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

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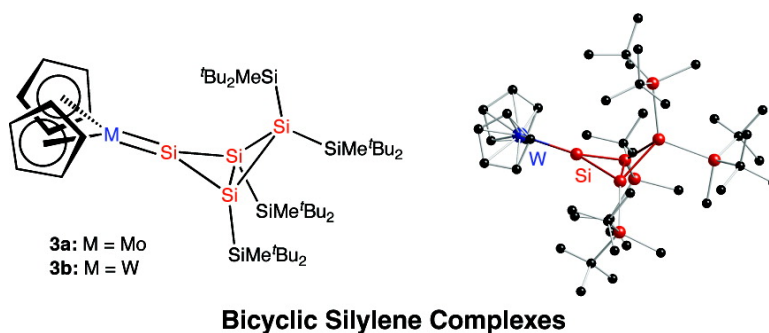**136** PUBLICATIONS   **2,172** CITATIONS

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Bicyclic Silylene Complexes

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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 $[(\eta^5-C_5Me_5)(Me_3P)_2Ru=SiPh_2(NCMe)]^+ \cdot BPh_4^-$, 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 $[(^tBu_2MeSi)_4Si_4]^{2-} \cdot 2K^+$ $1^{2-} \cdot 2K^+$,[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 $[(^tBu_2MeSi)_4Si_4]^{2-} \cdot Ca^{2+}$ $2^{2-} \cdot Ca^{2+}$, was readily available in 92% yield by the transmetalation of $1^{2-} \cdot 2K^+$ with CaI_2 in THF. The structure of $2^{2-} \cdot Ca^{2+}$ 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 $2^{2-} \cdot Ca^{2+}$ 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 $Cp_2M(\eta^1$-$Si_4R_4)$ (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 $2^{2-} \cdot Ca^{2+}$ 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
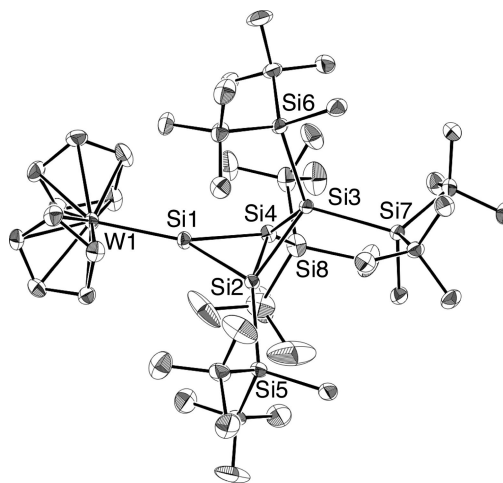

Figure 1. ORTEP drawing of $3b \cdot C_6H_{14}$ (30% probability level). Hydrogen atoms and crystallization solvent (hexane) molecule are omitted for clarity. Selected bond lengths (Å): Si1−W1 = 2.4202(14), Si1−Si2 = 2.3290(18), Si1−Si4 = 2.3231(19), Si2−Si4 = 2.4170(16), Si2−Si3 = 2.3769(16), Si3−Si4 = 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
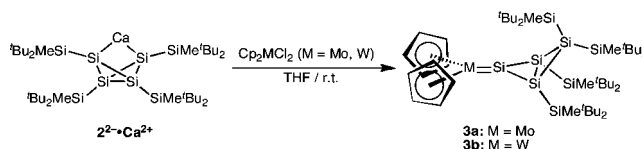
were observed as expected at high field for both bridging Si (−139.9 ppm for 3a and −147.7 ppm for 3b) and bridgehead Si (−101.2 ppm for 3a and −110.2 ppm for 3b).

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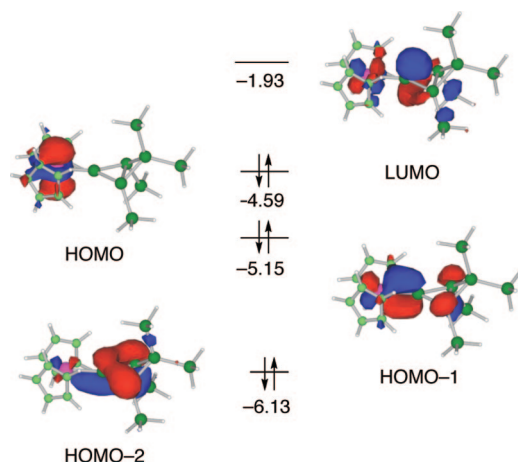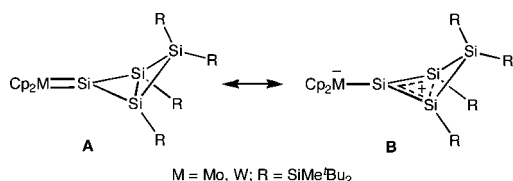
Figure 2. Frontier molecular orbitals of model silylene complex **3b′** (MO energy levels are given in eV).

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]

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.

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(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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