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Synthesis of new bis(trimethylsilylcyclopentadienyl) complexes of hafnium

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Abstract

The new trimethylsilylcyclopentadienyl hafnocene complexes, $(Me_3SiCp)_2Hf(Cl)(BH_4)$, $(Me_3SiCp)_2Hf(H)(BH_4)$, $(Me_3SiCp)_2HfMe_2$, $(Me_3SiCp)_2Hf(OR)_2$ (R = Me and Et), and $(Me_3SiCp)_2Hf(Cl)(OMe)$, have been prepared in good yield from the reactions of $(Me_3SiCp)_2HfCl_2$ with $LiBH_4$, MeLi, Et_3N/ROH (R = Me and Et), or NaOMe. All were isolated as volatile, low melting solids or oils. In the reaction of $(Me_3SiCp)_2HfCl_2$ with $LiBH_4$ in hexane, either the borohydride-chloride complex, $(Me_3SiCp)_2Hf(Cl)(BH_4)$ or the borohydride-hydride complex, $(Me_3SiCp)_2Hf(H)(BH_4)$, was isolated depending on the reaction temperature. Although the expected bis(borohydride) complex, $(Me_3SiCp)_2Hf(BH_4)_2$, was not obtained, ^{11}B NMR spectroscopy suggests that it may be formed as an intermediate which subsequently loses BH_3 to form $(Me_3SiCp)_2Hf(H)(BH_4)$.

Introduction

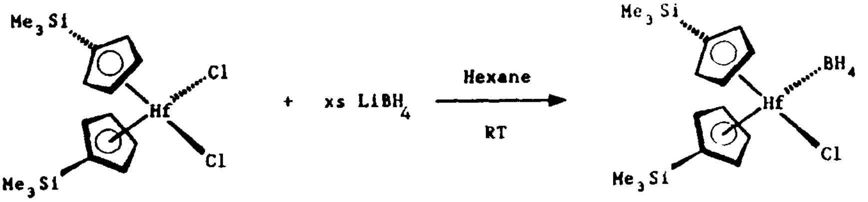
As part of a research program directed at the synthesis of volatile precursors for chemical vapor deposition (CVD), we had occasion to prepare several new bis(trimethylsilylcyclopentadienyl) (Me_3SiCp) complexes of hafnium. In particular, these included borohydride, alkyl, and alkoxide derivatives which are potential precursors to refractory hafnium boride, carbide, and oxide ceramic coatings, respectively. While the chemistry of the cyclopentadienyl (Cp) and related methylcyclopentadienyl (MeCp) hafnocene compounds is very extensive, the same is not true for the trimethylsilylcyclopentadienyl analogs [1]. The "parent" compound of this class, $(Me_3SiCp)_2HfCl_2$, **1**, has been reported [2], but few derivatives containing ligands other than chloride bound to the $(Me_3SiCp)_2Hf$ framework are known [1]. By analogy to the known reactions of Cp_2HfCl_2 with nucleophiles, derivatization of **1** by substitution of the chloride ligands with other anionic groups was expected to occur readily. This paper describes the preparation of several new Me_3SiCp hafnocene borohydride, alkyl, and alkoxide derivatives using this strategy.

Results and discussion

Preparation of bis(trimethylsilylcyclopentadienyl)hafnium(IV) borohydride complexes

Reaction of $(Me_3SiCp)_2HfCl_2$, **1**, with excess $LiBH_4$ in hexane at room temperature for two days gave 66% of the borohydride complex, $(Me_3SiCp)_2Hf(Cl)(BH_4)$, **2**

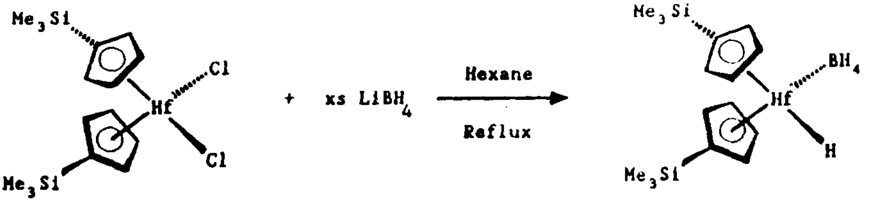
(Eq. 1). In refluxing hexane (4 days) both chlorides of **1** were removed, but the



