Cationic d^0/f^0 Metallocene Catalysts. Properties of Binuclear Organoborane Lewis Acid Cocatalysts and Weakly Coordinating Counteranions Derived Therefrom

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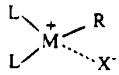
Received May 31, 1994®

Summary: Reaction of $^tBuCH_2CH(BCl_2)_2$ *with* LiC_6F_5 *yields the binuclear organo-Lewis acid* $^tBuCH_2CH[B(C_6F_5)_2]_2$*, which can be converted with* KEt_3BH*, followed by metathesis, into the salt* $[HN^nBu_3]^+\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$*. Reaction of this salt with* $Cp'_2Th(CH_3)_2$ *(*$Cp' = \eta^5\text{-}Me_5C_5$*) yields the cationic metallocene complex* $Cp'_2ThCH_3^+\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$ ***(5)****, which is a highly active catalyst for ethylene polymerization and 1-hexene hydrogenation. The THF adduct,* $Cp'_2Th(CH_3)THF^+\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$*, has been characterized by X-ray diffraction.*

Cationic metallocene alkyls and hydrides are key components of several broad, group 4- and actinide-based classes of homogeneous olefin polymerization catalysts[1–3] (**I**; L = cyclopentadienyl-type ligand; R = alkyl, H), the reactivities of which are highly sensitive to the nature of the counteranion (X^-).[1,4–6] **I** ion pairs are typically synthesized using neutral organo-Lewis acid alkide/hydride abstractors (e.g., $B(C_6F_5)_3$, MAO)[1,6,7] or salt-like abstracting/protonolyzing/redox reagents (e.g., $Ph_3C^+X^-$, $HNR'_3{}^+X^-$, Fc^+X^-).[1–3] We sought to produce more weakly coordinated/more reactive L_2MR^+ species by employing *chelating binuclear* fluoroaromatic (Ar^F)[8] boranes (**II**)/borates (**III**), connected by saturated hydrocarbon bridges,[8] which might better disperse the X^- negative charge[9] and bind the abstracted anionic functionality more strongly.[8] We report here the synthesis and some initial observations on the properties of the first binuclear structures of types **II** and **III**.[10]



I

II

III

Double hydroboration[11a] of *tert* -butylactylene with *in situ* generated $HBCl_2$[11b] yields the known[11a] diboryl **1** (Scheme 1). Subsequent arylation with *in situ* generated LiC_6F_5 yields binuclear borane **2** as a pale yellow, viscous oil.[12] Compound **2** could be characterized by NMR, mass spectrometry, and the synthesis of derivatives (*vide infra*), however attempts at purification by crystallization/precipitation (pentane at −78 °C) or short-path distillation indicate that **2** undergoes slow alkyl/aryl redistribution[13] to produce $B(C_6F_5)_3$ (detected by ^{19}F NMR)[14] and other unidentified boranes. Thus, traces of $B(C_6F_5)_3$ in purified samples increase to a

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® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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[12] Compound **1** (2.77 g, 11.0 mmol) was injected into a stirring −78 °C suspension of LiC_6F_5[6] in 300 mL of pentane (prepared from 12.6 g (51.0 mmol) of C_6F_5Br and 51 mmol of ^nBuLi in hexane). The mixture was warmed to 25 °C over the course of 12 h and filtered and the pentane removed under high vacuum to yield **2** as a pale yellow oil. ^{19}F NMR (C_6D_6): δ −130.3 (8F, d, J = 14 Hz), −146.7 (4F, t, J = 21 Hz), −160.3 (8F, "t", J = 18 Hz). ^1H NMR (C_6D_6): δ 0.76 (9H, s), 2.21 (2H, d, J = 4.6 Hz), 3.56 (1H, t, broad, J = 4.6 Hz). FAB MS: parent ion at m/e 787. The ^{19}F NMR and the MS also show the presence of $B(C_6F_5)_3$.[14]

