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A Stable Schrock-Type Hafnium−Silylene Complex

Norio Nakata, Toshiyuki Fujita, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tsukuba, Ibaraki 305-8571, Japan

Received October 10, 2006; E-mail: sekiguch@chem.tsukuba.ac.jp

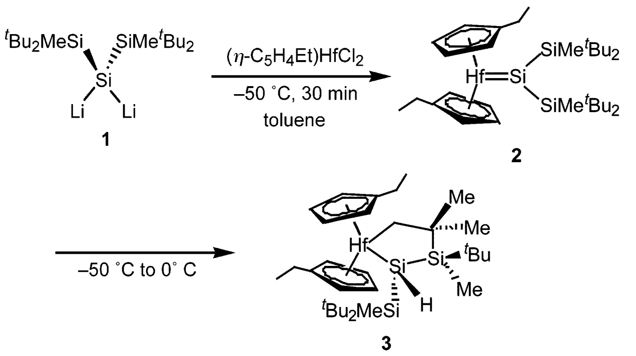
During the last two decades, transition-metal silylene complexes have become of interest as silicon analogues of carbene complexes and as potential intermediates in various metal-catalyzed syntheses and transformations of organosilicon compounds.[1] Since two base-stabilized silylene complexes, $(CO)_4Fe{=}Si(O^tBu)_2{\cdot}HMPA$[2] and $[Cp^*(PMe_3)_2Ru{=}SiPh_2{\cdot}NCMe]$ (BPh_4),[3] were independently isolated in 1987, several studies of base-stabilized or base-free transition-metal silylene complexes have been published to date. All of these complexes are classified as Fischer-type, which typically have electrophilic silicon and nucleophilic metals.[4] Although Tilley et al. have recently reported high oxidation-state tungsten−silylene complexes, $[Cp^*(dmpe)H_2W{=}SiR_2][B(C_6F_5)_4]$,[5] there are few examples of early transition-metal silylene complexes,[6,7] especially for group 4 metals, such as titanium, zirconium, and hafnium, owing to a lack of suitable synthetic methods.

Meanwhile, we have recently prepared 1,1-dilithiosilane (**1**) as an extremely useful coupling reagent, interaction of which with 1,1-difunctional electrophiles results in the formation of a variety of unsaturated derivatives containing heavier group 14 elements.[8] Using this synthetic approach, we quite recently succeeded in the first isolation of stable 1,3-disila-2-gallata- and -indataallenic anions[9] and amino-substituted silaborene,[10] featuring double bonds between a silicon atom and group 13 elements. Here, we present the synthesis and characterization of the first stable Schrock-type hafnium−silylene complex as a new application of the dilithiosilane derivative.

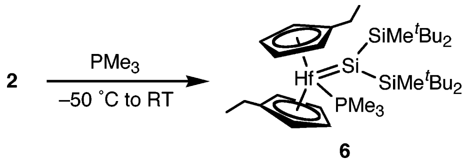
First, we attempted the coupling reaction of **1** with 0.9 equiv of $(\eta\text{-}C_5H_4Et)_2HfCl_2$ in dry toluene at −50 °C. The reaction mixture immediately changed to a dark-green solution, suggesting the generation of the 16-electron hafnium−silylene complex, $(\eta\text{-}C_5H_4Et)_2Hf{=}Si(SiMe^tBu_2)_2$ (**2**) (Scheme 1).[11,12] Unfortunately, silylene complex **2** could not be isolated because of its thermal instability, and decomposition of **2** occurs rapidly even at 0 °C to give a metallacycle (**3**), which most likely results from the intramolecular C−H insertion reaction of **2**.[11] However, indirect evidence for the formation of **2** was given by reaction with MeOH and D_2O at −50 °C to afford the corresponding dihydrosilane $(^tBu_2MeSi)_2SiH_2$ (**4**) and didueteriosilane $(^tBu_2MeSi)_2SiD_2$ (**5**) in nearly quantitative yields by nucleophilic attack on the Hf center.[11] The reactivities reported so far have shown that the M═Si double bond in the silylene complexes is highly polarized in a $M^{\delta-}{=}Si^{\delta+}$ manner.[4] Indeed, these complexes undergo nucleophilic attack at the silicon atom instead of the transition metal M. However, the present complex **2** has an opposite polarity $M^{\delta+}{=}Si^{\delta-}$ by the influence of two factors: the use of the early transition metal and the introduction of the electropositive $^tBu_2MeSi$ groups at the silylene center.

