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Base-Free Cationic Mono(cyclopentadienyl)zirconium Complexes: Synthesis, Structural Characterization, and Catalytic Activity in Olefin Polymerization

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Mono(cyclopentadienyl) Lewis-base-free cationic complexes $[(C_5R_5)Zr(CH_2Ph)_2]^+$-$[B(CH_2Ph)(C_6F_5)_3]^-$ (R = H (1), Me (2)) have been synthesized by abstraction of one benzyl ligand from the corresponding neutral $(C_5R_5)Zr(CH_2Ph)_3$ precursors with the strong Lewis acid $B(C_6F_5)_3$. A single-crystal X-ray diffraction analysis of 1 shows that the formally 10-electron $[(C_5H_5)Zr(CH_2Ph)_2]^+$ cation is stabilized by π-coordination of the Ph ring of the $[B(CH_2Ph)(C_6F_5)_3]^-$ anion. The coordination geometry around Zr is tetrahedral, with normal, undistorted η^1-benzyl ligands, while a considerable deviation from planarity is observed for the π-coordinated Ph ring. Crystal data are a = 15.813(7) Å, b = 11.014(8) Å, c = 25.402(11) Å, β = 102.65(3)°, V = 4316.7 Å^3, Z = 4, space group $P2_1/n$. A dynamic equilibrium involving the dissociation of the counteranion is observed in solution by variable-temperature NMR spectroscopy for both 1 and 2. Both 1 and 2 react rapidly with THF, affording the Lewis-base adducts $[(C_5R_5)Zr(CH_2Ph)_2(THF)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (3 and 4), and initiate the ring-opening polymerization of THF. 1 and 2 promote the polymerization of ethene at 25 °C and 1 atm of monomer pressure with fairly high activity, while under the same conditions polymerization of propene proceeds sluggishly.

Following the pioneering studies by Jordan[1] and Bochmann,[2] the chemistry of cationic bis(cyclopentadienyl) group 4 metal alkyl complexes $[Cp_2MR]^+$ has been extensively developed in the last few years,[3] mainly because complexes of this type are currently believed to be the true active species of the metallocene–methylalumoxane Ziegler–Natta catalytic systems for olefin polymerization.[4] In contrast, little attention has been paid to analogous mono(cyclopentadienyl) derivatives,[5] which also play a role in some homogeneous methylalumoxane-based Ziegler–Natta catalysts promoting polymerization of olefins,[6] syndiotactic-specific polymerization of styrene,[7] and *cis*-1,4-polymerization of butadiene and other conjugated diolefins.[8]

Following recent findings[9] that catalysts promoting the polymerization of olefins and styrene can be obtained from non-metallocene group 4 complexes, such as homoleptic hydrocarbyls or mono(cyclopentadienyl) derivatives, by *in situ* activation with either $[C_6H_5NMe_2H]^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$, we have turned our attention to the possibility of isolating and characterizing the resulting active species. In this respect, we have recently reported the synthesis and structural characterization of the Cp-free cationic complex $[Zr(CH_2Ph)_3]^+[B(CH_2Ph)(C_6F_5)_3]^-$,[10] which revealed an intriguing reactivity with α-olefins, affording either the single-insertion adducts or high-molecular-weight polymers, depending on the reaction conditions.[11]

This paper describes the synthesis, the structural characterization, and the reactivity of the related mono-Cp complexes $[(C_5R_5)Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$

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Table I. Atomic Fractional Coordinates and Thermal Parameters for $[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-\cdot PhMe$ (1)[a]

