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Articles

Synthesis and Reactivity of 16-Electron Hafnocene Silyl Hydride Complexes

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The synthesis and reactivity of monomeric, 16-electron hafnocene silyl hydride complexes are described. The complex $CpCp^*Hf[Si(SiMe_3)_3]H$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$), prepared by the reaction of $CpCp^*Hf(H)Cl$ with $(THF)_3LiSi(SiMe_3)_3$, reacts rapidly with both ethylene and diphenylacetylene with elimination of $HSi(SiMe_3)_3$ to afford the corresponding hafnacyclopentane and tetraphenylhafnacyclopentadiene complexes. Complex **1** reacts with acetone to give the insertion product $CpCp^*Hf(OCHMe_2)[Si(SiMe_3)_3]$ (**4**). Reaction of **1** with the secondary silane $H_2Si(SiMe_3)_2$ proceeds smoothly to the new silyl hydride complex $CpCp^*Hf[SiH(SiMe_3)_2]H$ (**5**), which was characterized by X-ray crystallography. Deuterium labeling experiments indicate that the latter reaction occurs with significant scrambling of label between the SiH and HfH positions. The tertiary silane Ph_3SiH does not react under comparable conditions. The silane $H_2Si(SiMe_3)_2$ undergoes a similar σ-bond metathesis reaction with $CpCp^*Hf[Si(SiMe_3)_3]Cl$, to give $CpCp^*Hf[SiH(SiMe_3)_2]Cl$ (**7**). For the latter reaction, there is a photochemical dependence on the rate and course of the reaction pathway. Exposure of the reaction mixture to room light is critical for complete conversion to **7**.

Introduction

From our investigations of the chemistry of d^0 metal−silicon bonds, we have found that zirconocene and hafnocene silyl complexes are active catalysts for the dehydropolymerization of hydrosilanes.[1] Other catalysts which have been reported appear to convert to metal silyl species during the polymerization.[2] On the basis of extensive mechanistic studies, we have suggested that this dehydropolymerization occurs by a purely σ-bond metathesis mechanism involving only two steps.[1] Other workers have suggested somewhat more complicated mechanisms,[3−5] but widespread attention has focused on the possible role of group 4 silyl hydride complexes, $Cp'Cp''MH(SiR_3)$ (Cp', Cp'' = cyclopentadienyl derivatives), as intermediates in the polymerization. Such complexes are thought to be highly reactive, since they possess two different bonds which should readily participate in σ-bond metathesis.[1] The possibility that such species might react via the reductive elimination of silane, as has been observed for related alkyl hydride derivatives,[6] has been suggested by Corey.[4] It is therefore important to more thoroughly establish the chemical properties for d^0 metallocene silyl hydride complexes.

Postulates concerning the possible role of 16-electron silyl hydride complexes in catalytic cycles have been difficult to test, given the fact that none have been isolated. However, closely related titanium(III) dimeric complexes have been isolated by Harrod,[3,7] and Lewis base adducts of the type $Cp_2MH(SiR_3)(PMe_3)$ have been prepared by Buchwald.[8] Here we describe the synthesis of monomeric, 16-electron hafnocene silyl hydride complexes and their structural and chemical properties.

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Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere of nitrogen or argon using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. To remove olefin impurities, pentane and benzene were pretreated with concentrated $\mathrm{H_2SO_4}$ and then 0.5 N $\mathrm{KMnO_4}$ in 3 M $\mathrm{H_2SO_4}$, followed by $\mathrm{NaHCO_3}$ and finally $\mathrm{MgSO_4}$. All solvents were distilled from sodium benzophenone ketyl. Benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy. ^{1}H NMR yields were determined by relative integration against $\mathrm{Cp_2Fe}$, using a long delay time and a short pulse width. CpCp*Hf(H)Cl,[1d] $\mathrm{(THF)_3LiSi(SiMe_3)_3}$,[9] CpCp*Hf[$\mathrm{Si(SiMe_3)_3}$]Cl,[1c] and $\mathrm{H_2Si(SiMe_3)_2}$[10] were prepared according to literature procedures. Elemental analyses were performed by Mikroanalytisches Labor Pascher or the Microanalytical Laboratory in the Department of Chemistry at the University of California at Berkeley. NMR spectra were recorded on AMX-300, Varian UN-500, and VBAMX-400 spectrometers, and infrared spectra were recorded on a Perkin-Elmer 1330 instrument.

