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Zirconium and hafnium diene and dienyl half-sandwich complexes: synthesis, polymerization catalysis and deactivation pathways. The molecular structures of [M(η^3-C_3H_5)(2,3-$Me_2C_4H_4$){η-$C_5H_3(SiMe_3)_2$-1,3}] (M = Zr or Hf) and [Hf(η^3-C_3H_5){η^3-$CH_2CMeCMeCH_2B(C_6F_5)_3$}{$\eta$-$C_5H_3(SiMe_2)$-1,3}]†

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The reduction of [MCl_3Cp''] [M = Zr or Hf; Cp″ = η-$C_5H_3(SiMe_3)_2$-1,3] with sodium amalgam in the presence of dienes gave the compounds [MCl(diene)Cp″] which are alkylated with MeMgBr or RMgCl (R = allyl) to give [MX(diene)Cp″] (X = CH_3 or η^3-C_3H_5; diene = 2,3-dimethylbuta-1,3-diene or isoprene). The reduction of [ZrCl(CHCMeCMeCH)Cp″] with an excess of Na–Hg leads to the binuclear η^4(5e)-butadienyl complex [Zr(μ-η^1:η^4-$C_4H_3Me_2$-2,3)Cp″]$_2$, also formed from [ZrMe($C_4H_4Me_2$)Cp″] by methane elimination. The butadiene complex [Zr(η^3-$CH_2CMeCHCH_2$)(η^4-C_4H_6)Cp″] is obtained directly from [$ZrCl_3Cp''$] and $MeCHCHCH_2MgCl$. The complexes [M(allyl)(diene)Cp″] react with $B(C_6F_5)_3$ to give the zwitterionic complexes [$Cp''M^+$(η^3-C_3H_5)-{η^3-$C_4H_4R^1R^2B^-(C_6F_5)_3$}] which contain a 14-electron [CpM(allyl)$_2$]$^+$ core stabilised by agostic bonding of the B–CH_2 methylene hydrogens. These zwitterions catalyse the polymerisation of ethene to high molecular weight polyethene. Catalysts with similar activities are obtained by the activation of [M(allyl)(diene)Cp″] with [CPh_3]-[$B(C_6F_5)_4$]. The thermal stability of the zwitterionic active species depends strongly on the steric requirements of the dienyl ligands and decreases sharply in the order $R^1 = R^2 = Me > R^1 = Me, R^2 = H \gg R^1 = H, R^2 = H$; *i.e.* the dimethylbutadiene derivatives are stable at room temperature, while in the latter case decomposition is significant even at −60 °C. The complexes [Zr(η^3-CH_2CHCHR^1){η^3-$CH_2CR^2MeCHCH_2B(C_6F_5)_3$}Cp″] ($R^1$ = H, R^2 = Me, **9a**; R^1 = Me, R^2 = H, **10**) decompose *via* an unusual C–H activation pathway, with alkene elimination and concomitant migration of a C_6F_5 substituent from boron to zirconium, to give the catalytically inactive boryldiene complexes [Zr(C_6F_5){η^4-$CH_2CR^1CHCHB(C_6F_5)_2$}Cp″]. The crystal structures of [M(C_3H_5)($Me_2C_4H_4$)Cp″] (M = Zr or Hf) and [Hf(η^3-C_3H_5){η^3-$CH_2CMeCMeCH_2B(C_6F_5)_3$}Cp″] are reported.

Early-transition-metal cyclopentadienyl complexes have in recent years provided a series of important classes of olefin polymerisation catalysts. Best known are the extensively investigated metallocenes [MX_2Cp_2] (Cp = η-C_5H_5), which, on addition of suitable activators, give rise to cationic 14-electron compounds [Cp_2MR]$^+$ as the catalytically active species.[1] With the possible exception of ‘constraint geometry’ complexes of the type [{$Me_2Si(Cp)(NR)$}MX_2],[2] the potential of monocyclopentadienyl complexes [MX_3Cp] as catalyst precursors has been less well investigated, although their ability to generate syndiotactic polystyrene,[3] and the high electronic unsaturation and reduced steric hindrance in the active species [$CpMR_2$]$^+$ would make them very promising catalyst systems.[4] On the other hand, there are indications that catalysts based on half-sandwich complexes may be less long lived and show reactivity patterns not found in metallocene chemistry. As part of our studies on ligand control of the reactivity, catalyst efficiency and deactivation pathways in methylaluminoxane (MAO)-free metal alkyl catalysts[5] we have become interested in the synthesis of cationic allyl complexes [CpM(η^3-allyl)$_2$]$^+$ which are isoelectronic to, but possibly more stable than, the active species in metallocene-based catalysts, [Cp_2MR]$^+$. We report here the synthesis of a series of monocyclopentadienyl complexes of the type [MX(1,3-diene)Cp] (X = Cl, methyl or allyl), their activation to catalytically active zwitterionic π-allyl complexes, and unexpectedly facile C–H activation reactions which provide novel catalyst deactivation pathways for these species.

Results and Discussion

Neutral complexes

The reduction of [MCl_3Cp''] [Cp″ = η-$C_5H_3(SiMe_3)_2$-1,3] with 2 equivalents of sodium amalgam in tetrahydrofuran (thf) in the presence of 2,3-dimethylbuta-1,3-diene leads to the 14-electron complexes [MCl(2,3-$Me_2C_4H_4$)Cp″] (M = Zr **1a** or Hf **1b**), which are isolated in high yield as violet (Zr) or yellow-orange (Hf) solids, respectively. The isoprene complexes [MCl(2-MeC_4H_5)Cp″] (M = Zr **2a** or Hf **2b**) are prepared similarly (Scheme 1). Throughout this study the $C_5H_3(SiMe_3)_2$-1,3 ligand was chosen as the stabilising cyclopentadienyl derivative; this ligand is comparable in bulk and electronic characteristics to be more commonly employed η-C_5Me_5 (Cp*) ligand but is sterically more flexible since it is able to adopt different conformations, and often imparts enhanced stability and subtly different reactivity patterns.

The synthesis of complexes **1** and **2** is in principle analogous to that of the known Cp* derivatives[6] [MCl(diene)Cp*]. However, whereas the Cp* complexes retain co-ordinated thf which has to be removed by sublimation, the Cp″ complexes afford thf-free complexes in higher yields and require the use of only stoichiometric amounts of sodium amalgam.

Unexpectedly, in the presence of an excess of sodium amalgam, mixtures of [$ZrCl_3Cp''$] and 2,3-dimethylbuta-1,3-diene did not give **1a** but instead afforded the deep red binuclear butadienyl complex **3**. The same complex is obtained when **1a** is further treated with sodium; apparently **1a** is reduced to an unstable Zr^{III} intermediate which dimerizes through an intermolecular C–H bond activation step losing H_2, to afford the

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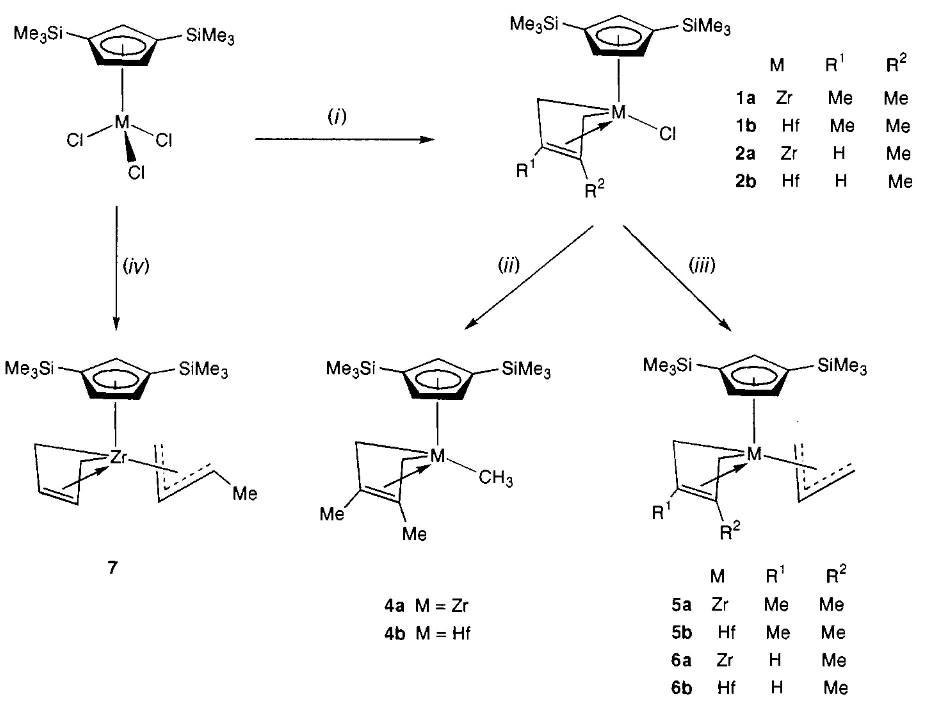
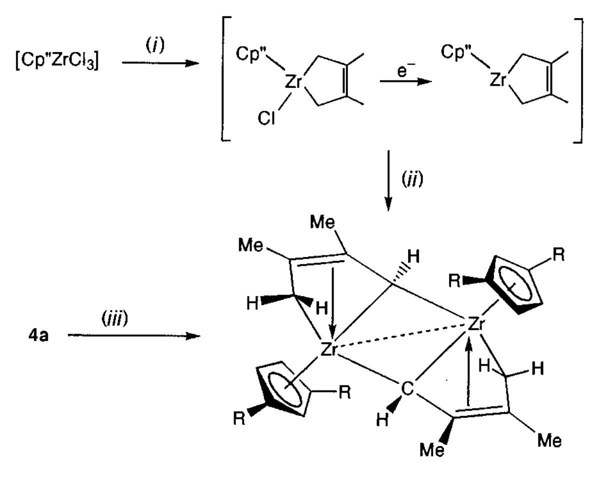
† In memoriam Geoffrey Wilkinson, an inspired and inspiring chemist.



Scheme 1 (*i*) $CH_2=C(R^1)C(R^2)=CH_2$, 2 Na–Hg, thf, −78 °C to room temperature (r.t.); (*ii*) MeLi, Et_2O; (*iii*) C_3H_5MgCl, thf–Et_2O; (*iv*) C_4H_7MgCl, thf, 0 °C to r.t.



3

Scheme 2 R = $SiMe_3$. (*i*) 2,3-Dimethylbuta-1,3-diene, 4 Na–Hg, thf, r.t., 24 h; (*ii*) $-H_2$; (*iii*) hexane, r.t. to −16 °C, 38 h, $-CH_4$

binuclear Zr^{IV} product **3** (Scheme 2). Such a redox process is less likely for hafnium, and indeed there is no evidence for the formation of a hafnium analogue of **3**.

Compounds **1a** and **2a** react with methylmagnesium chloride in diethyl ether between −78 °C and room temperature to give the methyl complexes **4a** (M = Zr) and **4b** (M = Hf) as a red solid and a spectroscopically pure orange oil, respectively. In the absence of solvent these complexes are stable at room temperature over a period of days. However, as we reported recently,[7] on attempted recrystallization from light petroleum at −16 °C, **4a** slowly undergoes C–H bond activation and evolves methane, to give again complex **3**.

The hafnium compound **4b** is also accessible from the reaction of **1b** with $Li[AlMe_4]$ in thf. The expected tetramethylaluminate is not formed, most probably because of the facile abstraction of $AlMe_3$ as the adduct $Me_3Al{\cdot}thf$. Not unexpectedly, compound **4b** is more stable than the Zr analogue **4a** but decomposes slowly in solution to unknown products. Variable-temperature NMR investigations provided no evidence for the hafnium analogue of **3**.

The reaction of **1a**, **1b** or **2a**, **2b** with allylmagnesium chloride in diethyl ether generates the thermally stable η^3-allyl complexes $[M(\eta^3\text{-}C_3H_5)(\text{diene})Cp'']$ **5a**, **5b** (diene = 2,3-dimethylbuta-1,3-diene) and **6a**, **6b** (diene = isoprene) as red (Zr) or yellow (Hf) crystalline solids (Scheme 1). They are readily recrystallised from light petroleum and show none of the decomposition reactions of the related 14-electron methyl complexes. As is well known, another route to η^3-allyl derivatives is the direct reaction of cyclopentadienylzirconium trihalides with allyl Grignard reagents.[8] This method was chosen to synthesize **7** from $[ZrCl_3Cp'']$ and 3 equivalents of $CH_3CH=CHCH_2MgCl$.

