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Enhanced Reactivity of Cationic Hafnocene Complexes toward σ-Bond Metathesis Reactions. Si−H and Si−C Bond Activations in Stoichiometric and Catalytic Organosilane Conversions

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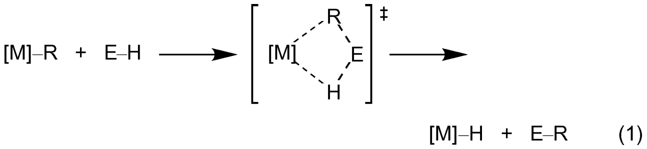
Interest in developing highly active catalysts for processes involving σ-bond metathesis steps led to a study directly comparing neutral, zwitterionic, and cationic derivatives of CpCp*Hf− in reactions with silanes. In stoichiometric transformations, comparisons of the reactivities of $CpCp^*HfMe_2$ (**1**), CpCp*HfMe(OTf) (**2**), $CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3$ (**3**), and $[CpCp^*HfMe][B(C_6F_5)_4]$ (**4**) with organosilanes indicate that the cationic character in the complex influences the activity of the Hf−Me bond toward reactions with Si−H bonds. Enhanced activity in catalytic σ-bond metathesis reactions of $PhSiH_3$ was also observed with zwitterionic hafnium hydride complexes. Neutral CpCp*HfHCl (**7**) reacts slowly with $PhSiH_3$ to give oligomers, while zwitterionic $CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3$ (**6**) reacts ca. 10 times faster, activating both Si−C and Si−H bonds of $PhSiH_3$, to give redistribution and dehydrocoupling products. A mechanism based on σ-bond metathesis is evidenced by identical experimental rate laws (rate $\propto$ [catalyst]$[PhSiH_3]^2$) for both the neutral and zwitterionic systems. The cationic complex **4** is an extremely reactive catalyst precursor and undergoes rapid redistribution and dehydropolymerization of $PhSiH_3$ to give highly cross-linked insoluble materials of the type $H-(PhSiH)_n-(SiH)_m-H$.

Introduction

Facile σ-bond activations by electrophilic, high-valent organometallic complexes hold considerable promise for the development of catalytic processes. These σ-bond metathesis reactions are typically associated with metal centers in their highest oxidation states and involve concerted steps and four-center electrocyclic transition states.[1] Such transition states have been postulated for intramolecular ligand metalations[2] and in C−H bond activations of hydrocarbons such as methane and benzene, by Cp^*_2MR ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Sc, Lu, Y; R = hydride, alkyl) complexes.[3] These reactive complexes possess several features that are required for σ-bond metathesis transformations, including electrophilicity, coordinative unsaturation, and a reactive M−R bond. However, the utilization of these C−H bond activation steps for catalytic hydrocarbon conversions has developed slowly.[4−6]

Several catalytic processes appear to involve σ-bond metathesis, and these are based on reactions of E−H bonds (E = H, Si, B, Sn, P) with high-valent organometallic species containing reactive M−R σ-bonds (R = H, C, Si, P, Sn). For olefin hydrogenations,[7] hydrosilations,[8] and hydroborations[9] mediated by early (d^0)-transition-metal and lanthanide complexes, the key carbon−element bond formation proceeds via the interaction of an M−C bond with dihydrogen, a silane, or a borane, respectively (eq 1). In silane, stannane, and



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phosphine dehydropolymerizations,[10−12] two sequential E−H (E = Si, Sn, P) bond activations produce dihydrogen and an element−element bond. Mechanistic studies

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indicate that these transformations are possible because, unlike carbon, certain main-group elements can occupy the β-position of a four-centered transition state (eq 1).[7−13] Thus, the accessibility of such transition states allows for various bond-forming reactions involving main-group elements.

σ-Bond metathesis reactions are potentially useful in the development of new catalytic processes, but a wider application of this chemistry in catalysis requires a more thorough understanding of the factors that influence reactivity and selectivity and the development of more reactive metal complexes. For example, studies of C−H and Si−H bond activations in hydrocarbons and hydrosilanes, mediated by the reactive $\mathrm{Cp^*_2ScR}$ derivatives ($\mathrm{R = H, Me, CH_2CMe_3}$), have led to the discovery of the first examples of catalytic methane conversions based on σ-bond metathesis.[5,6]

A strategy for the design of new bond activation catalysts is suggested by the similarities between olefin polymerization and σ-bond metathesis. Both mechanisms proceed via four-centered electrocyclic transition states ($2_\sigma + 2_\sigma$ vs $2_\sigma + 2_\pi$) and require electrophilic metal centers containing an open coordination site and a reactive σ-bond to the metal.[14] However, the most efficient dehydropolymerization catalysts are neutral, 16-electron, group 4 metal hydride complexes containing a single, low-lying, vacant d orbital, while effective group 4 metallocene-based olefin polymerization catalysts are cationic 14-electron complexes with two available d orbitals.[15] This comparison suggests that cationic group 4 metallocene derivatives might be highly reactive in σ-bond metathesis.

The rich C−H bond activation chemistry for neutral scandium group and lanthanide complexes of the type $\mathrm{Cp^*_2LnR}$ has not been observed for isoelectronic, cationic group 4 complexes of the type $\mathrm{[Cp'_2MR]^+}$. For the cationic complex $\mathrm{[Cp^*_2ZrH][HB(C_6F_5)_3]}$, C−H bond activation is apparently involved in rapid deuterium exchange between the zirconium hydride position and benzene-d_6.[17] In addition, the catalytic alkylation of pyridine with α-olefins has been reported for the cationic complex $\mathrm{[Cp_2ZrH(THF)][BPh_4]}$.[18] These examples suggest that cationic centers should also be reactive toward silanes and Si−H bond activations.

Interestingly, previous attempts to employ cationic catalysts in the dehydropolymerization of organosilanes did not yield increased molecular weights for the polysilane products.[14a,18] As we have learned in studies with active, lanthanide-based catalysts, low-molecular-weight polysilanes may result from the action of highly active catalysts which promote competing redistribution processes.[19] Thus, the molecular weights of polysilanes produced in a dehydropolymerization are not a good measure of a catalyst's activity toward σ-bond metathesis processes. For this reason, we have attempted to make direct comparisons between the activities of analogous neutral and cationic complexes in well-defined σ-bond metathesis steps. The study presented here addresses this fundamental question by comparing the reactivity of neutral and cationic complexes toward silanes in stoichiometric Si−C bond-forming reactions and in catalytic organosilane dehydropolymerizations. These findings, which have been communicated previously,[20] indicate that cationic complexes show enhanced reactivity toward silanes in σ-bond metathesis reactions.