CpCp*Hf[$\mathbf{Si(SiMe_3)_3}$]H (1). CpCp*Hf(H)Cl (0.484 g, 1.17 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (0.544 g, 1.15 mmol) were combined in an aluminum-foil-covered Schlenk flask. Benzene (30 mL) was added, and the solution was stirred for 15 min at room temperature. The volatiles were removed *in vacuo,* and the crude material was extracted with pentane (20 mL). The pentane extract was filtered, concentrated (to ~10 mL), and cooled (to −40 °C) to afford complex **1** as bright orange needles in 32% yield (0.228 g, 0.364 mmol). IR (toluene, NaCl, cm^{-1}): 3028 (m), 2949 (m), 2895 (m), 2050 (w), 1638 (br m, Hf−H), 1495 (m), 1446 (w sh), 1439 (w), 1394 (w sh), 1387 (w), 1242 (s), 1017 (m), 837 (s sh), 833 (vs), 825 (s sh), 762 (m). ^{1}H NMR (benzene-d_6, 500 MHz, 24 °C): δ 15.69 (s, 1 H, Hf−H), 6.02 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 1.94 (s, 15 H, $\mathrm{C_5}\mathit{Me}_5$), 0.47 (s, 27 H, $\mathrm{Si}\mathit{Me}_3$). ^{13}C{^{1}H} NMR (toluene-d_8, 125.7 MHz, −30 °C) δ 118.5 ($\mathit{C}_5\mathrm{Me_5}$), 109.8 ($\mathit{C}_5\mathrm{H_5}$), 13.15 ($\mathrm{C_5}\mathit{Me}_5$), 6.93 ($\mathrm{Si}\mathit{Me}_3$). ^{29}Si NMR (toluene-$d_8$, 99.3 MHz, −30 °C): δ −4.61 ($\mathrm{Si(}\mathit{Si}\mathrm{Me_3)_3}$), −67.1 ($\mathit{Si}\mathrm{(SiMe_3)_3}$). Anal. Calcd for $\mathrm{C_{24}H_{48}HfSi_4}$: C, 45.94; H, 7.71. Found: C, 45.85; H, 8.03.

CpCp*$\overline{\mathbf{Hf[CH_2(CH_2)_2C}}\mathbf{H_2]}$ (2). A pentane solution (15 mL) of CpCp*Hf(H)Cl (0.215 g, 0.516 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (0.243 g, 0.516 mmol) was stirred under an atmosphere of ethylene (1 atm) for 15 min. The initial orange color turned yellow. Filtration and evaporation of the filtrate provided a yellow powder. Crystallization from pentane at −35 °C gave a pale yellow powder (0.140 g, 62%). ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 5.82 (s, 5 H, $\mathrm{C_5H_5}$), 2.39 (m, 2 H, H_β), 2.06 (m, 2 H, H_β), 1.74 (s, 15 H, $\mathrm{C_5Me_5}$), 0.96 (m, 2 H, H_α), 0.37 (m, 2 H, H_α). Anal. Calcd for $\mathrm{C_{19}H_{28}Hf}$: C, 52.47; H, 6.49. Found: C, 51.03; H, 6.19. The low carbon value is presumably due to loss of ethylene under vacuum and/or during the combustion analysis.

