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Base-Free Molybdenum and Tungsten Bicyclic Silylene Complexes Stabilized by a Homoaromatic Contribution

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Transition metal silylene complexes have been postulated as key intermediates in a number of the metal-catalyzed reactions of organosilicon compounds (for example, dehydrogenative coupling of hydrosilanes).[1] The first transition metal silylene complexes, in which Lewis acidic silylene ligands were stabilized by coordination to Lewis bases, $(OC)_4Fe{=}Si(O^tBu)_2[OP(NMe_2)_3]$ and $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2Ru{=}SiPh_2(NCMe)]^+\cdot BPh_4^-$, were reported in 1987 by the groups of Tilley and Zybill.[2] As the other breakthrough, the syntheses of the first Lewis base-free silylene transition metal complexes,[1] including those of the *N*-heterocyclic silylenes,[3] are also worthy of mention.

Recently, we reported the isolation of the first derivative of tetrasilacyclobutadiene dianion $[({}^tBu_2MeSi)_4Si_4]^{2-}\cdot 2K^+$ $\mathbf{1^{2-}\cdot 2K^+}$,[4] which was successfully utilized as a new ligand for transition metal complexes[5a−c] as well as polycyclic compounds.[5d] Moreover, we have also prepared disiladigermabicyclo[1.1.0]butane-2,4-diide as its alkaline-earth metal salts $[({}^tBu_2MeSi)_4Si_2Ge_2]^{2-}\cdot M^{2+}$ (M = Mg, Ca, Sr),[6] which could also serve as a promising ligand for transition metal complexes. In this contribution, we report the synthesis of the all-silicon analogue $[({}^tBu_2MeSi)_4Si_4]^{2-}\cdot Ca^{2+}$ and its unusual reaction with group 6 transition metals, forming unprecedented bicyclic silylene Mo and W complexes stabilized by the homoaromatic contribution.

The key dianionic precursor, the calcium salt of 1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)tetrasilabicyclo[1.1.0]butane-2,4-diide $[({}^tBu_2MeSi)_4Si_4]^{2-}\cdot Ca^{2+}$ $\mathbf{2^{2-}\cdot Ca^{2+}}$, was readily available in 92% yield by the transmetalation of $\mathbf{1^{2-}\cdot 2K^+}$ with CaI_2 in THF. The structure of $\mathbf{2^{2-}\cdot Ca^{2+}}$ was established by its NMR spectra (diagnostic shielding of the bridging and especially bridgehead silicons, observed at −129.5 and −224.9 ppm, respectively).[7] The reaction of $\mathbf{2^{2-}\cdot Ca^{2+}}$ with Cp_2MCl_2 (M = Mo, W; Cp = η^5-C_5H_5) in THF performed at room temperature resulted in the clean formation of the bicyclic silylene complexes, bis(η^5-cyclopentadienyl){η^1-[1,3,4,4-tetrakis(di-*tert*-butylmethylsilyl)tetrasilabicyclo[1.1.0]butan-2-ylidene]}molybdenum and -tungsten $Cp_2M(\eta^1\text{-}Si_4R_4)$ (**3a**, M = Mo; **3b**, M = W; R = $SiMe{}^tBu_2$), isolated as highly air- and moisture-sensitive red crystals in 73 and 81% yields (Scheme 1).[7] Although the mechanism for the formation of silylene complex **3** by the reaction of $\mathbf{2^{2-}\cdot Ca^{2+}}$ with Cp_2MCl_2 is not known, we can suggest that it may involve several consective steps: transmetalation at the anionic silicon followed by the ring inversion and anionic rearrangement, ending with the elimination of $CaCl_2$ finally to form **3**.

Very characteristic low-field resonances of the doubly bonded Si were observed at 323.6 ppm for **3a** and 260.9 ppm for **3b**, being within the range of values previously reported for silylene−Mo (139.3−414.1 ppm)[8a−e] and silylene−W (97.8−380.9 ppm)[8f−i] complexes, indicative of the presence of base-free silylene ligands. The large value of the ${}^1J_{Si-W}$ coupling constant of 278.2 Hz clearly testifies to the presence of an Si=W bond. Other skeletal silicons were observed as expected at high field for both bridging Si (−139.9 ppm for **3a** and −147.7 ppm for **3b**) and bridgehead Si (−101.2 ppm for **3a** and −110.2 ppm for **3b**).