All of these compounds are very air sensitive. The alkyl and allyl derivatives are soluble in all common hydrocarbon solvents whereas the chloride complexes are sparingly soluble. The complexes decompose rapidly in chlorinated solvents to give the trichlorides $[MCl_3Cp'']$.

The ^1H and ^{13}C NMR spectroscopic data of all new compounds are given in Table 1, ^{19}F NMR data in Table 2. For the diene ligands the geminal coupling constants $|^2J_{HH}|$ of the methylene groups (7.0–11.4 Hz) and the $^1J_{CH}$ coupling constants (139.8–146.9 Hz) are larger and smaller, respectively, than in the case of the conventional η^4-diene complexes;[9] such features are indicative of the distinct σ^2-π-metallacyclopentane character of conjugated *s-cis* dienes co-ordinated to early-transition-metal centres.[10]

At room temperature the ^1H NMR spectra of **1a**, **1b** and **2a**, **2b** show only broad peaks. Cooling solutions of **1a**, **1b** at −40 °C resolves two isomers, at ratios of 6:1 for M = Zr and 12:1 for M = Hf. Since the possibility of *s-trans* diene co-ordination is ruled out by the magnitude of the geminal coupling constant $^2J_{HH}$ (M = Zr: 8.5 Hz for the major, and 8.7 for the minor isomer),[11] the two isomers arise most probably from the diene adopting prone and supine conformations. The NMR data for the complexes **5**, **6** and **7** are in agreement with η^3-bonded allylic ligands.[6,12]

Structures of $[Mn(\eta^3\text{-allyl})(\eta^4\text{-diene})Cp'']$ 5

Crystals of **5a** and **5b** suitable for an X-ray diffraction study were grown from diethyl ether at −20 °C. The molecular structure of **5a** is shown in Fig. 1; crystal data are listed in Table 3, and selected distances and angles in Table 4. Complex **5b** is isostructural to **5a**.

Table 1 Proton and ^{13}C NMR data for the zirconium and hafnium complexes[a]

	^{1}H NMR		^{13}C NMR	
Complex	δ	Assignment	δ	Assignment
1a [ZrCl($C_4H_4Me_2$-2,3)Cp″] ([$^2H_8$]toluene, −40 °C)	0.31 (s, 18 H)	$SiMe_3$	0.30 (q, *J* = 119.1)	$SiMe_3$
	0.66 (d, 2 H, *J* = 8.5)	=CH_2 *anti*	23.01 (q, *J* = 125.0)	diene-Me
	1.70 (d, 2 H, *J* = 8.5)	=CH_2 *syn*	65.35 (t, *J* = 142.1)	=CH_2
	2.28 (s, 6 H)	diene-Me	123.10 (m)	$C^{1,3}$ of C_5H_3
	6.29 (br s, 1 H)	H^2 of C_5H_3	125.59 (d, *J* = 168.0)	$C^{4,5}$ of C_5H_3
	7.09 (br s, 2 H)	$H^{4,5}$ of C_5H_3	125.73 (d, *J* = 168.0)	C^2 of C_5H_3
			127.17 (m)	=*C*Me
1b [HfCl($C_4H_4Me_2$-2,3)Cp″] ([$^2H_8$]toluene, −40 °C)	0.23 (d, 2 H, *J* = 9.8)	=CH_2 *anti*	0.18 (q, *J* = 119.2)	$SiMe_3$
	0.31 (s, 18 H)	$SiMe_3$	23.05 (q, *J* = 126.5)	diene-Me
	1.36 (d, 2 H, *J* = 9.8)	=CH_2 *syn*	65.24 (t, *J* = 141.8)	=CH_2
	2.42 (s, 6 H)	diene-Me	121.56 (d, br, *J* = 168)	$C^{4,5}$ of C_5H_3
	6.20 (br s, 1 H)	H^2 of C_5H_3	123.54 (m)	$C^{1,3}$ of C_5H_3
	7.01 (br s, 2 H)	$H^{4,5}$ of C_5H_3	124.62 (d, *J* = 168.6)	C^2 of C_5H_3
			126.86 (m)	=*C*Me
2a [ZrCl(C_4H_5Me-2)Cp″] [$^2H_8$]thf	0.40, 0.41 (s, 9 H, each)	$SiMe_3$	−0.12, 0.00 (q, *J* = 119.1)	$SiMe_3$
	0.72 (d, 1 H, *J* = 6.9)	=CH_2 *anti*	25.45 (q, *J* = 126.0)	diene-Me
	0.91 (t, 1 H, *J* = 8.3)	=CH_2 *anti*	52.84, 57.42 (t, *J* = 143, 141.9)	=CH_2
	1.31 (d, 1 H, *J* = 6.9)	=CH_2 *syn*	118.46 (d, *J* = 159.2)	=CH
	1.44 (t, 1 H, *J* = 8.3)	=CH_2 *syn*	120.42, 121.64 (d, *J* = 169)	$C^{4,5}$ of C_5H_3
	2.14 (s, 3 H)	diene-Me	123.3 (d, *J* = 166.8)	C^2 of C_5H_3
	5.61 (t, 1 H, *J* = 8.3)	=CH	126.06, 126.2 (m)	$C^{1,3}$ of C_5H_3
	6.63, 6.77, 6.8 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3	135.95 (m)	=*C*Me
2b [HfCl(C_4H_5Me-2)Cp″] (C_6D_6)	0.14 (d, 1 H, *J* = 10.1)	=CH_2 *anti*	0.19, 0.26 (q, *J* = 119.3)	$SiMe_3$
		$SiMe_3$	26.70 (q, *J* = 128.9)	diene-Me
	0.31 (s, 18 H)	=CH_2 *syn*	58.18, 60.88 (t, *J* = 139.8, 141.3)	=CH_2
	1.61 (d, 1 H, *J* = 10.1)	=CH_2 *syn*	117.68 (d, *J* = 154.7)	=CH
	1.70 (t, br, 1 H)	diene-Me	123.1, 123.89 (br d, *J* = 169.0)	$C^{4,5}$ of C_5H_3
	2.42 (s, 3 H)	=CH	124.20 (d, *J* = 168.3)	C^2 of C_5H_3
	6.04 (t, br, 1 H)	$H^{2,4,5}$ of C_5H_3	123.61, 123.47 (m)	$C^{1,3}$ of C_5H_3
	6.25, 6.85, 6.79 (s, br, 1 H each)		135.88 (m)	=*C*Me
3 [Zr(μ-η^1:η^4-$C_4H_3Me_2$-2,3)Cp″] (C_6D_6)	0.06, 0.52 (s, 9 H each)	$SiMe_3$	0.70, 0.80 (q, *J* = 119.0)	$SiMe_3$
	1.50 (s, 1 H)	ZrCHZr	24.0, 25.4 (q, *J* = 126.0, 126.2)	diene-Me
	1.80, 1.85 (s, 3 H each)	diene-Me	65.60 (t, *J* = 144.5)	=CH_2
	2.03, 3.78 (d, 1 H, *J* = 5.7)	=CH_2	111.20, 111.80 (m)	$C^{1,3}$ of C_5H_3
	4.58, 6.20 (d, 1 H each, *J* = 1.9)	$H^{4,5}$ of C_5H_3	116.0, 116.7 (d, *J* = 168.3)	$C^{4,5}$ of C_5H_3
	6.60 (t, 1 H, *J* = 1.9)	H^2 of C_5H_3	119.9 (d, *J* = 169.0)	C^2 of C_5H_3
			127.5 (m)	=*C*Me
			174.9 (d, *J* = 11)	ZrCHZr
4a [ZrMe($C_4H_4Me_2$-2,3)Cp″] (C_6D_6)	−0.30 (s, br, 3 H)	Zr-Me	0.11 (q, *J* = 119.0)	$SiMe_3$
	0.27 (s, 18 H)	$SiMe_3$	23.27 (q, *J* = 126.1)	diene-Me
	0.45 (d, 2 H, *J* = 9.6)	=CH_2 *anti*	45.15 (br q, *J* = 113.2)	Zr−Me
	2.00 (s, 6 H)	diene-Me	63.16 (t, *J* = 142.3)	−CH_2
	2.34 (d, 2 H, *J* = 9.6)	=CH_2 *syn*	117.37 (d, *J* = 169.8)	$C^{4,5}$ of C_5H_3
	6.04 (s, br, 2 H)	$H^{4,5}$ of C_5H_3	119.84 (m)	$C^{1,3}$ of C_5H_3
	7.10 (s, br, 1 H)	H^2 of C_5H_3	122.58 (d, *J* = 167.5)	C^2 of C_5H_3
			123.38 (m)	=*C*Me
4b [HfMe($C_4H_4Me_2$-2,3)Cp″] (C_6D_6)	−0.65 (s, 3 H)	Hf-Me	0.70 (q, *J* = 119.1)	$SiMe_3$
	−0.21 (d, 2 H, *J* = 11.4)	=CH_2 *anti*	23.20 (q, *J* = 126.1)	diene-Me
	0.25 (s, 18 H)	$SiMe_3$	53.35 (q, br, *J* = 111.4)	Hf−Me
	2.11 (s, 6 H)	diene-Me	68.02 (t, *J* = 139.5)	=CH_2
	2.33 (d, 2 H, *J* = 11.4)	=CH_2 *syn*	117.24 (d, *J* = 169.0)	$C^{4,5}$ of C_5H_3
	6.00 (s, 2 H, *J* = 1.8)	$H^{4,5}$ of C_5H_3	122.37 (d, *J* = 168.3)	C^2 of C_5H_3
	6.91 (t, 1 H, *J* = 1.8)	H^2 of C_5H_3	123.66 (m)	$C^{1,3}$ of C_5H_3
			126.80 (m)	=*C*Me
5a [Zr(C_3H_5)($C_4H_4Me_2$-2,3)Cp″] (C_6D_6)	−0.45 (d, 2 H, *J* = 7.2)	=CH_2 *anti*	0.42 (q, *J* = 119.0)	$SiMe_3$
	0.26 (s, 18 H)	$SiMe_3$	22.39 (q, *J* = 125.9)	diene-Me
	1.64 (d, 2 H, *J* = 14.5)	CH_2 of C_3H_5	53.41 (t, *J* = 145.2)	=CH_2
	1.79 (m, 4 H)	CH_2 of C_3H_5 and =CH_2	59.33 (t, *J* = 152.5)	CH_2 of C_3H_5
	1.86 (s, 6 H)	diene-Me	117.86 (m)	=*C*Me
	5.70 (m, 1 H)	CH of C_3H_5	119.70 (d, *J* = 167.5)	$C^{4,5}$ of C_5H_3
	6.29 (t, 1 H, *J* = 1.9)	H^2 of C_5H_3	120.80 (m)	$C^{1,3}$ of C_5H_3
	6.48 (d, 2 H, *J* = 1.9)	$H^{4,5}$ of C_5H_3	122.70 (d, *J* = 166.0)	C^2 of C_5H_3
			127.82 (d, *J* = 153.2)	CH of C_3H_5

