

Allyldimethylsilylcyclopentadienyl Hafnium Complexes: Formation and Trapping of Hafnocenium Cations

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The mixed silyl-stannyl-cyclopentadiene $C_5H_4[SiMe_2(CH_2CH=CH_2)][Sn(nBu)_3]$ was synthesized by reaction of the lithium salt $Li[C_5H_4\{SiMe_2(CH_2CH=CH_2)\}]$ with the corresponding chlorotrialkyltin and then reacted with $HfCl_4$ to prepare the monocyclopentadienyl complex $[Hf\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}Cl_3 \cdot DME]$ (DME = dimethoxyethane). Reaction of this compound with $Na(C_5H_5)$ or $Li(C_5H_5)$ afforded low yields of the dichloro hafnocene $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}Cl_2]$, which was also isolated more efficiently by transmetalation of the lithium salt $Li[C_5H_4\{SiMe_2(CH_2CH=CH_2)\}]$ with $[Hf(\eta^5-C_5H_5)Cl_3 \cdot DME]$. Alkylation of the mono- and dicyclopentadienyl complexes with $MgCl(CH_2Ph)$ or $LiMe$ gave the tribenzyl monocyclopentadienyl $[Hf\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}(CH_2Ph)_3]$ or the dialkyl hafnocene derivatives $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}R_2]$ ($R = Me, CH_2Ph$). The reaction of the dibenzyl hafnocene with the Lewis acid $B(C_6F_5)_3$ was monitored by NMR spectroscopy at variable temperature. Formation of the hafnocenium cationic species $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}(CH_2Ph)]^+$ was initially observed, which then slowly transformed into the metallacyclic alkyl $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2CH_2CH(CH_2Ph)-\eta^1-CH_2\}]^+$ cation, resulting from the benzyl migratory insertion of the allylic alkene moiety. Reaction of these intermediate cationic species with $KOtBu$ gave the neutral dicyclopentadienyl hafnocene compounds $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}(CH_2Ph)(OtBu)]$ and $[Hf(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2[CH_2CH(CH_2Ph)-\eta^1-CH_2]\}(OtBu)]$, which were characterized by elemental analyses and NMR spectroscopy.

Introduction

Group 4 metallocenes are well-known precursors for single-site alkene polymerization catalysts.^{1–9} The active metal alkyl cation is formed by reaction of these precursors with different alkylating agents and strong Lewis acid activators^{10–21} (MAO, $B(C_6F_5)_3$, $[CPh_3]-[B(C_6F_5)_4]$). Alkene coordination to the metal alkyl

cation followed by alkyl migration to the coordinated alkene is the generally accepted mechanism of propagation. Studies of the group 4 metallocene alkyl-alkene cations $[MCp_2R(alkene)]^+$ have generated a great deal of interest because the cations are key intermediates in metallocene-catalyzed alkene polymerization. Many efforts have been made to evaluate the kinetic barriers for alkene complexation, inversion at the metal, and migratory alkene insertion into the metal–alkyl bond. Models required for these studies have been based on d^0 neutral yttrium^{22–24} and cationic zirconium metallocenes with chelating alkoxy-alkene^{25–27} and alkyl-

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alkene^{28–34} ligands, which provide additional stability to the weak metal–alkene interaction, which lacks d– π^* back-donation. These species show a highly polarized and unsymmetrically coordinated alkene with a partial positive charge on the internal olefinic carbon.

We reported³⁵ that formation of the cationic species $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}(\text{CH}_2\text{Ph})]^+$ was stabilized by the β -Si substituent of the allylsilyl alkene tethered to one of the cyclopentadienyl ligands, which favors a partial positive charge on the internal olefinic carbon³⁶ of the d⁰ metal–alkene complex. This effect was verified more recently^{37,38} by comparing the coordination of allyltrimethylsilane and 4,4-dimethyl-1-pentene to $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{OtBu})(\text{ClCD}_2\text{Cl})]^+$, which shows additional stabilization against insertion due to the presence of the alkoxo ligand.

Similar studies were also reported³⁹ for related neutral titanium and zirconium dialkyl compounds and their cationic derivatives $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{R}]^+$ (M = Ti, R = Me, CH₂Ph; M = Zr, R = Me), although kinetic parameters could not be evaluated.

In this paper we describe the synthesis and characterization of new monocyclopentadienyl hafnium complexes $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\text{X}_3]$ (X = Cl, CH₂-Ph) and neutral hafnocenes $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\text{X}_2]$ (X = Cl, Me, CH₂Ph), studies related to the formation of the cationic hafnocenium species $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}(\text{CH}_2\text{Ph})]^+[(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})\text{-}\eta^1\text{-CH}_2\}]^+[(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3]^-$ between –80 and –20 °C, and their trapping and characterization as the neutral *tert*-butyl alkoxides $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}(\text{CH}_2\text{Ph})(\text{OtBu})]$ and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})\text{-}\eta^1\text{-CH}_2\}(\text{OtBu})]$.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or an M. Braun drybox. Solvents used were previously dried and freshly distilled under argon. Deuterated solvents from Scharlau were degassed, dried, and stored over molecular sieves. SiMe₂(CH₂CH=CH₂)Cl, Sn(*n*Bu)₃Cl, Mg(CH₂-Ph)Cl, *n*BuLi, MeLi, HfCl₄, KOTf, and SiMe₂ were obtained from commercial sources and used as received with the exception of Sn(*n*Bu)₃Cl, which was previously distilled. Na-

(C₅H₅)₄⁴⁰ B(C₆F₅)₃⁴¹ and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3\cdot\text{DME}]$ ⁴² were isolated by reported methods. ¹H and ¹³C NMR spectra were recorded on a Varian Unity VXR-300 or Varian Unity 500 Plus instrument. Chemical shifts, (δ) in ppm, are measured relative to residual ¹H and ¹³C resonances for C₆H₆-d₆, CHCl₃-d₁, and CH₂-Cl₂-d₂ used as solvents and coupling constants are in Hz. C, H analyses were carried out with a Perkin-Elmer 240-C analyzer.

