Unexpected reactions of pentafluorophenyl boron compounds with η-cyclopentadienyl(benzamidinato)zirconium derivatives †

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The compounds $[Zr(\eta\text{-}C_5R_5)\{\eta\text{-}CPh(NSiMe_3)_2\}R'_2]$ (R = H, R' = Me or CH_2Ph; R = Me, R' = Me) reacted with $[Ph_3C][B(C_6F_5)_4]$ giving $[\{Zr(\eta\text{-}C_5H_5)[\eta\text{-}CPh(NSiMe_3)_2]\}_2(\mu\text{-}Cl)][BX(C_6F_5)_3]_2$ [R = H, X = Me or CH_2Ph; R = Me, X = C_6F_5 (crystal structure)]. Treatment of $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}Me_2]$ with $B(C_6F_5)_3$ gave $[(C_6F_5)\{\eta\text{-}(Me_3SiN)_2PhC\}(\eta\text{-}C_5H_5)Zr(\mu\text{-}Me)B(C_6F_5)_3]$ (crystal structure). The compound $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}(CH_2Ph)_2]$ with $B(C_6F_5)_3$ in benzene or dichloromethane gave $[Zr^{III}(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}L][B(CH_2Ph)(C_6F_5)_3]$ (L = C_6H_6 or CH_2Cl_2).

It is well established that the catalytic activity of bent d^0 zirconocene compounds is associated with the so-called 'base free' cations of general formulation $[Zr(\eta\text{-}C_5H_5)_2R]^+[A]^-$, where R = alkyl and A^- is a non- or weakly co-ordinating anion such as $[BPh_4]^-$ or $[B(C_6F_5)_4]^-$.[1] These bent metallocene derivatives of the Group 4 metals are the most extensively studied class of homogeneous catalysts for α-olefin polymerisation.[2] Relatively little attention has been paid to mono(cyclopentadienyl) and non-cyclopentadienyl derivatives.[3] Jordan and co-workers[4] have studied d^0 cationic compounds $[ML(R)]^+$ (L = N_4 macrocycle) which have analogy with the metallocene system.[5] We have recently described the synthesis of neutral mixed-ligand η-cyclopentadienyl–benzamidinato complexes $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}X_2]$ (X = Cl or Me) because the hard basic benzamidinate ligand, which acts as a formal three-electron donor, would present substantially different electronic and steric properties at the zirconium centre compared with those of the $[Zr(\eta\text{-}C_5H_5)_2X_2]$ compounds.[6,7] Here we describe further studies of $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}X_2]$ compounds which were initially concerned with attempts to prepare base-free cationic cyclopentadienyl–benzamidinato zirconium alkyl derivatives, namely $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}R]^+A^-$. A preliminary account of part of this work has been published.[8]

Results and Discussion

Treatment of the previously reported[6,7] compounds $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}R_2]$ (R = Me **1** or CH_2Ph **2**) or $[Zr(\eta\text{-}C_5Me_5)\{\eta\text{-}CPh(NSiMe_3)_2\}Me_2]$ **3** with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 at −40 °C gave orange microcrystalline solids of $[\{Zr(\eta\text{-}C_5H_5)[\eta\text{-}CPh(NSiMe_3)_2]\}_2(\mu\text{-}Cl)_2][BR(C_6F_5)_3]_2$ (R = Me **4** or CH_2Ph **5**) or $[\{Zr(\eta\text{-}C_5Me_5)[\eta\text{-}CPh(NSiMe_3)_2]\}_2(\mu\text{-}Cl)_2][B(C_6F_5)_4]_2$ **6**, respectively. The analytical and spectroscopic data which characterise compounds **4–6** and all the other new compounds described in this work are given in Table 1.

The crystal structure of compound **6** has been determined. Crystals suitable for X-ray determination were grown by slow cooling of a CH_2Cl_2 solution of **6** at −40 °C. The molecular structure is shown in Fig. 1 and selected distances and angles are listed in Table 2. The molecular structure shows discrete dinuclear units in which the pairs of zirconium atoms are bridged by two chlorine atoms. Each Zr atom is in a distorted-tetrahedral environment chelated by a η-cyclopentadienyl, a benzamidinate and two bridging chloride ligands. A similar
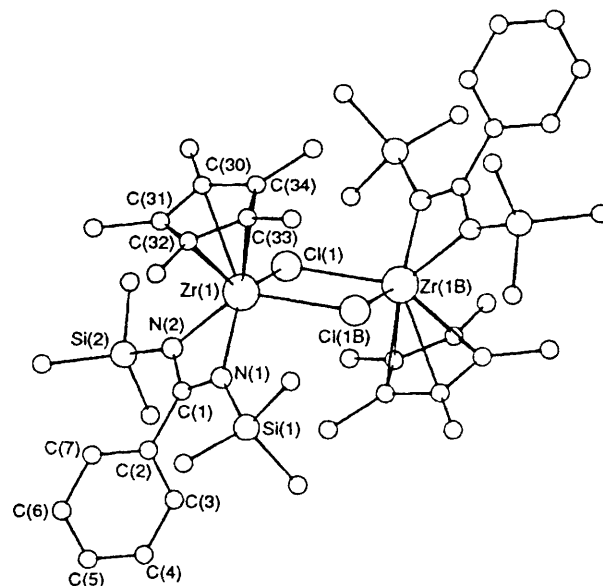
† Non-SI units employed: G = 10^{-4} T, atm = 101 325 Pa.

Fig. 1 Molecular structure of $[\{Zr(\eta\text{-}C_5Me_5)[\eta\text{-}CPh(NSiMe_3)_2]\}_2$-$(\mu\text{-}Cl)_2][B(C_6F_5)_4]_2$ **6**. The molecule lies across a crystallographic inversion centre. Atoms labelled B are related to their counterparts by the symmetry operator $-x$, $-y$, $-z$. Hydrogen atoms are omitted for clarity

$Zr(\mu\text{-}Cl)_2Zr$ moiety is suggested in $[\{Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)\}_2]^{2+}$·$2BF_4^-$.[9] The Cp(centroid)–Zr distance for **6** (2.181 Å) compares well with values observed for other pentamethyl-cyclopentadienylzirconium(IV) structures.[10,11] The Zr–Cl bond lengths of 2.552(1) and 2.563(1) Å and the Cl–Zr–Cl angle of 80.70(4)° are longer and smaller respectively than those found for neutral derivatives $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}$-$Cl_2]$ [2.421(1) and 2.422(1) Å, 90.95(4)°],[6] $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cl_2]$ [2.442(1) Å, 97.78(5)°][11] and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ (2.446 Å, 97.1°).[12] The Zr–N bond distances of 2.179(3) and 2.169(3) Å are short compared with other neutral mixed cyclopentadienyl–benzamidinate zirconium derivatives[6,7] but are similar to those in $[\{Zr[\eta\text{-}CPh(NSiMe_3)_2]Cl_3\}_2]$ [2.189(3) and 2.140(3) Å].[13] The four-membered rings ZrN_2C of **6** are slightly puckered with a dihedral angle between N(1)–Zr(1)–N(2) and N(1)–C(1)–N(2) of 4.51°. The geometry of the Zr_2Cl_2 core is planar and the Zr(1) ··· Zr(1B) distance of 3.898(1) Å is longer than found for $[\{Zr(\eta\text{-}C_5H_5)_2S\}_2]$ [3.529(2) Å][14] or $[\{Zr(\eta\text{-}C_5H_5)_2I\}_2]$ [3.649(1) Å][15] which excludes a metal–metal bond.

The compounds **4–6** are thermally stable but moisture sensitive and insoluble in aromatic and aliphatic hydrocarbons.