CpCp*$\overline{\mathbf{Hf[C(Ph)C(Ph)C(Ph)C}}$(Ph)] (3). A pentane solution (15 mL) of CpCp*Hf(H)Cl (0.305 g, 0.734 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (0.347 g, 0.735 mmol) was added to diphenylacetylene (0.262 g, 1.47 mmol), and the resulting reaction mixture was stirred in the dark for 12 h. The reaction mixture was filtered, and the volatile material was removed *in vacuo* to afford a yellow-orange powder. Crystallization from hexamethyldisiloxane (~5 mL) at −35 °C yielded complex **4** as a yellow solid (0.290 g, 54%). ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 7.00−6.71 (m, 20 H, $\mathrm{C_6H_5}$), 6.01 (s, 5 H, $\mathrm{C_5H_5}$), 1.80 (s, 15 H, $\mathrm{C_5Me_5}$). Anal. Calcd for $\mathrm{C_{43}H_{40}Hf}$: C, 70.24; H, 5.48. Found: C, 70.14; H, 5.50.

CpCp*Hf[$\mathbf{Si(SiMe_3)_3}$]($\mathbf{OCHMe_2}$) (4). Acetone (0.002 mL) was added to a benzene-d_6 solution (1 mL) of CpCp*Hf(H)Cl (0.008 g, 0.0193 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (0.009 g, 0.0191 mmol) at room temperature, and the reaction was monitored by ^{1}H NMR spectroscopy. The initial orange color of the solution turned dark blue and then colorless almost immediately. Assignment of the structure was based purely on ^{1}H NMR spectroscopy and comparison of the spectrum to spectra for closely related derivatives.[8a] ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 5.92 (s, 5 H, $\mathrm{C_5H_5}$), 4.20 (sept, J_{HH} = 6.0 Hz, 1 H, $\mathrm{OC}\mathit{H}\mathrm{Me_2}$), 1.89 (s, 15 H, $\mathrm{C_5Me_5}$), 1.08 (d, J_{HH} = 6.0 Hz, 3 H, $\mathrm{OCH}\mathit{Me}_2$), 0.89 (d, J_{HH} = 6.0 Hz, 3 H, $\mathrm{OCH}\mathit{Me}_2$), 0.55 (s, 27 H, $\mathrm{Si(Si}\mathit{Me}_3\mathrm{)_3}$).

CpCp*Hf[$\mathbf{SiH(SiMe_3)_2}$]H (5). CpCp*Hf(H)Cl (0.484 g, 1.17 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (0.544 g, 1.15 mmol) were combined in an aluminum-foil-covered Schlenk flask. Diethyl ether (30 mL) was added, and the solution was stirred for 5 min at room temperature. Subsequently, a diethyl ether solution (5 mL) of $\mathrm{H_2Si(SiMe_3)_2}$ (0.265 g, 1.50 mmol) was added. Immediately, the color of the reaction mixture changed from light orange to dark orange. The reaction mixture was then stirred at room temperature for 1 h. The reaction mixture was filtered, and the volatile material was removed from the filtrate by vacuum transfer to afford an orange residue. The residue was dissolved in pentane (ca. 25 mL), and the resulting filtered pentane solution was concentrated and cooled to −35 °C to afford orange platelike crystals of complex **5** in 72% yield. IR (toluene, NaCl, cm^{-1}): 2036 (Si−H), 1635 (Hf−H). ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 15.85 (s, 1 H, Hf-H), 6.00 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 2.71 (s, 1 H, $\mathrm{Si}\mathit{H}\mathrm{(SiMe_3)_2}$), 1.95 (s, 15 H, $\mathrm{C_5}\mathit{Me}_5$), 0.36 (s, 9 H, $\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$), 0.32 (s, 9 H, $\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 24 °C): δ 118.4 ($\mathit{C}_5\mathrm{Me_5}$), 108.9 ($\mathit{C}_5\mathrm{H_5}$), 12.84 ($\mathrm{C_5}\mathit{Me}_5$), 5.36 ($\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$), 4.82 ($\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$). ^{29}Si{^{1}H} NMR (benzene-d_6, 99.3 MHz, 20 °C): δ −4.85 ($\mathrm{SiH(}\mathit{Si}\mathrm{Me_3)_2}$), −4.89 ($\mathrm{SiH(}\mathit{Si}\mathrm{Me_3)_2}$), −29.7 ($\mathit{Si}\mathrm{H(SiMe_3)_2}$). Anal. Calcd for $\mathrm{C_{21}H_{40}HfSi_3}$: C, 45.42; H, 7.26. Found: C, 45.50; H, 7.20.

