Ionic, Base-Free Zirconocene Catalysts for Ethylene Polymerization

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In this communication we describe the syntheses and structural characterization of unique ionic, base-free zirconocene complexes which are highly active for the polymerization of ethylene.

Single-sited olefin polymerization catalysts based on bis(cyclopentadienyl)titanium(IV) or -zirconium(IV) with AlR_3[1] or methylalumoxane[2] are presumed to be ion pairs $[Cp'_2MR][aluminate]$.[3,4] This has been supported by theoretical studies[5] and the polymerization activity of the neutral Cp^*_2MR compounds (M = group III or lanthanide metal),[6] but characterization of the three-coordinate metallocene cation has proved difficult due either to the instability of the catalyst[7] or the complexity of the cocatalyst and the dynamic nature of the adduct.[8]

Active aluminum-free polymerization catalysts based on the formula $[Cp'_2MR][A]$ have proven difficult to prepare: classic "noncoordinating" anions (BF_4^-, PF_6^-) are either likely to be degraded by the metallocene cation[9] or are displaced by incoming olefin either slowly or not at all.[10] Discrete base-coordinated adducts of the type $[Cp_2MR(THF)][BPh_4]$ (M = Ti, Zr; R = CH_3, CH_2Ph) polymerize ethylene slowly due to the presence of a Lewis base.[11]

We have discovered that the use of peralkylated zirconocenes prevents anion degradation, obviates the need for a solvating Lewis base, maximizes lability of the anion to incoming olefin, and leads to highly active polymerization catalysts. The reaction of $[n\text{-}Bu_3NH][BPh_4]$ with $Cp^*_2ZrMe_2$ ($Cp^* = C_5Me_5$) in toluene results in gas evolution and an insoluble orange crystalline precipitate, **1a**, which rapidly polymerizes ethylene at ambient temperatures and pressures. Controlled-atmosphere solid-state ^{13}C NMR spectroscopy of this compound[12] indicated that this was not the target monomethyl cation but the zwitterion $Cp^*_2Zr\text{-}(+)\text{-}(m\text{-}C_6H_4)\text{-}B^{(-)}Ph_3$ (**1a**), probably formed by reaction of a monomethyl cation intermediate with the tetraphenylborate anion (eq 1). Reactions with tributylammonium salts of para-substituted tetraarylborates gave similar, toluene-soluble products **1b**,**c**.[13] The X-ray crystal structure of **1c** is shown in Figure 1.[14]

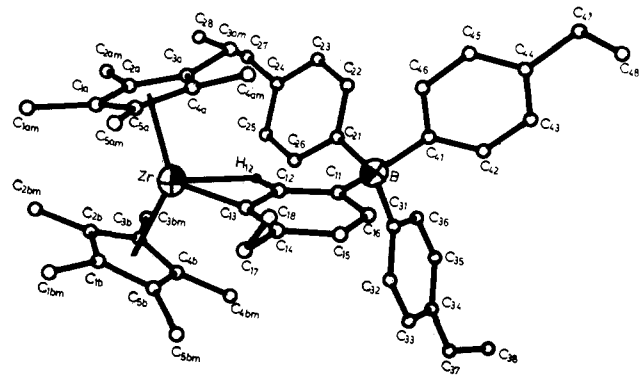


Figure 1. Molecular structure of **1c**. Important bond distances (Å) and angles (deg): Zr–C(13) = 2.154 (4), Zr–C(12) = 2.515 (4), Zr–H(12) = 2.14 (3), Zr–ring centroid = 2.205, C(12)–C(13)–Zr = 87.2 (2), C(14)–C(13)–Zr = 155.0 (3), C(12)–H(12)–Zr = 100 (2), ring centroid–Zr–ring centroid = 140.7. Thermal ellipsoids encompass 50% of their electron density.

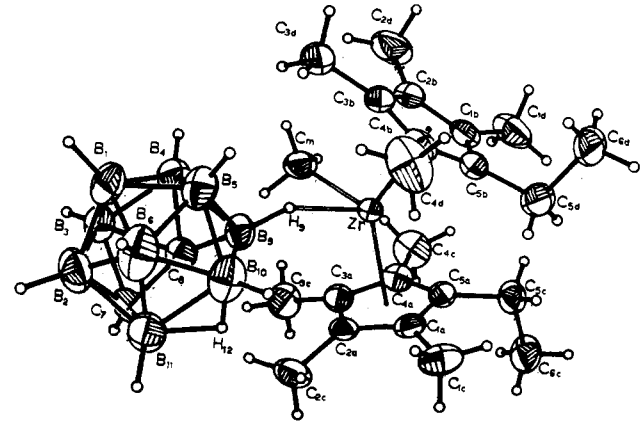
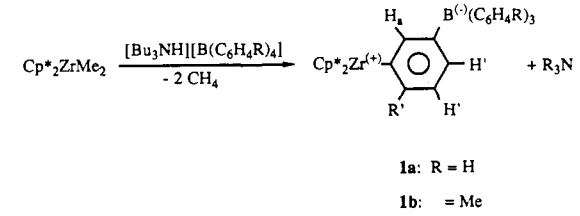


