Synthesis and Characterization of the Series of d^0 Arene Complexes $[Cp^*MMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ (M = Ti, Zr, Hf)

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Treatment of the neutral trimethyl compounds Cp^*MMe_3 (M = Ti, Zr, Hf) with the highly electrophilic borane $B(C_6F_5)_3$ in methylene chloride in the presence of various arenes results in methyl carbanion abstraction and coordination of the arene to form complexes of the type $[Cp^*MMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ (M = Ti, Zr, Hf; arene = benzene, toluene, *m*- and *p*-xylene, anisole, styrene, mesitylene). Indications of relative metal−arene affinities have been gleaned from a variety of low-temperature ^1H NMR experiments, and it seems that both steric and electronic factors play significant roles in determining stabilities. The crystal and molecular structures of $[Cp^*HfMe_2(\eta^6\text{-toluene})][MeB(C_6F_5)_3]$ have been determined; as anticipated, there are no significant contacts between anion and cation, and the latter assumes a bent-metallocene type of structure.

In earlier papers,[1] we have discussed the structure and chemistry of $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$, in which the borate anion appears to coordinate in an η^2 fashion, analogous to metallocene compounds with bridging methyl groups linking this same borate anion to transition-metal ions.[2] Similar, as yet poorly characterized, species are formed by treating the zirconium and hafnium compounds Cp^*MMe_3 (M = Zr, Hf) with the highly electrophilic borane $B(C_6F_5)_3$.[1a] The cationic dimethyl complexes of all three metals are of interest because they and similar species are extremely active olefin polymerization initiators.[1b,3]

In this paper we discuss reactions of $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ and its zirconium and hafnium analogues with aromatic solvents to form $[Cp^*MMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ (M = Ti, Zr, Hf), complexes of a type which, aside from their catalytic activities, are of significant interest in their own right. Thus, while a number of arene complexes of these metals in lower oxidation states are known,[4a] relatively few such complexes of these metals in the +4 oxidation state (d^0) have been reported.[4a] Typical examples are $Zr(CH_2Ph)_3\{\eta^6\text{-}PhBPh_3\}$[4b] and $Zr(CH_2Ph)_3\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}$,[4c] containing anionic arene ligands, and cationic complexes of electron-rich arenes such as $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$, formed by dissolving $TiCl_4$ in hexamethylbenzene.[4d,e]

Aspects of this work have appeared previously as a communication.[1a] Since then, the properties and the X-ray crystal structure of the similar complex $[\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}HfMe_2(\eta^6\text{-toluene})][MeB(C_6F_5)_3]$ have also been reported.[5]

Experimental Section

All experiments were carried out under nitrogen using standard Schlenk line techniques, a Vacuum Atmospheres glovebox, and dried, thoroughly deoxygenated solvents. ^1H, ^{13}C, and ^{19}F NMR spectra were run using a Bruker AM 400 spectrometer operating at 400.14, 100.6, and 376.5 MHz, respectively; ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced with respect to internal TMS, using residual proton or carbon resonances, respectively, of the solvents; ^{19}F spectra are referenced to external $CFCl_3$. ^1H and $^{13}C\{^1H\}$ NMR data are listed in Tables 1 and 2. The $^{13}C\{^1H\}$ NMR spectra of all compounds containing a free $[MeB(C_6F_5)_3]^-$ anion exhibited C_6F_5 resonances at δ ~150 (d, J_{CF} ~240 Hz, *o*-CF), ~138 (d, J_{CF} ~230 Hz, *m*-CF), ~136 (d, J_{CF} ~250 Hz, *p*-CF), and ~125 (br, *ipso*-C), while the ^{19}F spectra exhibited resonances at δ ~−123 (m, 2F, *o*-F), ~−126.1 (t, 2F, *m*-F) and ~−157 (t, 1F, *p*-F). Since these parameters are essentially independent of temperature, solvent, *etc.*, they vary little and are not useful for purposes of characterization and are therefore omitted from

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Table 1. ^{1}H NMR Data for the Complexes [$Cp^*MMe_2(\eta^6$-arene)][$MeB(C_6)_3$] (CD_2Cl_2)

arene	δ(M−Me)	δ(Cp*Me)	δ(arene) (*J*, Hz)
			M = Ti
toluene[a]	0.11	1.90	7.74 (d, *o*-H), 7.2 (t, *m*-H), 6.70 (t, *p*-H), 2.78 (s, Me)
mesitylene[a]	0.09	1.93	7.34 (s, Ph H), 2.52 (s, Me)
			M = Zr
benzene[a]	−0.15	1.89	7.64 (s, PhH) (free benzene at 7.39)
toluene[b]	−0.11	1.96	7.78 (d, *m*-H), 7.38 (t, *m*-H), 7.04 (t, *p*-H), 2.71 (s, Me)
p-xylene[d]	−0.10	1.94	7.48 (s, Ph H), 2.42 (s, Me)
m-xylene[d]	−0.29	1.89	8.26 (s, 1 H, H-2), 7.10 (d, 2H, H-4,6), 6.97 (t, 1H, H-5), 2.54 (s, Me)
mesitylene[c]	−0.15	1.96	7.29 (s, Ph H), 2.47 (s, Me)
styrene[a]	−0.23	1.89	7.95 (d, *o*-H), 7.41 (t, *m*-H), 7.11 (t, *p*-H), 6.82 (dd, C*H*=CH$_2$), 6.34 (d, *J* = 17.2, CH=C*H*$_2$), 6.04 (d, *J* = 10.9, CH=C*H*$_2$)
			M = Hf
toluene[b]	−0.28	2.10	7.55 (d, *m*-H), 7.32 (t, *m*-H), 7.28 (t, *p*-H), 2.76 (s, Me)
p-xylene[d]	−0.46	1.93	7.44 (s, PhH), 2.35 (s, Me)
m-xylene[d]	−0.41	2.02	7.81 (s, 1 H, H-2), 7.13 (d, 2H, H-4,6), 6.97 (t, 1H, H-5), 2.58 (s, Me)
styrene[d]	−0.37	2.02	7.94 (d, *o*-H), 7.47 (t, *m*-H), 7.21 (t, *p*-H), 6.80 (dd, C*H*=CH$_2$), 6.33 (d, *J* = 17.5, CH=C*H*$_2$), 6.08 (d, *J* = 10.9, CH=C*H*$_2$)
anisole[d]	−0.49	1.95	7.47 (t, *m*-H), 7.15 (d, *o*-H), 6.74 (t, *p*-H), 4.05 (s, OMe)
mesitylene[d]	−0.47	1.95	7.28 (s, Ph H), 2.44 (s, Me)

