

Synthesis and Structure of Donor-Ligand-Stabilized Tris(cyclopentadienyl)zirconium Cations

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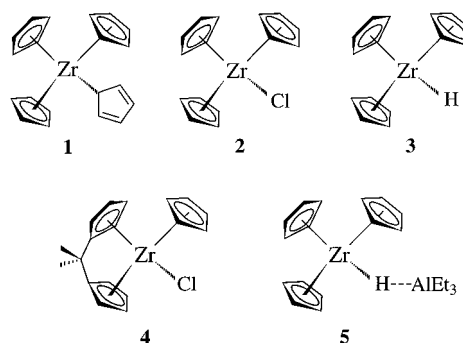
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Treatment of $\text{Cp}_2\text{Zr}(\text{Cl})\text{CH}_3$ (**6**) with sodium cyclopentadienide gives Cp_3ZrCH_3 (**7**). Its reaction with dimethylanilinium tetraphenylborate yields the $\text{Cp}_3\text{Zr}(\text{THF})^+$ cation. $[\text{Cp}_3\text{Zr}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ (**9**) is generated by treatment of **7** with tris(pentafluorophenyl)borate. Nitriles add to **9** to form the ligand-stabilized tris(η^5 -cyclopentadienyl)zirconium cation systems $\text{Cp}_3\text{Zr}(\text{N}\equiv\text{CR})^+$. With *tert*-butyl isocyanide, **9** is transformed to yield the donor-ligand-stabilized $[\text{Cp}_3\text{Zr}(\text{C}\equiv\text{NCMe})_3^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ salt **12**. Carbon monoxide adds to **9** to give the cationic metal carbonyl complex $[\text{Cp}_3\text{Zr}(\text{CO})^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ (**13**). Both cation complexes **12** and **13** were characterized by X-ray diffraction.

Introduction

While an enormous amount of knowledge about the chemistry of bis(cyclopentadienyl)zirconium(IV) compounds has been accumulated in recent years,¹ relatively little is known about the corresponding Cp_3Zr systems. According to Hoffmann et al. the molecular orbital situation of the $\text{Cp}_3\text{Zr}^{\text{IV}}$ fragment (in idealized D_{3h} symmetry with all three Cp ligands η^5 -coordinated) is such that the HOMO is almost completely ligand centered (a_2) and that there is a metal-centered LUMO (mostly of d_z^2 origin) that is mainly extended along the 3-fold axis.² Therefore, the Cp_3Zr^+ cation should have a tendency of picking up a suitable donor ligand L to form stable pseudotetrahedral $\text{Cp}_3\text{Zr}-\text{L}^+$ cations. It is expected that the Cp_3Zr^+ cation might become available by reacting the usual anion-abstracting reagents (e.g. $\text{HNR}_3^+\text{BPh}_4^-$, methylalumoxane (MAO), $\text{Ph}_3\text{C}^+\text{BPh}_4^-$, or $\text{B}(\text{C}_6\text{F}_5)_3$)³ with a suitable tris(cyclopentadienyl)zirconium hydrocarbyl $\text{Cp}_3\text{Zr}-\text{R}$ substrate. However, it was not clear a priori whether these reactions would proceed in the usual way leading to a clean R^- abstraction or if the reaction of any of these electrophilic reagents with the rather electron rich (and therefore probably increased basic) Cp ligand of the tris(cyclopentadienyl)zirconium system would compete or even become dominant. A review of the literature was not decisive about this question. A number of $\text{Cp}_3\text{Zr}-\text{R}$ or $\text{Cp}_3\text{Zr}-\text{X}$ type systems had been reported (see Chart 1)

Chart 1. Selected Examples of $\text{Cp}_3\text{Zr}-\text{R}$ Type Complexes That Were Previously Described



and a few had been treated with electrophiles, but to our knowledge a $\text{Cp}_3\text{Zr}-\text{L}^+$ cation, isolated from its counterion, had not been observed so far. A few Cp_3Zr^+ -containing ion pairs (e.g. **5**) had been described, and the catalytic ethene polymerization activity of the **4**/MAO system might have to be contributed to a tris(cyclopentadienyl)Zr-type complex generated in situ.⁴

In this study we have found a favored pathway for generating Cp_3Zr^+ and for the preparation of a number

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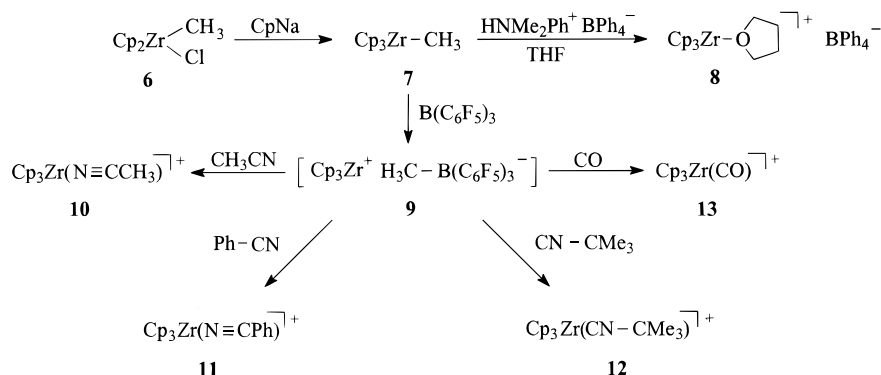
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Scheme 1. Synthesis of Tris(cyclopentadienyl)zirconium Complexes (Cations 10–13 with $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ Anion)



of ligand-stabilized $\text{Cp}_3\text{Zr-L}^+$ systems. These new complexes can readily be prepared and isolated and may become the basic starting materials for developing the organometallic chemistry of pseudotetrahedral cationic group 4 metal complexes containing the Cp_3Zr^+ unit. We here describe a series of first examples of this interesting class of new cationic zirconium(IV) complexes.

