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FULL PAPER

Reaction of $B(C_6F_5)_3$ with zirconium and hafnium benzyl diene complexes. The crystal and molecular structures of $Cp''Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ and $[Cp''Hf(2,3\text{-}Me_2C_4H_4)(OEt_2)][PhCH_2B(C_6F_5)_3]$ [$Cp'' = 1,3\text{-}(SiMe_3)_2C_5H_3$]

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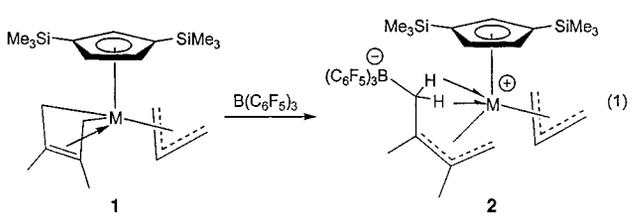
The zirconium and hafnium diene complexes $Cp''MCl(\eta^4\text{-}CH_2CMeCR^1CH_2)$ react with benzylmagnesium chloride to give the benzyl complexes $Cp''M(\eta^4\text{-}CH_2CMeCR^1CH_2)(CH_2Ph)$ (M = Zr, R^1 = Me or H; M = Hf, R^1 = Me) which react with $B(C_6F_5)_3$ selectively under benzyl abstraction to give the zwitterionic products $Cp''M(\eta^4\text{-diene})\text{-}\{\eta''\text{-}PhCH_2B(C_6F_5)_3\}$. The zirconium derivative exists as a mixture of two isomers which interchange *via* ring-flipping of the diene ligand, whereas the Hf compound is rigid. The isoprene analogue $Cp''Zr(CH_2CMeCHCH_2)\{PhCH_2\text{-}B(C_6F_5)_3\}$ decomposes at room temperature under C–H activation and C_6F_5 migration from boron to zirconium to give toluene and the structurally characterised boryldiene complex $Cp''Zr(C_6F_5)\{CH_2CMeCHCHB(C_6F_5)_2\}$. In the hafnium (but not zirconium) complexes, the $[PhCH_2B(C_6F_5)_3]^-$ anion is displaced by CH_2Cl_2. The addition of diethyl ether leads to the ionic compound $[Cp''Hf(2,3\text{-}Me_2C_4H_4)(OEt_2)]^+[PhCH_2B(C_6F_5)_3]$ which was characterised by X-ray diffraction.

Introduction

As part of a systematic study of mono-cyclopentadienyl complexes of the general formula Cp″M(dianion)(R) as potential precursors for new olefin polymerisation or oligomerisation catalysts we have recently reported the synthesis of the compounds $Cp''M(\eta^4\text{-diene})(R)$ (R = Me, η^3-allyl)[1] and $Cp''M(\eta^4\text{-diazadiene})(R)$ (R = Me, CH_2Ph),[2] where M = Zr or Hf and $Cp'' = 1,3\text{-}(SiMe_3)_2C_5H_3$. These 14- and 16-electron compounds are not themselves catalytically active but are activated by suitable Lewis or Brønsted acids,[3] for example, the allyl complexes $Cp''M(diene)(\eta^3\text{-allyl})$ **1** are attacked by $B(C_6F_5)_3$ exclusively at the less substituted terminal carbon atom of the diene ligand to give zwitterionic complexes **2** which readily polymerise ethene to high molecular weight polymers [eqn. (1)].[4] In no case was



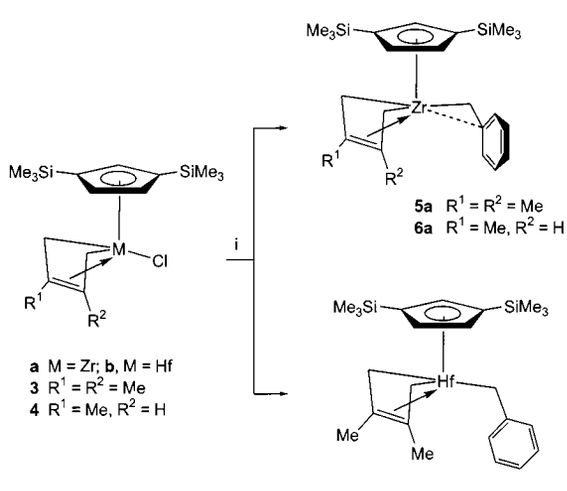
1 **2**

there evidence for an attack of $B(C_6F_5)_3$ on the allyl ligand. We now report the reaction of $B(C_6F_5)_3$ with related benzyl complexes $Cp''M(diene)(CH_2Ph)$ which show a very different selectivity.

Results and discussion

The chloro complexes $Cp''MCl(\eta^4\text{-}C_4H_4Me_2\text{-}2,3)$ (**3a**, M = Zr; **3b**, M = Hf) and $Cp''ZrCl(\eta^4\text{-}C_4H_5Me\text{-}2)$ **4a**,[1] react with benzylmagnesium chloride in diethyl ether at −78 °C to room temperature to give the corresponding benzyl complexes **5a**, **5b** and **6a** as dark red solids in the case of zirconium and as spectroscopically pure orange oils for hafnium (Scheme 1).

These benzyl complexes are thermally significantly more stable than the analogous methyl derivatives and can be isolated



Scheme 1 i, $PhCH_2MgCl$, Et_2O, −78 °C.

and stored at ambient conditions without appreciable decomposition. Compound **5a** is stable in benzene solution up to 60 °C but at higher temperature starts to decompose to give a mixture of products, including the previously identified dinuclear compound $[Cp''Zr(\mu,\eta^1\text{:}\eta^4\text{-}C_4H_3Me_2)]_2$.[5] The hafnium compound **5b** is more stable and decomposes in solution only above 80 °C to a mixture of unknown products; there was no evidence for the formation of an analogue to the dinuclear zirconium complex. All benzyl complexes are very soluble in hydrocarbon solvents and decompose rapidly in chlorinated solvents to the corresponding trichlorides, $Cp''MCl_3$. The compounds are extremely air sensitive and for this reason the oily products did not give satisfactory elemental analyses.

