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Synthesis of Base-Free Cationic Zirconium Methyl and Benzyl Complexes. The Crystal and Molecular Structure of $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$

Manfred Bochmann* and Simon J. Lancaster

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

Michael B. Hursthouse and K. M. Abdul Malik

School of Chemistry and Applied Chemistry, University of Wales Cardiff, Cardiff CF1 3TB, U.K.

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The reaction of the dimethyl complexes *rac*-$Me_2Si(Ind)_2ZrMe_2$ (**1a**) (Ind = η^5-indenyl) and $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe_2$ (**2a**) with $B(C_6F_5)_3$ gives the zwitterionic compounds *rac*-$Me_2Si(Ind)_2Zr(Me)(\mu\text{-}Me)B(C_6F_5)_3$ (**1b**) and $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (**2b**), respectively. The crystal structure of **2b** has been determined. The compound possesses a bridging methyl group with a long zirconium-carbon distance of 2.667(5) Å and an almost linear Zr-C-B arrangement [bond angle 170.5(3)°]. Two of the bridging methyl hydrogens show close Zr-H contacts of 2.47(3) and 2.44(3) Å. In contrast to the zwitterionic structure of **2b**, the reaction of $B(C_6F_5)_3$ with the dibenzyl complexes $Cp'_2Zr(CH_2Ph)_2$ [Cp'_2 = *rac*-$Me_2Si(Ind)_2$ (**1c**), $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2$ (**2c**), $(C_5H_5)_2$ (**3c**), *rac*-$C_2H_4(Ind)_2$ (**4c**), $Me_2C(C_5H_4)(Flu)$ (**5c**)] in dichloromethane at -50 °C leads to the ionic compounds $[Cp'_2Zr(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$ (**1d**-**5d**) which contain η^2-coordinated benzyl ligands and noncoordinated $[PhCH_2B(C_6F_5)_3]^-$ counteranions. The complexes are thermally unstable in dichloromethane solution but stable in hydrocarbons. Complexes with bridging benzyl ligands are not observed. In the case of the hydrocarbon-soluble complex $[\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Zr(\eta^2\text{-}CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$ (**2d**) it is shown that the ionic structure is maintained in toluene-d_8 solution at 60 °C, i.e. under polymerization conditions. By contrast, the mono(cyclopentadienyl) complex $CpZr(CH_2Ph)_3$ reacts with $B(C_6F_5)_3$ to give $CpZr(\eta^1\text{-}CH_2Ph)_2(\eta^6\text{-}PhCH_2B(C_6F_5)_3$ (**7**), where the phenyl ring of the anion is π-coordinated to the metal. The reaction of **1c** with $[CPh_3][B(C_6F_5)_4]$ gives the related complex $[Me_2Si(Ind)_2Zr(\eta^2\text{-}CH_2Ph)][B(C_6F_5)_4]$ (**1e**). The complexes are highly active catalysts for the polymerization of ethene and propene.

Cationic group 4 metal alkyl complexes of the type $[Cp_2M\text{-}R]^+$ (M = Ti, Zr, Hf) have been identified as the catalytically active species in homogeneously catalyzed alkene polymerization reactions.[1,2] In conventional catalytic systems, typically containing metallocene dihalides with methylaluminoxane (MAO) as activator, they are present in equilibrium with neutral species (eq 1).

$$Cp_2MR_2 + MAO \rightleftharpoons [Cp_2M\text{-}R]^+[R\text{-}MAO]^- \quad (1)$$

Alternatively, the reaction of dialkylmetallocenes with triphenylcarbenium salts of weakly coordinating anions, notably X = $B(C_6F_5)_4$,[3] in nonbasic solvents leads quantitatively to cationic complexes (eq 2). Coordinatively

$$Cp_2MR_2 + [CPh_3]^+X^- \rightarrow [Cp_2M\text{-}R]^+X^- + Ph_3CR \quad (2)$$

unsaturated species such as $[Cp_2M\text{-}R]^+$ complexes are potent electrophiles and may be expected to establish a series of solution equilibria by interacting with any available nucleophile, such as the solvent, the anion, neutral metal alkyls, or the olefin substrate, prior to polymerization (Scheme 1).[3b,4] In the absence of a coordinating solvent the cation-anion interactions are the most important of these and have a dramatic influence on catalyst activity. For example, BPh_4^- can form tight ion pairs or act as a ligand to give η^3- to η^6-complexes,[5] and the coordinative ability of even fluorinated tetraarylborate anions has been amply documented, e.g. in the case of $[B(C_6H_4F)_4]^-$,[6] $[BH(C_6F_5)_3]^-$,[7] and $[B(C_6F_5)_4]^-$,[8] while carboranyl and metallacarboranyl anions exhibit even more pronounced donor characteristics.[9]

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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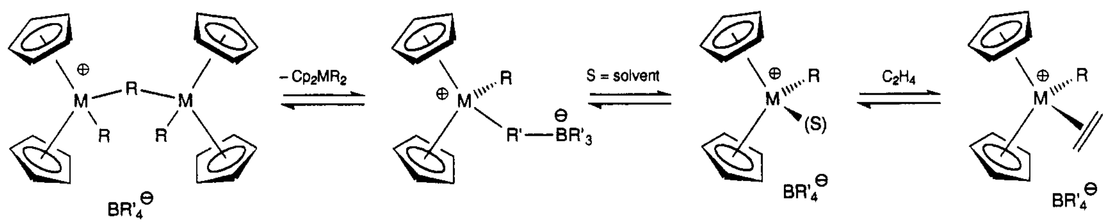
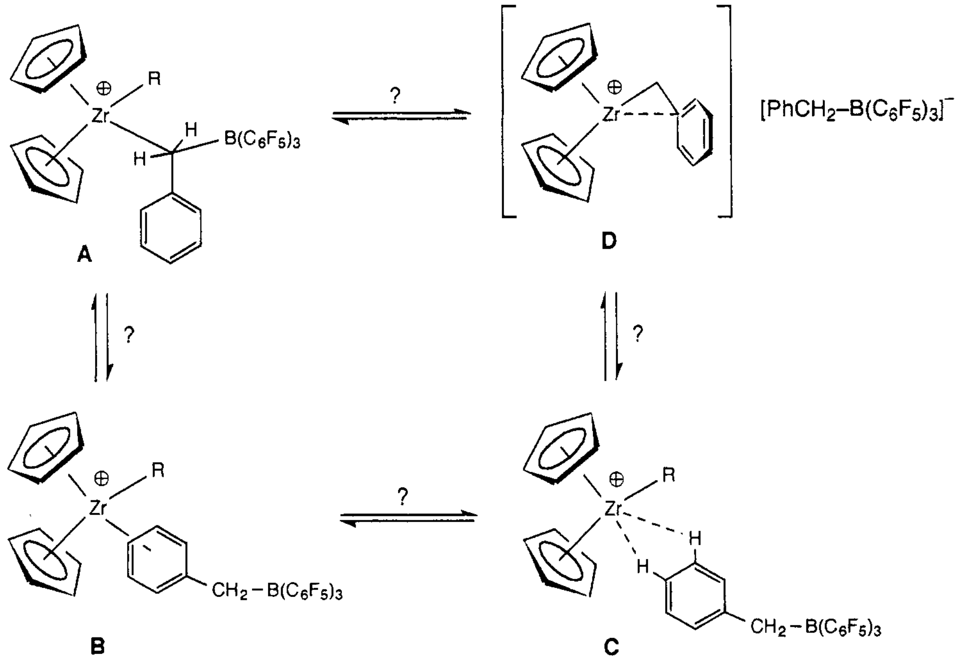
Scheme 1



Scheme 2



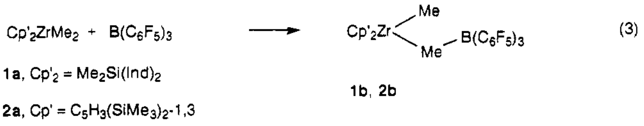
An alternative method for generating "cation-like" metal alkyl complexes of significant catalytic activity was recently introduced by Marks et al.[10] who showed that zirconocene dimethyls react with $B(C_6F_5)_3$ to give the zwitterionic complexes $Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ ($Cp' = C_5H_5$, $C_5H_3Me_2$, C_5Me_5). Here $[MeB(C_6F_5)_3]^-$ acts as a strongly coordinating ligand. The dissociation equilibrium which must be established before alkene polymerization can be initiated is shifted strongly to the left:

$$Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3 \rightleftharpoons [Cp'_2ZrMe]^+[MeB(C_6F_5)_3]^-$$