Table 1 *Continued*

	^{1}H NMR		^{13}C NMR	
Complex	δ	Assignment	δ	Assignment
5b [Hf(C_3H_5)($C_4H_4Me_2$-2,3)Cp″] (C_6D_6)	−0.83 (d, 2 H, *J* = 8.4)	=CH_2 *anti*	0.73 (q, *J* = 119.7)	$SiMe_3$
	0.25 (s, 18 H)	$SiMe_3$	22.17 (q, *J* = 125.6)	diene-Me
	1.64 (m, 4 H)	CH_2 of C_3H_5 and CH_2 *syn*	51.50 (t, *J* = 142.5)	=CH_2
	1.93 (s, 6 H)	diene-Me	57.13 (t, *J* = 152.0)	CH_2 of C_3H_5
	5.65 (m, 1 H)	CH of C_3H_5	116.30 (m)	=*C*Me
	6.19 (t, 1 H, *J* = 1.9)	H^2 of C_5H_3	119.06 (d, *J* = 168.3)	$C^{4,5}$ of C_5H_3
	6.40 (d, 2 H, *J* = 1.9)	$H^{4,5}$ of C_5H_3	121.05 (m)	$C^{1,3}$ of C_5H_3
			121.70 (d, *J* = 166.8)	C^2 of C_5H_3
			127.87 (d, *J* = 152.4)	CH of C_3H_5
6a [Zr(C_3H_5)(C_4H_5Me-2)Cp″] (C_6D_6)	−0.59, −0.52 (d, *J* = 7.2, m, 1 H each)	=CH_2 *anti*	0.48 (q, *J* = 119.1)	$SiMe_3$
	0.25, 0.26 (s, 9 H each)	$SiMe_3$	26.2 (q, *J* = 126.0)	diene-Me
	1.33, 1.64 (d, 1 H each, *J* = 14.5)	CH_2 of C_3H_5	46.69, 51.25 (t, *J* = 146.9, 147.5)	=CH_2
	1.57, 2.01 (m, 1 H each)	CH_2 of C_3H_5	56.96, 59.56 (t, *J* = 152.2)	CH_2 of C_3H_5
	1.89 (s, 3 H)	diene-Me	110.01 (d, *J* = 162.2)	=CH
	2.01 (m, 2 H)	=CH_2 *syn*	119.7, 119.8 (d, *J* = 167.5)	$C^{4,5}$ of C_5H_3
	5.14 (t, 1 H, *J* = 9.8)	=CH	120.65, 120.8 (m)	$C^{1,3}$ of C_5H_3
	6.03 (m, 1 H)	CH of C_3H_5	122.74 (d, *J* = 166)	C^2 of C_5H_3
	6.21 (t, 1 H, *J* = 1.9)	H^2 of C_5H_3	123.31 (m)	=*C*Me
	6.42, 6.44 (m, 1 H each)	$H^{4,5}$ of C_5H_3	125.70 (d, *J* = 153.2)	CH of C_3H_5
6b [Hf(C_3H_5)(C_4H_5Me-2)Cp″] (C_6D_6)	−0.93 (m, 2 H)	=CH_2 *anti*	0.39 (q, *J* = 119.1)	$SiMe_3$
	0.22, 0.25 (s, 9 H each)	$SiMe_3$	26.09 (q, *J* = 125.8)	diene-Me
	1.32, 1.45, 1.75 (m, 1 H, 1 H, 4 H)	CH_2 of C_3H_5 and CH_2 *syn*	44.47, 48.93 (t, *J* = 144.3, 145)	=CH_2
	2.0 (s, 3 H)	diene-Me	54.7, 57.31 (t, *J* = 151.2)	CH_2 of C_3H_5
	5.11 (t, 1 H, *J* = 9.1)	=CH	109.40 (d, *J* = 163.0)	=CH
	6.02 (m, 1 H)	CH of C_3H_5	119.1, 119.13 (d, *J* = 167)	$C^{4,5}$ of C_5H_3
	6.10 (t, 1 H, *J* = 1.9)	H^2 of C_5H_3	120.8, 121.0 (m)	$C^{1,3}$ of C_5H_3
	6.32, 6.39 (m, 1 H each)	$H^{4,5}$ of C_5H_3	121.74 (d, *J* = 166.0)	C^2 of C_5H_3
			121.90 (m)	=*C*Me
			126.06 (d, *J* = 153.9)	CH of C_3H_5
7 [Zr(C_3H_4Me-1)(C_4H_6)Cp″] (C_6D_6)	−0.70, −0.37 (m, 1 H each)	=CH_2 *anti*	0.33, 0.40	$SiMe_3$
	0.25, 0.26 (s, 9 H each)	$SiMe_3$	18.56	CH*Me*
	1.01, 1.28 (d, 1 H each, *J* = 13)	CH_2 of C_4H_7	46.78, 50.31	=CH_2
	1.43 (d, 3 H, *J* = 5.7)	Me of C_4H_7	50.84, 73.47	CH_2, *C*HMe of C_4H_7
	1.82, 2.17 (t, 1 H each, *J* = 8.3)	=CH_2 *syn*	112.03, 112.15	=CH
	2.06 (m, 1 H)	CHMe of C_4H_7	119.44, 120.36, 122.37	$C^{2,3,5}$ of C_5H_3
	5.43, 5.63 (m, 1 H)	=CH	120.49, 120.97	$C^{1,3}$ of C_5H_3
	5.87 (m, 1 H)	CH of C_4H_7	127.12	CH of C_4H_7
	6.2, 6.45, 6.45 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3		
8a [Zr(C_3H_5){CH_2CMeCMeCH_2B-(C_6F_5)$_3$}Cp″] (CD_2Cl_2, −40 °C)	−1.78, −0.33 (s, br, 1 H each)	=CH_2B	−0.55, −0.23 (q, *J* = 119)	$SiMe_3$
	0.19, 0.36 (s, 9 H each)	$SiMe_3$	16.93, 23.77 (q, *J* = 129.5, 127.8)	diene-Me
	1.41, 2.52 (d, 1 H each, *J* = 8.3)	=CH_2	31 (s, vbr)	=CH_2B
	1.68, 1.76 (s, 3 H each)	diene-Me	59.64 (t, *J* = 150.1)	=CH_2
	1.96, 2.66, 3.19 (m, d, d, 2 H, 1 H, 1 H, *J* = 15.3)	CH_2 of C_3H_5	67.12, 71.03 (t,*J* = 155.9, 158.6)	CH_2 of C_3H_5
	5.96 (m, 1 H)	CH of C_3H_5	112.91, 125.28, 129.26, 138 (m)	$C^{1,3}$ of C_5H_3 and =*C*Me
	6.44, 6.51, 6.96 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3	117.53, 124, 131.45 (d, *J* = 170.5, 169.8, 172)	$C^{2,4,5}$ of C_5H_3
8b [Hf(C_3H_5){CH_2CMeCMeCH_2B-(C_6F_5)$_3$}Cp″] (CD_2Cl_2, −30 °C)	−1.39, −0.51 (s, br, 1 H each)	=CH_2B	−0.46, −0.23 (q, *J* = 119.7)	$SiMe_3$
	0.19, 0.39 (s, 9 H each)	$SiMe_3$	16.39, 23.72 (q, *J* = 128, 127.7)	diene-Me
	1.08, 2.26 (d, 1 H each, *J* = 9.9)	=CH_2	29 (vbr s)	=CH_2B
	1.68, 1.9 (m, d, 1 H each, *J* = 15.2)	CH_2 of C_3H_5	55.66 (t, *J* = 147.7)	=CH_2
	1.72, 1.84 (s, 3 H each)	diene-Me	64.36, 67.21 (t, *J* = 152.7, 153.6)	CH_2 of C_3H_5
	2.4, 3.19 (m, d, 1 H each, *J* = 15.2)	CH_2 of C_3H_5	111.53, 125.15, 128.12, 138 (m)	$C^{1,3}$ of C_5H_3 and =CMe
	6.07 (m, 1 H)	CH of C_3H_5	116.44, 122.93, 130.25 (d, *J* = 170, 163, 169)	$C^{2,4,5}$ of C_5H_3
				ipso-C_6F_5
	6.32, 6.37, 6.77 (m , 1 H each)	$H^{2,4,5}$ of C_5H_3	122 (s, vbr)	*m*-C_6F_5
			136.9 (d, J_{CF} = 246.8)	*p*-C_6F_5
			139.2 (d, J_{CF} = 252.8)	CH of C_3H_5
			142.67 (d, *J* = 153.2)	*o*-C_6F_5
			148.1 (d, J_{CF} = 233.2)	
9a [Zr(C_3H_5){CH_2CMeCHCH_2B-(C_6F_5)$_3$}Cp″] ([$^2H_8$]toluene, −40 °C)	−1.72 (s, br, 1 H)	=CH_2B	−0.86, −0.27 (q, *J* = 119.5)	$SiMe_3$
	−1.05 (d, 1 H, *J* = 14.1)	=CH_2B	25 (s, vbr)	=CH_2B
	−0.06, 0.05 (s, 9 H each)	$SiMe_3$	25.55 (q, *J* = 128.4)	diene-Me
	0.90, 1.07 (m, 1 H each)	CH_2 of C_3H_5	62.01 (t, *J* = 152.1)	=CH_2
	1.01, 2.57 (d, 1 H each, *J* = 7.4)	=CH_2	64.55, 71.01 (t, *J* = 158, 159.9)	CH_2 of C_3H_5
	1.11 (s, 3 H)	diene-Me	103.98 (d, *J* = 169.8 Hz)	=CH