To provide further evidence for the generation of **2**, we carried out an addition of PMe_3 to the hafnium center of **2**. Thus, treatment of **2** with excess amounts of PMe_3 at −50 °C resulted in the formation of the hafnium−silylene phosphine complex, $(\eta\text{-}C_5H_4Et)_2(PMe_3)Hf{=}Si(SiMe^tBu_2)_2$ (**6**), which was isolated as air-sensitive red crystals in 33% yield after crystallization from pentane at −30 °C (Scheme 2).[13] Complex **6** represents the first example of a compound with a Si═Hf double bond as well as a Schrock-type 18-electron silylene complex, and it was characterized by spectroscopic data. In the ^1H and ^{13}C NMR spectra of **6**, the resonance signals of the two ethylcyclopentadienyl and $^tBu_2MeSi$ groups became nonequivalent owing to the Si═Hf double bond. The ^{29}Si NMR spectrum of **6** showed three doublet signals at 16.8, 24.7, and 295.4 ppm with J_{SiP} coupling constants of 2.6, 4.5, and 15.0 Hz, which are assignable to two $^tBu_2MeSi$ groups and a silylene ligand, respectively. The remarkable downfield shift of the silylene signal (295.4 ppm) is characteristic of base-free silylene complexes and is consistent with those reported for the tungsten−silylene complexes, $[Cp^*(dmpe)H_2W{=}SiR_2][B(C_6F_5)_4]$ (286−314 ppm).[5] The ^{31}P NMR spectrum of **6** displayed a signal at −8.6 ppm.

Scheme 1



Scheme 2



The molecular structure of **6** was unambiguously determined by X-ray crystallographic analysis, and an ORTEP drawing of **6** is shown in Figure 1.[14] The most important feature is the Si1−Hf1 bond length of 2.6515(9) Å, which is approximately 5% shorter than those of related complexes with Si−Hf single bonds, $(CpCp^*Hf(SiH_2Ph)Cl$, 2.729(3) Å;[15] $Cp_2Hf[Si(SiMe_3)_3]_2$, 2.850(4) Å;[16] $Cp_2(PMe_3)Hf(Me_3Si)_2Si{=}Si(SiMe_3)_2$, 2.8309(6) and 2.8332(5) Å[17]), obviously indicating the double-bond character between the silicon and hafnium atoms. The silylene ligand has a planar geometry, with the sum of the bond angles around the silicon center being 359.8°. The hafnium atom of **6** lies 2.18−2.19 Å from the C_5H_4Et ring centroid, and the centroid−Hf−centroid angle (128.7°) is similar to typical hafnocene derivatives. Furthermore, the Hf1−P1 bond length (2.6619(9) Å) is slightly shorter than that found in the

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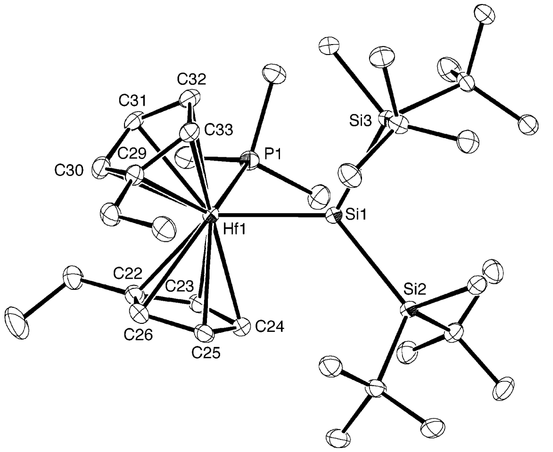

Figure 1. ORTEP drawing of hafnium−silylene phosphine complex **6** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Hf1 = 2.6515(9), Hf1−P1 = 2.6619(9), Si1−Si2 = 2.4512(13), Si1−Si3 = 2.4643(13), Hf1−C22 = 2.544(4), Hf1−C23 = 2.477(4), Hf1−C24 = 2.446(4), Hf1−C25 = 2.461(3), Hf1−C26 = 2.521(4), Hf1−C29 = 2.554(3), Hf1−C30 = 2.510(4), Hf1−C31 = 2.465(3), Hf1−C32 = 2.463(4), Hf1−C33 = 2.509(3), Selected bond angles (deg): Si1−Hf1−P1 = 91.19(3), Hf1−Si1−Si2 = 127.74(4), Hf1−Si1−Si3 = 123.77(4), Si2−Si1−Si3 = 108.27(5), Cp1−Hf1−Cp2 = 128.7.

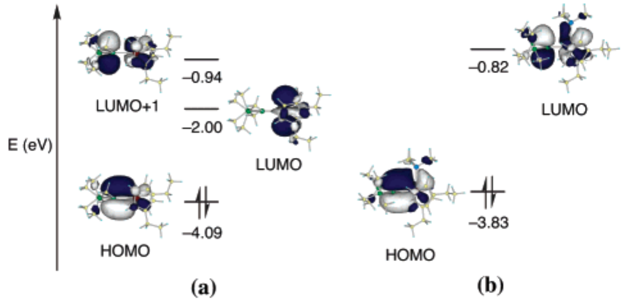

Figure 2. Representation of the frontier molecular orbitals of model complexes (η-$C_5H_4Et)_2Hf{=}Si(SiMe_3)_2$ **7** (a) and (η-$C_5H_4Et)_2(PMe_3)Hf{=}Si(SiMe_3)_2$ **8** (b).

hafnocene disilene complex, $Cp_2(PMe_3)Hf(Me_3Si)_2Si{=}Si(SiMe_3)_2$ (2.705(3) Å).[17]

