Organometallics **2006,** *25,* 1554−1556

Synthesis and Reactivity of a Donor-Free (Silyl)(silylene)molybdenum Complex: Novel Insertion Reaction of an Isocyanide into a Si−C Bond

Masakazu Hirotsu,[†] Takehiko Nunokawa,[‡] and Keiji Ueno*,[‡]

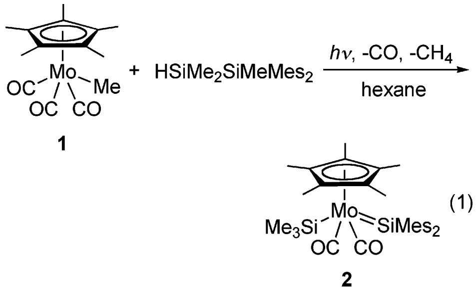
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu 376-8515, Japan, and
Department of Material Science, Graduate School of Science, Osaka City University,
Osaka 558-8585, Japan

Received January 9, 2006

*Summary: Photolysis of Cp*Mo(CO)$_3$Me (**1**; Cp* = η-C_5Me_5) in the presence of the hydrodisilane $HSiMe_2SiMeMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) resulted in the formation of the donor-free (silyl)(silylene)molybdenum complex Cp*Mo(CO)$_2$(=$SiMes_2$)($SiMe_3$) (**2**). The reaction of complex **2** with $^tBuCH_2CMe_2NC$ at 60 °C caused insertion of the isocyanide into the Si−C bond of the silylene ligand to give an intramolecular donor-stabilized silyl silylene complex, Cp*Mo(CO)$_2$(=Si(Mes)C(Mes)NCMe$_2$-CH$_2$^{t}Bu)($SiMe_3$) (**3**).*

The chemistry of silylene−transition-metal complexes is a current topical area of organometallic chemistry.[1] The silyl silylene complexes $L_nM(=SiR_2)(SiR_3)$ have attracted much interest, since many transition-metal-mediated reactions of organosilicon compounds are thought to proceed via such intermediates.[2−4] These unsaturated intermediates are very reactive toward nucleophilic molecules and have been isolated as donor-stabilized silyl silylene complexes.[2,5] Although donor-free silyl silylene complexes ought to be more informative and contribute to an understanding of the reaction mechanism, only a few donor-free silyl silylene complexes have been isolated.[6] Recently, we have synthesized donor-free (silyl)(silylene)-tungsten and -iron complexes by introducing bulky aryl substituents on silicon.[7] The isolation of silyl silylene complexes has allowed us to investigate the reactivity in detail; however, little has been discovered yet.[8] In this paper, we report the synthesis of the first donor-free (silyl)(silylene)molybdenum complex, **2**, and its novel reactivity with isocyanide. The latter reaction afforded an *intramolecular* base-stabilized silyl silylene complex via formal isocyanide insertion into the Si−C bond of the silylene ligand.

Photolysis of Cp*Mo(CO)$_3$Me (**1**) in the presence of $HSiMe_2SiMeMes_2$ in hexane resulted in the formation of the donor-free (silyl)(silylene)molybdenum complex Cp*Mo(CO)$_2$(=$SiMes_2$)($SiMe_3$) (**2**) (eq 1).[9] Complex **2** was isolated as orange crystals in 54% yield. The structure of **2** was confirmed by a crystal structure analysis (Figure 1).[10] The overall geometry of **2** is similar to that of the tungsten complex Cp*W(CO)$_2$(=$SiMes_2$)($SiMe_3$) reported previously.[7a] The molybdenum−silylene bond (Mo−Si(2) = 2.3872(7) Å) in **2** is remarkably shorter than the molybdenum−silyl bond in the same molecule (Mo−Si(1) = 2.6391(7) Å) and the usual Mo−Si single-bond



(1)

---

* To whom correspondence should be addressed. Tel and FAX: +81-277-30-1260. E-mail: ueno@chem.gunma-u.ac.jp.

[†] Osaka City University.

[‡] Gunma University.

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 2, Chapter 24. (b) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271. (c) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 494.

(2) Ogino, H. *Chem. Rec.* **2002**, *2*, 291.

(3) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

(4) (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (b) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (c) Hashimoto, H.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1995**, *499*, 205. (d) Pestana, D. C.; Koloski, T. S.; Berry, D. H.; *Organometallics* **1994**, *13*, 4173. (e) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (f) Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403. (g) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043.

(5) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835. (d) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545. (e) Ueno, K.; Ito, S.; Endo, K.; Tobita, H.; Inomata, S.; Ogino, H. *Organometallics* **1994**, *13*, 3309. (f) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459. (g) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1861. (h) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1997**, 437. (i) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315. (j) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023. (k) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138. (l) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2844. (m) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2850. (n) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1999**, *18*, 2694.