Results and Discussion

"Jordan's cation" ($\text{Cp}_2\text{ZrCH}_3^+\cdot\text{THF}$) is prepared by methyl anion abstraction from dimethylzirconocene.⁵ Therefore, the probably best suited starting material for generating Cp_3Zr^+ and its derivatives should be $\text{Cp}_3\text{Zr-CH}_3$ (**7**). We have prepared **7** by treatment of $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ (**6**)⁶ with sodium cyclopentadienide (ca. 1.5 molar equiv) in toluene solution. Using a larger excess of the CpNa reagent leads to a lower product yield due to subsequent formation of Cp_4Zr . Under optimized reaction conditions an 80% yield of **7** was obtained (Scheme 1). Complex **7** was identified by its characteristic NMR spectra [$^1\text{H}/^{13}\text{C}$ NMR in benzene- d_6 : δ 5.33/110.2 ($^1J_{\text{CH}} = 171$ Hz) (Cp), 0.52/14.3 ($^1J_{\text{CH}} = 122$ Hz) (CH_3); the ^{13}C methyl resonance of the starting material $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ appears at a substantially higher δ value of 32.1 ppm] and by a (disordered) X-ray crystal structure analysis (tetragonal space group $\bar{4}$; for details see the Supporting Information). The Zr–C(methyl) distance in **7** is close to the typical Zr–C(sp^3)-value of 2.3 Å (i.e. 2.295(10) Å).⁷ The average Zr–C-(cyclopentadienyl) distance is 2.59(1) Å which is only marginally longer than the average Zr–C($\eta^5\text{-Cp}$) of the Cp_3Zr unit in Cp_4Zr (**1**, 2.58(3) Å; the corresponding Zr– $\sigma\text{-Cp}$ bond length in Cp_4Zr (**1**) is 2.447(6) Å).^{4a} The single Zr–C(Cp) distances in Cp_3ZrCH_3 (**7**) deviate not much from the average (see Figure 1); all three (symmetry equivalent) cyclopentadienyl ring systems appear to be η^5 -coordinated.

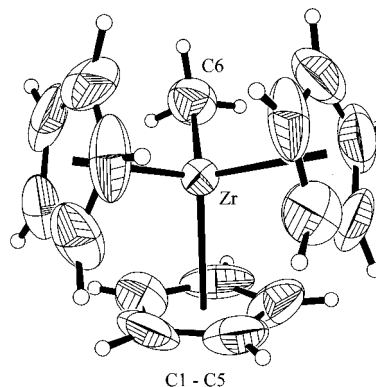


Figure 1. View of the molecular structure of the complex $\text{Cp}_3\text{Zr-CH}_3$ (**7**) (30% probability).

Cp_3ZrCH_3 (**7**) was treated with a slight excess (1.3 molar equiv) of *N,N*-dimethylanilinium tetraphenylborate at low temperature in tetrahydrofuran to give the THF-stabilized tris(cyclopentadienyl)zirconium cation (**8**) that was isolated, albeit in a low yield of ca. 30%. In THF- d_8 solution the yellow colored $\text{Cp}_3\text{Zr}(\text{THF})^+$ system exhibits a ^1H NMR Cp singlet at δ 6.24 (which is by ca. 0.6 ppm shifted to higher δ values as compared to the neutral $\text{Cp}_3\text{Zr-CH}_3$ starting material).

Probably donor-ligand-free Cp_3Zr^+ was generated by treatment of Cp_3ZrCH_3 with the strong organometallic Lewis-acid tris(pentafluorophenyl)borane in dichloromethane. The reaction was carried out at low temperature (-78°C) and its rapid progress monitored directly by ^1H and ^{13}C NMR spectroscopy. Methyl transfer from zirconium to boron was complete within minutes as evidenced by the broad $^1\text{H}/^{13}\text{C}$ NMR methyl singlet of the $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ anion at δ 0.48/8.9 ppm. Again a pronounced shift of the Cp resonance is observed relative to the formation of the Cp_3Zr^+ cation system **9** ($^1\text{H}/^{13}\text{C}$ NMR: δ 6.30/117.6 (Cp); **7**, δ 5.65/110.9 in dichloromethane- d_2). Unfortunately, the donor-ligand-free $[\text{Cp}_3\text{Zr}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ salt could not be isolated due to some unidentified mode of decomposition during attempted workup at higher temperature. However, the addition of suitable donor ligands to the solution containing the in situ generated reactive Cp_3Zr^+ system resulted in clean addition in a 1:1 stoichiometry to yield the respective considerably more stable $\text{Cp}_3\text{Zr-L}^+$ systems, four examples of which we were able to isolate and adequately characterize.