Results and Discussion

Generation of Neutral and Cationic Derivatives of $\mathrm{CpCp^*HfMe_2}$. A series of hafnium methyl complexes, $\mathrm{CpCp^*HfMe_2}$ (**1**),[21] $\mathrm{CpCp^*HfMe(OTf)}$ (**2**), $\mathrm{CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3}$ (**3**), and $\mathrm{[CpCp^*HfMe][B(C_6F_5)_4]}$ (**4**), were synthesized to evaluate the effect of cationic character on stoichiometric σ-bond metathesis reactions with silanes. Compound **1** was prepared by the literature method,[21] and **2** was obtained by an adaptation of the reported synthesis of $\mathrm{[Cp_2ZrMe(THF)][BPh_4]}$.[21] Thus, reaction of **1** with 1 equiv of AgOTf in benzene-d_6 at room temperature rapidly yielded **2**, ethane, and $\mathrm{Ag^0}$ (eq 2). The ^{1}H NMR spectrum of **2** in

$$\underset{\mathbf{1}}{\mathrm{CpCp^*HfMe_2}} + \mathrm{AgOTf} \xrightarrow{\text{benzene-}d_6} \underset{\mathbf{2}}{\mathrm{CpCp^*HfMe(OTf)}} + \mathrm{C_2H_6} + \mathrm{Ag^0} \tag{2}$$

benzene-d_6 contains singlets corresponding to the Cp, Cp*, and HfMe ligands in the expected ratio of 5:15:3. The HfMe resonance of **2** is downfield-shifted relative to that of the hafnium dimethyl, from −0.48 to 0.18 ppm. The relatively high solubility of **2** in nonpolar solvents such as pentane indicates that the $\mathrm{OTf^-}$ ligand is covalently bonded to the hafnium center.

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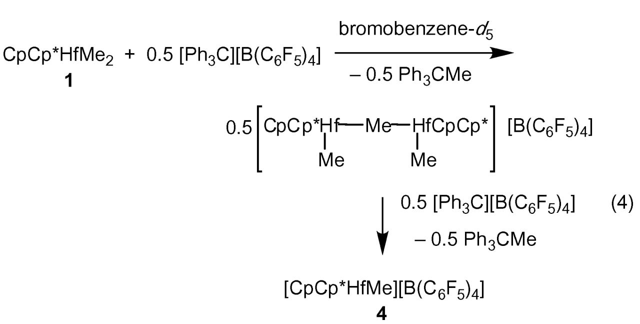
By analogy to the literature synthesis of $Cp^*{}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$,[16] the reaction of $CpCp^*HfMe_2$ (**1**) with the strong Lewis acid $B(C_6F_5)_3$ at room temperature rapidly (<5 min) and quantitatively produced the zwitterionic complex $CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3$ (**3**; eq 3).

$$\underset{\mathbf{1}}{CpCp^*HfMe_2} + B(C_6F_5)_3 \rightarrow \underset{\mathbf{3}}{CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3} \quad (3)$$

Compound **3** is soluble in benzene-d_6 and bromobenzene-d_5 but insoluble in aliphatic hydrocarbon solvents such as pentane and hexamethyldisiloxane (HMDS). Although both **1** and $B(C_6F_5)_3$ are extremely soluble in pentane at room temperature, when the two reagents were mixed in that solvent, complex **3** precipitated as an analytically pure, colorless powder. The ^1H NMR spectrum of **3** in benzene-d_6 reveals singlets corresponding to Cp, Cp*, and HfMe at 5.35 (5 H), 1.33 (15 H), and 0.09 ppm (3 H). A broad resonance at 0.15 ppm (3 H) corresponds to the methylborate counterion. Both methyl resonances are shifted downfield in comparison to the dimethyl peak in **1**. A singlet in the ^{11}B NMR spectrum (δ −17.5) and a $^1H-^{11}B$ HMQC experiment confirm the formation of the methylborate anion. With less than 1 equiv of $B(C_6F_5)_3$, mixtures of **3** and the dimeric, diastereomeric hafnium monocationic complexes $[(CpCp^*HfMe)_2(\mu\text{-}Me)][MeB(C_6F_5)_3]$ were formed. The ^1H NMR spectrum of the two diastereomers consists of two sets of peaks corresponding to Cp and Cp* ligands, bridging methyl groups (−1.81 and −1.85 ppm; 3 H each), and terminal methyl groups (−0.40 and −0.44; 6 H each). Upon addition of a full 1 equiv of $B(C_6F_5)_3$ to this mixture, **3** was formed quantitatively. Attempts to grow X-ray-quality crystals of **3** by cooling concentrated toluene solutions or by slow diffusion of pentane into toluene solutions were unsuccessful.

Reaction of colorless **1** with a benzene-d_6 solution of $[Ph_3C][B(C_6F_5)_4]$ induced a color change from the intense orange (for the Ph_3C^+ solution) to pale yellow. This reaction produced Ph_3CMe, but the desired $[CpCp^*HfMe][B(C_6F_5)_4]$ was not formed. Instead, mixtures containing large amounts of unreacted **1** and two other CpCp*-containing products were observed by ^1H NMR spectroscopy. In THF-d_8, Ph_3CMe and a single complex containing peaks corresponding to the Cp, Cp*, and methyl ligands in a ratio of 5:15:3 was formed. However, after 12 h the solution solidified, apparently due to the formation of polymeric THF.

The use of haloarene solvents proved critical in the synthesis of the desired cationic complex. Thus, addition of bromobenzene-d_5 or fluorobenzene solutions of $[Ph_3C][B(C_6F_5)_4]$ to **1** quantitatively produced deep red solutions of $[CpCp^*HfMe][B(C_6F_5)_4]$ (**4**) and Ph_3CMe after 1 h (eq 4). Initially, both diastereomers of $[(CpCp^*HfMe)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ formed, but within 1 h the dimeric products were quantitatively converted to **4**. Addition of 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ to **1** in bromobenzene-d_5 resulted in quantitative formation of the two dimeric diastereomers. Interestingly, the ^1H NMR spectra of the cationic hafnium fragment of the diastereomeric complexes $[(CpCp^*HfMe)_2(\mu\text{-}Me)][MeB(C_6F_5)_3]$ and $[(CpCp^*HfMe)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ are identical in bromobenzene-d_5, suggesting that separation of the cation and anion occurs in that solvent. The reaction of this pair of diastereomers with 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ then converted the mixture to **4**.



$$\underset{\mathbf{1}}{CpCp^*HfMe_2} + 0.5\,[Ph_3C][B(C_6F_5)_4] \xrightarrow[-0.5\,Ph_3CMe]{\text{bromobenzene-}d_5} 0.5\left[\underset{Me}{CpCp^*Hf}-Me-\underset{Me}{HfCpCp^*}\right][B(C_6F_5)_4] \xrightarrow[-0.5\,Ph_3CMe]{0.5\,[Ph_3C][B(C_6F_5)_4]} \underset{\mathbf{4}}{[CpCp^*HfMe][B(C_6F_5)_4]} \quad (4)$$

The ^1H NMR spectrum of **4** contained the expected three singlets, and as in **2** and **3**, the shift for the HfMe group is downfield relative to that for neutral **1**. At room temperature, no interaction between the cation and anion was detected by ^{19}F NMR spectroscopy. In fact, the ^{19}F NMR spectra of $[Ph_3C][B(C_6F_5)_4]$ and **4** are identical, and both contain three resonances at −132 (6 F), −162 (3 F), and −166 ppm (6 F). Unfortunately, all attempts to isolate **4** were unsuccessful. Reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ in pentane induced rapid precipitation of the insoluble dimeric monocations, thus inhibiting complete conversion to **4**. Therefore, the studies of σ-bond metathesis reactions involving **4** and silanes required in situ generation of the starting hafnium compound.