Table 1 *Continued*

Complex	^{1}H NMR δ	Assignment	^{13}C NMR δ	Assignment
9a $[Zr(C_3H_5)\{CH_2CMeCHCH_2B(C_6F_5)_3\}Cp'']$ ([$^2H_8$]toluene, −40 °C)	2.42, 2.65 (d, 1 H each, J = 15.1)	CH_2 of C_3H_5	118.28, 124.34, 130.71 (d, J = 169, 172, 168.3)	$C^{2,4,5}$ of C_5H_3
	4.40 (d, 1 H, J = 14.1)	=CH	122 (s, vbr)	*ipso*-C_6F_5
	5.62 (m, 1 H)	CH of C_3H_5	126.81, 143.18 (m)	$C^{1,3}$ of C_5H_3 and =*C*Me
	5.91, 6.12, 6.33 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3	135.93 (d, J = 155.4)	CH of C_3H_5
			137.2 (d, J_{CF} = 249)	*m*-C_6F_5
			139.3 (d, J_{CF} = 249.8)	*p*-C_6F_5
			148.3 (d, J_{CF} = 240.7)	*o*-C_6F_5
9b $[Hf(C_3H_5)\{CH_2CMeCHCH_2B(C_6F_5)_3\}Cp'']$ ([$^2H_8$]toluene, −20 °C)	−1.78 (s, br, 1 H)	$=CH_2B$	−0.84, −0.31 (q, J = 119)	$SiMe_3$
	−0.85 (d, 1 H, J = 14)	$=CH_2B$	23 (s, vbr)	$=CH_2B$
	−0.3, 0.05 (s, 9 H each)	$SiMe_3$	25.64 (q, J = 128.6)	diene-Me
	0.80 (m, 2 H)	CH_2 of C_3H_5 and $=CH_2$	57.11 (t, J = 146.8)	$=CH_2$
	1.05 (d, 1 H, J = 14.6)	CH_2 of C_3H_5	61.61, 67.13 (t, J = 151.7, 152)	CH_2 of C_3H_5
	1.22 (s, 3 H)	diene-Me	103.6 (d, J = 167.5)	=CH
	2.17, 2.76 (d, 1 H each, J = 14.9)	CH_2 of C_3H_5	116.91, 123.02, 129.21 (d, J = 170, 172.8, 168.9)	$C^{2,4,5}$ of C_5H_3
	2.37 (d, 1 H, J = 8.9)	$=CH_2$	122 (s, vbr)	*ipso*-C_6F_5
	4.34 (d, 1 H, J = 14)	=CH	126.40, 143.89 (m)	$C^{1,3}$ of C_5H_3 and =*C*Me
	5.79 (m, 1 H)	CH of C_3H_5	137.51 (d, J = 156.4)	CH of C_3H_5
	5.87, 6.13, 6.18 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3	137.4 (d, J_{CF} = 249.8)	*m*-C_6F_5
			139.4 (d, J_{CF} = 249.8)	*p*-C_6F_5
			148.3 (d, J_{CF} = 240)	*o*-C_6F_5
10 $[Zr(C_4H_7)\{CH_2CHCHCH_2B(C_6F_5)_3\}Cp'']$ ([$^2H_8$]toluene, −30 °C)	−1.68 (s, br, 1 H)	$=CH_2B$	−0.91, −0.71	$SiMe_3$
	−1.58 (d, 1 H, J = 14.4)	$=CH_2B$	18.49	CH*Me*
	−0.22, 0.09 (s, 9 H each)	$SiMe_3$	28 (br)	$=CH_2B$
	0.92 (d, 3 H, J = 5.6)	CH*Me*	57.58	$=CH_2$
	1.98, 2.21 (m, 1 H each)	$=CH_2$	61.18	CH_2 of C_4H_7
	1.65, 2.0 (d, J = 13.4, 1 H each)	CH_2 of C_4H_7	83.45	*C*HMe
	1.71 (m, 1 H)	C*H*Me	106.45, 133.09	=CH
	4.58 (d, 1 H, J = 9.87)	=CH	118.56, 124.43, 125.61	$C^{2,4,5}$ of C_5H_3
	5.01 (m, 1 H)	CH of C_4H_7	126.35 (br)	$C^{1,3}$ of C_5H_3
	5.17 (m, 1 H)	=CH	137.37	CH of C_4H_7
	5.87, 5.93, 6.63 (m, 1 H each)	$H^{2,4,5}$ of C_5H_3	137.23 (J_{CF} = 142.2)	*m*-C_6F_5
			139.42 (J_{CF} = 153)	*p*-C_6F_5
			148.23 (J_{CF} = 138.4)	*o*-C_6F_5
11A/B $[Zr\{CH_2CHCHCHB(C_6F_5)_2\}(C_6F_5)Cp'']$ ([$^2H_8$]toluene, 25 °C)	−0.14, 0.05 (s, 9 H each)	$SiMe_3$	−0.95, −0.73 (q, J = 119.5)	$SiMe_3$
	0.59, 2.19 (t, 1 H each, J = 8.9)	$=CH_2$	67.62 (t, J = 150.0)	$=CH_2$
	2.21 (d, 1 H, J = 12.6)	=CHB	93.64 (d, br, J ≈ 137)	=CHB
	5.99, 6.23 (br t, q, 1 H each, J = 9.2)	=CH	120.54, 127.22, 129.53 (d, J = 170.5, 169.0, 160.7)	$C^{2,4,5}$ of C_5H_3
	6.48, 6.65, 7.6 (s, br, 1 H each)	$H^{2,4,5}$ of C_5H_3	124.65, 135.64, (d, J = 167.5, 166)	=CH
			127.4, 134.56 (m)	$C^{1,3}$ of C_5H_3
11C $[Zr\{CH_2CHCHCHB(C_6F_5)_2\}(C_6F_5)Cp'']$ ([$^2H_8$]toluene, 25 °C)	−0.15, 0.03 (s, 9 H each)	$SiMe_3$	−1.39, −0.47 (q, J = 119.6)	$SiMe_3$
	1.44, 3.42 (m, dd, 1 H each, J = 8.9 and 6.6)	$=CH_2$	82.31 (t, J = 152.8)	$=CH_2$
	5.1, 5.82 (m, 1 H each)	=CH	97.17 (d, br, J ≈ 137)	=CHB
	5.34 (d, 1 H, J = 12)	=CHB	123.96, 134.05 (m)	$C^{1,3}$ of C_5H_3
	5.97, 7.01, 7.7 (s, br, 1 H each)	$H^{2,4,5}$ of C_5H_3	125.68, 129.68 (d, J = 165)	=CH
			125.9, 128.13, 135.11 (d, J = 172)	$C^{2,4,5}$ of C_5H_3
12a $[Zr\{CH_2CMeCHCHB(C_6F_5)_2\}(C_6F_5)Cp'']^b$ ([$^2H_8$]toluene)	−0.13, 0.06 (s, 9 H each)	$SiMe_3$	−0.93, −0.68 (q, J = 119.6)	$SiMe_3$
	0.60 (d, 1 H, J = 10.9)	$=CH_2$ *anti*	26.63 (q, J = 127.8)	diene-Me
	1.33 (s, 3 H)	diene-Me	71.50 (t, J = 146.7)	$=CH_2$
	2.05 (d, 1 H, J = 10.9)	$=CH_2$ *syn*	96.95 (d, br, J ≈ 140)	=CHB
	3.19 (d, 1 H, J = 11.7)	=CHB	120.59, 127.26 (d, J = 170.5, 170.5) and one under [$^2H_8$]-toluene signals	$C^{2,4,5}$ of C_5H_3
	5.89 (d, 1 H, J = 11.7)	=CH	121.48 (d, J = 169)	=CH
	6.6, 6.7, 7.5 (s, br, 1 H each)	$H^{2,4,5}$ of C_5H_3	134.75, 149.7 (m)	$C^{1,3}$ of C_5H_3 and =*C*Me
12b $[Hf\{CH_2CMeCHCHB(C_6F_5)_2\}(C_6F_5)Cp'']^b$ ([$^2H_8$]toluene)	−0.13, −0.08 (s, 9 H each)	$SiMe_3$	−0.9, −0.6	$SiMe_3$
	0.78 (d, 1 H, J = 11.4)	$=CH_2$ *anti*	26.83	diene-Me
	1.47 (s, 3 H)	diene-Me	70.07	$=CH_2$
	1.67 (d, 1 H, J = 10.9)	$=CH_2$ *syn*	94.01	=CHB
	2.88 (d, 1 H, J = 11.3)	=CHB	120.23, 126.07 and one under [$^2H_8$]toluene signals	$C^{2,4,5}$ of C_5H_3
	5.74 (d, 1 H, J = 11.3)	=CH	120.62	=CH
	6.45, 6.6, 7.47 (s, br, 1 H each)	$H^{2,4,5}$ of C_5H_3	132.95, 148.72	$C^{1,3}$ of C_5H_3 and =*C*Me

[a] All shifts are in ppm and J values in Hz. [b] Carbon-13 NMR signals for the C_6F_5 groups for these complexes have been omitted.

Table 2 Fluorine-19 NMR data*

Complex	δ	Assignment
8a $[Zr\{CH_2CMeCMeCH_2B(C_6F_5)_3\}(C_3H_5)Cp'']$ $(CD_2Cl_2, -50\ °C)$	−129.6, −130, 132.2, −132.6, −134, −134.7 (d, 1 F each, J_{FF} = 19.6)	*ortho*-F
	−159.9, −160.1, −160.6 (t, 1 F each, J_{FF} = 19.7)	*para*-F
	−164.2, −165.1, −165.6, −167 (m, 2 F, 1 F, 2 F, 1 F)	*meta*-F
8b $[Hf(C_3H_5)\{CH_2CMeCMeCH_2B(C_6F_5)_3\}Cp'']$ $(CD_2Cl_2, -30\ °C)$	−129.4 (d, 1 F, J_{FF} = 22.6); −132.4 (d, 1 F, J_{FF} = 22.6); −132, −133.6 (m, 1 F, 3 F)	*ortho*-F
	−160.5, −161 (m, 2 F, 1 F)	*para*-F
	−164.2, −165.3, −165.9 (m, 1 F, 2 F, 3 F)	*meta*-F
9a $[Zr(C_3H_5)\{CH_2CMeCHCH_2B(C_6F_5)_3\}Cp'']$ ($[^2H_8]$toluene, −40 °C)	−133.1 (br s, 6 F)	*ortho*-F
	−158.8 (br s, 3 F)	*para*-F
	−164.2 (br s, 6 F)	*meta*-F
9b $[Hf(C_3H_5)\{CH_2CMeCHCH_2B(C_6F_5)_3\}Cp'']$ ($[^2H_8]$toluene, −20 °C)	−132.6 (br s, 6 F)	*ortho*-F
	−158.7 (t, 3 F, J_{FF} = 19.7)	*para*-F
	−164.2 (br s, 6 F)	*meta*-F
10 $[Zr(C_3H_5)\{CH_2CHCHCH_2B(C_6F_5)_3\}Cp'']$ ($[^2H_8]$toluene, −60 °C)	−131.2, −132.9, −135.1 (vbr s, 1 F, 4 F, 1 F)	*ortho*-F
	−158.9 (vbr s, 3 F)	*para*-F
	−164.3 (vbr s, 6 F)	*meta*-F
11A, **11B** $[Zr(C_6F_5)\{CH_2CHCHCHB(C_6F_5)_2\}Cp'']$ ($[^2H_8]$toluene, −40 °C)	−114.1 (vbr s, 2 F); −130.1 (d, 2 F, J_{FF} = 19.7); −130.6, −169.9 (br s, 1 F each)	*ortho*-F
	−149.3 (br s, 1 F); −150.7 (t, 1 F, J_{FF} = 21.1); −153.6 (t, 1 F, J_{FF} = 19.7)	*para*-F
	−156.2, −159.5 (br s, 1 F each); −161.2 (m, 4 F)	*meta*-F
11C $[Zr(C_6F_5)\{CH_2CHCHCHB(C_6F_5)_2\}Cp'']$ ($[^2H_8]$toluene, −40 °C)	−118.7 (d, 2 F, J_{FF} = 25.3); −129.4 (br s, 1 F); −131.4 (d, 2 F, J_{FF} = 16.9); −184.1 (br s, 1 F)	*ortho*-F
	−151.6, −155.3 (t, 1 F each, J_{FF} = 19.7); −152.2 (t, 1 F, J_{FF} = 21.1)	*para*-F
	−157.1 (vbr s, 1 F); −160.5, −162.2 (m, 2 F each) and 1 F overlapping with *m*-F of **11A**	*meta*-F
12a $[Zr(C_6F_5)\{CH_2CMeCHCHB(C_6F_5)_2\}Cp'']$ ($[^2H_8]$toluene, −20 °C)	−106, −123 (vbr s, 1 F each); −130, −130.4, −168 (br s, 2 F, 1 F, 1 F)	*ortho*-F
	−149, −152.9 (br s, 1 F each); −150.7 (t, 1 F, J_{FF} = 19.1)	*para*-F
	−156, −158 (vbr s, 1 F each); −160 (br s, 4 F)	*meta*-F

* All shifts are in ppm and *J* values in Hz.

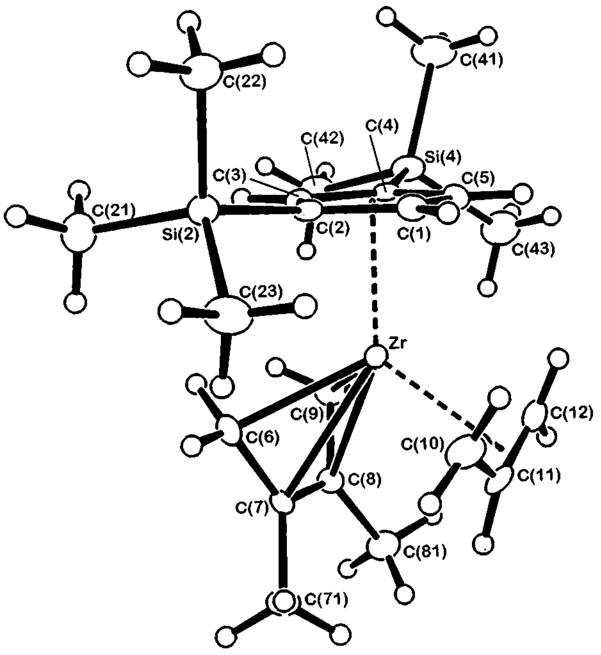


Fig. 1 Crystal structure of complex **5a**, showing the atomic numbering scheme (H atoms omitted for clarity). Ellipsoids are drawn at 40% probability

The co-ordination geometry about M is essentially square pyramidal with an apical η^5-Cp″ ligand in which the η^3-allyl and the η^4-butadiene ligand occupy the basal positions both oriented in the supine configuration with respect to Cp″. This contrasts with the prone conformations adopted by both the allyl and the diene ligands in $[Hf(1,2,3\text{-}Me_3C_3H_2)(1,2\text{-}Me_2C_4H_4)Cp]$.[8a] The C–C bond distances in the allyl ligand in **5a** are slightly shorter than in the parent compound $[Zr(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)Cp]$ [1.388(6) *vs.* 1.440(8) Å].[14] The bond length distribution within the diene ligand, in particular the short C(7)–C(8) bond, is in keeping with the σ^2,π-metallacyclopent-3-ene character of the C_4M unit. The distances from the metal centre to the diene methylene carbon atoms are in the normal range for M–C σ-bonds, with the Hf–C(6) and Hf–C(9) bonds being slightly shorter.[6,8a,15] The diene methylene carbons are much closer to the metal than the internal diene carbons C(7) and C(8), a further indication for the 'folded envelope' metallacyclopentane structure of this ligand. The distance difference $\Delta d = \frac{1}{2}[d\{M–C(6)\} + d\{M–C(9)\}] - \frac{1}{2}[d\{M–C(7)\} - d\{M–C(8)\}]$ = 0.189 Å is much longer than in predominantly η^4-bonded diene complexes.[16]