(1)

1 2 66%

expected bis(borohydride) derivative, $(Me_3SiCp)_2Hf(BH_4)_2$, **4**, was not obtained. Instead, the borohydride-hydride complex, $(Me_3SiCp)_2Hf(H)(BH_4)$, **3**, was isolated in 90% yield (Eq. 2). This is in contrast to the corresponding reactions of Cp_2HfCl_2

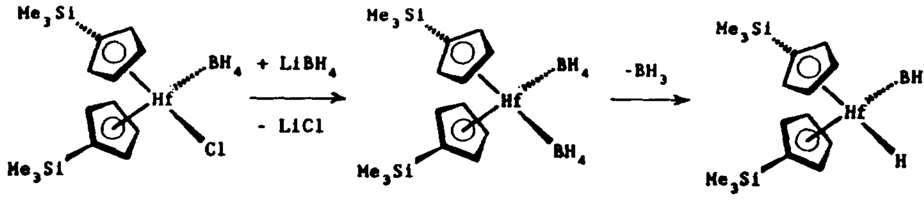


(2)

1 3 90%

or $(MeCp)_2HfCl_2$ with excess $LiBH_4$ which yield $Cp_2Hf(BH_4)_2$ [3] or $(MeCp)_2Hf(BH_4)_2$ [4], respectively. The borohydride ligands of the new compounds, **2** and **3**, displayed quintets in the ^{11}B NMR spectra at −8.21 (J(B–H) = 86.1 Hz) and 7.28 (J(B–H) = 84.8 Hz) ppm, respectively. The corresponding borohydride resonances in the ^1H NMR spectra, however, were not well resolved. In **3**, the borohydride signal appeared as a very broad quartet (partially obstructed by the Me_3Si resonance) centered at δ 0.69 (J(B–H) = 85.1 Hz). This is consistent with ^1H NMR data reported for $Cp_2Hf(BH_4)_2$ (δ 1.55, J(B–H) = 85.0 Hz) [3], $(MeCp)_2Hf(BH_4)_2$ (δ 1.53, J(B–H) = 84.9 Hz) [4], and $Cp_2Zr(BH_4)_2$ (δ 0.75, J(B–H) = 85.7 Hz) [3,5]. In **2**, $(Me_3SiCp)_2Hf(Cl)(BH_4)$, the expected borohydride quartet was not resolved at all, but instead appeared as a slight baseline rise centered at δ ~ 1.6 and integrating to four protons. Unexpectedly, the hydride resonance in **2** appeared far downfield at δ 9.26. Although most metal hydrides give rise to ^1H NMR signals upfield from tetramethylsilane [6], this low field signal is consistent with the ^1H NMR spectrum of $Cp_2Hf(H)(BH_4)$ which shows a hydride resonance at δ 9.5 [7]. Complexes **2** and **3** both gave satisfactory carbon–hydrogen combustion analyses as well as consistent field desorption mass spectra which showed the expected eight line isotope pattern for molecular ions at 504 and 470 amu, respectively.