	x	y	z	B_{iso} (Å^2)		x	y	z	B_{iso} (Å^2)
				Cation and Anion					
Zr	0.5864(1)	0.1523(2)	0.3210(1)		C30	0.3875(13)	–0.4738(20)	0.5104(9)	5.9(5)
C1	0.5870(14)	0.3463(22)	0.2710(9)	7.0(5)	C31	0.3276(14)	–0.4777(20)	0.4643(9)	5.9(5)
C2	0.5727(13)	0.3758(19)	0.3236(9)	6.4(5)	C32	0.3279(12)	–0.3849(17)	0.4278(8)	5.1(4)
C3	0.6551(13)	0.3437(21)	0.3569(8)	6.2(4)	F1	0.5070(7)	–0.2114(10)	0.4960(4)	6.9(2)
C4	0.7109(13)	0.2950(19)	0.3290(9)	6.1(5)	F2	0.5071(7)	–0.3816(10)	0.5667(4)	6.6(3)
C5	0.6705(15)	0.2964(20)	0.2771(9)	6.8(5)	F3	0.3896(8)	–0.5636(12)	0.5484(5)	8.1(3)
C6	0.6499(12)	0.0829(18)	0.4063(7)	5.1(4)	F4	0.2684(9)	–0.5665(13)	0.4541(5)	8.6(3)
C7	0.7425(12)	0.1115(16)	0.4310(7)	4.6(4)	F5	0.2625(7)	–0.3927(10)	0.3821(5)	6.7(3)
C8	0.8089(12)	0.0450(18)	0.4150(8)	5.2(4)	C33	0.2994(11)	–0.0913(16)	0.4059(7)	3.9(3)
C9	0.8949(14)	0.0707(21)	0.4389(9)	6.6(5)	C34	0.2106(11)	–0.0962(17)	0.3859(7)	4.4(4)
C10	0.9140(14)	0.1608(22)	0.4775(8)	6.7(5)	C35	0.1502(12)	–0.0266(18)	0.4006(8)	5.0(4)
C11	0.8497(14)	0.2254(20)	0.4932(8)	6.2(5)	C36	0.1768(13)	0.0585(19)	0.4398(8)	5.6(4)
C12	0.7628(12)	0.2008(18)	0.4706(8)	5.3(4)	C37	0.2583(12)	0.0687(18)	0.4638(7)	4.9(4)
C13	0.6613(12)	0.0373(18)	0.2724(8)	5.2(4)	C38	0.3193(11)	–0.0042(16)	0.4475(7)	4.1(4)
C14	0.6411(13)	–0.0958(19)	0.2637(8)	5.6(4)	F6	0.1790(7)	–0.1788(10)	0.3470(4)	5.8(2)
C15	0.6615(14)	–0.1824(20)	0.3038(9)	6.6(5)	F7	0.0669(8)	–0.0385(11)	0.3772(5)	7.0(3)
C16	0.6361(16)	–0.3061(23)	0.2919(10)	8.0(6)	F8	0.1177(8)	0.1309(12)	0.4550(5)	8.0(3)
C17	0.5954(17)	–0.3414(27)	0.2429(11)	9.4(7)	F9	0.2867(7)	0.1492(12)	0.5032(5)	7.3(4)
C18	0.5717(15)	–0.2574(23)	0.2009(10)	7.7(6)	F10	0.4017(7)	0.0067(9)	0.4752(4)	5.4(2)
C19	0.5967(13)	–0.1348(21)	0.2118(8)	6.5(5)	C39	0.3474(10)	–0.2259(16)	0.3269(7)	3.9(3)
B	0.3737(13)	–0.1756(19)	0.3899(8)	4.2(4)	C40	0.3785(11)	–0.3315(18)	0.3103(7)	4.8(5)
C20	0.4701(10)	–0.1076(15)	0.3911(6)	3.9(3)	C41	0.3687(12)	–0.3671(18)	0.2560(7)	5.1(4)
C21	0.4622(10)	–0.0080(16)	0.3507(7)	3.9(3)	C42	0.3225(13)	–0.2901(20)	0.2191(8)	5.8(4)
C22	0.4723(11)	–0.0363(16)	0.2976(7)	4.3(4)	C43	0.2924(13)	–0.1865(19)	0.2304(8)	5.7(5)
C23	0.4514(12)	0.0546(18)	0.2573(7)	5.0(4)	C44	0.3048(10)	–0.1550(18)	0.2854(6)	4.2(3)
C24	0.4240(12)	0.1718(19)	0.2685(8)	5.5(4)	F11	0.4263(7)	–0.4095(10)	0.3548(4)	5.7(2)
C25	0.4203(12)	0.2008(18)	0.3219(8)	5.3(4)	F12	0.4029(7)	–0.4717(11)	0.2439(4)	6.6(3)
C26	0.4424(12)	0.1123(17)	0.3624(7)	4.7(4)	F13	0.3126(8)	–0.3221(12)	0.1657(5)	8.0(3)
C27	0.3839(11)	–0.2922(16)	0.4335(7)	4.1(3)	F14	0.2493(7)	–0.1100(11)	0.1934(5)	6.9(3)
C28	0.449(11)	–0.2927(17)	0.4826(7)	4.4(4)	F15	0.2761(6)	–0.0438(9)	0.2946(4)	5.0(2)
C29	0.443(12)	–0.3857(17)	0.5194(8)	5.1(4)					
				Toluene Molecule (Standard Geometry Imposed)					
C45	–0.1045(10)	0.5960(15)	0.4165(6)	11.3(9)	C49	0.0171(10)	0.4614(15)	0.4187(6)	13.2(10)
C46	–0.0642(10)	0.6846(15)	0.3914(6)	12.7(10)	C50	–0.0638(10)	0.4844(15)	0.4303(6)	10.1(8)
C47	0.0167(10)	0.6617(15)	0.3799(6)	11.0(8)	C51	–0.1931(10)	0.6212(15)	0.4291(6)	16.2(13)
C48	0.0573(10)	0.5501(15)	0.3936(6)	12.0(9)					
				Centroids of C1–C2–C3–C4–C5 (Cp) and C22–C23–C24–C25–C26 (Ph) Systems					
Cp	0.6392	0.3314	0.3115		Ph	0.4421	0.1006	0.3015	

[a] Anisotropic thermal parameters B_{ij} (Zr only) are as follows (Å^2): $B_{11} = 4.97(8)$, $B_{22} = 3.88(7)$, $B_{33} = 3.86(7)$, $B_{12} = 0.41(8)$, $B_{13} = 0.82(5)$, $B_{23} = 0.01(8)$.

(R = H (1), Me (2)), which are active *single-component* olefin polymerization catalysts. 1 is the first structurally characterized cationic base-free mono(cyclopentadienyl) group 4 metal derivative.

Results

Synthesis and Crystal Structure of $[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (1). The reaction of $CpZr(CH_2Ph)_3$ with 1 equiv of $B(C_6F_5)_3$ in toluene at room temperature results in the precipitation of $[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (1) as a red crystalline solid (95%, eq 1). Complex 1 is sparingly soluble in

$$CpZr(CH_2Ph)_3 + B(C_6F_5)_3 \xrightarrow{\text{toluene},25\,°C} \underset{\textbf{1}}{[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-} \quad (1)$$

aromatic hydrocarbons and decomposes in chlorinated solvents such as CH_2Cl_2 and 1,1,2,2-$C_2H_2Cl_4$ at room temperature.