[a] *T* = 223 K. [b] *T* = 298 K. [c] *T* = 273 K. [d] *T* = 213 K.

Table 2. $^{13}C\{^1H\}$ NMR Data for the Complexes [$Cp^*MMe_2(\eta^6$-arene)][$MeB(C_6F_5)_3$] (CD_2Cl_2)

arene	δ(M−Me)	δ(Cp* ring)	δ(Cp* Me)	δ(arene)
			M = Ti	
toluene[d]	65.2	138.1	12.9	
			M = Zr	
benzene[a]	45.3	123.1	11.6	131.6 (free benzene 128.2)
toluene[b]	45.5	123.6	12.0	147.0, 134.8, 130.9, 129.2 (ring), 22.4 (Me)
p-xylene[d]	45.2	123.6	11.9	141.6, 134.8 (ring), 21.4 (Me)
m-xylene[d]	45.6	122.5	11.6	146.6, 136.9, 138.1 (ring), 22.0 (Me)
mesitylene[c]	40.7	122.4	11.7	141.1, 132.4 (ring), 21.3 (Me)
styrene[a]	44.6	122.9	11.7	140.8, 126.5 (C=C), 130.7, 129.6, 126.8, 126.5 (ring)
			M = Hf	
toluene[b]	46.5	121.7	11.6	146.8, 134.7, 130.5, 124.7 (ring), 31.8 (Me)
p-xylene[d]	47.2	121.0	11.4	140.6, 132.4 (ring), 21.2 (Me)
m-xylene[d]	50.3	122.3	11.9	147.6, 138.9, 138.1, 128.9 (ring), 22.5 (Me)

[a] *T* = 223 K. [b] *T* = 298 K. [c] *T* = 273 K. [d] *T* = 213 K.

the data compilations appearing below. Elemental analyses were performed by Canadian Microanalytical Services or at E. I. DuPont de Nemours, Central Research and Development, Wilmington, DE.

The following compounds were prepared as described previously: Cp^*MMe_3 (M = Ti,[6a] Zr,[6b] Hf[6c]), $B(C_6F_5)_3$.[6d]

Synthesis of [$Cp^*TiMe_2(\eta^6$-toluene)][$MeB(C_6F_5)_3$] and [$Cp^*TiMe_2(\eta^6$-1,3,5-$C_6H_3Me_3$)][$MeB(C_6F_5)_3$]. Attempted Syntheses of [$Cp^*TiMe_2(\eta^6$-arene)][$MeB(C_6F_5)_3$] (arene = Benzene, Hexamethylbenzene, *p*-Xylene, Chlorobenzene, Styrene). To a solution of $Cp^*TiMe_2(\mu$-Me)$B(C_6F_5)_3$ (0.04 mmol in 0.6 mL of CD_2Cl_2) prepared as before,[1] at 195 K, was added 21.0 μL of toluene (0.2 mmol). The sample was then placed in the NMR spectrometer probe at 223 K. Resonances of $Cp^*TiMe_2(\mu$-Me)$B(C_6F_5)_3$ and of free toluene were observed, as well as a new set of resonances, attributable to [$Cp^*TiMe_2(\eta^6$-toluene)][$MeB(C_6F_5)_3$] by comparison with spectra of the more stable zirconium and hafnium analogues (see below). Conversion to [$Cp^*TiMe_2(\eta^6$-toluene)][$MeB(C_6)_3$] was ~30%. ^{1}H NMR (CD_2Cl_2 at 223 K): δ 7.74, ~7.2, 6.70 (all Ph), 2.78 (s, 3H, toluene Me), 1.90 (s, 15H, Cp*), 0.38 (br s, 3H, BMe), 0.11 (s, 6H, TiMe).

A similar experiment with mesitylene showed ~50% conversion to [$Cp^*TiMe_2(\eta^6$-1,3,5-$C_6H_3Me_3$)][$MeB(C_6F_5)_3$]. ^{1}H NMR (CD_2Cl_2 at 223 K): δ 7.34 (s, 3H, ring CH), 2.52 (s, 9H, ring Me), 1.93 (s, 15H, Cp*), 0.39 (br s, 3H, BMe), 0.09 (s, 6H, TiMe). The ^{1}H NMR spectra for similar experiments with benzene, *p*-xylene, hexamethylbenzene, and chlorobenzene exhibited only the resonances of $Cp^*TiMe_2(\mu$-Me)$B(C_6F_5)_3$ and free arene; no [$Cp^*TiMe_2(\eta^6$-arene)][$MeB(C_6F_5)_3$] appeared to have been formed. Similar experiments with styrene, even at 173 K, resulted in very rapid polymerization to atactic polystyrene.[1b]