CpCp*Hf[$\mathbf{SiH(SiMe_3)_2}$]Cl (7). To a benzene solution (ca. 20 mL) of CpCp*Hf[$\mathrm{Si(SiMe_3)_3}$]Cl (0.200 g, 0.302 mmol) was added $\mathrm{H_2Si(SiMe_3)_2}$ (0.160 g, 0.910 mmol) at room temperature, and the reaction mixture was stirred in the presence of ambient room light for 12 h. The volatiles were removed *in vacuo*, to afford a yellow oil which was extracted with pentane (2 × 10 mL). The combined extracts were filtered, concentrated, and cooled to −40 °C to afford the product in 32% yield (0.057 g). The reaction proceeds in 67% yield, as determined by ^{1}H NMR spectroscopy. IR (toluene, NaCl, cm^{-1}): 2950 (m), 2900 (m), 2890 (m), 2860 (m), 2850 (m), 2052 (w), 2015 (w), 1493 (m), 1427 (w), 1244 (m), 841 (s sh), 810 (s sh). ^{1}H NMR (benzene-d_6, 300 MHz, 22 °C): δ 5.85 (s, 5 H, $\mathrm{C_5H_5}$), 2.81 (s, 1 H, $\mathrm{Si}\mathit{H}\mathrm{(SiMe_3)_2}$), 1.85 (s, 15 H, $\mathrm{C_5}\mathit{Me}_5$), 0.46 (s, 9 H, $\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$), 0.40 (s, 9 H, $\mathrm{SiH(Si}\mathit{Me}_3\mathrm{)_2}$). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 22 °C): δ 119.75 ($\mathit{C}_5\mathrm{Me_5}$), 111.01 ($\mathrm{C_5H_5}$), 12.61 ($\mathrm{C_5}\mathit{Me}_5$), 4.88 ($\mathrm{Si}\mathit{CH}_3$), 4.82 ($\mathrm{Si}\mathit{CH}_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 22 °C): −4.69 ($\mathrm{SiH(}\mathit{Si}\mathrm{Me_3)_2}$), −6.18 ($\mathrm{SiH(}\mathit{Si}\mathrm{Me_3)_2}$), −48.64 ($\mathit{Si}\mathrm{H(SiMe_3)_2}$). Anal. Calcd for $\mathrm{C_{21}H_{39}ClHfSi_3}$: C, 42.77; H, 6.67. Found: C, 42.99; H, 6.79.

X-ray Crystallography. Orange platelike crystals were obtained from a concentrated pentane solution at −35 °C. A crystal of dimensions 0.24 × 0.15 × 0.06 mm was mounted on a glass fiber using paratone N hydrocarbon oil. Data were collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10 s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using ω scans of 0.3°. Frame data were integrated (*XY* spot spread 1.60°; *Z* spot spread 0.60°) using the program SAINT (SAX Area-Detector Integration Program, V4.024, Siemens Industrial Automation, Inc., Madison, WI, 1995). The data were corrected for Lorentz and polarization effects. An absorption correction was performed using XPREP (part of the SHELXTL Crystal Structure Determination Package, Siemens Industrial Automation, Inc., Madison, WI, 1995; μR = 0.20, $T_{\max}$ = 0.79, $T_{\min}$ = 0.53). The

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Table 1. Summary of Crystallographic Data