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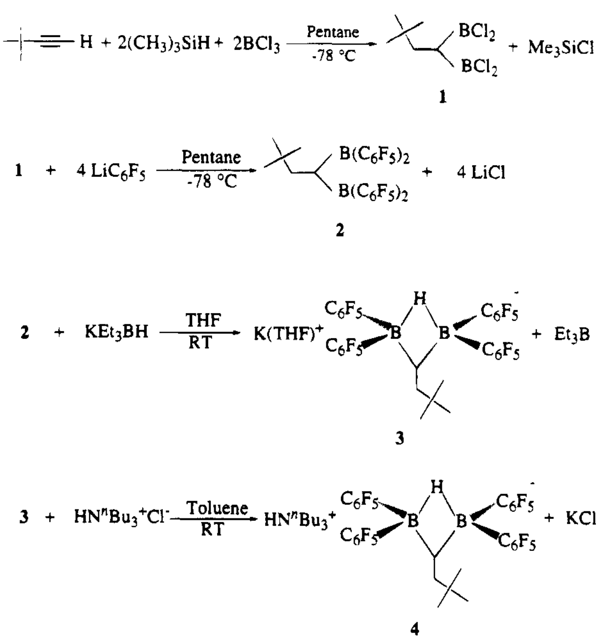
Scheme 1



steady state of ~17% over the course of 6 h at 25 °C. Initial experiments with **2** and Cp'_2ZrH_2 using procedures described elsewhere,[6,15] indicate high activity for ethylene polymerization (1.0(2) × 10^6 g of polyethylene (mol of Zr)$^{-1}$ h^{-1} atm^{-1}; $N_t \approx 10(2)$ s^{-1} at 25 °C), however, exact assessment of these results is complicated by possible competing $B(C_6F_5)_3$ cocatalysis.[16]

Reaction of borane **2** with KEt_3BH affords the binuclear borate **3** (Scheme 1), which can be converted by metathesis to tributylammonium salt **4**.[17] Unlike **2**, **4** does not undergo redistribution over periods of days at 25 °C in solution. Protonolytic reaction[4c] of **4** with $Cp'_2Th(CH_3)_2$ yields the thorocene cation **5** (eq 1).[18]

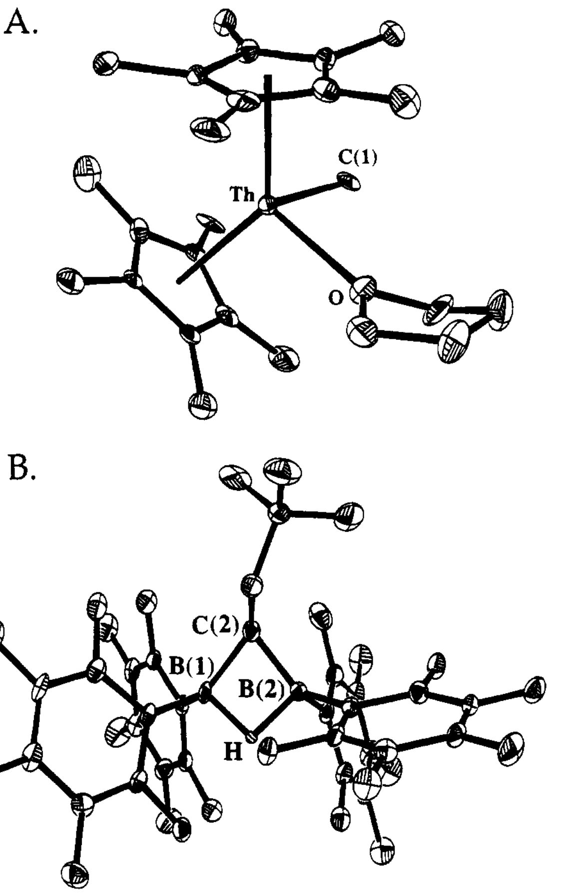


Figure 1. (A) Structure of the cation portion of **8**. Important bond distances (Å) and angles (deg) are as follows: Th–C(1) = 2.433(7), Th–O(1) = 2.455(4), Th–C_{ring} = 2.486 (av); ring centroid–Th–ring centroid = 137.1. (B) Structure of the anion portion of **8**. Important bond distances (Å) and angles (deg) are as follows: B(1)–H = 1.35(6), B(2)-H = 1.34(6); B(1)–H–B(2) = 91.9, H–B(1)–C(2) = 95.2, H–B(2)–C(2) = 95.4, B(1)–C(2)–B(2) = 75.0. Thermal ellipsoids are drawn at the 35% probability level.