Cation–anion interactions are not least due to attractive electrostatic forces, and although firm evidence for their existence is mostly based on observations in the solid state, they are likely to persist in solution, particularly in solvents of low dielectric constant such as toluene, which is commonly employed in olefin polymerization reactions. Having previously established the use of η^2-benzyl complexes such as $[Cp_2Zr(\eta^2\text{-}CH_2Ph)]^+$ in combination with the anion $[B(C_6F_5)_4]^-$, for which no evidence for association could be detected, as highly active polymerization catalysts,[2] we were therefore interested in probing the consequences of anion association firstly on the structure of cationic metal alkyl complexes and secondly on the activity and especially the stereoselectivity of these complexes as catalysts in polymerization reactions. We report here the synthesis of zirconocene alkyl cations in the presence of $[MeB(C_6F_5)_3]^-$ and $[PhCH_2B(C_6F_5)_3]^-$ in comparison with $[B(C_6F_5)_4]^-$. For $[PhCH_2B(C_6F_5)_3]^-$, for example, several different kinds of interaction with the cationic metal center could be envisaged (Scheme 2), including the formation of alkyl bridges (**A**) in analogy to $Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, π-interaction with the metal (**B**), or bonding to phenyl hydrogens (**C**). Anion coordination of this kind could be expected to lead to a reduction in catalytic activity compared to the case of $[B(C_6F_5)_4]^-$. A preliminary report on anion effects in the syndiospecific polymerization of propene has appeared.[11]

Results and Discussion

Methyl Complexes. Treatment of *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**1**) with MeLi in diethyl ether gives pale-yellow *rac*-$Me_2Si(Ind)_2ZrMe_2$ (**1a**) in high yield. According to the method of Marks et al., addition of $B(C_6F_5)_3$ to a solution of **1a** in petroleum ether gives *rac*-$Me_2Si(Ind)_2Zr(Me)(\mu\text{-}Me)B(C_6F_5)_3$ (**1b**) in high yield which is isolated as orange needles on recrystallization from toluene (eq 3). The



$$Cp'_2ZrMe_2 + B(C_6F_5)_3 \longrightarrow Cp'_2Zr\overset{Me}{\underset{Me}{<}}B(C_6F_5)_3 \quad (3)$$

1a, $Cp'_2 = Me_2Si(Ind)_2$

2a, $Cp' = C_5H_3(SiMe_3)_2\text{-}1,3$

1b, 2b

complex $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (**2b**) was similarly obtained for $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe_2$ (**2a**) as pale-yellow crystals whose good solubility in toluene indicates a nonionic structure; this is confirmed by X-ray

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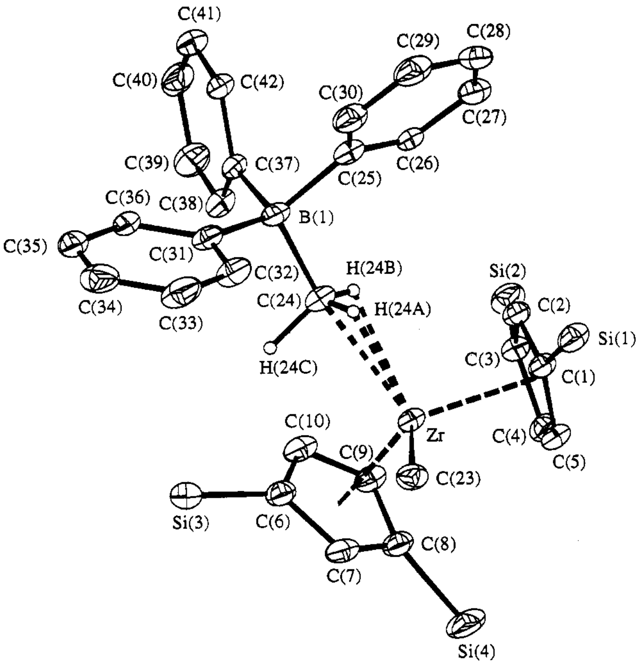


Figure 1. Molecular structure of $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (**2b**), showing the atomic numbering scheme. Ellipsoids correspond to 30% probability. The F atoms and the $SiMe_3$ methyl groups have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\{C_5H_3(SiMe_3)_2\}ZrMe(\mu\text{-}Me)B(C_6F_5)_3\cdot0.5C_7H_8$ (2b)

Zr–C(1)	2.593(4)	Zr–C(2)	2.531(4)
Zr–C(3)	2.499(4)	Zr–C(4)	2.470(4)
Zr–C(5)	2.492(5)	Zr–C(6)	2.554(5)
Zr–C(7)	2.534(4)	Zr–C(8)	2.528(5)
Zr–C(9)	2.484(5)	Zr–C(10)	2.509(4)
Zr–C(23)	2.260(4)	Zr–C(24)	2.667(5)
Zr···C(01)[a]	2.212	Zr···C(02)[a]	2.217
Zr···H(24A)	2.47(3)	Zr···H(24B)	2.44(3)
Zr···H(24C)	2.73(3)	C(4)–C(5)	1.399(6)
Si(1)–C(1)	1.879(5)	C(1)–C(2)	1.430(6)
Si(2)–C(3)	1.880(5)	C(3)–C(4)	1.432(6)
Si(3)–C(6)	1.885(5)	B(1)–C(31)	1.690(6)
Si(4)–C(8)	1.878(5)	B(1)–C(37)	1.714(6)
C(1)–C(5)	1.402(6)	C(24)–B(1)	1.684(7)
C(2)–C(3)	1.402(6)	B(1)–C(25)	1.710(6)
C(23)–Zr–C(24)	97.1(1)	C(24)–Zr–C(01)[a]	108.6
C(23)–Zr–C(01)[a]	102.8	C(5)–C(1)–Si(1)	128.2(4)
C(02)[a]–Zr–C(01)[a]	132.4	C(31)–B(1)–C(25)	114.0(4)
C(23)–Zr–C(02)[a]	102.9	C(31)–B(1)–C(37)	111.3(3)
C(24)–Zr–C(02)[a]	108.6	C(25)–B(1)–C(37)	104.8(3)
C(5)–C(1)–C(2)	104.0(4)	C(31)–B(1)–C(24)	106.8(3)
C(2)–C(1)–Si(1)	126.1(3)	C(24)–B(1)–C(25)	108.0(4)
B(1)–C(24)–Zr	170.5(3)	C(24)–B(1)–C(37)	112.0(4)

[a] The points C(01) and C(02) denote the centroids of the Cp rings through the C(1) to C(5) and C(6) to C(10) atoms, respectively.

diffraction (Figure 1). Selected bond lengths and angles are given in Table 1.

In **2b** the $[MeB(C_6F_5)_3]^-$ anion is coordinated to a $[Cp'_2ZrMe]^+$ fragment to give a zwitterionic arrangement analogous to that of $(C_5H_3Me_2\text{-}1,2)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$.[10] The structure of **2b** differs from the latter in the significantly longer bond between zirconium and the bridging methyl group [2.667(5) Å, compared to 2.549(3) Å] and in the almost linear (as opposed to bent) Zr–C–B moiety which forms an angle of 170.5(3)°. The hydrogens of the bridging methyl group were located. Two of these show relatively close contacts to zirconium, with Zr–H distances of 2.47(3) and 2.44(3) Å, indicative of a weak α-agostic interaction, compared to a nonbonding distance of 2.73(3) Å to the third hydrogen atom. This Zr–H bonding pattern reflects that found in $(C_5H_3Me_2\text{-}1,2)_2ZrMe(\mu\text{-}M)B(C_6F_5)_3$, although in that case the agostic Zr–H contacts are much shorter, 2.25(3) and 2.30(3) Å.[10]

The geometries around zirconium and boron are normal. The Me–Zr–Me angle of 97.1(2)° in **2b** is 5° wider than that in $(C_5H_3Me_2\text{-}1,2)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. The trimethylsilyl groups are bent slightly out of the C_5 plane. Although these structural parameters, in particular the long Zr–C(24) distance, illustrate the high degree of steric hindrance in **2b**, the strong coordination of the $[MeB(C_6F_5)_3]^-$ anion is still apparent and is maintained in toluene solution.