The molecular structure of 1 was established by single-crystal X-ray diffraction analysis of its toluene solvate. Atomic coordinates and relevant bond distances and angles are given in Tables I and II, while crystallographic data and technical details are reported in the Experimental Section. As shown in Figure 1, the molecular structure of 1 consists of a $[CpZr(CH_2Ph)_2]^+$ cation π-coordinated to a $[B(CH_2Ph)(C_6F_5)_3]^-$ anion through metal–arene bonding of BCH_2*Ph*. The coordination geometry around Zr, as defined by the methylene benzyl carbons C6 and C13 and the centers of gravity of the Cp and the Ph ligands, is tetrahedral. The angle Cp centroid–Zr–Ph centroid is 126°.

The two benzyl groups of the cation behave as normal, undistorted η^1 ligands, without significant $Zr\cdots C_{ipso}$ interactions (Zr–C7 = 3.33(2) Å, Zr–C15 = 3.30(2) Å, Zr–C6–C7 and Zr–C13–C14 = 120°). $Zr–CH_2$ distances (2.31(2) and 2.27(2) Å), as well as the other parameters within the benzyl ligands, are in the typical range of values observed for Zr benzyl compounds.[1b,d,12] The Cp ligand is unexceptional: the average Zr–C distance is 2.48 Å, and the Zr–Cp centroid distance is 2.18 Å (for similar complexes Zr–Cp distances range between 2.16 and 2.24 Å).[1a,b,3b,e,h,12b]

The Ph ring of the anion is coordinated to Zr unsymmetrically. In particular, the ipso carbon is significantly farther from Zr than the other ones: compare the Zr–C21 distance (2.86(2) Å) with the average of the remaining five (2.68 Å). Moreover, in spite of the limited accuracy of the present analysis, a significant distortion from planarity is observed for the Ph ring: the five atoms C22⋯C26 lie in

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Table II. Relevant Bond Distances and Bond Angles for $[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-\cdot PhMe$ (1)

	Bond Distances (Å)		
Zr–C1	2.49(2)	C3–C4	1.36(3)
Zr–C2	2.47(2)	C4–C5	1.33(3)
Zr–C3	2.45(2)	C5–C1	1.41(3)
Zr–C4	2.49(2)	C6–C7	1.50(2)
Zr–C5	2.49(2)	C13–C14	1.51(3)
Zr–C6	2.31(2)	C20–C21	1.49(2)
Zr–C13	2.27(2)	C21–C22	1.43(2)
Zr–C21	2.86(2)	C22–C23	1.42(2)
Zr–C22	2.73(2)	C23–C24	1.41(2)
Zr–C23	2.61(2)	C24–C25	1.41(2)
Zr–C24	2.63(2)	C25–C26	1.40(2)
Zr–C25	2.68(2)	C26–C21	1.41(2)
Zr–C26	2.74(2)	B–C27	1.68(2)
Zr–Cp[a]	2.18	B-C33	1.62(2)
Zr–Ph[a]	2.30	B–C39	1.66(2)
C1–C2	1.44(3)	B–C20	1.69(2)
C2–C3	1.43(3)		
	Bond Angles (deg)		
C6–Zr–C13	98.8(7)	C20–B–C33	116(2)
C6–Zr–Cp	107	C27–B–C33	104(1)
C6–Zr–Ph	109	C20–B–C39	101(1)
C13–Zr–Cp	101	C27–B–C39	110(1)
C13–Zr–Ph	111	C33–B–C39	113(1)
Cp–Zr–Ph	126	C21–C20–B	112(1)
C2–C1–C5	109(2)	C20–C21–C22	119(1)
C1–C2–C3	101(2)	C20–C21–C26	122(1)
C2–C3–C4	113(2)	C22–C21–C26	119(2)
C3–C4–C5	107(2)	C22–C23–C24	122(2)
C1–C5–C4	110(2)	C23–C24–C25	119(2)
Zr–C6–C7	120(1)	C24–C25–C26	119(2)
Zr–C13–C14	120(1)	C21–C26–C25	122(2)
C20–B–C27	112(1)		

[a] Cp and Ph denote the centroids of the C1, ..., C5 and C21, ..., C26 rings, respectively.

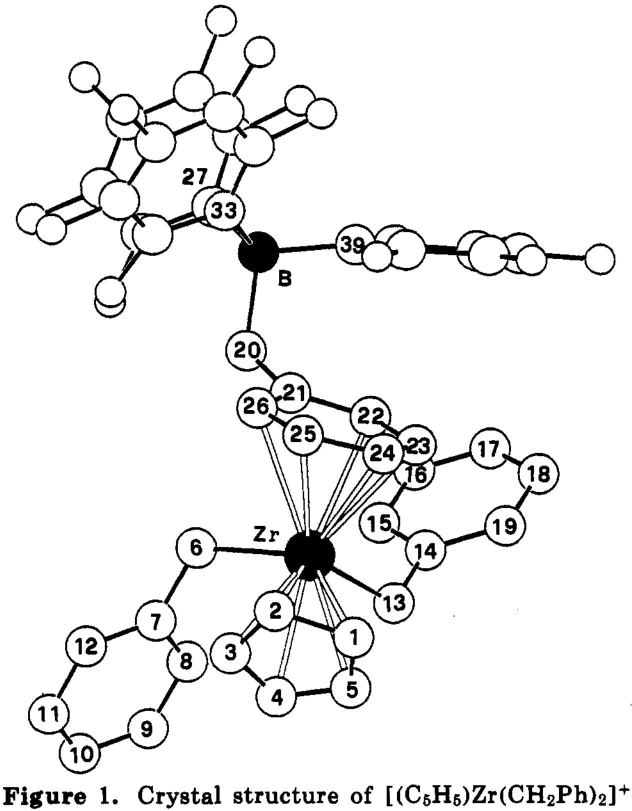

Figure 1. Crystal structure of $[(C_5H_5)Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (1).

