Unexpected Reactions of Pentafluorophenylboron Compounds with η-Cyclopentadienyl(benzamidinato)zirconium Derivatives

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The new base-free compounds $[\{Zr(\eta\text{-}C_5R_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2]Cl\}][B(C_6F_5)_3X]_2]$ (R = H, X = Me, CH_2Ph or R = Me, X = C_6F_5*) and $[\{(\eta\text{-}C_5H_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](C_6F_5)\}Zr(\mu\text{-}Me)B(C_6F_5)_3\}]$,* are prepared; the formation of the latter requires the transfer of a C_6F_5 group from $[B(C_6F_5)_4]$:* indicates the crystal structure has been determined.

We have recently described the chloro and alkyl derivatives of the mono-η-cyclopentadienyl(benzamidinato)zirconium $[Zr(\eta\text{-}C_5R_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}X_2]$, where R = H, Me and $X_2 = Cl_2$, $(CH_2Ph)Cl$, $(CH_2Ph)_2$[1] or Me_2.[2] Some of these, in the presence of methylaluminoxane (MAO), gave systems which were modestly active catalysts for the polymerisation of ethene and propene.[1] It is well established that the catalytic activity of bent zirconocene compounds is associated with the so-called 'base-free' cations of general formulation $[Zr(\eta\text{-}C_5R_5)_2(alkyl)]^+A^-$, where A^- is a weakly coordinating anion such as $[BPh_4]^-$ or, especially, $[B(C_6F_5)_4]^-$.[3] Here we report unexpected reactions which occurred in attempt to synthesize 'base free' derivatives of the dialkyl compounds $[Zr(\eta\text{-}C_5R'_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}R_2]$ (R′ = Me, R = Me **1** or R′ = H and R = Me **2** or CH_2Ph **3**), using $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$.

The initial objective was to prepare the 'base-free cation' compounds $[Zr(\eta\text{-}C_5R'_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}R][B(C_6F_5)_4]$ (R = Me or CH_2Ph). The compound $[Zr(\eta\text{-}C_5Me_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}Me_2]$ **1** was treated with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane but the expected salt $[Zr(\eta\text{-}C_5Me_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}Me][B(C_6F_5)_4]$ was not isolated and the product, in *essentially quantitative combined yield* (NMR), was the dichloro bridged salt $[\{Zr(\eta\text{-}C_5Me_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](\mu\text{-}Cl)\}_2[B(C_6F_5)_4]_2\}$ **4**. The crystal structure of **4** has been determined† and the molecular structure of the cation is shown in Fig. 1. Similarly, treatment of $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}Me_2]$ **2** with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane gave $[\{Zr(\eta\text{-}C_5H_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](\mu\text{-}Cl)\}_2][B(C_6F_5)_3Me]_2$ **5**. Clearly the formation of **4** and **5** requires the efficient abstraction of chlorine from the solvent dichloromethane and, for **5** the loss of a $C_6F_5^-$ group from the anion $[B(C_6F_5)_4]^-$. The reaction between the dibenzyl compound $[Zr(\eta\text{-}C_5H_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](CH_2Ph)_2]$ and $[CPh_3][B(C_6F_5)_4]$ proceeds in an essentially identical manner giving $[\{Zr(\eta\text{-}C_5Me_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](\mu\text{-}Cl)\}_2][B(C_6F_5)_3CH_2Ph]_2$ **6**, again in high yield. The compounds **4**–**6** are detected even at −80 °C.

In a different approach to the 'base-free cation' compound $[Zr(\eta\text{-}C_5R_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}Me][B(C_6F_5)_3Me]$, the dimethyl compound **2** in benzene was treated with the neutral molecule $B(C_6F_5)_3$ giving the yellow crystalline compound $[\{(\eta\text{-}C_5H_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](C_6F_5)]\}Zr\{\mu\text{-}MeB(C_6F_5)_3\}]$ **7** in 45% yield. The crystal structure of **7** has been determined† and the molecular structure is shown in Fig. 2. In this compound the Zr–C(Me) bond length and the almost linear angle for Zr–C–B are comparable to those of related M–Me–B systems in the compounds $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,2\}_2Me][BMe(C_6F_5)_3]$ [2.667(5) Å, 170.5(3)°][4] and $[Zr(\eta\text{-}C_5H_3Me_2\text{-}1,2)_2Me][BMe(C_6F_5)_3]$ [2.549(3) Å, 161.8(2)°].[5] The hydrogens of the bridging methyl group were located and have relatively close contacts to the zirconium atom with similar distances to those found in the cation $[Zr\{\mu\text{-}C_5H_3(SiMe_3)_2\text{-}1,2\}_2Me]$, [2.47(3) and 2.44(3) Å].[4] This suggests the presence of weak α-agostic interactions. Also, a five-coordinated carbon system related to that in **7** was first observed in the compound $[(\eta\text{-}C_5Me_5)_2Lu(\mu\text{-}Me)LuMe(\eta\text{-}C_5Me_5)_2]$.[6] The formation of **7** requires transfer of a C_6F_5 group from boron to zirconium.