Synthesis of [$Cp^*Ti(^{13}CH_3)_2(\eta^6$-toluene)][$^{13}CH_3B(C_6F_5)_3$]. To a solution of $Cp^*Ti(^{13}CH_3)_2(\mu$-$^{13}CH_3)B(C_6F_5)_3$[1b,c] (0.042 mmol in 0.4 mL of CD_2Cl_2) at 195 K was added 27.0 μL of toluene (0.26 mmol). The sample was then placed in the NMR spectrometer probe at 223 K. Resonances of $Cp^*Ti(^{13}CH_3)_2(\mu$-$^{13}CH_3)B(C_6F_5)_3$[1c] and of free toluene were observed, as well as a new set of resonances, attributed to [$Cp^*Ti(^{13}CH_3)_2(\eta^6$-toluene)][$^{13}CH_3B(C_6F_5)_3$] (see above). ^{1}H NMR (CD_2Cl_2 at 223 K): δ 7.74, ~7.2, 6.70 (Ph), 2.78 (s, 3H, toluene Me), 1.90 (s, 15H, Cp*), 0.44 (br d, 3H, J_{HC} 112.6 Hz, BMe), 0.167 (d, 6H, J_{HC} 120.1 Hz, TiMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 223 K): δ 138.1 (w, Cp* ring C), 65.2 (vs, Ti−Me), 12.9 (w, Cp* Me).

Synthesis of [$Cp^*ZrMe_2(\eta^6$-toluene)][$MeB(C_6F_5)_3$]. A solution of 0.511 g of $B(C_6F_5)_3$ (1.0 mmol) in 200 mL of hexanes, cooled to 273 K, was added dropwise over 45 min to a well-stirred solution of 0.272 g of Cp^*ZrMe_3 (1.0 mmol) in 20 mL of toluene cooled to 273 K. The resulting yellow suspension was stirred for a further few minutes, and the product was collected by filtration, washed five times with cold hexanes, and dried *in vacuo* for 30 min at room temperature. Yield: 0.82 g (94% yield). Anal. Calcd for $C_{38}H_{32}BF_{15}Zr$: C, 52.12; H, 3.68. Found: C, 52.40; H, 3.75. ^{1}H NMR (CD_2Cl_2 at 298 K): δ 7.78 (d, 2H, *o*-Ph), 7.38 (t, 2H, *m*-Ph), 7.04 (t, 1H, *p*-Ph), 2.71 (s, 3H, toluene Me), 1.96 (s, 15H, Cp*), 0.48 (br s, 3H,

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BMe), −0.11 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 147.0, 134.8, 130.9, 129.2 (*ipso-*, *o-*, *m-*, *p*-Ph, respectively), 123.6 (Cp* ring C), 45.5 (ZrMe), 22.4 (toluene Me), 11.5 (Cp* Me), 10.2 (br, BMe).

Synthesis of [Cp*ZrMe$_2$(η^6-1,3,5-$C_6H_3Me_3$)][MeB(C_6F_5)$_3$]. This compound was prepared as above, with mesitylene substituted for toluene, and the orange product was obtained in 89% yield. Anal. Calcd for $C_{40}H_{36}BF_{15}Zr$: C, 53.16; H, 4.01. Found: C, 53.28; H, 4.12. ^1H NMR (CD_2Cl_2 at 273 K): δ 7.29 (s, 3H, ring CH), 2.47 (s, 9H, ring Me), 1.96 (s, 15H, Cp*), 0.50 (br s, 3H, BMe), −0.15 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 278 K): δ 141.1, 132.4 (mesitylene ring), 122.4 (Cp* ring C), 40.7 (ZrMe), 21.3 (mesitylene Me), 11.7 (Cp* Me), 10.2 (br, BMe).

Synthesis of [Cp*ZrMe$_2$(η^6-benzene)][MeB(C_6F_5)$_3$]. This compound was prepared as above, with benzene substituted for toluene. Although a yellow, solid product could be obtained in 88% yield at 273 K, it readily decomposed at room temperature and was therefore characterized spectroscopically at low temperature. ^1H NMR (CD_2Cl_2 at 223 K): δ 7.64 (s, 6H, benzene), 1.89 (s, 15H, Cp*), 0.53 (br s, 3H, BMe), −0.15 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 278 K): δ 131.6 (benzene), 123.1 (Cp* ring C), 45.3 (ZrMe), 11.6 (Cp* Me), 9.2 (br, BMe).

Synthesis of [Cp*ZrMe$_2$(η^6-styrene)][MeB(C_6F_5)$_3$]. This compound could not be prepared as above because of thermal instability. It was therefore generated in an NMR tube and characterized spectroscopically at low temperature. ^1H NMR (CD_2Cl_2 at 223 K): δ 7.95, 7.41, 7.11 (Ph), 6.82 (dd, 1H, PhC*H*=), 6.34 (d, 1H, J_{HH} 10.9 Hz, *cis* =CH_2), 6.04 (d, 1H, J_{HH} 17.2 Hz, *trans* =CH_2), 1.89 (s, 15H, Cp*), 0.41 (br s, 3H, BMe), −0.23 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 223 K): δ 152.1 (Ph*C*=), 140.8 (=*C*H_2), 130.7, 129.6, 126.8, 126.5 (Ph), 122.9 (Cp* ring C), 44.6 (ZrMe), 11.7 (Cp* Me), 9.8 (br, BMe). When the product stood at 223 K for 2 h, polymerization of styrene was observed. When a freshly prepared sample was warmed to 273 K, complete polymerization of styrene was observed and several resonances appeared in the Cp* region.