Although the bis(borohydride) complex $(Me_3SiCp)_2Hf(BH_4)_2$, **4**, was not isolated from the reaction of $(Me_3SiCp)_2HfCl_2$ with excess $LiBH_4$, it may have formed as a transient intermediate to the final substitution product $(Me_3SiCp)_2Hf(H)(BH_4)$, **3**. When the reaction of **1** with excess $LiBH_4$ in refluxing hexane was monitored by ^{11}B NMR spectroscopy, three products in an approximate ratio of 1 : 4 : 2 were



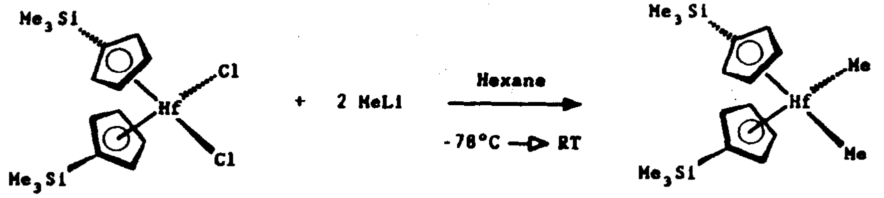
2 4 3

Scheme 1

observed at δ 7.6, -8.2, and -16.0 after 30 minutes. The signal at δ -8.2 is assigned to the borohydride-chloride product, $(Me_3SiCp)_2Hf(Cl)(BH_4)$, **2**, while the signal at δ 7.6 is assigned to the borohydride-hydride product, $(Me_3SiCp)_2Hf(H)(BH_4)$, **3**. The resonance at δ -16.0 (quintet, $J(B-H) = 86.0$ Hz) is attributed to the bis(borohydride) complex **4**, in agreement with the chemical shift of -16.5 ppm ($J(B-H) = 85$ Hz) reported for $Cp_2Hf(BH_4)_2$ [3]. After 1.5 h, the signal for the hydride complex, **3**, has grown considerably at the expense of the chloride complex, **2**, and after 17 h, complex **2** has disappeared completely, the major product now being **3**. After three days, the presumed intermediate **4** at δ -16.0 also has disappeared leaving only $(Me_3SiCp)_2Hf(H)(BH_4)$, **3**. It is believed that after initial formation of $(Me_3SiCp)_2Hf(Cl)(BH_4)$, **2**, the intermediate $(Me_3SiCp)_2Hf(BH_4)_2$, **4**, is formed by substitution of the second chloride with BH_4^- (Scheme 1). Apparently, this species is unstable in refluxing hexane and spontaneously loses BH_3 to yield the final product $(Me_3SiCp)_2Hf(H)(BH_4)$, **3**. Since each borohydride ligand likely bonds to the hafnium center through two hydride bridges (see ref. 4 for the neutron diffraction structure determination of the MeCp analog to **4**), facile loss of BH_3 to form the hydride complex certainly is plausible.

Preparation of bis(trimethylsilylcyclopentadienyl) dimethyl hafnium(IV)

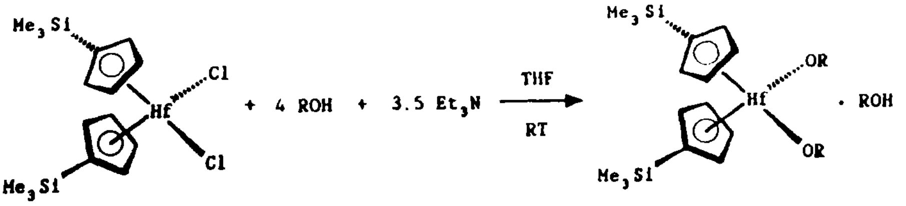
Reaction of $(Me_3SiCp)_2HfCl_2$, **1**, with two equivalents of methyllithium generated the dimethyl substituted product $(Me_3SiCp)_2Hf(CH_3)_2$, **5**, in 81% yield (Eq. 3).