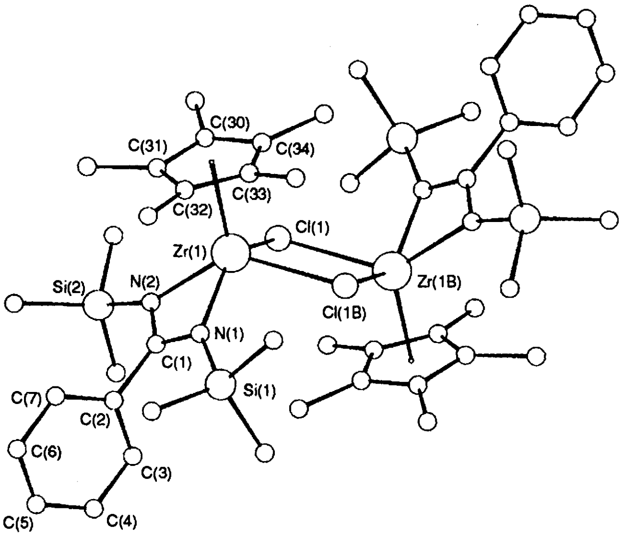


Fig. 1 Molecular structure of the cation of $[\{Zr(\eta\text{-}C_5Me_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ **4**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zr(1)–N(1) 2.179(3), Zr(1)–N(2) 2.169(3), Zr(1)–C(1) 2.555(4), Zr(1)–Cp_{cent} 2.181, Zr(1)–Cl(1) 2.552(1), Zr(1)–Cl(1B) 2.563(1), N(1)–Zr(1)–N(2) 63.4(1), Cl(1)–Zr(1)–Cl(1B) 80.70(4), where Cp_{cent} refers to the computed η-C_5H_5 centroid.

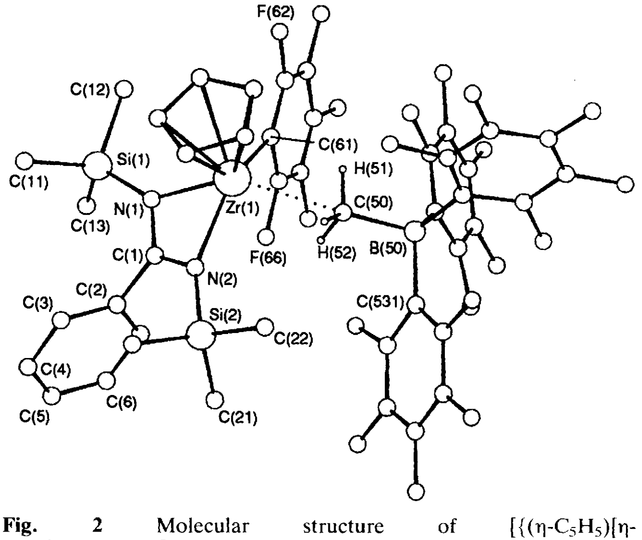
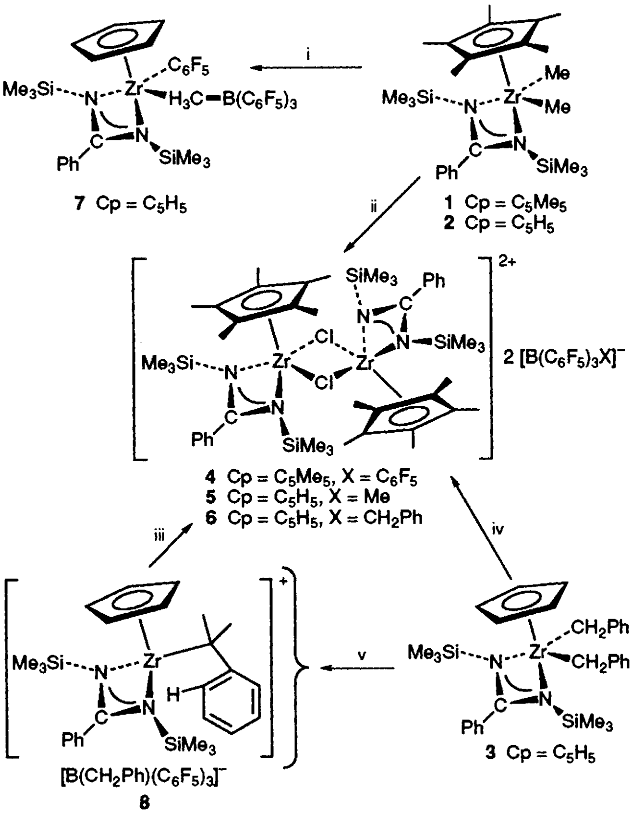