the same plane (root mean square deviation (rmsd) from the least-squares plane is 0.008 Å); C20, C21, C22, and C26 are also coplanar (rmsd 0.007 Å); the dihedral angle between the two planes is 9° (esd 1°). In view of that, we believe that a η^5-coordination mode is the most appropriate formulation for the Zr–arene bonding. It is worth noting that in the case of the related complex $[Zr(CH_2Ph)_3]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (5), for which an analogous cation–anion interaction was described as η^6-arene–metal coordination,[10] the same effect is also present, but to a much lesser extent ($Zr–C_{ipso}$ = 2.76 Å vs average $Zr–C_{Ph}$ = 2.68; the above interplanar angle is 3°). It has been previously anticipated[13] that structural forms intermediate between the idealized η^6, η^4, and η^2 formulations for arene–metal coordination could exist also in the ground state. The different degrees of distortion from an idealized η^6-Ph coordination found for 1 and for the essentially isostructural 5 could be explained on the basis of the lower unsaturation of the cation in the former (in 5 a η^2-benzyl replaces a η^5-Cp group).

The four B–C bonds in $[B(CH_2Ph)(C_6F_5)_3]^-$ are tetrahedrally arranged, with some distortion of the valence angles around B (see Table II). Both the coordination geometry around B and the conformations of C_6F_5 and CH_2Ph ligands observed for the anions in 1 and 5 are quite similar, in spite of the different crystal packings.

Solution Structure of 1. Due to the poor solubility of 1 in aromatic hydrocarbon, its solution behavior was studied by NMR spectroscopy in CD_2Cl_2 at low temperature. The zwitterionic structure found in the solid state is maintained in solution at −70 °C, as suggested by the two doublets of a AB system observed at δ 1.80, 2.07 for the diastereotopic $Zr–CH_2Ph$ protons, while the corresponding ortho Ph protons resonate at δ 6.77, in the usual range for normal, undistorted η^1-benzyls.[1b,12] The chemical shifts of the BCH_2Ph protons differ significantly from those of the "free" anion[10] (see the Experimental Section). The ^{13}C NMR spectrum (CD_2Cl_2, −70 °C) confirms this picture: particularly telling is the J_{CH} coupling constant (122 Hz) found for $Zr–CH_2Ph$, which is a typical value for η^1-benzyl ligands.[1b,12] At increasing temperature, a fluxional process involving the dissociation of the counterion is clearly suggested by a considerable broadening of both the $Zr–CH_2Ph$ ^1H resonance, reaching coalescence at 0 °C in a broad signal centered at δ 2.2, and the ^1H aromatic resonances. At this temperature and above, rapid decomposition occurs, possibly through Cl abstraction from the solvent, precluding further analysis. A ^1H NMR spectrum recorded at 25 °C in chlorobenzene-d_5 (in which 1 is only poorly soluble) shows a rather broad singlet at δ 1.78 for $Zr–CH_2Ph$ and a complex pattern of broad resonances for the aromatic protons, partially obscured by residual solvent peaks, consistent with a dynamic equilibrium between the zwitterion and the solvent-separated ion pair.

Synthesis and Characterization of $[Cp^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (2). The reaction of $Cp^*Zr(CH_2Ph)_3$ (Cp^* = C_5Me_5) with $B(C_6F_5)_3$ in 1,2,4-trichlorobenzene/toluene at room temperature results in the slow precipitation of $[Cp^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (2) as yellow crystals (eq 2, 90%). Complex 2 is considerably more soluble and stable than 1 in solvents such as chlorobenzene or bromobenzene and could be characterized by ^1H and ^{13}C NMR analysis in chlorobenzene-d_5 at 25 °C. Noteworthy in the ^1H NMR spectrum are a singlet observed at δ 2.15 for the $Zr–CH_2Ph$ protons and an unusually high-field broad resonance at δ 4.50 for

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[13] Muetterties, E. L.; Bleeke, J. R.; Wucherer, J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

$$\mathrm{Cp^*Zr(CH_2Ph)_3 + B(C_6F_5)_3 \xrightarrow[25\ ^\circ C]{\text{trichlorobenzene/toluene}} \underset{\textbf{2}}{[Cp^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-}} \quad (2)$$

the corresponding ortho Ph protons: the former finding, consistent with the equivalence of the Zr–CH_2Ph protons, suggests that the solvent-separated ion pair is the prevailing species under these conditions; the latter indicates a very strong η^n interaction[1b,12] of the benzyl ligands with the highly electrophilic Zr in the "naked" cation. The upfield shift of the ^{13}C resonance of Zr–CH$_2$ carbons (δ 62.0 ppm) confirms the above η^n interaction, although the broadness of the signal precluded evaluation of the J_{CH} coupling constant. The broadness of ^{1}H and ^{13}C resonances for ZrCH$_2$Ph groups suggests a rotational dynamics of the η^n-benzyl ligands at room temperature. Low-temperature ^{1}H NMR experiments performed in CD$_2$Cl$_2$ showed some other dynamic process, probably involving some cation–anion interaction, but did not allow us to "freeze" a zwitterionic structure analogous to that of **1** (at −70 °C a sharp singlet at δ 2.10 is found for the Zr–CH_2Ph protons).