Thus, the addition of acetonitrile to the in situ generated $[\text{Cp}_3\text{Zr}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ system gave $[\text{Cp}_3\text{Zr-}$

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($\text{N}\equiv\text{CCH}_3$)⁺ $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ (**10**), which was isolated as a yellow solid from the dichloromethane solution after precipitation with pentane (ca. 70% yield). Complex **10** exhibits a ¹H NMR Cp signal at δ 6.08 (in dichloromethane-*d*₂), i.e. by 0.33 ppm to higher δ values relative to the neutral $\text{Cp}_3\text{Zr}-\text{CH}_3$ starting material, but shifted by 0.22 ppm to a lower δ value relative to the non-donor-ligand-stabilized parent system [$\text{Cp}_3\text{Zr}^+-\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$] (**9**). The CH_3CN signal of **10** is observed at δ 2.62 (broadened singlet due to exchange with some residual free acetonitrile). The coordinated acetonitrile gives rise to two IR bands (in KBr) at $\tilde{\nu}$ = 2321 and 2295 cm^{-1} that are markedly shifted compared to free acetonitrile ($\tilde{\nu}$ = 2369, 2346 cm^{-1}). The typical IR features of the coordinated acetonitrile in the $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{N}\equiv\text{C}-\text{CH}_3)^+$ cation ($\tilde{\nu}$ = 2310, 2283 cm^{-1} in Nujol) are similar as observed here for **10**.⁸

Analogously, the reaction of **9** with benzonitrile furnished the stable complex [$\text{Cp}_3\text{Zr}(\text{N}\equiv\text{CPh})^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$] (**11**). Again, the characteristic shifting of the ¹H/¹³C NMR Cp resonances is observed (δ 6.13/114.8). The ¹³C NMR nitrile carbon signal of the $\text{PhC}\equiv\text{N}$ ligand appears at δ 137.2 (in dichloromethane-*d*₂; free benzonitrile, δ 118.7), and the IR (coordinated $-\text{C}\equiv\text{N}$) band is observed at $\tilde{\nu}$ = 2251 cm^{-1} , almost identical with free PhCN ($\tilde{\nu}$ = 2250 cm^{-1}). The $\tilde{\nu}(\text{C}=\text{C})_{\text{arom.}}$ band of **11** ($\tilde{\nu}$ = 1642 cm^{-1}) is shifted considerably relative to free benzonitrile ($\tilde{\nu}$ = 1600 cm^{-1}). A similar effect was observed for $\text{Cp}_2\text{ZrR}(\text{benzonitrile})^+$ cation complexes.⁹

Treatment of the in situ generated Cp_3Zr^+ cation with *tert*-butyl isocyanide gave the complex [$\text{Cp}_3\text{Zr}(\text{CNCMe}_3)^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$] (**12**) that was isolated in >70% yield. The ¹H NMR Cp signal is even further shifted to lower δ values (5.91 ppm) compared to **9** than observed in the nitrile adducts **10** and **11**, which probably indicates an even more effective delocalization of the positive charge by the isonitrile ligand, consequently leading to an increased electronic stabilization. The ¹³C NMR spectrum of **12** exhibits a Cp signal at δ 111.7 (in dichloromethane-*d*₂), the signals of the *tert*-butyl group (δ 29.4 and 61.3), and the CNR resonance at δ 145.4 ppm. The IR (CN $^-$) stretching vibration in **12** is found at $\tilde{\nu}$ = 2209 cm^{-1} , which is—as expected for a d^0 -configured isonitrile metal complex¹⁰—shifted to higher wavenumbers compared to the free ligand ($\tilde{\nu}$ = 2140 cm^{-1}).

The tris(cyclopentadienyl)(*tert*-butyl isocyanide)zirconium cation complex **12** was characterized by an X-ray crystal structure analysis. Single crystals of **12** were obtained from a dichloromethane solution at -30°C . In the crystal there are discrete $\text{Cp}_3\text{Zr}(\text{CNCMe}_3)^+$ units that are cleanly separated from their $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ counterions. The anion exhibits the usual alkyl tris(pentafluorophenyl)borate molecular geometry.¹¹ The

cation shows a distorted pseudotetrahedral arrangement of ligands around zirconium. The cyclopentadienyl groups are equally and very uniformly η^5 -coordinated to the early transition metal center. The corresponding Zr–C(Cp) bond distances are found to lie within a very close interval between 2.541(3) and 2.634(3) Å. The average Zr–C(Cp) bond length amounts to 2.580(3) Å which is identical with the observed value of the Cp_3Zr unit in Cp_4Zr^4 or the average zirconium–Cp–carbon distance in the paramagnetic complex $\text{Cp}_3\text{Zr}^{12}$.

The CNCMe_3 ligand occupies the fourth position to complete the distorted $\text{Cp}_3\text{Zr}-\text{L}^+$ tetrahedron. The Zr–C(isocyanide) bond length is 2.313(3) Å, which is just within the typical zirconium–carbon σ -bond range.⁷ As expected, the Zr–C \equiv N–unit is linear (Zr–C1–N2 = 178.4(2)°) and the C1–N2 bond length is 1.145(4) Å which is identical to the C–N distance in the free uncoordinated isonitrile.¹³ Contrary to the ubiquitously observed lengthening of the C=O or C \equiv NR bonds in the respective late transition metal carbonyl or isonitrile complexes, coordination to the d^0 -configured Cp_3Zr^+ cation is not expected to significantly alter the C \equiv X bond order¹⁰ as there is no electron density available for any substantial metal to ligand (π^*) back-bonding.¹⁴

The Cp(centroid)–Zr–Cp(centroid) angles in complex **12** are closely around 118.7°. This marked distortion from the ideal tetrahedral angle is probably due to the accumulated steric bulk of three η^5 -cyclopentadienyl ligands. Consequently, the average Cp(centroid)–Zr–C1 angle is only 96.6°. Nevertheless, the $\text{Cp}_3\text{ZrC}\equiv\text{NC}(\text{CH}_3)_3^+$ cation attains a conformational arrangement in the solid state where the *tert*-butyl methyl groups are found in an eclipsed arrangement with the Zr–Cp(centroid) vectors (see Figure 2).

