

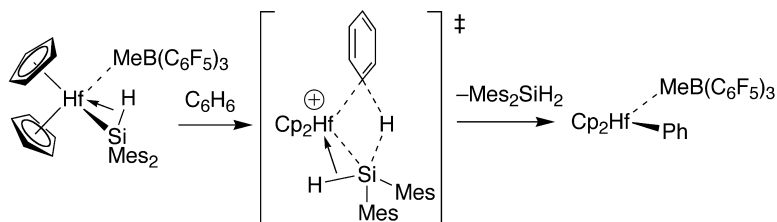
Article

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## Cationic Hafnium Silyl Complexes and Their Enhanced Reactivity in $\sigma$ -Bond Metathesis Processes with Si–H and C–H Bonds

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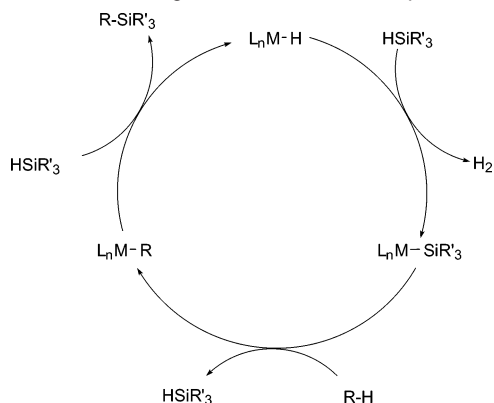
**Abstract:** Reaction of the mixed-ring silyl methyl complex  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$  (**4**) with  $\text{B}(\text{C}_6\text{F}_5)_3$  in bromobenzene- $d_5$  yielded the zwitterionic hafnium silyl complex  $[\text{CpCpHfSi}(\text{SiMe}_3)_3][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7**), which is stable for at least 12 h in solution. Addition of  $\text{PhSiH}_3$  to **7** rapidly produced  $\text{HSi}(\text{SiMe}_3)_3$ ,  $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ , and oligomeric silane products. Reactions of  $\text{CpCp}^*\text{Hf}(\text{SiR}_3)\text{Me}$  ( $\text{SiR}_3 = \text{Si}^i\text{BuPh}_2$ ,  $\text{SiHMes}_2$ ) with  $\text{B}(\text{C}_6\text{F}_5)_3$  rapidly produced  $\text{HSiR}_3$  in quantitative yield along with unidentified hafnium-containing species. However, reactions of  $\text{Cp}_2\text{Hf}(\text{SiR}_3)\text{Me}$  ( $\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3$  (**8**),  $\text{Si}^i\text{BuPh}_2$  (**9**),  $\text{SiPh}_3$  (**10**)) with  $\text{B}(\text{C}_6\text{F}_5)_3$  quantitatively produced the corresponding cationic hafnium silyl complexes **12–14**. The complex  $\text{Cp}_2\text{Hf}(\text{Si}^i\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**13**) was isolated by crystallization from toluene at  $-30^\circ\text{C}$  and fully characterized, and its spectroscopic properties and crystal structure are compared to those of its neutral precursor **9**. The  $\sigma$ -bond metathesis reaction of **13** with  $\text{Mes}_2\text{SiH}_2$  yielded  $\text{HSi}^i\text{BuPh}_2$  and the reactive species  $\text{Cp}_2\text{Hf}(\eta^2\text{-SiHMes}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**, benzene- $d_6$ ), which was also generated by reaction of  $\text{Cp}_2\text{Hf}(\text{SiMes}_2\text{H})\text{Me}$  (**11**) with  $\text{B}(\text{C}_6\text{F}_5)_3$ . Spectroscopic data provide evidence for an unusual  $\alpha$ -agostic Si–H interaction in **16**. At room temperature, **16** reacts with benzene to form  $\text{Cp}_2\text{Hf}(\text{Ph})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**17**), and with toluene to give isomers of  $\text{Cp}_2\text{Hf}(\text{C}_6\text{H}_4\text{Me})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**18–20**) and  $\text{Cp}_2\text{Hf}(\text{CH}_2\text{Ph})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**21**). The reaction with benzene is first order in both **16** and benzene. Kinetic data including activation parameters ( $\Delta H^\ddagger = 19(1)$  kcal/mol;  $\Delta S^\ddagger = -17(3)$  eu), a large primary isotope effect ( $k_H/k_D = 6.9(7)$ ), and the experimentally determined rate law are consistent with a mechanism involving a concerted transition state for C–H bond activation.

### Introduction

$\sigma$ -Bond metathesis holds considerable promise for the development of new catalytic transformations. This fundamental bond activation mechanism, which involves concerted, four-centered electrocyclic transition states, was first described for hydrogenations of  $d^0$  metal alkyl complexes.<sup>1</sup> Such processes are mediated by electrophilic, high valent transition metal or f-element centers ( $d^0$  or  $f^0d^0$ ) containing at least one open coordination site adjacent to a reactive  $\sigma$ -bond.<sup>2</sup>  $\sigma$ -Bond metathesis steps have been implicated in catalytic reactions of main group element-hydrogen bonds (E–H, E = B, Si, P, Sn), including dehydropolymerizations and the addition of E–H bonds to olefins.<sup>3–8</sup> Activations of the element-hydrogen bonds

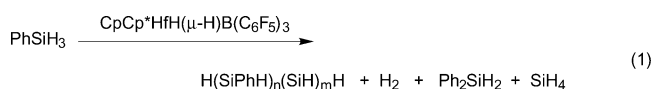
(e.g., Si–H) are generally more facile than C–H bond activations and may therefore be mediated by moderately electrophilic, 16-electron group 4 complexes of the type  $\text{Cp}'_2\text{MR}_2$  (M = Ti, Zr, Hf;  $\text{Cp}'_2 = \text{Cp}_2$ ,  $\text{CpCp}^*$ ,  $\text{Cp}^*_2$ , where  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ; R = H, alkyl, silyl).<sup>3,9</sup> A more reactive class of compounds are 14-electron complexes of the type  $\text{Cp}^*_2\text{MR}$  (M = Sc, Lu, Y; R = hydride, alkyl), which can react with inert hydrocarbons, including methane.<sup>10,11</sup> However, although high valent complexes capable of activating C–H bonds by  $\sigma$ -bond metathesis

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**Scheme 1.** A Possible Catalytic Cycle for Hydrocarbon Functionalization Involving  $\sigma$ -Bond Metathesis Steps

have been known for almost 20 years, catalytic cycles incorporating these reactions have been limited to the alkylation of pyridine.<sup>12</sup> Recently, we reported the first examples of methane conversions involving  $\sigma$ -bond metathesis steps, the hydro-methylation of propene, and the dehydrosilation of methane.<sup>13,14</sup>

The study described here targets the development of new  $d^0$  complexes designed to expand the chemistry of element-hydrogen bond activations and mediate new catalytic reactions. The electrophilic complexes of interest are cation-like group 4 complexes that are expected to be highly reactive in  $\sigma$ -bond metathesis reactions, based on analogies to cationic catalysts in olefin polymerization.<sup>15,16</sup> Previous studies have shown that zwitterionic and cationic hafnium complexes containing methyl and hydride ligands are highly reactive toward organosilanes and more reactive than analogous neutral complexes.<sup>17</sup> For example, the zwitterionic hafnium hydride complex  $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$  rapidly catalyzes the conversion of  $\text{PhSiH}_3$  to cross-linked oligosilanes and  $\text{Ph}_2\text{SiH}_2$  by dehydrocoupling and redistribution reactions involving Si-H and Si-C bond activations, respectively (eq 1). The corresponding neutral complex  $\text{CpCp}^*\text{HfHCl}$  more slowly (by  $> 1$  order of magnitude) catalyzes only the dehydropolymerization of  $\text{PhSiH}_3$ .<sup>3,4</sup>

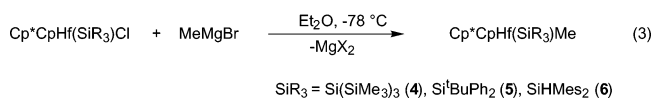
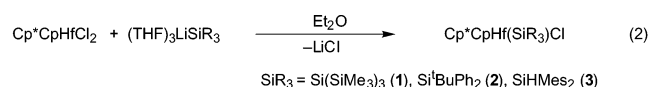


Strategies for the development of catalytic hydrocarbon conversions might be based on activation of a C-H bond by a reactive metal silyl derivative, since metal-silicon bonds in  $d^0$  complexes are generally quite reactive (e.g., more reactive than comparable metal-carbon bonds).<sup>3,9</sup> A possible catalytic process involving  $\sigma$ -bond metathesis is the dehydrosilation of hydrocarbons, which would couple C-H and Si-H bonds to give an Si-C bond and hydrogen. A three-step catalytic cycle for this reaction (Scheme 1) involves (1) a C-H bond activation step, (2) the well-known transfer of an organic group from the metal

to silicon, and (3) the dehydrocoupling of Si-H and M-H bonds to form a metal silyl derivative.<sup>18</sup> The latter two steps of this cycle have precedent in observed reactions of  $d^0$  complexes, including those of hafnium.<sup>3,4,17,19</sup> However, the activation of C-H bonds via  $\sigma$ -bond metathesis with a metal-silicon bond has not previously been reported. To develop more reactive  $d^0$  silyl complexes which might exhibit this chemistry, efforts were directed toward the synthesis and study of zwitterionic hafnium silyl complexes and their ability to activate Si-H and C-H bonds.

## Results

**Synthesis of  $\text{CpCp}^*\text{Hf}(\text{SiR}_3)\text{Me}$  ( $\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3$ ,  $\text{Si}^t\text{BuPh}_2$ ,  $\text{SiHMes}_2$ ) Complexes.** The neutral mixed-ring hafnium silyl methyl complexes  $\text{CpCp}^*\text{Hf}(\text{SiR}_3)\text{Me}$  ( $\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3$ ,  $\text{Si}^t\text{BuPh}_2$ ,  $\text{SiHMes}_2$ ) were prepared via silylation of  $\text{CpCp}^*\text{HfCl}_2$ , followed by methylation. The hafnium silyl chloride complexes **1–3** were prepared by the method of eq 2. Treatment of compounds **1–3** with methyl Grignard in diethyl ether at  $-78$  °C afforded the desired hafnium silyl methyl complexes **4–6** (eq 3). Compounds **1–6** are yellow, crystalline materials, which are somewhat thermally and photochemically sensitive and decompose in the solid state over 1 week at room temperature.<sup>9,21</sup> Thus, the complexes may be stored for extended periods ( $\sim 3$  months) in the dark at  $-30$  °C.



**Generation of  $[\text{CpCp}^*\text{HfSi}(\text{SiMe}_3)_3][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7**).** The strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  has been reported to react with early transition metal methyl complexes, such as  $\text{Cp}^*_2\text{ZrMe}_2$ , via methide abstraction.<sup>22</sup> Similarly, in bromobenzene- $d_5$ , compound **4** reacted with  $\text{B}(\text{C}_6\text{F}_5)_3$  to produce  $[\text{CpCp}^*\text{HfSi}(\text{SiMe}_3)_3][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7**), which is stable in solution at room temperature for several hours. The  $^1\text{H}$  NMR spectrum of **7** contains two sharp singlets corresponding to the Cp and  $\text{Cp}^*$  ligands and two broad singlets for the  $\text{Si}(\text{SiMe}_3)_3$  (0.3 ppm, 14 Hz width at half-height) and  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  (1.28 ppm, 18 Hz at half-height) groups. The  $\text{Si}(\text{SiMe}_3)_3$  resonance is further broadened at  $-20$  °C (to 90 Hz at half-height) but begins to sharpen at the low temperature limit for the bromobenzene- $d_5$  solvent (mp =  $-31$  °C). At that temperature, the resonance splits into several new  $\text{SiMe}_3$  peaks, suggesting hindered rotation about the Hf-Si

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bond. The latter methyl borate resonance is shifted significantly downfield from that of the HfMe groups of **4** and CpCp\*HfMe-( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (−0.55 and 0 ppm, respectively)<sup>3c,17</sup> and from that of the bridging methyl borate group of CpCp\*HfMe( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (ca. 0 ppm, bromobenzene-*d*<sub>5</sub>).<sup>17</sup> This downfield-shifted resonance for the methyl group of MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> suggests greater cation–anion separation than in CpCp\*HfMe( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (in benzene-*d*<sub>6</sub> and bromobenzene-*d*<sub>5</sub>). Compound **7** is sparingly soluble in benzene-*d*<sub>6</sub> and benzene-*d*<sub>6</sub>/bromobenzene-*d*<sub>5</sub> mixtures (the compound precipitates from solution as an oil over 10 min). The solubility properties and the <sup>1</sup>H NMR spectrum of **7** imply that it contains significant charge separation. However, in these relatively nonpolar, noncoordinating solvents, tight ion pairing is expected.<sup>22</sup>

The upfield-shifted singlet at −15.04 ppm in the <sup>11</sup>B NMR spectrum of **7** indicates the presence of a four-coordinate borate anion.<sup>23</sup> Interestingly, the <sup>29</sup>Si{<sup>1</sup>H} NMR resonances of **7** (−5.10 ppm, Si(SiMe<sub>3</sub>)<sub>3</sub>; −87.45 ppm, Si(SiMe<sub>3</sub>)<sub>3</sub>) are not significantly shifted from those of the precursor **4**, suggesting that the electronic environment of the silyl ligand is not notably affected by the change in formal charge at the hafnium center. Within 24 h at room temperature, **7** decomposed to HSi(SiMe<sub>3</sub>)<sub>3</sub> and several unidentified hafnium-containing products. The compound was stable overnight in solution at −30 °C as a bromobenzene-*d*<sub>5</sub> solution but did not crystallize and could not be isolated free of impurities.

Other attempts to isolate the zwitterionic complex **7** were unsuccessful. In benzene-*d*<sub>6</sub>, reaction of compound **4** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> resulted in formation of a deep red solution; as noted above, after ca. 10 min a red oil precipitated from solution. The <sup>1</sup>H NMR spectrum of the reaction mixture contained several broad resonances corresponding to Cp, Cp\*, Si(SiMe<sub>3</sub>)<sub>3</sub>, and MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> groups, and the quantitative formation of HSi(SiMe<sub>3</sub>)<sub>3</sub> was observed after 24 h. Dissolution of **4** in pentane followed by addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> immediately produced a red powdery precipitate, but the <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>) of this product is the same as that of the mixture formed in benzene-*d*<sub>6</sub>. Although **7** reacted with THF in benzene-*d*<sub>6</sub> to form Cp\*CpHf[Si(SiMe<sub>3</sub>)<sub>3</sub>](THF)[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**7**-THF; as indicated by <sup>1</sup>H NMR spectroscopy), the complex could not be isolated free from HSi(SiMe<sub>3</sub>)<sub>3</sub>.

Reactions of **7** with primary and secondary silanes such as PhSiH<sub>3</sub>, Ph<sub>2</sub>SiH<sub>2</sub>, and H<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>2</sub> at room temperature in bromobenzene-*d*<sub>5</sub> rapidly produced CpCp\*HfH( $\mu$ -H)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, HSi(SiMe<sub>3</sub>)<sub>3</sub>, and unidentified silane products (*t*<sub>1/2</sub> ≈ 5 min). By comparison, reaction of the neutral hafnium silyl CpCp\*Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl with 3 equiv of PhSiH<sub>3</sub> proceeded with a much longer half-life (*t*<sub>1/2</sub> ≈ 2 h) and yielded the previously reported complex CpCp\*Hf(SiH<sub>2</sub>Ph)Cl.<sup>3</sup> Like the  $\sigma$ -bond metathesis reactions of borane-activated complexes CpCp\*HfMe( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and CpCp\*HfH( $\mu$ -H)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with silanes,<sup>17</sup> those of the cationic complex **7** exhibit dramatically enhanced rates relative to those of neutral analogues.