(6) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599.

(7) (a) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326. (b) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221.

(8) During the review process, reactions of a (silyl)(silylene)iron complex with nitriles were reported: Hashimoto, H.; Matsuda, A.; Tobita, H. *Organometallics* **2006**, *25*, 472.

(9) Data for **2**: ^1H NMR (300 MHz, C_6D_6) δ 0.73 (s, 9H, $SiMe_3$), 1.71 (s, 15H, Cp*), 2.07 (s, 6H, *p*-Me), 2.61 (s, 12H, *o*-Me), 6.69 (s, 4H, *m*-H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.4 ($SiMe_3$), 11.2 ($C_5\mathit{Me}_5$), 21.1 (*p*-Me), 24.3 (*o*-Me), 103.6 (C_5Me_5), 129.1, 139.6, 140.5, 144.6 ($\mathit{C}_6H_2Me_3$), 230.6 (CO); ^{29}Si NMR (59.6 MHz, C_6D_6, INEPT) δ 35.0 ($SiMe_3$), 414.1 ($SiMes_2$); IR (KBr) ν_{CO} 1893, 1828 cm^{-1}. Anal. Calcd for $C_{33}H_{46}MoO_2Si_2$; C, 63.23; H, 7.40. Found: C, 62.77; H, 7.52.

(10) Crystallographic data for **2**: formula $C_{33}H_{46}MoO_2Si_2$, fw = 626.82, monoclinic, space group *Cc*, $a = 22.0107(18)$ Å, $b = 12.6962(10)$ Å, $c = 15.0501(13)$ Å, $\beta = 128.556(2)°$, $V = 3288.9(5)$ Å^3, $Z = 4$, $T = 113(2)$ K, $\rho_{calcd} = 1.266$ g cm^{-3}, $\mu = 0.498$ mm^{-1}, $F(000) = 1320$, θ range 1.99−27.50°, 357 variables refined with 5781 independent reflections to final *R* indices ($I > 2\sigma(I)$) of $R1 = 0.0306$ and $wR2 = 0.0788$, GOF = 1.077.

10.1021/om060022f CCC: $33.50

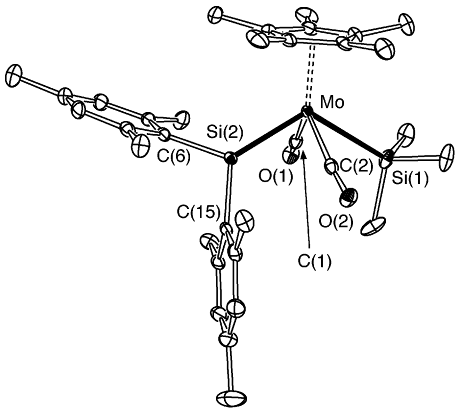
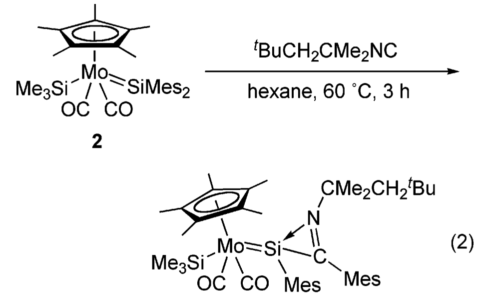


Figure 1. ORTEP drawing of **2** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo−Si(1) = 2.6391(7), Mo−Si(2) = 2.3872(7), Mo−C(1) = 1.968(3), Mo−C(2) = 1.954(3); Si(1)−Mo−Si(2) = 118.67(3), C(1)−Mo−C(2) = 106.55(11), Mo−Si(2)−C(6) = 127.33(8), Mo−Si(2)−C(15) = 125.19(8), C(6)−Si(2)−C(15) = 107.43(11).

lengths (Mo−Si = 2.513−2.670 Å).[11] The Mo−Si(2) bond distance is even shorter than those of known (silylene)-molybdenum complexes (2.4125(13)−2.5008(9) Å), except for the hydrido(silylene)molybdenum complexes Cp*Mo(H)(dmpe)(=SiMesCl) (2.288(2) Å) and Cp*Mo(H)(dmpe)(=SiR$_2$) (2.315(2)−2.343(10) Å).[5n,12] The geometry around the silicon atom of the silylene ligand is planar (sum of the three bond angles around Si(2): 359.95(14)°). These results clearly show the double-bond character of the molybdenum−silylene bonding in **2**. The ^{29}Si NMR spectrum of **2** showed two signals at 35.0 and 414.1 ppm, which can be assigned to the silyl and silylene ligands, respectively. The silylene resonance for **2** appeared at slightly lower magnetic field than that of the tungsten complex Cp*W(CO)$_2$(=SiMes$_2$)(SiMe$_3$) (380.9 ppm).[7a] The remarkable low-field shift of the silylene signal is consistent with the fact that complex **2** contains a three-coordinate, sp^2-hybridized silicon atom.