Figure 2. Molecular structure of **2b**. Important bond distances (Å) and angles (deg): Zr–H(9) = 2.12 (4), B(9)–H(9) = 1.19 (4), Zr–C(m) = 2.240 (4), Zr–ring centroid (a) = 2.231, Zr–ring centroid (b) = 2.215, Zr–H(9)–B(9) = 154 (2), H(9)–Zr–C(m) = 82.5 (9), ring centroid–Zr–ring centroid = 138.4. Thermal ellipsoids encompass 50% of their electron density.



(1)

1a: R = H

1b: = Me

1c: = Et

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(13) **1a**: Solid-state ^{13}C NMR, see Supplementary Material for details. **1b**: ^1H NMR (toluene-d_8, 100 MHz, room temperature) δ 1.35 (s, 30 H, $C_5(CH)_5$), 1.93 (s, 3 H, CH'_3), 2.37 (s, 9 H, CH_3), 4.65 (br s, 1 H, $C_6H'_2H_aMe$), 6.8–7.9 (m, 14 H, H' and C_6H_4Me). **1c**: ^1H NMR (room temperature, toluene-d_8) δ 0.95 (t, 3 H, $^2J_{HH}$ = 8 Hz, CH'_3), 1.25 (t, 9 H, $^2J_{HH}$ = 8 Hz, CH_3), 1.35 (s, 30 H, $C_5(CH_3)_5$), 2.10 (q, 2 Hz, $^2J_{HH}$ = 8 Hz, CH'_2), 2.65 (q, 6 Hz, $^2J_{HH}$ = 8 Hz, CH_2), 4.60 (br s, 1 H, H_a), 6.9–7.8 (m, 14 H, $C_6H'_2H_aEt$ and C_6H_4Et).

(14) Performed by Crystalytics Co., Lincoln, NE. Compound **1c** crystallizes from hot benzene with two C_6H_6 molecules of crystallization. Crystallographic data for **1c**·$2C_6H_6$: triclinic crystal system, a = 11.330 (2) Å, b = 11.994 (2) Å, c = 23.739 (5) Å, α = 92.60 (2)°, β = 112.16 (2)°, γ = 109.10 (2)°, V = 2770 (1) Å^3, Z = 2 for space group $P1\text{-}C_1^1$ (No. 2). R = 0.044 for 6103 reflections observed. H(12) was located from a difference Fourier synthesis and refined as an independent isotropic atom.

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One of the aryl rings of the $[BPh'_4]^-$ anion is metallated in the meta position with a Zr-C(13) distance of 2.154 (4) Å. The C-H bond ortho to boron acts as a ligand to the zirconium atom through an agostic interaction,[15] with a Zr-H(12) distance of 2.14 (3) Å. This unique proton appears in the ^1H NMR spectrum of **1c** at 4.77 δ. The metallated aryl ring is highly distorted with a Zr-C(13)-C(14) angle of 155.0 (3)° and a Zr-C(13)-C(12) angle of 87.2 (2)°. This distortion, which might be considered a static intermediate between aryl and benzyne hydride resonance structures, may be due to the coulombic interaction between the zirconium cation and boron anion; the related d^0 complex $(C_5Me_5)_2Sc(C_6H_5)$ shows no similar agostic interactions.[16]

The large size and chemical inertness of high-nuclearity polyhedral carboranes also make them compatible anions. $Cp^*_2ZrMe_2$ and $(etmcp)_2ZrMe_2$ (etmcp = C_5Me_4Et) (10% excess) react with the diprotic carborane complex *nido*-$C_2B_9H_{13}$[17] in pentane to form the monomethyl complexes $Cp'_2ZrMe(C_2B_9H_{12})$ (**2a**,**b**) in high yield as bright yellow precipitates (eq 2).[18]

$$Cp'_2ZrMe_2 + C_2B_9H_{13} \xrightarrow{-CH_4} Cp'_2ZrMe(C_2B_9H_{12}) \quad (2)$$