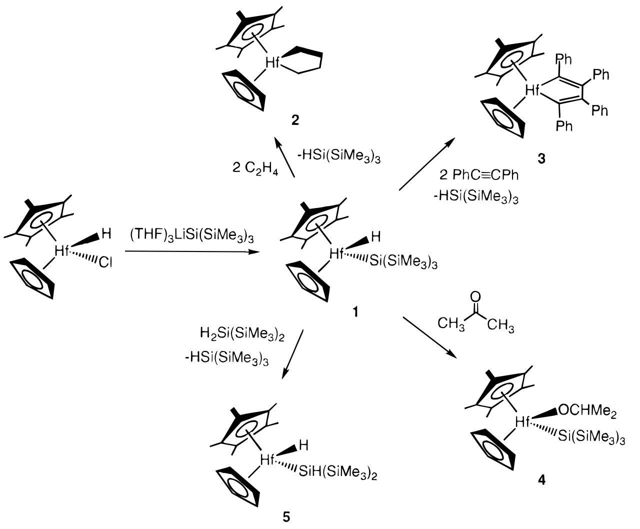
empirical formula	$HfSi_3C_{21}H_{40}$
fw	555.29
cryst color, habit	orange, plate
cryst dimens	0.24 × 0.15 × 0.06 mm
crys syst	monoclinic
cell determn (2θ range)	8192 (0.0−46.5°)
lattice params	$a = 11.4044(2)$Å $b = 17.2453(1)$ Å $c = 13.9402(2)$ Å $\beta = 113.338(1)°$ $V = 2517.34(6)$ Å^3
space group	$P2_1/n$ (No. 14)
Z	4
D_{calcd}	1.465 g/cm^3
μ(Mo Kα)	42.82 cm^{-1}
diffractometer	Siemens SMART
radiation	Mo Kα ($\lambda = 0.710$ 69 Å), graphite monochromated
temp	−149 °C
scan type	ω (0.3° per frame)
no. of rflns measd	total, 10 616; unique, 3757 ($R_{int} = 0.078$)
no. of observns ($I > 3.00\ \sigma(I)$)	3108
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
residuals: R; R_w	0.032; 0.039
R(all): R; R_w	0.036; 0.042
max peak in final diff map	1.67 e/Å^3
min peak in final diff map	−2.55 e/Å^3

10 616 integrated reflections were averaged in point group $2/m$ to give 3757 unique reflections ($R_{int} = 0.078$), but only 3108 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. Inspection of the systematic absences uniquely defined the space group as $P2_1/n$. The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan software. The non-hydrogen atoms were refined anisotropically. Peaks were found in the Fourier difference map at the expected locations for the hydrogen atoms bonded to Hf(1) and Si(1) (corresponding to Hf−H and Si−H distances of 1.76 and 1.25 Å, respectively). However, these H atoms could not be refined well in these locations and were not included in the final refinement. The number of variable parameters was 226, giving a data/parameter ratio of 13.75. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.67 and −2.55 e/Å^3, near the Hf atom. $R = 0.032$, $R_w = 0.039$, and GOF = 1.15. The crystallographic data are summarized in Table 1.

Results and Discussion

The silyl hydride complex CpCp*Hf[$Si(SiMe_3)_3$]H (**1**) was prepared by the addition of $(THF)_3LiSi(SiMe_3)_3$ to CpCp*Hf(H)Cl in benzene at room temperature (Scheme 1). An analytically pure sample was obtained from pentane at −35 °C as light-sensitive, thermally unstable orange needles in 32% yield. Evidence supporting a monomeric complex follows from ^{1}H NMR and IR spectroscopy. More specifically, the ^{1}H NMR spectrum of complex **1** reveals a characteristic downfield shift for a terminal hydride ligand (15.68 ppm),[1d,11] and the IR spectrum contains a strong absorption at 1638 cm^{-1} which is consistent with the presence of a terminal Hf−H bond.[1d,11] Despite the low recovery of complex **1**, the conversion is quantitative (by ^{1}H NMR spectroscopy). Complex **1** can be stored in the dark at −30 °C for several days without significant decomposition, but much shorter lifetimes are observed in solution ($t_{1/2} \approx$ 24 h). Therefore, for reactivity studies, it is most convenient to generate complex **1** *in situ*.