The ^1H and ^{13}C NMR spectroscopic data of all new compounds are given in Table 1, ^{19}F NMR data are collected in Table 2. The spectroscopic data, in particular the geminal $^2J_{HH}$ coupling constants (7.0–11.4 Hz) and the $^1J_{CH}$ coupling constants (139.8–146.9 Hz) of the diene methylene groups are con-

Table 1 ^{1}H and ^{13}C NMR data of zirconium and hafnium complexes[a]

Complex	^{1}H NMR (δ)	Assignment	^{13}C NMR (δ)	Assignment
Cp′Zr(CH_2Ph)-($2,3$-$Me_2C_4H_4$) **5a** (C_6D_6, 20 °C)	0.19 (d, J = 9, 2H)	=CH_2 *anti*	0.33 (q, J = 119)	$SiMe_3$
	0.23 (s, 18H)	$SiMe_3$	23.98 (q, J = 125.9)	diene-Me
	2.05 (s, 6H)	diene-Me	57.77 (t, J = 138.3)	*C*H_2Ph
	2.24 (s, 2H)	CH_2Ph	60.4 (t, J = 142.3)	=CH_2
	2.37 (d, J = 9, 2H)	=CH_2 *syn*	117.51 (d, J = 160)	*o*-Ph
	5.57 (d, J = 2, 2H)	4,5-C_5H_3	119.31, 123.64 (m)	=*C*Me, 1,3-C_5H_3
	5.72 (t, J = 2, 1H)	2-C_5H_3	121.14 (d, J = 166.8)	2-C_5H_3
	6.08 (d, J = 7.2, 2H)	*o*-Ph	121.4 (d, J = 160)	*p*-Ph
	6.7 (t, J = 7.2, 1H)	*p*-Ph	122.14 (d, J = 168.3)	4,5-C_5H_3
	7.05 (t, J = 7.2, 2H)	*m*-Ph	133.96 (d, J = 157.7)	*m*-Ph
			138.53 (m)	*ipso*-Ph
Cp′Hf(CH_2Ph)-($2,3$-$Me_2C_4H_4$) **5b** (C_6D_6, 20 °C)	−0.18 (d, J = 11.1, 2H)	=CH_2 *anti*	0.18 (q, J = 119.1)	$SiMe_3$
	0.21 (s, 18H)	$SiMe_3$	23.5 (q, J = 126)	diene-Me
	1.23 (s, 2H)	CH_2Ph	66.45 (t, J = 139.3)	=CH_2
	2.12 (s, 6H)	diene-Me	71.22 (t, J = 122.1)	*C*H_2Ph
	2.31 (d, J = 11.1, 2H)	=CH_2 *syn*	121.42, 125.37 (m)	=*C*Me, 1,3-C_5H_3
	5.86 (t, J = 1.9, 1H)	2-C_5H_3	121.87 (d, J = 169)	4,5-C_5H_3
	5.99 (d, J = 1.9, 2H)	4,5-C_5H_3	121.9 (d)	*p*-Ph
	65.53 (d, J = 7.2, 2H)	*o*-Ph	122.02 (d, J = 167.5)	2-C_5H_3
	6.86 (t, J = 7.2, 1H)	*p*-Ph	122.77 (d, J = 153.2)	*o*-Ph
	7.19 (t, J = 7.2, 2H)	*m*-Ph	130.28 (d, J = 153.2)	*m*-Ph
			154.2 (m)	*ipso*-Ph
Cp′Zr(CH_2Ph)-(2-MeC_4H_5) **6a** (C_6D_6, 20 °C)	−0.56, 0.35 (d, m, J = 9, 1H, each)	=CH_2 *anti*	0.3, 0.43 (q, J = 119)	$SiMe_3$
	0.23, 0.3 (s, 9H each)	$SiMe_3$	26.1 (q, J = 125.6)	diene-Me
	1.1, 2.18 (d, J = 8, 1H each)	CH_2Ph	52.04, 60.6 (t, J = 144.6, 145)	=CH_2
	1.82 (s, 3H)	diene-Me	53.85 (t, J = 137.8)	*C*H_2Ph
	1.93, 2.24 (t, d, J = 9, 1H each)	=CH_2 *syn*	117.73 (d, J = 154)	*o*-Ph
	4.33 (t, J = 9, 1H)	CH	!19.68, 121.69 (d, J = 168.3, 167.5)	4,5-C_5H_3
	6.02, 6.35 (m, 1H each)	4,5-C_5H_3	120.4 (d, J = 155)	CH