Cationic species

Treatment of a toluene solution of $[Hf(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CMeCMeCH_2)Cp'']$ **5b** with 1 equivalent of $B(C_6F_5)_3$ at −78 °C leads to a colour change from orange to pale yellow. The compound $B(C_6F_5)_3$ attacks exclusively one of the terminal carbons of the diene ligand, to give the zwitterionic hafnium bis(allyl) complex $[Hf^+(\eta^3\text{-}C_3H_5)\{\eta^3\text{-}CH_2CMeCMeCH_2B^-(C_6F_5)_3\}Cp'']$ **8b** (Scheme 3). The reaction is analogous to that of $B(C_6F_6)_3$ with **5a** to give **8a** which was the subject of a preliminary communication.[17]

Complex **8b** is chiral and shows seven ^1H resonances (Table 1) in the allylic region (five from the C_3H_5 ligand and two from the dienyl unit) together with two broadened doublets for the CH_2–B moiety which appear at an unusually high field, δ −0.51 and −1.39, suggestive of agostic CH···Hf interactions; this bonding mode was confirmed by the single crystal X-ray structure of **8b** (see below). The single ^{11}B NMR resonance at δ −13 confirms the formation of a triarylborate. The ^{19}F NMR (Table 2) at −10 °C shows three different resonances in the *ortho*-F region, an indication of a significant barrier of rotation around the B–CH_2 bond, while free rotation around the B–C_6F_5 bonds is still possible. This contrasts with the $B(C_6F_5)_3$ group in the analogous unsubstituted butadiene complex **10** (below) which is still freely rotating at −40 °C. Evidently the steric hindrance provided by the diene-methyl substituents plays an important role in the solution dynamics of these complexes, a facet that is also relevant to the decom-

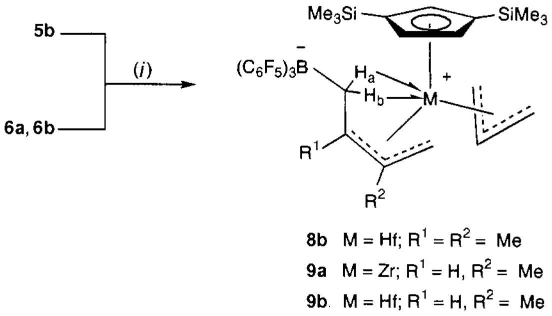
Table 3 Crystal data for compounds **5a**, **5b** and **8b**

	5a	**5b**	**8b**
Formula	$C_{20}H_{36}Si_2Zr$	$C_{20}H_{36}HfSi_2$	$C_{38}H_{36}BF_{15}HfSi_2 \cdot 0.5C_6H_5CH_3$
M	423.96	511.16	1069.21
Crystal dimensions/mm	0.28 × 0.28 × 0.21	0.28 × 0.145 × 0.145	0.30 × 0.21 × 0.15
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	6.9403(5)	6.916(2)	11.4036(8)
b/Å	20.191(3)	20.192(2)	11.5811(7)
c/Å	15.951(9)	15.902(7)	18.4053(11)
α/°			71.908(6)
β/°	98.200(7)	98.101(12)	89.541(7)
γ/°			68.383(6)
U/Å^3	2212.4(13)	2198.6(12)	2132.4(2)
Z	4	4	2
D_c/g cm^{-3}	1.273	1.544	1.665
μ/mm^{-1}	0.530	4.853	2.598
$F(000)$	896	1024	1058
Absorption correction	DIFABS[13]	DIFABS[13]	ψ scans
Maximum, minimum transmission factors	1.018, 0.855	1.198, 0.315	0.681, 0.401
θ Range/°	$2.02 \leq 2\theta \leq 24.83$	$2.02 \leq 2\theta \leq 24.99$	$1.93 \leq 2\theta \leq 25.00$
Index range	$-8 \leq h \leq 8$, $-22 \leq k \leq 23$, $-18 \leq l \leq 12$	$-8 \leq h \leq 5$, $-23 \leq k \leq 23$, $-18 \leq l \leq 17$	$-13 \leq h \leq 13$, $-12 \leq k \leq 13$, $0 \leq l \leq 21$
Reflections collected	7517	8076	7506
Unique reflections, n	3195 (R_{int} = 0.092)	3303 (R_{int} = 09.071)	7506
Reflections with $F_c^2 > 2.0\sigma(F_c^2)$	2794	3007	7003
Number of parameters, p	252	252	592
Goodness of fit on F^2, S^a	1.025	1.058	1.093
$R1^b$	0.0378	0.0326	0.0242
$wR2^c$	0.0905	0.0811	0.0588
Weighting parameters a, b^d	0.0435, 0.0000	0.044, 0.0000	0.0252, 3.7847
Extinction parameter^e	—	—	0.000 50(14)
Largest difference peak and hole/e Å^{-3}	0.531, −0.554	1.519, −1.126	0.737, −0.812

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{-\frac{1}{2}}$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [d] $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [e] $F_c' = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$.

Table 4 Selected interatomic distances (Å) and angles between interatomic vectors (°) for complexes **5a** [M = Zr] and **5b** [M = Hf] with estimated standard deviations (e.s.d.s) in parentheses

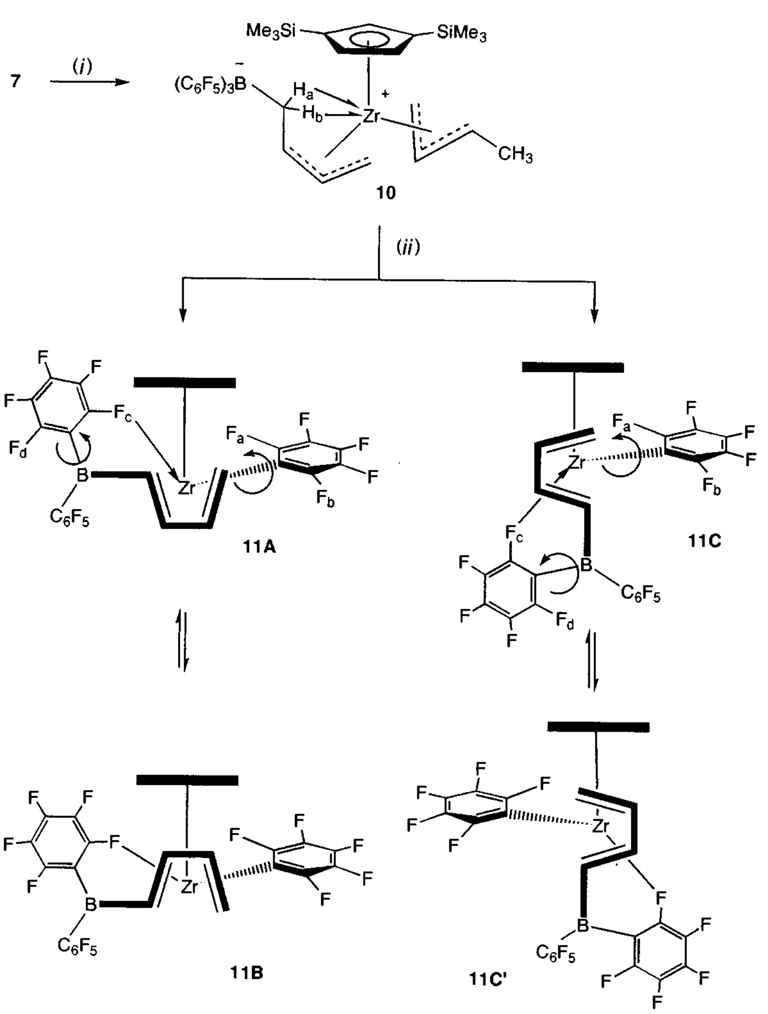
	5a	**5b**
M–C(1)	2.537(3)	2.505(5)
M–C(2)	2.546(3)	2.521(5)
M–C(3)	2.522(3)	2.511(5)
M–C(4)	2.541(3)	2.516(5)
M–C(5)	2.528(3)	2.506(5)
M–C(6)	2.312(3)	2.271(5)
M–C(7)	2.497(3)	2.496(5)
M–C(8)	2.500(3)	2.510(5)
M–C(9)	2.308(3)	2.264(5)
M–C(10)	2.435(4)	2.452(6)
M–C(11)	2.469(3)	2.442(5)
M–C(12)	2.475(4)	2.409(6)
C(6)–C(7)	1.443(5)	1.448(8)
C(7)–C(8)	1.387(5)	1.388(7)
C(7)–C(71)	1.517(5)	1.504(7)
C(8)–C(9)	1.444(5)	1.477(7)
C(8)–C(81)	1.504(5)	1.493(8)
C(10)–C(11)	1.389(6)	1.368(9)
C(11)–C(12)	1.388(6)	1.386(10)
C(7)–C(6)–H(6a)	118(2)	122(4)
C(7)–C(6)–H(6b)	119(2)	111(3)
H(6a)–C(6)–H(6b)	112(3)	111(5)
C(8)–C(7)–C(6)	120.6(3)	120.7(5)
C(7)–C(8)–C(9)	119.9(3)	118.3(5)
C(8)–C(9)–H(9a)	115(3)	127(4)
C(8)–C(9)–H(9b)	113(2)	116(4)
H(9a)–C(9)–H(9b)	115(3)	98(5)
H(10a)–C(10)–H(10b)	117(3)	107(5)
C(12)–C(11)–C(10)	123.0(4)	123.6(6)
H(12a)–C(12)–H(12b)	119(3)	114(5)



Scheme 3 (*i*) $B(C_6F_5)_3$, toluene

position reactions of these compounds (see below). A high-field ^{19}F NMR chemical shift of one of the *ortho*-F signals that might indicate a metal···*o*-F co-ordination is not observed. By contrast, the co-ordinated *ortho*-F in $[Zr\{C_3H_4CH_2B(C_6F_5)_3\}Cp_2]$ experiences an upfield shift of *ca.* 80 ppm to δ −213.2.[18]

The reaction of $B(C_6F_5)_3$ with the isoprene complexes **6a** gives the corresponding zwitterionic complexes **9a** as a yellow microcrystalline solids in high yield. The analogous hafnium complex **9b** was generated in solution, in essentially quantitative yield (by NMR spectroscopy). The spectroscopic data of these compounds are very similar to those of **8b**. Formation of a triarylborate is indicated by the ^{11}B NMR singlet at *ca.* δ −12, and the high-field shift of the ^{1}H NMR resonance for the CH_2–B moiety, δ −1.05 and −1.72 for **9a** and −0.85 and −1.78 for **9b**, again shows agostic CH···M interactions. At *ca.* −30 °C, the ^{19}F NMR spectra show only one resonance for the *ortho*-F atoms, without evidence for M···F bonding.



Scheme 4 (*i*) $B(C_6F_5)_3$, toluene, −60 °C; (*ii*) −60 °C to 25 °C, but-2-ene

Attack by $B(C_6F_5)_3$ on the isoprene ligand could, in principle, occur on C^1 or C^4, to give rise to two stereoisomers. However, only one single isomer is actually formed, and $B(C_6F_5)_3$ attacks exclusively the less hindered CH_2 terminus. Diagnostic for this stereochemistry is, for example, the coupling between the CH_2–B moiety and the neighbouring proton of the =CH group of the isoprene ligand.