Scheme 1



The reactivity of complex **1** toward selected small molecules is summarized in Scheme 1. The reaction with ethylene affords complex **2** in 62% yield. The structure of **2** was assigned on the basis of analysis of both the ^{1}H and ^{13}C NMR spectra and comparisons to spectroscopic data for the analogous $Cp_2Hf[CH_2(CH_2)_2CH_2]$ complex previously reported by Erker.[12] Similarly, the reaction of complex **1** with diphenylacetylene affords the tetraphenylmetallacyclopentadiene complex **3** (in 54% yield), which was independently prepared by the reaction of $CpCp^*HfCl_2$ with LiC(Ph)=C(Ph)C(Ph)=C(Ph)Li. The reactions with ethylene and diphenylacetylene produce $HSi(SiMe_3)_3$ (by ^{1}H NMR spectroscopy), and these reactions probably proceed by initial coordination of the incoming alkene or alkyne, followed by reductive elimination of the silane.[6] In contrast, complex **1** reacts rapidly with 1 equiv of acetone in benzene-d_6 at room temperature via insertion, to produce the isopropoxy complex **4**. Therefore, silyl hydride **1** behaves analogously to the phosphine-stabilized complex $Cp_2Zr(H)(SiPh_3)(PMe_3)$ described by Buchwald.[8a]

Previous studies have demonstrated that d^0 M−Si and M−H bonds are highly active toward σ-bond metathesis processes.[1] Due to their proposed role in catalytic silane polymerizations, the reactivity of silyl hydride complex **1** toward a series of silanes was investigated. The reaction of **1** with 1 equiv of $PhSiH_3$ in benzene-d_6 at room temperature is very complex and occurs rapidly to give numerous unidentified products, including many which contain Si−H bonds. The reaction of **1** with 1 equiv of Ph_2SiH_2 under analogous conditions proceeds similarly, but at a slower rate. In contrast, complex **1** does not react with Ph_3SiH (benzene-d_6 solution). Given our previous success with the synthesis and isolation of lanthanide−$SiH(SiMe_3)_2$ com-

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(11) Diagnostic ^{1}H NMR shifts and IR stretches for terminal Hf−H: (a) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. (b) Kablitz, H.-S.; Wilke, G. *J. Organomet. Chem.* **1973**, *51*, 241. (c) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793. (d) Highcock, W. J.; Mills, R. M.; Spencer, H. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 821. (e) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1989**, *6*, 1041.

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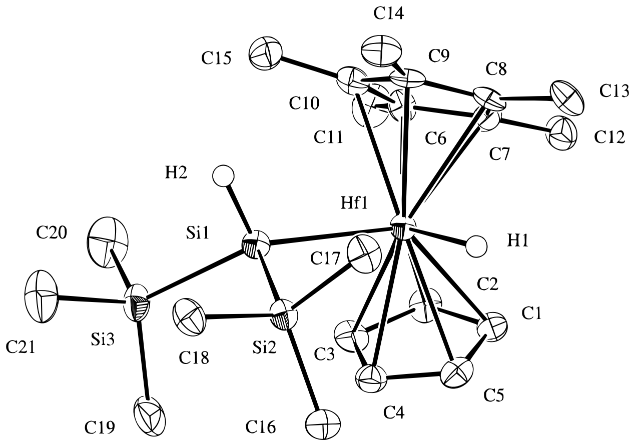


Figure 1. ORTEP view of the molecular structure of $Cp^*CpHf[SiH(SiMe_3)_2]H$ (**5**).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Cp^*CpHf[SiH(SiMe_3)_2]H$ (5)

(a) Bond Distances			
Hf(1)−Si(1)	2.744(1)	Si(1)−Si(2)	2.352(2)
Si(1)−Si(3)	2.348(2)	Si(2)−C(16)	1.880(5)
Si(2)−C(17)	1.880(5)	Si(2)−C(18)	1.876(5)
Si(3)−C(19)	1.883(7)	Si(3)−C(20)	1.882(7)
Si(3)−C(21)	1.896(6)	C(1)−C(2)	1.437(7)
Hf(1)−Cp[a]	2.184	Hf(1)−Cp*[a]	2.174
(b) Bond Angles			
Si(2)−Si(1)−Si(3)	109.00(7)	Cp−Hf(1)−Cp*	135.94
Hf(1)−Si(1)−Si(3)	122.35(6)	Si(1)−Hf(1)−Cp	105.48
Si(1)−Hf(1)−Cp[a]	109.90	Hf(1)−Si(1)−Si(2)	108.20(6)

[a] Cp and Cp* denote the centroids of the respective rings.