Synthesis of $[\text{C}_5\text{H}_4\{\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\{\text{Sn}(\text{nBu})_3\}]$ (1). Sn(*n*Bu)₃Cl (5.63 mL, 15.00 mmol) was slowly added at 0 °C to a suspension of Li[C₅H₄{SiMe₂(CH₂CH=CH₂)}] (3.00 g, 17.60 mmol) in hexane (150 mL). The mixture was stirred overnight. After filtration to remove LiCl, the solvent was removed under vacuum to give **1** as a yellow viscous liquid (6.10 g, 13.46 mmol, 89%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.11 (s, 6H, Si(CH₃)₂), 0.88 (m, 9H, –CH₃(*n*Bu)), 1.29 (m, 6H, –CH₂-(*n*Bu)), 1.42 (m, 12H, –CH₂-(*n*Bu)), 1.50 (d, 2H, *J* = 8.2, SiCH₂), 4.82 (2m, 2H, =CH₂), 5.70 (m, 1H, CH=), 6.14 (m, 2H, C₅H₄), 6.59 (m, 2H, C₅H₄).

Synthesis of $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\text{Cl}_3\cdot\text{DME}]$ (2). Dimethyl sulfide (1.64 mL, 22.33 mmol) was added at room temperature to a stirred suspension of HfCl₄ (3.57 g, 11.16 mmol) in 150 mL of dichloromethane. The resulting clear solution was then treated dropwise with **1** (4.98 g, 11.00 mmol). The reaction mixture was stirred for 18 h, and then DME (2.00 mL, 19.10 mmol) was added and stirred for an additional 1 h. The suspension was filtered, and the solvent was removed under reduced pressure. The residue was washed with hexane (4 × 20 mL) and dried under vacuum to yield **2** as a grayish white solid (3.51 g, 6.52 mmol, 59%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.58 (s, 6H, Si(CH₃)₂), 1.88 (d, 2H, *J* = 8.4, SiCH₂), 3.00–3.40 (m, 10H, DME), 4.80 (m, 2H, =CH₂), 5.82 (m, 1H, CH=), 6.34 (m, 2H, C₅H₄), 6.60 (m, 2H, C₅H₄). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ –2.1 (Si(CH₃)₂), 25.3 (SiCH₂), 60.0–70.0 (DME), 113.4 (=CH₂), 120.0 (C₅H₄), 124.1 (C₅H₄), 126.4 (C_{ipso}-Si C₅H₄), 135.3 (CH=). Anal. Calcd for C₁₄H₂₅SiO₂Cl₃Hf: C, 31.24; H, 4.68. Found: C, 31.22; H, 4.67.

Synthesis of $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}(\text{CH}_2\text{Ph})_3]$ (3). A 2 M THF solution of MgCl(CH₂Ph) (1.40 mL, 2.90 mmol) was added at –78 °C to a solution of **2** (0.50 g, 0.98 mmol) in Et₂O (20 mL), and the suspension was stirred for 18 h while warming slowly to room temperature. After filtration the solvent was removed under reduced pressure, and the residue was extracted into hexane (40 mL) to separate the white insoluble solid. The solvent was removed under reduced pressure and the residue dried under vacuum to give **3** as a yellow oily solid (0.19 g, 0.32 mmol, 33%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.16 (s, 6H, Si(CH₃)₂), 1.58 (d, 2H, *J* = 8.3, SiCH₂), 1.64 (s(a), 6H, CH₂Ph), 4.90 (m, 2H, =CH₂), 5.68 (m, 2H, C₅H₄), 5.69 (m, 1H, CH=), 5.96 (m, 2H, C₅H₄), 6.70, 6.86–7.26 (3m, 15H, C₆H₅). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ –2.3 (Si(CH₃)₂), 25.1 (SiCH₂), 69.7 (CH₂Ph), 114.1 (=CH₂), 117.5 (C₅H₄), 118.6 (C₅H₄), 125.6 (C_{ipso}-Si C₅H₄), 126.1 (C_{para} C₆H₅), 128.7 (C_{meta} C₆H₅), 129.2 (C_{ortho} C₆H₅), 134.2 (CH=), 144.2 (C_{ipso} C₆H₅). Anal. Calcd for C₃₁H₃₆SiHf: C, 60.52; H, 5.90. Found: C, 59.88; H, 5.09.