Finally, the salt **9** was exposed to a carbon monoxide atmosphere (ambient pressure and temperature). A very sensitive carbonyl complex **13** of the composition [$\text{Cp}_3\text{Zr}(\text{CO})^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$] was formed that could be isolated as single crystals from dichloromethane at -30°C . The $\text{Cp}_3\text{Zr}(\text{CO})^+$ cation shows ¹H/¹³C NMR Cp signals at δ 6.05/112.7. The ¹³C NMR CO resonance appears at δ 206.9. The IR spectrum of **13** (in KBr) shows a strong $\tilde{\nu}(\text{C}\equiv\text{O})$ band at 2150 cm^{-1} which is slightly above the free CO infrared stretching wavenumber.

The carbonyl complex **13** was characterized by an X-ray crystal structure analysis. The overall coordination geometry around Zr is similar as observed for **12** (see above). The C1–O2 distance in **13** is very short (1.110(7) Å), and the coordinated C \equiv O ligand in **13** is very similar in length to the free carbon monoxide molecule. The Zr–C1 bond length in **13** is 2.311(6) Å, and the Zr–C1–O2 angle 178.8(6)°. A view of the cation $\text{Cp}_3\text{Zr}(\text{CO})^+$ is given in Figure 3.

We have carried out a few ethene polymerization experiments employing catalyst solutions containing the donor-ligand-free Cp_3Zr^+ cation system. Generation of **9** by treatment of $\text{Cp}_3\text{Zr}-\text{CH}_3$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in dichloromethane followed by exposure of the solution to

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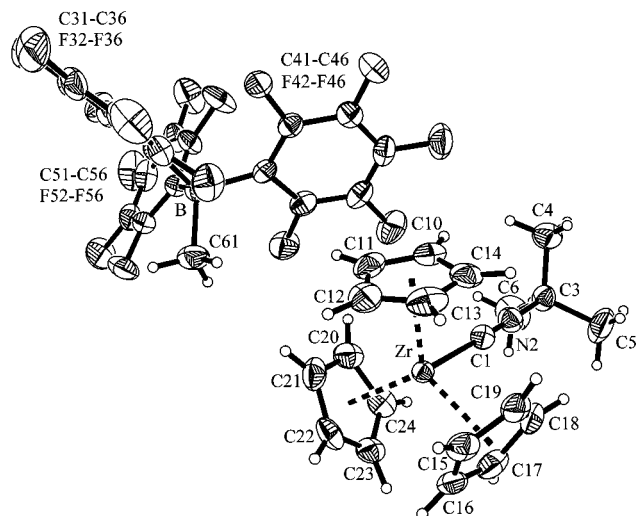


Figure 2. View of the molecular geometry of the $[\text{Cp}_3\text{Zr}(\text{C}\equiv\text{NC}(\text{CH}_3)_3)^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-]$ complex **12** in the crystal (50% probability). Selected bond lengths (Å) and angles (deg): Zr–C10 2.606(3), Zr–C11 2.637(3), Zr–C12 2.552(3), Zr–C13 2.553(3), Zr–C14 2.559(3), Zr–C15 2.568(3), Zr–C16 2.569(3), Zr–C17 2.560(3), Zr–C18 2.608(3), Zr–C19 2.634(3), Zr–C20 2.557(3), Zr–C21 2.551(3), Zr–C22 2.541(3), Zr–C23 2.617(3), Zr–C24 2.592(3), (centroid C10–C14)–Zr–(centroid C15–C19) 118.8, (centroid C10–C14)–Zr–(centroid C20–C24) 118.7, (centroid C15–C19)–Zr–(centroid C20–C24) 118.6, (centroid C10–C14)–Zr–C1 95.9, (centroid C15–C19)–Zr–C1 97.0, (centroid C20–C24)–Zr–C1 96.9, Zr–C1 2.313(3), C1–N2 1.145(4), N2–C3 1.465(3), C3–C4 1.510(4), C3–C5 1.522(4), C3–C6 1.521(4), C1–N2–C3 178.9(3), Zr–C1–N2 178.4(2), N2–C3–C4 107.5(2), N2–C3–C5 107.1(2), N2–C3–C6 106.2(2), B–C61 1.645(4), B–C31 1.653(4), B–C41 1.659(4), B–C51 1.663(4), C41–B–C61 107.2(2), C51–B–C61 106.8(2), C31–B–C61 112.0(2), C41–B–C51 112.0(2), C31–B–C51 111.2(2), C41–B–C31 107.6(2).