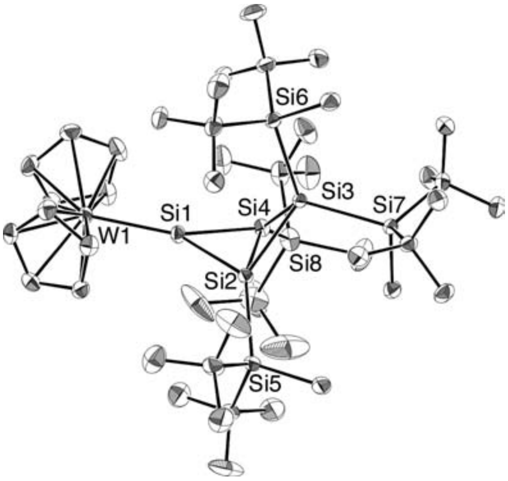
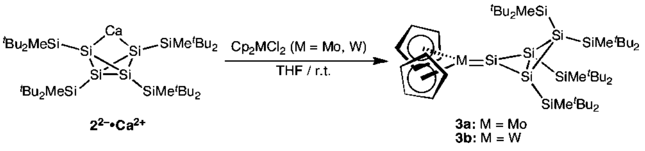


Figure 1. ORTEP drawing of $\mathbf{3b}\cdot C_6H_{14}$ (30% probability level). Hydrogen atoms and crystallization solvent (hexane) molecule are omitted for clarity. Selected bond lengths (Å): Si1−W1 = 2.4202(14), Si1−Si2 = 2.3290(18), Si1−Si4 = 2.3231(19), Si2−Si4 = 2.4170(16), Si2−Si3 = 2.3769(16), Si3−Si4 = 2.3708(17). Selected bond angles (deg): W1−Si1−Si2 = 148.21(6), W1−Si1−Si4 = 149.13(7), Si2−Si1−Si4 = 62.60(5), Si2−Si3−Si4 = 61.21(5), Si1−Si2−Si4 = 58.58(5), Si1−Si4−Si2 = 58.82(5), Si3−Si2−Si4 = 59.27(5), Si2−Si4−Si3 = 59.52(5).

Scheme 1



X-ray diffraction analysis of **3b** revealed that the coordination sites of tungsten are occupied by the two Cp ligands and η^1-silylene ligand, in which the low-coordinate silicon center is incorporated into the bicyclic R_4Si_4 system (Figure 1).[9] It should be emphasized that such transition metal−bicyclic silylene complexes are unprecedented. The geometry about the silylene center is planar with the sum of the bond angles around the Si1 atom being 359.94° (W1−Si1−Si2, 148.21(6); W1−Si1−Si4, 149.13(7); Si2−Si1−Si4, 62.60(5)°). The Si1=W1 double bond length of 2.4202(14) Å of **3b** is one of the longest among those reported for base-free silylene−tungsten complexes.[8f,h,i] On the other hand, the bonds between silylene silicon Si1 and bridgehead silicons Si2 and Si4 of 2.3290(18) and 2.3231(19) Å are somewhat shorter than for typical Si−Si single bonds (2.34 Å)[10] and ca. 5% shorter than Si−Si bonds in the bis(silyl)silylene−hafnium complex (η^5-

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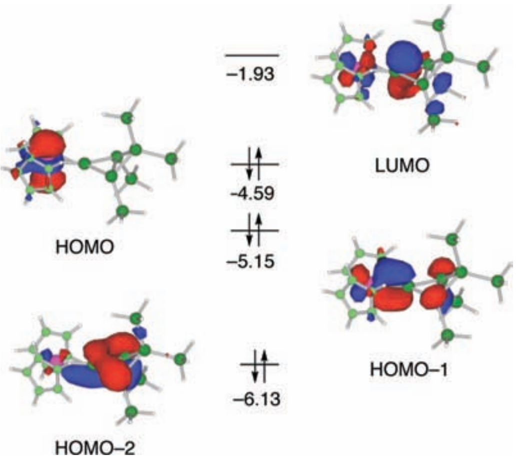
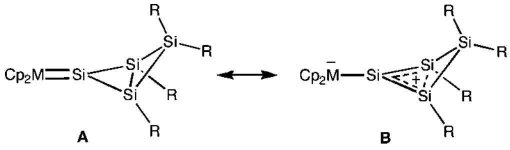


Figure 2. Frontier molecular orbitals of model silylene complex **3b′** (MO energy levels are given in eV).

Chart 1



M = Mo, W; R = SiMe^{t}Bu$_2$

C$_5$H$_4$Et)$_2$(Me$_3$P)Hf═Si(SiMe^{t}Bu$_2$)$_2$ (2.4512(13)−2.4643(13) Å).[11] Of particular importance is the extreme elongation of the Si2−Si4 bridge of **3b**, which is stretched to 2.4170(16) Å, being even longer than that of the long-bond isomer of the 1,3-disilabicyclo[1.1.0]butane derivative (2.412(1) Å).[12] However, in marked contrast, the interplanar angle Si1Si2Si4/Si3Si2Si4 of **3b** is rather acute (116.5(6)°) compared with the very wide interplanar angle of 1,3-disilabicyclo[1.1.0]butane (141.1(1)°).[12] Clearly, such mutually opposed structural features of **3b** (*very long* bridging Si−Si bond and *acute* interplanar angle) do not meet the requirements of conventional models of either short-bond or long-bond isomers of bicyclo[1.1.0]butane. Instead, these unusual geometrical characteristics of **3b** could be explained in the framework of a contribution of another resonance extreme, represented by the zwitterionic structure **B** featuring the homoaromatic cyclotetrasilenylium ion (Chart 1).[13] The contribution of resonance form **B** results in the stretching of the Si1−W1 bond and Si2−Si4 bridge and shortening of the Si1−Si2 and Si1−Si4 skeletal bonds.