Synthesis of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\text{Cl}_2]$ (4). A THF (20 mL) solution of Li[C₅H₄{SiMe₂(CH₂CH=CH₂)}] (3.35 g, 19.7 mmol) was added dropwise to a suspension of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3\cdot\text{DME}]$ (8.70 g, 19.7 mmol) in THF (40 mL) at –78 °C. The cooling bath was removed, and the reaction mixture was stirred for 18 h at room temperature. After solvent removal under vacuum the residue was extracted into toluene (150 mL) and the solution was concentrated to 10 mL and treated with hexane (80 mL) to give **4** as a colorless crystalline solid, which was separated by filtration and dried

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under vacuum (5.70 g, 12.90 mmol, 65%). ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.34 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.69 (d, 2H, $J_{\text{H-H}} = 8.1$, SiCH_2), 4.90 (2m, 2H, $=\text{CH}_2$), 5.73 (m, 1H, $\text{CH}=\text{}$), 5.80 (m, 2H, C_5H_4), 5.86 (s, 5H, C_5H_5), 6.25 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 0.31 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.69 (d, 2H, $J_{\text{H-H}} = 8.1$, SiCH_2), 4.82 (2m, 2H, $=\text{CH}_2$), 5.71 (m, 1H, $\text{CH}=\text{}$), 6.34 (s, 5H, C_5H_5), 6.43 (m, 2H, C_5H_4), 6.59 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ -2.4 ($\text{Si}(\text{CH}_3)_2$), 24.9 (SiCH_2), 113.9 ($=\text{CH}_2$), 114.4 (C_5H_5), 114.7 (C_5H_4), 114.9 ($\text{C}_{\text{ipso-Si}} \text{C}_5\text{H}_4$), 124.3 (C_5H_4), 134.6 ($\text{CH}=\text{}$). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{SiCl}_2\text{Hf}$: C, 37.73; H, 4.23. Found: C, 37.17; H, 4.10.

Synthesis of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})_2]$ (5). A 2 M THF solution of $\text{MgCl}(\text{CH}_2\text{Ph})$ (2.30 mL, 4.60 mmol) was added at -78 °C to a solution of **4** (1.04 g, 2.10 mmol) in Et_2O (50 mL), and the suspension was stirred for 18 h while warming slowly to room temperature. After filtration the solvent was removed under reduced pressure and the residue extracted with hexane to separate the white insoluble solid. The solution was concentrated to 20 mL and cooled to -35 °C. Complex **5** was collected as a yellow solid and dried under vacuum (0.42 g, 0.70 mmol, 45%). ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.05 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.69 (m, 4H, HfCH_2), 1.74 (d, 2H, $J_{\text{H-H}} = 7.9$, SiCH_2), 4.88 (2m, 2H, $=\text{CH}_2$), 5.58 (m, 1H, $\text{CH}=\text{}$), 5.61 (s, 5H, C_5H_5), 5.79 (m, 2H, C_5H_4), 5.82 (m, 2H, C_5H_4), 6.93 (m, 6H, H_{meta} , H_{para} C_6H_5), 7.26 (m, 4H, H_{ortho} C_6H_5). ^{13}C NMR (500 MHz, CD_2Cl_2 , 25 °C): δ 0.27 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.54 (d, 2H, $J_{\text{H-H}} = 10.7$, HfCH_2), 1.61 (d, 2H, $J_{\text{H-H}} = 10.7$, HfCH_2), 1.67 (d, 2H, $J_{\text{H-H}} = 7.9$, SiCH_2), 4.89 (m, 2H, $=\text{CH}_2$), 5.75 (m, 1H, $\text{CH}=\text{}$), 5.89 (s, 5H, C_5H_5), 6.04 (m, 2H, C_5H_4), 6.20 (m, 2H, C_5H_4), 6.83 (m, 2H, H_{para} C_6H_5), 6.84 (m, 4H, H_{meta} C_6H_5), 7.21 (m, 4H, H_{ortho} C_6H_5). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ -2.5 ($\text{Si}(\text{CH}_3)_2$), 25.1 (SiCH_2), 65.3 (CH_2Ph), 111.8 (C_5H_5), 113.1 ($=\text{CH}_2$), 114.1 ($\text{C}_{\text{ipso-Si}} \text{C}_5\text{H}_4$), 116.0 (C_5H_4), 119.9 (C_5H_4), 121.7, 126.7, 128.5 (C_6H_5), 134.3 ($\text{CH}=\text{}$), 152.5 ($\text{C}_{\text{ipso}} \text{C}_6\text{H}_5$). Anal. Calcd for $\text{C}_{29}\text{H}_{34}\text{SiHf}$: C, 59.02; H, 5.97. Found: C, 59.23; H, 6.00.

Synthesis of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{Me}_2)]$ (6). A 1.6 M Et_2O solution of methylolithium (2.60 mL, 4.20 mmol) was added at -78 °C to a solution of **4** (1.04 g, 2.00 mmol) in Et_2O (20 mL). The reaction mixture was stirred for 18 h while it was warmed slowly to room temperature. The solvent was removed under vacuum, and the residue was extracted into hexane (30 mL). After solvent removal under reduced pressure the residue was washed with cold hexane (-78 °C) and complex **6** (0.43 g, 0.98 mmol, 45%) was obtained as a colorless oily solid, which could not be crystallized. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ -0.29 (s, 6H, HfMe_2), 0.14 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.58 (d, 2H, $J_{\text{H-H}} = 7.9$, SiCH_2), 4.92 (2m, 2H, $=\text{CH}_2$), 5.38 (m, 2H, C_5H_4), 5.63 (m, 1H, $\text{CH}=\text{}$), 5.71 (s, 5H, C_5H_5), 5.90 (m, 2H, C_5H_4). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ -2.5 ($\text{Si}(\text{CH}_3)_2$), 25.3 (SiCH_2), 36.9 (HfMe_2), 110.1 (C_5H_5), 110.3 (C_5H_4), 113.6 ($=\text{CH}_2$), 113.7 ($\text{C}_{\text{ipso-Si}} \text{C}_5\text{H}_4$), 129.3 (C_5H_4), 134.8 ($\text{CH}=\text{}$). Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{SiHf}$: C, 46.35; H, 6.05. Found: C, 46.72; H, 5.99.