Table 1 Analytical and spectroscopic data [a]

Compound	Spectroscopic data
4 Orange C, 45.45 (45.2); H, 2.7 (3.2); Cl, 3.1 (3.6); N, 2.1 (2.85)	^{1}H (233 K):[b] 6.79 (5 H, s, C_5H_5), 0.49 (3 H, s, BCH_3), −0.03 (2 × 9 H, s, $SiMe_3$)[c] ^{13}C (233 K):[b] 174.1 [$CPh(NSiMe_3)_2$], 147.8 (C_o, C_6F_5, J_{CF} = 225.6), 137.0 (C_p, C_6F_5, J_{CF} = 250.3), 135.4 (C_{ipso}, C_6H_5), 136.0 (C_m, C_6F_5, J_{CF} = 248.0),[d] 130.1 (C_6H_5), 126.2 (C_6H_5),[c] 119.3 (C_5H_5), 10.4 (BCH_3), 1.1 ($SiMe_3$) ^{11}B (244 K):[b] −15.3 ^{19}F (200 K):[b] −133.3 (F_o, C_6F_5), −163.8 (F_p, C_6F_5), −166.5 (F_m, C_6F_5)
5 Orange C, 48.5 (48.8); H, 2.9 (3.3); Cl, 3.0 (3.35); N, 2.5 (2.65)	Identical signals to **4** for the free cation. Free anion: ^{1}H (293 K)[b] 6.91 (2 H, d, J_{HH} = 7.4), 2.88 (2 H, br, BCH_2Ph) ^{13}C (233 K)[b] 148.9 (C_{ipso}, $BCH_2C_6H_5$), 148.3 (C_o, C_6F_5, J_{CF} = 246.2), 142.2 (C_{ipso}, C_6F_5), 137.6 (C_p, C_6F_5, J_{CF} = 246.8), 136.4 (C_m, C_6F_5, J_{CF} = 249.2), 122.5 (C_p, $BCH_2C_6H_5$);[c] ^{11}B (293 K):[b] − 13.1
6 Bright yellow C, 46.9 (46.85);; H, 3.3 (3.2); Cl, 2.7 (2.9); N, 2.4 (2.3)	^{1}H (233 K):[b] 7.54 (m, C_6H_5),[e] 2.26 (15 H, s, C_5Me_5), −0.03 (2 × 9 H, s, $SiMe_3$) ^{13}C (253 K):[b] 185.1 [$CPh(NSiMe_3)_2$], 148.0 (C_o, C_6F_5, J_{CF} = 240.7), 138.1 (C_p, C_6F_5, J_{CF} = 243.5), 136.9 (C_m, C_6F_5, J_{CF} = 246.4), 127.1 (C_5Me_5), 123.5 (C_{ipso}, C_6F_5), 12.4 (C_5Me_5), 2.6 ($SiMe_3$)[c] ^{11}B (253 K):[b] −17.1
7 Yellow solution	^{1}H (293 K):[d] 6.99 (5 H, br, C_6H_5), 6.59 (5 H, br, C_5H_5), 1.43 (3 H, Br, MeB), −0.42 (2 × 9 H, br, $SiMe_3$) ^{13}C (293 K):[c] 181.7 [$CPh(NSiMe_3)_2$], 117.9 (C_5H_5), 23.8 (MeB), 1.4 ($SiMe_3$)
8 Yellow C, 46.9 (46.35); H, 3.1 (2.8); N, 2.6 (2.5)	^{1}H (293 K):[d] 7.10–6.80 (5 H, m, C_6H_5), 6.50 (5 H, s, C_5H_5), 1.48 (3 H, br, MeB), −0.57 (2 × 9 H, s, $SiMe_3$); (293 K):[b] 7.57–7.30 (5 H, m, C_6H_5), 7.10 (5 H, s, C_5H_5), 1.09 (3 H, br, MeB), −0.26 (2 × 9 H, s, $SiMe_3$) ^{13}C (233 K):[b] 182.0 [$CPh(NSiMe_3)_2$], 148.1 (C_o, C_6F_5, J_{CF} = 234.9), 138.4 (C_p, C_6F_5, J_{CF} = 245.6), 136.6 (C_m, C_6F_5, J_{CF} = 255.5), 119.1 (C_5H_5), 1.3 ($SiMe_3$)[e] ^{11}B (293 K):[d] −14.0 ^{19}F (211 K):[b] 132.2 (1 F_o), 133.7 (6 F_o), 150.1 (1 F_p), 157.8 (1 F_o), 160.3 (3 F_p), 164.0 (1 F_m), 164.9 (6 F_m), 166.7 (1 F_m)
9 Violet C, 53.6 (53.4); H, 4.15 (3.7); N, 2.45 (2.5)	Paramagnetic EPR:[b] g 1.98 (9 G)
10 Dark red solution	^{1}H (244 K):[b] 7.47–6.65 (14 H, m, C_6H_5), 6.19 (5 H, s, C_5H_5), 5.56 (1 H, d, J_{HH} = 7.71, H_o of C_6H_5), 3.79 (2 H, s, $ZrCH_2Ph$), 2.82 (2 H, br, BCH_2Ph), −0.06 (2 × 9 H, s, $SiMe_3$) ^{13}C (244 K):[b] 183.5 [$CPh(NSiMe_3)_2$], 148.3 (C_{ipso}, $BCH_2C_6H_5$), 147.7 (C_o, C_6F_5, J_{CF} = 236.8), 137.4 (C_{ipso}, $ZrCH_2C_6H_5$), 137.2 (C_p, C_6F_5, J_{CF} = 242.9), 136.9 (C_{ipso}, C_6H_5), 136.1 (C_m, C_6F_5, J_{CF} = 248.0),[d] 133.3 (C_m, $ZrCH_2C_6H_5$), 130.0 (C_6H_5), 128.4 (C_o, $BCH_2C_6H_5$), 128.0 (C_6H_5), 127.0 (C_6H_5), 126.7 (C_m, $BCH_2C_6H_5$), 125.1 (C_p, $ZrCH_2C_6H_5$), 122.3 (C_p, $BCH_2C_6H_5$), 117.9 (C_o or C_m, $ZrCH_2C_6H_5$), 109.6 (C_5H_5), 113.5 (C_o or C_m, $ZrCH_2C_6H_5$), 102.6 (C_o, $ZrCH_2C_6H_5$), 85.3 ($ZrCH_2C_6H_5$), 31.3 ($BCH_2C_6H_5$), 2.2 ($SiMe_3$) ^{11}B (244 K):[b] −13.2
11 Violet C, 48.1 (47.7); H, 3.9 (3.3); N, 2.6 (2.5)	Paramagnetic

[a] Analytical data given as found (calculated) %; the data for complex **4** are poor due to its extreme sensitivity. ^{1}H NMR at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 282.2 MHz relative to CFCl$_3$ and ^{11}B relative to BF$_3$·OEt$_2$ at 96.2 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (in Hz) and assignment. [b] In [^{2}H$_2$]dichoromethane. [c] Rest of the signals overlapping with those of MeCPh$_3$ or PhCH$_2$CPh$_3$. [d] In [^{2}H$_6$]benzene. [e] C_{ipso} obscured.