Reactivity with THF. Addition of THF to **1** and **2** generated *in situ* in toluene-d_8 results in the immediate precipitation of the Lewis-base adducts $[(C_5R_5)Zr(CH_2Ph)_2(THF)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (R = H, orange oil, **3**; R = Me, yellow oil, **4**), which have been characterized by NMR analysis in 1,1,2,2-C$_2$D$_2$Cl$_4$. For both **3** and **4**, resonances for two coordinated molecules of THF and for the "free" anion are detected in the ^{1}H NMR spectra (see the Experimental Section). The upfield shift for the ortho Ph ^{1}H resonances, observed at δ 6.71 for **3** and δ 6.67 for **4**, and a J_{CH} value of 134 Hz observed for **4** indicate some η^n interaction of the benzyl ligands with Zr, as previously found by Jordan *et al.*[5] for the analogous mono-THF complex $[Cp^*Zr(CH_2Ph)_2(THF)]^+[BPh_4]^-$. Interestingly, the latter was found to decompose in solution through Ph abstraction from BPh$_4^-$, while **3** and **4** are stable for days in C$_2$D$_2$Cl$_4$, probably due to the higher coordinative saturation of Zr and the lower reactivity of the $[B(CH_2Ph)(C_6F_5)_3]^-$ counterion. Complexes **3** and **4** initiate the ring-opening polymerization of THF: poly(tetrahydrofuran), characterized by NMR and DSC analysis, was produced when **1**–**4** were dissolved in THF. It is worth noting that cationic zirconocenes are stable in THF solution, with the exception of $[Cp_2Zr(Ph)(THF)]^+[BPh_4]^-$, which slowly decomposes over several days, producing some poly(tetrahydrofuran).[14] The higher reactivity of **3** and **4** in the ring-opening polymerization of THF reflects the higher electrophilicity of mono-Cp cations with respect to the analogous bis-Cp derivatives.

Catalytic Activity in Olefin Polymerization. We have previously reported that complexes **1** and **2** generated *in situ* promote the polymerization of ethene and propene in toluene solution at 50 °C and 5 atm of monomer pressure.[9c] We have now investigated the olefin polymerization activity of **1** and **2** and, for comparison, of the related Cp-free complex **5**[10] under milder conditions. The results summarized in Table III show that the activities of **1** and **2** are comparable, while **5** is much less active. This finding could be related to the lower tendency of the zwitterionic **5** to dissociate,[10] at least in aromatic solvents (see below for further discussion).

Table III. Ethene Polymerization with Mono-Cp and Cp-Free Cationic Zr Complexes

run no.	catalyst	temp (°C)	time (min)	yield (mg)	activity (kg of PE (mol of Zr)$^{-1}$ h^{-1})
1[a]	1	0	15	37	5.9
2[a]	1	27	5	183	88
3[a]	1	50	2.5	91	87
4[a]	2	26	5	88	42
5[a]	2	47	2.5	33	32
6[a]	5	26	30	trace	
7[b]	5	50	30	48	1.9

[a] Polymerization conditions: monomer pressure 1 atm, solvent 25 mL of toluene, [Zr] = 1 mM. [b] [Zr] = 2 mM.

However, it is worth noting that evaluation of the activity of single-component cationic catalysts, in the absence of scavengers such as aluminum alkyls or even an excess of the Zr hydrocarbyl, is always affected by an uncertainty due to the sacrificial function of a fraction of the catalyst in scavenging impurities of the solvent and/or the monomer.[9,15] This fact, as well as the usually short lifetimes of these Al-free catalysts,[15] should be considered in the comparison of their activity with that of the methylalumoxane-based systems.

Polymerization tests under similar conditions were performed with propene by using **1**, **2**, or **5** (see the Experimental Section): in every case, only traces of solid polymer were obtained. In the case of **1**, the polymerization mixture was hydrolyzed with acidified water and pentane was added. Separation of the organic layer and solvent evaporation left a waxy residue, which was identified by ^{13}C NMR analysis as an oligomeric atactic poly(propylene) analogous to that obtained in the presence of CpZr(CH$_2$Ph)$_3$–methylalumoxane.[9a]

1 promotes polymerization of ethene also in the solid state: a microcrystalline powder of **1** (50 mg) was placed in contact with ethene (5 mmol) at room temperature. After 3 weeks, almost quantitative polymerization had occurred on the surface of the solid catalyst, producing high-molecular-weight linear poly(ethylene), characterized by NMR and DSC analysis (mp 139 °C).

Discussion

Several synthetic approaches have been followed in order to generate cationic d^0 group 4 metal complexes from the neutral precursors, including (a) one-electron oxidation with AgBPh$_4$ or [Cp$_2$Fe][BPh$_4$],[1] (b) protonolysis with $[HNR_3]^+[B(C_6X_5)_4]^-$ (X = H, F),[2,3a–c] (c) abstraction of an anionic ligand with the carbenium salt[3d,i,j] $[CPh_3]^+[B(C_6X_5)_4]^-$, and (d) abstraction of an anionic ligand with the strong Lewis acid B(C$_6$F$_5$)$_3$.[3g,9b,c,15a] As recently pointed out by Siedle *et al.*,[16] reactions a–c are mainly driven by the irreversible formation of byproducts in addition to the targeted cationic complexes, while method d is based on the equilibrium transfer of an R$^-$ group from the transition metal to boron (see, e.g., eqs 1 and 2). The above observation could account for the experimental finding that stable, isolable, and in some cases structurally characterizable cationic complexes are typically obtained from metallocenes as well as from mono-Cp and Cp-free

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[14] Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.