**Attempted Syntheses of [CpCp\*HfSiR<sub>3</sub>][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (SiR<sub>3</sub> = Si<sup>t</sup>BuPh<sub>2</sub>, SiHMes<sub>2</sub>).** With the hope that other silyl ligands might impart stability and/or crystallinity to a cationic hafnium silyl complex, the precursor hafnium silyl methyl compounds CpCp\*Hf(Si<sup>t</sup>BuPh<sub>2</sub>)Me (**5**) and CpCp\*Hf(SiHMes<sub>2</sub>)Me (**6**) were

synthesized. Unfortunately, the addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to these compounds resulted in rapid elimination of the corresponding silane, and no hafnium complexes could be isolated from the reaction mixtures. Reactions of **5** or **6** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub> or bromobenzene-*d*<sub>5</sub> produced a rapid color change to red that was immediately followed by a bleaching to pale yellow. The reactions of **5** and **6** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in the presence of Lewis bases (PMe<sub>3</sub>, pyridine, DMSO) also quantitatively produced the corresponding free silane (<sup>1</sup>H NMR spectroscopy, benzene-*d*<sub>6</sub>, 5 min at room temperature). Methide abstraction from **5** in the presence of diphenylacetylene (room temperature, benzene-*d*<sub>6</sub>) quantitatively produced HSi<sup>t</sup>BuPh<sub>2</sub> along with a single hafnium-containing product. The <sup>1</sup>H NMR spectrum of this product contains a singlet for the Cp ligand (4.91 ppm, 5 H) and a complicated set of resonances corresponding to the Cp\* ligand. This species was not isolated, but based on its <sup>1</sup>H NMR spectrum, we postulate that the Cp\* ligand is involved in a decomposition of the initially formed silyl complex.

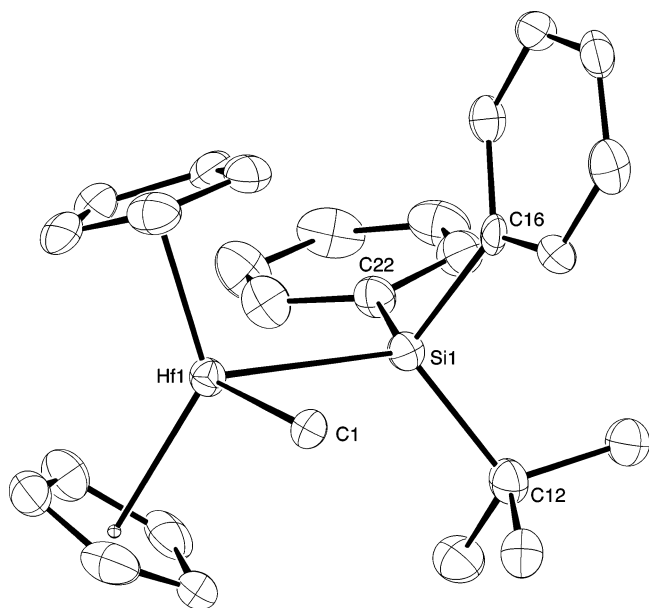
**Synthesis of Neutral Precursor Complexes Cp<sub>2</sub>Hf(SiR<sub>3</sub>)-Me (SiR<sub>3</sub> = Si(SiMe<sub>3</sub>)<sub>3</sub> (**8**), Si<sup>t</sup>BuPh<sub>2</sub> (**9**), SiPh<sub>3</sub> (**10**), SiHMes<sub>2</sub> (**11**)).** The possible involvement of the Cp\* ligand in the rapid decomposition of [CpCp\*Hf(SiR<sub>3</sub>)]<sup>+</sup> species suggested that cationic hafnium silyl complexes might be isolable for ligand sets possessing more inert C–H bonds (e.g., Cp<sub>2</sub>). The complexes Cp<sub>2</sub>Hf(SiR<sub>3</sub>)Me (SiR<sub>3</sub> = Si(SiMe<sub>3</sub>)<sub>3</sub> (**8**), Si<sup>t</sup>BuPh<sub>2</sub> (**9**)) were prepared by a two-step method analogous to the synthesis of the mixed-ring hafnium silyl methyl derivatives, involving reactions of Cp<sub>2</sub>HfCl<sub>2</sub> with the appropriate silyl anion reagent, followed by reaction of the resulting silyl complex with methyl Grignard. The compounds Cp<sub>2</sub>Hf(SiPh<sub>3</sub>)Me (**10**) and Cp<sub>2</sub>Hf(SiHMes<sub>2</sub>)Me (**11**) were prepared by the reaction of Cp<sub>2</sub>-HfMeCl with the corresponding silyl anion reagent. Notably, the reaction of Cp<sub>2</sub>HfCl<sub>2</sub> with (THF)<sub>2</sub>LiSiHMes<sub>2</sub> (in toluene or Et<sub>2</sub>O, at −78 °C in the dark) did not yield Cp<sub>2</sub>Hf(SiHMes<sub>2</sub>)Cl.<sup>21c</sup> Like the mixed-ring complexes **1–6**, the compounds **8–11** are somewhat thermally unstable and moderately sensitive to room light. These compounds decomposed to HSiR<sub>3</sub> and unidentified hafnium-containing products over 1 week under ambient lighting at room temperature but were stable for at least 4 months when stored in the dark at −30 °C. The X-ray crystal structure of **9** was determined (Figure 1), and relevant structural parameters for **9** are listed in Tables 1 and 2.

**Synthesis of Cp<sub>2</sub>Hf(SiR<sub>3</sub>)( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (SiR<sub>3</sub> = Si(SiMe<sub>3</sub>)<sub>3</sub> (**12**), Si<sup>t</sup>BuPh<sub>2</sub> (**13**), SiPh<sub>3</sub> (**14**)).** The bright yellow solutions (benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub>) of **8–10** turned deep red upon addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at room temperature, and <sup>1</sup>H NMR spectroscopy confirmed the quantitative formation of Cp<sub>2</sub>Hf(SiR<sub>3</sub>)( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (SiR<sub>3</sub> = Si(SiMe<sub>3</sub>)<sub>3</sub> (**12**), Si<sup>t</sup>BuPh<sub>2</sub> (**13**), SiPh<sub>3</sub> (**14**); eq 4). Unlike the mixed ring system, compounds **12–14** were stable in benzene-*d*<sub>6</sub> solution in the dark for approximately 12 h. Complex **13** was isolated by crystallization from toluene at −30 °C and characterized by X-ray crystallography. Compounds **12** and **14** did not crystallize from toluene (−78 °C) and were isolated as impure oils after the solvent was removed under reduced pressure.



(23) Kidd, R. G. *NMR of Newly Accessible Nuclei*, Vol. 2; Academic Press: 1983.





**Figure 1.** ORTEP diagram of  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)\text{Me}$  (**9**). The hydrogen atoms on the Cp rings and on the substituents on the silyl ligand were removed for clarity.

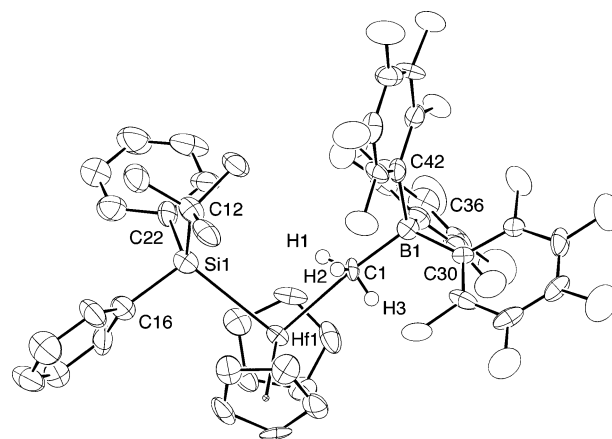
**Table 1.** Selected Bond Lengths (Å) for  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)\text{Me}$  (**9**) and  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**13**)

	<b>9</b>	<b>13</b>
Hf1–Si1	2.835(2)	2.851(3)
Hf1–C1	2.287(6)	2.48(1)
B1–C1	na	1.66(2)
Si–C12 ('Bu)	1.957(7)	1.92(1)
Si1–C16 (Ph)	1.899(7)	1.88(1)
Si1–C22 (Ph)	1.907(7)	1.90(1)
Hf1–Cp <sub>cent</sub>	2.200(2)	2.1605(5)
Hf1–Cp <sub>cent</sub>	2.1677(5)	2.1694(5)

**Table 2.** Selected Bond Angles for  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)\text{Me}$  (**9**) and  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**13**)

	<b>9</b>	<b>13</b>
Si1–Hf1–C1	93.6(2)	97.1(3)
Hf1–Si1–C12 ('Bu)	119.7(2)	117.2(4)
Hf1–Si1–C16 (Ph)	105.9(2)	105.7(4)
Hf1–Si1–C22 (Ph)	113.6(2)	116.2(4)
C12–Si1–C16	106.7(3)	110.4(6)
C12–Si1–C22	104.6(3)	101.7(6)
C16–Si1–C22	105.4(3)	105.1(6)
Hf1–C1–B1	na	162.0(9)
Cp <sub>cent</sub> –Hf1–Cp <sub>cent</sub>	132.41(1)	129.77(2)
C1–B1–C30	na	113(1)
C1–B1–C36	na	104(1)
C1–B1–C42	na	111(1)

Formation of zwitterionic **13** in benzene- $d_6$  results in the appearance of a broad signal at  $-0.25$  ppm in the  $^1\text{H}$  NMR spectrum, attributed to the bridging methyl group. For comparison, the  $^1\text{H}$  NMR resonance of free  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  (as the counterion of  $[\text{t}^n\text{Bu}_3\text{NCH}_2\text{Ph}]^+$ ) appears at 1.12 ppm in benzene- $d_6$ .<sup>24</sup> This indicates that in **13** there is a significant interaction between the methide and the hafnium center. Also, cross-peaks in the  $^1\text{H}$  NOESY spectrum of **13** confirm that the methide remains in close proximity to the ligands on hafnium. Formation of a tetrahedral methyl borate is confirmed by the presence of



**Figure 2.** ORTEP diagram of  $\text{Cp}_2\text{Hf}(\text{Si}'\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**13**). The hydrogen atoms on the Cp rings and on the substituents on the silyl ligand were removed for clarity.

a singlet in the  $^{11}\text{B}$  NMR spectrum ( $-13.03$  ppm) and by a cross-peak between the methyl group and the boron in a  $^1\text{H}$ – $^{11}\text{B}$  HMQC spectrum. As in mixed-ring zwitterionic **7**, the  $^{29}\text{Si}\{^1\text{H}\}$  NMR resonance of zwitterionic **13** is not shifted significantly from that of the neutral precursor **9** (48.76 vs 52.66 ppm). Crystals of **14** were stable for at least 4 months at  $-30$  °C but decomposed at room temperature over 2 days. Compound **14** decomposed slowly over the course of 4 days in benzene- $d_6$ , at room temperature in the dark, with elimination of  $^t\text{BuPh}_2\text{-SiH}$ .

The spectroscopic features of zwitterionic hafnium silyl species **12** and **14** are similar to those of **13**. In compounds **12** and **14**, the  $^{11}\text{B}$  NMR resonances ( $-13.10$  and  $-13.11$  ppm, respectively, benzene- $d_6$ ) establish the presence of a tetrahedral borate center, and broad  $^1\text{H}$  NMR resonances ( $-0.33$  and  $-0.15$  ppm, respectively) corresponding to the abstracted methide groups indicate the presence of bridging  $\text{Hf}\cdots\text{Me}-\text{B}$  interactions. The  $^{29}\text{Si}\{^1\text{H}\}$  NMR signal of **14** (39.41 ppm) does not shift significantly from that of the neutral precursor **10** (37.18 ppm). In complex **12**, however, the  $^{29}\text{Si}\{^1\text{H}\}$  resonance of the central Si (bonded to Hf) appears at  $-21.39$  ppm, which is substantially downfield of that of the neutral precursor ( $-84.12$  ppm). In the  $^1\text{H}$  NMR spectrum of **12** at 190 K (toluene- $d_8$ ), the  $\text{SiMe}_3$  resonance splits into two broad singlets at 0.18 and 0.03 ppm, which integrate to 18 and 9 H, respectively, while the Cp ligands remain equivalent. This low temperature  $^1\text{H}$  NMR spectrum is consistent with a structure in which rotation of the  $\text{Si}(\text{SiMe}_3)_3$  group with respect to the  $\text{Cp}_2\text{Hf}$ -framework is hindered. Complexes **12** and **14** slowly decomposed at room temperature over several days to produce the free silane and mixtures of unidentified hafnium-containing products.

X-ray quality crystals of **13** were obtained from a concentrated toluene solution cooled to  $-30$  °C. The solid-state structure confirms the formation of the zwitterionic species (Figure 2, see Table 3 for data collection parameters). Selected bonds lengths and angles are listed in Tables 1 and 2 along with relevant structural parameters for **9**. The Hf–C(Me) bond distance (2.48(1) Å) is longer than that in **9** (2.287(6) Å); the difference of hafnium–carbon(Me) distances (in **13** vs **9**; 0.19 Å) is smaller than those reported by Marks for  $\text{Cp}^R_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{Cp}^R = \text{C}_5\text{Me}_5, \text{C}_5\text{H}_3\text{Me}_2, \text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ;  $\text{Zr}\cdots\text{Me} = 0.297\text{--}0.407$  Å).<sup>22</sup> The shorter  $\text{M}\cdots\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3$  distance in **13** is likely a consequence of weaker steric pressure exerted

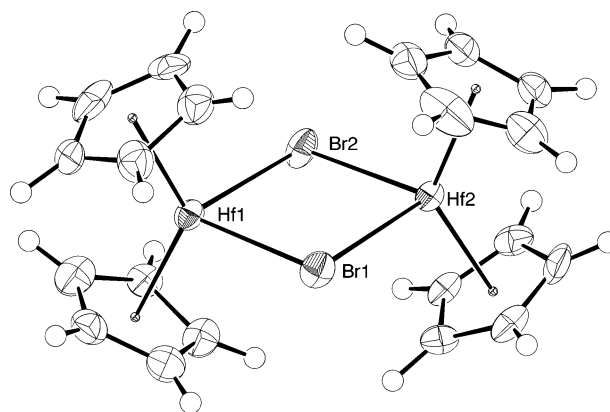
(24) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