Table 2 Selected bond lengths (Å) and angles (°) for [{Zr(η-C_5Me_5)-[η-CPh(NSiMe$_3$)$_2$]}$_2$(μ-Cl)$_2$][B(C$_6$F$_5$)$_4$]$_2$ **6** with estimated standard deviations (e.s.d.s) in parentheses

Zr(1)–Cl(1)	2.552(1)	Zr(1)–C(1)	2.555(4)
Zr(1)–Cl(1B)	2.563(1)	Zr(1) ··· Zr(1B)	3.898(1)
Zr(1)–N(1)	2.179(3)	Zr(1)–Cp	2.181
Zr(1)–N(2)	2.169(3)		
Cl(1B)–Zr(1)–N(2)	132.6(1)	Zr(1)–N(1)–C(1)	90.0(2)
N(1)–Zr(1)–N(2)	63.4(1)	Zr(1)–N(2)–C(1)	89.9(2)
Cl(1B)–Zr(1)–C(1)	114.06(9)	N(1)–C(1)–N(2)	116.5(3)
Cl(1B)–Zr(1)–C(1)	111.29(9)	Zr(1)–C(1)–C(2)	177.1(3)
Zr(1)–Cl(1)–Zr(1B)	99.30(4)	Cp–Zr(1)–Cl(1)	109.80
Cl(1)–Zr(1)–Cl(1B)	80.70(4)	Cp–Zr(1)–Cl(1B)	109.96
Cl(1)–Zr(1)–N(1)	133.2(1)	Cp–Zr(1)–Zr(1B)	116.49
Cl(1B)–Zr(1)–N(1)	88.26(9)	Cp–Zr(1)–Cl(1)	123.09
Cl(1)–Zr(1)–N(2)	91.7(1)		

Cp refers to the computed η^5-C_5Me_5 ring centroid.

They are soluble in CH$_2$Cl$_2$ but these solutions decompose at room temperature over 24 h giving the corresponding neutral dichlorides [Zr(η-C$_5$R$_5$){η-CPh(NSiMe$_3$)$_2$}Cl$_2$] in near-quantitative yields. The ^{1}H and ^{13}C NMR spectra (see Table 1) show signals corresponding to the free anions and for the C$_5$R$_5$ rings lower-field resonances than for the corresponding neutral [Zr(η-C$_5$R$_5$){η-CPh(NSiMe$_3$)$_2$}Cl$_2$] where, for R = H, δ 6.41

and 115.7 and for R = Me, δ = 2.12 and 126.1.[6] These shifts are consistent with a higher electron deficiency on the metal centre in the dications of **4–6**. A striking feature in the formation of compounds **4** and **5** is the observation of the counter anions [BMe(C$_6$F$_5$)$_3$]$^-$ and [B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ respectively which shows that the [B(C$_6$F$_5$)$_4$]$^-$ anion has a key role in the formation of the cation [{Zr(η-C$_5$H$_5$)[η-CPh(NSiMe$_3$)$_2$]}$_2$(μ-Cl)$_2$]$^{2+}$. The reactions giving **4** and **5** were monitored by NMR spectroscopy and showed the formation of the compounds Ph$_3$CMe or Ph$_3$CCH$_2$Ph respectively but, even at −80 °C, provided no evidence for the formation of zirconium–alkyl bonds assignable to the cations [Zr(η-C$_5$R$_5$){η-CPh(NSiMe$_3$)$_2$}R′]$^+$ which might be expected as intermediates.

An alternative approach to the cations [Zr(η-C$_5$H$_5$){η-CPh(NSiMe$_3$)$_2$}R]$^+$ (R = Me or CH$_2$Ph) via reaction of **1** or **3** with the neutral B(C$_6$F$_5$)$_3$ was investigated. Treatment of **1** with 1 equivalent of B(C$_6$F$_5$)$_3$ in benzene gave bright yellow crystals of [(C$_6$F$_5$){η-(Me$_3$SiN)$_2$PhC}(η-C$_5$H$_5$)Zr(μ-Me)B(C$_6$F$_5$)$_3$] **8** in which the presence of a pentafluorophenyl group attached to the Zr atom was certainly not anticipated. Compound **8** is sparingly soluble in aromatic solvents but soluble and stable in chlorinated solvents at low temperature.

The crystal structure of complex **8** has been determined and the molecular structure is shown in Fig. 2. The Zr–Me bond length and the almost linear angle Zr–Me–B (Table 3) are
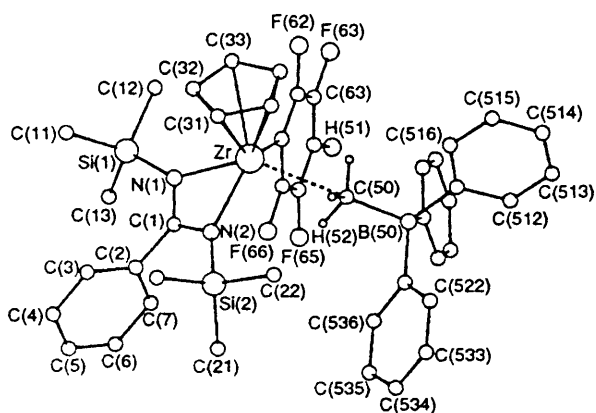
Fig. 2 Molecular structure of [(C₆F₅){η-(Me₃SiN)₂PhC}(η-C₅H₅)Zr(μ-Me)B(C₆F₅)₃] **8**. All hydrogen atoms except those of the bridging methyl group omitted for clarity as are the fluorine atoms of the B(C₆F₅)₃ groups

Table 3 Selected bond lengths (Å) and angles (°) for [(C₆F₅)-{η-(Me₃SiN)₂PhC}(η-C₅H₅)Zr(μ-Me)B(C₆F₅)₃] **8** with e.s.d.s in parentheses

Zr–N(1)	2.178(9)	N(2)–C(1)	1.33(1)
Zr–N(2)	2.177(9)	C(1)–C(2)	1.50(1)
Zr–C(1)	2.55(1)	N(1)–Si(1)	1.789(9)
Zr–C(61)	2.329(8)	N(2)–Si(2)	1.77(1)
Zr–C(50)	2.62(1)	C(50)–B(50)	1.67(2)
Zr–H(51)	2.48(9)	B(50)–C(511)	1.65(2)
Zr–H(52)	2.44(9)	B(50)–C(521)	1.68(1)
Zr–H(53)	2.60(8)	B(50)–C(531)	1.65(1)
N(1)–C(1)	1.32(1)	Zr–Cp	2.183
N(1)–Zr–N(2)	62.4(3)	Zr–C(50)–B(50)	166.0(8)
C(61)–Zr–C(50)	83.3(3)	C(50)–B(50)–C(511)	115.2(9)
Zr–N(1)–C(1)	90.1(7)	C(50)–B(50)–C(521)	106.7(9)
Zr–N(2)–C(1)	90.0(6)	C(50)–B(50)–C(531)	104.4(9)
N(1)–C(1)–N(2)	116.5(10)	Cp–Zr–C(61)	114.79
Zr–C(1)–C(2)	170.1(7)	Cp–Zr–C(50)	109.19

Cp refers to the computed η⁵-C₅Me₅ ring centroid.

comparable to those of related M–Me–B systems in the compounds [Zr(η-1,2-Me₂C₅H₃)₂Me][BMe(C₆F₅)₃] [2.549(3) Å. 161.8(2)°] [16] and [Zr{η-1,2-(Me₃Si)₂C₅H₃}₂Me]-[BMe(C₆F₅)₃] [2.667(5) Å, 170.5(3)°]. [17] The hydrogens of the bridging methyl group were located and two have relatively close contacts to the zirconium atom with similar distances to those found in the cation [Zr{η-1,2-(Me₃Si)₂C₅H₃}₂Me]⁺ [2.47(3) and 2.44(3) Å]. [17] The third one seems to afford a non-bonding interaction. This suggests the presence of weak α-agostic interactions. There is no evidence for Zr–F–C_{ortho} interactions involving the Zr–C₆F₅ group, as shown by the distances Zr ··· F_{ortho} [2.911(7) and 3.797(7) Å] and C–F_{ortho} [1.352(7) and 1.356(7) Å] compared to those found in the compounds [Zr(η-C₅Me₅)₂H][BH(C₆F₅)₃] [Zr–F_o 2.416(3) Å and C–F_o 1.396(5) Å] [18] and [(η-C₅Me₅)₂Zr(μ-O)B(C₆F₅)₃] [Zr–F_o 2.346(3), C–F_o 1.406(5) and C–F(average) 1.350(6) Å]. [19] The Zr–Cp distance of 2.183 Å in **8** compares well with those in [Zr(η-C₅H₅)₂Me(thf)]⁺ (thf = tetrahydrofuran) (2.174 Å) [20] or [Zr(η-C₅H₅){η-CPh(NSiMe₃)₂}Cl₂] (2.186 Å) [6b] but is appreciably shorter than those found in [Zr(η-C₅H₅)₂Me₂] (2.23 Å) [21] or [Zr(η-C₅H₅){η-CPh(NSiMe₃)₂}Me₂] (2.216 Å). [7] The four-membered ZrN₂C ring is slightly puckered, with a dihedral angle between N(1)–Zr–N(2) and N(1)–C(1)–N(2) of 10.65°. The trigonal-bipyramidal five-co-ordinated carbon system in **8** is rare. It was first observed in the compound [(η-C₅Me₅)₂Lu(μ-Me)LuMe(η-C₅Me₅)₂]. [22]