These zwitterionic complexes are very air sensitive but thermally quite stable in the solid state. They are readily isolable and can be stored at room temperature for months. The solubility is very dependent on the degree of substitution of the diene, *e.g.* whereas **8b** is soluble in aromatic solvents **9a**, **9b** are only sparingly soluble. In solution **8a** and **8b** decompose slowly, over a period of days, to give a mixture of unknown compounds. The complexes **9** are less stable than **8**.

The reaction of the unsubstituted butadiene complex **7** with $B(C_6F_5)_3$ is more complex. Monitoring the reaction by NMR spectroscopy at −60 °C shows that as in the previous cases a zwitterionic complex **10** is formed which is structurally analogous to **8** and **9**. Even at this low temperature, the reaction is accompanied by the formation of two decomposition products. One isomer, **11C**, is formed initially, but with increasing temperature a second isomer becomes dominant. The reaction is accompanied by the formation of but-2-ene. Warming solutions of **10** to room temperature leads to complete conversion to **11**. Cooling this solution to −80 °C shows that **11** consists of three isomers: isomer **11C** already mentioned, and isomers **11A** and **11B** which above −60 °C interconvert rapidly on the NMR time-scale (Scheme 4).

Each of these compounds is chiral and highly fluxional and possesses three different C_6F_5 groups. Compared to **10**, the ^{11}B NMR signal for **11** is high-field shifted by *ca.* 55 ppm to δ +43, indicative of the transformation of a four-co-ordinate borato group into a three-co-ordinate boryl substituent.‡ Evidently, **10** decomposes cleanly under C–H activation and but-2-ene elimination with concomitant migration of a C_6F_5 substituent from boron to zirconium (Scheme 4).

The nature of the products formed and the fluxionality they exhibit are conveniently elucidated using variable-temperature ^{19}F NMR spectroscopy. The *ortho*-F atoms of the Zr–C_6F_5 group are observed at relatively high field, well separated from other *o*-F signals, at δ −114 to −119. The isomers **11A** and **11B** are most probably prone and supine diene conformers which interconvert *via* a ring-flipping process[20] with a low activation barrier which is slow only at −80 °C. The diene moiety in **11C** adopts a different configuration, approximately perpendicular to the cyclopentadienyl ring, as seen in the crystallographically characterised C_5Me_5 analogue $[Zr(C_6F_5)\{\eta^4\text{-}C_4H_5B(C_6F_5)_2\}\text{-}Cp^*]$ which shows quite similar spectroscopic properties.[17] There is apparently no interchange of **C** with **A** and **B**. Isomer **C** does of course also undergo a ring-flipping motion, though in this case this produces the enantiomer **11C′** and hence is not detected spectroscopically.

In all three isomers one of the two B–C_6F_5 groups rotates freely. One *o*-F atom of the second B–C_6F_5 group is co-ordinated to the metal centre, as seen from the ^{19}F NMR signals at δ −170 (**11A/B**) and −184 (**11C**) (Table 2). This B–C_6F_5 substituent shows hindered rotation which becomes slow at

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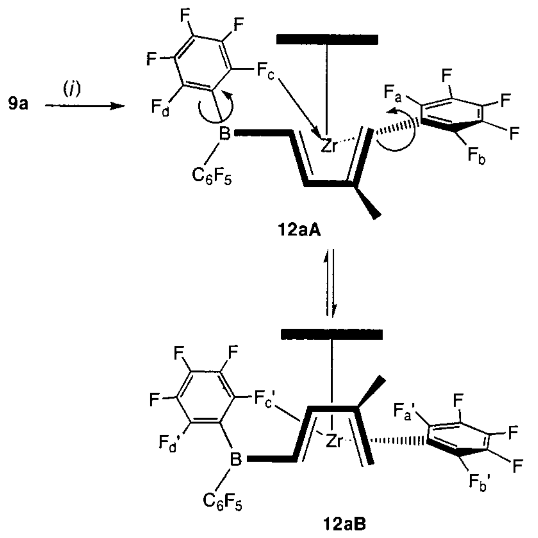
‡ The ^{11}B NMR chemical shift of δ 43 suggests some double bond character of the CH–B bond, comparable to π contributions present in $(C_6F_5)_2BOEt$ (δ 43.1) and $Li(C_5H_4BPr^i_2)$ (δ 40), whereas higher shifts are observed where such interactions are absent, as in $[TiCl_3\{C_5H_4B(C_6F_5)_2\}]$.[19]



Scheme 5 (*i*) Room temperature, 20 h, −propene

−60 °C and the signals for F_a F_b, F_c and F_d (Scheme 4) are resolved. Similar hindered rotation and slow exchange of F_a and F_b is observed for the Zr–C_6F_5 ligand in **11A** and **11B**, whereas in the sterically less encumbered isomer **11C** this group rotates freely.

In view of the general lack of reactivity of the B–C bond in $B(C_6F_5)_3$ towards electrophiles, the C_6F_5 migration to the electrophilic zirconium centre at temperatures of −60 °C and below seems unusually facile and is evidently the response to the very specific steric conditions in the case of **10**. Even a slight increase in steric hindrance of the diene, as in the isoprene complexes **9**, significantly raises the barrier for this rearrangement. Thus toluene solutions of **9a** decompose only at much higher temperatures ($\tau_{\frac{1}{2}} \approx 3$ h in $[^2H_8]$toluene at 25 °C), *via* a similar α-H elimination with formation of propene and the product **12a** (Scheme 5). The same decomposition process is observed for **9b** to give **12b**, but although the hafnium complex is more stable and the decomposition is slower, it is not as clean and gives a mixture of products, either because it is not selective or because **12b** decomposes further to as yet unknown compounds.

The formation of **12a** is among other things readily seen in the ^{13}C NMR spectrum where the signal at δ 25 for the sp^3-CH_2B is replaced by one at *ca.* δ 97 for into an sp^2-CHB, with $J_{CH} = 140$ Hz. At ambient temperature the ^{19}F NMR spectrum of **12a** shows three inequivalent C_6F_5 groups. The C_6F_5 group bound to zirconium shows again *o*-F resonances at relatively high field; at −20 °C F_a and F_a' are resolved and occur at δ −106 and −123. For **12a**, the rotation of the Zr–C_6F_5 and one B–C_6F_5 groups becomes completely 'frozen out' on the NMR time-scale below −20 °C, and one *o*-F signal of the B–C_6F_5 group is now found at low field, δ −168, indicating *ortho*-fluorine co-ordination to zirconium. The presence of the methyl substituent in the isoprene ligand of **12a** has evidently led to a significant increase of the rotational barriers compared with the butadiene complex **11**.

In contrast to **11**, compound **12a** forms only two isomers of type **A** and **B** which are well resolved at −60 °C. The activation barrier for the interchange, estimated from the coalescence of the isoprene-Me signal, is $\Delta G^{\ddagger}(233\ K) = 47.4$ kJ mol^{-1}, compared to $\Delta G^{\ddagger}(213\ K) = 37.5$ kJ mol^{-1} for **11**. A structure of type **C** is not found in the case of **12a**, possibly because this conformation would lead to unfavourable steric interactions between the isoprene-methyl group and the Cp″ ligand.

The fluxional processes in the case of **12a** are conveniently followed by ^{19}F NMR and are illustrated in Fig. 2. Cooling to 253 K allows three (broad) *ortho*-F signals for F_a, F_b and F_c to be distinguished. At this temperature interconversion of **A** and **B** is still fast. On further cooling the presence of two isomers begins to be detectable and leads to two well resolved sets of signals, (F_a, F_b and F_c, for one, F_a', F_b' and F_c' for the other isomer; the assignment to **A** and **B** is arbitrary). Similar behaviour is observed for the *m*-F signals which are however in a more crowded part of the spectrum (as is the signal for F_d).

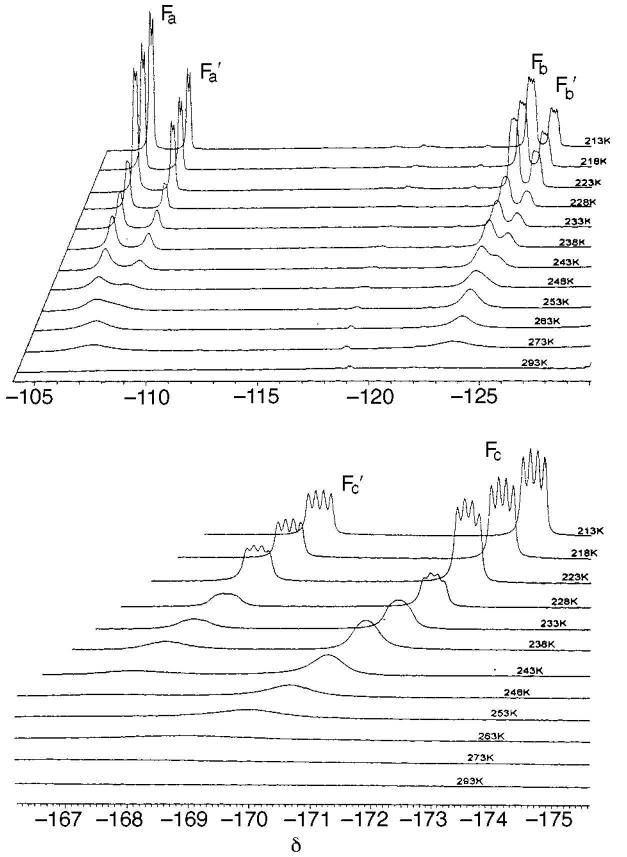


Fig. 2 Stacked plot of the variable-temperature ^{19}F NMR of complex **12a**, showing the region for the *o*-F atoms of the Zr–C_6F_5 (F_a, F_b) and the co-ordinated B–C_6F_5 groups. The signal for F_d (*cf.* Scheme 5) is close to those of the freely rotating B–C_6F_5 substituent and has been omitted for clarity

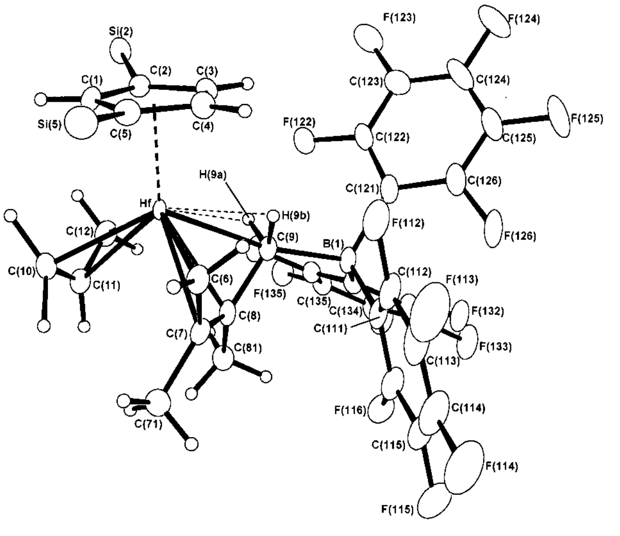


Fig. 3 Crystal structure of complex **8b**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability

Crystal structure of 8b

The structure of **8b**·0.5toluene was confirmed by a single-crystal X-ray diffraction study. Crystals were obtained by recrystallization from toluene at −20 °C. The structure is shown in Fig. 3. Important bond lengths and angles are collected in Table 5.