(3)

1 5 81%

In this instance the two chloride ligands of **1** were cleanly replaced by two methyl substituents derived from the MeLi. Characterization of this new complex was straightforward with the exception of the field desorption mass spectrum which did not confirm the identity of the molecular ion; instead, a signal exhibiting the



(4)

1

6 R = Me 72%

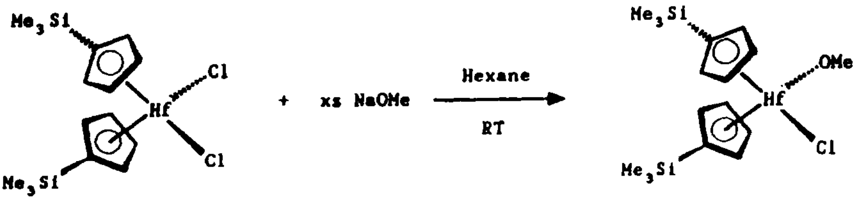
7 R = Et 61%

expected eight line isotope pattern for loss of CH_3 from the molecular ion was observed. The most striking feature of the ^1H NMR spectrum was the upfield shift relative to tetramethylsilane of the methyl singlet (δ −0.25), but this is in agreement with ^1H NMR spectra reported for Cp_2HfMe_2 and Cp_2ZrMe_2 [8].

Preparation of bis(trimethylsilylcyclopentadienyl)hafnium(IV) alkoxide complexes

In analogy to the preparation of hafnocene bis(alkoxides) [9], reaction of $(Me_3SiCp)_2HfCl_2$, **1**, with a two-fold excess of methanol or ethanol at room temperature in the presence of excess triethylamine generated the corresponding solvated bis(alkoxide) complexes $(Me_3SiCp)_2Hf(OMe)_2 \cdot MeOH$, **6**, or $(Me_3SiCp)_2Hf(OEt)_2 \cdot EtOH$, **7**, in good yields (Eq. 4). The compounds were isolated as volatile, clear oils which could be sublimed repeatedly (~100 °C and 0.07 mmHg) to liberate the alcohol of solvation. Subsequent characterization of the unsolvated complexes, $(Me_3SiCp)_2Hf(OMe)_2$, **8**, and $(Me_3SiCp)_2Hf(OEt)_2$, **9**, by the standard spectroscopic techniques was straightforward. In addition, these new complexes gave satisfactory carbon/hydrogen combustion analyses and field desorption mass spectra which showed the expected eight line isotope pattern corresponding to molecular ions at 516 and 544 amu, respectively. In both reactions, excess alcohol and triethylamine were found to be necessary to avoid the formation of inseparable mixtures of mono- and di-substituted alkoxide products.

In contrast to the reaction of $(Me_3SiCp)_2HfCl_2$, **1**, with excess methanol/triethylamine, reaction of **1** with excess sodium methoxide in hexane cleanly generated the singly substituted alkoxide complex $(Me_3SiCp)_2Hf(Cl)(OMe)$, **10**, in 91% yield (Eq. 5). The new compound tested positive for halogen by the Beilstein



(5)

1

10 91%

flame test and showed the expected eight line isotope pattern corresponding to the molecular ion at 520 amu in the field desorption mass spectrum. The ^1H NMR spectrum showed the methyl resonance at δ 3.88 (integrating to three protons), and the Cp resonances appeared as a complex multiplet in contrast to the Cp resonances of the disubstituted compounds, **8** or **9**, which each appeared as two triplets. Although reaction of **1** with excess NaOMe generated solely the mono-substituted product **10**, the corresponding reaction with NaOEt generated an inseparable mixture of mono- and di-substituted ethoxide products as indicated by ^1H NMR spectroscopy.

Experimental

General comments

Unless otherwise specified, all reactions and manipulations were carried out under prepurified tank argon. Hexane was distilled from lithium aluminum hydride and purged with argon prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and purged with argon prior to use. Ethyl alcohol and methyl alcohol were distilled from the respective magnesium alkoxides and purged with argon prior to use. Triethylamine was distilled from barium oxide and purged with argon prior to use. Lithium borohydride, sodium methoxide, and methyllithium (1.40 *M*) were purchased from Aldrich and used as received. Bis(trimethylsilylcyclopentadienyl) hafnium dichloride, $(Me_3SiCp)_2HfCl_2$, was prepared by a literature method [2].