**Table 3.** Crystallographic Data for Compounds **9**, **13**, and **15**

	<b>9</b>	<b>13</b>	<b>15</b>
empirical formula	HSiC <sub>27</sub> H <sub>32</sub>	HfSiC <sub>45</sub> BF <sub>15</sub> H <sub>32</sub>	Hf <sub>2</sub> B <sub>2</sub> Br <sub>4</sub> C <sub>79</sub> F <sub>40</sub> H <sub>25</sub>
formula weight	563.13	1075.11	2432.22
crystal color, habit	yellow, blocks	red, blocks	yellow, plates
crystal size (mm <sup>3</sup> )	0.27 × 0.12 × 0.08	0.17 × 0.13 × 0.10	0.46 × 0.35 × 0.06
crystal system	triclinic	orthorhombic	triclinic
space group	<i>P</i> 1(#2)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2(#18)	<i>P</i> 1(#2)
<i>a</i> (Å)	8.2187(2)	20.1825(2)	14.6430(2)
<i>b</i> (Å)	9.3202(2)	21.1290(5)	15.23140(10)
<i>c</i> (Å)	17.0472(4)	10.0160(2)	17.3616(3)
α (deg)	104.346(2)	90	95.234(1)
β (deg)	91.339(2)	90	100.754(1)
γ (deg)	110.93(8)	90	104.326(1)
<i>V</i> (Å <sup>3</sup> )	1172.5(4)	4271.2(3)	3647.31(9)
orientation reflection: number, 2θ range (deg)	3330, 3.5–45.0	4849, 3.5–45.0	9636, 3.5–45.0
<i>Z</i>	2	4	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.595	1.672	2.214
<i>F</i> <sub>000</sub>	560.00	2112.00	2306.00
μ (Mo Kα) (cm <sup>-1</sup> )	45.02	25.64	51.89
diffractometer	SMART	SMART	SMART
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Temperature (K)	151	174	151
scan type	ω(0.3° per frame)	ω(0.3° per frame)	ω(0.3° per frame)
scan rate	10.0 s per frame	10.0 s per frame	10.0 s per frame
data collected,	52.3	52.3	49.4
2θ <sub>max</sub> (deg)			
reflections measured	total: 5673 unique: 3978	total: 20740 unique: 7615	total: 18385 unique: 11518
<i>R</i> <sub>int</sub>	0.025	0.073	0.039
transmission factors	<i>T</i> <sub>max</sub> = 0.65 <i>T</i> <sub>min</sub> = 0.46	<i>T</i> <sub>max</sub> = 0.81 <i>T</i> <sub>min</sub> = 0.61	<i>T</i> <sub>max</sub> = 0.90 <i>T</i> <sub>min</sub> = 0.41
structure solution	SIR92	SIR92	SIR92
no. of observed data [ <i>I</i> > 3σ( <i>I</i> )]	3194	3988	8562
no. of parameters refined	262	594	1111
data/parameter ratio	12.19	6.71	7.71
final residuals:	0.033; 0.036; 0.048	0.037; 0.036; 0.091	0.047; 0.059; 0.064
<i>R</i> ; <i>R</i> <sub>w</sub> ; <i>R</i> <sub>all</sub>			
goodness of fit indicator	1.14	0.97	1.64
max shift/error	0.00	0.14	0.00
final cycle			
max and min peaks, final diff. map (e <sup>-</sup> /Å <sup>3</sup> )	0.89, -1.88	1.08, -0.79	2.07, -2.85

by its substantially smaller, unsubstituted Cp rings. The Si–Hf–C(Me) angle increases from 93.6(2)° to 97.1(3)° upon formation of the zwitterionic species. The B–C1 bond distance of 1.66(2) Å is identical to the corresponding distance reported for Cp\*<sub>2</sub>ZrMe(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>22</sup> The locations of the hydrogen atoms on the bridging methide were calculated based on a tetrahedral geometry for the carbon, and their positions were allowed to freely refine. In the resulting structure, the hydrogens are directed toward the Hf center. The crystal structure also confirms that partial methide abstraction does not significantly perturb the overall coordination environment of the silicon atom. The Hf–Si bond distance in **13** is lengthened by only 0.016 Å relative to that in **9**, and the only Si–C bond distance that changes upon methide abstraction is that involving the <sup>t</sup>Bu group (lengthened by 0.04 Å).

Compounds **8–10** reacted with the methide abstraction agent [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (benzene-*d*<sub>6</sub>, room temperature) with rapid elimination of the corresponding free silane. However, in bromobenzene-*d*<sub>5</sub>, the reaction of **9** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] produced Ph<sub>3</sub>CCH<sub>3</sub> and one organometallic species, which was crystallized by slow diffusion of pentane into the bromobenzene-*d*<sub>5</sub> solution at room temperature. X-ray crystallographic analysis

**Figure 3.** ORTEP diagram of the cation in [Cp<sub>2</sub>Hf(μ-Br)]<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (**15**).

revealed the product to be the dimeric, dicationic complex [Cp<sub>2</sub>Hf(μ-Br)]<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (**15**; Figure 3). Reaction of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with **9** in fluorobenzene produced a mixture of unidentified products.

**Synthesis and Characterization of Cp<sub>2</sub>Hf(η<sup>2</sup>-SiHMe<sub>2</sub>)(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**16**) in Solution.** As in the formation of **12–14**, the reaction of **11** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> yielded the partially

**Table 4.** Spectroscopic Data for Mes<sub>2</sub>SiH<sub>2</sub>, **11**, and **16**

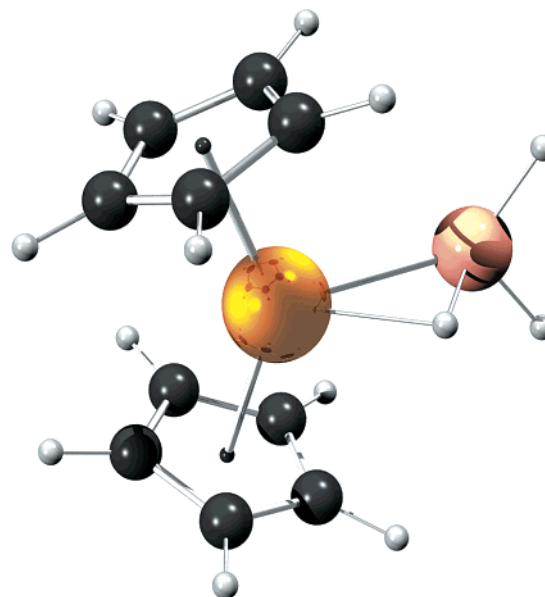
	Mes <sub>2</sub> SiH <sub>2</sub>	<b>11</b>	<b>16</b> (C <sub>6</sub> D <sub>6</sub> )
<sup>1</sup> H NMR (SiH)	5.29	4.98	1.80
<sup>1</sup> J <sub>SiH</sub> (Hz)	195	145	57
<sup>29</sup> Si{ <sup>1</sup> H} NMR	-61	8.25	158
ν(SiH)	2151	2077	1414

methide-abstracted hafnium silyl product, Cp<sub>2</sub>Hf(η<sup>2</sup>-SiHMe<sub>2</sub>)-(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**16**, quantitatively). At room temperature, however, the resulting cationic hafnium silyl complex reacts with benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub>, as described below. The reaction of **11** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in fluorobenzene, hexafluorobenzene, chlorobenzene, and bromobenzene also produced **16** in good yield (by <sup>1</sup>H NMR spectroscopy), but in these solvents, the complex decomposed to mixtures of products. In nonaromatic hydrocarbon solvents such as pentane or cyclohexane, addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **11** rapidly induced precipitation of a powder that contained **16** but was contaminated with Mes<sub>2</sub>SiH<sub>2</sub>. Thus, complex **16** was generated and studied at -40 °C (in toluene-*d*<sub>8</sub>), and under these conditions, it is stable for at least 8 h.

The most notable structural feature of **16** is an α-agostic SiH interaction, which can be deduced from several distinctive spectroscopic characteristics (see Table 4 for spectroscopic data of Mes<sub>2</sub>SiH<sub>2</sub>, **11**, and **16**). In the <sup>1</sup>H NMR spectrum of **16**, the SiH resonance at 1.80 ppm is far upfield of the typical range for silicon hydrides (5–3.5 ppm).<sup>25</sup> The <sup>29</sup>Si NMR resonance for the dimethylsilyl ligand in **16** (158 ppm), detected via a <sup>1</sup>H–<sup>29</sup>Si HMQC experiment, lies far downfield from the resonance in **11** (8.3 ppm), indicating a substantial change in the electronic environment of the silicon atom. The <sup>1</sup>J<sub>SiH</sub> coupling constant of 57 Hz is dramatically decreased from the corresponding value in **11** (150 Hz). This decrease is consistent with substantial weakening of the Si–H bond resulting from the α-agostic interaction with the cationic Hf center.<sup>26</sup> The strongly red-shifted Si–H stretching frequency at 1415 cm<sup>-1</sup> (ν(SiD) = 1015 cm<sup>-1</sup>) is also highly unusual and provides additional support for the proposed α-agostic structure in **16**.

Compound **16** reacts with DMSO to form the base-stabilized complex Cp<sub>2</sub>Hf(SiHMe<sub>2</sub>)(DMSO)MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Coordination of DMSO to the cationic hafnium center disrupts the α-agostic interaction, to produce a complex with spectroscopic data corresponding to a typical hydrosilyl ligand (<sup>1</sup>H NMR: SiH = 5.14 ppm, <sup>1</sup>J<sub>SiH</sub> = 145 Hz).<sup>21</sup>

Although this is the first example of a d<sup>0</sup> α-agostic SiH interaction, coordination of silicon–hydrogen bonds to transition metal centers is common.<sup>25–28</sup> For example, intramolecular coordination of the β-Si–H bond (i.e., β-agostic) to the d<sup>0</sup> centers in Cp<sub>2</sub>Zr[N(SiHMe<sub>2</sub>)<sup>t</sup>Bu]X (X = hydride, halide) complexes results in similar upfield <sup>1</sup>H NMR shifts for the silicon hydride at 1.21–2.94 ppm, low <sup>1</sup>J<sub>SiH</sub> coupling constants of 113–135 Hz, and reduced values for the ν(SiH) stretching frequency (1912–1998 cm<sup>-1</sup>).<sup>25</sup> Similarly, Me<sub>2</sub>Si(η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>-2-

**Figure 4.** Calculated gas-phase structure of [Cp<sub>2</sub>HfSiH<sub>3</sub>]<sup>+</sup> (A).

Me<sub>2</sub>YN(SiHMe<sub>2</sub>)<sub>2</sub>, with a β-agostic Si–H bond, exhibits a <sup>1</sup>H NMR shift of 2.97 ppm, a <sup>1</sup>J<sub>SiH</sub> value of 142 Hz, and a ν(SiH) frequency of 1804 cm<sup>-1</sup>.<sup>27</sup> Note that these comparisons suggest strong donation of electron density from the Si–H bond to the electrophilic hafnium center of **16**. Harrod and co-workers have isolated and spectroscopically characterized dimeric, dicationic zirconocene hydrosilyl complexes formulated as [Cp'<sub>2</sub>Zr(μ-H)-(SiHR)]<sub>2</sub><sup>2+</sup> (R = Ph, CH<sub>2</sub>Ph; Cp' = Cp, Cp\*, C<sub>5</sub>H<sub>4</sub>Me), in which very small SiH coupling constants (ca. 20 Hz) imply that there is no direct interaction between the Zr–H and the Si atom.<sup>28</sup> α-Agostic interactions in alkyl complexes have been extensively investigated due to their importance in olefin polymerization.<sup>29</sup> The α-agostic SiH interaction reported here may be important in σ-bond metathesis reactions (*vide infra*), as complexes featuring such characteristics (i.e., **16**) react with the C–H bonds of arenes, while complexes lacking this agostic interaction do not.

**Density Functional Theory (DFT) Calculations on the Model Compounds Cp<sub>2</sub>HfSiH<sub>3</sub><sup>+</sup> (A) and Cp<sub>2</sub>HfSiH(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub><sup>+</sup> (B).** To further explore the unusual bonding in **16**, density functional theory (B3LYP/LACVP\*\*++) was used to model the gas-phase structure of **16**.<sup>30–32</sup> The resulting structures represent unsolvated, counterion-free models of compound **16**. The initial geometry of Cp<sub>2</sub>HfSiH<sub>3</sub><sup>+</sup> (A), modeled as a normal hafnium silyl species with an Hf–Si σ-bond, a tetrahedral geometry at silicon, and an overall charge of +1 (i.e., Hf<sup>IV</sup>), was minimized on the potential energy surface (PES). The final geometry contains an α-agostic SiH moiety coordinated to the Hf center and is consistent with the proposed structure of **16** (Figure 4, Table 5). The geometry of the silicon atom is severely

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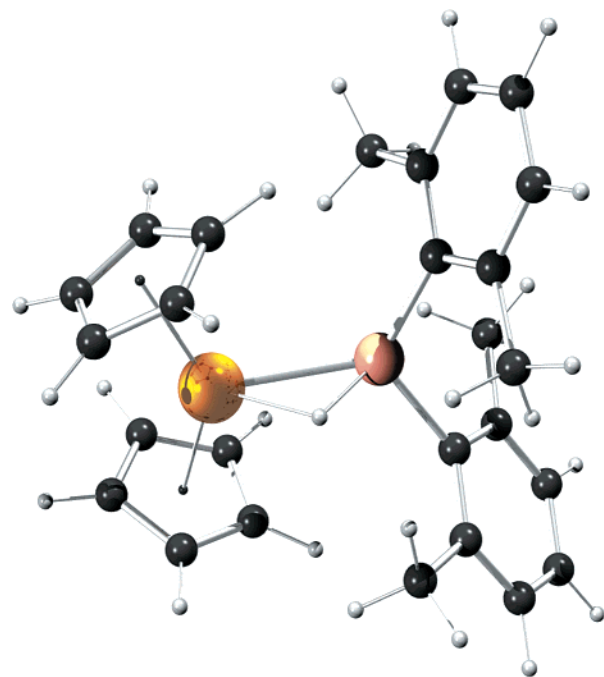
**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for the Calculated Structure  $\text{Cp}_2\text{HfSiH}_3^+$  (**A**)

bond lengths			
Hf–Si	2.59	Si–H <sub>term</sub>	1.49
Hf–H <sub>bridge</sub>	2.05	Hf–C <sub>pcent</sub>	2.17
Si–H <sub>bridge</sub>	1.63		
bond angles			
Hf–Si–H <sub>bridge</sub>	52.3	H <sub>term</sub> –Si–H <sub>term</sub>	108.0
Hf–H <sub>bridge</sub> –Si	88.6	H <sub>bridge</sub> –Si–H <sub>term</sub>	103.3
Hf–Si–H <sub>term</sub>	124.6	C <sub>pcent</sub> –Hf–C <sub>pcent</sub>	140.8

distorted to trigonal monopyramidal, with the bridging hydride occupying the pseudoaxial position. The Hf–Si–H<sub>bridge</sub> and H<sub>term</sub>–Si–H<sub>bridge</sub> angles are 52.3° and 88.6°, respectively. The Hf–Si–H<sub>term</sub> angles are identical (124.6°), and the H<sub>term</sub>–Si–H<sub>term</sub> angle is 108.0°. The sum of these three angles is 357.3°, indicating the near planarity of the silicon, the Hf, and the two H<sub>term</sub> atoms (the equatorial substituents). The Si–H<sub>bridge</sub> bond distance of 1.63 Å is longer than that of Si–H<sub>term</sub> (1.49 Å) and that of a 16-electron neutral complex  $\text{Cp}_2\text{Hf}(\text{SiH}_2\text{Cy})\text{Cl}$  (1.51 Å). This neutral complex, which was isolated and fully characterized previously,<sup>9</sup> was modeled for comparison. The Hf–Si bond distance in **A** is 2.60 Å, 0.17 Å shorter than the corresponding distance calculated for  $\text{Cp}_2\text{Hf}(\text{SiH}_2\text{Cy})\text{Cl}$  (2.76 Å). A calculation of the normal vibrational modes of structure **A** confirms that it is indeed a minimum geometry on the potential energy surface. The calculated Si–H stretching frequency  $\nu(\text{SiH})$  of 1475 (after normalization to the ratio  $\nu(\text{SiH})_{\text{calculated}}/\nu(\text{SiH})_{\text{experimental}}$ , 2121  $\text{cm}^{-1}/2030 \text{ cm}^{-1}$ , for  $\text{Cp}_2\text{Hf}(\text{SiH}_2\text{Cy})\text{Cl}$ ) is consistent with the experimentally observed value ( $\nu_{\text{SiH}} = 1415$ ), indicating that the proposed  $\alpha$ -agostic structure and the calculated structure are similar. According to the calculations, the  $\alpha$ -SiH's of the 16-electron complex  $\text{Cp}_2\text{Hf}(\text{SiH}_2\text{Cy})\text{Cl}$  do not coordinate to the Hf center, as the Hf–Si–H bond angles (110.0° and 112.4°) and Hf⋯H through-space distances (3.62 and 3.59 Å) preclude such interactions. It is also interesting to note that the minimized geometry for the isoelectronic neutral compound  $\text{Cp}_2\text{ScSiH}_3$  does not exhibit an  $\alpha$ -agostic structure.<sup>33</sup> This is consistent with the spectroscopic features of the isolated and crystallographically characterized compound  $\text{Cp}^*\text{ScSiH}_2\text{SiPh}_3$ , which exhibits normal  $\eta^1$  bonding of the silyl group to scandium.<sup>33</sup>

The minimized geometry of  $\text{Cp}_2\text{Hf}[\text{SiH}(2,6\text{-Me}_2\text{C}_6\text{H}_4)_2]^+$  (**B**) (Figure 5, Table 6) also contains the  $\alpha$ -agostic SiH structure found in **A** and **16**. The Hf–Si–H<sub>bridge</sub> angle is severely distorted to 50.4°, and the Si–H<sub>bridge</sub> bond distance is elongated to 1.67 Å. The Hf–Si bond distance of 2.62 Å is shorter than the calculated distance for  $\text{Cp}_2\text{Hf}(\text{SiH}_2\text{Cy})\text{Cl}$  (2.75 Å) or the X-ray crystallographically determined distance of  $\text{Cp}_2\text{Hf}(\text{Si}^i\text{BuPh}_2)\text{Me}$  (2.835 Å). The Hf–Si–C bond angles are 121.1° and 123.7°, and the C–Si–C angle is 114.3°. The sum of the angles around silicon (ignoring the  $\alpha$ -hydrogen substituent) is 359.1°, indicating the nearly trigonal planar geometry of the silicon and its equatorial substituents. It is clear from these calculations that the coordinatively unsaturated, electron-poor metal centers of **16**, **A**, and **B** are stabilized by the  $\alpha$ -agostic SiH interaction.