NMR Characterization of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})]$ [$(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3$] (7) and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})\text{-}\eta^1\text{-CH}_2]\}[(\text{CH}_2\text{-Ph})\text{B}(\text{C}_6\text{F}_5)_3]$ (8). An equimolar mixture of **5** (20.00 mg, 0.037 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (19.00 mg, 0.037 mmol) was charged into a Teflon-valved NMR tube, and after being cooled to -78 °C CD_2Cl_2 was transferred under vacuum to give complex **7**. ^1H NMR (500 MHz, CD_2Cl_2 , -80 °C): δ 0.27 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.52 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 2.19 (m, 2H, SiCH_2), 2.38 (m, 1H, $=\text{CHH}_{\text{trans}}$), 2.59 (d, 1H, $J_{\text{H-H}} = 10.7$, HfCH_2), 2.69 (s, b., CH_2B), 2.97 (d, 1H, $J_{\text{H-H}} = 10.7$, HfCH_2), 3.39 (m, 1H, $=\text{CHH}_{\text{cis}}$), 5.36 (m, 1H, C_5H_4), 6.07 (s, 5H, C_5H_5), 6.29 (m, 1H, C_5H_4), 6.63 (m, 1H, C_5H_4), 6.65 (m, 1H, C_5H_4), 7.35 (m, 1H, $\text{CH}_2=\text{}$), 6.61, 6.80-6.90, 7.09-7.15, 7.20, 7.50 (C_6H_5). ^{13}C NMR (75 MHz, CD_2Cl_2 , -80 °C): δ 1.3 ($\text{Si}(\text{CH}_3)_2$), 2.1 ($\text{Si}(\text{CH}_3)_2$), 28.1 (SiCH_2), 45.7 (HfCH_2), 92.3 ($=\text{CH}_2$), 109.2 (C_5H_5), 108.2, 108.5, 110.0, 112.5, 114.6, 118.5, 118.9, 119.7, 149.1 ($\text{C}_5\text{H}_4+\text{C}_6\text{H}_5$), 171.1 ($\text{CH}=\text{}$).

^{19}F NMR (CD_2Cl_2 , -80 °C): δ -169.3 (*m*-F), -164.9 (*p*-F), -120.9 (*o*-F).

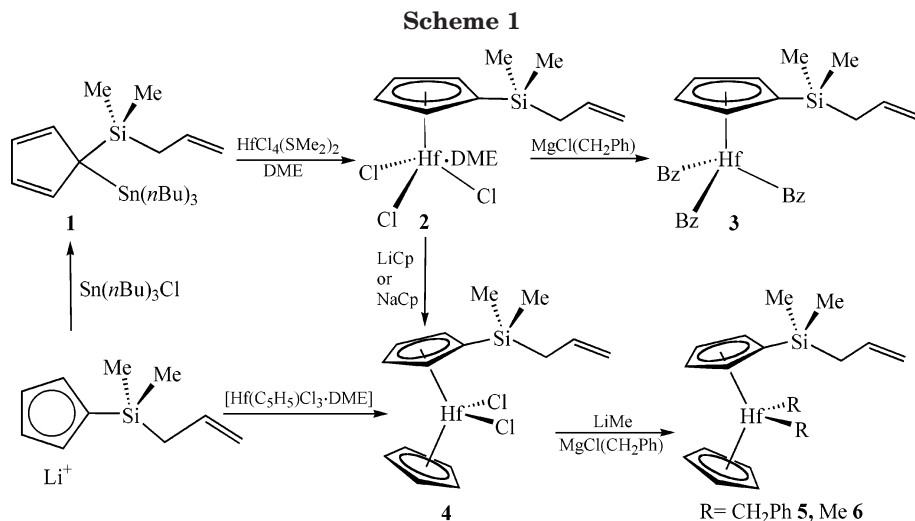
This reaction mixture was heated to -40 °C, kept for 1 h at this temperature, and then heated to -20 °C to give complex **8** as a mixture of two diastereomers, **8a** and **8b**. ^1H NMR (500 MHz, CD_2Cl_2 , -20 °C): δ 0.08×bb/0.07^b (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.24×bb^b (m, 1H, HfCH_2), 0.27×bb/0.26^b (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.99×bb^b (m, 2H, SiCH_2), 1.44×bb^b (m, 1H, HfCH_2), 1.93×bb^b (m, 1H, CH), 2.24×bb^b (m, 1H, CH_2Ph), 2.78×bb^b (s.a, 2H CH_2B), 2.84×bb^b (m, 1H, CH_2Ph), 5.92×bb/5.96^b (s, 5H, C_5H_5), 6.18×bb/6.02^b (m, 1H^a, 2H^b, C_5H_4), 6.22×bb/6.46^b (m, 1H^a, 2H^b, C_5H_4), 6.57×bb^b (m, 1H, C_5H_4), 6.63×bb^b (m, 1H, C_5H_4), 6.80×bb/7.40^b (m, 15H, C_6H_5). ^{13}C NMR (75 MHz, CD_2Cl_2 , -20 °C): δ -4.8^a/4.9^b ($\text{Si}(\text{CH}_3)_2$), 0.3^{a,b} ($\text{Si}(\text{CH}_3)_2$), 24.8×bb^b (SiCH_2), 30.2^{a,b} (CH_2B), 42.3×bb/42.6^b (CH), 52.5×bb/52.6^b (CH_2Ph), 78.7^a/78.9^b (CH_2Hf), 110.2^a/110.3^b (C_5H_4), 114.0^a/114.1^b (C_5H_4), 114.2×bb^b (C_5H_4), 114.3×bb^b (C_5H_4), 114.5, 122.2, 122.5, 122.9, 123.0, 126.9, 128.3, 128.6, 129.4, ^{a,b}(C_5H_6), 141.5×bb/141.6^b($\text{C}_{\text{ipso}} \text{C}_5\text{H}_6$). ^{19}F NMR (CD_2Cl_2 , -20 °C): δ -167.3 (*m*-F), -164.3 (*p*-F), -120.9 (*o*-F).