	6.05 (m, 1H)	2-C_5H_3	120.63, 128.87 (m)	=CMe, 1,3-C_5H_3
	6.19 (d, J = 7.3, 2H)	*o*-Ph	121.83 (d, J = 166.8)	2-C_5H_3
	6.88 (t, J = 7.2, 1H)	*p*-Ph	122.63 (d, J = 162.2)	*p*-Ph
	7.05 (t, J = 7.2, 2H)	*o*-Ph	131.51 (d, J = 158.5)	*m*-Ph
			134.61 (m)	*ipso*-Ph
Cp″Zr($2,3$-$Me_2C_4H_4$)-{η^6-$PhCH_2B(C_6F_5)_3$} **7a**, major isomer, (CD_2Cl_2, −40 °C)	−1.53 (d, J = 10.5, 2H)	=CH_2 *anti*	−0.32 (q, J = 119.5)	$SiMe_3$
	0.09 (s, 18H)	$SiMe_3$	23.11 (q, J = 127.5)	diene-Me
	1.31 (s, 6H)	diene-Me	34.4 (vbr)	CH_2-B
	3.0 (d, J = 10.5, 2H)	=CH_2 *syn*	66.19 (t, J = 144)	=CH_2
	3.34 (br s, 2H)	CH_2-B	116.4	2-C_5H_3
	4.4 (br s, 1H)	2-C_5H_3	116.67	4,5-C_5H_3
	4.6 (t, J = 7, 1H)	*p*-Ph	118.07 (d, J = 169.8)	*m*-Ph
	5.4 (t, J = 7, 2H)	*m*-Ph	121.9 (d, J = 171)	*o*-Ph
	5.63 (d, J = 1.8, 2H)	4,5-C_5H_3	123.93	*p*-Ph
	6.15 (d, J = 7, 2H)	*o*-Ph	136.28 (d, J_{CF} = 249.8)	*m*-C_6F_5
			137.82 (d, J_{CF} = 246.8)	*p*-C_6F_5
			147.5 (d, J_{CF} = 237)	*o*-C_6F_5
			155.92 (m)	*ipso*-Ph
Minor isomer, (CD_2Cl_2, −40 °C)	−1.8 (d, J = 9.3, 2H)	=CH_2 *anti*	0.30 (q, J = 119.5)	$SiMe_3$
	−0.01 (s, 18H)	$SiMe_3$	24.97 (q, J = 127.8)	diene-Me
	1.47 (s, 6H)	diene-Me	33.1 (vbr)	CH_2-B
	underneath	CH_2-B	71.34 (t, J = 145.3)	=CH_2
	3.55 (d, J = 9.3, 2H)	=CH_2 *syn*	105.71 (d, J = 173.5)	*m*-Ph
	4.5 (d, J = 1.7, 2H)	4,5-C_5H_3	109.39 (d, J = 169.8)	*p*-Ph
	5.27 (br s, 1H)	2-C_5H_3	113.81 (d, J = 169.8)	2-C_5H_3
	5.72 (t, J = 7, 1H)	*p*-Ph	114.64	4,5-C_5H_3
	6.07 (t, J = 7, 2H)	*m*-Ph	119.64 (d, J = 167.5)	*o*-Ph
	6.25 (d, J = 7, 2H)	*o*-Ph	160.32 (m)	*ipso*-Ph
Cp″Hf($2,3$-$Me_2C_4H_4$)-{η^6-$PhCH_2B(C_6F_5)_3$} **7b** (C_7D_8, −20 °C)	−1.69 (d, J = 12, 2H)	=CH_2 *anti*	−0.31 (q, J = 119.7)	$SiMe_3$
	0.09 (s, 18H)	$SiMe_3$	22.03 (q, J = 126.5)	diene-Me
	1.43 (s, 6H)	diene-Me	35 (vbr s)	CH_2-B
	2.51 (d, J = 12, 2H)	=CH_2 *syn*	60.07 (t, J = 140)	=CH_2
	3.35 (br s, 2H)	CH_2-B	104.16 (d, J = 175.8)	*p*-Ph
	4.53 (t, J = 6, 1H)	*p*-Ph	114.87 (d, J = 169.8)	4,5-C_5H_3
	4.6 (br s, 1H)	2-C_5H_3	116.78 (d, J = 169)	2-C_5H_3
	5.37 (br s, 2H)	4,5-C_5H_3	119.32 (d, J = 169.8)	*o*-Ph
	5.55 (t, J = 6, 2H)	*m*-Ph	123.1 (d, J = 169.8)	*m*-Ph
	6.15 (d, J = 6, 2H)	*o*-Ph	124.46, 126.46 (m)	=CH_2, 1,3-C_5H_3
			137.18 (d, J_{CF} = 249)	*m*-C_6F_5
			138.68 (d, J_{CF} = 248.3)	*p*-C_6F_5
			148.5 (d, J_{CF} = 238.4)	*o*-C_6F_5
			157.7 (m)	*ipso*-Ph