The (silyl)(silylene)molybdenum complex **2** reacted with ^{t}BuCH$_2$CMe$_2$NC in hexane at 60 °C to give the product **3**, which was isolated as yellow crystals in 39% yield (eq 2).[13] Elemental analysis data indicated the formation of a 1:1 adduct of **2** and the isocyanide. The IR spectrum of **3** showed two CO stretching bands in the terminal CO region (1856 and 1777 cm^{-1}). The ^{29}Si NMR spectrum of **3** showed two signals at 34.8 and 58.6 ppm, which are assignable to the silyl and silylene ligands, respectively. The significant high-field shift of the silylene signal compared to the signal for the donor-free complex **2** as well as the red shift of CO stretching bands in the IR spectrum implies the formation of a donor-stabilized silyl silylene complex: e.g., Cp*Mo(CO)$_2$(=SiMes$_2$·CNCMe$_2$CH$_2$^{t}Bu)(SiMe$_3$) (**A**). However, ^{1}H and ^{13}C NMR studies revealed that two mesityl groups as well as two carbonyl ligands are inequivalent. This implies that complex **3** is not a simple adduct such as **A**.



2

3

(2)

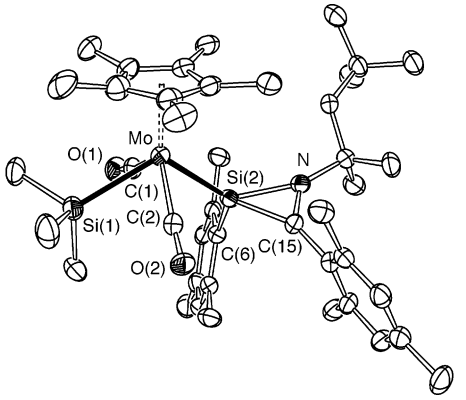


Figure 2. ORTEP drawing of **3** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo−Si(1) = 2.6031(14), Mo−Si(2) = 2.4439(14), Mo−C(1) = 1.964(5), Mo−C(2) = 1.960(5), Si(2)−C(6) = 1.904(5), Si(2)−C(15) = 1.900(5), Si(2)−N = 1.939(4), N−C(15) = 1.292(6); C(1)−Mo−C(2) = 109.6(2), Si(1)−Mo−Si(2) = 115.66(5), Mo−Si(2)−C(6) = 122.61(14), Mo−Si(2)−C(15) = 130.55(15), C(6)−Si(2)−C(15) = 102.8(2), C(15)−Si(2)−N = 39.33(17).

To elucidate the structure of complex **3**, a crystal structure analysis was carried out.[14] As shown in Figure 2, complex **3** is a base-stabilized silyl silylene complex with an iminoacyl substituent on the silylene ligand. The iminoacyl group is coordinated to the silylene silicon atom through C and N to form a Si−C−N three-membered ring with an acute C−Si−N angle (39.33(17)°). The molybdenum−silylene bond (Mo−Si(2) = 2.4439(14) Å) is longer than that of complex **2** but is in the range of reported Mo−Si bond lengths of silylene complexes (2.4125(13)−2.5008(9) Å),[5n,12] and is significantly shorter than the molybdenum−silyl bond (Mo−Si(1) = 2.6031(14) Å) in **3**. The Si−N bond length (1.939(4) Å) is comparable to those of nitrogen donor coordinated silylene complexes (1.908(2)−2.007(9) Å) and longer than the usual Si−N single-bond lengths (1.70−1.76 Å).[5e,n,15,16] The silylene silicon is slightly pyramidalized (the sum of the three valence bonds, except for that to the nitrogen atom, is 356.0(2)°), indicating weak coordination of the iminoacyl nitrogen to the silylene silicon atom.

---

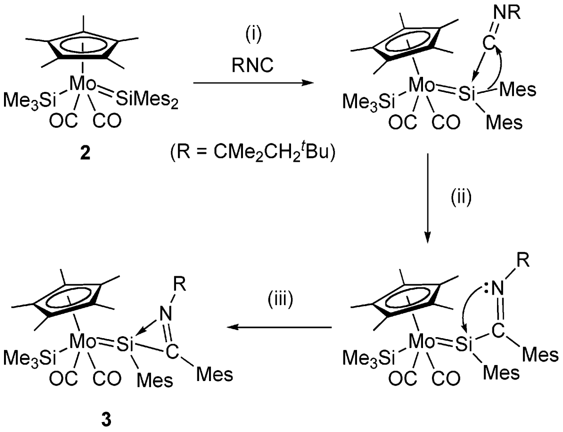
(11) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(12) (a) Petri, S. H. A.; Eikenberg, D.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **1999**, *18*, 2615. (b) Clendenning, S. B.; Gehrhus, B.; Hitchcock, P. B.; Moser, D. F.; Nixon, J. F.; West R. *J. Chem. Soc., Dalton Trans.* **2002**, 484. (c) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357. (d) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428.