Zirconium Benzyl Complexes. The zirconocene dibenzyl complexes *rac*-$Me_2Si(Ind)_2Zr(CH_2Ph)_2$ (**1c**), $Cp_2Zr(CH_2Ph)_2$ (**3c**), *rac*-$C_2H_4(Ind)_2Zr(CH_2Ph)_2$ (**4c**), and $Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)_2$ (**5c**) were prepared from the corresponding zirconocene dichlorides and 2 equiv. of $PhCH_2MgCl$. For these complexes the use of a large excess of Grignard reagent, as recommended earlier,[12] or of KCH_2Ph[13] was not found to be necessary to obtain halide-free products. However, the attempted synthesis of $\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)_2$ (**2c**) in the same fashion led to high yields of $\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)(Cl)$. The desired product **2c** was obtained using the "KCH_2Ph" procedure employed by Jordan et al.[14] and modified because of the very high solubility of the product. The spectroscopic data for the new compounds are given in Table 2.

The hydrogens of the benzylic CH_2 groups of the *ansa*-metallocene complex **1c** are inequivalent and appear as a set of two doublets, similar to **4c**, **5c**,[2] and *rac*-$(EBTHI)_2Zr(CH_2Ph)_2$ (EBTHI = ethylenebis(tetrahydroindenyl)).[14]

The reactions of **1c** and **3c**–**5c** with $B(C_6F_5)_3$ in CD_2Cl_2 proceed smoothly at −50 °C to give the corresponding cationic zirconium benzyl complexes $[Cp'_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**1d**, **3d**, **4d**, and **5d**) *in situ* (eq 4). The

$$Cp'_2Zr(CH_2Ph)_2 + B(C_6F_5)_3 \longrightarrow \underset{\textbf{1d - 5d}}{[Cp'_2Zr(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-} \qquad (4)$$

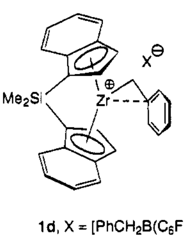
1c, $Cp'_2 = Me_2Si(Ind)_2$

2c, $Cp' = C_5H_3(SiMe_3)_2\text{-}1,3$

3c, $Cp' = C_5H_5$

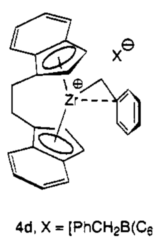
4c, $Cp'_2 = C_2H_4(Ind)_2$

5c, $Cp'_2 = Me_2C(C_5H_4)(Flu)$



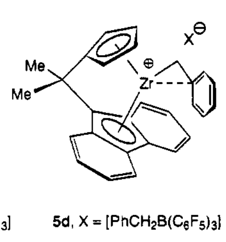
1d, X = $[PhCH_2B(C_6F_5)_3]$

1e, X = $[B(C_6F_5)_4]$



4d, X = $[PhCH_2B(C_6F_5)_3]$

4e, X = $[B(C_6F_5)_4]$



5d, X = $[PhCH_2B(C_6F_5)_3]$

5e, X = $[B(C_6F_5)_4]$

progress of the reaction is conveniently followed by NMR. For the bulky complex **2c** it proved necessary to warm the sample to −40 °C for a period of 1 h in the spectrometer in order to achieve quantitative conversion to the cationic species **2d**. The reactions are normally accompanied by

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Table 2. ^1H and ^{13}C NMR Data for Zirconium Alkyl Complexes

compd	^1H NMR	assgnt[a]	^{13}C NMR	assgnt[a]
$Me_2Si(Ind)_2ZrMe_2$ (**1a**) [C_6D_6, 21 °C]	−0.45 (s, 6 H)	Zr–Me	−1.90	Si–Me
	1.05 (s, 6 H)	Si–Me	37.04	Zr–Me
	6.20 (d, 2 H, *J* = 3.3 Hz)	C_5	84.39	C_5–Si
	7.22 (d, 2 H, *J* = 3.3 Hz)	C_5	111.38	C_5
	7.35 (t, 2 H, *J* = 7.8 Hz)	C_6	117.88	C_5
	7.66 (t, 2 H, *J* = 6.6 Hz)	C_6	124.55	C_6
	7.73 (d, 2 H, *J* = 9.7 Hz)	C_6	124.89	C_6
	7.98 (d, 2 H, *J* = 8.6 Hz)	C_6	124.96	C_6
			125.99	C_6
			126.22	C_6
			130.3	C_6
(**1a**) [CD_2Cl_2, 21 °C]	−1.43 (s, 6 H)	Zr–Me		
	0.91 (s, 6 H)	Si–Me		
	5.92 (d, 2 H, *J* = 3.3 Hz)	C_5		
	6.84 (d, 2 H, *J* = 3.3 Hz)	C_5		
	6.98 (t, 2 H, *J* = 7.8 Hz)	C_6		
	7.25 (t, 2 H, *J* = 6.6 Hz)	C_6		
	7.36 (d, 2 H, *J* = 9.7 Hz)	C_6		
	7.62 (d, 2 H, *J* = 8.6 Hz)	C_6		
$Me_2Si(Ind)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (**1b**) [toluene-d_8, 21 °C]	0.09 (s, 3 H)	Zr–Me terminal	20.7 (br)	$Zr(\mu\text{-}CH_3)B$
	0.16 (s, br, 3H)	$Zr(\mu\text{-}Me)B$	49.89 ($J_{C\text{-}H}$ 123 Hz)	Zr–CH_3 terminal
	0.91 (s, 3 H)	Si–Me	87.93	Si–C_5
	1.07 (s, 3 H)	Si–Me	89.19	Si–C_5
	5.66 (d, 1 H, *J* = 3.3 Hz)	C_5	111.40	C_5
	6.33 (d, 1 H, *J* = 3.3 Hz)	C_5	116.21	C_5
	6.83 (d, 1 H, *J* = 3.3 Hz)	C_5	116.98	C_5
	6.92 (t, 1 H, *J* = 3.3 Hz)	C_6 of Ind	121.01	C_6
	7.24 (d, 1 H, *J* = 3.3 Hz)	C_5	123.47	C_6
	7.28–7.36 (m, 2H)	C_6	124.87	C_6
	7.56–7.73 (m, 4 H)	C_6	124.93	C_6
	8.11 (d, 1 H, *J* = 8.6 Hz)	C_6	126.51	C_6
			126.78	C_6
			127.33	C_6
			127.37	C_6
			132.24	C_6
			133.00	C_6
			138.2 (d, $J_{C\text{-}F}$ = 249 Hz)	*m*-C of C_6F_5
			139.8 (d, $J_{C\text{-}F}$ = 255 Hz)	*p*-C of C_6F_5
			148.8 (d, $J_{C\text{-}F}$ = 237 Hz)	*o*-C of C_6F_5
$\{C_5H_3(SiMe_3)_2\}_2ZrMe_2$ (**2a**) [C_6D_6, 21 °C]	0.01 (s, 6 H)	Zr–Me	0.44	Si–Me
	0.27 (s, 36 H)	Si–Me	30.72	Zr–Me
	6.02 (d, 4 H, *J* = 2.02 Hz)	4,5-C_5H_2	115.73	4,5-C_5
	7.00 (t, 2 H, *J* = 2.02 Hz)	2-C_5H	123.74	1,3-C_5
			133.71	2-C_5
$\{C_5H_3(SiMe_3)_2\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (**2b**) [toluene-d_8, 20 °C]	−0.03 (s, 36 H)	Si–Me	−0.66	Si–CH_3
	0.41 (br, 3 H)	$Zr(\mu\text{-}Me)B$	16.55	$Zr(\mu\text{-}CH_3)B$
	0.64 (s, 3 H)	Zr–Me terminal	43.19	Zr–CH_3 terminal
	6.18 (s, br, 2 H)	2-C_5	123.20	2-C_5
	6.84 (s, br, 4 H)	4,5-C_5	137.49	4,5-C_5
			137.54 (d, $J_{C\text{-}F}$ = 249 Hz)	*m*-C of C_6F_5
			139.7 (d, $J_{C\text{-}F}$ = 260 Hz)	*p*-C of C_6F_5
			148.81 (d, $J_{C\text{-}F}$ = 237 Hz)	*o*-C of C_6F_5
$\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Zr(CH_2Ph)_2$ (**2c**) [toluene-d_8, 50 °C]	0.07 (s, 36 H)	Si–CH_3	0.74	Si–CH_3
	1.99 (s, 4 H)	Zr–CH_2	61.69 ($J_{C\text{-}H}$ = 117.8 Hz)	Zr–CH_2
	5.97 (s, 4 H)	4,5-Cp	121.48	*p*-C, Ph
	6.68 (t, 2 H, *J* = 7.92 Hz)	*p*-H, Ph	126.62	*m*-C, Ph
	6.93–6.96 (m, 6 H)	*o*-H, Ph, 2-Cp	128.63	*o*-C, Ph
	7.04 (t, 4 H, *J* = 7.59 Hz)	*m*-H, Ph	129.20[b]	4,5-Cp
			137.86[b]	2-Cp
			152.56	*ipso*-C, Ph
$Me_2Si(Ind)_2Zr(CH_2Ph)_2$ (**1c**) [$CDCl_3$]	−0.45 (d, 2 H, *J* = 11.2 Hz)	Zr–CH_2	−1.63	Si–CH_3
	0.63 (d, 2 H, *J* = 11.2 Hz)	Zr–CH_2	69.02 ($J_{C\text{-}H}$ = 120.9 Hz)	Zr–CH_2
	0.95 (s, 6 H)	Si–CH_3	84.35	C_5–Si
	5.66 (d, 2 H, *J* = 3.3 Hz)	C_5	114.88	C_5
	5.93 (d, 2 H, *J* = 3.3 Hz)	C_5	118.33	C_5
	6.59 (d, 4 H, *J* = 7.1 Hz)	*o*-H, Ph	120.88	*p*-C, Ph
	6.85 (t, 2 H, *J* = 7.3 Hz)	*p*-H, Ph	125.12	*m*-C, Ph
	7.1–7.3 (m, 10 H)	*m*-H and C_6	125.16	C_6
	7.50 (d, 2 H, *J* = 8.57 Hz)	C_6	125.28	C_6
			125.62	C_6
			125.67	C_6
			126.65	C_6
			128.09	*o*-C, Ph
			131.43	C_6
			152.42	*ipso*-C, Ph