Table 5 Selected bond distances (Å) and angles between interatomic vectors (°) for complex **8b** with e.s.d.s in parentheses

Hf−C(6)	2.279(4)	Hf−C(9)	2.411(3)
Hf−C(10)	2.417(4)	Hf−C(12)	2.442(4)
Hf−C(11)	2.458(3)	Hf−C(3)	2.474(3)
Hf−C(8)	2.477(3)	Hf−C(4)	2.480(3)
Hf−C(1)	2.491(3)	Hf−C(5)	2.503(3)
Hf−C(2)	2.506(3)	Hf−C(7)	2.522(3)
Hf−H(9a)	2.33(3)	Hf−H(9b)	2.26(3)
C(6)−C(7)	1.437(5)	C(6)−H(6a)	0.88(4)
C(6)−H(6b)	0.93(4)	C(7)−C(8)	1.388(5)
C(7)−C(71)	1.518(5)	C(8)−C(9)	1.511(5)
C(8)−C(81)	1.515(5)	C(9)−B(1)	1.703(5)
C(9)−H(9a)	0.96(4)	C(9)−H(95b)	0.81(4)
C(10)−C(11)	1.406(6)	C(11)−C(12)	1.384(6)
B(1)−C(111)	1.643(5)	B(1)−C(131)	1.657(5)
B(1)−C(121)	1.661(5)		
C(6)−Hf−C(9)	77.51(13)	C(6)−Hf−C(10)	91.51(14)
C(9)−Hf−C(10)	131.39(13)	C(6)−Hf−C(12)	134.32(14)
C(9)−Hf−C(12)	94.25(13)	C(10)−Hf−C(12)	60.52(14)
C(6)−Hf−C(3)	112.91(12)	C(9)−Hf−C(3)	88.53(11)
C(10)−Hf−C(3)	137.94(12)	C(12)−Hf−C(3)	111.67(13)
C(11)−Hf−C(3)	141.82(12)		
C(7)−C(6)−Hf	82.1(2)	C(7)−C(6)−H(6a)	117(2)
Hf−C(6)−H(6a)	125(2)	C(7)−C(6)−H(6b)	118(2)
Hf−C(6)−H(6b)	98(2)	H(6a)−C(6)−H(6b)	113(3)
C(8)−C(7)−C(6)	121.0(3)	C(8)−C(7)−C(71)	121.7(3)
C(6)−C(7)−C(71)	116.5(3)	C(7)−C(8)−C(9)	121.8(3)
C(7)−C(8)−C(81)	122.1(3)	C(9)−C(8)−C(81)	115.8(3)
C(8)−C(9)−B(1)	116.3(3)	C(8)−C(9)−Hf	74.4(2)
B(1)−C(9)−Hf	166.5(2)	C(8)−C(9)−H(9a)	110(2)
B(1)−C(9)−H(9a)	108(2)	Hf(1)−C(9)−H(9a)	74(2)
C(8)−C(9)−H(9b)	111(3)	B(1)−C(9)−H(9b)	98(3)
Hf−C(9)−H(9b)	69(3)	H(9a)−C(9)−H(9b)	113(3)
C(12)−C(11)−C(10)	122.7(4)		
C(111)−B(1)−C(131)	116.3(3)	C(111)−B(1)−C(121)	111.9(3)
C(131)−B(1)−C(121)	101.0(3)	C(111)−B(1)−C(9)	101.4(3)
C(131)−B(1)−C(9)	114.6(3)	C(121)−B(1)−C(9)	112.3(3)

The compound is the first example of a structurally characterised complex of the type $[\mathrm{CpHf}(\eta^3\text{-allyl})_2]^+$. The co-ordination around the metal atom is very close to the neutral precursor, with approximately square-pyramidal geometry and the $\eta^3\text{-}C_3H_5$ and $\eta^3\text{-}CH_2CMeCMeCH_2B(C_6F_5)_3$ ligands occupying basal positions in supine conformations. The presence of two $SiMe_3$ substituents and the $B(C_6F_5)_3$ unit ensures a very crowded ligand sphere, as shown by the orientation of the $SiMe_3$ groups away from $B(C_6F_5)_3$. The $\eta^3\text{-}CH_2CMeCMeCH_2B(C_6F_5)_3$ moiety has a *syn* conformation, which reflects its formation from the metallacyclopentene 'envelope' structure of **5b**. By contrast, in the related bis(cyclopentadiene) complex $[Zr\{C_3H_4CH_2B(C_6F_5)_3\}Cp_2]$ the allylic ligand adopts an *anti* arrangement. In our case no intra or inter-molecular M $\cdots$ F interactions are observed.

The most significant feature in the structure of **8b** is the $Hf{-}CH_2{-}B$ moiety. The Hf−C−B arrangement is almost linear [angle 166.5(2)°], with a Hf−C distance at 2.411(3) Å, and is comparable to related methyl-bridged zirconium systems, for example $[(\eta\text{-}C_5H_3Me_2\text{-}1,2)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$[21] [Zr−C−B 161.8(2)°], $[Cp''_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$[22] [170.5(3)°] and $[CpZr\{\eta^2\text{-}PhC(NSiMe_3)_2\}(C_6F_5)(\mu\text{-}Me)B(C_6F_5)_3]$[23] [166.0(8)°]. The hydrogens of the bridging methylene group were located and show relatively close contacts to the hafnium atom, with Hf−H distances of 2.33(3) and 2.26(3) Å. A similar stabilisation of the Lewis-acidic metal centre through agostic M $\cdots$ H bonds to two of the $\mu\text{-}CH_3$ hydrogens is found in $[(\eta\text{-}C_5H_3Me_2\text{-}1,2)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$, with Zr $\cdots$ H of 2.25(3) and 2.30(3) Å, while the metal–hydrogen distances in the more crowded $[Cp''_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$ are significantly longer [2.47(3) and 2.44(3) Å].

The C−C distances in the C_4 ligand of **8b** are comparable to those in **5b**. However, the Hf−C bond lengths to the diene-CH_2 carbons are significantly different: Hf−C(6) is a short 2.279(4) Å, very similar to that in **5b** and comparable to the $Hf{-}CH_3$ distances in the $[HfMe_2Cp''(C_6H_5CH_3)]^+$ cation [2.245(7) Å],[5g] while the bond length to the bridging carbon C(9) is substantially longer, 2.411(3) Å. For comparison, the $Hf{-}CH_3$ bond distances in $[HfMe_2Cp_2]$ are 2.318(8) and 2.382(7) Å.[24] In agreement with a bis(allylic) structure of the zwitterion, the C(8)−C(9) bond length is elongated from 1.477(7) Å in the metallacyclopentene **5b** to 1.511(5) Å in **8b** and approaches the value of a C−C single bond. The bond lengths between the hafnium atom and the cyclopentadienyl carbons are essentially identical to those found in **5b**.

Ethene polymerisation

The combination of Group 4 metal alkyls with cation generating agents, such as $B(C_6F_5)_3$ or $E[B(C_6F_5)_4]$ ($E = CPh_3$ or $NHMe_2Ph$) affords highly efficient methylaluminoxane-free alkene polymerisation catalysts.[1] Diene and allyl complexes have so far not been used in this context, with few exceptions. Erker and co-workers[18a] showed that $[Cp_2Zr\{\eta^3\text{-}C_3H_4CH_2B(C_6F_5)_3\}]$, obtained from $[Cp_2Zr(C_4H_6)]$ and $B(C_6F_5)_3$, polymerises ethene with good activity, and Devore *et al.*[25] employed $Me_2Si(C_5Me_4)(NBu^t)Ti(\text{diene}){-}B(C_6F_5)_3$ mixtures for the co-polymerisation of ethene with oct-1-ene, without identifying the nature of the active species. In view of the high activity of monocyclopentadienyl complexes such as $[TiMe_3(\eta\text{-}C_5Me_5)]{-}B(C_6F_5)_3$ for the polymerisation of ethene and propene, even at very low temperatures where bis(cyclopentadienyl) complexes are no longer appreciably active,[26] we became interested in the polymerisation activity of diene monocyclopentadienyl complexes. The results are collected in Table 6.

Mixtures of **5a** or **5b** with $B(C_6F_5)_3$ in toluene under 1 bar ethene give linear polyethene of relatively high molecular weight. The activities are good but not exceptional. This may in part be the result of the crowded ligand sphere, and in part due to the need for an η^3-allyl to rearrange to η^1 before alkene insertion into the M−C bond and polymer chain growth can occur, a process that is likely to increase the activation barrier for the first insertion step. The polymer molecular weight distributions are comparable to those of metallocene catalysts at low temperatures but broaden significantly with increasing temperature, possibly due to the formation of more than one active species. Isoprene and particularly butadiene complexes are less active since in these cases the formation of deactivation products such as **11** and **12** becomes significant at temperatures <0 °C.

Whereas $B(C_6F_5)_3$ or CPh_3^+ react with metallocene dialkyls $[MR_2Cp_2]$ to give identical active species $[Cp_2MR]^+$, this is obviously not the case with diene complexes [CpMX(diene)] which afford products with diene−$B(C_6F_5)_3$ or diene−CPh_3 ligands, respectively. Consequently, rather different catalytic behaviour may be expected. In our case mixtures of **5a** or **5b** and $[CPh_3][B(C_6F_5)_4]$ show increased productivity and, in some cases, significantly higher molecular weight (up to $M_w = 1.3 \times 10^6$) but with broader polydispersities. Uptake of propene under these conditions was not detected.§

Conclusion

Zirconium and hafnium diene monocyclopentadienyl complexes $[M(\eta^3\text{-allyl})(\eta^4\text{-diene})Cp'']$ are readily activated by $B(C_6F_5)_3$ or CPh_3^+ to give the cationic bis(allyl) complexes of the type $[M(\eta^3\text{-allyl})_2Cp]^+$ which catalyse the polymerisation of ethene. The zwitterionic 14-electron complexes $[M(\eta^3\text{-allyl})\{\eta^3\text{-}CH_2CRCRCH_2B(C_6F_5)_3\}Cp'']$ are isolable and stabilised by the

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§ Mixtures of $[Hf(\eta^3\text{-}C_4H_7)_3Cp^*]$ and $[CPh_3][B(C_6F_5)_4]$ oligomerise propene.[27]

Table 6 Ethene polymerisations with complexes **5a** and **5b**[a]

Catalyst	Activator[b]	*T*/°C	*t*/min	Polymer yield/g	Productivity[c]	M_w	M_w/M_n
5a	**I**	0	3.5	0.144	98.7	201	3.5
5a	**I**	20	5	0.132	63.3	181	4.7
5a	**I**	60	10	0.190	45.6	77.3	7.6
5a	**II**	0	10	0.284	68.1	1230	68
5a	**II**	20	5	0.138	66.2	1060	27
5b	**I**	20	4	0.201	120.6	115	5.7
5b	**I**	60	10	0.062	15	316	17
5b	**II**	0	10	0.163	39.1	312	6.5
5b	**II**	20	10	0.114	27	247	8.5

[a] Conditions: 25 µmol of catalyst, 25 µmol of activator, 20 cm^3 of toluene, ethene 1 bar. [b] **I**, $B(C_6F_5)_3$; **II**, $[CPh_3][B(C_6F_5)_4]$. [c] In 10^3 g polyethene (mol M)$^{-1}$ h^{-1}.

Table 7 Analytical data of zirconium and hafnium diene and dienyl complexes

			Analysis* (%)		
Complex	Colour	Yield (%)	C	H	Cl
1a $[ZrCl(Me_2C_4H_4)Cp'']$	Violet	58	48.9 (48.8)	7.8 (7.5)	8.6 (8.5)
1b $[HfCl(Me_2C_4H_4)Cp'']$	Orange	81	40.1 (40.4)	6.4 (6.2)	7.1 (7.0)
2a $[ZrCl(MeC_4H_5)Cp'']$	Violet	72	47.1 (47.6)	6.8 (7.2)	8.7 (8.5)
2b $[HfCl(MeC_4H_5)Cp'']$	Orange	80	39.5 (39.1)	6.2 (6.0)	7.2 (7.2)
3 $[Zr(Me_2C_4H_3)Cp'']_2$	Deep red	38	53.2 (53.4)	7.8 (7.9)	
5a $[Zr(C_3H_5)(Me_2C_4H_4)Cp'']$	Red	83	56.1 (56.7)	9.3 (8.6)	
5b $[Hf(C_3H_5)(Me_2C_4H_4)Cp'']$	Yellow	76	47.3 (46.9)	7.4 (7.1)	
6a $[Zr(C_3H_5)(MeC_4H_5)Cp'']$	Red	80	52.6 (52.7)	8.3 (8.4)	
6b $[Hf(C_3H_5)(MeC_4H_5)Cp'']$	Yellow	83	45.3 (45.9)	7.2 (6.9)	
7 $[Zr(C_4H_7)(C_4H_6)Cp'']$	Purple	87	52.3 (52.7)	8.2 (8.4)	
8b $[Hf(C_3H_5)\{Me_2C_4H_4B(C_6F_5)_3\}Cp'']\cdot 0.5C_6H_5Me$	Pale yellow	83	47.0 (46.7)	3.6 (3.8)	
9a $[Zr(C_3H_5)\{MeC_4H_5B(C_6F_5)_3\}Cp'']\cdot C_6H_5Me$	Yellow	89	52.8 (52.1)	4.4 (4.1)	
12a $[Zr\{MeC_4H_4B(C_6F_5)_2\}(C_6F_5)Cp'']$	Red	92	46.5 (46.4)	3.3 (3.2)	

* Required values given in parentheses.

agostically bonded CH_2B moiety. Their stability and propensity towards C–H activation and decomposition depends crucially on the steric requirements of the ligand sphere and particularly on the substituents R. Unlike related bis(cyclopentadienyl) complexes, these monocyclopentadienyl compounds are able to undergo facile C–H activation and rearrangement reactions which provide a novel catalyst deactivation pathway. The sensitivity of these reactions to mainly steric ligand influences illustrates the importance of detailed reactivity studies for the understanding of activity, lifetime and ligand design requirements in potential catalysts.