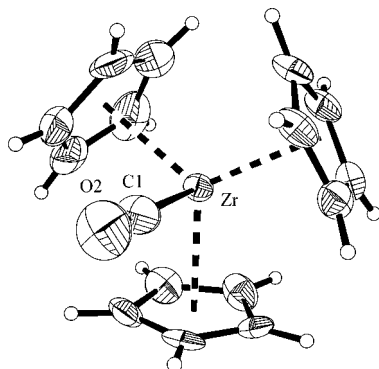


Figure 3. Molecular structure of **13** (only the cation $\text{Cp}_3\text{Zr}(\text{CO})^+$ is depicted). Selected bond lengths (Å): Zr–C1 2.311(6), Zr–C11 2.546(6), Zr–C10 2.553(6), Zr–C24 2.553(5), Zr–C20 2.553(6), Zr–C14 2.559(5), Zr–C17 2.561(5), Zr–C18 2.562(5), Zr–C21 2.567(6), Zr–C16 2.578(5), Zr–C13 2.596(5), Zr–C12 2.605(5), Zr–C23 2.609(6), Zr–C15 2.615(5), Zr–C19 2.632(5), Zr–C22 2.650(6), C1–O2 1.110(7), C10–C11 1.395(9), C10–C14 1.410(8), C11–C12 1.406(9), C12–C13 1.379(8), C13–C14 1.406(8), C15–C19 1.409(8), C15–C16 1.415(9), C16–C17 1.410(8), C17–C18 1.402(8), C18–C19 1.404(8), C20–C24 1.353(10), C20–C21 1.432(12), C21–C22 1.427(11), C22–C23 1.386(10), C23–C24 1.409(10).

ethene at a constant pressure of 1 bar produced polyethylene ($F_p \approx 121^\circ\text{C}$), albeit with a very low catalyst activity of $a = 11$ g of polymer/g of $[\text{Zr}] \cdot \text{h} \cdot \text{bar}$. Activation

of $\text{Cp}_3\text{Zr}-\text{CH}_3$ with excess methylalumoxane ($\text{Al}:\text{Zr} = 500$) in toluene solution yielded a solution that catalyzed the polymerization of ethene with a similarly low catalyst activity. At present it cannot be excluded that actually a very small (and thus not directly detected) amount of the very active $\text{Cp}_2\text{Zr}-\text{CH}_3^+$ cation^{3,5}—formed from **7** by a competing Cp abstraction—is actually responsible for the observed low activity polymerization reaction of these solutions. Although the Cp_3Zr^+ cation seems to be a poor catalyst for the polymerization of simple α -olefins, we expect it to serve as a useful Lewis-acid catalyst in organic synthesis.¹⁵ Studies aimed at exploring such use of the Cp_3Zr^+ cation and related systems are currently being carried out in our laboratory.

Experimental Section

Reactions with organometallic substrates and reagents were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. Instrumentation used for physical characterization included Bruker AC 200 P (^1H , 200 MHz; ^{13}C , 50 MHz) and Varian Unity plus (^1H , 600 MHz, ^{13}C , 150 MHz) NMR spectrometers and a Nicolet 5 DXC FT infrared spectrometer. Elemental analyses: Foss Heraeus CHNO-Rapid. Melting points: DuPont 2910 DSC (STA Instruments). X-ray crystal structure analyses: Enraf-Nonius MACH 3 diffractometer (programs used: SHELX 86, SHELX 93, XP, and SCHAKAL). Tris(pentafluorophenyl)borane¹⁶ and chlorobis(η^5 -cyclopentadienyl)methylzirconium (**6**)⁶ were prepared according to literature procedures.

Tris(η^5 -cyclopentadienyl)methylzirconium (7). A solution of 10.0 g (36.8 mmol) of chlorobis(η^5 -cyclopentadienyl)methylzirconium (**6**) in 50 mL of toluene was added dropwise with stirring to a suspension of 4.9 g (55.3 mol) of sodium cyclopentadienide in 150 mL of toluene at ambient temperature. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was concentrated in vacuo to a volume of ca. 30 mL. Pentane (70 mL) was added. The resulting precipitate was collected by filtration, washed with pentane, and dried in vacuo. An additional product fraction was precipitated from the filtrate by adding more pentane. Combined yield of **7**: 8.9 g (80%), mp 232°C . Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{Zr}$ (301.5): C, 63.73; H, 6.02. Found: C, 62.93; H, 6.09. ^1H NMR (benzene- d_6): δ 5.33 (s, 15H, Cp), 0.52 (s, 3H, CH_3). ^{13}C NMR (benzene- d_6): δ 110.2 ($^1J_{\text{CH}} = 171$ Hz, Cp), 14.3 ($^1J_{\text{CH}} = 122$ Hz, CH_3). IR (KBr): $\tilde{\nu} = 3087, 2930, 2891, 2825, 1439, 1010, 804$ cm^{-1} . Single crystals of **7** were obtained from toluene at -30°C . X-ray crystal structure analysis of **7**: formula $\text{C}_{16}\text{H}_{18}\text{Zr}$, $M = 301.52$, $0.4 \times 0.3 \times 0.2$ mm, $a = 8.136(1)$ Å, $c = 15.726(1)$ Å, $V = 668.0(1)$ Å³, $\rho_{\text{calc}} = 1.499$ g cm^{-3} , $\mu = 7.98$ cm^{-1} , empirical absorption correction