The formation of complex **8** requires transfer of a C₆F₅ group from boron to zirconium. The reaction was monitored in

C₆D₆ by NMR spectroscopy. An initial product **7** was observed but the spectrum showed no resonances assignable to a terminal ZrMe moiety. Compound **7** decomposed giving, among other things a precipitate of **8** and an unidentified brown oil. There was no evidence for the expected product, namely [Me{η-(Me₃SiN)₂PhC}(η-C₅H₅)Zr(μ-Me)B(C₆F₅)₃], which is analogous to [Me(η-C₅H₃R₂)₂Zr(μ-Me)B(C₆F₅)₃] (R = Me [16] or SiMe₃ [17]). Both **7** and **8** show in the ¹H and ¹³C NMR spectra the presence of a unsymmetrical Zr(μ-Me)B bridge, δ 1.43 and 1.48 respectively. These resonances are highly shifted downfield with respect to the Marks [16] and Bochmann [17] derivatives, indicating a high degree of electron deficiency in the benzamidinato compounds. Similar reactivity has been observed in the partial hydrogenolysis of [Me(C₅H₅)₂Zr(μ-Me)B(C₆F₅)₃] affording [H(C₅H₅)₂Zr(μ-Me)B(C₆F₅)₃] in which the methyl bridge is not apparently involved in the reaction. [18] The ¹⁹F NMR study disclosed that the structure of **8** in CD₂Cl₂ solution is essentially that established for the solid state. At −60 °C the ¹⁹F NMR spectrum displays eight resonances. Three correspond to the F atoms of the [BMe(C₆F₅)₃]⁻ fragment and the other five are attributed to the unsymmetrical C₆F₅⁻ group attached to the metal. One of the fluorine resonances that is shifted upfield by over 20 ppm from the typical region of F_o in C₆F₅ rings is assigned to the o-F of the C₆F₅⁻ ring since it is nearest the metal centre and a ¹⁹F chemical shift of δ > 50 has been observed for the compound [(C₅Me₅)₂Zr(μ-O)B(C₆F₅)₃] where both solution and solid state are in agreement with the existence of a Zr ··· F–C interaction. [19] Despite the absence of structural evidence in **8** there may be a weak Zr ··· F–C_o interaction.

Treatment of complex **2** with B(C₆F₅)₃ in benzene afforded violet paramagnetic microcrystals which, on the basis of the analytical and spectroscopic data and the chemical behaviour, we tentatively propose to be the benzene adduct [Zr^{III}(η-C₅H₅){η-CPh(NSiMe₃)₂}(C₆H₆)][B(CH₂Ph)(C₆F₅)₃] **9**. The ¹H and ¹¹B NMR spectra showed only signals corresponding to the free anion. The EPR spectrum gave a single peak [g = 1.98 (9 G)] consistent with a monomeric zirconium(III) complex. [23]

The reaction between complex **2** and B(C₆F₅)₃ was also monitored in CD₂Cl₂ at −40 °C. In this case a diamagnetic intermediate was observed which the NMR data suggest is the compound [Zr(η-C₅H₅)[η-CPh(NSiMe₃)₂](CH₂Ph)][B(CH₂-Ph)(C₆F₅)₃] **10**. The ¹H NMR spectrum at −40 °C showed signals corresponding to the free anion [B(CH₂Ph)(C₆F₅)₃]⁻, a singlet (δ 3.79) appropriate for Zr–CH₂Ph methylene protons and a doublet at an unusually high field (δ 5.56) assignable to an o-hydrogen of a benzyl group. In the ¹³C NMR spectrum resonances at δ 137.4 and 102.6 corresponding to C_{ipso} and C_o respectively also confirm the existence of a η^n-benzyl group (n > 1). [3a,24] We note that the downfield resonances of the methylene group of Zr–CH₂Ph (δ 85.3) with respect to the neutral dibenzyl derivative [Zr(η-C₅H₅){η-CPh(NSiMe₃)₂}-(CH₂Ph)₂] [7] is not ascribed to the presence of a η² co-ordination mode as found for [Zr(η-C₅H₅)₂(CH₂Ph)-(MeCN)]⁺[BPh₄]⁻. [25]

Compound **10** was only stable in solution and at low temperature and attempts to isolate it, even at low temperatures, were unsuccessful. Decomposition occurred as solvent was removed giving a new paramagnetic compound which on the basis of microanalysis and chemical behaviour is tentatively proposed to be [Zr^{III}(η-C₅H₅){η-CPh(NSiMe₃)₂}-(CH₂Cl₂)][B(CH₂Ph)(C₆F₅)₃] **11**. Solutions of both **9** and **11** in CD₂Cl₂ decomposed at room temperature giving **5** in high yields. The mechanism of formation of **9** and **11** appears to involve homolytic cleavage of a benzyl group from the intermediate **10**. Proton NMR data show that CH₃Ph and CH₂DPh were formed but there was no evidence for bibenzyl.

The reactivity of complex **10** towards the formation of paramagnetic cationic species is quite different from that of the related benzyl zirconocene [Zr(η-C₅H₅)₂(CH₂Ph)]⁺ [3a,24,26]
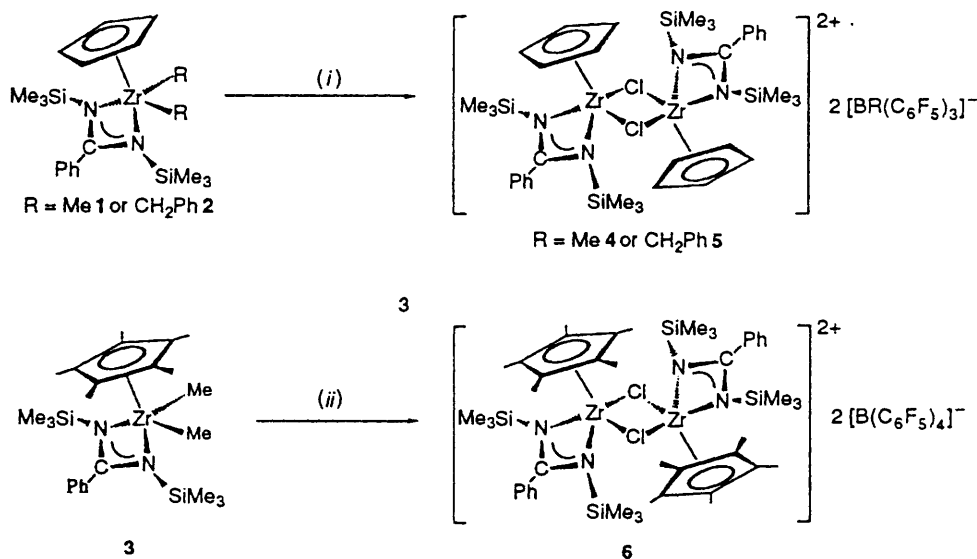
Scheme 1 (i) [Ph₃C][B(C₆F₅)₄], in CH₂Cl₂ for 30 min, −80 °C, 4 (62), 5 (71%); (ii) [Ph₃C][B(C₆F₅)₄], in CH₂Cl₂ for 30 min, −30 °C, 6 (79%)

but is comparable to that of the analogous titanocenes [Ti-(η-C₅H₅)₂(CH₂Ph)L]⁺ (L = MeCN or thf).[27] The differences between cationic zirconocene and benzamidinato compounds would be due to a greater metal electron deficiency and a higher degree of metal unsaturation.