Synthesis of [Cp*ZrMe$_2$(η^6-*p*-xylene)][MeB(C_6F_5)$_3$]. This compound could not be isolated analytically pure as above because of thermal instability, and it was therefore generated in an NMR tube and characterized spectroscopically at low temperature. ^1H NMR (CD_2Cl_2 at 213 K): δ 7.48 (s, 4H, ring H), 2.42 (s, 6H, ring Me), 1.94 (s, 15H, Cp*), 0.46 (br s, 3H, BMe), −0.10 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 141.6, 134.8 (xylene ring C), 123.6 (Cp* ring C), 45.2 (ZrMe), 21.4 (xylene Me), 11.9 (Cp* Me), 10.5 (br, BMe).

Synthesis of [Cp*ZrMe$_2$(η^6-*m*-xylene)][MeB(C_6F_5)$_3$]. This compound could not be isolated analytically pure as above because of thermal instability, and it was therefore generated in an NMR tube and characterized spectroscopically at low temperature. ^1H NMR (CD_2Cl_2 at 213 K): δ 8.26 (s, 1H, xylene ring H-2), 7.10 (d, 2H, xylene ring H-4,6), 6.97 (t, 1H, xylene ring H-5), 2.54 (s, 6H, xylene ring Me), 1.89 (s, 15H, Cp*), 0.41 (br s, 3H, BMe), −0.29 (s, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 213 K): δ 146.6, 139.6, 138.1, 126.4 (xylene ring C), 122.5 (Cp* ring C), 45.6 (ZrMe), 22.0 (xylene Me), 11.6 (Cp* Me), 10.5 (br, BMe).

Attempted Syntheses of [Cp*ZrMe$_2$(η^6-arene)][MeB(C_6F_5)$_3$] (arene = PhCl, C_6Me_6). Low-temperature (223 K) NMR experiments designed to detect these complexes revealed no resonances which could be attributed to arene species.

Synthesis of [Cp*HfMe$_2$(η^6-toluene)][MeB(C_6F_5)$_3$]. This compound was prepared as above for the zirconium analogue. Anal. Calcd for $C_{38}H_{32}BF_{15}Hf$: C, 47.38; H, 3.32. Found: C, 46.62; H, 3.41. ^1H NMR (CD_2Cl_2 at 293 K): δ 7.55 (d, 2H, *o*-Ph), 7.32 (t, 2H, *m*-Ph), 7.28 (t, 1H, *p*-Ph), 2.76 (s, 3H, toluene Me), 2.10 (s, 15H, Cp*), 0.56 (br s, 3H, BMe), −0.28 (s, 6H, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 146.8, 134.7, 130.5, 124.7 (*ipso-*, *o-*, *m-*, *p*-Ph, respectively), 121.7 (Cp* ring C), 46.5 (ZrMe), 31.8 (toluene Me), 11.6 (Cp* Me), 10.2 (br, BMe).

Synthesis of [Cp*HfMe$_2$(η^6-*p*-xylene)][MeB(C_6F_5)$_3$]. This compound was prepared as above. Anal. Calcd for $C_{39}H_{34}BF_{15}Hf$: C, 47.95; H, 3.51. Found: C, 46.62; H, 3.59. ^1H NMR (CD_2Cl_2 at 213 K): δ 7.44 (s, 4H, ring H), 2.35 (s, 6H, ring Me), 1.93 (s, 15H, Cp*), 0.41 (br s, 3H, BMe), −0.46 (s, 6H, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 140.6, 132.4 (xylene ring C), 121.0 (Cp* ring C), 47.2 (HfMe), 21.2 (xylene Me), 11.4 (Cp* Me), 10.5 (br, BMe).

Synthesis of [Cp*HfMe$_2$(η^6-*m*-xylene)][MeB(C_6F_5)$_3$]. This compound was prepared as above; although apparently thermally stable at room temperature, it could not be obtained analytically pure and was characterized spectroscopically. ^1H NMR (CD_2Cl_2 at 213 K): δ 7.81 (s, 1H, xylene ring H-2), 7.13 (d, 2H, xylene ring H-4,6), 6.97 (t, 1H, xylene ring H-5), 2.58 (s, 6H, xylene ring Me), 2.02 (s, 15H, Cp*), 0.52 (br s, 3H, BMe), −0.41 (s, 6H, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 213 K): δ 147.6, 138.9, 138.1, 128.9 (xylene ring C), 122.3 (Cp* ring C), 50.3 (HfMe), 22.5 (xylene Me), 11.9 (Cp* Me), 10.5 (br, BMe).

Synthesis of [Cp*HfMe$_2$(η^6-anisole)][MeB(C_6F_5)$_3$]. This compound could not be prepared analytically pure because of thermal instability but was generated in an NMR tube and characterized spectroscopically at low temperature. ^1H NMR (CD_2Cl_2 at 213 K): δ 7.47 (t, 2H, *m*-H), 7.15 (d, 2H, *o*-H), 6.74 (t, 1H, *p*-H), 4.05 (s, 3H, OMe), 1.95 (s, 15H, Cp*), 0.39 (br s, 3H, BMe), −0.49 (s, 6H, HfMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 213 K): δ 163.8, 133.5, 121.2, 115.5 (Ph), 116.9 (Cp* ring C), 44.6 (HfMe), 11.4 (Cp* Me), 10.2 (br, BMe). When the compound was warmed to 295 K in the presence of free anisole, coalescence of the phenyl ^1H resonances of free and coordinated anisole to broad bands at δ ~7.37 (2H) and δ ~6.95 (3H) and of the OMe resonances of free and coordinated anisole to a broad band at δ ~3.9 was observed. The Hf−Me resonance of the anisole complex (δ −0.38) was also noticeably broadened.