Synthesis of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})(\text{OtBu})]$ (9). Toluene (20 mL) was added at -78 °C to a mixture of **5** (0.24 g, 0.40 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.21 g, 0.40 mmol), and the reaction mixture was stirred for an additional 1 h at this temperature. The resulting clear yellow solution was then treated with a THF solution of KOtBu (0.40 mL, 0.40 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The solvent was removed at reduced pressure, and the residue was extracted into hexane (20 mL). After filtration, the solvent was removed at reduced pressure and the residue was dried under vacuum to give a yellow oily solid characterized as **9** (0.09 g, 0.15 mmol, 42%). ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 0.23 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.25 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 1.07 (s, 9H, $t\text{BuO}$), 1.61 (d, 2H, $J = 7.9$, SiCH_2), 2.13 (d, 1H, $J = 11.4$, CH_2Ph), 2.32 (d, 1H, $J = 11.4$, CH_2Ph), 4.93 (m, 2H, $=\text{CH}_2$), 5.70 (m, 1H, $\text{CH}=\text{}$), 5.74 (s, 5H, C_5H_5), 5.81 (m, 1H, C_5H_4), 5.92 (m, 2H, C_5H_4), 5.95 (m, 1H, C_5H_4), 6.99 (m, 1H, H_{para} C_6H_5), 7.16 (m, 2H, H_{meta} C_6H_5), 7.30 (m, 2H, H_{ortho} C_6H_5). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ -1.9 ($\text{Si}(\text{CH}_3)_2$), -1.8 ($\text{Si}(\text{CH}_3)_2$), 25.6 (SiCH_2), 32.3 ($\text{CMe}_3\text{-}t\text{Bu}$), 50.3 ($\text{CMe}_3\text{-}t\text{Bu}$), 70.8 (CH_2Ph), 110.4 (C_5H_5), 112.3 ($=\text{CH}_2$), 114.5 ($\text{C}_{\text{ipso-Si}} \text{C}_5\text{H}_4$), 119.9 (C_5H_4), 121.2 (C_5H_4), 121.5 (C_5H_4), 125.6 (C_5H_4), 126.1 (C_{para} C_6H_5), 128.5 (C_{ortho} C_6H_5), 128.7 (C_{meta} C_6H_5), 134.7 ($=\text{CH}$), 154.2 ($\text{C}_{\text{ipso}} \text{C}_6\text{H}_5$). Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{SiOHf}$: C, 54.70; H, 6.30. Found: C, 53.83; H, 6.24.

Synthesis of $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})\text{-}\eta^1\text{-CH}_2]\}(\text{OtBu})]$ (10). The same procedure described to prepare **9** was followed using **5** (0.24 g, 0.40 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.21 g, 0.40 mmol). The reaction mixture was stirred for an additional 2 h at -20 °C, and then a THF solution of KOtBu (0.40 mL, 0.40 mmol) was added to give **10** as a yellow-orange oil (0.06 g, 0.12 mmol, 30%). ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 0.06 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.21 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.40 (m, 1H, CH_2Hf), 0.75 (m, 1H, SiCH_2), 0.90 (m, 1H, SiCH_2), 1.02 (m, 9H, $t\text{BuO}$), 1.25 (m, 1H, CH_2Hf), 2.05 (m, 1H, CH), 2.65 (q, 1H, $J = 13.1$, 11.8, CH_2Ph), 2.80 (q, 1H, $J = 13.1$, 11.8, CH_2Ph), 5.28 (m, 1H, C_5H_4), 5.68 (m, 5H, C_5H_5), 5.90 (m, 1H, C_5H_4), 5.93 (m, 1H, C_5H_4), 6.20 (m, 1H, C_5H_4), 6.99 (m, 2H, H_{meta} C_6H_5), 7.05 (m, 1H, H_{para} C_6H_5), 7.25 (m, 2H, H_{ortho} C_6H_5). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ -3.6 (SiCH_3), 0.6 (SiCH_3), 24.8 (SiCH_2), 31.7 ($\text{CMe}_3\text{-}t\text{Bu}$), 38.1 (CH), 50.1 ($\text{CMe}_3\text{-}t\text{Bu}$), 50.7 (HfCH_2), 54.3 (CH_2Ph), 105.4 (C_5H_4), 109.8 (C_5H_5), 115.1 (C_5H_4), 115.8 (C_5H_4), 119.6 (C_5H_4), 126.1 (C_{meta} C_6H_5), 129.2 (C_{para} C_6H_5), 129.9 (C_{ortho} C_6H_5), 140.2 ($\text{C}_{\text{ipso-Si}} \text{C}_5\text{H}_4$), 140.2 ($\text{C}_{\text{ipso}} \text{C}_6\text{H}_5$). Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{SiOHf}$: C, 54.70; H, 6.30. Found: C, 53.21; H, 5.90.