[15] (a) Ewen, J. A.; Elder, M. J. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 179. (b) Chien, J. C. W.; Tsai, W.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 141.

[16] Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Stevens, J.; Richardson, D. E.; Ryan, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 215.

derivatives by using method d, while methods a–c usually afford Lewis-base adducts such as $[(Cp)_nZr(R)_{3-n}(L)_m]^+$ (L = THF, CH_3CN, PR_3) or produce generally unstable, unisolable base-free cationic complexes.[17]

According to the literature,[1–4] unreactive and poorly coordinating anions, such as $[BPh_4]^-$, $[B(C_6H_4F)_4]^-$, and $[B(C_6F_5)_4]^-$, are required in order to obtain fairly stable cationic complexes functioning as catalysts for olefin polymerization. The activity increases while the coordinating ability of the anion decreases, in the order $[BPh_4]^- < [B(C_6H_4F)_4]^- < [B(C_6F_5)_4]^-$. Of course, reaction of $B(C_6F_5)_3$ with neutral $(Cp)_nMR_{4-n}$ ($n = 0$–2) compounds results in the production of $[B(R)(C_6F_5)_3]^-$ anions, which can show different coordination properties depending on R. As a matter of fact, Marks *et al.*[3g] reported the synthesis of $[(C_5H_3Me_2)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$, in which the $[B(Me)(C_6F_5)_3]^-$ anion is coordinated to Zr through the BMe group. Very recently, while this work was near completion, a preliminary communication[18] reported the synthesis of $[Cp^*MMe_2(\eta^6\text{-arene})]^+[B(Me)(C_6F_5)_3]^-$ (M = Zr, Hf), for which NMR analysis indicates that the solvent-separated ion pairs, stabilized by the coordination of the aromatic solvent, are the prevailing species. In the case of **1** and **2**, in contrast, it turns out that the electronic deficiency of Zr is relieved either by the coordination of the Ph ring of the $[B(CH_2Ph)(C_6F_5)_3]^-$ counterion (as occurs for **1** in the solid state and in solution at low temperature) or by η^n coordination of the Zr-bound benzyl ligands (as found for **2** in solution at room temperature). There is no evidence of the coordination of aromatic solvents either in solution or in the solid-state structure of **1**, in which solvated toluene molecules showing no significant interactions with Zr are actually present. These findings indicate that a wide spectrum of interactions involving the cation, the anion, and the solvent can influence the structure and consequently the activity of such cationic catalysts.[19,20]

The activity in ethene polymerization of **1**, **2**, and **5** parallels the extent of the dissociation for the equilibrium

$$[(C_5R_5)_nZr(CH_2Ph)_{3-n}(\eta^6\text{-}PhCH_2B(C_6F_5)_3)] \rightleftarrows [(Cp)_nZr(CH_2Ph)_{3-n}]^+[B(CH_2Ph)(C_6F_5)_3]^- \quad (3)$$

$$n = 0, 1$$

In fact, while **1** and **2**, for which extensive dissociation occurs in solution at room temperature, promote the polymerization of ethene in toluene at 25 °C and 1 atm of monomer pressure with a minimum activity of (0.5–1) $\times 10^5$ g of PE (mol Zr)$^{-1}$, under the same conditions **5**, for which coordination of the counterion is maintained in toluene solution up to 100 °C,[10] is almost inactive. The observed increase of the extent of the dissociation in the order $5 < 1 \leq 2$ is reasonably expected on the basis of the relative electrophilicities of the respective cations. Actually, the different strengths of the cation–anion bonding interactions in **1** and **5** are reflected also in their solid-state structures. However, it is hazardous to anticipate polymerization activity simply from electrophilicity of the cationic catalysts, since other factors, e.g. steric factors, should be taken in account.

We have recently found[11] that reaction of propene with **5** at 25 °C affords quantitatively the single-insertion adduct $[Zr(\eta^2\text{-}CH_2Ph)_2(CH_2CHMeCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$, in which the cation is coordinatively saturated through η^6 coordination of the Ph ring of the $CH_2CHMeCH_2Ph$ group. Polymerization of propene occurs only under more severe conditions and is accompanied by the formation of $CH_2{=}CMeCH_2Ph$, suggesting that propagation probably occurs after β-hydrogen elimination in the monoinsertion adduct. Extension of this study to mono-Cp derivatives, to be reported elsewhere, suggests that the formation of stable single-insertion adducts is a typical feature for the reaction of cationic Zr–benzyl complexes with α-olefins, accounting for the observed low activity of **1**, **2**, and **5** in the polymerization of propene under mild conditions.