2a: Cp' = Cp*

2b: = etmcp

The solubility of **2a**,**b** in aromatic hydrocarbons suggested a tight ion pairing between the zirconocene monomethyl cation and the $[C_2B_9H_{12}]^-$ anion, but there was no spectroscopic evidence for an interaction. A single-crystal X-ray study of **2b** (Figure 2)[19] shows the $[(etmcp)_2ZrMe]^+$ cation is bound to the $[C_2B_9H_{12}]^-$ anion solely through a Zr-H-B bond to a terminal hydride on the nido face of the anion. The Zr-H(9) distance of 2.12 (4) Å is much longer than that of terminal M-H (1.6-1.7 Å) or bridging M-H-M (ca. 1.8 Å) bonds.[20] Both the large size of the anion and the peralkylcyclopentadienyl ligands limit any closer approach of the anion to the metal. The B(9)-H(9) distance, 1.19 (4) Å, is about 0.1 Å longer than the average of the other terminal B-H distances in the cage (1.08 Å). A similar, but greater perturbation occurs in $Fe(TPP)(CB_{11}H_{12})$: the Fe-H-B distance is shorter (1.82 Å) while the B-H(br) distance is about 0.2 Å longer than the other B-H distances.[21] However, the problem of accurately determining hydrogen atom positions in an X-ray experiment is well known.[22]

Both **1a-c** and **2a**,**b** function as catalysts for the polymerization of ethylene to linear polyethylene under mild conditions.[23] Unlike the base-coordinated metallocene catalyst $[Cp_2ZrMe(THF)][BPh_4]$, **1** and **2** show high activity even in low-dielectric solvents such as toluene or hexane. In the case of **1a-c**, there is no evidence that the tetraarylborate anion is the head group of the polymer chain. Our investigations into the chemistry of these compounds, the mechanisms of chain initiation, polymerization behavior of the catalysts, and the characteristics of the polymer formed will be presented in future publications.

Acknowledgment. We thank Dr. C. S. Day of Crystalytics Co. for carrying out the crystal structure studies, Dr. H. C. Welborn for consultations, and S. M. Wapp, D. J. Upton, and J. L. Zamora for expert technical assistance.

Supplementary Material Available: Solid-state NMR experimental details and X-ray structure details and tables of crystal data, final atomic positional and isotropic thermal parameters, bond distances and angles, and anisotropic displacement parameters for **1c** and **2b** (48 pages); tables of observed and calculated structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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(18) **2a**: ^1H NMR (room temperature, toluene-d_8) δ 1.67 (30 H, $C_5(CH_3)_5$), 0.23 (3 H, Zr-CH_3). **2b**: ^1H NMR (room temperature, toluene-d_8) δ 2.24 (q, $^2J_{HH}$ = 7 Hz, 4 H, -CH_2CH_3), 1.77 (d, J_{HH} = 8 Hz, 24 H, $C_4Et(CH_3)_4$), 0.80 (t, $^2J_{HH}$ = 7 Hz, 6 H, -CH_2CH_3), 0.30 (s, 3 H, Zr-CH_3).

(19) Performed by Crystalytics, Co., Lincoln, NE. Crystallographic data for **2b**: monoclinic crystal system, a = 10.538 (3) Å, b = 10.876 (3) Å, c = 13.029 (3) Å, β = 92.73 (2)°, V = 1491.6 (7) Å^3, Z = 2 in space group *Pn-an* alternate of *Pc*-C_s^2 (No. 7). R = 0.03 for 3495 observed reflections. Hydrogen atoms on $C_2B_9H_{12}$ were located by Fourier synthesis and refined as independent isotropic atoms.

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(23) Polymerizations were carried out in a 1-L stainless-steel autoclave. **1b** has an activity of 375 g PE/mmol **1b**·h·atm (0.13 mmol **1b** in 100 mL of toluene, 90 psig ethylene, 80 °C). **2a** has an activity of 265 g PE/mmol **2a**·h·atm (0.043 mmol **2a** in 250 mL of toluene, 240 psig ethylene, 40 °C). Compare to the activity of $[Cp_2ZrMe(THF)][BPh_4]$ (ca. 12 g PE/mmol catalyst·h·atm, CH_2Cl_2 solution, 1-4 atm ethylene, 25 °C).[11a]

Dopamine β-Monooxygenase Catalyzed Aromatization of 1-(2-Aminoethyl)-1,4-cyclohexadiene: Redirection of Specificity and Evidence for a Hydrogen Atom Transfer Mechanism

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Dopamine β-monooxygenase (DBM, E.C.1.14.17.1), a copper-dependent mammalian monooxygenase, catalyzes the conversion of dopamine to the neurotransmitter norepinephrine in the sympathetic nervous system.[1-4] Recent attention has been directed toward understanding the details of its catalytic mechanism for the purpose of rational development of specific inhibitors and alternate substrates as potential therapeutic agents for the modulation of adrenergic activity in vivo.[5-7] We now report that DBM catalyzes aromatization of 1-(2-aminoethyl)-1,4-cyclohexadiene [(I); (CHDEA)] in a facile process which exhibits the characteristics of the normal DBM reductive monooxygenation pathway but apparently does not entail oxygen transfer to the organic substrate.

CHDEA was synthesized, characterized,[8] and shown to be an excellent substrate for soluble bovine adrenal chromaffin granule DBM, with kinetic parameters comparable to those of the most

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