(15) See e.g.: Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406; *Synlett* **1990**, 74. Young, J. R.; Stille, J. R. *Organometallics* **1990**, *9*, 3022. Erker, G.; van der Zeijden, A. A. H. *Angew. Chem.* **1990**, *102*, 543; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 512. Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123. Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* **1992**, *33*, 1005. Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. Halterman, R. L.; Ramsey, T. M. *Organometallics* **1993**, *12*, 2879. Erker, G.; Schamberger, J.; van der Zeijden, A. A. H.; Dehnicke, S.; Krüger, C.; Goddard, R.; Nolte, M. *J. Organomet. Chem.* **1993**, *459*, 107. Lee, N. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. Rieger, B.; Jany, G. *Chem. Ber.* **1994**, *127*, 2417. Review: Hoveyda, A.; Morken, J. P. *Angew. Chem.* **1996**, *108*, 1378; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262 and references cited therein.

(16) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

via ψ -scan data ($0.925 \leq C \leq 0.999$), $Z = 2$, tetragonal, space group $I\bar{4}$ (No. 82), $\lambda = 0.710\ 73\ \text{\AA}$, $\omega/2\theta$ scans, 818 reflections collected ($+h, +k, \pm l$), $[(\sin \theta)/\lambda]_{\max} = 0.62\ \text{\AA}^{-1}$, 716 independent and 647 observed reflections [$I \leq 2\sigma(I)$], 48 refined parameter, $R = 0.067$, $wR^2 = 0.170$, maximum residual electron density $0.55\ (-0.61)\ \text{e}\ \text{\AA}^{-3}$; refinement, Zr anisotropic, Cp ring as rigid group, restraints on anisotropic thermal parameters for all carbon atoms (similar U_{ij} of neighbouring atoms, quasi-isotropic behavior), occupancy(C1–C5) = 0.75, occupancy(C6) = 0.25, hydrogens calculated and riding.

Generation of Tris(η^5 -cyclopentadienyl)zirconium Methyltris(pentafluorophenyl)borate (9). In a 5 mm NMR tube was reacted 16.0 mg (31.3 μmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ with 9.0 mg (29.8 μmol) of Cp_3ZrCH_3 (**7**) in 0.6 mL of benzene- d_6 or dichloromethane- d_2 , respectively. A pale yellow solution of **9** was obtained. At ambient temperature the $[\text{Cp}_3\text{Zr}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ salt is decomposed after several hours. At $-30\ ^\circ\text{C}$ in dichloromethane- d_2 it can be kept without decomposition for several days. The salt **9** could not be isolated as yet. It was characterized spectroscopically. ^1H NMR (benzene- d_6): δ 5.31 (s, 15H, Cp), 0.12 (br s, 3H, $\text{CH}_3\text{-B}$). ^1H NMR (dichloromethane- d_2): δ 6.30 (s, 15H, Cp), 0.48 (br s, 3H, $\text{CH}_3\text{-B}$). ^{13}C NMR (dichloromethane- d_2): δ 148.7 ($^1J_{\text{CF}} = 240\ \text{Hz}$), 140.0 ($^1J_{\text{CF}} = 234\ \text{Hz}$), 136.9 ($^1J_{\text{CH}} = 245\ \text{Hz}$) and 129.0 (br s, o-, p-, m-, and ipso-C of $\text{MeB}(\text{C}_6\text{F}_5)_3^-$), 117.6 (Cp), 8.9 (B-CH_3).

[Tris(η^5 -cyclopentadienyl)(tetrahydrofuran)zirconium] Tetraphenylborate (8). Tris(η^5 -cyclopentadienyl)methylzirconium (**6**) (457 mg, 1.52 mmol) was treated with 950 mg (2.15 mmol) of *N,N*-dimethylanilinium tetraphenylborate at $-78\ ^\circ\text{C}$ in 25 mL of THF. The reaction mixture was stirred for 1 h at $-78\ ^\circ\text{C}$ and then for 4 h at $0\ ^\circ\text{C}$. After ca. 2 h the product began to precipitate. It was collected by filtration and washed with pentane to give 325 mg (32%) of **8**, mp $52\ ^\circ\text{C}$ (dec). ^1H NMR (THF- d_8): δ 6.24 (s, 15H, Cp), 3.62 (m, 4H) and 1.77 (m, 4H, THF); BPh_4^- anion, δ 7.40–7.20 (m, 8H), 7.00–6.80 (m, 8H), 6.80–6.65 (m, 4H). IR (KBr): $\tilde{\nu} = 3119, 3069, 3051, 2980, 2851, 1591, 1479, 1431, 1240, 1015, 885, 802, 735\ \text{cm}^{-1}$.