Compound 8 is not active in polymerisation of ethene probably due to a strong Zr–C₆F₅ bond that will not undergo olefin insertion. In contrast, a mixture of 1 and B(C₆F₅)₃ does polymerise ethene [activity = 1.2 × 10⁴ (mol Zr)⁻¹ h⁻¹ atm⁻¹] where the intermediate 7 is presumably the precursor to the active species. None of the other complexes, 4–6, 9 and 11, was active for ethene polymerisation under Kaminsky conditions.[2a] A mixture of 2 and B(C₆F₅)₃ at −40 °C was not active either. The observed tendency of the [Zr(η-C₅R₅){η-CPh(NSiMe₃)₂}] to form the dimeric dication [{Zr(η-C₅H₅)[η-CPh-(NSiMe₃)₂]}₂(μ-Cl)₂]²⁺ suggests that dimer formation may account, in part, for the lack of catalytic activity.

The new reactions and the structures proposed for the new compounds are shown in Schemes 1 and 2. The mechanisms for the formation of the compounds 4–11 are not known. The anions of 4 and 5 show that the [B(C₆F₅)₄]⁻ anion is not inert and can undergo replacement of a C₆F₅ group by an alkyl group derived from a ZrR system. Similarly, the transfer in high yields of a C₆F₅ group from B(C₆F₅)₃ to zirconium occurs in the formation of 8. The formation of 10 presumably proceeds by initial cleavage of a zirconium-alkyl group by the B(C₆F₅)₃ Lewis acid. The loss of the second alkyl group giving the paramagnetic cations in 9 and 11 may proceed by loss of the alkyl radical, as indicated by the formation of toluene. The reactions of 9 and 11 with dichloromethane giving the dimeric cation 5 have parallels in the chemistry of neutral zirconium(III) complexes which afford zirconium(IV) derivatives[28] and are consistent with the existence of low oxidation states in 9 and 11. The decomposition of the expected species [Zr(η-C₅H₅){η-CPh(NSiMe₃)₂}R]⁺ via abstraction of Cl from the chlorinated solvent affording 4–6 has no precedent in the chemistry of the analogous cationic zirconocenes [Zr(η-C₅H₅)₂R]⁺ which decompose at room temperature giving neutral complexes by degradation of the anion or reaction with the solvent.[29] However, there is no obvious overall mechanistic scheme which rationalises all the different pathways implied by the observed products and further studies are in progress.

Experimental

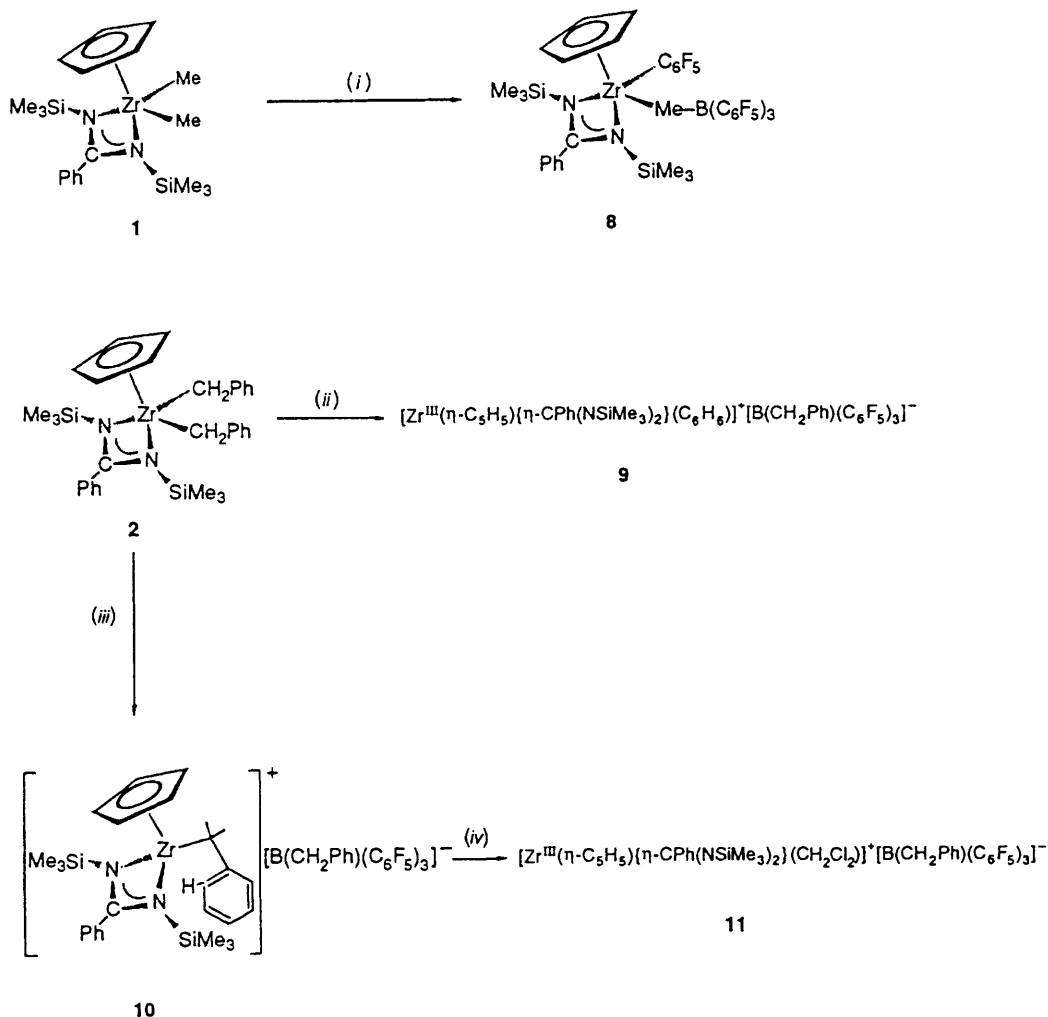All manipulations of air- and moisture-sensitive materials were performed using either standard Schlenk-line techniques under an atmosphere of argon, which had been purified by passage over BASF catalyst and 4 Å molecular sieves, or in an inert-atmosphere box containing dinitrogen unless stated otherwise. Solvents were predried by standing over 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentaoxide (dichloromethane), sodium (toluene, benzene), potassium–benzophenone (thf) or sodium–potassium alloy (1:3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents for NMR studies were stored in Young's ampoules under an atmosphere of dinitrogen over sodium–potassium alloy ([²H₆]benzene) or molecular sieves ([²H₂]dichloromethane). The NMR spectra were recorded on a Brüker AM 300 spectrometer [300 (¹H) or 75 MHz ¹³C-{¹H}] referenced internally using the residual protio solvent (¹H) or solvent (¹³C) resonances relative to tetramethylsilane (δ 0); 282.2 MHz (¹⁹F) relative to CFCl₃; 96.2 MHz (¹¹B) relative to BF₃·OEt₂; EPR spectra using an X-band Varian spectrometer and an Oxford Instruments cryostat. Elemental analyses were performed by the analytical department of this laboratory. The compounds Li[PhC(NSiMe₃)₂],[30] B(C₆F₅)₃[31] and [Ph₃C]-[B(C₆F₅)₄][32] were prepared as reported.