Interestingly, the nature of the cyclopentadienyl ancillary ligands affects the rate of formation of the monomeric cationic complexes. A survey of related abstraction reactions indicates that the rates of conversion to the monomeric cationic complexes $[Cp'_2HfMe][B(C_6F_5)_4]$ from the dimeric intermediate follow the trend $Cp_2Hf- < CpCp^*Hf- < Cp^*{}_2Hf-$. This trend appears to reflect the destabilization of the dimeric intermediates by the sterically demanding Cp* ligand. The $Cp^*{}_2Hf$ derivative further reacted in bromobenzene-d_5 (over ca. 12 h) to form two unidentified compounds (by ^1H NMR spectroscopy). Compound **4** was stable for at least 1 week in bromobenzene-d_5 at room temperature under an N_2 atmosphere, but exposure of this solution to air resulted in rapid decomposition to a black material.

Cationic complex **4** reacted cleanly with PMe_3 to form the colorless adduct $[CpCp^*HfMe(PMe_3)][B(C_6F_5)_4]$ (**5**), which was isolated by crystallization from bromobenzene-d_5 or fluorobenzene solution layered with pentane. The ^1H NMR shift of the HfMe group in the 16-electron PMe_3 adduct is upfield (−0.47 ppm) relative to that of the formally 14-electron, zwitterionic, cationic hafnium methyl complexes **3** and **4**. An attempt to remove the datively bound phosphine ligand by exposure of crystals of **5** to dynamic vacuum (ca. 1.3 Pa) for 6 h was unsuccessful.

σ-Bond Metathesis Reactions of CpCp*HfMe(X) (X = Me, OTf, $MeB(C_6F_5)_3$, $B(C_6F_5)_4$) with Silanes. Phenylsilane was added to compounds **1**−**4** to evaluate the relative reactivity of their respective Hf−C bonds toward σ-bond metathesis. No reaction occurred between the neutral hafnocene **1** and 1 equiv of $PhSiH_3$ at room temperature in benzene-d_6 over 1 week. The hafnium triflate **2** also did not react with $PhSiH_3$ in benzene-d_6 after 5 days at 25 °C or over 12 h at 70 °C.

In contrast, the zwitterionic complex **3** reacted with 1 equiv of $PhSiH_3$ (room temperature, 3 h, benzene-d_6) to quantitatively form $PhMe_2SiH$ and $CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3$ (**6**, eq 5). Thus, both the hafnium methyl and

$$\underset{\mathbf{3}}{CpCp^*HfMe_2(\mu\text{-}Me)B(C_6F_5)_3} + PhSiH_3 \rightarrow \underset{\mathbf{6}}{CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3} + PhMe_2SiH \quad (5)$$

a methyl group from the borate of **3** were transferred to $PhSiH_3$, and methane was not detected in the ^1H NMR spectrum. Although the reaction required approximately 3 h to proceed to completion, the presumed mixed hydride/methyl intermediates $CpCp^*HfH(\mu\text{-}Me)B(C_6F_5)_3$ and $CpCp^*HfMe(\mu\text{-}H)B(C_6F_5)_3$ were not detected by ^1H NMR spectroscopy. However, the intermediate silane product $PhMeSiH_2$ was observed. The reaction of **3** with 0.5 equiv of $PhSiH_3$ yielded $PhMe_2SiH$ and a 1:1 mixture of **3** and **6**. Ligand exchange between **3** and **6**, to give the mixed hydrido/methyl species, also did not occur. Addition of excess $PhSiH_3$ (ca. 5 equiv) to **3** rapidly produced **6** and 2 equiv of $PhMeSiH_2$ ($t_{1/2} < 5$ min) at room temperature.

Many σ-bond metathesis reactions of silanes, including dehydropolymerizations,[10,22] are accelerated by light. However, reactions of **3** proceed identically under ambient light or in the dark. Due to the crowded nature of the concerted transition states, the reaction rate is sensitive to steric effects imposed by substituents on the silane.[23] Thus, larger silanes reacted more slowly than smaller silanes with **3** (1 equiv of silane in benzene-d_6 at room temperature), following the trend $PhSiH_3 > CySiH_3 > MesSiH_3 > Ph_2SiH_2 > Mes_2SiH_2$ (Cy = C_6H_{13}, Mes = 2,4,6-trimethylphenyl). Thus, the initial buildup of the $PhMeSiH_2$ intermediate results from the relative rates of the reactions of **3** with $PhSiH_3$ vs $PhMeSiH_2$. Tertiary silanes, such as $PhMe_2SiH$, Ph_3SiH, and Et_3SiH, did not react with **3** (1:1) in benzene-d_6 at room temperature over 1 week.

Note that the reaction of **3** with $PhSiH_3$ models the Si−C bond-forming step in the hydrosilation of olefins, as catalyzed by early-transition-metal and lanthanide complexes.[8] Also, $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ was reported to be a diene cyclization−hydrosilation catalyst precursor.[24] Similar stoichiometric Si−C bond formations have been observed in the reactions of lanthanide methyl compounds $[Cp'_2LnMe]_2$ (Cp′ = Cp*, Ln = Lu, Y; Cp′ = $C_5H_4{}^tBu$, Ln = Lu, Sm, Nd) with silanes.[25]

The cationic hafnium methyl complex **4** reacted rapidly with primary and secondary organosilanes in bromobenzene-d_5 at room temperature, to give complicated mixtures of products; however, some characteristic features of the reaction mixtures could be identified. For example, spectroscopically identical organometallic species were formed regardless of the silane reagent. The major product contained resonances at 5.60 and 1.86 ppm for the Cp and Cp* ligands, respectively, and the resonances for a minor product were observed at 5.84 and 1.64 ppm. Methane was detected in the reaction mixture, which contrasts with the quantitative Si−C bond formation observed in reactions of **3** with organosilanes. As with **3**, compound **4** reacts with unhindered organosilanes more rapidly than with bulky silanes: $PhSiH_3 \approx CySiH_3 \approx HexSiH_3 > MesSiH_3 > Ph_2SiH_2 > Mes_2SiH_2 \approx Ph_3SiH$. In reactions with less hindered primary silanes, **4** was completely consumed before an initial spectrum could be obtained. Thus, this cationic hafnium methyl complex appears to be extremely reactive toward organosilanes.

The reaction of dihydrogen with **4** produced methane and the same two organometallic products that are produced in the presence of silanes. Therefore, the species formed in the reactions described above are not cationic hafnium silyl complexes.[26] Although $[CpCp^*HfH][B(C_6F_5)_4]$ could not be spectroscopically identified, its formation is suggested by the observed reaction chemistry (see below). A compound analogous to this putative cationic hafnium hydride, $[Cp^*_2ZrH][B(C_6F_5)_4]$, was previously reported.[27] Attempts to isolate $[CpCp^*HfH][B(C_6F_5)_4]$ via the procedure used for the zirconium species (H_2 in toluene at −78 °C) were not successful. The broad dihydrogen resonance (or the broad SiH resonance observed upon reaction of **4** and hydrosilanes) suggests that rapid hydrogen exchange processes may obscure the hafnium hydride resonance of $[CpCp^*HfH][B(C_6F_5)_4]$. Note that the hydride resonance in isoelectronic Cp^*_2ScH could not be detected by ^1H NMR spectroscopy, due in part to similar rapid exchange with reagents used to generate this hydride (H_2 or hydrosilanes).[3,5] Interestingly, under an atmosphere of H_2 this mixture catalyzed H/D exchange among the meta position of bromobenzene-d_5, cyclooctane, and the Cp ligands. Thus, deuterium was incorporated into the typically inert secondary methylene groups of cyclooctane such that 92% of the cyclooctane was deuterated after 24 h. This H/D exchange is presumed to proceed via metalation of bromobenzene-d_5 and elimination of HD or D_2, followed by hydrogenolysis to form bromobenzene-d_4 and a cationic hafnium deuteride complex. Surprisingly, the ortho and para positions of bromobenzene-d_5 and Ph_3CMe were unaffected.