(13) Data for **3**: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.79 (s, 9H, SiMe$_3$), 0.91 (s, 9H, CMe$_3$), 1.51 (s, 6H, CMe$_2$), 1.79 (s, 15H, Cp*), 1.83 (s, 2H, CH$_2$), 1.97 (br, 6H, *o*-Me), 2.01 (s, 3H, *p*-Me), 2.10 (s, 3H, *p*-Me), 2.70 (br, 6H, *o*-Me), 6.62 (s, 2H, *m*-H), 6.70 (br, 2H, *m*-H); ^{13}C NMR (125.7 MHz, C$_6$D$_6$) δ 6.9 (SiMe$_3$), 11.3 (C$_5$*Me*$_5$), 20.8 (*p*-Me), 21.2 (*p*-Me), 22.2 (*o*-Me), 24.5 (*o*-Me), 27.5 (CH$_2$), 31.6 (C*Me*$_2$), 31.8 (C*Me*$_3$), 52.3 (*C*Me$_2$), 69.3 (*C*Me$_3$), 101.5 (*C*$_5$Me$_5$), 128.2, 128.3, 128.8, 131.3, 134.2, 137.6, 138.3, 140.6 (*C*$_6$H$_2$Me$_3$), 143.4 (N=C), 224.0 (CO), 237.7 (CO); ^{29}Si NMR (99.3 MHz, C$_6$D$_6$, INEPT) δ 34.8 (SiMe$_3$), 57.5 (Si(Mes)C(Mes)NCMe$_2$CH$_2$^{t}Bu); IR (KBr) ν_{CO} 1856, 1777, ν_{CN} = 1609 cm^{-1}. Anal. Calcd for C$_{42}$H$_{63}$MoNO$_2$Si$_2$: C, 65.85; H, 8.29; N, 1.57. Found: C, 66.02; H, 8.56; N, 2.00.

(14) Crystallographic data for **3**: formula C$_{42}$H$_{63}$MoNO$_2$Si$_2$, fw = 766.05, monoclinic, space group *P*2/*n*, a = 13.5552(8) Å, b = 12.8074(7) Å, c = 24.5519(17) Å, β = 104.986(2)°, V = 4117.4(4) Å^3, Z = 4, T = 133(2) K, ρ_{calcd} = 1.236 g cm^{-3}, μ = 0.411 mm^{-1}, F(000) = 1632, θ range 1.72−27.50°, 452 variables refined with 9202 independent reflections to final R indices ($I > 2\sigma(I)$) of $R1$ = 0.0754 and $wR2$ = 0.1858, GOF = 1.296.

Scheme 1



Formation of complex **3** by the reaction of silylene complex **2** with isocyanide can be rationalized by the mechanism depicted in Scheme 1: (i) coordination of isocyanide to a silylene ligand, (ii) 1,2-migration of a Mes group to the isocyanide carbon to give an iminoacyl substituent, and (iii) coordination of the imino nitrogen to the silylene ligand to form complex **3**. We have recently reported that the reaction of a donor-free (silyl)-(silylene)iron complex with ^{t}BuNC caused 1,2-migration of the silyl group to the silylene ligand to give a disilanyl complex.[7b] The remarkable difference in reactivity between complex **2** and the iron complex is attributable to the difference in the geometries of the silyl and silylene ligands; that is, a mutual trans geometry for the molybdenum complex, compared to a mutual cis geometry for the iron complex, prevents 1,2-migration of the silyl ligand.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 16033212) and for Scientific Research (Nos. 17655022 and 15350030) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Text and tables giving complete experimental details, including the synthesis and characterization data, for all new compounds and crystal structure data; X-ray crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060022F

---

(15) (a) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geibt, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (b) Probst, R.; Leis, C.; Gamper, S.; Herdtweck, E.; Zybill, C.; Auner, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1132. (c) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518. (d) Kobayashi, H.; Ueno, K.; Ogino, H. *Organometallics* **1995**, *14*, 5490. (e) Braunstein, P.; Veith, M.; Blin, J.; Huch, V. *Organometallics* **2001**, *20*, 627. (f) Choo, T. N.; Kwok, W.-H.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2002**, *645*, 235. (g) Okazaki, M.; Suzuki, E.; Miyajima, N.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4633.

(16) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 3.