Table 1 (*Contd.*)

Complex	^{1}H NMR (δ)	Assignment	^{13}C NMR (δ)	Assignment
[Cp″Hf(2,3-$Me_2C_4H_4$)-(CD_2Cl_2)$_n$]$^+$ [$PhCH_2$-$B(C_6F_5)_3$]$^-$ **8b** (CD_2Cl_2, 0 °C)	−2.38 (br d, J = 5.5, 1H)	=CH_2	−0.39, 0.31 (q, J = 119.8)	$SiMe_3$
	0.22, 0.25 (s, 9H each)	$SiMe_3$	23.78, 24.45 (q, J = 127.8, 128)	diene-Me
	2.23, 2.37 (s, 3H each)	diene-Me	31 (vbr s)	CH_2-B
	2.51 (br d, J = 3.5, 1H) and another underneath diene-Me	=CH_2	73.37 (t, J = 120.7)	=CH_2
			76.29 (t, J = 150)	=CH_2
	2.81 (br s, 2H)	CH_2-B	116.1, 133.95, 148.85 (m)	=CH_2, 1,3-C_5H_3
	3.6 (br d, J = 5.5, 1H)	=CH_2	119 (vbr)	4,5-C_5H_3
	6.71 (m, 2H)	4,5-C_5H_3	122.56 (d, J = 158.4)	*o*-Ph
	6.74 (d, J = 7, 2H)	*o*-Ph	126.97 (d, J = 157.7)	*m*-Ph
	6.88 (m, 3H)	*m*-Ph, *p*-Ph	128.7	2-C_5H_3
	7.24 (m, 1H)	2-C_5H_3	128.83 (d, J = 156.2)	*o*-Ph
			130.02 (d, J = 171.3)	4,5-C_5H_3
			136 (d, J_{CF} = 244)	*m*-C_5F_5
			135.9 (d, J_{CF} = 260)	*p*-C_6F_5
			148 (d, J_{CF} = 246)	*o*-C_6F_5
			157.7 (m)	*ipso*-Ph
[Cp″Hf($C_4H_4Me_2$-2,3)(OEt_2)]$^+$ [$PhCH_2$-$B(C_6F_5)_3$]$^-$ **12b** (CD_2Cl_2, −60 °C)	−0.04 (d, J = 12.8, 2H)	=CH_2 *anti*	−0.85 (q, J = 119.7)	$SiMe_3$
	0.23 (s, 18H)	$SiMe_3$	11.9 (q, J = 128.3)	(CH_3CH_2)$_2$O
	1.08 (t, J = 7, 6H)	(CH_3CH_2)$_2$O	23.22 (q, J = 127.7)	diene-Me
	2.15 (s, 6H)	diene-Me	31 (vbr s)	CH_2-B
	2.71 (br s, 2H)	CH_2-B	68.44 (t, J = 151)	(CH_3CH_2)$_2$O
	2.86 (d, J = 12.8, 2H)	=CH_2 *syn*	72.6 (t, J = 142.2)	=CH_2
	3.45 (q, J = 7, 4H)	(CH_3CH_2)$_2$O	122.21 (d, J = 159.2)	*p*-Ph
	5.61 (t, J = 1.8, 1H)	2-C_5H_3	122.68 (d, J = 169.8)	4,5-C_5H_3
	6.76 (d, J = 1.8, 2H)	4,5-C_5H_3	123.42, 129.24 (m)	=CH_2, 1,3-C_5H_3
	6.64 (d, J = 7.1, 2H)	*o*-Ph		
	6.88 (m, 3H)	*m*-Ph, *p*-Ph	126.59 (d, J = 158.5)	*m*-Ph
			126.7 (d, J = 167.5)	2-C_5H_3
			128.08 (d, J = 156)	*o*-Ph
			135.9 (d, J_{CF} = 256)	*m*-C_6F_5
			136.9 (d, J_{CF} = 242.2)	*p*-C_6F_5
			147.39 (d, J_{CF} °C = 235.5)	*o*-C_6F_5
			147.91 (m)	*ipso*-Ph

Table 2 ^{19}F NMR data of new zirconium and hafnium complexes

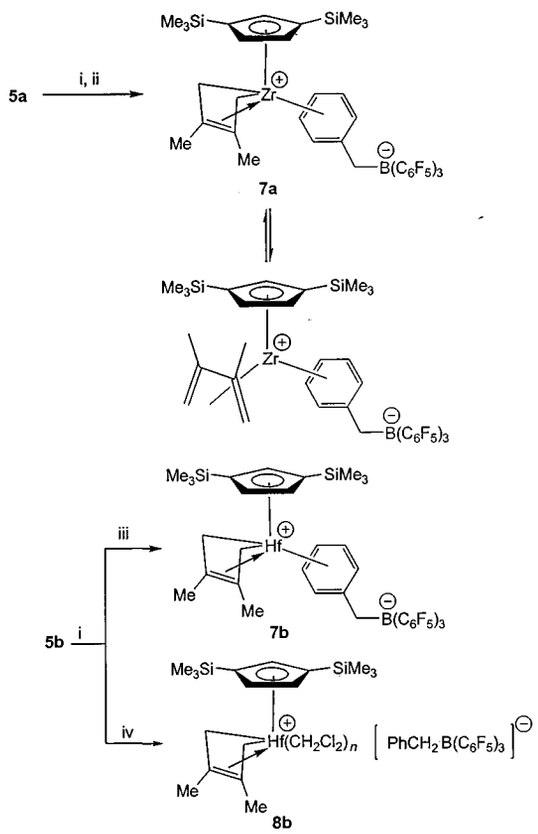
Complex	^{19}F NMR (δ)	Assignment	$\Delta\delta(m-p)$
Cp″Zr(2,3-$Me_2C_4H_4$){η^6-$PhCH_2B(C_6F_5)_3$}	−131.3 (d, J = 19.7, 6F)	*ortho*-F	
7a, C_6D_6 (20 °C), major isomer	−161.2 (t, J = 21.1, 3F)	*para*-F	
	−165.3 (m, 6F)	*meta*-F	4.1
C_6D_6 (20 °C), minor isomer	−130.8 (d, J = 19.7, 6F)	*ortho*-F	
	−161.52 (t, J = 21.1, 3F)	*para*-F	
	−165.4 (m, 6F)	*meta*-F	3.9
[Hf(2,3-$Me_2C_4H_4$){η^6-$PhCH_2B(C_6F_5)_3$}Cp″]	−131.1 (d, J = 19, 6F)	*ortho*-F	
7b C_7D_8 (−20 °C)	−161.0 (t, J = 21.1, 3F)	*para*-F	
	−164.9 (m, 6F)	*meta*-F	3.9
[Cp″Hf(2,3-$Me_2C_4H_4$)(CD_2Cl_2)$_n$][η^6-$PhCH_2B(C_6F_5)_3$]	−131.9 (d, J = 22.6, 6F)	*ortho*-F	
8b, CD_2Cl_2 (−40 °C)	−164.4 (t, J = 21.1, 3F)	*para*-F	
	−167.4 (m, 6F)	*meta*-F	3.0
[Cp″Hf(2,3-$Me_2C_4H_4$)(OEt_2)][η^6-$PhCH_2B(C_6F_5)_3$]	−132.1 (d, J = 22, 6F)	*ortho*-F	
12b, CD_2Cl_2 (−60 °C)	−164.1 (t, J = 21.1, 3F)	*para*-F	
	−167.2 (m, 6F)	*meta*-F	3.1

sistent with *s-cis* coordinated diene ligands with pronounced $\sigma^2\pi$ metallacyclopentene character.