**$\sigma$ -Bond Metathesis Reactions of  $\text{Cp}_2\text{Hf}(\text{Si}^i\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**13**).** With the zwitterionic hafnium silyl complex **13** in hand, we began to explore its reactivity in  $\sigma$ -bond metathesis

**Figure 5.** Calculated gas-phase structure of  $[\text{Cp}_2\text{HfSiH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]^+$  (**B**).**Table 6.** Selected Bond Lengths (Å) and Angles (deg) for the Calculated Structure  $\text{Cp}_2\text{HfSiH}(2,6\text{-C}_6\text{Me}_2\text{H}_3)_2^+$  (**B**)

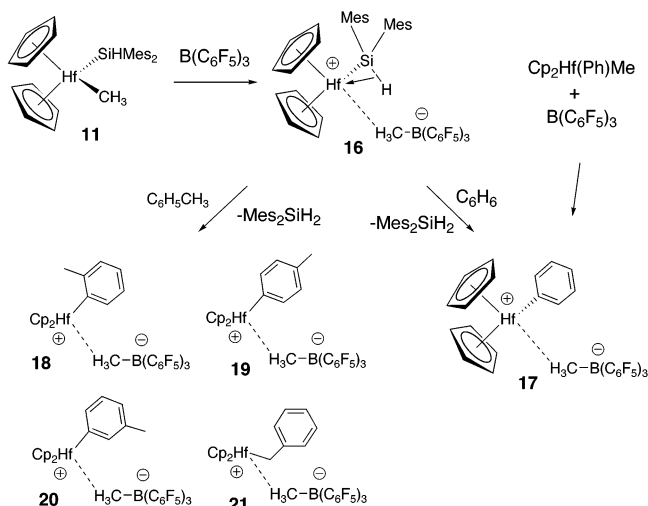
bond lengths			
Hf–Si	2.63	Si–C1	1.90
Hf–H <sub>bridge</sub>	2.02	Si–C2	1.91
Si–H <sub>bridge</sub>	1.67	Hf–C <sub>pcent</sub>	2.18
Hf–C <sub>pcent</sub>	2.18		
bond angles			
Hf–Si–H <sub>bridge</sub>	50.4	H <sub>bridge</sub> –Si–C	103.2
Hf–H <sub>bridge</sub> –Si	90.1	H <sub>bridge</sub> –Si–C	108.8
Hf–Si–C	121.1	C <sub>pcent</sub> –Hf–C <sub>pcent</sub>	137.8
Hf–Si–C	123.7		

reactions with silanes. Compound **13** rapidly reacted with 1 equiv of  $\text{PhSiH}_3$  to produce an immediate color change from red to pale yellow, with formation of  $\text{HSi}^i\text{BuPh}_2$ ,  $\text{PhMeSiH}_2$ , and unidentified hafnium-containing species (by  $^1\text{H}$  NMR spectroscopy). In contrast, the reaction of the neutral hafnium silyl chloride complex  $\text{Cp}_2\text{Hf}(\text{Si}^i\text{BuPh}_2)\text{Cl}$  with  $\text{PhSiH}_3$  produced  $[\text{Cp}_2\text{HfHCl}]_x$ ,  $^i\text{BuPh}_2\text{SiH}$ , and a mixture of oligomeric silanes over 3 days in benzene- $d_6$ . The reactions of **13** with primary and secondary silanes, such as  $\text{MesSiH}_3$ ,  $\text{Ph}_3\text{SiSiH}_3$ ,  $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$ ,  $(\text{Me}_3\text{Si})_2\text{SiH}_2$ , and  $\text{Ph}_2\text{SiH}_2$ , rapidly produced  $\text{HSi}^i\text{BuPh}_2$  and unidentified organometallic products at room temperature ( $t_{1/2} < 5 \text{ min}$ ,  $^1\text{H}$  NMR spectroscopy).

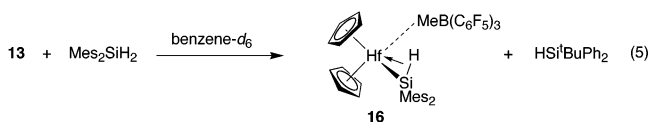
The reaction of **13** with  $\text{Mes}_2\text{SiH}_2$  at room temperature produced  $\text{Cp}_2\text{Hf}(\text{SiHMe}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**) in approximately 25% yield (by  $^1\text{H}$  NMR spectroscopy) in benzene- $d_6$  after 2.5 h (eq 5). The byproduct  $^i\text{BuPh}_2\text{SiH}$  was formed quantitatively, and the low yield of compound **16** results from its subsequent reaction with benzene to form  $\text{Cp}_2\text{HfPh}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**17**, *vide infra*). After 4 h, **17** was the primary hafnium-containing product. Compounds **16** and **17** were identified by comparisons of their  $^1\text{H}$  NMR spectra to the spectra of independently synthesized samples (prepared via reactions of **11** and  $\text{Cp}_2\text{Hf}(\text{Ph})\text{Me}$ , respectively, with  $\text{B}(\text{C}_6\text{F}_5)_3$ ). In the absence of  $\text{Mes}_2\text{SiH}_2$ , **17** was not formed from complex **13** in benzene- $d_6$  ( $^1\text{H}$  NMR spectroscopy). Interestingly, the steric bulk

(33) Sadow, A. D.; Tilley, T. D. Manuscript in preparation.



**Scheme 2.** Synthesis of  $\text{Cp}_2\text{Hf}(\eta^2\text{-SiHMes}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**) and Its Reactions with Arenes via  $\text{Mes}_2\text{SiH}_2$  Elimination

of  $\text{Mes}_2\text{SiH}_2$  and the  $\text{Si}^i\text{BuPh}_2$  substituent did not inhibit this transformation; it is quite facile. Second-order plots of  $\ln\{[\text{Mes}_2\text{SiH}_2]/[\mathbf{13}]\}$  vs time were linear over three half-lives ( $k = 8.3 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$  at  $26^\circ\text{C}$ ). The first-order dependence of the rate on both  $\text{Mes}_2\text{SiH}_2$  and **13** supports the hypothesis that the reaction proceeds via a concerted,  $\sigma$ -bond metathesis mechanism.



**C–H Bond Activation by  $\text{Cp}_2\text{Hf}(\eta^2\text{-SiHMes}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**).** At room temperature, compound **16** rapidly reacted with benzene- $d_6$  ( $t_{1/2} = 54 \text{ min}$ ) to form  $\text{Cp}_2\text{Hf}(\text{Ph-}d_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**17-d**), with elimination of  $\text{Mes}_2\text{SiHD}$  (Scheme 2). The  $\text{Mes}_2\text{SiHD}$  was identified by its 1:1:1 SiH triplet resonance in the  $^1\text{H}$  NMR spectrum ( $^2J_{\text{HD}} = 3.6 \text{ Hz}$ ) and by comparison to an authentic sample of  $\text{Mes}_2\text{SiH}_2$ .  $\alpha$ -Agostic **16** also reacted with toluene- $d_8$  (as solvent; over ca. 2.5 h at room temperature) to give the four possible products of C–D bond activation,  $\text{Cp}_2\text{Hf}(o\text{-tolyl-}d_7)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**18-d**),  $\text{Cp}_2\text{Hf}(p\text{-tolyl-}d_7)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**19-d**) (relative percentages of compounds **18** and **19** could not be resolved by  $^1\text{H}$  NMR spectroscopy but represent 45% of the total products),  $\text{Cp}_2\text{Hf}(m\text{-tolyl-}d_7)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**20-d**, 32%), and  $\text{Cp}_2\text{Hf}(\text{benzyl-}d_7)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**21-d**, 23%). The identity of each product was confirmed by its independent synthesis from the appropriate  $\text{Cp}_2\text{Hf}(\text{C}_7\text{H}_8)\text{Me}$  derivative.

Kinetic investigations of the reaction of **16** with benzene provide information regarding the mechanism of the C–H bond activation step. In neat benzene- $d_6$ , linear plots of  $\ln[\mathbf{16}]$  versus time established first-order rate dependence on the cationic hafnium silyl complex. Attempts to determine the order in benzene were complicated by the difficulty of finding an inert solvent in which the zwitterionic complex was soluble; compound **16** precipitated even from benzene solutions containing low concentrations of nonaromatic hydrocarbon solvents. Polar solvents such as diethyl ether and  $\text{CH}_3\text{CN}$  interfered with the C–H bond activation chemistry. However, it was possible to vary the concentration of benzene over a small range by the

addition of small amounts of hexafluorobenzene (ca. 7–13%). The results of these experiments indicate first-order dependence of the rate on benzene and suggest a rate law of  $\text{rate} = k[\mathbf{16}][\text{C}_6\text{D}_6]$  ( $k = 5.0 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ,  $13.5^\circ\text{C}$ ). The existence of a large primary kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 6.9(7)$ ) confirmed that benzene is involved in the rate-determining step. Furthermore, the magnitude of this isotope effect is consistent with transfer of hydrogen from carbon to silicon in the  $\beta$ -position of a concerted transition state.<sup>34</sup> An Eyring plot provided activation parameters of  $\Delta H^\ddagger = 19(1) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -17(3) \text{ eu}$ , which implicate an ordered transition state.<sup>35</sup> These data are all consistent with a  $\sigma$ -bond metathesis mechanism in which Hf–Si bond cleavage and Hf–Ph bond formation occur simultaneously.

The cationic character of the reactive species and the role of the borate anion were investigated by monitoring benzene activations in the presence of excess  $[\text{Bu}_3\text{NCH}_2\text{Ph}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (10 and 20 equiv). Since these rates were identical to those observed in the absence of excess borate anion, it appears that the dissociation of  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  is not involved in the rate-determining step for C–H activation. Marks and co-workers have studied the solution dynamics of cationic zirconium and hafnium alkyl complexes with  $\text{MeB}(\text{C}_6\text{F}_5)_3^-$  counterions, based on the coalescence of the diastereotopic methyl groups in the  $\text{C}_5\text{H}_3\text{Me}_2$  ligand in fluxional cation–anion pairs, and have determined the barriers for cation/anion separation.<sup>36</sup> The values for  $\Delta G^\ddagger$  and  $\Delta H^\ddagger$  (14.0(2) kcal/mol and 15(2) kcal/mol, respectively;  $20^\circ\text{C}$  in toluene) for the first-order cation–anion reorganization process were reported for the compound  $(\text{C}_5\text{H}_3\text{Me}_2)_2\text{Hf}(\text{CH}_2\text{SiMe}_3)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>36</sup> Comparisons of these barriers with those of the second-order C–H bond activation process for **16** ( $\Delta G^\ddagger = 24 \text{ kcal/mol}$  at  $20^\circ\text{C}$ ;  $\Delta H^\ddagger = 19(1) \text{ kcal/mol}$ , temperature range of  $5\text{--}50^\circ\text{C}$  in benzene- $d_6$ ) suggest that the reaction of **16** with benzene is slower than cation–anion separation. Furthermore, these activation barriers and the fact that the neutral complexes **4**, **6**, and **11** do not react with benzene imply that the reactive form of **16** contains considerable cationic character.

Given the well-documented role of  $\alpha$ -agostic assistance in olefin polymerization,<sup>16,29</sup> the  $\alpha$ -agostic SiH interaction in **16** may be an important factor in the C–H bond activation step. The negligible secondary isotope effect ( $k_{\text{H}}/k_{\text{D}} = 1.1(1)$ ) determined for the rate of benzene- $d_6$  activation by  $\text{Cp}_2\text{Hf}(\eta^2\text{-SiDMes}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16-d**) versus **16** indicates that the Si–H $\cdots$ Hf interaction is not disrupted in the transition state for C–H activation. Furthermore, the cationic hafnium silyl complexes **12–14** do not contain an  $\alpha$ -SiH and do not react with C–H bonds. These observations suggest that the  $\alpha$ -agostic Si–H interaction plays an important role in activating the Hf–Si bond toward  $\sigma$ -bond metathesis.

## Discussion

The zwitterionic hafnium silyl complexes reported here are significantly more reactive than corresponding neutral species

- (34) Concerted four-centered transition states in which an H atom is transferred in the  $\beta$ -position typically exhibit large primary isotope effects. For example, see: Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425.  
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in  $\sigma$ -bond metathesis reactions. For example, the enhanced reactivity of **13** is illustrated by its reaction with the sterically hindered  $\text{Mes}_2\text{SiH}_2$  to form **16**, presumably through a very hindered transition state. The high reactivity of **16** is demonstrated by its ability to activate the C–H bonds of arenes. The mechanism of the reactions of **16** with arene C–H bonds appears to proceed via a concerted transition state, of the type normally associated with  $\sigma$ -bond metathesis.<sup>1,2</sup>

The metalation of arenes by **16** is the first example of a direct  $\sigma$ -bond metathesis reaction between a  $d^0$  metal–silyl and an arene C–H bond. In previous studies, the scandium–silyl complex  $\text{Cp}_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$  was found to react with  $\text{HC}\equiv\text{CPh}$  to yield the products  $[\text{Cp}_2\text{ScC}\equiv\text{CPh}]_2$  and  $\text{HSi}(\text{SiMe}_3)_3$ , via activation of the alkyne C–H bond.<sup>37</sup> While the Ta<sup>III</sup> complex  $\text{Cp}_2\text{Ta}(\text{SiH}^t\text{Bu}_2)(\text{PMe}_3)$  reacts with benzene in a process which is similar to that of Scheme 2, the mechanism of this metalation involves oxidative addition of a C–H bond followed by reductive elimination of an Si–H bond.<sup>38</sup> Interestingly, the microscopic reverse of the reaction of **16** with benzene, the direct reaction of a  $d^0$  metal phenyl with a hydrosilane to form a metal–silicon bond, with elimination of arene, is also rare.<sup>33</sup> Silanes typically react with  $d^0$  metal phenyl (and alkyl) complexes to form Si–C bonds and metal hydride species, as in lanthanide-catalyzed organosilane redistribution and olefin hydrosilation.<sup>6,39</sup>

Cationic ( $d^0$ ) hafnium alkyl complexes containing  $\alpha$ -agostic interactions have been documented.<sup>40</sup> Furthermore,  $\alpha$ -agostic assistance (i.e., the coordination of an  $\alpha$ -hydrogen to the metal center in the transition state for olefin insertion into an M–C bond) has been proposed as an important effect in the polymerization of olefins. This assertion is based on the detection of small secondary isotope effects ( $k_H/k_D \approx 1.2$ ) for the olefin insertion step.<sup>29</sup> The participation of  $\alpha$ -agostic structures in  $\sigma$ -bond metathesis has been suggested by theoretical studies of gas-phase model molecules. For example, the ground-state, gas-phase structure of 14-electron  $\text{Cp}_2\text{ZrMe}^+$  contains an  $\alpha$ -agostic interaction, which is maintained upon coordination of  $\text{H}_2$  to the cationic Zr center and in the transition state structure for Zr–C bond hydrogenolysis.<sup>41a</sup> Also, an  $\alpha$ -Si–H bond is coordinated to the scandium center in the calculated transition state structure for the  $\sigma$ -bond metathesis reaction of  $\text{Cl}_2\text{ScSiH}_3$  with  $\text{SiH}_4$ .<sup>41b</sup> Additionally, in the isolated compound  $\text{Cp}^*\text{Th}(\text{CH}_2\text{CMe}_3)_2$ , the  $\alpha$ -C–H bonds of one  $\text{CH}_2\text{CMe}_3$  ligand are coordinated to the Th center and this compound reacts via intramolecular C–H bond activation and  $\text{CMe}_4$  elimination to form the cyclometalated complex  $\text{Cp}^*\text{Th}(\kappa^2\text{-CH}_2\text{CMe}_2\text{CH}_2)$ .<sup>42</sup> In C–H bond activation reactions with **16**, participation of the  $\alpha$ -agostic SiH in the transition state appears to contribute to the high reactivity of the Hf–Si bond. The negligible secondary isotope effect ( $k_H/k_D = 1.1(1)$ ) suggests either that the agostic interaction is broken prior to the rate determining step or that it

is maintained as the reaction passes through the transition state. The latter interpretation is supported by the fact that cationic hafnium silyl complexes lacking an  $\alpha$ -SiH moiety, such as **12–14**, do not react with aromatic or aliphatic C–H bonds.