^1H, ^{13}C, and ^{11}B (referenced to external $BF_3 \cdot Et_2O$) NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200, 50.3, and 64.2 MHz, respectively. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Field desorption mass spectra were completed by VG Instruments, Savannah Labs, using a VG 70-250 S/SE spectrometer. Isotope patterns were calculated with the Isotope Envelope Prediction Program using the following naturally occurring isotopes: ^1H, ^2H, ^{10}B, ^{11}B, ^{12}C, ^{13}C, ^{16}O, ^{17}O, ^{18}O, ^{28}Si, ^{29}Si, ^{30}Si, ^{35}Cl, ^{37}Cl, ^{174}Hf, ^{176}Hf, ^{177}Hf, ^{178}Hf, ^{179}Hf, and ^{180}Hf.

Synthesis of $(Me_3SiCp)_2Hf(Cl)(BH_4)$

To a 200 mL Schlenk flask was added 1.50 g (2.86 mmol) of $(Me_3SiCp)_2HfCl_2$ and 0.36 g (16.6 mmol) of $LiBH_4$ in a glove box. Outside of the glove box the flask was attached to a Schlenk line and subsequently charged with 80 mL of hexane by syringe. After stirring at room temperature for 2 d, the reaction mixture was filtered under argon and the solvent concentrated *in vacuo* to a few milliliters. The product, 0.95 g (1.89 mmol, 66%) of $(Me_3SiCp)_2Hf(Cl)BH_4$, **2**, crystallized out of solution as white needles, m.p.: 88–92 °C; subl: ~ 120 °C/0.07 mmHg. The solid tested positive for halogen by the Beilstein flame test.

Anal. Found: C, 38.19; H, 6.10. $C_{16}H_{30}BClHfSi_2$ calcd.: C, 38.18; H, 6.01%. ^1H NMR (C_6D_6): δ 0.30 (s, 18H, $Si(CH_3)_3$); 1.6 (broad rise in baseline, 4H, BH_4); 5.60, 5.79, 6.11, and 6.34 (all m, 8H, cyclopentadienyl H). ^{11}B NMR (hexane): δ −8.21 (quintet, $J(B-H) = 86.1$ Hz, BH_4). ^{13}C NMR (C_6D_6): δ 0.39 (q, $J(C-H) =$ 119.6 Hz, $Si(CH_3)_3$); 110.32 (dq, $J(C-H) = 173.7$ and 6.8 Hz, cyclopentadienyl CH); 111.95 (dq, $J(C-H) = 173.6$ and 6.7 Hz, cyclopentadienyl CH); 120.12 (s,

C-Si(CH$_3$)$_3$); 122.84 (dq, J(C–H) = 172.0 and 7.5 Hz, cyclopentadienyl CH); 125.31 (dq, J(C–H) = 176.2 and 7.5 Hz, cyclopentadienyl CH). FD (+) mass spectrum: M^+ at 504 with the expected eight line isotope pattern.

Synthesis of (Me$_3$SiCp)$_2$Hf(H)BH$_4$

To a 300 mL three necked, round bottom flask equipped with a reflux condenser and argon inlet (gas adapter), glass stopper, rubber septum, and stir bar was added 1.51 g (2.88 mmol) of (Me$_3$SiCp)$_2$HfCl$_2$ and 0.37 g (16.7 mmol) of LiBH$_4$ in a glove box. Outside of the glove box the flask was attached to a Schlenk line and subsequently charged with 30 mL of hexane by syringe. After heating at reflux for 4d, the reaction mixture was filtered under argon and the solvent subsequently removed to yield 1.22 g (2.59 mmol, 90%) of (Me$_3$SiCp)$_2$Hf(H)BH$_4$, **3**, as a white solid, m.p.: 60–62°C after sublimation at ~ 100°C/0.05 mmHg.