X-ray Structure Determination of [Cp*HfMe$_2$(η^6-toluene)][MeB(C_6F_5)$_3$]. Crystals of this complex were grown by slow diffusion of hexanes into an *o*-dichlorobenzene solution at 243 K over several weeks, and a platelike sample was mounted on a glass fiber with epoxy cement and sealed under an argon atmosphere in a thin glass capillary. Table 3 presents the crystal data, details of the experimental measurements, and a summary of refinement parameters. The cell constants were obtained from least-squares refinement of 25 reflections with 34° ≤ 2θ ≤ 36°. Intensity data were collected by $\omega-2\theta$ scans. Three standard reflections monitored throughout the data collection showed significant degradation of the compound (30% at the end of data collection), and a correction based on the variation of the standards' intensities was applied.[7] The data were corrected for absorption using the program DIFABS.[8] The structure was solved by heavy-atom methods (Patterson and Fourier maps) using the program SHELXS86.[9] Full-matrix least-squares refinement on F^2 data with the anisotropic displacement parameters for all non-H atoms was performed using the program SHELXL92[10] (the neutral atom scattering factors and anomalous dispersion corrections used are those from ref 11). The structure has shown the presence of one solvent molecule of toluene per two pairs of complex cations. It was found disordered around the inversion center at $^1/_2$, 0, $^1/_2$ and was refined originally as a rigid group (as an ideal hexagon with ring C−C bonds of 1.390 Å and a single C−C bond of 1.51 Å) with common isotropic displacement parameters. In the last cycles, the restrained anisotropic refinement was used and the $C_{phenyl}-C_{methyl}$ bond

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Table 3. Crystallographic Data for $[Cp^*HfMe_2(\eta^6\text{-toluene})][MeB(C_6F_5)_3]$

(a) Crystal Parameters	
formula	$C_{41.5}H_{36}BF_{15}Hf$
fw	1009.00
cryst syst	triclinic
space group	$P\bar{1}$(No. 2)
a, Å	9.380(3)
b, Å	17.639(3)
c, Å	12.335(2)
α, deg	82.37(1)
β, deg	101.14(2)
γ, deg	96.32(2)
V, Å^3	1977.2(8)
Z	2
D_{calcd}, g/cm^3	1.695
μ(Mo Kα), cm^{-1}	27.39
cryst dimens, mm	0.18 × 0.50 × 0.70
cryst color	yellow-brown
(b) Data Collection	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα ($\gamma = 0.710\ 69$ Å)
monochromator	graphite
temp, K	298
data collected	$-11 \le h \le 10$, $-20 \le k \le 20$, $0 \le l \le 14$
θ scan range, deg	1.2−25.00
no. of rflns collected	7176
no. of indep rflns	6921 ($R_{int} = 0.031$)
no. of indep obsd reflns ($I > 2\sigma(I)$)	4598
abs cor	empirical (transmissn factors 0.587−1.249)
(c) Structure Solution and Refinement	
solution method	Patterson and Fourier methods
refinement method	full-matrix least squares on F^2 (for all indep data)
no. of variables	554
no. of restraints	60
data/variables ratio	12.5
function minimized	$\sum w(F_o^2 - F_c^2)^2$
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
R,[a] $wR2$,[b] indep obsd rflns	0.0448, 0.1222
R,[a] $wR2$,[b] all indep rflns	0.0729, 0.1436
goodness-of-fit indicator[c]	1.094 (all indep data)
max shift/error, final cycle	0.008
max resid electron dens, e/Å^3	1.379
min resid electron dens, e/Å^3	−1.484

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit on F^2: $S = \{[\sum w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{var})\}^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1

Hf−C1	2.219(9)	C5−C6	1.424(11)
Hf−C2	2.204(9)	C6−C7	1.408(12)
Hf−Cg(1)[a]	2.172(4)	C3−C8	1.499(13)
Hf−Cg(2)[b]	2.334(6)	C4−C9	1.488(12)
Hf−C3	2.487(8)	C5−C10	1.478(12)
Hf−C4	2.480(7)	C6−C11	1.490(12)
Hf−C5	2.481(8)	C7−C12	1.477(12)
Hf−C6	2.487(7)	C13−C14	1.387(14)
Hf−C7	2.480(8)	C13−C18	1.42(2)
Hf−C13	2.805(9)	C13−C19	1.48(2)
Hf−C14	2.666(9)	C14−C15	1.31(2)
Hf−C15	2.623(11)	C15−C16	1.36(3)
Hf−C16	2.62(2)	C16−C17	1.33(3)
Hf−C17	2.710(14)	C17−C18	1.34(2)
Hf−C18	2.768(10)	B−C20	1.665(11)
C3−C4	1.397(11)	B−C30	1.668(10)
C3−C7	1.421(12)	B−C40	1.647(11)
C4−C5	1.420(11)	B−C50	1.628(10)
C1−Hf−C2	93.6(5)	C20−B−C30	103.7(6)
C1−Hf−Cg(1)[a]	108.5(3)	C20−B−C40	112.2(5)
C1−Hf−Cg(2)[b]	102.1(3)	C20−B−C50	113.0(6)
C2−Hf−Cg(1)[a]	108.4(3)	C30−B−C40	113.6(6)
C2−Hf−Cg(2)[b]	103.2(3)	C30−B−C50	109.7(6)
Cg(1)[a]−Hf−Cg(2)[b]	133.8(2)	C40−B−C50	104.9(6)
C50−B−C20−C21	3.2(10)	C50−B−C30−C35	−128.4(8)
C50−B−C20−C25	−173.3(6)	C50−B−C40−C41	−111.6(8)
C50−B−C30−C31	55.2(9)	C50−B−C40−C45	61.2(8)

[a] Cg(1): center of gravity of the C3−C7 five-membered ring. [b] Cg(2): center of gravity of the C13−C18 six-membered ring.

