

Chemistry of Half-Sandwich Compounds of Zirconium: Evidence for the Formation of the Novel *ansa* Cationic–Zwitterionic Complex [Zr(η : η -C₅H₄CMe₂C₆H₄Me-*p*)(μ -MeB(C₆F₅)₃)]⁺[MeB(C₆F₅)₃][–]

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The compound [Zr(η -C₅H₄CMe₂C₆H₄Me-*p*)Cl₃(dme)] (**1**) has been prepared. Methylation affords the compound [Zr(η -C₅H₄CMe₂C₆H₄Me-*p*)Me₃] (**2**), and benzylation of **1** yields [Zr(η -C₅H₄CMe₂C₆H₄Me-*p*)(CH₂Ph)₃] (**3**). Reaction of **2** with [Ph₃C]⁺[B(C₆F₅)₄][–] at –60 °C gives the *ansa* complex [Zr(η : η -C₅H₄CMe₂C₆H₄Me-*p*)Me₂]⁺[B(C₆F₅)₄][–] (**4a**), which has been characterized by 1D and 2D NMR spectroscopy. Reaction of **2** with an excess (1.5 equiv) of B(C₆F₅)₃ yields not only the *ansa* complex [Zr(η : η -C₅H₄CMe₂C₆H₄Me-*p*)Me₂]⁺[MeB(C₆F₅)₃][–] (**4b**) but also the novel cationic zwitterionic *ansa* complex [Zr(η : η -C₅H₄CMe₂C₆H₄Me-*p*)(μ -MeB(C₆F₅)₃)]⁺[MeB(C₆F₅)₃][–] (**5**). The dynamic behavior of complexes **4b** and **5** was extensively studied by NMR spectroscopy. Reaction of **3** with [Ph₃C]⁺[B(C₆F₅)₄][–] at –60 °C yields the *ansa* complex [Zr(η : η -C₅H₄CMe₂C₆H₄Me-*p*)(CH₂Ph)₂]⁺[B(C₆F₅)₄][–] (**6**), containing σ -bound benzyl ligands.

Introduction

Cationic zirconocene complexes are of great interest as catalysts for hydrogenation,¹ isomerization,² and especially olefin polymerization reactions.^{3–11} The donor-free 14-electron [Zr(η -C₅H₅)₂R]⁺ cation is believed to be an active species in Ziegler–Natta type olefin polymerization. However, these species are extremely reactive and have not been isolated.

The half-sandwich complexes [M(η -Cp')R₃] (Cp' = C₅H₅, substituted Cp; M = Ti, Zr, Hf) have received less attention, although they are used as precursors for the catalytic polymerization of styrene¹² and propene.¹³ Baird et al. have demonstrated the formation of arene adducts [M(η -C₅Me₅)Me₂(η -arene)]⁺ (arene = benzene, toluene, *m*- and *p*-xylene, anisole, styrene, mesitylene; M = Ti, Zr, Hf).^{14,15} Bochmann et al.¹⁶ reported the

solid-state structure of [Zr(η -C₅H₃(SiMe₃)₂-1,3)(η -toluene)Me₂]⁺. Recently, Rausch^{12,17} has reported the 16-electron *ansa* complex [Zr(η : η -C₅Me₄CH₂CH₂C₆H₅)Me₂]⁺[B(C₆F₅)₄][–] and used this complex as a model for styrene polymerization. In this model the cationic complex [Zr(η : η -C₅Me₄CH₂CH₂C₆H₅)Me₂]⁺ is considered to be the resting state for styrene polymerization; the incoming monomer displaces the coordinated phenyl ring and subsequently inserts into the metal–carbon bond (see Scheme 1).

Competitive complexation to the metal of the tethered phenyl ring and the phenyl ring attached to the growing chain can be expected, since other cationic half-sandwich complexes of zirconium are known¹⁸ in which the benzyl moiety is coordinated in an η^3 and η^7 fashion, respectively.

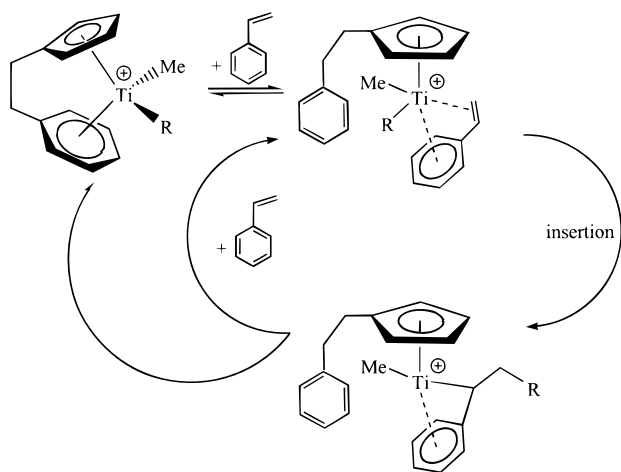
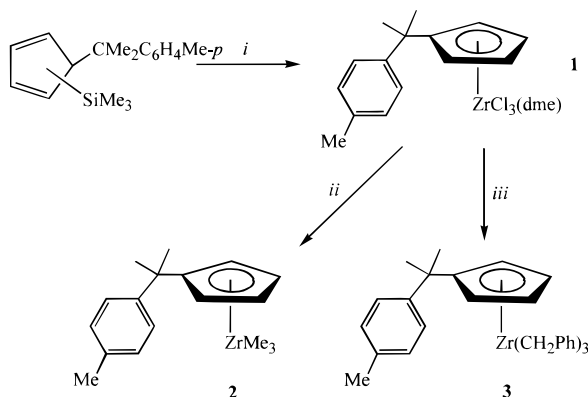
To investigate the coordination mode of the benzyl moiety and the pendant phenyl group, the compound [Zr(η -C₅H₄CMe₂C₆H₄Me-*p*)(CH₂Ph)₃] (**3**) was prepared. Here, the methyl group in the *para* position of the tethered phenyl ring serves as an NMR probe.