From past observations,[4,6] two features of **5** qualitatively

$$Cp'_2Th(CH_3)_2 + \mathbf{4} \xrightarrow[25\ °C]{toluene} [Cp'_2ThCH_3]^+\{{}^tBuCH_2CH[B(C_6F_5)_2]_2H\}^- \quad (1)$$
$$\mathbf{5}$$

suggest reduced cation–anion interaction/greater metallocene cationic character. These are very low solubility in toluene (lower than that of $Cp'_2ThCH_3^+B(C_6F_5)_4^-$ (**6**)[4b] and $Cp'_2ThCH_3^+B(C_6H_5)_4^-$ (**7**)[4c]) as well as displacement of $\delta(Th-{}^{13}CH_3)$ to low field (δ 80 for **5** by CPMAS NMR versus δ 78 for **6**[4b] and 73 for **7**,[4c] consistent with reduced Th electron density). Although crystals of **5** suitable for diffraction could not be obtained, crystals of a mono-THF adduct (**8**) could be

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[16] Using previous activity data,[6a] it can be estimated that the presence of 17% $B(C_6F_5)_3$ could contribute as much as ~[0.5(1)] × 10^6 g of polyethylene (mol of Zr)$^{-1}$ h^{-1} atm^{-1} to the observed activity.

[17] Crude **2** (5.0 g, ~6.3 mmol) was dissolved in 100 mL of THF, and 6.0 mL (6.0 mmol) of 1 M KEt_3BH was slowly added with stirring. After 6 h, the solvent was removed *in vacuo* to yield a viscous oil, which solidified on washing with pentane. Recrystallization from toluene/pentane afforded 2.7 g (50%) of **3** as a colorless solid. ^1H NMR (C_6D_6): δ 1.32 (9H, s), 1.39 (4H, m), 1.42 (2H, d, *J* = 6.0 Hz), 2.19 (1H, b), 2.37 (1H, b), 3.48 (4H, m). ^{19}F NMR (C_6D_5): δ −130.8 (4F, b), −133.7 (4F, b), −157.5 (2F, t, *J* = 21 Hz), −158.0 (2F, t, *J* = 21 Hz), −163.4 (4F, b), −163.8 (4F, b). Satisfactory elemental analyses could not be obtained, presumably due to loss of varying amounts of THF. Compound **3** (3.0 g, 5.6 mmol) and 1.20 g (5.6 mmol) of $HN^nBu_3^+Cl^-$ were stirred in toluene for 8 h. Next, precipitated KCl was removed by filtration, the filtrate evaporated *in vacuo*, and the crude product recrystallized from CH_2Cl_2/pentane to yield 5.1 g (90%) of **4** as a colorless solid. ^1H NMR (C_6D_6): δ 0.69 (9H, m), 0.88 (12H, m), 1.30 (9H, s), 1.67 (2H, d, *J* = 5.0 Hz), 2.18 (6H, m), 2.20 (1H, b), 3.05 (1H, b). ^{19}F NMR (C_6D_6): δ - 128.9 (4F, b), −131.3 (4F, b), −159.3 (2F, t, *J* = 20 Hz), −159.8 (2F, t, *J* = 20 Hz), −165.0 (4F, "t", *J* = 17 Hz), −165.4 (4F, b). Anal. Calcd for $C_{42}H_{41}NB_2F_{20}$: C, 52.46; H, 4.30; N, 1.45. Found: C, 51.67; H, 4.14; N, 1.20.

[18] $Cp'_2Th(CH_3)_2$ (0.10 g, 0.19 mmol) and **4** (0.18 g, 0.19 mmol) were stirred in 30 mL of benzene for 3 h. A colorless precipitate formed, which was collected by filtration and washed to yield 0.22 g (90%) of **5**. ^1H NMR (THF-d_8): δ 0.17 (3H, s), 1.30 (9H, s), 1.62 (30H, s), 1.73 (2H, d, *J* = 5.0 Hz), 2.27 (1H, b). ^{19}F NMR (THF − d_8): δ −129.2 (4F, b), −131.4 (4F, b), −159.0 (2F, t, *J* = 21 Hz), −159.5 (2F, t, *J* = 21 Hz), −164.2 (4F, b), −164.8 (4F, b). Anal. Calcd for $ThC_{51}H_{46}B_2F_{20}$: C, 47.39; H, 3.59; N, 0.00. Found: C, 47.08; H, 3.35; N, 0.00.