The rapid reactions of **4** with silanes clearly indicate that this cationic complex is considerably more reactive toward silanes than the zwitterionic compound **3**. The relative rates of reactions with hydrosilanes (conversion of the hafnium methyl species) follow the trend **4** > **3** > **2** ≈ **1**. Thus, cationic character appears to significantly impact the reactivity of a complex toward σ-bond metathesis.

Synthesis and Characterization of $CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3$ (6). The zwitterionic hafnium hydride complex **6** was prepared by vigorously stirring a pentane suspension of **3** with 1.5 equiv of $PhSiH_3$ for 3 h at room temperature. Alternatively, compound **6** could be synthesized via reaction of **3** with H_2 (1 atm, pentane). The

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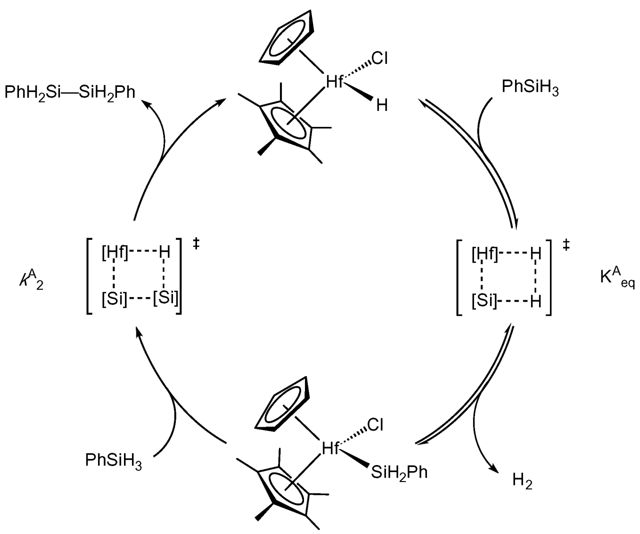
Scheme 1

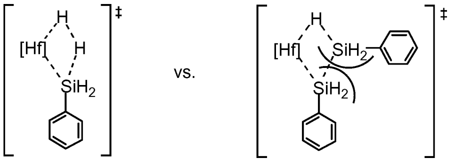


^1H NMR spectrum of **6** (benzene-d_6) contains a hydride peak at 12.84 ppm (1 H), in addition to the Cp and Cp* resonances. Due to the quadrupolar boron nucleus, the hydridoborate signal was broadened into the baseline and could not be detected directly by ^1H NMR spectroscopy, but it was identified using a $^1H-^{11}B$ HMQC experiment (at 0.5 ppm). The ^{11}B NMR resonance (−16.91 ppm) and the $^1H-^{11}B$ HMQC data indicate the presence of an anionic hydroborate counterion. Moreover, the $^1J_{BH}$ coupling constant (50 Hz) and the boron−hydrogen stretching frequency (1950 cm^{-1}) are consistent with a hydride bridging the boron and hafnium centers, Hf−(μ-H)−B. For comparison, the crystallographically characterized, cationic zirconocene hydride $[Cp^*_2ZrH][HB(C_6F_5)_3]$ was shown to contain a terminal boron hydride (ν(B−H) 2346 cm^{-1}) and aryl fluorides bridging to the unsaturated Zr center.[28] Interestingly, the compound $[Cp^*_2ZrH][MeB(C_6F_5)_3]$ was isolated by the reaction of $[Cp^*_2ZrMe][MeB(C_6F_5)_3]$ with H_2 in pentane,[16,28] while the mixed hafnium hydride/methyl borate CpCp*HfH(μ-Me)B$(C_6F_5)_3$ was never detected. In contrast to $[Cp^*_2ZrH][HB(C_6F_5)_3]$, which reacts rapidly with benzene-d_6 to incorporate deuterium into its hydride position, zwitterionic **6** does not react with benzene-d_6 at room temperature over 1 week.

Reactions of CpCp*HfHX (X = Cl, HB$(C_6F_5)_3$) with Silanes. Organosilane Dehydropolymerization and Redistribution. Dehydropolymerizations of excess $PhSiH_3$ by zwitterionic **6** (2 mol %, 2 days, neat substrate) produced polysilanes of similar molecular weight ($M_n \approx 1000$) to those formed by neutral CpCp*HfHCl (**7**) under analogous conditions. Although these low molecular weights are consistent with previous findings regarding $PhSiH_3$ polymerizations by cationic group 4 complexes,[14,18] the studies described above comparing reactions of neutral vs cationic hafnium methyl compounds with silanes indicate that cationic species should be significantly more reactive toward σ-bond metathesis. These seemingly contradictory observations prompted a closer examination of neutral and cationic hafnocene hydride complexes in silane dehydropolymerizations.

The catalytic cycle of Scheme 1 was proposed on the basis of studies on observed stoichiometric reactions, which represent the two steps of this cycle. These mechanistic studies involved neutral, mixed-ring hafnium derivatives of the type CpCp*HfRCl (R = H, SiH_2Ph).[11b,23] However, the kinetics of the overall catalytic process (i.e. monomer consumption) has not been reported. To better understand the relationship between σ-bond metathesis reactivity and the molecular weights of polysilanes produced by a catalytic dehydropolymerization, we investigated the kinetics of the dehydropolymerization of $PhSiH_3$, as catalyzed by **6** and **7**.

Chart 1



Addition of $PhSiH_3$ to **7** (neat or in benzene-d_6), which is known to react with silanes via four-centered transition states,[10] produced low-molecular-weight polysilanes (neat, $M_n \approx 1000$ by GPC analysis). The initial stages of the reaction were monitored by ^1H NMR spectroscopy in benzene-d_6, which revealed that the silane reacted to form dehydrocoupling products. Thus, H_2, $PhH_2Si-SiH_2Ph$, and $PhH_2Si-(SiHPh)-SiH_2Ph$ were detected, and after 1 day mixtures of linear and cyclic silicon chains were formed (identified by their characteristic ^1H NMR chemical shifts).[11d,29] Additionally, the hafnium hydride **7** was partially converted to the corresponding silyl compound CpCp*Hf(SiH_2Ph)Cl.[11d] For reactions in sealed NMR tubes, plots of 1/$[PhSiH_3]$ vs time were linear for approximately 2 half-lives but indicated that the reaction slowed after extended reaction times at high $PhSiH_3$ conversions (due to a buildup of the H_2 concentration; vide infra). However, when the reaction vessel was opened to a N_2 atmosphere (i.e., H_2 was allowed to escape), the reaction exhibited pseudo-second-order kinetics for greater than 3 half-lives. Plots of the observed second-order rate constant k_{obs} vs [**7**] demonstrate first-order dependence on the hafnium hydride catalyst, indicating that silicon−silicon bond formation occurs at the metal center. A mechanism consistent with these observations involves reversible, concurrent silane metalation and H_2 elimination with **7** (Scheme 1). As expected, the addition of 1 atm of H_2 inhibited the polymerization. Overall second-order dependence on substrate concentration is expected for a condensation polymerization reaction;[30] another 1 equiv of $PhSiH_3$ is required for a single turnover of the catalytic cycle. The rate law for such a mechanism, rate = k_{obs}[**7**]$[PhSiH_3]^2$ ($k_{obs} = K^A{}_{eq}k^A{}_2$), is consistent with the experimentally determined rate law ($k_{obs} = 3.3 \times 10^{-3}$ s^{-1} M^{-2} at 51.2 °C). The buildup of CpCp*Hf(SiH_2Ph)Cl indicates that the silicon−silicon bond formation step of the cycle is rate-limiting, at least during the early stages of the polymerization. This conclusion is consistent with the postulate that σ-bond metathesis steps involving hindered transition states are slow (Chart 1). Thus, these results are consistent with the previously proposed catalytic cycle (Scheme 1).[10b,11d]