[(Acetonitrile)tris(η^5 -cyclopentadienyl)zirconium] Methyltris(pentafluorophenyl)borate (10). A Schlenk flask was charged with Cp_3ZrCH_3 (**7**) (100 mg, 0.33 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (175 mg, 0.34 mmol) and then cooled to $-78\ ^\circ\text{C}$. At that temperature 15 mL of cold ($-78\ ^\circ\text{C}$) dichloromethane was added. The mixture was then slowly allowed to warm with stirring until a clear orange colored solution was obtained. The solution was then cooled again to $-78\ ^\circ\text{C}$, and 0.09 mL (68 mg, 1.66 mmol) of acetonitrile was added dropwise. The resulting pale yellow solution was allowed to warm to room temperature and then concentrated to ca. half of its original volume in vacuo. Addition of pentane (15 mL) precipitated the product **10**, which was collected by filtration, washed with pentane, and dried in vacuo (yield 195 mg, 69%), mp $109\ ^\circ\text{C}$. ^1H NMR (10:1 dichloromethane- d_2 /THF- d_8): δ 6.08 (s, 15H, Cp), 2.62 (br s, 3H, CH_3CN), 0.48 (br s, 3H, $\text{CH}_3\text{-B}$). IR (KBr): $\tilde{\nu} = 3138, 2985, 2938, 2907, 2321, 2295, 1642, 1513, 1457, 1266, 1086, 936, 845, 819, 736\ \text{cm}^{-1}$.

[(Benzonitrile)tris(η^5 -cyclopentadienyl)zirconium] Methyltris(pentafluorophenyl)borate (11). A solid mixture of Cp_3ZrCH_3 (**7**) (100 mg, 0.33 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (175 mg, 0.34 mmol) was cooled to $-78\ ^\circ\text{C}$. Then 15 mL of cold ($-78\ ^\circ\text{C}$) dichloromethane was added and the mixture cleared at a slightly elevated temperature. Benzonitrile (170 mg, 1.65 mmol) was then added at $-78\ ^\circ\text{C}$. The mixture was warmed to room temperature during 30 min, 50% of the solvent removed in vacuo, and 20 mL of pentane added. The product **11** was collected by filtration, washed with a small amount of pentane, and dried in vacuo to yield 184 mg (61%) of **11**, mp $139\ ^\circ\text{C}$. Anal. Calcd for $\text{C}_{41}\text{H}_{23}\text{BNF}_{15}\text{Zr}$ (916.6): C, 53.72; H, 2.53. Found: C, 53.91; H, 2.95. ^1H NMR (dichloromethane- d_2): δ 7.92 (m, 2H), 7.90 (m, 1H), and 7.69 (m, 2H, o-, p-, m-H of Ph), 6.13 (s, 15H, Cp), 0.47 (br s, 3H, $\text{CH}_3\text{-B}$). ^{13}C NMR (dichloromethane- d_2): δ 148.3 ($^1J_{\text{CF}} = 240\ \text{Hz}$), 137.4 ($^1J_{\text{CF}} =$

243 Hz), 136.2 ($^1J_{\text{CF}} = 245\ \text{Hz}$) and 128.7 (br s; o-, p-, m-, and ipso-C of $\text{B}(\text{C}_6\text{F}_5)_3^-$), 137.2 (Ph-CN), 136.8, 133.0, 130.1, 107.5 (p-, o-, m-, and ipso-C of Ph), 114.8 (Cp), 10.0 (br, B-CH_3). IR (KBr): $\tilde{\nu} = 3130, 2975, 2926, 2251, 1642, 1511, 1266, 1088, 951, 810\ \text{cm}^{-1}$.

[(tert-Butyl isocyanide)tris(η^5 -cyclopentadienyl)zirconium] Methyltris(pentafluorophenyl)borate (12). As described above, the $[\text{Cp}_3\text{Zr}]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ salt **9** was generated by treatment of 100 mg (0.33 mmol) of **7** with 175 mg (0.34 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ in 15 mL of dichloromethane. At $-78\ ^\circ\text{C}$ 0.19 mL (137 mg, 1.65 mmol) of *tert*-butyl isocyanide was added, the mixture allowed to warm to room temperature, and then the solution concentrated to half of its volume in vacuo. Pentane (20 mL) was added and the precipitated product **12** collected by filtration, washed with a small amount of pentane, and dried in vacuo to yield 215 mg (73%) of **12**, mp $113\ ^\circ\text{C}$. Anal. Calcd for $\text{C}_{39}\text{H}_{27}\text{BNF}_{15}\text{Zr}$ (896.7): C, 52.24; H, 3.04; N, 1.56. Found: C, 51.37; H, 3.14; N, 1.62. ^1H NMR (dichloromethane- d_2): δ 5.91 (s, 15H, Cp), 1.77 (br s, 9H, $\text{C}(\text{CH}_3)_3$), 0.51 (br s, 3H, B-CH_3). ^{13}C NMR (dichloromethane- d_2): δ 148.0 ($^1J_{\text{CF}} = 241\ \text{Hz}$), 137.4 ($^1J_{\text{CF}} = 243\ \text{Hz}$), 136.3 ($^1J_{\text{CF}} = 245\ \text{Hz}$), and 128.6 (br s, o-, p-, m-, and ipso-C of $\text{RB}(\text{C}_6\text{F}_5)_3^-$), 145.4 (br s; RN(C), 111.7 (Cp), 61.3 and 29.9 (CMe_3), 10.0 (br s, B-CH_3). IR (KBr): $\tilde{\nu} = 3134, 2990, 2961, 2209, 1641, 1511, 1456, 1266, 1081, 957, 820\ \text{cm}^{-1}$. Single crystals were obtained from dichloromethane at $-30\ ^\circ\text{C}$. X-ray crystal structure analysis of **12**: formula $\text{C}_{39}\text{H}_{27}\text{BF}_{15}\text{NZr}$, $M = 896.65$, $0.7 \times 0.5 \times 0.4\ \text{mm}$, $a = 13.330(1)\ \text{\AA}$, $b = 13.152(1)\ \text{\AA}$, $c = 21.062(1)\ \text{\AA}$, $\beta = 100.54(1)^\circ$, $V = 3630.2(4)\ \text{\AA}^3$, $\rho_{\text{calc}} = 1.641\ \text{g}\ \text{cm}^{-3}$, $\mu = 4.11\ \text{cm}^{-1}$, empirical absorption correction via ψ -scan data ($0.980 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.710\ 73\ \text{\AA}$, $\omega/2\theta$ scans, 7575 reflections collected ($\pm h, -k, \pm l$), $[(\sin \theta)/\lambda]_{\max} = 0.62\ \text{\AA}^{-1}$, 7372 independent and 5943 observed reflections [$I \leq 2\sigma(I)$], 518 refined parameter, $R = 0.039$, $wR^2 = 0.124$, maximum residual electron density $0.57\ (-0.79)\ \text{e}\ \text{\AA}^{-3}$, hydrogens calculated and riding.

