Anionic and Zwitterionic Metallocene Complexes derived from Novel Boratocyclopentadienyl Ligands

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Borate-substituted di- and tri-anionic cyclopentadienyl ligands $[X_3B{-}C_5H_4]^{2-}$ and $[X_2B(C_5H_4)_2]^{3-}$ (X = C_6F_5) give anionic group 4 metallocene complexes which provide a facile route to zwitterionic 'single-component' alkene polymerisation catalysts.

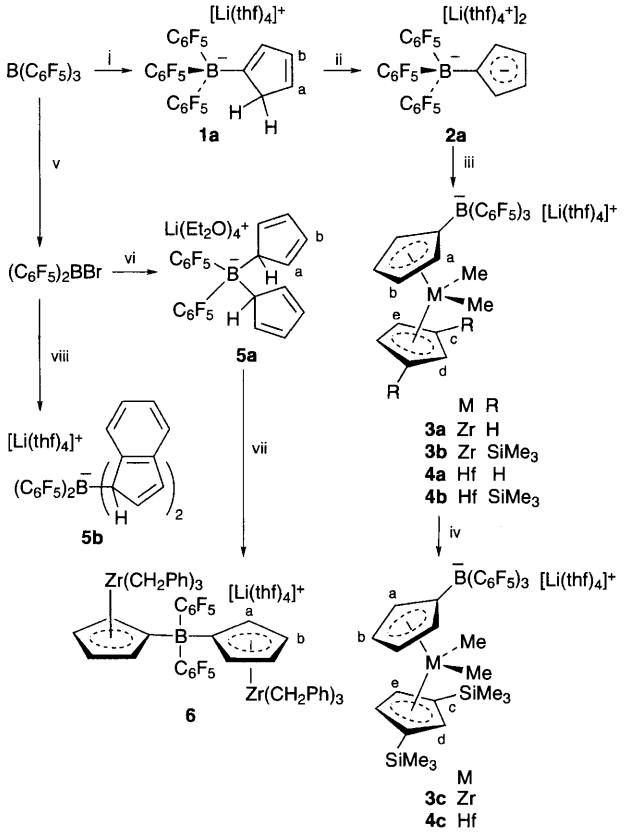
The role of cationic 14-electron metal–alkyl complexes $[(\eta\text{-}C_5H_5)_2M\text{–}R]^+$ (M = Ti, Zr, Hf) as the active species in homogeneously catalysed olefin polymerisations is now well documented.[1–3] Several attempts have been made to explore the role of the positive charge and of the counter anion in these systems by preparing neutral group 4 metal analogues of the type $[M(R)(L)(\eta\text{-}C_5H_5)]$, for example where L^{2-} = $[C_2B_9H_{11}]^{2-}$ (M = Ti, Zr, Hf).[4] As a route to such complexes, a number of anionic complexes $[(\eta\text{-}C_5H_5)(L)M(\mu\text{-}Cl)_2Li(OEt_2)_2]$ have been made based on dianionic $\eta^5\text{-}C_5H_4BNPr^i_2$ and $\eta^4\text{-}C(CH_2)_3$ ligands.[5,6] In such compounds there is significant accumulation of negative charge on the metal centre and the chloride ligands which leads to the coordination of the counter cation *via* stable halide bridges, a feature more commonly seen with anionic metallocene halides of lanthanide metals. Since coordinative unsaturation of the metal centre must be regarded as a key feature of a successful polymerisation catalysts, we are currently exploring routes to neutral complexes of the type $[MR(L)(\eta\text{-}C_5H_5)]$ in which the Lewis acidity of the complex is impaired as little as possible. Rather than using dianionic ligands L^{2-}, it seemed to us that this condition was more likely to be fulfilled by ligands of the type L = $Cp^{-}\text{–}Z^{-}$, *i.e.* a cyclopentadienyl ligand carrying an anionic substituent which does not itself coordinate to the metal, and we report here the synthesis of complexes derived from a new range of cyclopentadienyl ligands carrying borate substituents, $[X_3BC_5H_4]^{2-}$ and $[X_2B(C_5H_4)_2]^{3-}$ (X = C_6F_5), and their conversion to zwitterionic species.