The spectroscopic data for the Zr–CH_2Ph ligand differ significantly from that of the hafnium analogues. In the case of zirconium, the large $^1J_{CH}$ coupling constant of the Zr–CH_2 moiety (**5a**: 138.3 Hz; **6a**: 137.8 Hz), the upfield ^{13}C NMR shift of the *ipso*-C atoms (δ 138.5 and 134.6, respectively), and the high-field *ortho*-hydrogen resonances of the phenyl groups (δ 6.08 and 6.19 for **5a** and **6a**, respectively) clearly indicate the presence of an η^2-coordinate benzyl ligand.[6] By contrast, the benzyl ligand in the hafnium compound **5b** is η^1-coordinate, with a ^{13}C chemical shift for the *ipso*-carbon of δ 154.2 and a CH_2 $^1J_{CH}$ value of 122.1 Hz. Since the metal centre in **5a** is chiral, the hydrogen atoms of the benzylic CH_2 group are diastereotopic.

Treatment of toluene solutions of **5a** or **5b** with one equivalent of $B(C_6F_5)_3$ at −78 °C leads exclusively to the abstraction of the benzyl ligand (Scheme 2), in contrast to the selective attack on the diene ligand observed[1,4] in the case of Cp″Zr(diene)(allyl) **1**. The [$PhCH_2B(C_6F_5)_3$]$^-$ anion thus formed is coordinated to the metal centre *via* the phenyl group,[7] as shown by an upfield shift of the *m*- and *p*-phenyl resonances (above δ 6), a downfield ^{13}C NMR shift of the *ipso*-C of B-CH_2Ph (**7a**:δ 155.9; **7b**:δ 157.7), and a comparatively large ^{19}F chemical shift difference $\Delta\delta = \delta(m\text{-F}) - \delta(p\text{-F})$ of 3.9 ppm, indicative of coordinated pentafluorophenylborate.[8]

The ^{1}H NMR spectrum of **7a** consists of two sets of signals, in a ratio of *ca.* 60:40. The compound evidently exists as a mixture of two isomers which interchange slowly at room temperature in toluene-d_8 but broaden and coalesce on warming to 60 °C. These results are consistent with an interconversion of the *prone* and *supine* coordination modes of the diene ligand[9] *via* a 'ring-flipping' process (Scheme 2), similar to the fluxionality processes that have been seen in neutral metallocene diene



Scheme 2 i, $B(C_6F_5)_3$; ii, solvent toluene or dichloromethane, −78 °C; iii, toluene; iv, CH_2Cl_2.

complexes.[10] By contrast, the hafnium complex **7b** is not fluxional and exists only as a single isomer.

The reaction of **5a** with $B(C_6F_5)_3$ proceeds in an identical fashion whether toluene or dichloromethane is used as the solvent. However, while **5b** and $B(C_6F_5)_3$ give **7b** in toluene, the reaction in CD_2Cl_2 does not lead to **7b** but gives the ionic product **8b** in which the $[PhCH_2B(C_6F_5)_3]^-$ anion is not coordinated. The compound is chiral and shows two ^{1}H NMR resonances for the $SiMe_3$ groups. The geminal $^2J_{HH}$ coupling constants of *ca.* 5 Hz are smaller than in the zwitterionic **7b**, and the $\Delta[\delta(m\text{-F}) - \delta(p\text{-F})]$ value has decreased to 3 ppm (Table 2). Evidently the anion has been displaced by one or more dichloromethane molecules. Unfortunately, in spite of the clean NMR reaction, no solvated product could be crystallised. This facile displacement of a coordinated aryl by the chlorinated solvent is in contrast to the behaviour of the dimethyl complex $[Cp''HfMe_2(\eta^6\text{-}C_6H_5Me)][MeB(C_6F_5)_3]$, which can be recrystallised from dichloromethane without loss of toluene,[11] and is most probably due to the presence of the electron donating η^4-diene ligand in **8b**.

The reaction of the isoprene derivative **6a** with $B(C_6F_5)_3$ is more complex. Monitoring the reaction by NMR spectroscopy at low temperature gives very complicated spectra which are most probably the result of $B(C_6F_5)_3$ attack on both the diene and the benzyl ligand. Warming this mixture to room temperature for 16 h leads to complete conversion to the known[1] boryldiene complex, $Cp''Zr(C_6F_5)[\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2]$ **11a**, as well as one equivalent of toluene. This reaction is best explained by assuming an equilibrium between the benzylborate complex **9a** and the allylic zwitterion **10a**. Compound **10a** is capable of undergoing C–H activation to give toluene with concomitant migration of a C_6F_5 group from boron to zirconium, to generate **11a**. A similar reaction sequence has previously been observed in the case of the allyl compounds **2**.[1,4]

The structure of **11a** was confirmed by X-ray crystallography (Fig. 1). The 14-electron metal centre is stabilised by coordination to an *ortho*-F atom of one of the boryl-C_6F_5 groups.[12] The structure resembles that of the related C_5Me_5 complex $Cp^*Zr(C_6F_5)\{CH_2CHCHCHB(C_6F_5)_2\}$ reported previously;[4] however, whereas in that case the diene ligand adopted a conformation roughly perpendicular to the Cp* ligand (**A**), the present complex exists as the *supine* isomer (**B**). Selected bond lengths and angles are given in Table 3.