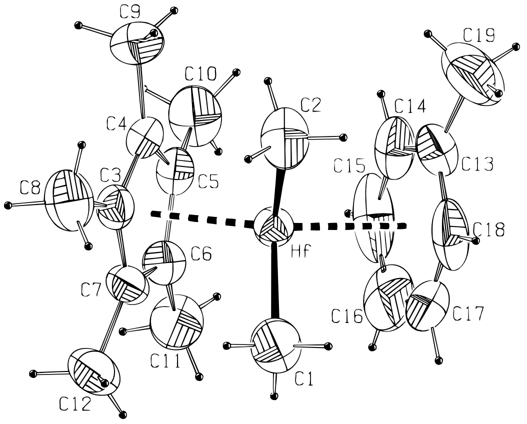

Figure 1. Molecular structure of $[Cp^*HfMe_2(\eta^6\text{-toluene})]$-$[BMe(C_6F_5)_3]$ showing 30% probability displacement ellipsoids. The toluene solvent molecule is shown in one of two positions related by a center of symmetry; H atoms were omitted for clarity.

length was allowed to vary. All atoms of the solvent toluene were refined with a site occupancy factor of 50%. The hydrogen atoms of the structure were placed in calculated positions (for toluene methyl groups in two positions rotated by 60° with half-occupancy each; for other methyl groups, the torsion angle was determined on the basis of the electron density map features). In the refinement, all H atoms were riding on the carbon atoms to which they are attached; their isotropic thermal displacement parameters were kept as $U_{iso}(H) = 1.2U_{eq}(C)$ (for aromatic H) or $U_{iso}(H) = 1.5U_{eq}(C)$ (for methyl H). The refinement converged at the final R value (conventional, based on F) of 0.0448. Selected bond lengths, bond angles, and torsion angles are listed in Table 4. Tables of all bond lengths and angles, positional parameters for non-H atoms, anisotropic displacement parameters for non-H atoms, hydrogen atom positional and thermal parameters, and least-squares planes data, as well as a diagram showing the disorder of the solvent molecule of toluene, are available as Supporting Information. The geometrical analysis of the structure was done with the programs SHELXL92[10] and PLATON.[12] An ORTEP[13] drawing of the complex ions and the solvent toluene molecule with the atom-numbering scheme is given in Figure 1. Figure 2 shows the arrangement of two pairs of the complex ions around the disordered solvent molecule of toluene, drawn with the program PLUTON.[14]

Results and Discussion

Synthesis of Arene Complexes of Zirconium and Hafnium. In general, addition of the highly electrophilic borane $B(C_6F_5)_3$ to solutions of Cp^*MMe_3 (M = Zr, Hf) in CD_2Cl_2 in the presence of excess arene (arene = benzene, toluene, styrene, *m*-xylene, *p*-xylene, anisole, mesitylene) at low temperatures results in the disappearance of the ^1H resonances of Cp^*MMe_3, in weaken-

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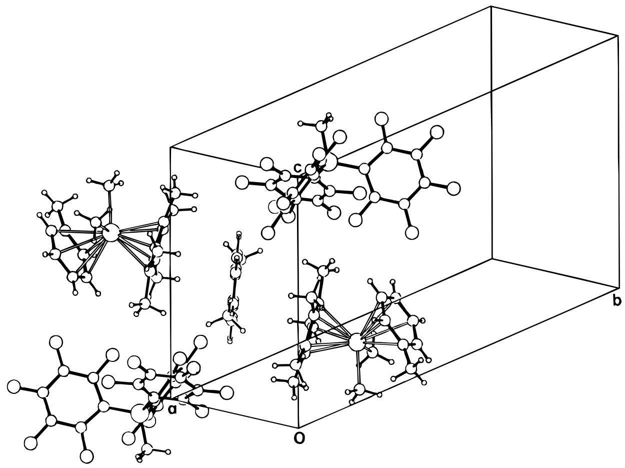

Figure 2. Packing diagram of [Cp*HfMe$_2$(η^6-toluene)]-[BMe(C$_6$F$_5$)$_3$], showing two pairs of the complex ions and two overlapped molecules of solvent toluene (50% occupation each) around the inversion center at $^1/_2$, 0, $^1/_2$.

ing of the resonances of the free arene, and in the appearance of new resonances attributable to free borate ion, [MeB(C$_6$F$_5$)$_3$]$^-$ (δ ~0.5),[1] and the new species [Cp*MMe$_2$(η^6-arene)]$^+$ (Table 1). In some cases, *e.g.* [Cp*ZrMe$_2$(η^6-toluene)][MeB(C$_6$F$_5$)$_3$], [Cp*ZrMe$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)][MeB(C$_6$F$_5$)$_3$], [Cp*HfMe$_2$(η^6-toluene)][MeB-(C$_6$F$_5$)$_3$], and [Cp*HfMe$_2$(η^6-*p*-xylene)][MeB(C$_6$F$_5$)$_3$], analytically pure compounds could be obtained as yellow solids by precipitation from CH$_2$Cl$_2$ with hexanes. However, many of the new compounds could not be obtained pure in this way but were instead characterized unambiguously by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Tables 1 and 2). NMR spectra of experiments involving the zirconium complex with hexamethylbenzene and the hafnium complex with chlorobenzene at 223 K resulted in the appearance of no ^{1}H resonances attributable to new arene complexes. In the case of zirconium, there appeared a number of new Cp* methyl resonances and a resonance at δ ~0.5 attributable to free borate but no resonances attributable to coordinated arene. In the case of hafnium, new Cp* and Hf−Me singlet resonances appeared at δ 2.09 and 0.09, respectively, as well as a broad singlet at δ ~0.9 but not at δ ~0.5. The broad resonance at δ ~0.9 is reminiscent of the boron-broadened (μ-Me resonance of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$, at δ ~1.1,[1] and it is possible that the compound formed is Cp*HfMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$.