Preparations

[{Zr(η-C₅H₅)[η-CPh(NSiMe₃)₂]}₂(μ-Cl)₂][BMe(C₆F₅)₃]₂ 4. A mixture of complex 1 (0.2 g, 0.445 mmol) and [Ph₃C][B(C₆F₅)₄] (0.4 g, 0.434 mmol) was cooled to −78 °C and CH₂Cl₂ (30 cm³), pre-cooled to −78 °C, was added. The mixture was stirred for 15 min at −78 °C giving a bright orange solution and which was stirred at −30 °C for 1 h. The solvent was removed at −30 °C giving a brown-orange oil, which was washed with benzene (20 cm³) and then with light petroleum (2 × 15 cm³) affording complex 4 as a brown-orange solid. Yield 0.27 g (62%).

[{Zr(η-C₅H₅)[η-CPh(NSiMe₃)₂]}₂(μ-Cl)₂][B(CH₂Ph)-(C₆F₅)₃]₂ 5. A mixture of complex 2 (0.2 g, 0.332 mmol) and [Ph₃C][B(C₆F₅)₄] (0.3 g, 0.325 mmol) was cooled to −78 °C and CH₂Cl₂ (20 cm³), pre-cooled to −78 °C, was added. The mixture was stirred for 15 min at −78 °C giving a bright orange solution which was stirred at −30 °C for 1 h. The solvent was removed at −30 °C giving a brown-orange oil, which was washed with benzene (20 cm³) and then with light petroleum (2 × 15 cm³) affording complex 5 as a brown-orange solid. Yield 0.25 g (71%).

[{Zr(η-C₅Me₅)[η-CPh(NSiMe₃)₂]}₂(μ-Cl)₂][B(C₆F₅)₄]₂ 6. A mixture of complex 3 (0.25 g, 0.482 mmol) and

Scheme 2 showing chemical structures 1, 8, 2, 9, 10, 11.

$[Zr^{III}(\eta-C_5H_5)\{\eta-CPh(NSiMe_3)_2\}(C_6H_6)]^{+}[B(CH_2Ph)(C_6F_5)_3]^{-}$ **9**

$[B(CH_2Ph)(C_6F_5)_3]^{-}$ **10**

$[Zr^{III}(\eta-C_5H_5)\{\eta-CPh(NSiMe_3)_2\}(CH_2Cl_2)]^{+}[B(CH_2Ph)(C_6F_5)_3]^{-}$ **11**

Scheme 2 (*i*) B(C$_6$F$_5$)$_3$, in benzene for 48 h, room temperature (r.t.), **8** (48%); (*ii*) B(C$_6$F$_5$)$_3$, in benzene for 12 h, r.t., **9** (75%); (*iii*) B(C$_6$F$_5$)$_3$, in CD$_2$Cl$_2$, −40 °C, **10** (>95% according to NMR spectroscopy); (*iv*) in CH$_2$Cl$_2$ under vacuum, −30 °C, **11** (37%)

[Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.44 g, 0.477 mmol) was cooled to −78 °C and CH$_2$Cl$_2$ (20 cm^3), pre-cooled to −78 °C, was added. The mixture was stirred for 15 min at −78 °C and then stirred at −30 °C for 1 h. The resulting yellow solution at −40 °C was reduced in volume to *ca.* 5 cm^3 and on standing at this temperature yellow crystals of complex **6** separated. Yield 0.46 g (79%).

Intermediate 7. To an NMR tube containing complex **1** (0.054 g, 0.120 mmol) and B(C$_6$F$_5$)$_3$ (0.060 g, 0.118 mmol) was added C$_6$D$_6$ (*ca.* 0.5 cm^3) at room temperature and then sealed. The tube was allowed to stand at room temperature with occasional shaking for 15 min to afford a yellow solution of complex **7** (*ca.* 98%, NMR spectroscopy).

[(C$_6$F$_5$){η-(Me$_3$SiN)$_2$PhC}(η-C$_5$H$_5$)Zr(μ-Me)B(C$_6$F$_5$)$_3$] 8. A mixture of complex **1** (0.3 g, 0.668 mmol) and B(C$_6$F$_5$)$_3$ (0.34 g, 0.664 mmol) was dissolved in benzene (20 cm^3) at room temperature and stirred for 1 h. The yellow solution was left at room temperature for 48 h giving a slow precipitation of bright yellow microcrystals of complex **8**. Yield 0.36 g (48%).

[Zr^{III}(η-C$_5$H$_5$){η-CPh(NSiMe$_3$)$_2$}(C$_6$H$_6$)][B(CH$_2$Ph)(C$_6$F$_5$)$_3$] 9. A mixture of complex **2** (0.3 g, 0.500 mmol) and B(C$_6$F$_5$)$_3$ (0.25 g, 0.488 mmol) was dissolved in benzene (30 cm^3) at room temperature. The mixture changed quickly from orange to dark red and then to violet. The solution was allowed to stir for 12 h, resulting in a slow precipitation of complex **9** as violet crystals. Yield 0.41 g (75%).

[Zr(η-C$_5$H$_5$){η-CPh(NSiMe$_3$)$_2$}(CH$_2$Ph)][B(CH$_2$Ph)-(C$_6$F$_5$)$_3$] 10. To an NMR sample tube containing complex **2** (0.042 g, 0.070 mmol) and B(C$_6$F$_5$)$_3$ (0.035 g, 0.068 mmol) was added CD$_2$Cl$_2$ (*ca.* 0.5 cm^3) by vacuum transfer at −196 °C and then the tube was sealed. The sample was warmed to −78 °C, agitated to effect mixing of the reactants and then slowly warmed to −30 °C to give a dark red solution of **10** (95%, NMR spectroscopy).

[Zr^{III}(η-C$_5$H$_5$){η-CPh(NSiMe$_3$)$_2$}(CH$_2$Cl$_2$)][B(CH$_2$Ph)-(C$_6$F$_5$)$_3$] 11. A mixture of complex **2** (0.3 g, 0.500 mmol) and B(C$_6$F$_5$)$_3$ (0.25 g, 0.488 mmol) at −40 °C was dissolved in CH$_2$Cl$_2$ (30 cm^3), pre-cooled to −40 °C and allowed to stir for 2 h at this temperature. Volatiles of the resulting dark red solution were removed under reduced pressure. The mixture changed from red to violet and a violet solid separated. This was washed with light petroleum (20 cm^3) and recrystallized from CH$_2$Cl$_2$ (5 cm^3) at −78 °C to give complex **11** as violet microcrystals. Yield 0.17 g (37%).

Ethene polymerisation studies

Ethene was dried by passage over potassium supported on glass-wool and then 4 Å molecular sieves. Polymerisation reactions were performed in a Fischer–Porter apparatus (500 cm^3) equipped with a thermocouple and a Teflon stirrer bar. Toluene (200 cm^3) were added to the apparatus and stirred at 25 °C under ethene at a pressure of 2 bar (2 × 10^5 Pa). Solutions of B(C$_6$F$_5$)$_3$ or [Ph$_3$C][B(C$_6$F$_5$)$_4$] (2.47 × 10^{-5} mol)

Table 4 Crystal data, details of the data collection and final refinements for complexes **6** and **8** *