The reactions of **16** with the C–H bonds of benzene and toluene expand the scope of possible approaches for the catalytic functionalization of arenes (e.g., Scheme 1). The three steps which comprise this potential cycle (C–H bond activation by a metal–silyl complex, aryl transfer from hafnium to the silicon center of a hydrosilane, and silane metalation by a metal hydride complex) have been observed as individual steps for cationic hafnium complexes.<sup>17,20</sup> The transfer of an aryl substituent from a metal center to silicon has been reported for several transition metal and f-block aryl complexes, including cationic hafnium complexes.<sup>17,43</sup> The dehydrocoupling of M–H and Si–H bonds to form a metal–silyl complex and dihydrogen has also been described in stoichiometric and catalytic reactions of primary and secondary silanes with several  $d^0$  and  $f^0d^0$  complexes.<sup>3,4,8,9</sup> In addition, the metalation of  $\text{Mes}_2\text{SiH}_2$  by  $\text{Cp}_2\text{Hf}(\text{Si}^t\text{BuPh}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  indicates that **16** may be formed via  $\sigma$ -bond metathesis (i.e., it is a viable participant in a catalytic cycle). Unfortunately, the synthesis of **16** from  $\text{Mes}_2\text{SiH}_2$  and  $\text{Cp}_2\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$  is not possible because the latter hafnium hydride complex appears to be unstable under the reaction conditions.

Efforts to effect the type of catalysis depicted in Scheme 1 using  $\text{Cp}_2\text{Hf}(\text{SiHMe}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**) were unsuccessful, and the selective activation of benzene by cationic hafnium–silyl complexes appears to be limited to the bis(cyclopentadienyl) ligand set and the dimethylsilyl substituent on **16**. Benzene- $d_6$  solutions of  $\text{Mes}_2\text{SiH}_2$  and **16** were heated to 60 °C for several days, but  $\text{Mes}_2(\text{C}_6\text{D}_5)\text{SiH}$  was not formed, probably because  $\text{Mes}_2\text{SiH}_2$  is too hindered to occupy the  $\beta$ -position of the four-centered transition state and participate in a phenyl-transfer reaction. Given the possibility that less hindered silanes might be more reactive toward phenyl derivatives that form by C–H bond activation,  $\text{PhSiH}_3$  and  $\text{Ph}_2\text{SiH}_2$  were investigated as components in **16**/ $\text{Mes}_2\text{SiH}_2$ /benzene reaction mixtures. Unfortunately, addition of  $\text{PhSiH}_3$  or  $\text{Ph}_2\text{SiH}_2$  simply facilitated the decomposition of **16** to  $\text{Mes}_2\text{SiH}_2$  and unidentified hafnium-containing products. Attempts to extend the C–H bond activation reactions to  $\text{CpCp}^*\text{Hf}$ -derivatives were also unsuccessful; the reaction of  $\text{CpCp}^*\text{Hf}(\text{SiHMe}_2)\text{Me}$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  (in benzene- $d_6$ ) did not produce identifiable quantities of either  $\text{CpCp}^*\text{Hf}(\text{SiHMe}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{CpCp}^*\text{Hf}(\text{C}_6\text{D}_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>17</sup> Additionally, attempts to initiate the catalytic dehydrosilation of benzene- $d_6$  (as solvent) with  $\text{Mes}_2\text{SiH}_2$  were unsuccessful with  $\text{Cp}_2\text{HfMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$  as potential catalyst precursors (no  $\text{Mes}_2(\text{C}_6\text{D}_5)\text{SiH}$  was detected after 2 d at 70 °C by  $^1\text{H}$  NMR or GC–MS). Clearly, successful hydrocarbon dehydrosilations by cationic group 4 complexes require species capable of mediating facile and selective hydrocarbon metalations via C–H bond activations. Despite the apparent lack of catalytic activity in the systems described here, the observation of C–H bond activations by **16** suggests that catalytic cycles for hydrocarbon functionalization might be based on electrophilic  $d^0$  metal–silyl species as the catalysts. This approach will

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require silyl complexes which are easily generated by the dehydrocoupling of M–H and Si–H species and which readily activate C–H bonds in a selective manner in the presence of the Si–H and Si–C bonds of silanes.

## Conclusion

The results reported here demonstrate that cationic character in a  $d^0$  silyl complex promotes  $\sigma$ -bond metathesis reactions of M–Si bonds with Si–H and C–H bonds. The electrophilic, coordinatively unsaturated, zwitterionic complex  $\text{Cp}_2\text{Hf}(\eta^2\text{-SiHMe}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  (**16**) has been shown to exhibit unusual spectroscopic features characteristic of an  $\alpha$ -agostic Si–H interaction with the hafnium center. The reactions described here, including those of **13** with  $\text{Me}_2\text{SiH}_2$  and **16** with benzene, constitute further evidence that cationic  $d^0$  metal complexes are highly reactive in  $\sigma$ -bond metathesis. Furthermore, we have observed three stoichiometric steps for a possible catalytic cycle, involving cationic hafnium complexes, that appear to represent a potential strategy for the catalytic functionalization of hydrocarbons.

## Experimental Section

**General.** All manipulations were performed under an atmosphere of nitrogen using Schlenk techniques and/or a glovebox. Dry, oxygen-free solvents were employed throughout. Removal of thiophenes from benzene and toluene was accomplished by washing each with  $\text{H}_2\text{SO}_4$  and saturated  $\text{NaHCO}_3$  followed by drying over  $\text{MgSO}_4$ . Olefin impurities were removed from pentane by treatment with concentrated  $\text{H}_2\text{SO}_4$ , 0.5 N  $\text{KMnO}_4$  in 3 M  $\text{H}_2\text{SO}_4$ , saturated  $\text{NaHCO}_3$ , and then the drying agent  $\text{MgSO}_4$ . 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. Bromobenzene- $d_5$  was placed over 4-Å molecular sieves and degassed by repeated freeze–pump–thaw cycles. The compounds  $\text{CpCp}^*\text{HfCl}_2$ ,<sup>44</sup>  $\text{Cp}_2\text{HfMeCl}$ ,<sup>45</sup>  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$  (**4**),<sup>3c</sup>  $\text{Cp}_2\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ ,<sup>46</sup>  $\text{B}(\text{C}_6\text{F}_5)_3$ ,<sup>47</sup>  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,<sup>47</sup>  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ ,<sup>48</sup>  $(\text{THF})_3\text{LiSi}^i\text{BuPh}_2$ ,<sup>48</sup>  $(\text{THF})_3\text{LiSiPh}_3$ ,<sup>48</sup> and  $(\text{THF})_2\text{LiSiMe}_2\text{H}^{21}$  were prepared according to literature procedures. The materials MeLi, MeMgBr, (*o*- $\text{C}_6\text{H}_4\text{Me}$ )MgCl, (*m*- $\text{C}_6\text{H}_4\text{Me}$ )MgCl, and (*p*- $\text{C}_6\text{H}_4\text{Me}$ )MgCl were purchased from Aldrich and used as received. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. Infrared spectra were recorded using a Mattson FTIR spectrometer at a resolution of 4  $\text{cm}^{-1}$ . All NMR spectra were recorded at room temperature in benzene- $d_6$  unless otherwise noted, using a Bruker AMX-300 spectrometer at 300 MHz ( $^1\text{H}$ ), 75.5 MHz ( $^{13}\text{C}$ ), a Bruker AM-400 spectrometer at 400 MHz ( $^1\text{H}$ ) 377 MHz ( $^{19}\text{F}$ ), or a Bruker DRX-500 at 500 MHz ( $^1\text{H}$ ), 125 MHz ( $^{13}\text{C}$ ), 160 MHz ( $^{11}\text{B}$ ), 100 MHz ( $^{29}\text{Si}$ ).

**$\text{CpCp}^*\text{Hf}(\text{Si}^i\text{BuPh}_2)\text{Cl}$  (**2**).** A 250-mL Schlenk flask was charged with  $\text{CpCp}^*\text{HfCl}_2$  (1.47 g, 3.28 mmol) and  $(\text{THF})_3\text{LiSi}^i\text{BuPh}_2$  (1.68 g, 3.64 mmol). The flask was wrapped in aluminum foil, and 75 mL of ether were added. The resulting solution was stirred at ambient temperature in the dark for 5 h. Solvent was then removed under reduced pressure, and the yellow solid was extracted with pentane (3  $\times$  30 mL). The pentane extracts were combined, concentrated to

approximately 10 mL, and cooled to  $-40^\circ\text{C}$  for crystallization. Yellow crystals were isolated by filtration and dried under vacuum to yield 1.70 g of **2** (2.61 mmol, 79.5%).  $^1\text{H}$  NMR (300 MHz):  $\delta$  7.94 (m, 2 H, Ph), 7.48 (m, 2 H, Ph), 7.28 (m, 5 H, Ph), 6.11 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 1.64 (s, 15 H,  $\text{C}_5\text{Me}_5$ ), 1.35 (s, 9 H,  $^i\text{Bu}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz):  $\delta$  138.7 (Ph), 138.1 (Ph), 128.3 (Ph), 127.8 (Ph), 127.7 (Ph), 127.4 (Ph), 121.4 ( $\text{C}_5\text{Me}_5$ ), 112.2 ( $\text{C}_5\text{H}_5$ ), 32.1 ( $\text{CMe}_3$ ), 25.5 ( $\text{CMe}_3$ ), 12.9 ( $\text{C}_5\text{Me}_5$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz):  $\delta$  51.48. IR (KBr,  $\text{cm}^{-1}$ ): 2113.6 (w), 1487 (m), 1454 (m), 1425 (s), 1379 (m), 1259 (m), 1174 (w), 1086 (s), 1026 (s), 816 (s). Anal. Calcd for  $\text{C}_{31}\text{H}_{39}\text{F}_3\text{HfSi}$ : C, 56.96; H, 6.01. Found: C, 56.60; H, 6.36. Mp: 100–102  $^\circ\text{C}$  (dec).

**$\text{CpCp}^*\text{Hf}(\text{SiHMe}_2)\text{Cl}$  (**3**).**  $\text{CpCp}^*\text{HfCl}_2$  (0.526 g, 1.17 mmol) and  $(\text{THF})_{2.5}\text{LiSiHMe}_2$  (0.635 g, 1.52 mmol) were separately dissolved in 25 mL of ether. The solution of  $(\text{THF})_{2.5}\text{LiSiHMe}_2$  was slowly added to the  $\text{CpCp}^*\text{HfCl}_2$  solution. The reaction mixture was stirred in the dark for 3 h. Solvent was removed under reduced pressure, and the resulting solid was extracted with pentane (3  $\times$  50 mL). The pentane extracts were concentrated to ca. 15 mL and cooled to 0  $^\circ\text{C}$ . Small yellow crystals were isolated by filtration and dried under vacuum to yield 0.13 g of **3** (0.191 mmol, 16.3%).  $^1\text{H}$  NMR (400 MHz):  $\delta$  6.90 (s, 2 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 6.86 (s, 2 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 5.77 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 5.32 (s, 1 H, SiH), 2.69 (s, 6 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.54 (s, 6 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.21 (s, 3 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.17 (s, 3 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 1.84 (s, 15 H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz):  $\delta$  141.6 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 139.7 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 136.3 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 136.4 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 128.6 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 127.8 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 127.5 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 119.9 ( $\text{C}_5\text{Me}_5$ ), 112.2 ( $\text{C}_5\text{H}_5$ ), 25.3 (*p*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 20.7 (*o*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 20.6 (*o*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 11.8 ( $\text{C}_5\text{Me}_5$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (100 MHz):  $\delta$  -0.423. IR (KBr,  $\text{cm}^{-1}$ ): 3589 (s), 3444 (br), 3226 (br), 3142 (br), 1421 (s), 1315 (s), 1265 (m), 1101 (m), 1051 (m), 976 (m), 831 (m). Anal. Calcd for  $\text{C}_{33}\text{H}_{43}\text{HfSi}$ : C, 58.14; H, 6.35. Found: C, 57.80; H, 6.42. Mp: 142–144  $^\circ\text{C}$  (dec).

**$\text{CpCp}^*\text{Hf}(\text{Si}^i\text{BuPh}_2)\text{Me}$  (**5**).** Compound **2** (0.329 g, 0.504 mmol) was dissolved in  $\text{Et}_2\text{O}$  (35 mL) and the solution was cooled to  $-78^\circ\text{C}$ .  $\text{MeMgBr}$  (0.20 mL, 3.0 M in diethyl ether, 0.60 mmol) was added to the solution. The flask was allowed to slowly warm to room temperature over 3 h. The volatile materials were removed from the bright yellow solution under reduced pressure. The resulting solid was extracted with pentane (3  $\times$  25 mL), which was subsequently removed under vacuum, affording a powdery solid. Analytically pure samples of **5** were obtained by recrystallization from ether (3 mL) at  $-30^\circ\text{C}$ . Yellow crystals were isolated by filtration, yielding 0.26 g (0.342 mmol, 67.8%) of **5**.  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.65 (d, 1 H, Ph), 7.39 (d, 1 H, Ph), 7.27 (m, 4 H, Ph), 7.19 (m, 4 H, Ph), 6.02 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 1.59 (s, 15 H,  $\text{C}_5\text{Me}_5$ ), 1.27 (s, 9 H,  $^i\text{Bu}$ ), -0.44 (s, 3 H, HfMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz):  $\delta$  147.3 (Ph), 147.1 (Ph), 128.7 (Ph), 128.6 (Ph), 128.0 (Ph), 127.8 (Ph), 127.5 (Ph), 119.2 ( $\text{C}_5\text{Me}_5$ ), 111.1 ( $\text{C}_5\text{H}_5$ ), 57.5 (HfMe), 32.0 ( $\text{CMe}_3$ ), 24.8 ( $\text{CMe}_3$ ), 12.5 ( $\text{C}_5\text{Me}_5$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (100 MHz):  $\delta$  48.76. IR (KBr,  $\text{cm}^{-1}$ ): 2360 (w), 1427 (m), 1085 (m), 1016 (m), 814 (s), 739 (s), 706 (s). Anal. Calcd for  $\text{C}_{32}\text{H}_{42}\text{HfSi}$ : C, 60.69; H, 6.68. Found: C, 60.43; H 6.88. Mp: 112–113  $^\circ\text{C}$  (dec).