Anal. Found: C, 40.83; H, 6.38. $C_{16}H_{31}BHfSi_2$ calcd.: C, 40.98; H, 6.66%. ^1H NMR (C_6D_6): δ 0.26 (s, 18H, Si(CH$_3$)$_3$); 0.69 (broad q partially obstructed by SiMe$_3$ resonance, 4H, J(B–H) = 85.1 Hz, BH$_4$); 4.46 (m, 2H, cyclopentadienyl H); 5.69 (m, 6H, cyclopentadienyl H); 9.26 (s, 1H, Hf-H). ^{11}B NMR (hexane): δ 7.58 (quintet, J(B–H) = 84.8 Hz, BH$_4$). ^{13}C NMR (C_6D_6): δ 0.38 (q, J(C–H) = 119.3 Hz, Si(CH$_3$)$_3$); 106.11 (dq, J(C–H) = 172.4 and 6.8 Hz, cyclopentadienyl CH); 107.20 (dq, J(C–H) = 172.6 and 6.7 Hz, cyclopentadienyl CH); 108.27 (dq, J(C–H) = 171.5 and 7.9 Hz, cyclopentadienyl CH); 112.64 (dq, J(C–H) = 172.4 and 7.5 Hz, cyclopentadienyl CH); 117.53 (s, C-Si(CH$_3$)$_3$). FD (+) mass spectrum: M^+ at 470 with the expected eight line isotope pattern.

Synthesis of (Me$_3$SiCp)$_2$Hf(CH$_3$)$_2$

To a 100 mL Schlenk flask was added 1.50 g (2.87 mmol) of (Me$_3$SiCp)$_2$HfCl$_2$ in a glove box. Outside of the glove box the flask was attached to a Schlenk line, charged with 30 mL of hexane by syringe, and subsequently cooled to −78°C. Methyllithium (4.09 mL, 1.40 M, 5.73 mmol) was then added slowly by syringe, and the flask subsequently was warmed to room temperature by removal of the cold bath. After stirring at room temperature for 18h, the reaction mixture was filtered under argon and the solvent removed to yield 1.13 g (2.33 mmol, 81%) of (Me$_3$SiCp)$_2$Hf(CH$_3$)$_2$, **5**, as a white solid, m.p.: 35–41°C after sublimation at ~ 70°C/0.02 mmHg.

Anal. Found: C, 44.56; H, 6.81. $C_{18}H_{32}HfSi_2$ calcd.: C, 44.75; H, 6.68%. ^1H NMR (C_6D_6): δ −0.25 (s, 6H, Hf(CH$_3$)$_2$); 0.19 (s, 18H, Si(CH$_3$)$_3$); 5.88 (t, J = 2.4 Hz, 4H, cyclopentadienyl H); 6.03 (t, J = 2.4 Hz, 4H, cyclopentadienyl H). ^{13}C NMR (C_6D_6): δ 0.27 (q, J(C–H) = 119.1 Hz, Si(CH$_3$)$_3$); 37.0 (q, J(C–H) = 115.1 Hz, Hf(CH$_3$)$_2$); 113.04 (dq, J(C–H) = 170.9 and 6.6 Hz, cyclopentadienyl CH); 118.22 (s, C-Si(CH$_3$)$_3$); 117.88 (dq, J(C–H) = 170.7 and 7.6 Hz, cyclopentadienyl CH). FD (+) mass spectrum: $M^+ -$ CH$_3$ at 469 with the expected eight line isotope pattern.

Synthesis of (Me$_3$SiCp)$_2$Hf(OEt)$_2$

To a 100 mL Schlenk flask was added 1.00 g (1.90 mmol) of (Me$_3$SiCp)$_2$HfCl$_2$ in a glove box. Outside of the glove box the flask was attached to a Schlenk line and successively charged with 30 mL of THF, 0.45 mL (7.60 mmol) of ethanol, and 0.79 mL (5.70 mmol) of triethylamine by syringe. After the reaction mixture stirred for 2 h at room temperature, the solvent was removed *in vacuo* to yield a white solid. Extraction with hexane (4 × 10 mL), filtration under argon, and removal of solvent gave 0.67 g (1.17 mmol, 61%) of $(Me_3SiCp)_2Hf(OEt)_2 \cdot EtOH$, **7**, as the a clear oil. The ethanol of solvation (δ 1.14 and 3.55 in the ^1H NMR spectrum) could be removed by repeated sublimation at ~ 110 °C/0.07 mmHg to give analytically pure $(Me_3SiCp)_2Hf(OEt)_2$, **9**.