Results and Discussion

Mixed metallocenes containing two different cyclopentadienyl rings may be prepared by any of the two



alternative methods based on reactions of monocyclopentadienylmetal halides with a cyclopentadienyl-transfer reagent. Reactions of either $[M\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_3]$ with $\text{Li}(\text{C}_5\text{R}_5)$ and $\text{Na}(\text{C}_5\text{R}_5)$ or $[M(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3]$ with $\text{Li}[\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ may therefore be appropriate methods to isolate the group 4 metallocenes $[M(\eta^5\text{-C}_5\text{R}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$. The monocyclopentadienyl titanium complex was isolated³⁹ by dechlorosilylation of the symmetric disilylcyclopentadiene $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]_2$ with TiCl_4 , whereas a similar reaction of the asymmetric $\text{C}_5\text{H}_4[\text{SiMe}_3][\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ was not a convenient method, as it afforded a mixture of the two possible desilylation products, $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_3]$ and $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_3]$. However no reaction was observed when the same procedure was carried out using the less reactive zirconium and hafnium halides (MCl_4). Transmetalation of these compounds with the corresponding lithium cyclopentadienide $\text{Li}[\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ was also unsuccessful, as it provided only the dicyclopentadienyl derivative.

The related tin compounds are usually better cyclopentadienyl-transfer reagents and have been extensively used^{43–45} to prepare many mono- and dicyclopentadienyl transition metal complexes. The mixed silyl-stannyl-cyclopentadiene $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)][\text{Sn}(\text{nBu})_3]$ (**1**) was prepared by reaction of the lithium salt $\text{Li}[\text{C}_5\text{H}_4\{\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}]$ with 1 equiv of the chlorotrialkyltin as shown in Scheme 1 and isolated as a yellow liquid, which was characterized by NMR spectroscopy as a single 1-silyl-1-stannylcyclopentadienyl isomer.

Reaction of **1** with 1 equiv of the hafnium adduct $\text{HfCl}_4(\text{SMe}_2)_2$ in dichloromethane and further addition of DME afforded the DME adduct of the hafnium monocyclopentadienyl complex $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_3\cdot\text{DME}]$ (**2**), isolated as a grayish white solid and characterized by elemental analysis and NMR spectroscopy (see Experimental Section). No reaction was observed when a similar procedure was followed

using the zirconium halide ZrCl_4 , making this method unsuitable to prepare the related monocyclopentadienyl zirconium complex. As shown in Scheme 1, benzylation of **2** with 3 equiv of $\text{MgCl}(\text{CH}_2\text{Ph})$ afforded the tribenzyl compound $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})_3]$ (**3**), which was isolated as a highly air sensitive yellow oily solid, soluble in all of the usual organic solvents. It was also a thermally unstable compound, which could not be stored for long periods at room temperature under an inert atmosphere. Compound **3** was characterized by elemental analysis and NMR spectroscopy.

Using the monocyclopentadienyl hafnium compounds $[\text{Hf}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_3\cdot\text{DME}]$ (**2**) and $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3\cdot\text{DME}]$,⁴² alternative methods may be followed to isolate the mixed hafnocene complex by reaction with the $\text{Li}(\text{C}_5\text{H}_5)$ or $\text{Na}(\text{C}_5\text{H}_5)$ and $\text{Li}[\text{C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ salts, respectively. However the silylated compound **2** resulted in a less advantageous and experimentally more demanding method, which always gave lower yields of the required metallocene. The most efficient method used the lithium salt of the allylsilylcyclopentadiene, which when reacted with the adduct $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3\cdot\text{DME}]$, gave the hafnocene compound $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (**4**), as shown in Scheme 1. Complex **4** was isolated as a white solid and was characterized by elemental analysis and NMR spectroscopy.

Alkylation of the dichlorometallocene **4** with 2 equiv of $\text{MgCl}(\text{CH}_2\text{Ph})$ afforded the dibenzyl hafnium derivative $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})_2]$ (**5**), and similar methylation with LiMe afforded the dimethyl derivative $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Me}_2]$ (**6**). Formation of a monomethyl complex similar to the titanium derivative reported previously³⁹ was not observed when 1 equiv of the alkylating agent was used.

Formation and Dynamic Behavior of Cationic Species. Reaction of the dibenzyl hafnocene complex **5** with $\text{B}(\text{C}_6\text{F}_5)_3$ was carried out in CD_2Cl_2 using a Teflon-valved NMR tube and monitored by ^1H , ^{13}C , and ^{19}F NMR spectroscopy at variable temperature.

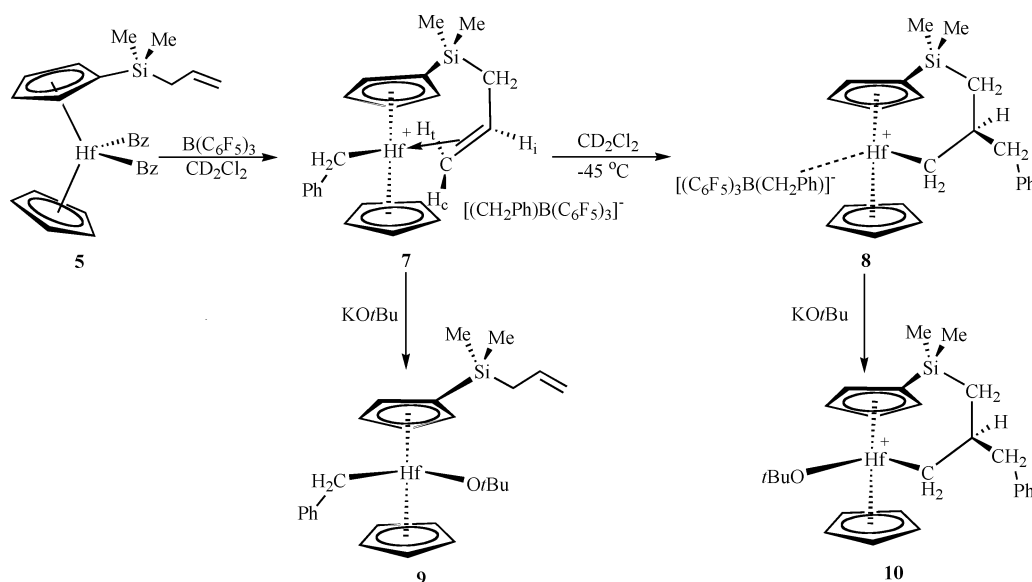
Addition of 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ at -78°C gave the alkene-coordinated species $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})_2]^+[(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**7**) (see Scheme 2). The ^1H NMR spectrum of **7** at -80°C shows the expected two SiMe singlets (δ 0.27, 0.52) and four