The addition of diethyl ether to a toluene solution of **7b**

Table 3 Selected bond lengths (Å) and angles (°) for $Cp''Zr(C_6F_5)[CH_2\text{-}CMeCHCHB(C_6F_5)_2]$ **11a**

Zr–C(1)	2.499(1)	Zr–C(12)	2.327(10)
Zr–C(2)	2.505(10)	Zr–C(13)	2.405(10)
Zr–C(3)	2..499(10)	Zr–C(14)	2.483(10)
Zr–C(4)	2.483(10)	Zr–C(15)	2.292(9)
Zr–C(5)	2.471(10)	Zr–C(21)	2.342(10)
B(1)–C(12)	1.514(15)	Zr–F(32)	2.441(7)
B(1)–C(31)	1.56(2)	C(12)–C(13)	1.435(13)
B(1)–C(41)	1.57(2)	C(13)–C(14)	1.365(13)
C(14)–C(15)	1.423(14)		
C(31)–B(1)–C(41)	120.4(9)	C(15)–Zr–C(21)	89.2(4)
C(31)–B(1)–C(12)	117.5(10)	C(12)–Zr–C(21)	129.8(4)
B(1)–C(12)–C(13)	125.0(10)	C(12)–Zr–C(15)	75.3(4)
C(12)–C(13)–C(14)	123.7(10)	C(13)–C(14)–C(16)	119.7(11)
C(13)–C(14)–C(15)	117.3(10)		

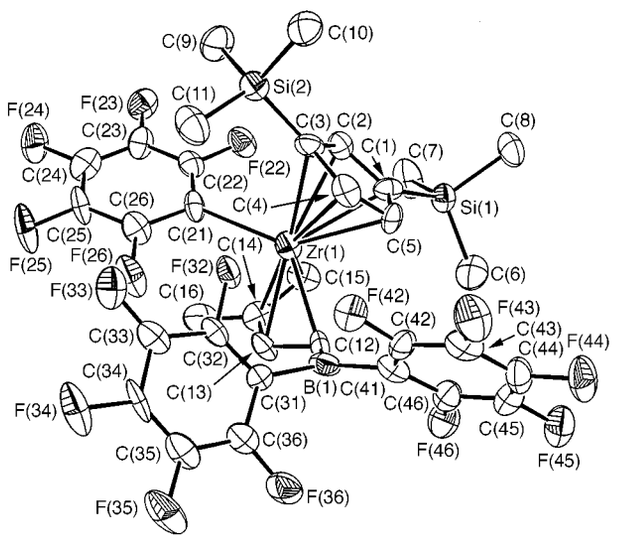
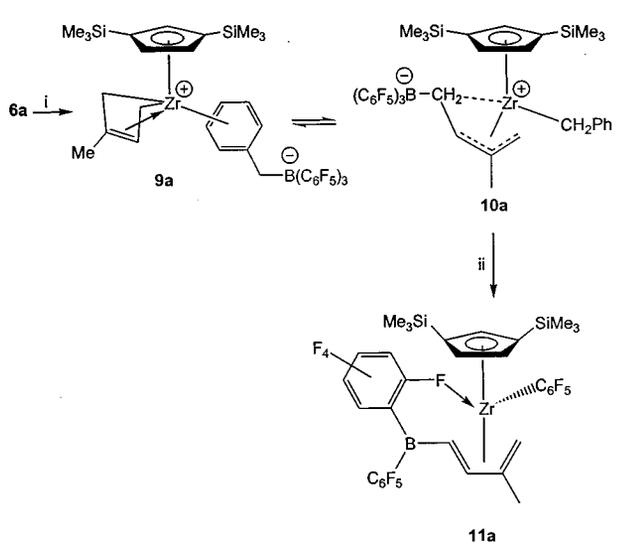


Fig. 1 Crystal structure of $Cp''Zr(C_6F_5)\{CH_2CMeCHCHB(C_6F_5)_2\}$ **11a**, showing the atomic numbering scheme; H-atoms are omitted for clarity, ellipsoids are drawn at 40% probability.



Scheme 3 i, $B(C_6F_5)_3$, −78 to 20 °C; ii, room temperature, −toluene.

Table 4 Selected bond lengths (Å) and angles (°) for [Cp″Hf(2,3-$Me_2C_4H_4$)(OEt_2)][$PhCH_2B(C_6F_5)_3$] **12b**

Hf–O(1)	2.148(2)	Hf–C(4)	2.488(2)
Hf–C(1)	2.491(3)	Hf–C(5)	2.495(2)
Hf–C(2)	2.441(2)	Hf–C(6)	2.199(3)
Hf–C(3)	2.482(2)	Hf–C(7)	2.466(3)
Hf–C(8)	2.473(3)	Hf–C(9)	2.207(3)
C(6)–C(7)	1.466(4)	C(7)–C(8)	1.377(4)
C(8)–C(9)	1.469(4)		
C(6)–Hf–O(1)	113.86(11)	C(9)–Hf–O(1)	114.59(10)
C(6)–C(7)–C(8)	120.6(3)	C(7)–C(8)–C(9)	120.7(2)
C(14)–O(1)–C(16)	116.7(3)	C(6)–Hf–C(9)	81.38(11)
C(14)–O(1)–Hf	109.6(2)	C(16)–O(1)–Hf	133.3(3)