Table 2 (Continued)

compd	^1H NMR	assgnt[a]	^{13}C NMR	assgnt[a]
$[Cp_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$	2.81 (s br, 2 H)	$\mathrm{PhC}\mathit{H}_2\mathrm{B}$	31.3 (br)	$\mathrm{B}\mathit{C}\mathrm{H_2Ph}$
(**3d**) $[CD_2Cl_2, -40\ °C]$	3.07	$Zr\text{–}CH_2$	47.49 ($J_{C\text{–}H}$ = 147.1 Hz)	$\mathrm{Zr}\mathit{C}\mathrm{H_2Ph}$
	6.18 (s, 10 H)	Cp	110.26	Cp
	6.99 (d, 2 H, *J* = 7.9 Hz)	*o*-H of $\mathrm{ZrCH_2}\mathit{Ph}$	121.17	*ipso*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.42 (t, 2 H, *J* = 7.8 Hz)	*m*-H of $\mathrm{ZrCH_2}\mathit{Ph}$	128.26	*o*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.52 (t, 1 H, *J* = 6.8 Hz)	*p*-H of $\mathrm{ZrCH_2}\mathit{Ph}$	130.62	*m*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
			130.71	*p*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	6.74 (d, 2 H, *J* = 6.9 Hz)	*o*-H of $\mathrm{BCH_2}\mathit{Ph}$	122.35	*p*-C of $\mathrm{BCH_2}\mathit{Ph}$
	6.84 (t, 1 H, *J* = 7.0 Hz)	*p*-H of $\mathrm{BCH_2}\mathit{Ph}$	126.72	*m*-C of $\mathrm{BCH_2}\mathit{Ph}$
	6.92 (t, 2 H, *J* = 7.3 Hz)	*m*-H of $\mathrm{BCH_2}\mathit{Ph}$	133.91	*o*-C of $\mathrm{BCH_2}\mathit{Ph}$
			136.05	*m*-C of C_6F_5
			137.10	*p*-C of C_6F_5
			142.84	*ipso*-C of C_6F_5
			147.70	*o*-C of C_6F_5
			148.10	*ipso*-C of $\mathrm{BCH_2}\mathit{Ph}$
$[\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)]^+$	0.17 (s, 36 H)	Si–Me	−0.31	Si–Me
(**2d**) $[CD_2Cl_2, -40\ °C]$[c]	3.54 (s, 2 H)	$\mathrm{Zr\text{–}C}\mathit{H}_2\mathrm{Ph}$	64.19 ($J_{C\text{–}H}$ = 146.5 Hz)	$\mathrm{Zr\text{–}}\mathit{C}\mathrm{H_2Ph}$
	7.10–7.26 (m, 5 H)	$\mathrm{Zr\text{–}CH_2}\mathit{Ph}$	122.78	*ipso*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.51 (s br, 4 H)	$\mathrm{4,5\text{-}C_5}\mathit{H}_3$	127.96	*o*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.67 (s br, 2 H)	$\mathrm{2\text{-}C_5}\mathit{H}_3$	129.00	4,5-C_5
			130.74	*m*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
			132.83	*p*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
			137.27	2-C_5
$[\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)]^+$	−0.11 (s, 36 H)	Si–Me	−0.32	Si–Me
(**2d**) [toluene-d_8, 60 °C][c]	3.17 (s, 2 H)	$\mathrm{Zr\text{–}C}\mathit{H}_2$	64.32 ($J_{C\text{–}H}$ = 146.5 Hz)	$\mathrm{Zr\text{–}}\mathit{C}\mathrm{H_2}$
	3.28 (s, br, 2 H)	$\mathrm{B\text{–}C}\mathit{H}_2$	123.02	*ipso*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	6.71–7.04 (m, 10 H)	Ph	126.99	*o*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.13 (d, 4 H, *J* = 2.02 Hz)	$\mathrm{4,5\text{-}C_5}\mathit{H}_3$	127.42	*m*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
	7.38 (t, 2 H, *J* = 2.02 Hz)	$\mathrm{2\text{-}C_5}\mathit{H}_3$	129.62	*p*-C of $\mathrm{ZrCH_2}\mathit{Ph}$
			128.54	4,5-C_5
			136.75	2-C_5
$[Me_2Si(Ind)_2Zr(CH_2Ph)]^+$	−1.23 (d, 1 H, *J* = 7.3 Hz)	$\mathrm{Zr\text{–}C}\mathit{H}_2$	−2.82	Si–Me
(**1d**) $[CD_2Cl_2, -50\ °C]$[c]	1.11 (s, 3 H)	Si–Me	−2.59	Si–Me
	1.12 (s, 3 H)	Si–Me	62.28 ($J_{C\text{–}H}$ = 147 Hz)	$\mathrm{Zr\text{–}}\mathit{C}\mathrm{H_2}$
	2.88 (s, 1 H, *J* = 7.3 Hz)	$\mathrm{Zr\text{–}C}\mathit{H}_2$	85.71	Si–C_5
	5.77–5.79 (m, 2 H)	C_5	87.60	Si–C_5
	6.24 (d, 2 H, *J* = 6.9 Hz)	*o*-H, $\mathrm{Zr\text{–}CH_2}\mathit{Ph}$	104.64	C_5
	6.38 (d, 1H, *J* = 3 Hz)	C_5	109.58	C_5
	6.92–7.72 (m, 12 H)	1 H (C_5), 3 H ($\mathrm{Zr\text{–}CH_2}\mathit{Ph}$), 8 H ($C_6$)	113.62	C_5
			113.71	C_5
			121.87	*ipso*-C of Ph
			126.93	*o*-C of Ph
			127.92	*m*-C of Ph
			132.1	*p*-C of Ph
			122.19	C_6
			122.60	C_6
			123.56	C_6
			123.88	C_6
			124.60	C_6
			128.25	C_6
			129.11	C_6
			130.00	C_6
			130.10	C_6
			130.31	C_6
			131.19	C_6
			135.27	C_6
$[Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)]^+$	−1.90 (d, 1 H, *J* = 6.9 Hz)	$\mathrm{Zr\text{–}C}\mathit{H}_2$	27.71	$\mathit{Me}_2\mathrm{C}$
(**5d**) $[CD_2Cl_2, -50\ °C]$[c]	2.27 (s, 3 H)	Me_2C	27.76	$\mathit{Me}_2\mathrm{C}$
	2.29 (s, 3 H)	Me_2C	39.8	$\mathrm{Me_2}\mathit{C}$
	2.88 (d, 1 H, *J* = 6.9 Hz)	$\mathrm{Zr\text{–}C}\mathit{H}_2$	59.78 ($J_{C\text{–}H}$ = 148 Hz)	$\mathrm{Zr\text{–}}\mathit{C}\mathrm{H_2Ph}$
	5.34 (s br, 1 H)	$\mathrm{C_5}\mathit{H}_4$	77.41	Me_2C–C_5 bridgehead C
	5.37 (s br, 1 H)	$\mathrm{C_5}\mathit{H}_4$	95.42	C_5
	5.80 (s br, 1 H)	$\mathrm{C_5}\mathit{H}_4$	101.96	C_5
	6.03 (d, 1 H, *J* = 6.3 Hz)	Flu	110.15	C_5
	6.36 (s br, 1 H)	$\mathrm{C_5}\mathit{H}_4$	110.71	Me_2C–Flu bridgehead C
	6.58 (d, 1 H, *J* = 7.9 Hz)	Flu	117.90	C_5
	7.14–7.44 (m, 6 H)	*o*-H of $\mathrm{Zr\text{–}CH_2}\mathit{Ph}$	118.18	Flu
	7.70 (t, 1 H, *J* = 7.6 Hz)	*p*-H of $\mathrm{Zr\text{–}CH_2}\mathit{Ph}$	119.53	Flu
	7.87 (t, 2 H, *J* = 8.4 Hz)	*m*-H of $\mathrm{Zr\text{–}CH_2}\mathit{Ph}$	119.67	Flu
	8.12 (d, 1 H, *J* = 8.3 Hz)	Flu	122.69	*ipso*-C of $ZrCH_2Ph$
	8.21 (d, 1 H, *J* = 8.3 Hz)	Flu	122.73	Flu
			122.89	Flu
			124.78	Flu
			125.84	Flu