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Scheme 2



resonances (δ 5.36, 6.29, 6.63, 6.65) for the silyl-substituted cyclopentadienyl ring protons corresponding to an asymmetric cation and a broad methylene resonance (δ 2.69) characteristic of the benzylborate $[(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion. The ^{19}F NMR spectrum shows signals for the *meta* (δ -169.3), *para* (δ -164.9), and *ortho* (δ -120.9) fluorine atoms with a difference $\Delta\delta(\text{meta} - \text{para}-\text{F}) = 4.4$, consistent⁴⁶ with the presence of the noncoordinated borate anion. The methylenic protons of the metal-bonded benzyl ligand are observed as an AB spin system shifted downfield (δ 2.59, 2.97) with respect to the value observed for the precursor neutral compound **5**, whereas the terminal vinylic H_t and H_c signals of the allyl moiety are shifted high-field (δ 2.38 and 3.39) and the internal H_i signal is shifted downfield (δ 7.35), demonstrating the high degree of polarization of the coordinated alkene known^{25,35} for this type of compound. Similar behavior was observed in the ^{13}C NMR spectrum, which shows the resonances for the external ($=\text{CH}_2$) and internal ($-\text{CH}=\text{}$) carbon atoms shifted high-field [δ 92.3, $\Delta\delta = \delta(\mathbf{7}) - \delta(\mathbf{5}) = -20.8$] and downfield [δ 171.1, $\Delta\delta = 36.8$], respectively, with respect to those found for compound **5**.

The NMR behavior observed at variable temperature between -80 and -45°C for the hafnocenium cation **7** was similar to that found³⁵ for the related zirconocenium derivative, with both showing the broadening of signals expected for rapid interconversion between the *endo-exo* diastereomers, formed by dissociation of the alkene followed by recomplexation to the opposite alkene enantioface, on the NMR time scale. Variable-temperature ^1H NMR spectra between -80 and -10°C for the zirconocenium cation were also consistent with reversible interconversion between the two enantiomers formed by inversion at zirconium, with a combined barrier for alkene dissociation and zirconium inversion estimated³⁵ at $11.7 \text{ kcal mol}^{-1}$. However, as expected from the higher energetic barriers evaluated by DFT calculations,⁴⁷ the same dynamic process was much slower for the hafno-

cenium cation **7**, for which a different irreversible transformation before coalescence was observed at -40°C .

When a solution of **7** was warmed to -40°C , a slow and irreversible transformation into a new species, $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})-\eta^1\text{-CH}_2]\}]^+[(\text{CH}_2\text{Ph})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**8**), was observed (Scheme 2). This transformation was almost quantitative after 30 min, or in shorter periods at temperatures higher than -40°C , and **8** was the unique species present in solution at -20°C . The complex could not be isolated because decomposition to unidentified products took place rapidly at temperatures higher than -10°C .

Compound **8** exhibited two stereogenic centers at hafnium and at the benzyl-bound tertiary carbon atom and was characterized by ^1H , ^{13}C , ^{19}F , DEPT, HOMO-DEC, TOCSY-1D, and HMQC-2D NMR techniques (see Supporting Information) as a mixture of two diastereomers **8a** and **8b** in a 1:1 molar ratio of the metallacyclic cation, resulting from the migratory insertion of the alkene into the hafnium-benzyl bond in both enantiomers of the *endo*-diastereoisomer, giving two series of close and identical signals in the ^1H and ^{13}C NMR spectra. A slight stabilization by a weak interaction of this coordinatively unsaturated cation with the benzylborate anion is consistent with the ^{19}F NMR spectrum, which shows resonances for *meta*- (δ -167.3), *para*- (δ -164.3), and *ortho*- (δ -120.9) fluorine atoms with a value of $\Delta\delta(\text{meta} - \text{para}-\text{F}) = 3.0$. Both diastereomers are easily distinguished by the singlets observed for the cyclopentadienyl ring (C_5H_5) and the silicon-methyl ($\text{Si}-\text{CH}_3$) protons (see Experimental Section). The most relevant feature of these spectra is the absence of the low-field signal for the internal olefinic $-\text{CH}=\text{}$ group, whereas signals [δ 1.93 (^1H) and 42.3–42.6 (^{13}C)] are observed for a tertiary CH group.