A solution of cyclopentadienyllithium in tetrahydrofuran (thf) reacts with BX_3 to give $[Li(thf)_4][X_3B(C_5H_5)]$ **1a** (X = C_6F_5). The indenylborate $[Li(thf)_4][X_3B(C_9H_7)]$ **1b** is obtained similarly. The yields are essentially quantitative. The borates **1** are readily deprotonated by butyllithium in thf to give dianions, *e.g.* $[Li(thf)_4]_2[X_3B(C_5H_4)]$ **2a**. Solutions of **2a** react with $[MLCl_3]$[7] to give $[Li(thf)_4][MCl_2L\{(\eta^5\text{-}C_5H_4)BX_3\}]$ [**3**$^-$, M = Zr; **4**$^-$, M = Hf; **a**, L = $\eta\text{-}C_5H_5$; **b**, L = $C_5H_3(SiMe_3)_2$-1,3] (Scheme 1). The compounds are isolated as off-white amorphous solids.† In contrast to the anionic zirconium halides mentioned above the lithium cation is associated with the borate substituent rather than the chloride ligands and is readily exchanged with $[NEt_4]BF_4$ in dichloromethane to give $[NEt_4][MCl_2L\{(C_5H_4)BX_3\}]$ (M = Zr, Hf).

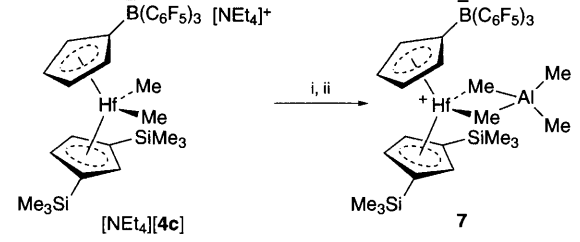
Alkylation of $[Li(thf)_4]$[**3b**] with methyllithium leads to the expected methyl complex $[Li(thf)_4][ZrMe_2\{C_5H_3(SiMe_3)_2\}\{(C_5H_4)BX_3\}]$ $\{[Li(thf)_4]$[**3c**]$\}$. Treatment of the NEt_4^+ salts of **3b** and **4b** with LiMe in diethyl ether similarly gives the dimethyl complexes, without lithium/NEt_4 exchange.

The reaction of X_2BBr‡ (X = C_6F_5) with 2 equivalents of cyclopentadienyllithium or indenyllithium affords $[Li(thf)_4][X_2B(C_5H_5)_2]$ **5a** and $[Li(thf)_4][X_2B(C_9H_7)_2]$ **5b**, respectively. Ligands of this nature have the potential to form boron-bridged *ansa*-metallocenes.§ However, a suspension of **5a** in toluene reacts with $Zr(CH_2Ph)_4$ to give the dinuclear zirconium tribenzyl complex **6** (Scheme 1), even in the presence of excess **5a**. Similar products are obtained from the reaction of **5a** with $Zr(NMe_2)_4$, although there is evidence for C_5H_5/NMe_2 exchange of the borate and the reaction is less clean.

The reaction of $[NEt_4]$[**4c**] with $[CPh_3][B(C_5F_5)_4]$ or $B(C_5F_5)_3$ in toluene leads to decomposition. However, mixing $[NEt_4]$[**4c**] with $[CPh_3][B(C_5F_5)_4]$ in the presence of 1 equivalent of $AlMe_3$ per Hf in toluene at 20 °C proceeds with methyl abstraction, indicated by the appearance of Ph_3CCH_3, to give $[NEt_4][B(C_5F_5)_4]$ and a single major organometallic product **7** (Scheme 2). Variable-temperature ^1H and ^{13}C NMR spectra and $^1H\text{–}^{13}C$ heteronuclear correlation experiments support the formulation of **7** as a methyl-bridged Hf–Al dimer, $[\{C_5H_3(SiMe_3)_2\}\{(\eta^5\text{-}C_5H_4)BX_3\}Hf(\mu\text{-}Me_2)AlMe_2]$. In contrast to the



Scheme 1 i, $Li(C_5H_5)$, thf, room temp.; ii, $LiBu^n$, thf, −78 °C; iii, $MLCl_3$ [L = C_5H_5 or $C_5H_3(SiMe_3)_2$], thf, −78 °C to room temp., 80–90%; iv, LiMe, Et_2O–thf, −78 °C to room temp., 50–60%; v, BBr_3, toluene, room temp.; vi, $Li(C_5H_5)$ (2 equiv.) Et_2O, −78 °C to room temp., 83%; vii, $Zr(CH_2Ph)_4$, toluene, room temp., 53%; viii, $Li(C_9H_7)$ (2 equiv.) thf, 90%