Table 2 (Continued)

compd	^{1}H NMR	assgnt[a]	^{13}C NMR	assgnt[a]
$[Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)]^+$ (**5d**) [CD_2Cl_2, −50 °C][c]			126.84	Flu
			127.58	Flu
			128.32	*o*-C of ZrCH$_2$*Ph*
			128.35	*m*-C of ZrCH$_2$*Ph*
			128.80	Flu
			129.52	*p*-C of ZrCH$_2$*Ph*
			131.82	Flu
			132.11	Flu
			137.90	Flu
$CpZr(CH_2Ph)_2(\eta^6\text{-}PhCH_2)B(C_6F_5)_3$ (**7**)	1.91 (d, 2 H, *J* = 11.9 Hz)	Zr-CH$_2$	ca. 37 (br)	B–*C*H$_2$Ph
	2.12 (d, 2 H, *J* = 11.9 Hz)	Zr-CH$_2$	71.39	Zr–*C*H$_2$Ph
	3.05 (s, br, 2 H)	B–CH$_2$	115.36	Cp
	6.04 (s, 5 H)	Cp	123.31	*p*-C of Zr–CH$_2$*Ph*
	6.83 (d, 4 H, *J* = 2.6 Hz)	*o*-H of Zr–CH$_2$*Ph*	124.71	*p*-C of B–CH$_2$*Ph*
	7.04 (t, 2 H, *J* = 2.6 Hz)	*p*-H of Zr–CH$_2$*Ph*	125.75	*o*-C of Zr–CH$_2$*Ph*
	7.29 (t, 4 H, *J* = 6.9 Hz)	*m*-H of Zr–CH$_2$*Ph*	128.71	*m*-C of Zr–CH$_2$*Ph*
	6.71 (d, 4 H, *J* = 6.27 Hz)	*o*-H of B–CH$_2$*Ph*[d]	129.52	*o*-C of B–CH$_2$*Ph*
			129.72	*m*-C of B–CH$_2$*Ph*
			147.83	*ipso*-C of Zr–CH$_2$ph
			157.91	*ipso*-C of B–CH$_2$*Ph*
			136.22 (d, J_{C-F} = 242.9 Hz)	*m*-C of C_6F_5
			137.9 (d, J_{C-F} = 257 Hz)	*p*-C of C_6F_5
			147.34 (d, J_{C-F} = 242.9 Hz)	*o*-C of C_6F_5

[a] C_5 = cyclopentadienyl, C_6 = C_6-ring of indenyl. [b] Si–C missing or obscured. [c] Data for the counteranion as given for **3d**. [d] *m*- and *p*-BCH$_2$*Ph* ^{1}H NMR signals obscured by Zr–CH$_2$*Ph*.

a darkening of the color of the reaction mixture, from orange to red-orange, while **2d** forms a dark-purple solution.

Comparison of the spectroscopic data for $[Cp_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**3d**) with those for $[Cp_2Zr(CH_2Ph)][B(C_6F_5)_4]$ (**3e**), prepared from $Cp_2Zr(CH_2Ph)_2$ and $[CPh_3][B(C_6F_5)_4]$ as described previously,[2] shows only minor changes due to the different solvents and temperatures at which the characterization took place. The cationic complexes have an identical structure in both cases, with η^2-bonded benzyl ligands. The Zr-C*H$_2$*Ph signal of **3d** is observed at δ 3.07 ppm (CD_2Cl_2, −40 °C), 1.01 ppm downfield from the benzyl resonance of the neutral precursor **3c** [δ 2.06 ($C_2D_2Cl_4$, 0 °C)]. There is no indication of the formation of benzyl-bridged species involving the anion in analogy to **1b**, and whereas reaction 2 in the presence of excess Cp_2ZrMe_2 gives the methyl-bridged cations $[\{Cp_2ZrMe\}_2(\mu\text{-}Me)]^+$,[4] no related dimeric benzyl cations could be detected with $Cp_2Zr(CH_2Ph)_2/[CPh_3]^+$ mixtures in ratios of 2:1 to 11:1.

As a consequence of the stereorigid ligand frameworks in complexes **1c**, **4c**, and **5c** the hydrogens of the benzylic CH_2 group are inequivalent and appear as a set of two doublets. Characteristic chemical shift trends are observed on going from the neutral to the cationic complexes, with the CH_2 resonances being shifted from δ −0.45 and +0.63 ppm in **1c** to −1.23 and +2.88 in **1d**, and from δ −0.61 and −0.23 in **5c** to −1.91 and +2.88 in **5d**. The increases in chemical shift differences between the two benzylic hydrogens (**1c**, $\Delta\delta$ = 1.08; **1d**, $\Delta\delta$ = 4.11; and **5c**, $\Delta\delta$ = 0.38; **5d**, $\Delta\delta$ = 4.79) are further evidence for the adoption of an η^2-bonding mode which places only one of the two benzylic CH_2 hydrogens in close proximity to the magnetically anisotropic indenyl or fluorenyl rings, while the other shows a chemical shift close to that of **3d**. Interestingly, in the case of the cationic complexes there is a characteristic reduction in the value of ^2J(H–H) for the diastereotopic benzylic hydrogens, from 11.2 Hz in **1c** to 7.3 Hz in **1d**, and from 10 Hz in **5c** to 6.9 Hz in **5d**. The η^2-coordination of the benzyl ligand of the cationic complexes is further confirmed by ^1J(C–H) values of ca. 147 Hz for the Zr–CH_2 moiety and by the high-field shifted *ipso*-carbons of the benzylic phenyl groups.[14,15]

In all cases essentially identical resonances for the anion $[PhCH_2B(C_6F_5)_3]^-$ are observed under these conditions in dichloromethane, supporting the notion that in contrast to methyl complexes such as **2b** the benzyl complexes **1d**–**5d** show no detectable anion coordination in solution. In agreement with this the benzyl complexes are significantly less soluble in toluene than **1b** or **2b** and are obtained on cooling as highly sensitive oils which refused to crystallize and could not be isolated without decomposition. Depending on the nature of the cyclopentadienyl ligands the cationic complexes are thermally unstable in CD_2Cl_2 and decompose with varying rates above −30 °C to give the dichlorides.