Experimental Section

General Procedures. All procedures were carried out under nitrogen by using standard Schlenk or glovebox techniques. Solvents were treated as follows: sulfur-free toluene,[9c] *n*-heptane, and THF were refluxed for 48 h over sodium–benzophenone and distilled before use; 1,2,4-trichlorobenzene was distilled from CaH_2. Deuteriated solvents were filtered through activated basic alumina before use. Polymerization-grade ethylene was used without purification, while propene was distilled over $Al(i\text{-}Bu)_3$. $CpZr(CH_2Ph)_3$, $Cp^*Zr(CH_2Ph)_3$, and $B(C_6F_5)$ were synthesized according to the literature.[21–23]

NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 250 MHz for ^1H and at 62.89 MHz for ^{13}C. The chemical shifts are reported vs tetramethylsilane and were determined by reference to residual ^1H and ^{13}C solvent peaks. Zr content in compounds **1** and **2** was determined by using a Perkin-Elmer 372 atomic absorption spectrophotometer.

$[CpZr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (1). To $CpZr(CH_2Ph)_3$ (570 mg, 1.3 mmol) dissolved in toluene (10 mL) was added a solution of $B(C_6F_5)_3$ (670 mg, 1.3 mmol) in 10 mL of toluene at room temperature: the solution changed immediately from yellow to red. The solution was kept overnight at 4 °C: **1**·PhMe precipitated as a red microcrystalline solid (95% isolated yield, 100% by NMR). ^1H NMR (CD_2Cl_2, −70 °C): $ZrCH_2Ph$, δ 7.23 (t, 4 H, *m* C_6H_5), 6.98 (t, 2 H, *p* C_6H_5), 6.77 (d, 4 H, *o* C_6H_5), 2.07, 1.80 (2 d, AB system, $^2J = 11.9$ Hz, CH_2); Cp, δ 5.98 (s, 5 H, C_5H_5); BCH_2Ph, δ 7.05 (t, 2 H, *m* C_6H_5), 7.02 (t, 1 H, *p* C_6H_5), 6.61 (d, 2 H, *o* C_6H_5), 2.95 (br s, 2 H, CH_2). ^{13}C NMR (CD_2Cl_2, −70 °C): $ZrCH_2Ph$, δ 147.8 (*ipso*), 128.6 (*m*), 125.6 (*o*), 123.2 (*p*), 71.3 (J_{CH} = 122 Hz, CH_2); BCH_2Ph, δ 157.7 (*ipso*), 129.5 (*m*), 129.3 (*o*), 124.6 (*p*); Cp, δ 115.2. Resonances for solvated toluene (1 equiv) are also observed. Anal. Calcd for $C_{51}H_{34}BF_{15}Zr$: Zr, 8.82. Found: Zr, 8.94.

$[Cp^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (2). Reaction of $Cp^*Zr(CH_2Ph)_3$ (250 mg, 0.5 mmol) with $B(C_6F_5)_3$ (255 mg, 0.5 mmol) in 1,2,4-trichlorobenzene (10 mL) at 25 °C, followed by the addition of toluene (10 mL), resulted in the precipitation of

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[17] A few base-free cationic metallocenes have been isolated by methods b and c: (a) Reference 3f. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840. (c) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (d) Bochmann, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992**, *424*, C5.

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[19] The influence of the coordination of aromatic solvents on the polymerization activity of catalysts based on group 4 metal complexes and methylalumoxane was realized long before we were able to isolate the true active complexes: (a) Oliva, L.; Pellecchia, C.; Cinquina, P.; Zambelli, A. *Macromolecules* **1989**, *22*, 1642. (b) References 4b and 7c.

[20] Temperature- and solvent-dependent cation–anion interactions have been suggested to play a role in both the activity and the stereospecificity of metallocene-based catalysts: (a) Reference 3h. (b) Eisch, J. J.; Caldwell, K. R.; Werner, S.; Kruger, C. *Organometallics* **1991**, *10*, 3417. (c) Reference 17d. (d) Herfert, N.; Fink, G. *Makromol. Chem.* **1992**, *193*, 773.

[21] Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419.

[22] Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

[23] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

2 as a yellow crystalline solid (90% isolated yield, 100% by NMR). ^{1}H NMR (C_6D_5Cl, 25 °C): $ZrCH_2Ph$, δ 6.38 (d, 2 H, *p* C_6H_5), 6.28 (t, 4 H, *m* C_6H_5), 4.50 (br s, 4 H, *o* C_6H_5), 2.15 (s, 4 H, CH_2); Cp*, δ 1.61 (s, 15 H, C_5Me_5); BCH_2Ph, δ 7.20 (d, 2 H, *o* C_6H_5), 7.04 (t, 2 H, *m* C_6H_5), 6.89 (t, 1 H, *p* C_6H_5), 3.40 (br s, 2 H, CH_2). ^{13}C NMR (C_6D_5Br, 25 °C; selected resonances): δ 119.8 (C_5Me_5), 62.0 (br, $ZrCH_2Ph$), 32.5 (br, BCH_2Ph), 12.3 (C_5Me_5); two broad signals at δ 115.2 and 110.0 are tentatively assigned to the ipso and ortho carbons of $ZrCH_2Ph$. Anal. Calcd for $C_{49}H_{36}BF_{15}Zr$: Zr, 9.02. Found: Zr, 9.45.