The ^{1}H NMR spectra of all the arene complexes exhibit Cp* methyl resonances at δ ~1.9−2.1 and metal−methyl resonances at δ ~0.1 (Ti), δ −0.1 to −0.2 (Zr), and δ −0.3 to −0.5 (Hf). The ^{13}C{^{1}H} NMR spectra of the zirconium and hafnium complexes exhibit metal−methyl, Cp* methyl, and Cp* ring resonances at δ 41−54, ~12, and ~122, respectively, and thus the chemical shifts vary little within these series of complexes, lending confidence to the assignments where pure compounds could not be obtained. In contrast, the ^{13}C{^{1}H} NMR spectrum of [Cp*TiMe$_2$(η^6-toluene)][MeB-(C$_6$F$_5$)$_3$] exhibits metal−methyl and Cp* ring resonances at considerably lower field: δ 65.2 and 138.1, respectively. However, this complex was ^{13}C-enriched at the Ti−Me site and thus, even though no ^{13}C{^{1}H} NMR spectra of other (arene)titanium complexes were obtained, the Ti−Me resonance of this compound is assigned quite unambiguously.

In the ^{1}H NMR spectra of the complexes, all arene resonances except for the ^{1}H resonances of the *p*-H atoms of the monosubstituted ligands toluene, styrene and anisole were found to be significantly deshielded relative to the chemical shifts of the free ligands. The *p*-H resonances were all found to be slightly shielded relative to the chemical shifts of the free ligands. We presume that the anisole ligand coordinates preferentially in an η^6 fashion because of these similarities in coordination shifts and because integrations of the ^{1}H NMR spectra of the hafnium anisole complex indicate quite clearly that only one arene ligand coordinates, not two. As shown previously, an analogous bis-THF complex, [Cp*ZrMe$_2$(THF)$_2$][BPh$_4$], is known.[15] However, coordination via the oxygen is also possible and probably occurs to some extent (see below).

The general trends seem reasonable, since the arenes are in each case coordinated to cationic complexes in which the metals are in the +4 oxidation state. Bonding of the arenes to the d^0 metal ions must involve essentially no metal−ligand back-bonding but rather significant net flow of electron density from arene to metal, a bonding model seemingly confirmed by the coordination shifts exhibited in the NMR spectra. The fact that chlorobenzene does not coordinate to either [Cp*TiMe$_2$]$^+$ or [Cp*HfMe$_2$]$^+$ seems to confirm this hypothesis.[16] The ^{13}C{^{1}H} resonances of the coordinated arenes also generally occur to low field relative to the corresponding resonances of the free arenes. The ^{1}H NMR spectra of most of the complexes of both metals are essentially unchanged on warming from 223 to 273 K, indicating reasonable thermal stabilities.

An exception is the anisole complex [Cp*HfMe$_2$(η^6-PhOMe)][MeB(C$_6$F$_5$)$_3$], for which all of the ^{1}H resonances except the Cp* resonance broaden on warming. We note, however, that the toluene of [Cp*ZrMe$_2$(η^6-toluene)][MeB(C$_6$F$_5$)$_3$] is readily displaced from the metal by amines and phosphines,[1b] and we suggest that the η^6-anisole ligand is displaced also, to some extent, from the highly oxophilic hafnium by the ether group of free anisole. Other exceptions are the styrene complexes [Cp*MMe$_2$(η^6-styrene)][MeB(C$_6$F$_5$)$_3$], in the presence of free styrene. The ^{1}H NMR spectra of these change quite drastically on warming to 273 K; atactic polystyrene is formed, and many new Cp* peaks appear.

Interestingly, spin saturation transfer experiments at 223 K with mixtures of free arenes and [Cp*ZrMe$_2$(η^6-arene)][MeB(C$_6$F$_5$)$_3$] (arene = benzene, toluene) suggest that exchange between free and coordinated arenes is not facile in these cases. Irradiation of the resonances of the coordinated arenes had no effect on the intensities of the resonances of the free arenes, and *vice versa.* Spin saturation was also not observed with the toluene compound on warming to 273 K but was observed with the benzene compound, consistent with exchange in the latter case. The lower reactivity of the toluene complex is consistent with the stronger arene−metal bonding anticipated on substitution of hydrogen by a more electron-releasing methyl group.