DFT computations at the B3PW91 level (basis sets: 6-31G(d) for H, C, Si, and LANL2DZ for W) on the model bicyclic silylene−tungsten complex (η^5-Cp)$_2$W{η^1-Si$_4$(SiH$_3$)$_4$} **3b′** and model acyclic bis(silyl)silylene−tungsten complex (η^5-Cp)$_2$W{η^1-Si[Si(SiH$_3$)$_3$]$_2$} **4** well support the above-discussed conclusion on the homoaromatic contribution of **B** to the overall structure of silylene−tungsten complex **3b**. Thus, the bond order between the W and Si atoms in **3b′** is lower (1.23) than that in **4** (1.29), pointing to a smaller degree of double−bond character in the former. Likewise, the bond order of the silylene center−bridgehead silicons in **3b′** is slightly higher (1.00) than that of the silylene center−silyl substituents in **4** (0.97). Accordingly, NPA analysis revealed less positive W and more positive Si‘s (one silylene center and two substituent silicons) in **3b′** compared with those in **4**: +0.06 (W) and −0.02 (for a total of three Si atoms) versus +0.10 (W) and −0.41 (for a total of three Si atoms). The homoaromatic contribution can also be seen in the frontier orbitals of the **3b′** model (Figure 2). Thus, apart from the W═Si d(π)−p(π) interaction, bonding and antibonding interactions between the π(W═Si) and σ(Si−Si bridge) orbitals can be noticed in HOMO−2 and HOMO−1, respectively, whereas LUMO is represented by the π* of the W═Si bond. Homoaromaticity of the Si$_3$ ring of **3b′** was also manifested in the negative values of its nucleus-independent chemical shift (NICS):[14] NICS(1) = −11.9 and NICS(−1) = −13.1.[15]

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Supporting Information Available: The experimental procedures and spectral data for **2^{2-}·Ca^{2+}** and **3a**,**b**, calculated atomic coordinates of **3b′** and **4**, tables of crystallographic data including atomic positional and thermal parameters for **3b**·C$_6$H$_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Latest reviews: (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (b) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

(2) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. L. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 699.

(3) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165.

(4) Lee, V. Ya.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758.

(5) (a) Takanashi, K.; Lee, V. Ya.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 5768. (b) Takanashi, K.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3269. (c) Takanashi, K.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2007**, 5741. (d) Takanashi, K.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2007**, *36*, 1158.

(6) Lee, V. Ya.; Takanashi, K.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6703.

(7) For the experimental procedures and the spectral data of **2^{2-}·Ca^{2+}**, **3a**, and **3b**, see the Supporting Information.

(8) Base-free silylene-molybdenum complexes, see: (a) Petri, S. H. A.; Eikenberg, D.; Newmann, 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. (e) Hirotsu, M.; Nunokawa, T.; Ueno, K. *Organometallics* **2006**, *25*, 1554. Base-free silylene tungsten complexes, see: (f) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702. (g) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. *J. Organomet. Chem.* **2001**, *636*, 17. (h) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326. (i) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 4375.

(9) Crystal data for **3b**·C$_6$H$_{14}$ at 150 K: MF = C$_{52}$H$_{108}$Si$_8$W, MW = 1141.95, monoclinic, $P2_1/c$, a = 11.7460(5), b = 13.3610(3), c = 41.3200(13) Å, β = 106.100(2)°, V = 6230.4(4) Å^3, Z = 4, D_{calcd} = 1.217 g·cm^{-3}. R = 0.0552 ($I_o > 2\sigma(I_o)$), R_w = 0.1425 (all data), GOF = 1.038.

(10) Kaftory, M.; Kapon, M.; Botoshansky, M. in *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, Chapter 5.

(11) Nakata, N.; Fujita, T.; Sekiguchi, A. *J. Am. Chem. Soc.* **2006**, *128*, 16024.

(12) Iwamoto, T.; Yin, D.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 12730.

(13) A related homoaromatic cyclotetrasilenylium derivative was recently isolated, see: Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250.

(14) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. van E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(15) However, given the characteristic high-field resonances of the bridgehead silicons in **3a**,**b** and unimportant alternation of bond orders and NPA charges in **3b′** vs **4**, it is likely that the extent of the homoaromatic contribution **B** is not predominant.

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