There was the possibility that the absence of anion coordination was a reflection of the polarity of the solvent used for NMR investigations (CD_2Cl_2). The compounds **1d** and **3d**–**5d** proved to be insufficiently soluble for NMR studies in toluene. However, the reaction of highly hydrocarbon-soluble $\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)_2$ (**2c**) with $B(C_6F_5)_3$ proceeds smoothly in toluene above 0 °C to give a dark-purple product that is only sparingly soluble at room temperature but forms a homogeneous solution on warming to 60 °C. For comparison the complex was also characterized at low temperature in CD_2Cl_2. The ^{13}C NMR spectra are almost identical in both solvents and at both temperatures, with only small temperature and solvent dependent chemical shift differences. Crucially, *J*(C–H) for the benzylic CH_2 group of **2d** in toluene is 147 Hz, indicating that the complex is thermally stable and the η^2-bonding mode is preserved in toluene solution at 60 °C (i.e. under polymerization conditions). The ^{1}H spectrum at 60 °C shows somewhat larger solvent- and temperature-

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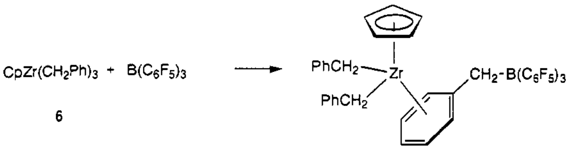
(15) (a) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T.; Piols, A. J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 677. (b) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T. *J. Chem. Soc. Chem. Commun.* **1971**, 1511. (c) Mintz, E. A.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4692. (d) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (e) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echolls, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (f) Scholz, J.; Rehbaum, F.; Thiele, K. H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93.

induced chemical shift differences but again confirms the presence of an η^2-coordinated zirconium benzyl cation and a noncoordinated $[PhCH_2B(C_6F_5)_3]^-$ anion.

For comparison the cationic complexes **1e** and **2e** were prepared from the zirconocene dibenzyls and $[CPh_3][B(C_6F_5)_4]$. The NMR data for zirconium species are identical to those of **1d** and **2d** and have therefore not been listed. **4e** has been reported previously.[2]

The reaction of $B(C_6F_5)_3$ with the more electron-deficient complex $CpZr(CH_2Ph)_3$ (**6**) in CD_2Cl_2 at −50 °C gives rise to $[CpZr(CH_2Ph)_2][PhCH_2B(C_6F_5)_3]$ (**7**). The ^1H NMR spectrum of **7** has a set of two doublets for the benzylic CH_2 groups at δ 1.92 and 2.12 ppm with a coupling constant of 11.9 Hz. The ^{13}C resonance for the benzylic CH_2 group is observed at δ 71.4 ppm, with $J(C-H) = 121$ Hz. These data indicate that in contrast to the cationic complexes described above **7** contains η^1-coordinated benzyl ligands. In agreement with this observation the ^1H NMR resonance for the $[PhCH_2B(C_6F_5)_3]^-$ anion show a different pattern from that of the free anion present in the bis(cyclopentadienyl) complexes, suggestive of anion coordination in the case of **7**. While it is not possible to unambiguously assign the coordination mode on the basis of the NMR data, we suggest that, in analogy to the recently reported arene complexes $[CpMMe_2(arene)][MeB(C_6F_5)_3]$[16] (M = Zr, Hf) and the crystallographically characterized $(PhCH_2)_3Zr\{\eta^6-C_6H_5CH_2B(C_6F_5)_3\}$[17] complex, **7** is a 16-electron complex containing a $[PhCH_2B(C_6F_5)_3]^-$ anion with a π-coordinated phenyl ring (eq 5).[18]



(5)

7

Preliminary studies show that the cationic complexes **1b** and **1d**–**4d** are highly active for the polymerization of ethene, while the activity of the sterically hindered complex **2b** and the monocyclopentadienyl compound **7** is about 1 order of magnitude less than that of **3d**. Similarly, **1d**–**4d** and **1e**–**4e** are highly active for the polymerization of propene at 0–60 °C and compare favorably with metallocene dihalide/MAO catalysts. A detailed study of the influence of the counteranion on catalyst productivity and stereoselectivity is in progress.

Conclusions

Zirconocene dimethyl complexes react with Lewis acids such as $B(C_6F_5)_3$ to give the zwitterionic complexes $Cp'_2ZrMe(\mu-Me)B(C_6F_5)_3$. The extent of anion coordination via a bridging methyl group is subject to steric hindrance of the Cp′ ligand but still strong even in the case of Cp′ = $1,3-C_5H_3(SiMe_3)_2$. By contrast, zirconocene dibenzyl compounds react with $B(C_6F_5)_3$ under transfer of a benzyl group to give the ionic complexes $[Cp'_2Zr(\eta^2-CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$. The structurally similar complexes $[Cp'_2Zr(\eta^2-CH_2Ph)]^+[B(C_6F_5)_4]^-$ are obtained from zirconocene dibenzyls and $[CPh_3][B(C_6F_5)_4]$, and it was confirmed that this structure is also adopted in toluene at 60 °C, i.e. under polymerization conditions. Species with bridging benzyl ligands are not found. Cationic benzyl complexes promise therefore to provide relatively simple systems for the systematic study of anion and ligand effects in polymerization catalysis.

Experimental Section

General Procedures. All manipulations are performed under dried argon using standard vacuum line techniques. $Cp_2Zr(CH_2Ph)_2$ (**3c**),[19] $CpZr(CH_2Ph)_3$ (**6**),[20] $\{C_5H_3(SiMe_3)_2\}_2ZrCl_2$,[21] *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**1**),[22] *rac*-$C_2H_4(Ind)_2Zr(CH_2Ph)_2$ (**4c**),[2] $Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)_2$ (**5c**),[2] $B(C_6F_5)_3$,[23] $[CPh_3][B(C_6F_5)_4]$,[3] and KCH_2Ph[13] were prepared according to literature procedures. Solvents were distilled under nitrogen from sodium (toluene), sodium–benzophenone (diethyl ether, THF, light petroleum (bp 40–60 °C)), or CaH_2 (CH_2Cl_2). Deuterated solvents were stored over activated 4-Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded on a JEOL EX270 instrument (reference TMS).

***rac*-$Me_2Si(Ind)_2Zr(CH_3)_2$ (1a).** To a suspension of 2.75 g of **1** (6.5 mmol) in 100 mL of diethyl ether at −78 °C was added dropwise with stirring 9.3 mL of a 1.4 M solution of MeLi in diethyl ether (13 mmol). The suspension was stirred for 0.5 h before being allowed to slowly warm to room temperature. Stirring was continued for 3 h. The diethyl ether was removed under reduced pressure and the residue extracted with 50 mL of toluene. The extract was centrifuged to remove the finely suspended LiCl. The toluene was concentrated to ca. 15 mL, 20 mL of petroleum ether was added, and the solution was cooled to −16 °C overnight, yielding light yellow crystals of **1a** (1.3 g, 3.2 mmol, 49%). Anal. Calcd for $C_{22}H_{24}SiZr$: C, 64.79; H, 5.94. Found: C, 64.77; H, 5.90.

***rac*-$Me_2Si(Ind)_2Zr(CH_3)(\mu-CH_3)B(C_6F_5)_3$ (1b).** A mixture of 0.35 g of **1a** (0.86 mmol) and 0.5 g of $B(C_6F_5)_3$ (0.98 mmol) was cooled to −78 °C, and 10 mL of petroleum ether was added. The resulting slurry was stirred for 0.5 h and then allowed to warm to room temperature, forming an orange slurry. After adding 20 mL of toluene followed by filtration the solution was concentrated to 10 mL and cooled to −16 °C. Cushions of very small orange-red needles crystallized over a period of 7 days which were collected and dried *in vacuo*, yield 0.5 g (0.54 mmol, 62.8%). The product is extremely air sensitive, decomposing to a red oil. Anal. Calcd for $C_{40}H_{24}BF_{15}SiZr$: C, 52.23; H, 2.64. Found: C, 52.63; H, 2.98.