**$\text{CpCp}^*\text{Hf}(\text{SiHMe}_2)\text{Me}$  (**6**).** Compound **3** (0.213 g, 0.312 mmol) was dissolved in  $\text{Et}_2\text{O}$  (ca. 40 mL) in a 100-mL Schlenk flask, which was cooled to  $-78^\circ\text{C}$ . Via a syringe, 3.0 M  $\text{MeMgBr}$  in ether (0.150 mL, 0.45 mmol, 1.4 equiv) was added. The flask was allowed to slowly warm to ambient temperature. Solvent was removed under reduced pressure and the solid residue was extracted with hexane (2  $\times$  30 mL). The hexane solution was concentrated to ca. 5 mL and cooled to  $-30^\circ\text{C}$ . A red solid was isolated, yielding 0.128 g of **6** (0.193 mmol, 62.1%) which was pure enough for reactivity studies. Analytically pure samples of **6** were obtained by recrystallization from ether at  $-40^\circ\text{C}$  to yield small red crystals.  $^1\text{H}$  NMR (300 MHz):  $\delta$  6.86 (s, 4 H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 5.73 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 5.00 (s, 1 H, SiH), 2.48 (s, 6 H, *o*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.35 (s, 6 H, *o*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.21 (s, 3 H, *p*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.20 (s, 3 H, *p*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 1.81 (s, 15 H,  $\text{C}_5\text{Me}_5$ ), -0.52 (s, 3 H, HfMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz):  $\delta$  144.65 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 142.48 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 142.42 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 136.82 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 136.72 ( $\text{C}_6\text{H}_2\text{Me}_3$ ), 129.34 ( $\text{C}_6\text{H}_2\text{Me}_3$ ),

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129.12 ( $C_6H_2Me_3$ ), 128.58 ( $C_6H_2Me_3$ ), 118.64 ( $C_5Me_5$ ), 111.61 ( $C_5H_5$ ), 53.62 (HfMe), 26.38 ( $p-C_6H_2Me_3$ ), 25.73 ( $p-C_6H_2Me_3$ ), 21.46 ( $o-C_6H_2Me_3$ ), 12.31 ( $C_5Me_5$ ).  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$  0.770. IR (KBr,  $cm^{-1}$ ): 2364 (w), 2063 (m), 1601 (w), 1448 (m), 1376 (w), 1140 (w), 1023 (m), 813 (s). Anal. Calcd for  $C_{34}H_{46}HfSi$ : C, 61.75; H, 7.01. Found: C, 61.42; H, 7.03. Mp: 157–159 °C (dec).

**[CpCp\*HfSi(SiMe<sub>3</sub>)<sub>3</sub>][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (7).** A bromobenzene-*d*<sub>5</sub> (~0.3 mL) solution of  $B(C_6F_5)_3$  (0.015 g, 0.028 mmol) was added to a bright yellow solution (~0.3 mL) of **4** (0.018 g, 0.028 mmol). Upon addition, the color instantaneously turned deep red.  $^1H$  NMR (500 MHz, bromobenzene-*d*<sub>5</sub>):  $\delta$  5.71 (s, 5 H,  $C_5H_5$ ), 1.81 (s, 15 H,  $C_5Me_5$ ), 1.08 (br s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 0.151 (br s, 27 H, Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (125 MHz, bromobenzene-*d*<sub>5</sub>):  $\delta$  122.75 ( $C_5Me_5$ ), 111.83 ( $C_5H_5$ ), 12.91 ( $C_5Me_5$ ), 6.50 (br, Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{29}Si\{^1H\}$  NMR (100 MHz, bromobenzene-*d*<sub>5</sub>):  $\delta$  -5.10 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -87.45 (Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{11}B$  NMR (161 MHz, bromobenzene-*d*<sub>5</sub>):  $\delta$  -15.07.  $^{19}F\{^1H\}$  NMR (377 MHz, bromobenzene-*d*<sub>5</sub>):  $\delta$  -131.9 (m, 6 F), -163.9 (br, 3 F), -166.4 (br, 6 F).

**Cp<sub>2</sub>Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]Me (8).** Cp<sub>2</sub>Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl (0.473 g, 0.800 mmol) was dissolved in diethyl ether, and the solution was cooled to -78 °C. A solution of MeMgBr (3.0 M, 0.29 mL) was added dropwise with a syringe, and the resulting mixture was allowed to warm to ambient temperature and stirred overnight in the dark. The solvent was removed under vacuum, and the resulting solid was extracted with pentane (2 × 50 mL). The solution was concentrated by evaporation under reduced pressure, and compound **8** crystallized from ca. 45 mL of pentane at -30 °C as small, needlelike, yellow crystals and was isolated by filtration (0.232 g, 0.405 mmol, 50.7%).  $^1H$  NMR (500 MHz):  $\delta$  5.86 (s, 10 H,  $C_5H_5$ ), 0.38 (s, 27 H, Si(SiMe<sub>3</sub>)<sub>3</sub>), -0.67 (s, 3 H, HfCH<sub>3</sub>).  $^{13}C\{^1H\}$  (125 MHz):  $\delta$  109.47 ( $C_5H_5$ ), 53.49 (HfMe), 5.81 (Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$  -5.37 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -84.12 (Si(SiMe<sub>3</sub>)<sub>3</sub>). IR (Nujol,  $cm^{-1}$ ): 2978 (w), 2845 (w), 1443 (s), 1144 (m), 1020 (s), 678 (s), 626 (s). Anal. Calcd for  $C_{20}H_{40}HfSi_4$ : C, 42.04; H, 7.05. Found: C, 41.93; H, 7.16. Mp: 140–142 °C.

**Cp<sub>2</sub>Hf(Si<sup>*i*</sup>BuPh<sub>2</sub>)Cl.** Cp<sub>2</sub>HfCl<sub>2</sub> (2.170 g, 5.72 mmol) and 1.05 equiv of (THF)<sub>3</sub>LiSi<sup>*i*</sup>BuPh<sub>2</sub> (2.70 g, 5.84 mmol) were placed in separate 250-mL Schlenk flasks, and ca. 75 mL of Et<sub>2</sub>O were added to each flask. The flask containing the Cp<sub>2</sub>HfCl<sub>2</sub>/Et<sub>2</sub>O slurry was cooled to -78 °C. Dropwise cannula addition of the (THF)<sub>3</sub>LiSi<sup>*i*</sup>BuPh<sub>2</sub>/Et<sub>2</sub>O solution to Cp<sub>2</sub>HfCl<sub>2</sub> produced a yellow solution and a white precipitate. This mixture was allowed to warm to room temperature and was then stirred for 1 h. Solvent was removed under dynamic vacuum, and the yellow residue was extracted with pentane (5 × 100 mL). The combined extracts were concentrated and cooled to -80 °C. A yellow crystalline solid was isolated by filtration (0.768 g, 1.32 mmol). The mother liquor was concentrated and cooled to -78 °C to yield a second batch of crystals of overall yield of 1.667 g (2.857 mmol, 49.9%).  $^1H$  NMR (500 MHz):  $\delta$  7.65 (d, 4 H, Ph), 7.28 (t, 4 H, Ph), 7.21 (t, 2 H, Ph), 5.73 (s, 10 H,  $C_5H_5$ ), 1.36 (s, 9 H, <sup>*i*</sup>Bu).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  146.30 (Ph), 137.52 (Ph), 128.68 (Ph), 12.91 (Ph), 111.02 ( $C_5H_5$ ), 31.93 (CMe<sub>3</sub>), 24.24 (CMe<sub>3</sub>).  $^{29}Si\{^1H\}$  NMR (99 MHz):  $\delta$  49.41. IR (KBr,  $cm^{-1}$ ): 2971 (w), 2943 (w), 2851 (m), 2364 (w), 2341 (w), 1425 (m), 1089 (m), 1021 (m), 822 (s), 738 (m), 705 (s), 497 (s). Anal. Calcd for  $C_{26}H_{29}HfSiCl$ : C, 53.52; H 5.01. Found: C, 53.67; H 5.29. Mp: 134–135 °C.

**Cp<sub>2</sub>Hf(Si<sup>*i*</sup>BuPh<sub>2</sub>)Me (9).** Cp<sub>2</sub>Hf(Si<sup>*i*</sup>BuPh<sub>2</sub>)Cl (0.667 g, 1.15 mmol) was placed in a 100-mL Schlenk flask, dissolved in diethyl ether (35 mL), and cooled to -78 °C. A solution of 3.0 M of MeMgBr (0.43 mL, 1.2 mmol) was added in a dropwise fashion from a syringe. The reaction mixture was allowed to warm to room temperature, and the resulting mixture was stirred for 1 h in the dark. The solvent was removed under reduced pressure, and the resulting solid was extracted with pentane (3 × 50 mL). The combined filtrates were concentrated to ca. 50 mL and cooled to -78 °C, yielding small yellow crystals (0.157 g, 2.79 mmol, 40.9%).  $^1H$  NMR (500 MHz):  $\delta$  7.49 (d, 4 H, Ph), 7.26 (t, 4 H, Ph), 7.19 (t, 2 H, Ph), 5.70 (s, 10 H,  $C_5H_5$ ), 1.25 (s,

9 H, CMe<sub>3</sub>), -0.57 (s, 3 H, HfMe).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  147.17 (Ph), 137.35 (Ph), 136.45 (Ph), 127.71 (Ph), 109.79 ( $C_5H_5$ ), 55.59 (HfMe), 31.84 (CMe<sub>3</sub>), 23.83 (CMe<sub>3</sub>).  $^{29}Si\{^1H\}$  NMR (99 MHz):  $\delta$  49.04. IR (KBr,  $cm^{-1}$ ): 3065 (w), 2971 (w), 2942 (w), 2851 (m), 1425 (m), 1089 (w), 1019 (m), 822 (s), 738 (m), 704 (s), 497 (s). Anal. Calcd for  $C_{27}H_{32}HfSi$ : C, 57.59; H, 6.13. Found: C, 57.30; H, 5.90. Mp: 116–121 °C.

**Cp<sub>2</sub>Hf(SiPh<sub>3</sub>)Me (10).** Cp<sub>2</sub>HfMeCl (0.607 g, 1.69 mmol) and (THF)<sub>3</sub>LiSiPh<sub>3</sub> (0.860, 1.77 mmol) were separately dissolved in Et<sub>2</sub>O (25 mL). The flask containing Cp<sub>2</sub>HfMeCl was cooled to -78 °C, and the solution of LiSiPh<sub>3</sub> was added in a dropwise fashion. The reaction flask was wrapped in foil, and the reaction mixture was allowed to warm to room temperature. The volatile materials were removed in vacuo, and the resulting residue was extracted with pentane (3 × 50 mL). The combined extracts were subsequently concentrated to 45 mL and cooled to -80 °C. A yellow powder was isolated by filtration at -78 °C (0.611 g, 1.05 mmol, 62.1%).  $^1H$  NMR (500 MHz):  $\delta$  7.56 (d, 6 H, Ph), 7.27 (t, 6 H, Ph), 7.17 (t, 3 H, Ph), 5.68 (s, 10 H,  $C_5H_5$ ), -0.50 (s, 3 H, HfMe).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  146.21 (Ph), 137.07 (Ph), 128.34 (Ph), 128.11 (Ph), 109.87 ( $C_5H_5$ ), 55.77 (HfMe).  $^{29}Si\{^1H\}$  NMR (99 MHz):  $\delta$  37.18. IR (KBr,  $cm^{-1}$ ): 3104 (w), 3062 (w), 3007 (w), 2933 (w), 1479 (w), 1426 (m), 1132 (w), 1090 (m), 1015 (m), 819 (s), 736 (m), 703 (s), 509 (s). Anal. Calcd for  $C_{29}H_{29}HfSi$ : C, 59.73; H, 4.84. Found: C, 59.54; H, 4.73. Mp: 188–190 °C.

**Cp<sub>2</sub>Hf(SiMes<sub>2</sub>H)Me (11).** Cp<sub>2</sub>HfMeCl (0.6073 g, 1.69 mmol) was placed in a 100-mL Schlenk flask. A separate 100-mL Schlenk flask was charged with (THF)<sub>2</sub>LiSiHMe<sub>2</sub> (0.714 g, 1.71 mmol), and both compounds were dissolved in Et<sub>2</sub>O (ca. 35 mL each). The solution of Cp<sub>2</sub>HfMeCl was cooled to -78 °C in a dry ice/acetone bath. The solution of (THF)<sub>2</sub>LiSiHMe<sub>2</sub> was slowly added to the cooled Cp<sub>2</sub>HfMeCl/Et<sub>2</sub>O solution. The reaction flask was stoppered and wrapped in aluminum foil. The reaction mixture was allowed to warm to room temperature and stirred in the dark for 2 h. All volatile material was removed under reduced pressure, and the remaining solids were extracted with pentane (3 × 50 mL). The resulting yellow extracts were combined, concentrated in vacuo to ca. 40 mL, and cooled to -78 °C. A powdery yellow solid precipitated at low temperature yielding 0.681 g (1.15 mmol, 68.2%) of **11**.  $^1H$  NMR (500 MHz):  $\delta$  6.87 (s, 4 H, *m*- $C_6H_2Me_3$ ), 5.72 (s, 10 H,  $C_5H_5$ ), 4.98 (s, 1 H, SiH), 2.36 (s, 12 H, *o*- $C_6H_2Me_3$ ), 2.21 (s, 6 H, *p*- $C_6H_2Me_3$ ), -0.49 (s, 3 H, HfMe).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  144.69 ( $C_6H_2Me_3$ ), 141.57 ( $C_6H_2Me_3$ ), 137.26 ( $C_6H_2Me_3$ ), 129.35 ( $C_6H_2Me_3$ ), 109.77 ( $C_5H_5$ ), 51.29 (HfMe), 25.64 ( $C_6H_2Me_3$ ), 21.45 ( $C_6H_2Me_3$ ).  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$  8.25. IR (KBr,  $cm^{-1}$ ): 2965 (s), 2916 (s), 2862 (m), 2077 (m), 1601 (m), 1442 (m), 1408 (m), 1017 (s), 819 (s), 804 (s), 749 (m). Anal. Calcd for  $C_{29}H_{36}HfSi$ : C, 58.92; H, 6.14. Found: C, 58.63; H, 6.42. Mp: 100–102 °C (dec).

**Cp<sub>2</sub>Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (12).** A benzene-*d*<sub>6</sub> solution (ca. 0.3 mL) of  $B(C_6F_5)_3$  (0.022 g, 0.043 mmol) was added to a solution (ca. 0.3 mL) of **8** (0.024 g, 0.042 mmol) in an NMR tube. This quantitatively produced **12**.  $^1H$  NMR (500 MHz):  $\delta$  5.82 (s, 10 H,  $C_5H_5$ ), 0.12 (s, 27 H, Si(SiMe<sub>3</sub>)<sub>3</sub>), -0.33 (br s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  149.94 (C<sub>6</sub>F<sub>5</sub>), 148.02 (C<sub>6</sub>F<sub>5</sub>), 142 (br, C<sub>6</sub>F<sub>5</sub>), 138.97 (C<sub>6</sub>F<sub>5</sub>), 137.04 (C<sub>6</sub>F<sub>5</sub>), 124 (br, C<sub>6</sub>F<sub>5</sub>), 111.92 ( $C_5H_5$ ), 33.7 (br, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 5.26 (Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{11}B$  NMR (161 MHz):  $\delta$  -13.10.  $^{29}Si\{^1H\}$  NMR (99 MHz):  $\delta$  -3.77 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -21.39 (Si(SiMe<sub>3</sub>)<sub>3</sub>).  $^{19}F\{^1H\}$  NMR (377 MHz):  $\delta$  -132.5 (6 F), -158.9 (3 F), -164.0 (6 F).

