ Hz, 1H, N$=$C*H*Me). **3b**: ^{1}H NMR (300 MHz, toluene-d_8, 250 K, δ): 0.43 (s, 27H, SiMe), 0.85 (t, $^3J_{\mathrm{HH}} = 7.5$ Hz, 3H, $C_5Me_4CH_2CH_3$), 1.63 (s, 3H, C_5Me_4Et), 1.66 (s, 3H, C_5Me_4Et), 1.70 (d, $^3J_{\mathrm{HH}} = 5.0$ Hz, 3H, N$=$CH*Me*), 1.79 (s, 3H, C_5Me_4-Et), 1.82 (s, 3H, C_5Me_4Et), 2.23 (q, $^3J_{\mathrm{HH}} = 7.5$ Hz 2H, $C_5Me_4CH_2CH_3$), 3.88 (s, 1H, SiH, $^1J_{\mathrm{SiH}} = 190.2$ Hz), 8.67 (q, $^3J_{\mathrm{HH}} = 5.0$ Hz, 1H, N$=$C*H*Me).

(6) See the Supporting Information for the details.

(7) Crystal data for **3b** (150 K): $C_{25}H_{49}NO_2Si_4W$; FW 691.86; triclinic; space group $P\bar{1}$ (No. 2); $a = 9.0355(6)$ Å, $b = 12.6226(12)$ Å, $c = 15.0883(11)$ Å, $\alpha = 66.075(3)°$, $\beta = 88.306(4)°$, $\gamma = 85.204(3)°$, $V = 1567.5(2)$ Å^3; density (calcd) 1.466 Mg/m^3, $Z = 2$. Final R indices $R = 0.0445$, Rw $= 0.1125$ for all data, 6988 unique reflections.[6]

(8) Based on a search of the Cambridge Structural Database, CSD version 5.26 (November 2004).

(9) Hashimoto, H.; Aratani, I.; Kabuto, C.; Kira, M. *Organometallics* **2003**, *22*, 2199.

(10) At 296 K, the ^{1}H signals of SiH and N$=$C*H*Me of both **3a** and **3b** became broad without any changes of the chemical shifts. The ^{13}C signals for carbonyl ligands of **3** also became broad at 296 K. The origins of these behaviors are unclear at present.

(11) (a) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 11870. (b) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 3087.

(12) **4a**: ^{1}H NMR (300 MHz, toluene-d_8, 250 K, δ): 0.42 (s, 27H, SiMe), 1.10 (s, 9H, N$=$CH^{t}Bu), 1.75 (s, 15H, C_5Me_5), 3.82 (s, 1H, SiH, $^1J_{\mathrm{SiH}} = 189.9$ Hz), 9.00 (s, 1H, N$=$CH^tBu). ^{29}Si{^{1}H} NMR (59.6 MHz, toluene-d_8, 250 K, δ): -50.5 (WSi, $^1J_{\mathrm{WSi}} = 52.7$ Hz), -0.3 (CSiMe). **5a**: ^{1}H NMR (300 MHz, C_6D_6, δ): -6.07 (s, 1H, WH, $^1J_{\mathrm{WH}} = 55.4$ Hz, $^2J_{\mathrm{SiH}} = 32.4$ Hz), 0.44 (s, 27H, SiMe), 1.09 (s, 3H, N$=$CH^{t}Bu), 1.97 (s, 15H, C_5Me_5), 7.75 (s, 1H, N$=$CH^tBu). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, δ): -1.1 (CSiMe), 188.3 (WSi, $^1J_{\mathrm{WSi}} = 130.8$ Hz).[6]

(13) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326.

(14) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428.

(15) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801.

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