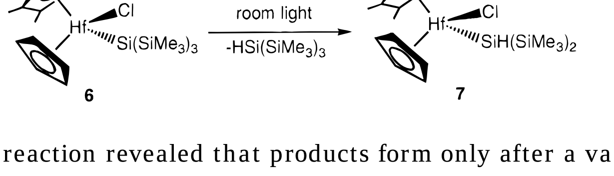
plexes obtained by σ-bond metathesis reactions of $H_2Si(SiMe_3)_2$,[13] we examined the interaction of complex **1** with this silane.

Complex **1** reacts rapidly with $H_2Si(SiMe_3)_2$ under ambient room light in benzene-d_6 to afford the new hydrido silyl complex $CpCp^*Hf[SiH(SiMe_3)_2]H$ (**5**) in 86% yield by ^1H NMR spectroscopy (Scheme 1). Our observations indicate that complex **5** is much more thermally and photochemically stable than **1**, presumably because of the less sterically demanding silyl ligand. The ^1H NMR spectrum contains a new Hf−H signal (15.85 ppm), a singlet at δ 2.71 attributed to the Si−H hydrogen, and two singlets for the diastereotopic trimethylsilyl groups (at δ 0.36 and 0.32). Infrared absorptions at 2036 and 1635 cm^{-1}, assigned to the Si−H and Hf−H stretches, respectively, are consistent with a monomeric structure.[1d,11] The molecular structure of complex **5** was confirmed by X-ray crystallography. The structure is shown in Figure 1, and selected bond distances and angles are summarized in Table 2. Electron density peaks in the final difference Fourier map were observed at the expected positions for the hydrogen atoms bonded to Hf and Si. The Hf-Si bond distance of 2.744(1) Å is comparable to analogous distances in $Cp^*Cl_2HfSi(SiMe_3)_3$ (2.748(4) Å)[14] and $Cp^*CpHf(SiH_2Ph)Cl$ (2.729(3) Å).[1c] Interestingly, these distances are considerably shorter than those observed for the independent Hf−Si bonds for $Cp^*CpHf[Si(SiMe_3)_3]Cl$, 2.881(4) and 2.888(4) Å, which are probably elongated by steric congestion in the molecule.[1c]

Mechanistically, the formation of complex **5** from **1** and $H_2Si(SiMe_3)_2$ could occur by several different pathways. One possibility is that the reaction proceeds via initial reductive elimination of $HSi(SiMe_3)_3$ from complex **1** to form the hafnocene CpCp*Hf, followed by oxidative addition of the Si−H bond of $H_2Si(SiMe_3)_2$. This mechanism would therefore involve formation of a Hf(II) species, which is expected to be a relatively high-energy process.[15] An alternative reaction pathway might involve a four-centered transition state resulting from interaction of Hf−Si and Si−H bonds. Other mechanistic possibilities include a chain reaction catalyzed by hydrogen[16] and processes involving metalation of the Cp* C−H bonds.[17]

To investigate the mechanism of this process, we carried out deuterium-labeling experiments. The reaction of **1** with $D_2Si(SiMe_3)_2$[18] occurred rapidly (<5 min) at room temperature or −70 °C under ambient room light to give significant (ca. 80%) incorporation of deuterium into the HfH hydride position, as determined by multiple integrations of ^1H NMR spectra against an internal ferrocene standard. The incomplete deuteration of this position suggests competing processes and, in particular, significant Hf−H/Si−H scrambling. In fact, this type of scrambling is expected to be quite rapid relative to other σ-bond metathesis processes.[1d] The reaction of $CpCp^*Hf[Si(SiMe_3)_3]D$ with 1.05 equiv of $H_2Si(SiMe_3)_2$ in benzene (or benzene-d_6) results in significant (but incomplete) transfer of deuterium to the Hf−H and Si−H positions of **5** and production of both $HSi(SiMe_3)_3$ (ca. 75%) and $DSi(SiMe_3)_3$ (by ^1H and ^2H NMR spectroscopy). No clear conclusion concerning the operative mechanism can be drawn from the above labeling experiments, but we interpret the observation of extensive deuterium scrambling as evidence for σ-bond metathesis processes.[1d,6c]