Scheme 2 i, $[CPh_3][B(C_6F_5)_4]$, toluene, 0.5 Al_2Me_6; ii, $-Ph_3CMe$, $-[NEt_4][B(C_6F_5)_4]$

related cationic Hf–Al analogue $[(\eta\text{-}C_5H_5)_2Hf(\mu\text{-}Me)_2AlMe_2]^+$ which is surprisingly non-fluxional,[9] the methyl groups of **7** exchange rapidly at room temperature and give rise to a singlet at δ −0.39 which splits into a broadened 1 : 1 doublet on cooling to −60 °C, indicative of bridging and terminal methyl ligands.

Although the bulky $-B(C_6F_5)_3$ substituents provide significant steric hindrance, complexes of type **3** and **4** are active polymerisation catalysts. For example, **3b** in the presence of methylaluminoxane (Al/Zr = 1800) polymerises ethylene at 1 bar/20 °C with a productivity of *ca.* 10^6 g PE (mol Zr)$^{-1}$ bar^{-1} h^{-1}. Mixtures of $[NEt_4][\mathbf{4c}]$ and $[CPh_3][B(C_5F_5)_4]$ in the presence of $AlBu^i_3$ (Al/Hf = 10) are similarly active.

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Footnotes

† Satisfactory elemental analyses were obtained for all new compounds. *Selected spectroscopic data*: **1a** (major isomer) ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.81 (br, 16 H, thf), 2.71 (s, 2 H, C_5), 3.66 (br, 16 H, thf), 5.99 (s, 1 H, C_5), 6.15 (d, 1 H, *J* 5.27 Hz, C_5), 6.29 (d, 1 H, *J* 5.27 Hz, C_5). ^{19}F NMR ($CDCl_3$, 84.1 MHz, 29 °C): δ −162.55 (br t, *m*-F), −157.72 (t, J_{F-F} 20, *p*-F), −135.49 (br, *o*-F). **1b** ^{1}H NMR (CD_2Cl_2, 270 MHz): δ 1.88 (br, 16 H, thf), 3.26 (s, 1 H, C_5), 3.76 (br, 16 H, thf), 6.34 (d, 1 H, C_5), 6.78 (d, 1 H, C_5), 7.05–7.50 (m, 4 H, C_6). ^{19}F NMR ($CDCl_3$): δ −166.80 (t, J_{F-F} 20.6 Hz, *m*-F), −162.08 (t, J_{F-F} 20.6 Hz, *p*-F), −139.41 (d, J_{F-F} 20.7 Hz, *o*-F). NMR data for complex anions: $[\mathbf{3a}]^-$ ^{1}H NMR (CD_2Cl_2, 270 MHz, 23 °C): δ 6.11 (t, 2 H, *J* 2.64 Hz, H^a), 6.32 (t, 2 H, *J* 2.64 Hz, H^b), 6.44 (s, 5 H, C_5H_5). ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 23 °C): δ 112.61 (C^a), 116.15(C_5H_5), 117.45 (C^b), 135.20 (CB), 137.29 (d, J_{C-F} 250 Hz, *m*-C), 148.28 (d, J_{C-F} 242 Hz, *o*-C). ^{19}F NMR (CD_2Cl_2): δ −167.61 (t, J_{F-F} 23.6 Hz, *m*-F), −162.99 (t, J_{F-F} 20.6 Hz, *p*-F), −139.53 (d, J_{F-F} 20.7 Hz, *o*-F). $[\mathbf{3b}]^-$ ^{1}H NMR (CD_2Cl_2, 270 MHz, 23 °C): δ 0.27 (s, 18 H, $SiMe_3$), 6.03 (t, 2 H, *J* 2.7 Hz, H^a), 6.29 (t, 2 H, *J* = 2.7 Hz, H^b), 6.85–6.90 (m, 3 H, C^d and C^e). ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 23 °C): δ 0.05 ($SiMe_3$), 110.69 (C^a), 119.08 (C^b), 128.32 (C^d), 129.07 (C^e), 131.27 (C^c), 135.20 (CB), 137.33 (d, J_{C-F} 236 Hz, *m*-C), 139.29 (d, J_{C-F} 248 Hz, *p*-C), 148.28 (d, J_{C-F} 222 Hz, *o*-C). ^{19}F NMR (CD_2Cl_2): δ −167.61 (t, J_{F-F} 17.7 Hz, *m*-F), −162.99 (t, J_{F-F} 20.6 Hz, *p*-F), −139.49 (d, J_{F-F} 23.6 Hz, *o*-F). $[\mathbf{4b}]^-$ ^{1}H NMR (CD_2Cl_2, 270 MHz, 23 °C): δ 0.27 (s, 18 H, $SiMe_3$), 5.94 (t, 2 H, *J* 2.64 Hz, H^a), 6.20 (t, *J* 2.64 Hz, H^b), 6.79 (d, 2 H, *J* 1.98 Hz, H^e), 6.81 (t, 1 H, *J* 1.98 Hz, C^d). ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 23 °C): δ 0.10 ($SiMe_3$), 109.37 (C^a), 117.76 (C^b), 125.63 (C^d), 128.37 (C^e), 130.74 (C^c), 132.92 (CB), 137.26 (d, J_{C-F} 249 Hz, *m*-C), 148.25 (d, J_{C-F} 239 Hz, *o*-C). ^{19}F NMR (CD_2Cl_2): δ −167.22 (t, J_{F-F} 17.7 Hz, *m*-F), −162.29 (t, J_{F-F} 20.7 Hz, *p*-F), −139.42 (d, J_{F-F} 23.6 Hz, *o*-F). $[\mathbf{3c}]^-$ ^{1}H NMR (C_6D_6, 270 MHz, 23 °C): δ −0.15 (s, 6 H, Zr–Me), 0.14 (s, 18 H, $SiMe_3$), 5.57 (t, 2 H, *J* 2.64 Hz, H^a), 5.81 (t, 2 H, *J* 2.64 Hz, H^b), 5.91 (t, 1 H, *J* 1.98 Hz, H^d), 6.65 (d, 2 H, *J* 1.98 H^e). ^{13}C NMR (C_6D_6): δ 0.22 ($SiMe_3$), 30.37 (Zr–Me, J_{CH} 117 Hz), 105.79 (C^a), 112.67 (C^b), 120.56 (C^d), 122.50 (C^e), 124.14 (C^c), 135.53 (CB). ^{19}F NMR (CD_2Cl_2): δ −167.43 (t, J_{F-F} 20.6 Hz, *m*-F), −162.85 (t, J_{F-F} 20.7 Hz, *p*-F), −139.88 (d, J_{F-F} 17.7 Hz, *o*-F). $[\mathbf{4c}]^-$ ^{1}H NMR (C_6D_6, 270 MHz, 23 °C): δ −0.34 (s, 6 H, Hf–Me), 0.15 (s, 18 H, $SiMe_3$), 5.55 (t, 2 H, *J* 2.64 Hz, H^a), 5.71 (t, 2 H, *J* 2.64 Hz, H^b), 5.92 (t, 1 H, *J* 1.98 Hz, H^d), 6.58 (d, 2 H, *J* 1.98 Hz, H^e). ^{13}C NMR (C_6D_6): δ 0.24 ($SiMe_3$), 36.43 (Hf–Me, J_{CH} 115.2 Hz), 105.40 (C^a), 112.15 (C^b), 121.24 (C^d), 123.87 (C^e), 125.63 (C^c), 129.28 (CB). ^{19}F NMR ($CDCl_3$): δ −166.66 (t, J_{F-F} 17.7 Hz, *m*-F), −161.90 (t, J_{F-F} 20.7 Hz, *p*-F), −139.34 (d, J_{F-F} 20.7 Hz, *o*-F). **5a** ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.16 (t, 24 H, Et_2O), 2.68 (br, 2 H, C_5), 3.57 (q, 16 H, Et_2O), 5.95 (br, 2 H, C_5), 6.04 (q, 2 H, *J* 2.65, C_5), 6.17 (s, 4 H, C_5). ^{13}C NMR (CD_2Cl_2): δ 14.48 (Et_2O), 56.26 (CB), 66.88 (Et_2O), 106.09 (C^a, C^b), 137.28 (*m*-C, J_{C-F} 234 Hz), 138.94 (*p*-C, J_{C-F} 258 Hz), 148.50 (*o*-J_{C-F} 237 Hz). ^{19}F NMR ($CDCl_3$): δ −167.36 (br t, *m*-F), −163.68 (t, J_{F-F} 39.1 Hz, *p*-F), −139.42 (br, *o*-F). **5b** ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.85 (m, 16 H, thf), 2.47 (br, 2 H, C_5), 3.71 (m, 16 H, thf), 6.45 (d, 2 H, *J* 5.60 Hz, C_5), 6.78 (d, 2 H, *J* 5.60 Hz, C_5), 7.1–7.5 (m, 8 H, C_6). ^{13}C NMR (CD_2Cl_2): δ 25.73 (thf), 50.62 (CB of C_5), 68.77 (thf), 121.33 (C_5), 123.04 (C_6), 125.07 (C_6), 126.85 (C_5), 131.32 (C_5), 139.28 (C_6), 144.72 (C_5/C_6), 147.85 (C_5/C_6), 137.28 (*m*-C, J_{C-F} 240 Hz), 139.20 (*p*-C, J_{C-F} 246 Hz), 148.22 (*o*-C, J_{C-F} 242 Hz). $[\mathbf{6}]^-$ ^{1}H NMR (CD_2Cl_2, 270 MHz, 25 °C): δ 1.43 (s, 12 H, CH_2Ph), 5.44 (t, 4 H, *J* 2.64 Hz, H^a), 5.71 (t, *J* 2.64 Hz, H^b), 6.47 (d, 12 H, *J* 8.24 Hz, *o*-Ph), 6.95–7.05 (m, 6 H, *p*-Ph), 7.10–7.20 (m, 12 H, *m*-Ph). ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 23 °C): δ 65.97 (CH_2Ph, J_{C-H} 128), 111.57 (C^a), 111.93 (C^b), 112.09 (CB of C_5), 123.41 (*p*-C of Ph), 127.53 (*m*-C of Ph), 130.01 (*o*-C of Ph), 143.77 (*ipso*-C of Ph), 139.12 (*m*-C, J_{C-F} 228 Hz), 139.45 (*p*-C, J_{C-F} 250 Hz), 148.38 (*o*-C, J_{C-F} 240 Hz). ^{19}F NMR (CD_2Cl_2): δ −167.26 (t, J_{F-F} 17.7 Hz, *m*-F), −162.64 (t, J_{F-F} 20.6 Hz, *p*-F), −139.77 (br, *o*-F). **7** ^{1}H NMR ([$^2H_8$]toluene, 270 MHz, 23 °C): δ −0.39 (br s, 12 H, AlMe), 0.07 (s, 18 H, $SiMe_3$), 5.46 (br, 2 H, H^a), 5.65 (br, H^b), 5.84 (br, 1 H, H^d), 6.48 (br, 2 H, H^f). ^{13}C NMR ([$^2H_8$]toluene 67.8 MHz, 23 °C): δ −7.06 (br, AlMe, J_{C-H} 114 Hz), 0.24 ($SiMe_3$), 35.46 (br, μ-CH_3, J_{C-H} 115 Hz), 105.9 (C^a), 112.4 (C^b), 121.49 (C^d), 123.99 (C^e), 127.75 (C^c), 130.50 (CB). ^{19}F NMR ([$^2H_8$]toluene): δ −166.73 (t, J_{F-F} 23.0 Hz, *m*-F), −163.23 (t, J_{F-F} 20.6 Hz, *p*-F), −138.79 (d, J_{F-F} = 23.6 Hz, *o*-F).

‡ $(C_6F_5)_2BBr$ was prepared in 78% yield by mixing BBr_3 in hexane with 2 equiv. of $B(C_6F_5)_3$ in toluene at −78 °C and warming to room temp.; ^{19}F NMR (C_6D_6, 25 °C): δ −121.6 (d, J_{F-F} 27.4 Hz, *o*-F), −135.0 (t, J_{F-F} 29.3 Hz, *p*-F), −153.0 (t, J_{F-F} 30.7 Hz, *m*-F).

§ A borate-bridged *ansa*-arene complex is known, $[Nb\{Ph_2B(\eta^6\text{-}Ph)_2\}(C_2Me_2)]$ (ref.8).

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