***rac*-$Me_2Si(Ind)_2Zr(CH_2Ph)_2$ (1c).** To 3 g of **1** (7.2 mmol) suspended in 30 mL of diethyl ether was added dropwise at −78 °C 100 mL of a 0.15 M solution of $PhCH_2MgCl$ in diethyl ether (15 mmol). The reaction was allowed to warm slowly to room temperature before stirring for 4 h. The diethyl ether was removed under reduced pressure. The solid was extracted with 200 mL of a 9:1 toluene/petroleum ether mixture. After concentration to ca. 40 mL and addition of ca. 100 mL of petroleum ether the solution was placed in the freezer overnight, yielding orange-red cubic crystals. This material contained some halide; a halide-free sample was obtained by recrystallization from toluene/petroleum ether 9:1. Yield: 1.0 g (1.8 mmol, 25%). Anal. Calcd for $C_{34}H_{32}SiZr$: C, 72.92; H, 5.77. Found: C, 72.05; H, 5.59.

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Table 3. Crystal Data for Compound 2b

formula	$C_{42}H_{48}BF_{15}Si_4Zr{\cdot}0.5C_7H_8$
fw	1098.27
cryst syst	triclinic
space group	$P1$ (No. 2)
cell dimens	
a, Å	11.807(3)
b, Å	13.068(4)
c, Å	19.487(2)
α, deg	77.81(2)
β, deg	74.04(3)
γ, deg	75.63(1)
V, Å^3	2767.2(11)
Z	2
D_{calcd}, g cm^{-3}	1.318
abs coeff, mm^{-1}	0.356
$F(000)$	1122
abs corr	0.854–1.031
θ range, deg	$2.3 \leq \theta \leq 30.2$
index range	$-10 \leq h \leq 16, -18 \leq k \leq 17, -18 \leq l \leq 25$
no. of reflns collcd	14 178
no. of ind reflns	12 290 [R_{int} = 0.0450]
no. of param	608
goodness-of-fit on F^2	0.753
final R indices[a] (for 4865 data with $I > 2\sigma(I)$)	$R_1 = 0.0527$, $wR_2 = 0.1328$
R indices (all 12290 data)	$R_1 = 0.1216$, $wR_2 = 0.1468$

[a] $R_1 = \sum(\Delta F)/\sum(F_o)$; $wR_2 = [\sum\{w(\Delta(F^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (0.068P)^2]$, where $P = [\max((F_o)^2, 0) + 2(F_c)^2]/3$.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound 2b·0.5C$_7$H$_8$

	x	y	z	U(eq)[a]
Zr	3887(1)	3215(1)	2390(1)	42(1)
Si(1)	1529(1)	6018(1)	2859(1)	59(1)
Si(2)	3384(1)	1918(1)	4456(1)	66(1)
Si(3)	6777(1)	2648(1)	718(1)	63(1)
Si(4)	2480(2)	912(1)	1989(1)	73(1)
C(1)	2093(4)	4535(4)	3046(2)	46(1)
C(2)	2826(4)	3991(4)	3540(2)	47(1)
C(3)	2846(4)	2890(4)	3695(2)	49(1)
C(4)	2087(4)	2736(4)	3282(2)	49(1)
C(5)	1676(4)	3718(4)	2886(2)	47(1)
C(6)	5516(4)	2205(4)	1466(2)	50(1)
C(7)	4400(4)	2120(4)	1377(2)	55(1)
C(8)	3747(4)	1540(4)	1992(3)	55(1)
C(9)	4525(4)	1242(4)	2480(2)	51(1)
C(10)	5575(4)	1634(3)	2165(2)	50(1)
C(11)	2755(5)	6766(4)	2478(3)	86(2)
C(12)	701(7)	6432(5)	3752(3)	113(3)
C(13)	498(6)	6299(5)	2245(3)	94(2)
C(14)	2706(6)	721(5)	4616(3)	102(2)
C(15)	5055(5)	1492(5)	4275(3)	85(2)
C(16)	2867(6)	2652(6)	5244(3)	116(3)
C(17)	8182(5)	2245(6)	1056(3)	94(2)
C(18)	6505(6)	4079(5)	399(3)	98(2)
C(19)	6841(6)	1964(7)	−38(3)	122(3)
C(20)	1135(6)	1909(5)	1828(4)	98(2)
C(21)	3131(7)	110(7)	1241(4)	148(4)
C(22)	2091(6)	−16(5)	2851(4)	103(2)
C(23)	3383(4)	4420(4)	1450(2)	57(1)
C(24)	5651(5)	4051(4)	2515(3)	48(1)
B(1)	6584(5)	4702(5)	2686(3)	50(1)
C(25)	5735(3)	5614(2)	3235(1)	50(1)
C(26)	4997(3)	5199(2)	3866(2)	53(1)
C(27)	4222(3)	5878(3)	4333(1)	59(1)
C(28)	4186(3)	6972(3)	4169(2)	76(2)
C(29)	4925(3)	7387(2)	3537(2)	73(2)
C(30)	5699(3)	6708(3)	3070(2)	63(1)
C(31)	7339(3)	5250(2)	1879(1)	50(1)
C(32)	6654(2)	5993(3)	1451(2)	66(2)
C(33)	7212(3)	6483(3)	781(2)	79(2)
C(34)	8456(4)	6230(3)	539(1)	81(2)
C(35)	9141(2)	5487(3)	967(2)	64(2)
C(36)	8583(3)	4997(2)	1637(2)	54(1)
C(37)	7552(3)	3868(3)	3174(2)	52(1)
C(38)	7761(3)	2761(3)	3246(2)	60(1)
C(39)	8495(3)	2131(2)	3690(2)	74(2)
C(40)	9022(3)	2610(4)	4061(2)	82(2)
C(41)	8814(3)	3718(4)	3989(2)	78(2)
C(42)	8079(3)	4347(3)	3546(2)	60(1)
F(26)	5038(2)	4183(2)	4092(1)	57(1)
F(27)	3508(3)	5503(3)	4934(1)	84(1)
F(28)	3412(3)	7667(3)	4599(2)	109(1)
F(29)	4906(4)	8441(3)	3387(2)	106(1)
F(30)	6416(3)	7152(2)	2511(2)	92(1)
F(32)	5471(3)	6254(3)	1638(2)	89(1)
F(33)	6545(4)	7185(3)	353(2)	113(1)
F(34)	8991(4)	6739(3)	−107(2)	113(1)
F(35)	10308(3)	5286(3)	732(2)	98(1)
F(36)	9288(2)	4306(3)	1986(1)	72(1)
F(38)	7349(3)	2266(2)	2882(2)	84(1)
F(39)	8691(3)	1086(3)	3751(2)	117(1)
F(40)	9700(3)	1982(4)	4506(2)	121(2)
F(41)	9331(3)	4150(4)	4349(2)	113(1)
F(42)	7969(3)	5387(3)	3483(2)	84(1)
C(43)[b]	7568(7)	9176(5)	1925(6)	86(4)
C(44)[b]	7554(9)	9075(6)	1231(7)	130(6)
C(45)[b]	8604(13)	9039(6)	688(5)	112(5)
C(46)[b]	9668(8)	9103(6)	837(5)	99(5)
C(47)[b]	9681(7)	9203(6)	1531(7)	97(4)
C(48)[b]	8631(11)	9240(5)	2075(4)	129(6)
C(49)[b]	8150(19)	9315(12)	2833(5)	165(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atoms of the disordered toluene molecule, each refined with a fixed occupancy of 0.50.