In order to perhaps gain more information on this σ-bond metathesis process, we examined the related and much slower reaction of $CpCp^*Hf[Si(SiMe_3)_3]Cl$[1c] (**6**) with $H_2Si(SiMe_3)_2$,which affords $Cp^*CpHf[SiH(SiMe_3)_2]Cl$ (**7**) in 67% yield, along with a quantitative amount of $HSi(SiMe_3)_3$, as determined by ^1H NMR spectroscopy (eq 1).[19] Initial efforts to follow the kinetics of this reaction revealed that products form only after a vari-



6 **7** (1)

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(19) $CpCp^*Hf[SiH(SiMe_3)_2]Cl$ can be prepared by two routes: the addition of methylene chloride to complex **5** at room temperature or the addition of $H_2Si(SiMe_3)_2$ to **6** in benzene at room temperature.

able induction time (ca. 0−3.3 h at 25 °C). Note that a similar observation was made for the σ-bond metathesis reaction of $Cp*_2SmCH(SiMe_3)_2$ with $H_2Si(SiMe_3)_2$, which appears to proceed by a chain reaction catalyzed by H_2.[16] However, the reaction in eq 1 is not catalyzed by hydrogen, and although CpCp*Hf(H)Cl does react with $H_2Si(SiMe_3)_2$ (very slowly over several days), the yield of **7** is extremely low (trace amounts by ^1H NMR spectroscopy; benzene-d_6 solution).

In addition, we have found that the reaction of complex **6** with $H_2Si(SiMe_3)_2$ is photochemically driven. When a benzene-d_6 solution of highly pure **6** (recrystallized at least three times) was treated with $H_2Si(SiMe_3)_2$ in the dark, complex **7** did not form and only the decomposition of **6** to $HSi(SiMe_3)_3$ and unidentified hafnium complexes was observed after several hours at room temperature. After a benzene-d_6 solution of **6** was exposed to room light for 2 h, the color of the solution changed from bright yellow to yellow-brown. By NMR spectroscopy the purity of the compound appeared unchanged; however, 10% of it had decomposed, as determined by reference to an internal standard. Addition of $H_2Si(SiMe_3)_2$ at this point, in the dark, resulted in only a 10% conversion to **7**. Exposure of this reaction mixture to ambient room light, however, resulted in a 70% conversion to **7** after 12 h. Thus, **6** is photochemically converted to a species which appears to be paramagnetic and may therefore contain Hf(III).[20] This is consistent with what we have previously observed for photochemical reactions of **6** and its zirconium analogue.[1c] Therefore, this reaction is photochemically driven and an efficient radical chain process does not appear to be operative.[21] However, the reaction is clearly mediated by a photochemically activated species. It may be that photochemical Hf−Si bond homolysis is necessary for this reaction to occur,[1c] but the nature and role of a potential Hf(III) intermediate is not known at this time.

In summary, the preparation and reactivity of the first monomeric, d^0, 16-electron silyl hydride metallocenes are reported. For these systems, we have observed reductive elimination, insertion, and σ-bond metathesis processes. As observed previously,[1c] the reaction of a hafnocene silyl complex (**6**) with a silane is photochemically driven. Future investigations will address the mechanism of this photochemical reaction.

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Supporting Information Available: Tables of crystal data, collection, and refinement parameters, positional parameters, bond distances and angles, and anisotropic displacement parameters (14 pages). Ordering information is given on any current masthead page.

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[20] Extended photolysis of **6** with a UV lamp (10 °C, benzene-d_6) produces significant quantities of $CpCp*HfCl_2$ and $HSi(SiMe_3)_3$, along with a dark precipitate.

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