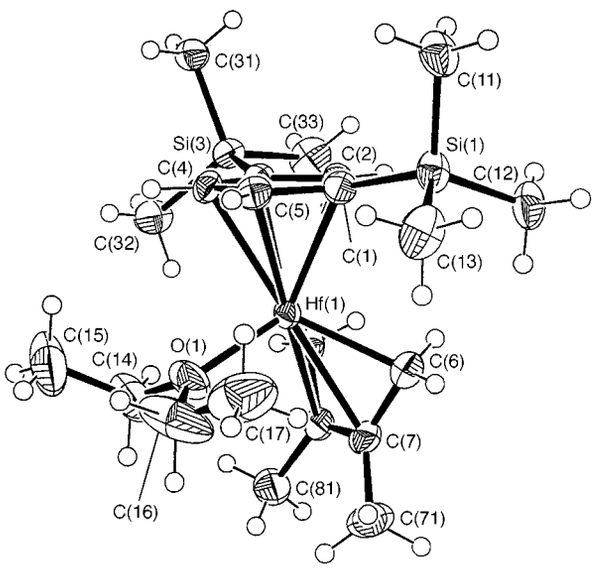
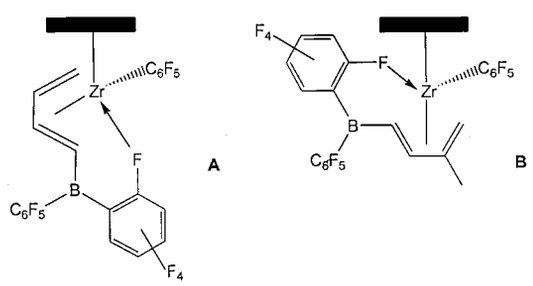
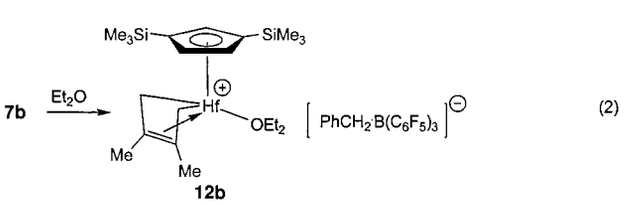


Fig. 2 Crystal structure of the cation [Cp″Hf(2,3-$Me_2C_4H_4$)(OEt_2)]$^+$ in compound **12b**, showing the atomic numbering scheme, ellipsoids are drawn at 40% probability.



results in the displacement of the benzylborate anion and the formation of the ionic product [Cp″Hf(2,3-$Me_2(C_4H_4)$-(OEt_2)]$^+$[$PhCH_2B(C_6F_5)_3$]$^-$ **12b** which was isolated as orange crystals [eqn. (2)]. The non-coordinating nature of the anion



(2)

is evident from the NMR spectroscopic data. The structure of the complex was confirmed by single-crystal X-ray diffraction (Fig. 2). The ether ligand in **12b** is quite tightly bonded, with a Hf–O distance of 2.148(2) Å, shorter than the bond lengths to the terminal diene carbon atoms. The ether-oxygen atom is trigonal-planar (angle sum 359.6°), with one Hf–O–C angle of 133.3(3)° being significantly larger than the other [109.6(2)°]. Selected geometric parameters are given in Table 4.

Conclusion

Whereas the 16-electron allyl complexes Cp″M(η^4-diene)-(η^3-allyl) (M = Zr or Hf) are attacked by $B(C_6F_5)_3$ selectively at the carbon terminus of the diene ligand, the related benzyl complexes Cp″M(η^4-diene)(CH_2Ph) react with abstraction of the benzyl ligand to give zwitterionic complexes where the anion is coordinated *via* the benzylic phenyl group. Displacement of the anion is facile and in the case of the hafnium compounds is observed even in dichloromethane, to give solutions of [Cp″Hf(2,3-$Me_2C_4H_4$)(CH_2Cl_2)$_n$][$PhCH_2B(C_6F_5)_3$], while the addition of diethyl ether leads to the stable adduct [Cp″Hf(2,3-$Me_2C_4H_4$)(OEt_2)][$PhCH_2B(C_6F_5)_3$]. In the case of the isoprene complex Cp″Zr(2-MeC_4H_5)(CH_2Ph) attack by $B(C_6F_5)_3$ can occur both at the diene and the benzyl ligand. Both products are in equilibrium with one another and decompose slowly *via* C–H activation to give a boryldiene complex, Cp″Zr(C_6F_5)[$CH_2CMeCHCHB(C_6F_5)_2$], another example of facile C_6F_5 transfer from boron to zirconium.

Experimental

General procedures

All manipulations were performed under dry nitrogen using Schlenk techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium–benzophenone (diethyl ether), sodium–potassium alloy [light petroleum (bp = 40–60 °C)] and calcium hydride (CH_2Cl_2). Deuteriated solvents were stored over activated 4A molecular sieves and degassed by several freeze–thaw cycles. The compounds Cp″MCl(η^4-diene) (diene = 2,3-dimethylbuta-1,3-diene or isoprene) and $B(C_6F_5)_3$ were prepared following literature procedures.[1,13] The NMR spectra were recorded using a Bruker DPX300 spectrometer; ^{1}H NMR spectra are referenced to the residual solvent protons. ^{19}F chemical shifts (282.2 MHz) are relative to $CFCl_3$, ^{11}B (96.2 MHz) relative to external BF_3·OEt_2.

Preparation of Cp″Zr(2,3-$Me_2C_4H_4$)(CH_2Ph) 5a

To a suspension of Cp″ZrCl(2,3-$Me_2C_4H_4$) (1.2 g, 2.87 mmol) in 30 cm^3 of diethyl ether at −78 °C was added *via* syringe 2.9 cm^3 of a 1.0 M solution of $PhCH_2MgCl$ (2.9 mmol) in Et_2O. The reaction mixture was allowed to warm to room temperature and stirred for a further 3 h. Removal of the solvent left a dark orange foam which was extracted with light petroleum (2 × 30 cm^3). Evaporation of the filtrate gave **5a** as a dark red solid (1.15 g, 84%) (Calc. for $C_{24}H_{38}Si_2Zr$: C, 60.8; H, 8.1. Found: C, 59.2; H, 7.6%).