[(Carbonyl)tris(η^5 -cyclopentadienyl)zirconium] Methyltris(pentafluorophenyl)borate (13). As described above, the salt **9** was generated by treatment of 100 mg (0.33 mmol) of **7** with 175 mg (0.34 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ in 20 mL of dichloromethane in a 100 mL Schlenk flask. The argon atmosphere was removed from the flask in vacuo and replaced with carbon monoxide. The mixture was stirred under a constant (1 bar) CO pressure for 20 min at ambient temperature. The reaction mixture was concentrated to half its volume in vacuo and then kept at $-30\ ^\circ\text{C}$ for several days to yield a number of yellow single crystals of **13** that were collected by filtration and dried in vacuo, yield 106 mg (38%). Anal. Calcd for $\text{C}_{35}\text{H}_{18}\text{BOF}_{15}\text{Zr}$ (842.4): C, 49.95; H, 2.16. Found: C, 49.24; H, 2.18. ^1H NMR (dichloromethane- d_2): δ 6.05 (s, 15H, Cp), 0.52 (br s, 3H, B-CH_3). ^{13}C NMR (dichloromethane- d_2): δ 206.9 (CO), 112.7 (Cp). IR (KBr): $\tilde{\nu} = 3118, 2934, 2855, 2150, 1650, 1518, 1459, 1274, 1090, 959, 827, 741\ \text{cm}^{-1}$. Single crystals were obtained from dichloromethane; they contained one molecule of CH_2Cl_2 per **13**. X-ray crystal structure analysis of **13**: formula $\text{C}_{36}\text{H}_{20}\text{BCl}_2\text{F}_{15}\text{OZr}$, $M = 926.45$, $0.5 \times 0.4 \times 0.2\ \text{mm}$, $a = 11.189(1)\ \text{\AA}$, $b = 11.549(1)\ \text{\AA}$, $c = 15.191(1)\ \text{\AA}$, $\alpha = 108.28(1)^\circ$, $\beta = 105.16(1)^\circ$, $\gamma = 100.29(1)^\circ$, $V = 1724.8(2)\ \text{\AA}^3$, $\rho_{\text{calc}} = 1.784\ \text{g}\ \text{cm}^{-3}$, $\mu = 5.87\ \text{cm}^{-1}$, empirical absorption correction via ψ -scan data ($0.946 \leq C \leq 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\ 73\ \text{\AA}$, $\omega/2\theta$ scans, 7381 reflections collected ($-h, \pm k, \pm l$), $[(\sin \theta)/\lambda]_{\max} = 0.62\ \text{\AA}^{-1}$, 7005 independent and 5940 observed reflections [$I \leq 2\sigma(I)$], 506 refined parameters, $R = 0.069$, $wR^2 = 0.234$, maximum residual electron density $1.49\ (-1.52)\ \text{e}\ \text{\AA}^{-3}$, hydrogens calculated and riding.

Ethene Polymerization Experiments. (A) In a Schlenk flask was combined 50 mg (0.17 mmol) of Cp_3ZrCH_3 (**7**) with 50 mL of a 10% methylalumoxane solution in toluene (4.35 g, 93.5 mmol of MAO). The flask was evacuated and then filled with ethene (1.3 bar) and kept under a constant ethene pressure for 2 h. After 10 min polymer began to

separate from the solution. The mixture was poured into 50 mL of half concentrated aqueous HCl. The precipitate was collected by filtration and dried to yield 1.2 g of polyethylene, mp 127 °C.

(B) Cp_3ZrCH_3 (100 mg, 0.33 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (175 mg, 0.34 mmol) were reacted at -78°C in 15 mL of dichloromethane as described above to give the $[\text{Cp}_3\text{Zr}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ salt (**9**). The solution was then warmed to room temperature during 15 min. The flask was evacuated, filled with ethene (1 bar), and kept under 1 bar of ethene for 3 h. Polymer began to precipitate within 10 min. A total of 895 mL (36 mmol) of ethene was consumed. The mixture was then hydrolyzed and the polyethylene collected by filtration (1.0 g), mp 121 °C.

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Supporting Information Available: Additional material concerning the X-ray crystal structure analyses of the complexes **7**, **12**, and **13** including complete listings of X-ray parameters, bond lengths and angles, and positional and thermal parameters (23 pages). Ordering information is given on any current masthead page.

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