	6	**8**
Formula	$C_{94}H_{76}B_2Cl_2F_{40}N_4Si_4Zr_2\cdot 0.6CH_2Cl_2$	$C_{43}H_{31}B_1F_{20}N_2Si_2Zr$
M	2459.9	1113.9
Crystal size/mm	0.21 × 0.33 × 0.69	0.12 × 0.19 × 0.34
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	14.110(2)	17.363(1)
b/Å	14.8799(8)	13.0700(9)
c/Å	15.394(1)	20.265(3)
$\alpha/°$	107.533(5)	
$\beta/°$	104.255(9)	94.365(8)
$\gamma/°$	109.591(9)	
U/Å^3	2678	4586
Z	1	4
D_c/g cm^{-3}	1.60	1.61
$F(000)$	1232	2224
μ/cm^{-1}	4.48	3.98
hkl Ranges	−16 to 16, −17 to 17, −1 to 17	−19 to 19, −1 to 15, −1 to 23
ω-Scan width/°	0.80 + 0.34 tan θ	0.75 + 0.35 tan θ
Horizontal aperture/mm	2.80 + 1.05 tan θ	2.70
Total data collected	9170	8525
Total unique data	8399	7185
Total observed data [$I > 3\sigma(I)$]	6020	2976
Merging R factor	0.0108	0.0286
Minimum, maximum absorption correction	1.00, 1.03	1.00, 1.13
No. parameters	679	354
Observations/parameters	9	8.8
Weighting coefficients	14.4, 2.69, 11.6, 2.78	11.4, −13.5, 9.0, −3.0
Minimum, maximum residual peaks/e Å^{-3}	−0.50, 1.86	−0.64, 0.66
R	0.0565	0.0720
R'	0.0630	0.0795

* Details in common: Mo-Kα radiation (λ = 0.710 69 Å); ω–2θ scans; θ_{min}, θ_{max} 1.0, 24.0°; Chebychev [33] weighting scheme; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 5 Fractional atomic coordinates for complex **6** with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Zr(1)	0.632 98(3)	0.131 78(3)	0.068 58(3)	F(45)	0.616 0(3)	0.535 1(3)	0.457 8(2)
Cl(1)	0.438 71(9)	0.055 74(9)	0.061 29(9)	F(46)	0.628 2(2)	0.427 1(2)	0.565 5(2)
N(1)	0.779 5(3)	0.120 4(3)	0.140 2(3)	C(51)	0.726 3(3)	0.561 5(3)	0.894 7(3)
N(2)	0.700 1(3)	0.201 1(3)	0.228 7(2)	C(52)	0.827 1(3)	0.648 8(3)	0.947 1(3)
Si(1)	0.867 4(1)	0.061 1(1)	0.117 1(1)	C(53)	0.868 9(3)	0.709 7(3)	1.046 8(3)
Si(2)	0.674 7(1)	0.262 4(1)	0.334 30(9)	C(54)	0.809 4(3)	0.685 6(3)	1.101 8(3)
C(1)	0.778 2(3)	0.167 7(3)	0.228 3(3)	C(55)	0.709 8(4)	0.598 4(4)	1.054 5(3)
C(2)	0.859 1(3)	0.184 3(3)	0.322 3(3)	C(56)	0.671 9(3)	0.539 0(3)	0.955 1(3)
C(3)	0.839 1(4)	0.107 4(4)	0.356 4(4)	F(52)	0.890 1(2)	0.680 4(2)	0.898 3(2)
C(4)	0.915 7(6)	0.122 3(6)	0.442 5(4)	F(53)	0.967 2(2)	0.795 2(2)	1.090 9(2)
C(5)	1.009 3(5)	0.213 8(6)	0.493 8(4)	F(54)	0.846 1(3)	0.745 0(3)	1.198 1(2)
C(6)	1.029 5(4)	0.290 3(5)	0.460 1(4)	F(55)	0.650 0(3)	0.571 8(3)	1.105 8(2)
C(7)	0.954 2(4)	0.276 7(4)	0.373 9(3)	F(56)	0.576 2(2)	0.452 5(3)	0.917 8(2)
C(11)	0.822 7(6)	−0.063 0(5)	0.131 8(7)	C(61)	0.564 2(3)	0.396 7(3)	0.724 9(3)
C(12)	0.853 1(5)	0.030 4(6)	−0.013 6(5)	C(62)	0.474 8(3)	0.417 6(3)	0.725 7(3)
C(13)	1.013 0(4)	0.148 2(5)	0.196 9(4)	C(63)	0.368 2(3)	0.342 2(4)	0.687 0(3)
C(21)	0.636(1)	0.172 7(9)	0.392 6(8)	C(64)	0.345 7(4)	0.239 2(4)	0.646 9(3)
C(22)	0.791 9(6)	0.389 5(7)	0.423 5(5)	C(65)	0.428 2(4)	0.212 2(3)	0.643 4(3)
C(23)	0.558 2(5)	0.288 5(6)	0.288 2(5)	C(66)	0.533 8(3)	0.290 1(3)	0.680 1(3)
C(30)	0.580 8(4)	0.260 3(3)	0.017 8(3)	F(62)	0.491 8(2)	0.517 5(2)	0.767 8(2)
C(31)	0.693 8(4)	0.312 3(3)	0.079 3(3)	F(63)	0.287 3(2)	0.370 9(3)	0.687 7(2)
C(32)	0.748 5(4)	0.265 3(3)	0.028 8(3)	F(64)	0.242 3(3)	0.164 5(3)	0.610 7(3)
C(33)	0.669 6(4)	0.184 7(4)	−0.063 7(3)	F(65)	0.406 9(3)	0.111 3(3)	0.603 5(3)
C(34)	0.565 8(4)	0.180 5(4)	−0.069 0(3)	F(66)	0.609 5(3)	0.255 3(2)	0.668 2(3)
C(35)	0.494 9(4)	0.292 9(4)	0.036 4(4)	C(71)	0.783 9(3)	0.459 6(3)	0.764 2(3)
C(36)	0.749 0(4)	0.411 9(4)	0.173 5(4)	C(72)	0.806 9(3)	0.400 1(3)	0.812 9(3)
C(37)	0.870 1(4)	0.307 2(4)	0.064 0(4)	C(73)	0.886 2(4)	0.365 6(4)	0.811 4(4)
C(38)	0.689 7(5)	0.123 5(5)	−0.148 3(4)	C(74)	0.947 3(3)	0.389 8(3)	0.758 4(3)
C(39)	0.460 8(4)	0.109 5(5)	−0.157 9(4)	C(75)	0.931 4(3)	0.450 2(3)	0.710 7(3)
B	0.687 2(4)	0.497 5(4)	0.774 9(3)	C(76)	0.852 8(3)	0.484 9(3)	0.715 9(3)
C(41)	0.675 7(3)	0.570 3(3)	0.714 0(3)	F(72)	0.747 6(3)	0.370 3(2)	0.864 9(2)
C(42)	0.691 1(3)	0.673 7(3)	0.752 3(3)	F(73)	0.902 4(3)	0.307 9(3)	0.860 1(3)
C(43)	0.685 2(3)	0.730 6(3)	0.697 3(3)	F(74)	1.023 5(3)	0.354 9(3)	0.753 6(3)
C(44)	0.659 5(4)	0.684 4(3)	0.598 4(3)	F(75)	0.993 3(2)	0.478 0(3)	0.660 8(2)
C(45)	0.641 1(3)	0.582 2(4)	0.555 3(3)	F(76)	0.850 9(2)	0.551 0(2)	0.672 3(2)
C(46)	0.647 9(3)	0.528 1(3)	0.613 2(3)	Cl(101)	0.240 9(5)	0.900 5(5)	0.379 3(5)
F(42)	0.711 2(2)	0.725 8(2)	0.848 5(2)	Cl(102)	0.092 7(6)	1.003 3(5)	0.365 4(5)
F(43)	0.703 6(3)	0.831 3(2)	0.740 8(2)	C(100)	0.170(2)	0.954(2)	0.306(1)
F(44)	0.653 8(4)	0.739 3(3)	0.543 8(3)				