$\{C_5H_3(SiMe_3)_2\}_2ZrMe_2$ (2a). $\{C_5H_3(SiMe_3)_2\}_2ZrCl_2$ (1.8 g, 3.1 mmol) was dissolved in 60 mL of diethyl and ether, and the solution was cooled to −78 °C before 4.5 mL of a 1.4 M solution of MeLi (6.2 mmol) was added via syringe. The mixture was allowed to warm slowly to room temperature and stirred for 5 h. The solvent was removed in vacuo and the residue extracted with 60 mL of petroleum ether. The filtrate was concentrated to 30 mL and cooled to −16 °C overnight to give large colorless crystals of **2a** (1.1 g, 20 mmol, 65%). Anal. Calcd for $C_{24}H_{48}Si_4Zr$: C, 53.34; H, 8.97. Found: C, 53.45; H, 8.92.

$\{C_5H_3(SiMe_3)_2\}_2Zr(\mu\text{-}CH_3)B(C_6F_5)_3$ (2b). Solid **2a** (0.85 g, 1.89 mmol) and 1.0 g of $B(C_6F_5)_3$ (1.95 mmol) were mixed, and 20 mL of precooled (−70 °C) petroleum ether was added. The mixture was stirred for 0.5 h before being allowed to warm to room temperature. To the yellow slurry was added 20 mL of toluene to give a yellow solution which was filtered and cooled to −16 °C to give pale-yellow cubes of **2b**·0.5(toluene) (1.3 g, 1.18 mmol, 62%). Anal. Calcd for $C_{42}H_{48}Si_4BF_{15}Zr{\cdot}0.5C_7H_8$: C, 49.74; H, 4.78. Found: C, 49.79; H, 4.47.

$\{C_5H_3(SiMe_3)_2\}_2ZrCl(CH_2Ph)$. $\{C_5H_3(SiMe_3)_2\}_2ZrCl_2$ (5.0 g, 8.6 mmol) was added in small portions to 200 mL of a 0.1 M solution of $PhCH_2MgCl$ in Et_2O at room temperature. The mixture was stirred for 24 h in the dark. After removal of the solvent the residue was extracted with 200 mL of petroleum ether and filtered. Since no solid was obtained on cooling, the filtrate was evaporated to leave an orange-red oil which solidified over 48 h at 5 °C (3.5 g, 5.49 mmol, 64%). ^{1}H NMR (C_6D_6, 21 °C): δ 0.18 (s, 18 H, Si-Me), 0.22 (s, 18 H, Si-Me), 2.52 (s, 2 H, Zr-CH_2), 6.15–6.26 (m, 4 H, 4,5-Cp), 6.97–6.98 (m, 2 H, 2-Cp). Anal. Calcd for $C_{29}H_{49}ClSi_4Zr$: C, 54.68; H, 7.77; Cl, 5.56. Found: C, 56.64; H, 7.65; Cl, 5.00.

$\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)_2$ (2c). To 10 mmol of "KCH_2Ph" were added 100 mL of THF and 2.9 g of $\{C_5H_3(SiMe_3)_2\}_2ZrCl_2$ (5 mmol). The solution rapidly became very dark. Light was excluded and the reaction was stirred overnight. When stirring was ceased, a white precipitate settled out from a dark brown solution. The THF was removed under reduced pressure and the solid extracted with 200 mL of petroleum ether. The petroleum fraction was concentrated but would not yield a solid even after cooling to −78 °C. After solvent removal a dark-yellow oil remained which slowly crystallized at 5 °C to give a yellow solid which was freed from the adhering brown oil by washing with 2 × 20 mL of petroleum ether at −50 °C. The solid was dried *in vacuo* to give 2.5 g of **2c** (3.6 mmol, 72%). Anal. Calcd for $C_{36}H_{56}Si_4Zr$: C, 62.43; H, 8.17. Found: C, 62.26; H, 8.08.

Generation of $[Me_2Si(Ind)_2Zr(CH_2Ph)][PhCH_3B(C_6F_5)_3]$ (1d). **1c** (43 mg, 0.08 mmol) and 40 mg of $B(C_6F_5)_3$ (0.08 mmol) were placed in two different Schlenk tubes, and each was dissolved in 0.4 mL of CD_2Cl_2. The solutions were cooled to −78 °C and mixed in an NMR tube to give a dark-orange solution which was spectroscopically characterized at −50 °C.

Generation of $[\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (2d). In CD_2Cl_2. **2c** (82 mg, 0.12 mmol) and 85 mg of $B(C_6F_5)_3$ (0.16 mmol) were combined in a Schlenk tube and cooled to −50 °C. On addition of 0.8 mL of precooled CD_2Cl_2 the solution rapidly developed a dark-purple color and was stirred for 1 h at −50 °C. The solution was transferred to an NMR tube and placed in the spectrometer at −50 °C.

In C_7D_8. **2c** (83 mg, 0.12 mmol) and 90 mg of $B(C_6F_5)_3$ (0.18 mmol) were each dissolved in C_7D_8 and transferred to an NMR tube. The reaction was followed over the temperature interval from −30 to +60 °C.

Generation of $[\{C_5H_3(SiMe_3)_2\}_2Zr(CH_2Ph)][B(C_6F_5)_4]$ (2e). In CD_2Cl_2. According to the procedure for **2d**, 66 mg of **2c** (0.1 mmol) and 100 mg of $[CPh_3][B(C_6F_5)_4]$ (0.11 mmol) were placed in two different Schlenk tubes, dissolved in 0.4 mL of CD_2Cl_2 each, cooled to −78 °C, and transferred to an NMR tube where the two solutions were mixed, giving a color change to purple.

In C_7D_8. **2c** (37 mg, 0.05 mmol) and 70 mg of $[CPh_3][B(C_6F_5)_4]$ (0.08 mmol) were mixed in 0.8 mL of C_7D_8 at room temperature for 10 min before being transferred to an NMR tube for spectroscopic characterization.

Generation of $[Cp_2Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (3d). $Cp_2Zr(CH_2Ph)_2$ (**3c**) (61 mg, 0.15 mmol) and 91 mg of $B(C_6F_5)_3$ (0.18 mmol) were placed in two different Schlenk tubes, and each was dissolved in 0.4 mL of CD_2Cl_2. The solutions were cooled to −78 °C and transferred to an NMR tube where mixing took place to give an orange solution which was spectroscopically characterized at −50 °C.

Generation of $[Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (5d). $Me_2C(C_5H_4)(Flu)Zr(CH_2Ph)_2$ (**5c**) (60 mg, 0.11 mmol) and 70 mg of $B(C_6F_5)_3$ (0.14 mmol) were handled in a similar fashion to the generation of **1d** to give an orange solution which was spectroscopically characterized at −50 °C.

Generation of $CpZr(CH_2Ph)_2(\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ (7). $CpZr(CH_2Ph)_3$ (85 mg, 0.19 mmol) and 95 mg of $B(C_6F_5)_3$ were separately dissolved in 0.4 mL of CD_2Cl_2 precooled to −78 °C and combined in an NMR tube, forming a dark-red solution. The product was identified spectroscopically. The compound is thermally sensitive, giving dark-brown decomposition products on warming.

X-ray Crystallography. The determinations of the X-ray structure of **2b** was carried out at 298 K using a crystal of dimensions 0.25 × 0.20 × 0.15 mm. Data were collected using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo Kα radiation [λ(Mo Kα) = 0.710 69 Å] by following the procedures described elsewhere.[24] Crystal data and a summary of the structure refinement are collected in Table 3; atomic positional parameters are given in Table 4. The compound contains disordered toluene of crystallization. The best fit was obtained by assuming half-occupancy for the carbon positions. The hydrogen atoms to the bridging methyl group C(24) were identified experimentally and refined freely with individual U_{iso}'s, those on the disordered toluene were ignored. The remaining hydrogens were included in idealized positions and their U_{iso}'s were set at 1.2 times (for CH) and 1.5 times (for CH_3) the U_{eq}'s of the parent carbons. The phenyl rings were refined as idealized hexagons (C–C 1.390 Å, C–C–C 120°). The structure was solved by the direct methods using SHELX-S[25] and refined on F_o^2 by full-matrix least squares techniques using SHELXL-93[26] with all data corrected for absorptions by DIFABS.[27] Figures were drawn by SNOOPI.[28] All calculations were made on a 486DX2/66 personal computer.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compound **2b** (7 pages). Ordering information is given on any current masthead page.

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