Experimental

General procedures

All manipulations were performed under dried nitrogen using Schlenk techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether, thf), sodium–potassium alloy (light petroleum, b.p. 40–60 °C) and CaH_2 (CH_2Cl_2). Deuteriated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. The compounds $[MCl_3Cp'']$ (M = Zr or Hf) were prepared according to published procedures;[28] 2,3-dimethylbuta-1,3-diene and isoprene were purchased from Aldrich and distilled immediately before use. The NMR spectra were recorded on a Bruker DPX300 spectrometer; ^{1}H spectra are referenced to the residual solvent protons, ^{19}F (282.2 MHz) is relative to $CFCl_3$, ^{11}B (96.2 MHz) relative to $BF_3\cdot OEt_2$. Elemental analyses are given in Table 7.

Preparation of $[ZrCl(C_4H_4Me_2\text{-}2,3)Cp'']$ 1a

A solution of $[ZrCl_3Cp'']$ (6 g, 14.7 mmol) and 2,3-dimethylbuta-1,3-diene (1.8 cm^3, 15.9 mmol) in thf (80 cm^3) was stirred with 1% Na–Hg (0.74 g, 32.3 mmol) at room temperature for 16 h. The solvent was removed and the brown-purple residue extracted several times with hot light petroleum. Concentration and cooling of this solution to −20 °C gave **1a** as a violet solid (3.58 g, 58%).

Preparation of $[HfCl(C_4H_4Me_2\text{-}2,3)Cp'']$ 1b

A solution of $[HfCl_3Cp'']$ (7.5, 15.1 mmol) and 2,3-dimethylbuta-1,3-diene (1.8 cm^3, 16 mmol) in thf (80 cm^3) was stirred with 1% Na–Hg (0.77 g, 33.4 mmol) at room temperature for 16 h. The thf was pumped off and the resultant orange solid extracted with toluene. Concentration and cooling at −20 °C gave an orange solid **1b** (6.51 g, 81%).

Preparation of $[MCl(C_4H_5Me\text{-}2)Cp'']$ (M = Zr 2a or Hf 2b)

Following the method described for **1a**, **2a** and **2b** were prepared as violet and orange solids in 72 and 80% yield, respectively.

Preparation of $[Zr(\mu\text{-}\eta^1:\eta^4\text{-}C_4H_3Me_2\text{-}2,3)Cp'']_2$ 3

A solution of $[ZrCl_3Cp'']$ (3 g, 7.4 mmol) and 2,3-dimethylbuta-1,3-diene (0.84 cm^3, 7.4 mmol) in thf (50 cm^3) was stirred at room temperature with a two-fold excess of 1% Na–Hg (86 g, 37 mmol) for 24 h. After removal of the solvent the dark brown oil was extracted with light petroleum (3 × 20 cm^3). The filtrate was concentrated to 10 cm^3 and cooled at −20 °C to give **3** as a deep red solid (2.1 g, 38%).

Preparation of $[ZrMe(C_4H_4Me_2\text{-}2,3)Cp'']$ 4a

To a suspension of **1a** (1.0 g, 2.4 mmol) in diethyl ether at −78 °C was added MeLi in diethyl ether (1.4 M, 1.8 cm^3, 2.4 mmol). The reaction mixture was allowed to warm to −20 °C and stirred for 3 h. After removal of the solvent the residue was extracted with light petroleum (30 cm^3). The resultant red solution was taken to dryness to give a red solid, **4a** (0.77 g, 81%).

Preparation of [HfMe($C_4H_4Me_2$-2,3)Cp″]

Following the method given for **4a**, **4b** was prepared giving a spectroscopically pure yellow oil.

Preparation of [Zr(C_3H_5)($C_4H_4Me_2$-2,3)Cp″] 5a

Into a solution of **1a** (2.0 g, 4.8 mmol) in thf (30 cm^3) at −78 °C was injected 2.4 cm^3 of a 2.0 M solution of C_3H_5MgCl in diethyl ether. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed and the residue extracted with light petroleum (3 × 20 cm^3). The filtrate was concentrated and left to crystallize at −20 °C to give a red crystalline material **5a** (1.68 g, 83%).

The other allyl complexes **5b**, **6a** and **6b** were prepared similarly. All of these compounds were obtained in 76–83% yields and gave satisfactory elemental analyses.

Preparation of [Zr(C_4H_7)(C_4H_6)Cp″] 7

A solution of [$ZrCl_3$Cp″] (3.85 g, 9.3 mmol) in 30 cm^3 of thf was added to a solution of C_4H_7MgCl (0.13 M, 218 cm^3, 28.4 mmol) in thf at 0 °C. The solution was allowed to warm to room temperature and stirred for 5 h. After removal of the thf, the residue was extracted with light petroleum (2 × 50 cm^3). The combined extracts were concentrated and cooled overnight to −20 °C to give **7** (3.32 g, 87%).

Preparation of [Hf(η^3-C_3H_5){η^3-$CH_2CMeCMeCH_2B$-$(C_6F_5)_3$}Cp″] 8b

To a solution of **5b** (1.5 g, 2.93 mmol) in toluene (50 cm^3) at −78 °C was added $B(C_6F_5)_3$ (1.51 g, 2.93 mmol) in toluene (20 cm^3). The reaction mixture was stirred at this temperature for 1 h and then allowed to warm to ambient temperature. The colour changed instantaneously from orange to pale yellow. Concentration to 20 cm^3 followed by cooling to −20 °C afforded **8b** as a pale yellow crystalline solid (2.6 g, 83%). ^{11}B-{^{1}H} NMR (−30 °C): δ −13.0.

Preparation of [Zr(η^3-C_3H_5){η^3-$CH_2CMeCHCH_2B(C_6F_5)_3$}Cp″] 9a

A solution of $B(C_6F_5)_3$ (2.5 g, 4.9 mmol) in toluene (30 cm^3) at −78 °C was added to a solution of **6a** (2 g, 4.88 mmol) in toluene (20 cm^3), also at −20 °C. The mixture was stirred at this temperature for 2 h during which a large quantity of microcrystalline yellow solid precipitated. Concentration and cooling to −20 °C afforded **9a** (4.4 g, 89%). ^{11}B-{^{1}H} NMR (−40 °C): δ −12.1.

Generation of [Hf(η^3-C_3H_5){η^3-$CH_2CMeCHCH_2B(C_6F_5)_3$}Cp″] 9b

To a solution of **6b** (40 mg, 0.08 mmol) in [$^2H_8$]toluene (0.3 cm^3) at −40 °C was added $B(C_6F_5)_3$ (42 mg, 0.08 mmol) in [$^2H_8$]toluene (0.3 cm^3). The colour changed instantaneously from bright to pale yellow. The conversion is 100% by ^{1}H NMR spectroscopy. ^{11}B-{^{1}H} NMR (0 °C): δ −12.5.

Generation of [Zr(η^3-C_4H_7){η^3-$CH_2CHCHCH_2B(C_6F_5)_3$}Cp″] 10

This compound is thermally sensitive and was therefore generated in solution and characterised spectroscopically. To a solution of **7** (42 mg, 0.1 mmol) in [$^2H_8$]toluene (0.3 cm^3) at −60 °C was added $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in [$^2H_8$]toluene (0.2 cm^3). The orange solution contained **10**, besides **11**. ^{11}B-{^{1}H} NMR (−60 °C): δ −12.6.

Generation of [Cp″Zr(C_6F_5){η^3-$CH_2CHCHCHB(C_6F_5)_2$}] 11

The compound was generated *in situ* from **7** and $B(C_6F_5)_3$ (1 equivalent) by warming a solution in [$^2H_8$]toluene from −60 °C to room temperature. The conversion is 100% by ^{1}H NMR spectroscopy. ^{11}B-{^{1}H} NMR (20 °C): δ 43.0.

Preparation of [Cp″Zr(C_6F_5){η^3-$CH_2CMeCHCHB(C_6F_5)_2$}] 12a

An orange solution of **9a** (2.3 g, 2.27 mmol) in toluene (100 cm^3) was stirred at ambient temperature for 20 h during which time the solution turned red. The solvent was removed under vacuum and the residue extracted with diethyl ether (50 cm^3). Concentration to 10 cm^3 and cooling to −20 °C yielded **12a** as a red microcrystalline solid (1.85 g, 92%). ^{11}B-{^{1}H} NMR (20 °C): δ 41.

Preparation of [Cp″Hf(C_6F_5){η^3-$CH_2CMeCHCHB(C_6F_5)_2$}] 12b

This compound was generated *in situ* and characterised spectroscopically. To a solution of **6b** (40 mg, 0.08 mmol) in [$^2H_8$]toluene (0.3 cm^3) at −40 °C was added $B(C_6F_5)_3$ (42 mg, 0.08 mmol) in [$^2H_8$]toluene (0.3 cm^3). The solution was left at room temperature for 5 h. The final orange solution contained **12b**, besides further unknown decomposition compounds. ^{11}B-{^{1}H} NMR (20 °C): δ 44.

General procedure for ethene polymerisation

A magnetically stirred 50 cm^3 reactor was flame dried *in vacuo* prior to being charged with 20 cm^3 of dry and degassed toluene. The solvent was heated to the desired polymerisation temperature and allowed to saturate with ethene at 1 bar of pressure. Aliquots of toluene solutions of the organometallic catalyst were injected, followed by a solution of activator in toluene. There was an immediate colour change, accompanied by monomer consumption. The pressure was maintained at 1 bar throughout. The reaction was terminated by injecting 2 cm^3 of methanol. The contents of the reactor were poured into methanol; the collected polymer was washed with methanol and dried at 60–80 °C for 24 h. Molecular weight determinations and NMR analysis were carried out on ‘as-prepared’ polymer samples without fractionation.

X-Ray crystallography

Data for **5a** and **5b** were collected at 150 K on a Delft Instruments FAST TV-area detector diffractometer positioned at the window of a rotating anode generator and following previously described procedures.[29] Data for **8b** were collected at 160 K on a Stoe STADI4 diffractometer operating in the ω–θ scan mode. All three data sets were collected using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Full details of crystal data, data collection and structure refinement are given in Table 3.

The structures of all three compounds were solved by standard heavy-atom methods using SHELXS 86.[30] The asymmetric unit of **8b** was found to contain a half molecule of toluene disordered across the centre of symmetry at $(1 - x, -y, 1 - z)$. Refinement, by full-matrix least squares on F^2 using SHELXL 93,[31] was essentially the same for all three compounds. Non-hydrogen atoms (including those of the toluene solvate molecule of **8b**) were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised positions using a riding model (with free rotation for methyl groups) with the exception of the hydrogen atoms attached to atoms C(6), C(9), C(10) and C(12) of all three complexes which were all located on Fourier-difference syntheses and freely refined with isotropic displacement parameters.

CCDC reference number 186/605.

Acknowledgements

We thank Professor M. B. Hursthouse (EPSRC National Crystallographic Service, University of Wales, Cardiff) for the collection of two X-ray data sets. G. J. P. thanks the Spanish Ministry for Education and Science for a research fellowship.

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Received 9*th May* 1997; *Paper* 7/03192K