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(30) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.

The reaction of neat $PhSiH_3$ with zwitterionic **6** resulted in effervescence, and a gelatinous oil formed after approximately 5 h (eq 6). Despite the visibly

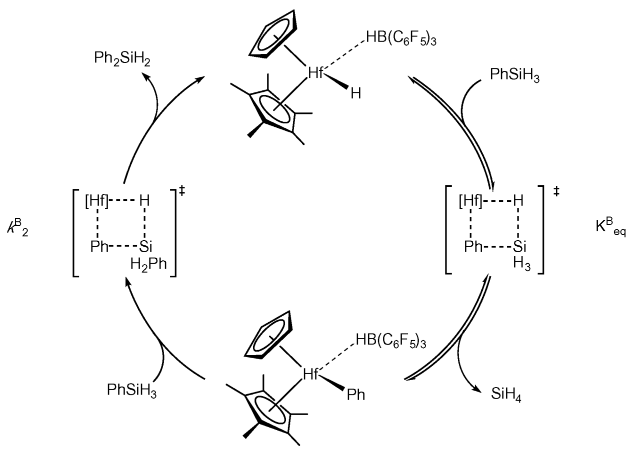
$$n\mathrm{PhSiH_3} \xrightarrow[\text{neat or in benzene-}d_6]{5\text{ mol \% }\mathbf{6}} \mathrm{H(SiPhH)}_n\mathrm{(SiH)}_m\mathrm{H} + \mathrm{H_2} + \mathrm{Ph_2SiH_2} + \mathrm{SiH_4} \quad (6)$$

vigorous reaction, gel-permeation chromatography (GPC) traces of the resulting product indicated only short oligosilane formation ($M_n \approx 1000$). The ^1H and ^{29}Si NMR spectra of the crude reaction revealed a mixture of polysilanes, Ph_2SiH_2, and unreacted $PhSiH_3$. Monitoring the reaction by ^1H NMR spectroscopy (benzene-d_6, sealed NMR tube) revealed that H_2 and SiH_4 formed as well. The $^{29}Si\{^1H\}$ NMR spectra of the polysilane produced by **6** exhibited two bands of resonances from −55 to −65 ppm and from −95 to −120 ppm. The former resonances are attributed to structures of the type $-(\mathrm{Ph}Si\mathrm{H})_n-$, on the basis of comparisons to resonances for polysilanes produced by **7** and other neutral group 4 catalysts.[10] A $^{29}Si\{^1H\}$ DEPT 90° spectra of the polysilane produced by **6** indicated that the latter set of resonances were due to $\mathrm{H}Si\mathrm{(Si_3)}$ centers, apparently resulting from incorporation of SiH_4 into the polymer backbone. Notably, the formation of Ph_2SiH_2 and SiH_4 demonstrate that organosilane redistribution, via Si−C bond activations, occurred. As in the $[Cp^*_2LnH]_2$ systems, the cleavage of Si−C bonds implies that the cationic metal−hydride species are highly reactive. The corresponding reaction between **6** and $CySiH_3$ (25 equiv) was slow (only 25% conversion after 3 days at room temperature in benzene-d_6), and the Si−C bond activation product Cy_2SiH_2 was formed. No reaction was observed between **6** and Ph_2SiH_2 (23 equiv) in benzene-d_6 after 3 days.

In contrast to the reaction of **7** with $PhSiH_3$, in which $CpCp^*Hf(SiH_2Ph)Cl$ was formed,[11d] the presumed cationic hafnium silyl intermediate $CpCp^*Hf(SiH_2Ph)(\mu\text{-}H)B(C_6F_5)_3$ was not detected in reaction mixtures of **6** with $PhSiH_3$ (by ^1H NMR spectroscopy, benzene-d_6, over 8 h at room temperature or 35 °C). Attempts to independently synthesize the cationic hafnium hydrosilyl complex $CpCp^*Hf(SiH_2Ph)(\mu\text{-}H)B(C_6F_5)_3$ were unsuccessful, and the synthesis and σ-bond metathesis chemistry of related cationic hafnium silyl complexes is presented elsewhere.[26] The cationic hafnium phenyl complex $CpCp^*HfPh(\mu\text{-}H)B(C_6F_5)_3$, which is the presumed intermediate in the redistribution of $PhSiH_3$ to Ph_2SiH_2 and SiH_4, was also not detected in this reaction mixture. Unfortunately, independent synthesis of the putative phenyl intermediate $CpCp^*HfPh(\mu\text{-}H)B(C_6F_5)_3$ was unsuccessful, as the reaction of $CpCp^*HfPhH$ with $B(C_6F_5)_3$ yielded a mixture of products. The only organometallic species observed in the reaction mixture was **6**, indicating that this cationic hafnium hydride complex represents the resting state of the catalyst.

Although the dehydropolymerization and redistribution of $PhSiH_3$ are both catalyzed by **6**, the observed kinetic behavior of this reaction system is remarkably simple. Second-order plots of $1/[PhSiH_3]$ vs time were linear for greater than 3 half-lives, and plots of k_{obs} vs [**6**] revealed first-order dependence on the catalyst concentration. The experimentally determined rate law, rate $= k_{obs}[\mathbf{6}][PhSiH_3]^2$ ($k_{obs} = 4.5 \times 10^{-2}\ s^{-1}\ M^{-2}$ at 35 °C), takes the same form as that of the simple dehydropolymerization reaction catalyzed by $CpCp^*HfHCl$. Notably, the observed rate constants are greater than those for dehydropolymerization, as catalyzed by the neutral catalyst **7**, by more than an order of magnitude. Unlike the $CpCp^*HfHCl$-catalyzed dehydropolymerization, the reaction could be performed in a sealed NMR tube. However, at high conversions of $PhSiH_3$ (<4 half-lives), the observed rate constant decreased slightly due to increased $[H_2]$ from the silane redistribution process. The redistribution process accounts for much of the $PhSiH_3$ conversion (ca. 66%), and therefore relatively large amounts of H_2 (relative to the silane dehydropolymerization catalyzed by compound **7**) are required to inhibit the catalysis. In related work, Rosenberg recently reported that the dehydrocoupling of Ph_2SiH_2 to Ph_2SiSiH_2, as catalyzed by $(PPh_3)_3RhCl$, could be favored over redistribution to $PhSiH_3$ and Ph_3SiH by rapid H_2 removal.[31]