As indicated above, the pattern of coordination shifts of the aromatic hydrogen and carbon atoms in the

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(16) While hexamethylbenzene would therefore be expected to coordinate strongly, steric factors might well weaken arene−metal interactions in the case of this potential ligand.

styrene complexes $[Cp^*MMe_2(\eta^6\text{-styrene})][MeB(C_6F_5)_3]$ (M = Zr, Hf) implies a coordination mode similar to that of the toluene complexes, *i.e.* an η^6-arene rather than an η^2-olefin mode of bonding. While this result seems surprising in view of the high activities exhibited by these complexes, and their titanium analogue, as styrene polymerization initiators,[1] a detailed examination of the vinyl hydrogen atom spin−spin coupling constants supports the conclusion. A number of styrene complexes of both types, η^2- and η^6-, are known, and while the vinyl H−H coupling constants of $(\eta^6\text{-styrene})Cr(CO)_3$[17a] and $[Cp^*Ru(\eta^6\text{-styrene})]^+$ [17b] are very similar to those of free styrene, the vinyl H−H coupling constants of $[CpFe(CO)_2(\eta^2\text{-styrene})]^+$ [17c] and $PtCl_2(\eta^2\text{-styrene})_2$[17d] are quite different, in accord with changes in hybridization on coordination. In the case of the complexes $[Cp^*MMe_2(\eta^6\text{-styrene})][MeB(C_6F_5)_3]$, the vinyl H-H coupling constants are essentially identical with those of free styrene, consistent only with the η^6 mode of bonding.

Synthesis of Arene Complexes of Titanium. Addition of borane to a solution of Cp^*TiMe_3 in CD_2Cl_2 in the presence of excess toluene results in disappearance of the ^1H resonances of Cp^*TiMe_3, weakening of the peaks of the free arene, and the appearance of new resonances attributable to the species $[Cp^*TiMe_2(\eta^6\text{-toluene})]^+$. The ^1H NMR spectrum also exhibits a resonance at $\delta \sim 0.5$, attributable to free borate, and the Cp* and BMe resonances of the complex $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$.[1] Thus, in contrast to the zirconium and hafnium systems, described above, an equilibrium is established between the neutral borate complex and the cationic arene complex, formed to the extent of ∼30% (eq 1). Similar results were obtained with mesitylene,

$$Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3 + \text{toluene} \rightleftarrows [Cp^*TiMe_2(\eta^6\text{-toluene})]^+ + [BMe(C_6F_5)_3]^- \quad (1)$$

but no reaction was observed with benzene or *p*-xylene at 213 K. Only the resonances of the free arene and $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ were present. The lack of coordination of benzene must reflect the lowered electron density on the ring of this ligand relative to the case with toluene, and we note the spin-saturation transfer experiments with $[Cp^*ZrMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ (arene = benzene, toluene), described above, which showed that the (benzene)zirconium complex is more labile than the toluene analogue. The reason for the lack of reactivity with *p*-xylene is less clear; possibly steric effects are important.

Structure of $[Cp^*HfMe_2(\eta^6\text{-toluene})][BMe(C_6F_5)_3]$. Usable crystals of $[Cp^*HfMe_2(\eta^6\text{-toluene})][BMe(C_6F_5)_3]$ were obtained by slow diffusion of hexanes into an *o*-dichlorobenzene solution at 243 K over several weeks. Figure 1 illustrates the structure of the complex cation, and Figure 2 gives a packing diagram showing two pairs each of both complex ions and two overlapped molecules of solvent toluene (50% occupation each) about the inversion center at $^1/_2$, 0, $^1/_2$. Crystal data, details of the experimental measurements, and a summary of refinement parameters are presented in Table 3 and important bond lengths and angles in Table 4.

As anticipated, the $[Cp^*HfMe_2(\eta^6\text{-toluene})]^+$ cation and the $[BMe(C_6F_5)_3]^-$ anion are well separated in the crystal lattice, and the former forms a bent-sandwich structure, analogous to the structures of $[\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}HfMe_2(\eta^6\text{-toluene})][MeB(C_6F_5)_3]$[5] and Cp_2HfMe_2.[18] The Hf−Me bond lengths of $[Cp^*HfMe_2(\eta^6\text{-toluene})]^+$ (2.219(9), 2.204(9) Å) are shorter than those of $[\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}HfMe_2(\eta^6\text{-toluene})]^+$ (2.245(7), 2.244(7) Å at 120 K)[5] and Cp_2HfMe_2 (2.318(8), 2.382(7) Å),[18] but the averages of the Hf−Cp* and Hf−toluene bond lengths (2.483, 2.669 Å, respectively) are very similar to those of $[\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}HfMe_2((\eta^6\text{-toluene})]^+$ (2.487, 2.689 Å, respectively).[5] The Me−Hf−Me and Cp* ring centroid−Hf−toluene ring centroid bond angles of $[Cp^*HfMe_2(\eta^6\text{-toluene})]^+$ are 93.6(5) and 133.8(2)°, respectively, very similar to those of $[\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}HfMe_2(\eta^6\text{-toluene})]^+$ (93.5(3), 134.2(2)°,[5] respectively). The corresponding angles in Cp_2HfMe_2 are 94.8(3) and 132.1°, respectively.[18]

The packing diagram of $[Cp^*HfMe_2(\eta^6\text{-toluene})][BMe(C_6F_5)_3]$ (Figure 2) shows that there are two pairs of each of the complex ions and two disordered molecules of solvent toluene around the inversion center. The dihedral angle between the plane of the toluene solvent molecule and the Cp* least-squares plane is 11(2)°, while the Cp*−toluene stacking distance is 3.6(2) Å; thus, the structure may be stabilized by $\pi-\pi$ stacking[19] in the solid state.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for financial support of this research (Research, Collaborative Research and Development, and Strategic Grants to M.C.B., Graduate Fellowship to D.J.G.), to the Government of Ontario for a graduate fellowship to D.J.G., and to DuPont Canada Inc. for both generous financial support and for a leave of absence to D.J.G.

Supporting Information Available: Tables of positional parameters, bond lengths and angles, anisotropic displacement parameters for non-H atoms, hydrogen atom positional and thermal parameters, and least-squares planes data and a diagram showing disorder of the solvent molecule of toluene (14 pages). Ordering information is given on any current masthead page.

OM960174I

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