The nucleophilic character of these new hafnium−silylene complexes was confirmed by density-functional theory (DFT) calculations for the model complexes (η-$C_5H_4Et)_2Hf{=}Si(SiMe_3)_2$ (**7**) and (η-$C_5H_4Et)_2(PMe_3)Hf{=}Si(SiMe_3)_2$ (**8**).[18] As expected, the natural population analysis (NPA) charge distributions for **7** and **8** revealed that the silicon atoms have substantial negative charges (Si, −0.40; Hf, 1.25 for **7**; and Si, −0.34; Hf, 0.78 for **8**). The UV−vis spectrum of silylene complex **6** in hexane shows three absorption maxima at 261 (ϵ 13300), 327 (ϵ sh, 2300), and 513 nm (ϵ 3800). The longest wavelength absorption band at 513 nm is attributable to the π(HOMO)→π^*(LUMO) transition of the Si=Hf double bond (Figure 2b). On the other hand, the UV−vis spectrum of **2** in hexane at 223 K shows characteristically red-shifted absorption maxima at 411 and 635 nm.[19] The former absorption band at 411 nm can be assigned to the π(HOMO)→π^*(LUMO + 1) transition of the Si=Hf double bond, while the latter at 635 nm would be assigned to the $\pi_{Si=Hf}$(HOMO) → d_{z^2}(LUMO) interaction (Figure 2a).

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Supporting Information Available: The experimental procedures of **2**−**6**, calculated geometries for **7** and **8**, table of crystallographic data including atomic positional and thermal parameters for **6** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the experimental procedures and spectral data of **2**−**5**, see the Supporting Information.
(12) The reaction of **1** with (η-$C_5H_4Et)_2ZrCl_2$ produced the corresponding silylene complex with several unidentified products; however, only Li-Cl exchange reaction occurred in the case of (η-$C_5H_4Et)_2TiCl_2$, and none of the silylene complex was formed.
(13) Spectral data for **6**: red crystals; mp 121−123 °C (dec). ^1H NMR (C_6D_6, δ): 0.80 (s, 3 H), 0.88 (s, 3 H), 0.94 (d, $J_{PH} = 6.3$ Hz, 9 H), 1.06 (t, $J_{CH} = 7.5$ Hz, 3 H), 1.07 (t, $J_{CH} = 7.5$ Hz, 3 H), 1.30 (s, 9 H), 1.44 (s, 9 H), 1.47 (s, 18 H), 1.81−2.09 (m, 4 H), 4.60 (m, 1 H), 4.67 (m, 1 H), 4.94 (m, 1 H), 5.54 (m, 1 H), 6.10 (m, 1 H), 6.54 (m, 1 H), 7.41 (m, 1 H), 7.66 (m, 1 H). ^{13}C NMR (C_6D_6, δ): 3.0 ($SiCH_3$), 5.0 ($SiCH_3$), 16.1 (CH_2CH_3), 17.3 (CH_2CH_3), 22.5 (d, $J_{PC} = 22.7$ Hz, PCH_3), 23.4 (CH_2CH_3), 23.6 (CH_2CH_3), 24.2 (CCH_3), 24.4 (CCH_3), 24.5 (CCH_3), 24.6 (CCH_3), 32.2 (CCH_3), 32.3 (CCH_3), 32.7 (CCH_3), 33.1 (CCH_3), 90.2 (Cp), 95.9 (Cp), 97.7 (Cp), 100.3 (Cp), 102.1 (Cp), 102.6 (Cp), 104.4 (Cp), 108.2 (Cp), 120.3 (Cp_{ipso}), 120.5 (Cp_{ipso}). ^{29}Si NMR (C_6D_6, δ): 16.8 (d, $^3J_{PSi} = 2.6$ Hz, $SiMe^tBu_2$), 24.7 (d, $^3J_{PSi} = 4.5$ Hz, $SiMe^tBu_2$), 295.4 (d, $^2J_{PSi} = 15.0$ Hz, $Si = Hf$). ^{31}P NMR (C_6D_6, δ): −8.6. UV−vis (hexane) λ_{max}/nm (ϵ): 261 (13300), 327 (2300), 513 (3800).
(14) Crystal data for **6** at 120 K: $C_{35}H_{69}Hf\,PSi_3$, MW = 783.63, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 19.1080(13)$, $b = 11.7660(9)$, $c = 19.6560(14)$ Å; $\beta = 118.138(4)°$, $V = 3896.9(5)$ Å^3, $D_{calcd} = 1.336$ g cm^{-3}, R_1 ($I > 2\sigma(I)$) = 0.0384, wR_2 (all data) = 0.1017 for 8638 reflections and 380 parameters, GOF = 1.031.
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(18) Geometry optimizations for **7** and **8** were carried out using the Gaussian 98 program with density-functional theory at the B3PW91 level using the 6−31G(d) basis set for the P, Si, C, and H atoms and the LANL2DZ level for the Hf atom. The NPA charge distributions for **8** were calculated at the B3LYP level using 6−31G(d) for the P, Si, C, and H atoms and the LANL2DZ level for the Hf atom.
(19) The molar absorption coefficient for **2** in the UV−vis spectrum could not be determined because of the instability of the compound.

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