Scheme 2



The significantly increased reaction rate for **6** appears to reflect the enhanced reactivity of the cationic system toward organosilanes. Furthermore, the similarity of the two experimentally determined rate laws suggests that the cationic hafnium catalyst mediates organosilane dehydrocoupling via a mechanism analogous to that of the neutral catalyst, involving σ-bond metathesis steps. Analysis of the kinetic data and the observed reaction products suggests that phenylsilane redistribution proceeds through a two-step mechanism involving reversible Si−C bond cleavage by **6** followed by transfer of the phenyl group from hafnium to silicon (Scheme 2). The summation of the rate laws for redistribution and dehydropolymerization (both first order in **6** and second order in $PhSiH_3$) yields an overall rate law (eq 7), for

$$\text{rate} = \left(\frac{K^{A}_{eq}k^{A}_{2}}{[H_2]} + \frac{K^{B}_{eq}k^{B}_{2}}{[SiH_4]}\right)[\mathbf{6}][PhSiH_3]^2 \qquad (7)$$

which the second term, $K^B_{eq}k^B_2/[SiH_4]$, is derived from the $PhSiH_3$ redistribution reaction. Because the first step of both pathways is an equilibrium, the relative rates of the pathways should be dependent on the concentrations of the H_2 and SiH_4 byproducts in the reaction mixture. In accord with this mechanism, ad-

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[31] Rosenberg, L.; Davis, C. W.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 5120.

dition of 1 atm of H_2 inhibited dehydrocoupling to favor redistribution (by a factor of 4:1 based on the amount of Ph_2SiH_2 relative to the initial $PhSiH_3$).

Rapid Organosilane Dehydropolymerization and Redistribution with [CpCp*HfMe][B(C_6F_5)$_4$] (4). Although the cationic hydride complex [CpCp*HfH]-[B(C_6F_5)$_4$] could not be isolated and studied in direct comparisons with **6** or **7**, the cationic hafnium methyl derivative **4** was extremely active as a catalyst precursor for both organosilane dehydropolymerization and redistribution processes. Thus, addition of excess $PhSiH_3$ (ca. 25 equiv) to bromobenzene-d_5 solutions of **4** resulted in vigorous gas evolution. After 5 min, a ^{1}H NMR spectrum of the reaction mixture indicated that approximately half of the $PhSiH_3$ had been converted to polysilanes and a mixture of Ph_2SiH_2 (ca. 40% of the organosilane species present) and small amounts of Ph_3SiH and SiH_4 (<5% each). After 1 h, the relative amounts of $PhSiH_3$ and Ph_2SiH_2 had changed only slightly (ca. 30% and 55%, respectively), but a large amount of white solid had formed in the NMR tube. After approximately 3 h, the $PhSiH_3$ was completely converted to Ph_2SiH_2 and the insoluble white precipitate. Addition of more $PhSiH_3$ to the mixture resulted in further effervescence and production of more flocculent solid. Once formed, the resulting precipitate was insoluble in all organic solvents tested, including THF and DMSO. This insolubility hindered its characterization by ^{29}Si NMR spectroscopy or gel permeation chromatography. Given the observation of SiH_4 in the reaction mixture, it is likely that this species participates as a cross-linking agent to produce insoluble polysilanes.

The concurrent redistribution and dehydropolymerization of organosilanes was also observed upon addition of [CpCp*HfMe][B(C_6F_5)$_4$] (**4**) to a large excess of $HexSiH_3$, $MesSiH_3$, or Ph_2SiH_2, as evidenced by formation of large amounts of insoluble products for each reaction. Interestingly, **4** reacted with more sterically hindered silanes such as $CySiH_3$ and Ph_2SiH_2. The polymer resulting from reaction of **4** and Ph_2SiH_2 was also insoluble in common organic solvents, making characterization difficult. Interestingly, this polymer exhibits a relatively sharp melting point, at 229−231 °C. Reaction of **4** with $CySiH_3$ did not result in precipitation of a polymer from bromobenzene-d_5. Instead, large amounts of Cy_2SiH_2 were formed (by ^{1}H NMR spectroscopy). The hindered silanes Cy_2SiH_2, Ph_3SiH, and Mes_2SiH_2 did not react with **4** after 1 week at room temperature (by ^{1}H NMR spectroscopy, bromobenzene-d_5).

Lewis acids, including [Ph_3C][B(C_6F_5)$_4$], are known to promote organosilane redistributions.[18a,32] Thus, the possibility that trace [Ph_3C][B(C_6F_5)$_4$] contamination could be responsible for the observed chemistry was considered. Reaction of **1** with 1 equiv of [Ph_3C]-[B(C_6F_5)$_4$] (bromobenzene-d_5) produced a solution of **4** and Ph_3CMe (1:1) in which the trityl reagent could not be detected (by ^{1}H NMR spectroscopy). To ensure that no free [Ph_3C][B(C_6F_5)$_4$] was available in solution, **1** was allowed to react with 0.8−0.99 equiv of [Ph_3C][B(C_6F_5)$_4$] (in bromobenzene-d_5) to produce mixtures of [CpCp*HfMe][B(C_6F_5)$_4$] and [(CpCp*HfMe)$_2$(μ-Me)]-[B(C_6F_5)$_4$]. These Ph_3C^+-free mixtures reacted with excess $PhSiH_3$ to form the same dehydropolymerization and redistribution products that were observed in reactions of $PhSiH_3$ with [CpCp*HfMe][B(C_6F_5)$_4$] (generated from 1:1 mixtures of **1** and [Ph_3C][B(C_6F_5)$_4$]). Additionally, the cationic hafnium complex [CpCp*HfMe]-[B(C_6F_5)$_4$] did not react with Ph_3SiH (room temperature, bromobenzene-d_5, 1 day), whereas [Ph_3C][B(C_6F_5)$_4$] rapidly reacted with Ph_3SiH.[18a,32] For example, a mixture of **1** and 1.1 equiv of [Ph_3C][B(C_6F_5)$_4$] (bromobenzene-d_5, 2 h) was allowed to react with 0.2 equiv of Ph_3SiH; after 1 day at room temperature, the cationic hafnium methyl **4** had not reacted, but the excess [Ph_3C]-[B(C_6F_5)$_4$] had been consumed (by ^{1}H NMR spectroscopy). This mixture retained the same activity toward reaction with $PhSiH_3$, and thus we conclude that [Ph_3C]-[B(C_6F_5)$_4$] is not the active catalyst in these silane dehydropolymerization and redistribution reactions.

Concluding Remarks

Previous to this work, it had been shown that neutral, 16-electron, mixed-ring zirconocene hydride or silyl complexes were among the most reactive catalysts for the dehydropolymerization of $PhSiH_3$.[10,11] Mechanistic studies have revealed that these neutral catalysts mediate the polymerization reaction through Si−H bond activations and silicon−silicon bond formations via four-centered transition states.[11d] Attempts to develop more efficient Si−H bond activations and silane dehydropolymerizations, for the production of high-molecular-weight polysilanes, prompted studies of more electrophilic metal centers as catalysts for these reactions. In this context, some reports in the literature suggest that cationic group 4 centers are more active catalysts for the synthesis of high-molecular-weight polysilanes,[14b,18] while other studies suggest that cationic centers are less active in silane dehydropolymerizations.[14a]

We have addressed this issue by comparing the activities of neutral and cationic hafnium complexes in reactions with silanes, in terms of both the molecular weights of the polysilanes produced and the rates at which analogous neutral and cationic complexes react. Polysilane molecular weights indicate that cationic hafnium-catalyzed polymerizations of $PhSiH_3$ do not produce longer polysilane chains (in comparison to analogous neutral catalysts). On the other hand, our investigations indicate that cationic hafnium centers react much more rapidly with silanes than comparable neutral hafnium compounds.