Fig. 2 Molecular structure of $[\{(\eta\text{-}C_5H_5)[\eta\text{-}CPh\{N(SiMe_3)\}_2](C_6F_5)\}Zr\{\mu\text{-}MeB(C_6F_5)_3\}]$ **7**. All hydrogen atoms except those of the bridging methyl group omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zr(1)–N(1) 2.178(9), Zr(1)–N(2) 2.177(9), Zr(1)–C(1) 2.55(1), Zr(1)–Cp_{cent} 2.183, Zr(1)–C(50) 2.62(1), Zr(1)–H(51) 2.48(9), Zr(1)–H(52) 2.44(9), Zr(1)–H(53) 2.60(8), C(50)–B(50) 1.67(2), N(1)–Zr(1)–N(2) 62.4(3), C(61)–Zr(1) –C(50) 83.3(3), Zr(1)–C(50)–B(50) 166.0(8), B(50)–C(50)–H(51) 104(6), B(50)–C(5)–H(52) 105(5), B(50)–C(50)–H(53) 116(5), where Cp_{cent} refers to the computed η-C_5H_5 centroid.



Scheme 1 *Reagents and conditions*: i, $B(C_6F_5)_3$ in benzene for 24 h, room temp., **7** (45%); ii, $[CPh_3][B(C_6F_5)_4]$ in CH_2Cl_2 for 30 min., −80 °C, **5** (62%), **4** (79%); iii, in CD_2Cl_2, remove solvent under vacuum, −40 °C, then in CD_2Cl_2 at room temp., **6** (>30% by NMR); iv, $[CPh_3][B(C_6F_5)_4]$, CD_2Cl_2 at room temp., **6** (>95% by NMR], or $B(C_6F_5)_3$ in benzene for 12 h, room temp., remove solvent then in CD_2Cl_2 at room temp., **6** (>60% by NMR); v, $B(C_6F_5)_3$ in CD_2Cl_2, −40 °C, **8** (>95% by NMR)

We have also studied the reaction between $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}(CH_2Ph)_2]$ **3** with $B(C_6F_5)_3$ in benzene and in dichloromethane. The reaction in CH_2Cl_2 was monitored by NMR spectroscopy at −40 °C. A red intermediate **8** which was only stable in solution and at low temperature was detected. The ^1H and ^{13}C NMR spectra of **8**† are consistent with the structure shown in Scheme 1. The ^1H NMR spectrum showed the presence of the free anion $[B(C_6F_5)_3(CH_2Ph)]^-$.[7,8] Attempts to isolate **8** at low temperature were unsuccessful due to decomposition as the solvent was removed, and formation of a new paramagnetic compound which in CH_2Cl_2 at room temp. decomposed to the dimer salt **6**. The reaction between $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh[N(SiMe_3)]_2\}(CH_2Ph)_2]$ **3** with $B(C_6F_5)_3$ in *benzene* gave an initial red colour, presumed to be **8**, which also rapidly decomposed giving red–violet paramagnetic microcrystals which in CH_2Cl_2 at room temp. further reacted to give **6**.

Compound **7** is not active in polymerisation of ethene, presumably due to the strength of the Zr–C_6F_5 bond, however, a mixture of **2** and $B(C_6F_5)_3$ polymerises ethene (activity: 1.2×10^4 g[mol Zr]$^{-1}$ h^{-1} atm^{-1}). In addition, **1**, **2** or **3**, together with $[CPh_3][B(C_6F_5)_4]$ do not polymerise ethene.

In conclusion, unexpected reactions of the so-called 'non-coordinating' anion $[B(C_6F_5)_4]^-$ have been identified. The transfer of the $C_6F_5^-$ group (for **7**) and the abstraction of Cl^- from dichloromethane in the formation of **4**–**6** suggests that there are intermediate cationic zirconium compounds which are exceptionally electrophilic.

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Footnote

† Satisfactory analysis have been obtained for all the new compounds isolated. The spectroscopic data which characterise the new compounds and further details of the structure determinations have been provided in full for the referees and will be published in the full paper to be submitted to Dalton Transactions.

Crystal data for **4**: $C_{94}H_{76}B_2Cl_2F_{40}N_4Si_4Zr_2\cdot0.6CH_2Cl_2$, M = 2459.9, triclinic, a = 14.110(2), b = 14.8799(8), c = 15.394(1) Å, α = 107.533(5), β = 104.255(9), γ = 109.591(9)°, space group $P\bar{1}$, V = 2678 Å^3, Z = 1, $F(000)$ = 1232, D_c = 1.60 g cm^{-3}; λ (Mo-Kα) = 0.71069 Å. 6020 reflections with $I > 3\sigma(I)$ were used in the refinement, to R = 5.65%, R_w = 6.30%.

Crystal data for **7**: $C_{43}H_{31}B_1F_{20}N_2Si_2Zr_1$, M = 1113.9, monoclinic, a = 17.363(1), b = 13.0700(9), c = 20.265(3) Å, β = 94.365(8)°, space group $P2_1/c$, V = 4586 Å^3, Z = 4, $F(000)$ = 2224, D_c = 1.61 g cm^{-3}; μ(Mo-Kα) = 3.98 cm^{-1}. 2976 reflections with $I > 3\sigma(I)$ were used in the refinement to R = 7.20%, R_w = 7.95%.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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