Table 6 Fractional atomic coordinates for complex **8** with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Zr	0.178 01(6)	0.429 64(9)	0.119 91(5)	C(511)	0.185 5(5)	0.048 5(7)	0.036 3(4)
N(1)	0.220 7(5)	0.558 4(7)	0.180 2(4)	C(512)	0.197 9(5)	−0.056 0(8)	0.035 3(4)
N(2)	0.286 9(5)	0.498 1(7)	0.096 8(5)	C(513)	0.150 7(6)	−0.122 7(7)	−0.002 8(5)
C(1)	0.285 3(6)	0.558 5(9)	0.149 5(5)	C(514)	0.090 8(5)	−0.088 5(7)	−0.040 7(4)
C(2)	0.354 4(5)	0.619 8(7)	0.174 3(4)	C(515)	0.076 4(5)	0.011 1(8)	−0.042 5(4)
C(3)	0.366 0(5)	0.717 7(8)	0.153 9(4)	C(516)	0.122 9(5)	0.078 5(6)	−0.004 4(4)
C(4)	0.433 0(6)	0.770 6(8)	0.177 5(5)	F(512)	0.260 9(4)	−0.093 5(6)	0.071 0(4)
C(5)	0.484 5(6)	0.724 6(9)	0.220 5(5)	F(513)	0.168 8(5)	−0.223 6(7)	0.002 9(5)
C(6)	0.473 8(5)	0.629(1)	0.241 7(5)	F(514)	0.045 9(5)	−0.158 6(7)	−0.074 9(4)
C(7)	0.407 4(6)	0.574 2(8)	0.218 4(4)	F(515)	0.015 8(5)	0.046 1(6)	−0.082 0(4)
Si(1)	0.193 8(2)	0.639 2(3)	0.245 8(2)	F(516)	0.100 0(4)	0.177 2(5)	−0.009 0(4)
Si(2)	0.356 1(2)	0.498 8(3)	0.036 9(2)	C(521)	0.243 6(5)	0.077 4(6)	0.157 7(4)
C(11)	0.173(1)	0.768(1)	0.209 6(9)	C(522)	0.304 0(5)	0.033 4(6)	0.196 0(4)
C(12)	0.102 5(9)	0.588(1)	0.274 5(8)	C(523)	0.296 1(6)	−0.004 2(6)	0.259 2(5)
C(13)	0.268(1)	0.648(2)	0.315(1)	C(524)	0.2277(6)	0.000 3(6)	0.285 5(4)
C(21)	0.453(1)	0.471(1)	0.076 0(8)	C(525)	0.166 9(5)	0.041 5(7)	0.250 7(4)
C(22)	0.330 0(8)	0.399(1)	−0.023 2(7)	C(526)	0.174 6(5)	0.079 7(6)	0.187 4(4)
C(23)	0.350 9(9)	0.622(1)	−0.007 7(8)	F(522)	0.372 5(4)	0.016 5(6)	0.171 3(4)
C(31)	0.113 8(6)	0.522(1)	0.024 1(6)	F(523)	0.357 9(5)	−0.046 5(7)	0.292 6(4)
C(32)	0.082 1(7)	0.560(1)	0.080 0(8)	F(524)	0.221 1(5)	−0.035 8(7)	0.347 3(4)
C(33)	0.040 2(7)	0.483(1)	0.107 4(6)	F(525)	0.097 4(5)	0.041 8(7)	0.275 6(4)
C(34)	0.045 9(6)	0.398(1)	0.069 5(7)	F(526)	0.109 9(4)	0.116 7(5)	0.155 4(3)
C(35)	0.091 5(6)	0.422(1)	0.018 0(6)	C(531)	0.330 7(5)	0.128 1(6)	0.051 3(4)
C(61)	0.154 6(5)	0.347 6(6)	0.218 4(4)	C(532)	0.348 7(5)	0.091 5(6)	−0.009 6(4)
C(62)	0.091 4(5)	0.316 4(6)	0.250 2(4)	C(533)	0.421 8(6)	0.096 0(7)	−0.032 8(4)
C(63)	0.099 0(5)	0.270 2(6)	0.311 8(4)	C(534)	0.480 1(5)	0.138 9(7)	0.004 7(5)
C(64)	0.168 9(6)	0.255 1(6)	0.341 5(4)	C(535)	0.466 6(5)	0.177 9(6)	0.064 2(5)
C(65)	0.232 9(5)	0.284 0(6)	0.313 9(4)	C(536)	0.393 2(5)	0.172 5(6)	0.086 5(4)
C(66)	0.224 3(5)	0.330 2(6)	0.252 1(4)	F(532)	0.295 5(4)	0.047 4(6)	−0.052 8(4)
F(62)	0.019 2(4)	0.329 0(6)	0.221 1(4)	F(533)	0.435 2(5)	0.057 4(7)	−0.093 1(4)
F(63)	0.034 3(5)	0.239 7(7)	0.339 6(4)	F(534)	0.551 8(5)	0.141 9(7)	−0.017 5(5)
F(64)	0.175 1(5)	0.204 9(7)	0.400 6(4)	F(535)	0.523 8(5)	0.223 1(6)	0.102 5(4)
F(65)	0.304 0(5)	0.267 1(7)	0.343 6(4)	F(536)	0.383 9(4)	0.217 9(5)	0.145 0(3)
F(66)	0.289 4(4)	0.357 8(5)	0.224 1(3)	H(51)	0.165(2)	0.243(7)	0.100(4)
C(50)	0.217 8(7)	0.246 0(9)	0.083 9(6)	H(52)	0.261(3)	0.281(6)	0.110(4)
B(50)	0.245 1(8)	0.124(1)	0.080 7(6)	H(53)	0.216(5)	0.285(6)	0.041(2)

and complex **1**, **2** or **3** (2.50 × 10⁻⁵ mol) in toluene (10 cm³) were allowed to react for 15 min and the mixture was then added via a cannula to the solution in the Fischer–Porter apparatus. After 1 h the polymerisation was quenched by adding a few drops of ethanol and dinitrogen was passed through the solution to remove the excess of ethene. The product mixture was then poured into an acidified ethanol solution and stirred overnight. The product polyethylene was filtered off, washed with water and ethanol and dried at 60 °C to constant weight.

Crystallography

Crystal data, data collection and processing parameters are given in Table 4. The general procedure was as follows. A crystal was sealed in a Lindemann capillary and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. The unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and measured every 3600 s of X-ray exposure time and three orientation controls were measured every 147 reflections.

Data were corrected for Lorentz and polarisation effects and an empirical absorption correction based on azimuthal scan data applied. The structures were solved by direct methods (SIR 92)[34] and Fourier-difference syntheses and refined using full-matrix least squares.

For compound **6** all non-hydrogen atoms were assigned anisotropic thermal parameters and throughout refinement the phenyl rings were restrained to their idealised geometries. The structure suffers from disorder in two dichloromethane solvent molecules which was modelled using partial occupancy. All atoms in the solvent molecules were refined isotropic-

ally with the C–Cl bond lengths restrained to a mean value. The hydrogen atoms were placed in calculated positions (C–H 1.0 Å and $U_{iso} = 1.25U_{eq}$ of adjacent atom) and were not included in the final cycles of refinement. A correction for anomalous dispersion was made in the final cycles of refinement.

For compound **8** the fluorine and carbon atoms associated with the phenyl groups and the carbon atoms of the trimethylsilyl groups were refined with isotropic thermal parameters. All other non-hydrogen atoms [Zr, Si, N, B, C(1), C(50), C atoms of the C_5H_5 ring] were refined with anisotropic thermal parameters. Throughout refinement the phenyl rings were restrained to their idealised geometries. The hydrogen atoms of the bridging methyl group were located from successive Fourier-difference syntheses and were refined with isotropic thermal parameters. Their C–H bond lengths were restrained to 1.00 Å. All other hydrogen atoms were placed in calculated positions (C–H 1.00 Å and $U_{iso} = 1.25U_{eq}$ of adjacent carbon atom) and were not included in the final cycles of refinement.

Crystallographic calculations were carried out using the CRYSTALS[35] program package on a MicroVAX 3800 computer. Atomic scattering factors were taken from the usual sources.[36] Fractional atomic coordinates of the non-hydrogen atoms for compound **6** are given in Table 5, those of **8** in Table 6.

Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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