One possible explanation for the lower molecular weights (despite enhanced rates in σ-bond metathesis reactions) is that σ-bond metathesis is not the mechanism for polysilane formation. Harrod has suggested that the mechanism for silane dehydropolymerization, as catalyzed by cationic group 4 metal centers, involves silyl radical coupling for Si−Si bond formation.[18] Our investigations of the kinetics of $PhSiH_3$ dehydropolymerizations implicate a mechanism for dehydropolymerization that involves a metal-mediated condensation polymerization.[30] Also, the general rate expressions for neutral and cationic hafnium-catalyzed monomer consumption in the silane dehydropolymerization reactions are identical $\{k_{obs}[\text{catalyst}][PhSiH_3]^2\}$. These observations provide support for σ-bond metathesis as the mechanism for silane dehydropolymerization, as catalyzed by these cationic hafnium complexes.

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(32) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3227.

The lower molecular weight products observed for highly active (e.g., cationic) catalysts may instead be attributed to the competitive organosilane redistribution process, via Si−C bond activation, which interferes with polysilane chain growth. The activation of Si−C bonds via four-centered transition states is more difficult than Si−H bond activation but has been observed in transformations of silanes with highly reactive lanthanide complexes $(Cp^*_2LnH)_2$ (Ln = Sm, Lu, Y).[25] Thus, the organosilane redistribution process further indicates that the cationic hafnium centers are highly reactive in σ-bond metathesis steps, more so than neutral hafnium centers. As is also evident from the σ-bond metathesis chemistry of f-element complexes, more reactive metal centers may react with both Si−H bonds and Si−C bonds. These results suggest that new catalytic bond activation processes may be based on cationic centers. However, successful strategies for bond activation catalysis based on σ-bond metathesis reactions require consideration of selectivity as well as activity.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of nitrogen using Schlenk techniques or a glovebox. Dry, oxygen-free solvents were employed throughout. Removal of thiophenes from benzene and toluene was accomplished by washing each with H_2SO_4 and saturated $NaHCO_3$ and treating with the drying agent $MgSO_4$. Olefin impurities were removed from pentanes by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, saturated $NaHCO_3$, and the drying agent $MgSO_4$. All solvents were distilled from sodium benzophenone ketyl, with the exception of benzene-d_6, which was purified by vacuum distillation from Na/K alloy. The compounds $CpCp^*HfMe_2$ (**1**),[21a] CpCp*Hf(H)Cl (**7**),[10] $B(C_6F_5)_3$,[33] and $[Ph_3C][B(C_6F_5)_4]$[33] were prepared according to literature procedures. All hydrosilanes were prepared via reduction of the corresponding chlorosilanes with $LiAlH_4$. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. Infrared spectra were recorded using a Mattson FTIR instrument at a resolution of 4 cm^{-1}. All NMR spectra were recorded at room temperature in benzene-d_6 unless otherwise noted, using a Bruker AM-400 spectrometer or a Bruker DRX-500 spectrometer.

CpCp*Hf(OTf)Me (2). Addition of a benzene solution of AgOTf (0.449 g, 1.75 mmol) to a benzene solution of $CpCp^*HfMe_2$ (0.711 g, 1.74 mmol) immediately induced formation of a black solution. The resulting mixture of **2** and Ag^0 was stirred for 1 h. The Ag^0 precipitate was removed by filtration of the solution, and analytically pure **2** was isolated by evaporation of the benzene solvent under reduced pressure (0.752 g, 1.39 mmol, 79.7%). ^1H NMR (400 MHz): δ 5.793 (s, 5 H, C_5H_5), 1.588 (s, 15 H, C_5Me_5), 0.152 (s, 3 H, HfMe). $^{13}C\{^1H\}$ NMR (100 MHz): δ 120.5 (C_5Me$_5$), 113.7 (C_5H_5), 38.0 (HfMe), 11.4 (C$_5$*Me*$_5$). ^{19}F NMR (377 MHz): δ −77.4 (OTf). IR (KBr, cm^{-1}): 2926 (w), 1350 (s), 1239 (m), 1200 (s), 834 (m), 632 (m). Anal. Calcd for $C_{17}H_{23}F_3HfO_3S$: C, 37.61; H, 4.27. Found: C, 37.94; H, 4.02. Mp: 142.5−143 °C.

CpCp*HfMe(μ-Me)B(C_6F_5)$_3$ (3). A 100 mL Schlenk flask was charged with $CpCp^*HfMe_2$ (0.406 g, 0.993 mmol), $B(C_6F_5)_3$ (0.509 g, 0.993 mmol), and pentane (ca. 35 mL). The resulting suspension was stirred vigorously for 3 h. The pentane was removed via filtration, and a white, powdery product was washed with pentane (3 × 25 mL). Residual solvent was removed under reduced pressure to yield **3** (0.606 g, 0.658 mmol, 66.3%). ^1H NMR (400 MHz): δ 5.35 (s, 5 H, C_5H_5), 1.33 (s, 15 H, C_5Me_5), 0.146 (br, 3 H, BMe), 0.088 (s, 3 H, HfMe). $^{13}C\{^1H\}$ NMR (100 MHz): δ 121.9 (C_5Me$_5$), 113.1 (C_5H_5), 42.5 (HfMe), 22.0 (BMe), 10.8 (C$_5$*Me*$_5$). ^{19}F NMR (377 MHz): δ −134 (m, 6 F), −159 (m, 2 F), −165 (m, 6 F). ^{11}B NMR (160 MHz): δ −17.5 (s). IR (KBr, cm^{-1}): 1645 (m), 1516 (s), 1462 (s), 1385 (m), 1281 (m), 1151 (w), 1097 (s), 1026 (m), 974 (s). Anal. Calcd for $BC_{35}F_{15}H_{26}Hf$: C, 45.65; H, 2.85. Found: C, 45.50; H, 2.97. Mp: 65−68 °C dec.

In Situ Generation of [CpCp*HfMe][B(C_6F_5)$_4$] (4). Bromobenzene-d_5 solutions of $CpCp^*HfMe_2$ (0.016 g, 0.038 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.035 g, 0.038 mmol) were mixed at room temperature. After 2 h, ^1H NMR spectroscopy indicated that the $[Ph_3C][B(C_6F_5)_4]$ was consumed and that **4** and Ph_3CMe were formed in a 1:1 ratio. ^1H NMR (500 MHz, bromobenzene-d_5): δ 5.54 (s, 5 H, C_5H_5), 1.73 (s, 15 H, C_5Me_5), 0.00 (s, 3 H, HfMe). $^{13}C\{^1H\}$ NMR (100 MHz, bromobenzene-d_5): δ 123.36 (C_5Me$_5$), 115.37 (C_5H_5), 50.76 (HfMe), 11.48 (C$_5$*Me*$_5$). ^{19}F NMR (377 MHz, bromobenzene-d_5): δ −132 (m, 8 F), −162, (m, 4 F), −166 (m, 8 F). ^{11}B NMR (160 MHz, bromobenzene-d_5): δ −16.85 (s).