Anal. Found: C, 44.18; H, 6.91. $C_{20}H_{36}HfO_2Si_2$ calcd.: C, 44.23; H, 6.68%. ^1H NMR (acetone-d_6): δ 0.22 (s, 18H, $Si(CH_3)_3$); 1.08 (*t*, $J = 6.9$ Hz, 6H, OCH_2CH_3); 4.01 (q, 4H, $J = 6.9$ Hz, OCH_2CH_3); 6.32 (t, $J = 2.5$ Hz, 4H, cyclopentadienyl H); 6.45 (t, $J = 2.5$ Hz, 4H, cyclopentadienyl H). ^{13}C NMR (acetone-d_6): δ 0.05 (q, J(C–H) = 118.9 Hz, $Si(CH_3)_3$); 20.53 (q, J(C–H) = 124.9 Hz, OCH_2CH_3); 68.03 (t, J(C–H) = 138.6 Hz, OCH_2CH_3); 112.84 (dq, J(C–H) = 169.6 and 6.8 Hz, cyclopentadienyl CH), 120.14 (dq, J(C–H) = 169.7 and 7.6 Hz, cyclopentadienyl CH); 121.50 (s, C–$Si(CH_3)_3$). FD (+) mass spectrum: M^+ at 544 with the expected eight line isotope pattern.

Synthesis of $(Me_3SiCp)_2Hf(OMe)_2$

To a 100 mL Schlenk flask was added 1.00 g (1.91 mmol) of $(Me_3SiCp)_2HfCl_2$ in a glove box. Outside of the glove box the flask was attached to a Schlenk line and successively charged with 20 mL of THF, 0.31 mL (7.63 mmol) of methanol, and 0.80 mL (5.72 mmol) of triethylamine by syringe. After the reaction mixture was stirred for 1 h at room temperature, the solvent was removed *in vacuo*. Extraction with hexane (4 × 10 mL), filtration under argon, and removal of solvent gave 0.75 g (1.37 mmol, 72%) of $(Me_3SiCp)_2Hf(OMe)_2 \cdot MeOH$, **6**, as a clear oil. The methanol of solvation (δ 3.29 in the ^1H NMR spectrum) could be removed by repeated sublimation at ~ 95 °C/0.07 mmHg to give analytically pure $(Me_3SiCp)_2Hf(OMe)_2$, **8**.

Anal. Found: C, 41.69; H, 6.32. $C_{18}H_{32}HfO_2Si_2$ calcd.: C, 41.97; H, 6.26%. ^1H NMR (acetone-d_6): δ 0.20 (s, 18H, $Si(CH_3)_3$); 3.80 (s, 6H, OCH_3); 6.34 (t, $J = 2.4$ Hz, 4H, cyclopentadienyl H); 6.45 (t, $J = 2.5$ Hz, 4H, cyclopentadienyl H). ^{13}C NMR (acetone-d_6): δ −0.11 (q, J(C–H) = 119.0 Hz, $Si(CH_3)_3$); 60.32 (q, J(C–H) = 138.5 Hz, OCH_3); 112.90 (dq, J(C–H) = 169.7 and 6.7 Hz, cyclopentadienyl CH); 119.77 (dq, J(C–H) = 169.6 and 7.5 Hz, cyclopentadienyl CH). FD (+) mass spectrum: M^+ at 516 with the expected eight line isotope pattern.