The following compounds were prepared similarly: Cp″Hf(2,3-MeC_4H_4)(CH_2Ph) **5b** as a spectroscopically pure orange oil (yield 85%) and Cp″Zr(η^4-$CH_2CMeCHCH_2$)-(CH_2Ph) **6a** as a dark red solid (yield 80%).

Preparation of Cp″Zr(2,3-$Me_2C_4H_4$){η''-$PhCH_2B(C_6F_5)_3$} 7a

To a solution of **5a** (1.1 g, 2.32 mmol) in 40 cm^3 toluene at −78 °C was added $B(C_6F_5)_3$ (1.2 g, 2.32 mmol) in 30 cm^3 toluene. The reaction was stirred at −78 °C for 2 h and filtered. The volatiles were removed *in vacuo* to afford a dark red solid which was washed with light petroleum (2 × 30 cm^3) to give **7a** (2.0 g, 87%) (Calc. for $C_{42}H_{38}BF_{15}Si_2Zr$: C, 51.1; H, 3.9. Found: C, 49.6; H, 3.8%). ^{11}B-{^{1}H} NMR(23 °C): δ −11.95.

Preparation of Cp″Hf(2,3-$Me_2C_4H_4$){η''-$PhCH_2B(C_6F_5)_3$} 7b

A solution of $B(C_6F_5)_3$ (2.14 g, 4.19 mmol) in 40 cm^3 toluene was added to a solution of **5b** (2.35 g, 4.19 mmol) in 20 cm^3 toluene. The mixture was stirred for 2 h. Concentration to 20 cm^3 followed by cooling to −20 °C afforded **7b** as orange crystals (3.81 g, 85%) (Calc. for $C_{42}H_{38}BF_{15}HfSi_2$: C, 47.0; H, 3.6. Found: C, 46.8; H, 3.6%). ^{11}B-{^{1}H} NMR(23 °C): δ −12.07.

Table 5 Crystal data for compounds **11a** and **12b**

	11a	**12b**
Formula	$C_{34}H_{28}BF_{15}Si_2Zr$	$C_{46}H_{48}BF_{15}HfOSi_2$
M	879.77	1147.32
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.068(7)	11.191(2)
b/Å	11.44(2)	13.146(2)
c/Å	16.22(2)	17.506(2)
α/°	96.79(3)	104.763(10)
β/°	105.19(5)	94.315(11)
γ/°	94.15(6)	103.276(10)
U/Å^3	1780(3)	2399.3(5)
Z	2	2
D_c/g cm^{-3}	1.642	1.588
μ/mm^{-1}	0.481	2.317
Reflections collected, unique	5906, 4532	8418, 8418
R_{int} [a]	0.0778	—
R_1 [b]	0.0734	0.0202
wR_2 [c]	0.1720	0.0483

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$.

Reaction of 6a with $B(C_6F_5)_3$

To a solution of **6a** (32 mg, 0.07 mmol) in toluene-d_8 (0.3 cm^3) at −78 °C was added $B(C_6F_5)_3$ (35.6 mg, 0.07 mmol) in 0.3 cm^3 toluene-d_8. After 12 h at room temperature the final product was identified by NMR spectroscopy as a 1:1 mixture of $Cp''Zr(C_6F_5)\{\eta^4\text{-}CH_2CMeCHCHB(C_6F_5)_2\}$ **11a** and toluene. From a similar reaction on a larger scale **11a** was obtained as red crystals which were suitable for X-ray diffraction.

Reaction of 5b with $B(C_6F_5)_3$ in CD_2Cl_2

To a solution of **5b** (0.136 g, 0.242 mmol) in 0.3 cm^3 CD_2Cl_2 at −40 °C was added a cold (−40 °C) solution of $B(C_6F_5)_3$ (0.124 g, 0.242 mmol) in 0.3 cm^3 CD_2Cl_2. A deep red mixture was produced which was characterised by NMR spectroscopy as $[Cp''Hf(2,3\text{-}Me_2C_4H_4)(CD_2Cl_2)_n]^+[PhCH_2B(C_6F_5)_3]^-$ **8b**. $^{11}B\text{-}\{^1H\}$ NMR (−40 °C): δ −12.4.

Preparation of $[Cp''Hf(2,3\text{-}Me_2C_4H_4)(OEt_2)]^+[PhCH_2\text{-}B(C_6F_5)_3]^-$ 12b

To a solution of **7b** (1.5 g, 1.4 mmol) in 30 cm^3 toluene at −78 °C was added 10 cm^3 Et_2O. The mixture was stirred at −20 °C for 10 h, filtered and concentrated to remove excess diethyl ether. An orange oil separated. The toluene supernatant was filtered off and the residue dried *in vacuo* to afford a dark orange solid (0.96 g, 60%). $^{11}B\text{-}\{^1H\}$ NMR(−30 °C): δ −12.5. Recrystallisation from toluene–Et_2O gave crystals suitable for X-ray diffraction (Calc. for $C_{46}H_{48}BF_{15}HfOSi_2$: C, 48.9; H, 2.6. Found: C, 47.8; H, 4.1%).

X-Ray crystallography

Data for **11a** were collected at 293 K on a Delft Instruments FAST TV-area detector diffractometer positioned at the window of a rotating anode generator and following previously described procedures.[14] Data for **12b** were collected at 160 K on a Stoe STADI4 4-circle diffractometer using the ω–θ scanning method. Both data sets were collected using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Full details of crystal data, data collection and refinement are given in Table 5. Both structures were solved by standard heavy-atom methods using SHELXS86[15] and were refined by full-matrix least squares (on F^2) using SHELXL93.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were constrained to idealised positions using a riding model (with free rotation for methyl groups).

CCDC reference number 186/1406.

See http://www.rsc.org/suppdata/dt/1999/1663/ for crystallographic files in .cif format.

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