[19] Crystal data: $C_{55}H_{54}B_2F_{20}OTh$; triclinic, space group $P\bar{1}$; *a* = 12.280(2), *b* = 14.417(4), *c* = 17.790(3) Å; α = 110.39, β = 94.46(1), γ = 110.42(2)°; *V* = 2695(3), Å^3; Z = 2; d_{calcd} = 1.681 g/cm^3; at −120 °C. The structure was solved by direct methods. The nonhydrogen atoms were refined anisotropically. The hydrogen atom between the borons was refined isotropically, and remaining hydrogen atoms were fixed in "idealized" positions. The final cycle of full-matrix least-squares refinement was based on 6546 observed reflections ($I > 3.00\sigma(I)$) and 716 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of R = 0.035 and R_w = 0.043.

grown by slow diffusion of pentane into THF solutions. The diffraction data[19] show well-separated $Cp'_2Th(CH_3)THF^+$ and $^tBuCH_2CH[B(C_6F_5)_2]_2H^-$ ions (Figure 1). The former exhibits an unexceptional, "bent metallocene" geometry similar to that of **6** and **7**. However, respective metrical parameters of **6**,[4b] **8**, and **7**[4c] reflect increasing Th coordinative saturation: $Th-CH_3$ = 2.399(8) (**6**), 2.433(7) (**8**), 2.49(1) (**7**) Å; $Th-C_{ring}$ = 2.754(3) (av) (**6**), 2.786(3) (av) (**8**), 2.80 (1) (av) (**7**) Å; Th–O = 2.455(4) in **8** vs 2.531(9) and 2.628(8) Å in **7**. The dinuclear counterion contains an essentially planar four-membered ring (sum of internal angles 357.5°) with significant steric screening of the μ-H functionality. The average $B-C_{aryl}$ distance of 1.62 Å in **8** is substantially shorter than that in **6** (1.70 Å)[4b] and in typical $CH_3B(C_6F_5)_3^-$ complexes (1.64–1.66 Å).[6] This likely reflects both enhanced boron electron deficiency in **8** as well as reduced steric congestion.

Catalytic experiments were carried out using previously described procedures[6,15] in mixed *o*-difluorobenzene–benzene solutions, in which these catalysts are soluble and stable for hours. At 25 °C, the activity of **5** for ethylene polymerization ($5.8(1.1) \times 10^6$ g of linear polyethylene[20] (mol of Th)$^{-1}$ h^{-1} atm^{-1}; $N_t \approx 58(11)$ s^{-1}) exceeds that of any homogeneous organothorium complex studied to date (e.g., **6**, $3.6(7) \times 10^6$ g of polyethylene (mol of Th)$^{-1}$ h^{-1} atm^{-1}, $N_t \approx 36(7)$ s^{-1}; **7**, ~ $[1.1(2)] \times 10^3$ g of polyethylene (mol of Th)$^{-1}$ h^{-1} atm^{-1}; $N_t \approx 0.01(2)$ s^{-1}). For 1-hexene hydrogenation, the activity of **5** at 25 °C, and 1 atm of H_2 (3 mM catalyst, 1.0 M substrate) slightly exceeds that of **6** (N_t = 6.0(1) vs 5.2(1) s^{-1}). Experiments to be discussed elsewhere also indicate that the ethylene polymerization activities of **4**-derived zirconocene catalysts rival or exceed those of the $B(C_6F_5)_3$-derived analogues.[10,21]

These results provide the first information on the binuclear, diboron analogues of cationic $B(C_6F_5)_3$ / $B(C_6F_5)_4^-$-based metallocene polymerization catalysts. Noteworthy is the ability to form metallocene complexes with low apparent coordinative saturation and high reactivity for olefin polymerization and hydrogenation.

Acknowledgment. This research was supported by the U. S. Department of Energy (Grant DE-FG02-86ER13511). X.Y. thanks Akzo Chemicals for a postdoctoral fellowship. We thank Dr. D. A. Kershner of Akzo for GPC analyses.

Supplementary Material Available: X-ray experimental details, including a structure report, tables of positional and anisotropic displacement parameters, and bond lengths and angles, completely labeled drawings, and packing diagrams (45 pages). Ordering information is given on any current masthead page.

OM940407A

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(20) $M_w = 2.8 \times 10^5$, $M_n = 1.2 \times 10^5$ by GPC.

(21) Jia, L.; Marks, T. J. Manuscript in preparation.