The structural assignments discussed above were confirmed when these intermediate cationic species **7** and **8** were trapped as the stable neutral complexes by addition of the strong nucleophile $\text{KO}t\text{Bu}$.³⁷ Addition of 1 equiv of $\text{KO}t\text{Bu}$ to a toluene solution containing an equimolar mixture of complex **7** and $\text{B}(\text{C}_6\text{F}_5)_3$ at -80°C

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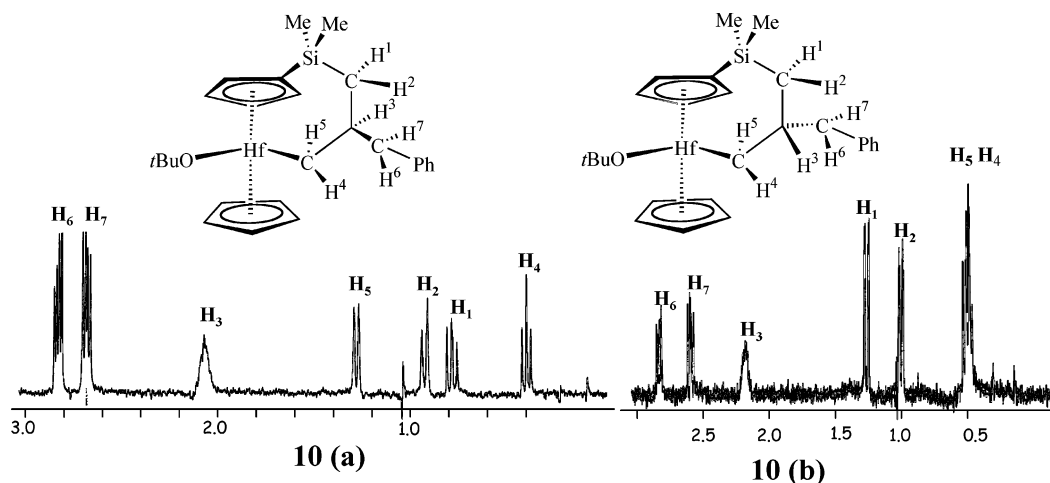


Figure 1. TOCSY-1D NMR spectrum for the major **10(a)** and minor **10(b)** isomers.

°C gave the *tert*-butoxo complex $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{CH}_2\text{Ph})(\text{OtBu})]$ **9** (Scheme 2) as a yellow oily solid after purification. Similar addition of KOtBu , after maintaining the solution at -20°C for 1 h, gave the *tert*-butoxo compound $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})-\eta^1\text{-CH}_2]\}(\text{OtBu})]$, **10** (see Scheme 2), which was isolated as a yellow-orange oil. In both reactions the nucleophile is bound to the metal, easily displacing the very weakly coordinated allylic alkene moiety of **7** and the borate anion of **8**. Complexes **9** and **10** could not be crystallized and were isolated as oily products, for which unsatisfactory analytical data were found for samples characterized as spectroscopically pure compounds by NMR spectroscopy.

Complex **9** shows the typical vinylic signals of the free allyl moiety (δ 4.93 and 5.70) with the signals for the diastereotopic methylenic protons of the benzyl ligand shifted downfield (δ 2.13, 2.32) with respect to those observed for **7**.

Compound **10** shows the two stereogenic centers observed for its precursor complex **8** and was characterized by ^1H , ^{13}C , DEPT, TOCSY-1D, and HMQC-2D NMR techniques as a mixture of two diastereomers. The ^1H NMR spectrum of the major component **10(a)** shows two SiCH_3 (δ 0.06, δ 0.21) and four silylcyclopentadienyl ring proton resonances (δ 5.28, 5.90, 5.93, 6.20) along with signals due to the aliphatic chain protons (see Experimental Section), whereas almost undetectable amounts of a second diastereomer **10(b)** were present. As shown in Figure 1, the TOCSY-1D NMR spectrum of **10(a)** shows the expected seven signals of the cyclic alkyl system, whereas only six were observed for the minor component **10(b)**, as the signals due to the H_4 and H_5 protons overlapped, probably due to the anisotropic effect of the phenyl ring.

Conclusions

New chloro and alkyl mono- $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{X}_3]$ ($\text{X} = \text{Cl}, \text{CH}_2\text{Ph}$) and dicyclopentadienyl $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Me}, \text{CH}_2\text{Ph}$) hafnium complexes containing a silyl-substituted cyclopentadienyl ligand with a pendant allyl moiety have been isolated and characterized by elemental analyses and NMR spectroscopy.

The dibenzyl hafnium complex reacts with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ at -80°C to generate the cationic species $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2-\eta^2\text{-CH}=\text{CH}_2)\}(\text{CH}_2\text{-Ph})]^+$, which exhibits dynamic behavior similar to that known for the zirconium derivative between -80 and -45°C , as monitored by ^1H and ^{13}C NMR spectroscopy. However at temperatures higher than -45°C this cationic species is irreversibly transformed into the metallacyclic alkyl cation $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-CH}_2\text{CH}(\text{CH}_2\text{Ph})-\eta^1\text{-CH}_2\}]^+$ by migratory insertion of the alkene into the metal–benzyl bond.

Both cationic species were characterized by NMR techniques, and their structures were confirmed after being trapped by reactions with KOtBu . In both cases the nucleophile displaces the coordinated olefin to form $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2-\eta^2\text{-CH}=\text{CH}_2)\}(\text{OtBu})\text{-}(\text{CH}_2\text{Ph})]$ or the borate anion to yield $[\text{Hf}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}(\text{CH}_2\text{Ph})-\eta^1\text{-CH}_2\}(\text{OtBu})]$.

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Supporting Information Available: Figures giving ^1H NMR spectra for **7**, **8**, and **10** and TOCSY-1D and HMQC-2D for **8** and **10** are available free of charge via the Internet at <http://pubs.acs.org>.

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