**Cp<sub>2</sub>Hf(Si<sup>*i*</sup>BuPh<sub>2</sub>)( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (13).** Compound **9** (0.100 g, 0.174 mmol) and  $B(C_6F_5)_3$  (0.092 g, 0.180 mmol) were dissolved in a minimal amount of toluene (ca. 2 mL) in the glovebox. The resulting red solution was cooled to -30 °C for several days until red blocklike crystals of **13** formed. The crystals were isolated by filtration from the mother liquor.  $^1H$  NMR (500 MHz):  $\delta$  7.26–7.11 (m, 10 H, Ph), 5.53 (s, 10 H,  $C_5H_5$ ), 0.90 (s, 9 H, <sup>*i*</sup>Bu), -0.25 (br s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>).  $^{13}C\{^1H\}$



NMR (125 MHz):  $\delta$  149.91 (C<sub>6</sub>F<sub>5</sub>), 148.02 (C<sub>6</sub>F<sub>5</sub>), 143.62 (C<sub>6</sub>H<sub>5</sub>), 139.03 (C<sub>6</sub>F<sub>5</sub>), 137.05 (C<sub>6</sub>F<sub>5</sub>), 136.61 (C<sub>6</sub>H<sub>5</sub>), 128.90 (C<sub>6</sub>H<sub>5</sub>), 128.48 (C<sub>6</sub>H<sub>5</sub>), 112.61 (C<sub>5</sub>H<sub>5</sub>), 40.05 (MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 30.62 (CMe<sub>3</sub>), 25.60 (CMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz):  $\delta$  52.66. <sup>11</sup>B NMR (161 MHz):  $\delta$  -13.03. <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz):  $\delta$  -132.2 (br, 6 F), -157.8 (br, 3 F), -163.2 (br, 6 F). IR (KBr, cm<sup>-1</sup>): 3121 (w), 3070 (w), 2943 (m), 2855 (m), 2690 (w), 2360 (w), 1645 (m), 1515 (s), 1462 (s), 1379 (m), 1282 (m), 1104 (s), 1015 (m), 974 (s), 902 (m), 838 (s), 803 (s), 735 (s), 705 (s), 498 (m). Anal. Calcd for C<sub>52</sub>H<sub>10</sub>BF<sub>15</sub>HfSi (including 1 C<sub>7</sub>H<sub>8</sub>): C, 53.51; H, 3.45. Found: C, 53.24; H, 3.07. Mp: 85–87 °C.

**Cp<sub>2</sub>Hf(SiPh<sub>3</sub>)( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (14).** Compound **9** (0.012 g, 0.020 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.011 g, 0.020 mmol) were dissolved separately in benzene-*d*<sub>6</sub> (~0.3 mL each). The solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was added to **9**, quantitatively producing **14** (by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.18 (m, 12 H, Ph), 7.12 (m, 3 H, Ph), 5.67 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), -0.15 (s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  149.83 (br, C<sub>6</sub>F<sub>5</sub>), 147.90 (br, C<sub>6</sub>F<sub>5</sub>), 143.03 (Ph), 137.50 (br, C<sub>6</sub>F<sub>5</sub>), 136.80 (br, C<sub>6</sub>F<sub>5</sub>), 136.36 (Ph), 129.49 (Ph), 128.92 (Ph), 112.57 (C<sub>5</sub>H<sub>5</sub>), 41.0 (br, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>11</sup>B NMR (161 MHz):  $\delta$  -13.11. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz):  $\delta$  39.41. <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz):  $\delta$  -133.3 (6 F), -159.1 (3 F), -164.3 (6 F).

**Cp<sub>2</sub>Hf( $\eta^2$ -SiHMe<sub>2</sub>)( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (16).** Compound **11** (0.014 g, 0.024 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.013 g, 0.025 mmol) were dissolved in toluene-*d*<sub>8</sub> (~0.7 mL) in an NMR tube. The solution was cooled to -78 °C before being placed into the precooled spectrometer (-40 °C) for analysis. The <sup>1</sup>H NMR spectrum of the red solution at -40 °C indicated that compound **16** had formed in quantitative yield. A <sup>1</sup>H-NOESY spectrum indicates through space interactions between the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> anion and the Cp ligands on hafnium and the mesityl substituents on silicon. A <sup>1</sup>H-<sup>11</sup>B HMQC reveals through bond coupling between the methide group and the boron center. The reaction was also performed in benzene, and the reaction mixture was immediately frozen. The benzene was removed by sublimation under reduced pressure in the dark at -30 °C, yielding a red powder (contaminated with Mes<sub>2</sub>SiH<sub>2</sub>) that was used for IR analysis. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, -40 °C, 500 MHz):  $\delta$  6.60 (s, 4 H, C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), 5.16 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 2.19 (s, 12 H, *o*-C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), 2.04 (s, 6 H, *p*-C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), 1.80 (s, 1 H, SiH), -0.25 (br s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, -40 °C, 125 MHz):  $\delta$  149.56 (C<sub>6</sub>F<sub>5</sub>), 147.63 (C<sub>6</sub>F<sub>5</sub>), 153.0 (br m, C<sub>6</sub>F<sub>5</sub>), 140.15 (Ar), 138.29 (C<sub>6</sub>F<sub>5</sub>), 137.60 (Ar), 137.15 (Ar), 136.38 (C<sub>6</sub>F<sub>5</sub>), 129.51 (Ar), 106.91 (C<sub>5</sub>H<sub>5</sub>), 24.60 (*o*-C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), 20.86 (*p*-C<sub>6</sub>Me<sub>3</sub>H<sub>2</sub>), -12.41 (MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, -40 °C, 100 MHz, detected via a <sup>1</sup>H-<sup>29</sup>Si HMQC experiment):  $\delta$  158. <sup>11</sup>B NMR (toluene-*d*<sub>8</sub>, -40 °C, 160 MHz):  $\delta$  -13.37. <sup>19</sup>F{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 377 MHz):  $\delta$  -133.10 (d, 6 F), -160.35 (t, 3 F), -164.86 (t, 6 F). IR (Nujol, cm<sup>-1</sup>): 1415 (m).

**Cp<sub>2</sub>HfPhMe.** A 100-mL Schlenk flask was charged with Cp<sub>2</sub>HfMeCl (0.538 g, 1.50 mmol) and solid PhLi (0.128 g, 1.52 mmol). Benzene (35 mL) was added, the flask was sealed, and the reaction mixture was stirred under N<sub>2</sub> for 3 h. The resulting solution was filtered and the volatile materials were removed under reduced pressure, yielding analytically pure Cp<sub>2</sub>HfPhMe (0.422 g, 1.05 mmol, 70.3%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.27 (t, 2 H, C<sub>6</sub>H<sub>5</sub>), 7.07 (m, 3 H, C<sub>6</sub>H<sub>5</sub>), 5.67 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 0.108 (s, 3 H, HfMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  194.01 (C<sub>6</sub>H<sub>5</sub>), 136.79 (C<sub>6</sub>H<sub>5</sub>), 127.84 (C<sub>6</sub>H<sub>5</sub>), 125.33 (C<sub>6</sub>H<sub>5</sub>), 111.25 (C<sub>5</sub>H<sub>5</sub>), 40.59 (HfMe). IR (KBr, cm<sup>-1</sup>): 3044 (m), 2922 (m), 1439 (w), 1411 (w), 1015 (s), 808 (s), 700 (s). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>Hf: C, 50.94; H, 4.53. Found: C, 50.54; H, 4.27. Mp: 78–80 °C (dec).

**Cp<sub>2</sub>HfPh( $\mu$ -Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (17).** Cp<sub>2</sub>HfPhMe (0.078 g, 0.194 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.109 g, 0.213 mmol) were placed in a 100-mL Schlenk flask, 30 mL of pentane was added, and the resulting suspension was stirred vigorously for ca. 2 h. The precipitate was allowed to settle, and the desired complex was isolated by filtration from the reaction mixture as a gray powder (0.103 g, 0.113 mmol, 58.4%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.42 (t, 2 H, *m*-C<sub>6</sub>H<sub>5</sub>), 6.930 (t, 1 H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.516 (d,

2 H, *o*-C<sub>6</sub>H<sub>5</sub>), 5.503 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 0.926 (br s, 3 H, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  186.76 (C<sub>6</sub>H<sub>5</sub>), 136.71 (C<sub>6</sub>H<sub>5</sub>), 127.60 (C<sub>6</sub>H<sub>5</sub>), 127.33 (C<sub>6</sub>H<sub>5</sub>), 114.65 (C<sub>5</sub>H<sub>5</sub>), 24.20 (MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). <sup>11</sup>B NMR (160 MHz):  $\delta$  -13.37. <sup>19</sup>F NMR (377 MHz):  $\delta$  -134 (6 F), -159 (3 F), -164 (6 F). IR (KBr, cm<sup>-1</sup>): 3045 (w), 2924 (w), 1649 (m), 1523 (m), 1468 (s), 1381 (m), 1321 (m), 1018 (m), 974 (s), 806 (s), 700 (w). Anal. Calcd for C<sub>35</sub>H<sub>18</sub>B<sub>15</sub>Hf<sub>1</sub>: C, 46.05; H, 1.99. Found: C, 46.00; H, 1.64. Mp: 135–136 °C.

**Cp<sub>2</sub>Hf(CH<sub>2</sub>Ph)Me.** Cp<sub>2</sub>HfMeCl (0.536 g, 1.49 mmol) and KCH<sub>2</sub>Ph (0.218 g, 1.68 mmol) were dissolved in THF (ca. 25 mL each) in separate 100-mL Schlenk flasks. The flask containing the Cp<sub>2</sub>HfMeCl/THF solution was cooled to -78 °C with a dry ice/acetone bath. The THF solution of KCH<sub>2</sub>Ph was added dropwise to the cold Cp<sub>2</sub>HfMeCl solution. The resulting mixture was allowed to slowly warm to ambient temperature and was then stirred under N<sub>2</sub> for 1 h. THF was removed under reduced pressure, and the salts were extracted with pentane (3 × 40 mL). The combined extracts were concentrated to ca. 25 mL and cooled to -78 °C. Yellow crystals of Cp<sub>2</sub>Hf(CH<sub>2</sub>Ph)Me were isolated by cold filtration in moderate yield (0.347 g, 0.836 mmol, 56.1%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.27 (t, 2 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.90 (t, 1 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.77 (d, 2 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.50 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 1.33 (s, 2 H, CH<sub>2</sub>Ph), -0.14 (s, 3 H, HfMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  152.81 (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 128.58 (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 127.18 (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 121.64 (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 110.8 (C<sub>5</sub>H<sub>5</sub>), 64.51 (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 38.44 (HfMe). IR (KBr, cm<sup>-1</sup>): 3091 (w), 3065 (w), 3014 (w), 2921 (w), 2864 (w), 1592 (m), 1484 (m), 1438 (w), 1207 (m), 1141 (w), 1016 (s), 811 (s), 751 (m), 704 (m). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Hf<sub>1</sub>: C, 52.12; H, 4.81. Found: C, 52.20; H, 4.64. Mp: 61–61.5 °C.

**Cp<sub>2</sub>Hf(*m*-C<sub>6</sub>H<sub>4</sub>Me)Me.** To a 100-mL Schlenk flask containing Cp<sub>2</sub>HfMeCl (0.459 g, 1.28 mmol) was added Et<sub>2</sub>O (50 mL). The flask was cooled to -78 °C, and a 1.0 M solution of (*m*-C<sub>6</sub>H<sub>4</sub>Me)MgCl in Et<sub>2</sub>O (1.28 mL) was added via syringe. The reaction mixture was allowed to warm to ambient temperature. After 0.5 h of stirring, the volatile materials were removed under reduced pressure and the salts were extracted with pentane (3 × 25 mL). The combined extracts were concentrated to ca. 30 mL and cooled to -78 °C. An off-white powder of Cp<sub>2</sub>Hf(*m*-C<sub>6</sub>H<sub>4</sub>Me)Me was isolated by cold filtration (0.400 g, 0.964 mmol, 75.4%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.231 (t, 1 H, C<sub>6</sub>H<sub>4</sub>Me), 6.987 (s, 1 H, C<sub>6</sub>H<sub>4</sub>Me), 6.89 (m, 2 H, C<sub>6</sub>H<sub>4</sub>Me), 5.69 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 2.29 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me), 0.132 (s, 3 H, HfMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  194.22 (C<sub>6</sub>H<sub>4</sub>Me), 137.28 (C<sub>6</sub>H<sub>4</sub>Me), 136.34 (C<sub>6</sub>H<sub>4</sub>Me), 133.75 (C<sub>6</sub>H<sub>4</sub>Me), 128.20 (C<sub>6</sub>H<sub>4</sub>Me), 126.17 (C<sub>6</sub>H<sub>4</sub>Me), 111.24 (C<sub>5</sub>H<sub>5</sub>), 40.54 (HfMe), 22.75 (C<sub>6</sub>H<sub>4</sub>Me). IR (cm<sup>-1</sup>): 3086 (w), 2989 (w), 2914 (m), 2862 (w), 2787 (w), 1570 (w), 1439 (w), 1144 (w), 1097 (w), 1014 (m), 814 (s), 766 (s), 704 (m), 461 (m). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Hf<sub>1</sub>: C, 52.12; H, 4.81. Found: C, 52.06; H, 5.10. Mp: 111–112 °C.

**Cp<sub>2</sub>Hf(*o*-C<sub>6</sub>H<sub>4</sub>Me)Me.** The preparation of this compound was similar to the synthesis described for Cp<sub>2</sub>Hf(*m*-tolyl)Me above, with the modification that 1.05 equiv of 1.0 M (*o*-C<sub>6</sub>H<sub>4</sub>Me)MgCl in Et<sub>2</sub>O were used instead of (*m*-C<sub>6</sub>H<sub>4</sub>Me)MgCl. Yield: 0.726 g of Cp<sub>2</sub>Hf(*o*-C<sub>6</sub>H<sub>4</sub>Me)Me (1.75 mmol, 78.6%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.12 (m, 3 H, C<sub>6</sub>H<sub>4</sub>Me), 7.08 (br, 1 H, C<sub>6</sub>H<sub>4</sub>Me), 5.665 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 1.983 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me), 0.185 (s, 3 H, HfMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  196.03 (C<sub>6</sub>H<sub>4</sub>Me), 145.98 (C<sub>6</sub>H<sub>4</sub>Me), 130.06 (C<sub>6</sub>H<sub>4</sub>Me), 129.04 (C<sub>6</sub>H<sub>4</sub>Me), 127.86 (C<sub>6</sub>H<sub>4</sub>Me), 126.23 (C<sub>6</sub>H<sub>4</sub>Me), 110.81 (C<sub>5</sub>H<sub>5</sub>), 57.13 (HfMe), 25.99 (C<sub>6</sub>H<sub>4</sub>Me). IR (KBr, cm<sup>-1</sup>): 3087 (m), 3044 (w), 2975 (w), 2912 (m), 2867 (m), 2793 (w), 1442 (s), 1145 (m), 1013 (s), 811 (s), 754 (s), 456 (s). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Hf<sub>1</sub>: C, 52.12; H, 4.81. Found: C, 51.95; H, 4.64. Mp: 67–68 °C.

**Cp<sub>2</sub>Hf(*p*-C<sub>6</sub>H<sub>4</sub>Me)Me.** The preparation of this compound was similar to the synthesis described for Cp<sub>2</sub>Hf(*m*-C<sub>6</sub>H<sub>4</sub>Me)Me above, with the modification that 1.05 equiv of 1.0 M (*p*-C<sub>6</sub>H<sub>4</sub>Me)MgCl in Et<sub>2</sub>O were used instead of (*m*-C<sub>6</sub>H<sub>4</sub>Me)MgCl. Yield: 0.410 g (0.989 mmol, 67.3%). <sup>1</sup>H NMR (500 MHz):  $\delta$  7.13 (d, 2 H, C<sub>6</sub>H<sub>4</sub>Me), 7.04 (d, 2 H, C<sub>6</sub>H<sub>4</sub>Me), 5.69 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 2.25 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me), 0.12 (s, 3 H, HfMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  190.01 (C<sub>6</sub>H<sub>4</sub>Me), 138.43 (C<sub>6</sub>H<sub>4</sub>Me),

Me), 136.92 ( $C_6H_4Me$ ), 134.23 ( $C_6H_4Me$ ), 111.24 ( $C_5H_5$ ), 40.38 (HfMe), 21.80 ( $C_6H_4Me$ ). IR (KBr,  $cm^{-1}$ ): 3045 (w), 2197 (w), 1441 (w), 1144 (w), 1046 (w), 1015 (m), 812 (s), 792 (s), 487 (m), 465 (m). Anal. Calcd for  $C_{18}H_{20}Hf$ : C, 52.12; H, 4.81. Found: C, 52.47; H, 4.72. Mp: 84–85 °C.