Synthesis of $(Me_3SiCp)_2Hf(Cl)(OMe)$

To a 100 mL Schlenk flask was added 1.00 g (1.91 mmol) of $(Me_3SiCp)_2HfCl_2$ and 0.31 g (5.72 mmol) of NaOMe in a glove box. Outside of the glove box the flask was attached to a Schlenk line and subsequently charged with 30 mL of hexane by syringe. After stirring at room temperature for 3.5 d, the reaction mixture was filtered under argon and the solvent subsequently removed to yield 0.90 g (1.73 mmol, 91%) of $(Me_3SiCp)_2Hf(Cl)(OMe)$, **10**, as a clear oil which solidified to a white solid (m.p.: 33.5–38.5 °C after sublimitation at ~ 70 °C/0.07 mmHg) over a period of several days. The product tested positive for halogen by the Beilstein flame test.

Anal. Found: C, 39.83; H, 5.41. $C_{18}H_{33}ClHfO_2Si_2$ calcd.: C, 39.30; H, 5.62%. ^1H NMR (acetone-d_6): δ 0.23 (s, 18H, $Si(CH_3)_3$); 3.88 (s, 3H, OCH_3); 5.95–6.55 (m, 8H, cyclopentadienyl H). ^{13}C NMR (acetone-d_6): δ 0.04 (q, J(C–H) = 119.4 Hz,

$Si(CH_3)_3$); 62.25 (q, J(C–H) = 140.2 Hz, OCH_3); 114.07 (dq, J(C–H) = 172.0 and 6.0 Hz, cyclopentadienyl CH); 117.66 (s, C-$Si(CH_3)_3$); 122.00 (dq, J(C–H) = 171.5 and 7.6 Hz, cyclopentadienyl CH); 123.60 (dq, J(C–H) = 171.9 and 7.6 Hz, cyclopentadienyl CH). FD (+) mass spectrum: M^+ at 520 with the expected eight line isotope pattern.

Reaction of $(Me_3SiCp)_2HfCl_2$ *with excess NaOEt*

To a 100 mL Schlenk flask was added 1.00 g (1.91 mmol) of $(Me_3SiCp)_2HfCl_2$ and 0.39 g (5.72 mmol) of NaOEt in a glove box. Outside of the glove box the flask was attached to a Schlenk line and subsequently charged with 30 mL of hexane by syringe. After stirring at room temperature for 3.5 d, the reaction mixture was filtered under argon and the solvent subsequently removed to yield 0.94 g of a cloudy, yellow oil identified by its ^1H NMR spectrum to be a mixture of $(Me_3SiCp)_2Hf(OEt)_2$, **9**, and $(Me_3SiCp)_2Hf(Cl)(OEt)$, **11**. The product mixture tested positive for halogen by the Beilstein flame test.

^1H NMR (acetone-d_6): δ 0.22 (s, $Si(CH_3)_3$, **9**), 0.24 (s, $Si(CH_3)_3$, **11**); 1.08 (t, $J = 6.9$ Hz, CH_2CH_3, **9**), 1.10 (t, $J = 6.9$ Hz, CH_2CH_3, **11**); 4.01 (q, $J = 6.9$ Hz, CH_2CH_3, **9**), 4.11 (q, $J = 6.9$ Hz, CH_2CH_3, **11**); 6.3–6.6 (m, cyclopentadienyl H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 0.09 (s, $Si(CH_3)_3$, **9**) 0.20 (s, $Si(CH_3)_3$, **11**); 19.64 (s, CH_2CH_3, **11**), 20.52 (s, CH_2CH_3, **9**); 68.01 (s, CH_2CH_3, **9**), 69.97 (s, CH_2CH_3, **11**); 112.86 (s, cyclopentadienyl CH, **9**), 113.64 (s, cyclopentadienyl CH, **11**); 113.97 (s, cyclopentadienyl CH, **11**), 120.16 (s, cyclopentadienyl CH, **9**); 121.45 (s, cyclopentadienyl CH, **9**); 122.90 (s, cyclopentadienyl CH, **11**); 123.27 (s, cyclopentadienyl CH, **11**).

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