Reactivity of 1 and 2 with THF. To a solution of either **1** or **2** (~0.1 mmol) prepared *in situ* in 2 mL of toluene-d_8 was added THF (0.05 mL) at room temperature: **2** or **3** deposited immediately as an orange (**3**) or a yellow (**4**) oil, respectively. ^{1}H NMR for **3** (1,1,2,2-$C_2D_2Cl_4$, 25 °C): $ZrCH_2Ph$, δ 7.54 (t, 4 H, *m* C_6H_5), 7.42 (t, 2 H, *p* C_6H_5), 6.71 (d, 4 H, *o* C_6H_5), 2.26 (br s, 4 H, CH_2); Cp, δ 6.49 (s, 5 H, C_5H_5); THF, δ 3.56 (br s, 8 H, α-CH_2), 1.91 (br s, 8 H, β-CH_2). ^{13}C NMR for **3** (1,1,2,2-$C_2D_2Cl_4$, 25 °C): $ZrCH_2Ph$, δ 133.9 (*ipso*), 129.8 (*m*), 128.4 (*o*), 126.6 (*p*), 72.5 (CH_2); Cp, δ 113.8; THF, δ 73.0 (br, α-CH_2), 25.4 (β-CH_2). ^{1}H NMR for **4** (1,1,2,2-$C_2D_2Cl_4$, 25 °C): $ZrCH_2Ph$, δ 7.49 (t, 4 H, *m* C_6H_5), 7.36 (t, 2 H, *p* C_6H_5), 6.67 (d, 4 H, *o* C_6H_5), 2.05 (br s, 4 H, CH_2); Cp*, δ 2.10 (s, 5 H, C_5Me_5); THF, δ 3.5 (br s, 8 H, α-CH_2), 1.9 (br s, 8 H, β-CH_2). ^{13}C NMR for **4** (1,1,2,2-$C_2D_2Cl_4$, 25 °C): $ZrCH_2Ph$, δ 137.4 (*ipso*), 131.1 (*m*), 129.5 (*o*), 124.5 (*p*), 79.5 (J_{CH} = 134 Hz, CH_2); Cp*, δ 124.8 (C_5Me_5), 11.8 (C_5Me_5); THF, δ 72.0 (α-CH_2), 25.4 (β-CH_2).

Identical signals for the "free" anion are found for both **1** and **2**. ^{1}H NMR: BCH_2Ph, δ 7.06 (t, 2 H, *m* C_6H_5), 7.02 (t, 1 H, *p* C_6H_5), 6.97 (d, 2 H, *o* C_6H_5), 3.07 (br s, 2 H, CH_2). ^{13}C NMR: δ 148.2 (*ipso*), 128.9 (*m*), 128.1 (*o*), 125.2 (*p*).

Attempts at crystallization lead to partial decomposition, probably due to the loss of some coordinated THF.[10b] Solution of either **1** or **2** in THF became more and more viscous over 3–4 h. In a typical experiment, 25 mg of **1** was dissolved in 2 mL of THF. After 3 h, addition of acidified methanol resulted in the precipitation of a waxy solid (0.1 g), which was identified by DSC (mp 45 °C) and ^{13}C NMR analysis as poly(tetrahydrofuran).[14] ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 25 °C): δ 67.4, 23.3.

5 also initiates the ring-opening polymerization of THF, while $B(C_6F_5)_3$ is not active.

Polymerization Experiments. Polymerizations of ethylene were carried out in 100-mL magnetically stirred glass flasks, which were charged with toluene; this solvent was thermostated at the desired temperature and saturated with the monomer at 1 atm. Polymerization runs were then initiated by injecting the solution of the catalyst, while the monomer pressure was kept constant, and terminated by injecting methanol. The reaction mixture was poured into acidified ethanol, and the resulting solid polymers were collected and dried *in vacuo* at 80 °C. Polymerizations of propene were performed similarly at 1 atm of monomer pressure and temperatures ranging between 25 and 50 °C, with catalyst concentrations of 1–10 mM, by using **1**, **2**, or **5**: in every case, only traces of solid polymer were obtained. In one case (run 8, temperature 50 °C, time 30 min, [**1**] = 10 mM, 5 mL of toluene) 30 mg of oligomeric poly(propylene) was recovered as described above.

X-ray Structural Analysis. Single crystals of **1** were obtained by allowing $CpZr(CH_2Ph)_3$ and $B(C_6F_5)_3$ to react in 1,2,4-trichlorobenzene and layering toluene over the solution obtained: red plates of **1**·PhMe deposited on standing 24 h at room temperature. Diffraction data were collected at 25 °C with an Enraf-Nonius CAD-4 diffractometer. Data for **1**·PhMe are as follows: empirical formula $C_{44}H_{26}BF_{15}Zr \cdot C_7H_8$; fw 1033.83; crystal size (mm) 0.4 × 0.4 × 0.1; space group $P2_1/n$; lattice constants $a = 15.813(7)$ Å, $b = 11.014(8)$ Å, $c = 25.402(11)$ Å, $\beta = 102.65(3)°$, $V = 4316.7$ Å^3, $Z = 4$, d(calcd) = 1.58 g/cm^3; radiation Mo Kα; scan ratio $2\theta/\omega = 0.70$, scan limit $2 < \theta < 26°$; scan speed 2.5°/min (measurement time was kept low since crystals of **1** partially decompose under radiation); data collected $\pm h,k,l$; 8770 reflections measured; 3325 reflections included in the structure analysis ($F > 2\sigma_F$); structure solved by Patterson and Fourier transform methods and refined using isotropic thermal parameters for all atoms, except Zr; H atoms neglected; weight factors unitary; data/parameter ratio 3325/198; maximum parameter shift/esd 0.070; maximum residual density 0.87 e/Å^3; final R factor 0.10. Calculations were made by using the SHELX-76 package.

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Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, and least-squares planes and deviations therefrom for **1**·PhMe (8 pages). Ordering information is given on any current masthead page.

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