**$Cp_2Hf(o-C_6H_4Me)(\mu-Me)B(C_6F_5)_3$  (18).** A pentane solution (15 mL) of  $B(C_6F_5)_3$  (0.352 g, 0.688 mmol) was added to a pentane solution (25 mL) of  $Cp_2Hf(o-C_6H_4Me)Me$  (0.284 g, 0.686 mmol) at  $-78$  °C. Immediately a white precipitate formed. The mixture was gradually warmed to room temperature, and the powdery solid was isolated by filtration. Residual solvent was removed in vacuo, and analytically pure **18** was isolated in good yield (0.532 g, 0.573 mmol, 83.6%).  $^1H$  NMR (toluene- $d_8$ , 500 MHz):  $\delta$  6.98 (m, 2 H,  $C_6H_4Me$ ), 6.89 (t, 1 H,  $C_6H_4Me$ ), 6.14 (br, 1 H,  $C_6H_4Me$ ), 5.49 (s, 10 H,  $C_5H_5$ ), 1.66 (s, 3 H,  $C_6H_4Me$ ), 1.04 (br s, 3 H, MeB( $C_6F_5$ ) $_3$ ).  $^{13}C\{^1H\}$  NMR (100 MHz):  $\delta$  192.2 ( $C_6H_4Me$ ), 146.7 ( $C_6H_4Me$ ), 132.0 ( $C_6H_4Me$ ), 126.3 ( $C_6H_4Me$ ), 122.4 ( $C_6H_4Me$ ), 113.6 ( $C_5H_5$ ), 25.2 ( $C_6H_4Me$ ).  $^{11}B$  NMR (160 MHz):  $\delta$   $-13.69$ .  $^{19}F$  NMR (377 MHz):  $\delta$   $-133$  (6 F),  $-159$  (3 F),  $-164$  (6 F). IR (KBr,  $cm^{-1}$ ): 3126 (w), 2978 (w), 1645 (m), 1516 (s), 1462 (s), 1379 (w), 1279 (w), 1099 (s), 1018 (w), 972 (s), 829 (s), 737 (m). Anal. Calcd for  $C_{36}H_{20}BF_{15}Hf$ : C, 46.65; H, 2.17. Found: C, 46.58; H, 2.10. Mp: 107–108 °C.

**$Cp_2Hf(p-C_6H_4Me)(\mu-Me)B(C_6F_5)_3$  (19).** A similar procedure to that for **18** was used, with  $Cp_2Hf(p-C_6H_4Me)Me$  (0.270 g, 0.651 mmol). Compound **19** was isolated in good yield (0.463 g, 0.499 mmol, 76.8%).  $^1H$  NMR (500 MHz):  $\delta$  6.931 (d, 2 H,  $C_6H_4Me$ ), 6.524 (d, 2 H,  $C_6H_4Me$ ), 5.482 (s, 10 H,  $C_5H_5$ ), 2.127 (s, 3 H,  $C_6H_4Me$ ), 0.895 (br s, 3 H, MeB( $C_6F_5$ ) $_3$ ).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  183.5 ( $C_6H_4Me$ ), 137.5 ( $C_6H_4Me$ ), 129.2 ( $C_6H_4Me$ ), 114.5 ( $C_5H_5$ ), 21.4 ( $C_6H_4Me$ ).  $^{11}B$  NMR (160 MHz):  $\delta$   $-13.36$ .  $^{19}F$  NMR (377 MHz):  $\delta$   $-134$  (6 F),  $-159$  (3 F),  $-164$  (6 F). IR (KBr,  $cm^{-1}$ ): 3120 (w), 2922 (s), 2756 (s), 1645 (m), 1516 (s), 1462 (s), 1281 (w), 1093 (s), 1016 (w), 974 (s), 829 (m). Anal. Calcd for  $C_{36}H_{20}BF_{15}Hf$ : C, 46.65; H, 2.17. Found: C, 46.37; H, 2.14. Mp: 87–88 °C (dec).

**$Cp_2Hf(m-C_6H_4Me)(\mu-Me)B(C_6F_5)_3$  (20).** A similar procedure to that of **18** was used, with  $Cp_2Hf(m-C_6H_4Me)Me$  (0.115 g, 0.277 mmol). **20** was isolated in modest yield (0.113 g, 0.122 mmol, 44.0%).  $^1H$  NMR (toluene- $d_8$ , 500 MHz):  $\delta$  7.02 (m, 1 H,  $C_6H_4Me$ ), 6.76 (d, 1 H,  $C_6H_4Me$ ), 6.44 (s, 1 H,  $C_6H_4Me$ ), 6.29 (d, 1 H,  $C_6H_4Me$ ), 5.72 (s, 10 H,  $C_5H_5$ ), 2.11 (s, 3 H,  $C_6H_4Me$ ), 0.94 (br s, 3 H, MeB( $C_6F_5$ ) $_3$ ).  $^{13}C\{^1H\}$  NMR (toluene- $d_8$ , 125 MHz):  $\delta$  187.39 ( $C_6H_4Me$ ), 149.96 ( $C_6H_4Me$ ), 148.09 ( $C_6H_4Me$ ), 138.14 ( $C_6H_4Me$ ), 136.66 ( $C_6H_4Me$ ), 133.88 ( $C_6H_4Me$ ), 114.63 ( $C_5H_5$ ), 21.94 ( $C_6H_4Me$ ).  $^{11}B$  NMR (160 MHz):  $\delta$   $-13.34$ .  $^{19}F$  NMR (377 MHz):  $\delta$   $-134$  (6 F),  $-159$  (3 F),  $-164$  (6 F). IR (KBr,  $cm^{-1}$ ): 2992 (w), 2923 (w), 1644 (m), 1516 (s), 1460 (s), 1381 (w), 1280 (w), 1091 (s), 1016 (m), 973 (s), 829 (s), 803 (m), 769 (m). Anal. Calcd for  $C_{36}H_{20}BF_{15}Hf$ : C, 46.65; H, 2.17. Found: C, 46.53; H, 2.38. Mp: 104–106 °C (dec).

**$Cp_2Hf(CH_2Ph)(\mu-Me)B(C_6F_5)_3$  (21).** A toluene- $d_8$  solution (ca. 0.3 mL) of  $B(C_6F_5)_3$  (0.017 g, 0.033 mmol) was added to a toluene- $d_8$  solution (0.3 mL) of  $Cp_2Hf(CH_2Ph)Me$  (0.014 g, 0.033 mmol) to quantitatively generate **21**.  $^1H$  NMR (toluene- $d_8$ , 500 MHz):  $\delta$  7.07 (s, 1 H,  $CH_2C_6H_5$ ), 6.77 (s, 2 H,  $CH_2C_6H_5$ ), 6.22 (s, 2 H,  $CH_2C_6H_5$ ), 5.40 (s, 10 H,  $C_5H_5$ ), 1.71 (s, 2 H,  $CH_2C_6H_5$ ), 0.57 (s, 3 H, MeB( $C_6F_5$ ) $_3$ ).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  129.1 ( $CH_2C_6H_5$ ), 126.9 ( $CH_2C_6H_5$ ), 124.3 ( $CH_2C_6H_5$ ), 114.0 ( $CH_2C_6H_5$ ), 113.3 ( $C_5H_5$ ), 67.3 ( $CH_2C_6H_5$ ).  $^{11}B$  NMR (160 MHz):  $\delta$   $-13.37$ .  $^{19}F$  NMR (377 MHz):  $\delta$   $-134$  (6 F),  $-159$  (3 F),  $-164$  (6 F).

**$Mes_2SiDCl$ .**  $Mes_2SiDCl$  was synthesized by an adaptation of a Corey and West synthesis for  $Ph_2SiHCl$ .<sup>49</sup>  $Mes_2SiD_2$  (2.67 g, 9.95 mmol) and  $Ph_3CCl$  were dissolved in toluene in a Teflon-sealed flask and heated to 115 °C for 2 days.  $Mes_2SiDCl$  was isolated in reasonable yield (2.21 g, 7.27 mmol, 73.1%) by cooling the reaction mixture to  $-78$  °C.  $^1H$  NMR (500 MHz):  $\delta$  6.63 (s, 4 H,  $C_6H_2Me_3$ ), 2.62 (s, 12 H,  $o-C_6H_2Me_3$ ), 2.03 (s, 6 H,  $p-C_6H_2Me_3$ ).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  114.87 ( $C_6H_2Me_3$ ),

141.02 ( $C_6H_2Me_3$ ), 130.20 ( $C_6H_2Me_3$ ), 128.74 ( $C_6H_2Me_3$ ), 23.58 ( $C_6H_2Me_3$ ), 21.43 ( $C_6H_2Me_3$ ).  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$   $-18.79$  (t,  $^1J_{SiD} = 35.67$  Hz). IR (KBr,  $cm^{-1}$ ): 2956 (s), 2926 (s), 2856 (s), 1604 (s), 1452 (s), 1411 (m), 1076 (m), 877 (m), 657 (s), 633 (s), 569 (s). Anal. Calcd for  $C_{18}H_{22}ClDSi$ : C, 71.14; H, 7.30. Found: C, 71.23; H, 7.44. Mp: 67–68 °C.

**$(THF)_{1.8}LiSiDMes_2$ .**  $(THF)_2LiSiMes_2D$  was synthesized by reduction of  $Mes_2SiDCl$  with 10 equiv of  $Li^0$  in THF at 0 °C, following the original synthesis of  $(THF)_{2.5}LiSiMes_2H$ .<sup>21</sup> Yield: 1.663 g, (4.11 mmol, 60.2%).  $^1H$  NMR (500 MHz):  $\delta$  6.91 (s, 4 H,  $C_6H_2Me_3$ ), 3.30 (t, 7.5 H,  $C_4H_8O$ ), 2.67 (s, 12 H,  $o-C_6H_2Me_3$ ), 2.25 (s, 6 H,  $p-C_6H_2Me_3$ ), 1.13 (t, 7.5 H,  $C_4H_8O$ ).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  145.36 ( $C_6H_2Me_3$ ), 144.28 ( $C_6H_2Me_3$ ), 134.65 ( $C_6H_2Me_3$ ), 129.66 ( $C_6H_2Me_3$ ), 68.80, 26.05, 25.61, 21.63.  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$   $-72.42$  (t,  $^1J_{SiD} = 18.92$  Hz). IR (KBr,  $cm^{-1}$ ): 2962 (s), 2916 (s), 1603 (m), 1458 (m), 1414 (w), 1261 (m), 1045 (s), 847 (m), 818 (s), 658 (m). Anal. Calcd for  $(OC_4H_8)_{1.8}LiSiC_{18}H_{22}D$ : C, 74.70; H, 9.05. Found: C, 74.88; H, 9.22. Mp: 94–98 °C (dec).

**$Cp_2Hf(SiDMes_2)Me$ .** The synthesis of  $Cp_2Hf(SiMes_2D)Me$  followed that of **11**, using  $(THF)_2LiSiMes_2D$  instead of  $(THF)_2LiSiMes_2H$ . Yield = 0.519 g (0.876 mmol, 80.0%).  $^1H$  NMR (500 MHz):  $\delta$  6.88 (s, 4 H,  $C_6H_2Me_3$ ), 5.72 (s, 10 H,  $C_5H_5$ ), 2.36 (s, 12 H,  $o-C_6H_2Me_3$ ), 2.21 (s, 6 H,  $p-C_6H_2Me_3$ ),  $-0.49$  (s, 3 H, HfMe).  $^{13}C\{^1H\}$  NMR (125 MHz):  $\delta$  144.71 ( $C_6H_2Me_3$ ), 141.55 ( $C_6H_2Me_3$ ), 137.26 ( $C_6H_2Me_3$ ), 129.35 ( $C_6H_2Me_3$ ), 109.78 ( $C_5H_5$ ), 51.40 (HfMe), 25.63 ( $C_6H_2Me_3$ ), 21.45 ( $C_6H_2Me_3$ ).  $^{29}Si\{^1H\}$  NMR (100 MHz):  $\delta$  6.97 (t,  $^1J_{SiD} = 50.72$  Hz). IR (KBr,  $cm^{-1}$ ): 2966 (m), 2916 (m), 1601 (w), 1512 (w), 1462 (s), 1261 (m), 1090 (m), 1016 (s), 850 (m), 822 (s), 621 (m), 579 (m). Anal. Calcd for  $C_{29}H_{35}DHfSi$ : C, 58.82; H, 5.96. Found: C, 59.02; H, 6.26. Mp: 75–79 °C (dec).

**Kinetics Measurements of the Reaction of 13 with  $Mes_2SiH_2$ .** The reaction was monitored by  $^1H$  NMR spectroscopy with a Bruker DRX500 spectrometer, using a 5 mm Wilmad NMR tube equipped with a J. Young Teflon screw cap. The sample was prepared by addition of benzene solutions of **9** (ca. 0.02 M) and  $B(C_6F_5)_3$  (1:1 molar ratio) to 5–10 equiv of  $Mes_2SiH_2$  in benzene- $d_6$ . The solution was frozen in liquid  $N_2$  immediately after preparation and thawed before being placed in the probe which was preheated to 26 °C. The probe temperature was calibrated using neat ethylene glycol and monitored with a thermocouple. Single scan spectra were acquired automatically at preset time intervals. The peak areas were integrated relative to cyclooctane as an internal standard. Rate constants were obtained by nonweighted linear least-squares fit of the second-order rate law,  $\ln\{[Mes_2SiH_2]/[13]\} = \ln\{[Mes_2SiH_2]_0/[13]_0\} + k\Delta t$ .

**Kinetic Measurements of Reactions of 16 and Benzene.** Reactions were monitored by  $^1H$  NMR spectroscopy with a Bruker DRX500 spectrometer, using 5 mm Wilmad NMR tubes equipped with J. Young Teflon screw caps. The samples were prepared by addition of a benzene- $d_6$  solution of  $B(C_6F_5)_3$  to a solution of **11**. The reaction solutions were frozen in liquid  $N_2$  immediately after preparation and thawed just before being placed in the probe which was precooled to the required temperature. The probe temperature was calibrated using neat ethylene glycol or methanol and monitored with a thermocouple. Single scan spectra were acquired automatically at preset time intervals. The peak areas were integrated relative to cyclooctane as an internal standard. Rate constants were obtained by nonweighted linear least-squares fit of the pseudo-first-order rate law,  $\ln[C] = \ln[C_0] + k_{obs}t$ . The benzene- $d_6$  concentration was varied by dilution with hexafluorobenzene.

**Computational Details.** The B3LYP/LACVP\*\*++<sup>30,31</sup> level of theory with “high” grid density as implemented in the Jaguar 4.0 quantum chemistry program package<sup>32</sup> was used for these studies. Full geometry optimization was performed for model compounds **A** and **B**. Analytical vibrational frequency calculation was performed for model compound **A**; this stationary point was characterized by exactly zero imaginary vibrational modes. No frequency analysis was performed for model compound **B**.

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**Supporting Information Available:** Supporting Information available: representative kinetics plots and Eyring plots for the reaction of **16** with benzene (PDF) and X-ray crystallographic data for **9**, **13**, and **15** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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