[CpCp*HfMe(PMe$_3$)][B(C_6F_5)$_4$] (5). $Cp^*CpHfMe_2$ (0.017 g, 0.041 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.038 g, 0.041 mmol) were mixed in bromobenzene-d_5. After 2 h, 1.2 equiv of PMe_3 was added, which resulted in an immediate color change from orange to pale yellow. The bromobenzene-d_5 solution was layered with pentane in an NMR tube, and after 1 day crystals of **5** formed (0.025 g, 0.022 mmol, 53.6%). ^1H NMR (400 MHz, bromobenzene-d_5): δ 5.69 (s, 5 H, C_5H_5), 1.64 (s, 15 H, C_5Me_5) 0.84 (d, 9 H, PMe_3), −0.47 (s, 3 H, HfMe). $^{13}C\{^1H\}$ NMR (100 MHz, bromobenzene-d_5): δ 121.82 (C_5Me$_5$), 113.41 (C_5H_5), 55.65 (HfMe), 14 (br, PMe_3), 11.59 (C$_5$*Me*$_5$). ^{19}F NMR (377 MHz, bromobenzene-d_5): δ −132.1 (d, 8 F), −162.3 (2, 4 F), −166.1 (t, 8 F). ^{11}B NMR (160 MHz, bromobenzene-d_5): δ −16.84. $^{31}P\{^1H\}$ NMR (162 MHz, bromobenzene-d_5): 36.70. IR (KBr, cm^{-1}): 2926 (m), 1644 (s), 1515 (s), 1462 (s), 1383 (m), 1089 (s), 979 (s), 824 (s), 774 (s), 662 (m). Anal. Calcd for $BC_{43}F_{20}H_{32}HfP$: C, 44.96; H, 2.81. Found: C, 45.06; H, 2.81. Mp: 165−167 °C dec.

CpCp*HfH(μ-H)B(C_6F_5)$_3$ (6). A 100 mL Schlenk flask was charged with **3** (0.781 g, 0.848 mmol), pentane (30 mL), and $PhSiH_3$ (0.1 g, 0.927 mmol). The flask was sealed, and the resulting mixture was stirred overnight. The solvent and silane were removed by filtration, and the resulting white powder was dried under reduced pressure to yield analytically pure **6** (0.361 g, 0.404 mmol, 47.6%). ^1H NMR (400 MHz): δ 12.84 (s, 1 H, HfH), 5.26 (s, 5 H, C_5H_5), 1.59 (s, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100 MHz): δ 120 (C_5Me$_5$), 110.1 (C_5H_5), 11.8 (C$_5$*Me*$_5$). ^{19}F NMR (377 MHz): δ −138 (m, 6 F), −157 (m, 3 F), −164 (m, 6 F). ^{11}B NMR (160 MHz): δ −16.91 (d, $^1J_{BH}$ = 50 Hz). IR (KBr, cm^{-1}): 2362 (w), 1950 (m), 1645 (m), 1516 (s), 1467 (s), 1381 (m), 1281 (m), 1111 (s), 968 (s), 835 (m). Anal. Calcd for $BC_{33}F_{15}H_{22}Hf$: C, 44.39; H, 2.48. Found: C, 44.06; H, 2.34. Mp: 86−89 °C dec.

CpCp*Hf(Ph)Me. A 250 mL Schlenk flask was charged with CpCp*Hf(OTf)Me (0.752 g, 1.38 mmol), PhLi (0.142 g, 1.69 mmol), and benzene (100 mL). The flask was sealed, and the resulting mixture was stirred overnight. All volatile materials were removed under reduced pressure, and the resulting solid was extracted with pentane (3 × 30 mL). The combined pentane extracts were concentrated to ca. 20 mL and cooled to −78 °C. The resulting white crystals were collected and dried under vacuum to give a yield of 58% (0.377 g, 0.798 mmol). ^1H NMR (400 MHz): δ 7.25 (t, 2 H, Ph), 7.05 (t, 1H, Ph), 6.95 (d, 2 H, Ph), 5.71 (s, 5 H, C_5H_5), 1.62 (s, 15 H, C_5Me_5), −0.05 (s, 3 H, HfMe). $^{13}C\{^1H\}$ NMR (100 MHz): δ 199.08 (Ph), 137.16 (Ph), 127.43 (Ph), 125.12 (Ph), 118.09 (C_5Me$_5$), 112.15 (C_5H_5), 42.69 (HfMe), 12.02 (C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 3046 (m), 2952 (s), 2922 (s), 2854 (s), 1455 (m), 1378 (m), 1143 (m), 1057 (m), 1017 (m), 807 (s), 705 (s). Anal. Calcd for $C_{22}H_{28}$-

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Hf: C, 56.37; H, 5.99. Found: C, 56.37; H, 5.91. Mp: 129.5−130.5 °C dec.

CpCp*HfPh(μ-Me)B(C_6F_5)$_3$. This complex was generated in situ by reaction of CpCp*Hf(Ph)Me with 1 equiv of B(C_6F_5)$_3$ in benzene-d_6 and characterized in solution. ^{1}H NMR (500 MHz): δ 7.15 (t, 2 H, Ph), 6.63 (t, 1 H, Ph), 6.63 (d, 2 H, Ph), 5.52 (s, 5 H, C_5H_5), 1.33 (s, 15 H, C_5Me_5), 0.712 (br, 3 H, *Me*B(C_5F_5)$_3$). ^{13}C{^{1}H} NMR (100 MHz): δ 193.35 (Ph), 150.15 (C_6F_5), 148.20 (C_6F_5), 139.02 (C_6F_5), 136.98 (C_6F_5), 136.39 (Ph), 127.00 (Ph), 124.67 (C_5Me$_5$), 115.32 (C_5H$_5$), 20.50 (*Me*B(C_6F_5)$_3$, 11.88 (C_5Me_5). ^{11}B NMR (160 MHz): δ −13.75.

Kinetic Measurements. Reactions were monitored by ^{1}H NMR spectroscopy with a Bruker DRX500 spectrometer using 5 mm Wilmad NMR tubes, equipped with J. Young Teflon screw caps. The samples were frozen in liquid N_2 immediately after preparation and defrosted just before being placed in the probe, which was preheated to the required temperature. When CpCp*HfHCl was used as the catalyst, the headspace of the NMR tube was evacuated while the benzene solution was frozen. The probe temperature was calibrated using an ethylene glycol standard and monitored with a thermocouple. Single-scan spectra were acquired automatically at preset time intervals. The peaks were integrated relative to cyclooctane as an internal standard. Rate constants were obtained by nonweighted linear least-squares fit of the integrated second-order rate law $1/[C] = 1/C_0 + k_{obs}t$.

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Supporting Information Available: Figures giving representative kinetics data for the reactions of **6** and **7** with PhSiH_3 and ^{29}Si NMR spectra for poly(phenylsilanes). This material is available free of charge via the Internet at http://pubs.acs.org.

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