Since Rausch's cation [Zr(η : η -C₅Me₄CH₂C₆H₄Me-*p*)Me₂]⁺ formally has the same electronic configuration as the neutral zirconocene compound [Zr(η -C₅R₅)₂Me₂] (R = H, Me), we sought to investigate the possibility of the formation of zwitterionic complexes similar to the well-known metallocene complexes [Zr(η -C₅R₅)₂Me(μ -Me)B(C₆F₅)₃] (R = H, Me).^{19,20} For this purpose the compound [Zr(η -C₅H₄CMe₂C₆H₄Me-*p*)Me₃] (**2**) was prepared.

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- (1) Qian, Y.; Li, G.; Huang, Y. *J. Mol. Catal.* **1989**, *54*, L 19.
- (2) Qian, Y.; Lu, J.; Xu, W. *J. Mol. Catal.* **1986**, *34*, 31.
- (3) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 225–270.
- (4) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1995**, *127*, 144–187.
- (5) Aulbach, M.; Küber, F. *Chem. Ums. Z.* **1994**, *28*, 197–208.
- (6) Brintzinger, H.-H.; Fischer, D.; Mühlhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255–1383.
- (7) Guram, A. S.; Jordan, R. F. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Pergamon: Oxford, U.K., 1995; Vol. 4.
- (8) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387.
- (9) Ushioda, T.; Green, M. L. H.; Haggitt, J.; Yan, X. *J. Organomet. Chem.* **1996**, *518*, 155–166.
- (10) Möhring, P. C.; Vlachakis, N.; Grimmer, N. E.; Coville, N. J. *J. Organomet. Chem.* **1994**, *483*, 159–166.
- (11) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447.
- (12) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 4944–4950.
- (13) Sassmannshausen, J.; Bochmann, M.; Rösch, J.; Lige, D. *J. Organomet. Chem.* **1997**, *548*, 23–28.
- (14) Gillis, D. J.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543–2545.

- (15) Gillis, D. J.; Quyoum, R.; Tudoret, M. J.; Wang, Q.; Jeremic, D.; Roszak, A. W.; Baird, M. C. *Organometallics* **1996**, *15*, 3600–3605.
- (16) Bochmann, M.; Robinson, O. B.; Lancaster, S. J.; Hursthouse, M. B.; Coles, S. J. *Organometallics* **1995**, *14*, 2456–2462.
- (17) Blais, M. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 3775–3783.
- (18) Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773–3775.

Scheme 1^a^a R = growing polymer chain.Scheme 2^a

^a Legend: (i) (a) $\text{ZrCl}_4(\text{dms})_2$, CH_2Cl_2 , room temperature, (b) dme; (ii) MgMeCl , Et_2O , -78°C ; (iii) $\text{Mg}(\text{CH}_2\text{Ph})\text{Cl}$, Et_2O , room temperature.

Results and Discussion

The compound $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)\text{Cl}_3(\text{dme})]$ (**1**) was prepared by a modified literature procedure²¹ by reacting the ligand $\text{C}_5\text{H}_4(\text{SiMe}_3)(\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)$ with $[\text{ZrCl}_4(\text{Me}_2\text{S})_2]$ in dichloromethane followed by precipitation of the zirconium compound **1** as the dimethoxyethane adduct. **1** was used without further purification. Methylation of **1** was performed with MgMeCl in diethyl ether at -78°C to furnish the compound $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_3]$ (**2**) as an air- and moisture-sensitive dark brown microcrystalline solid, which is best handled under argon (Scheme 2). Benzylation of **1** was performed with $\text{Mg}(\text{CH}_2\text{Ph})\text{Cl}$ in diethyl ether at ambient temperature; the product $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)(\text{CH}_2\text{Ph})_3]$ (**3**) crystallizes as yellow needles from light petroleum.

The reaction of **2** with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 was monitored by NMR spectroscopy. At -60°C the reaction proceeds cleanly to the *ansa*-metallocene $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)_2\text{Me}_2]^+$ (**4a**; $\text{B}(\text{C}_6\text{F}_5)_4^-$ counterion). Typical for such complexes is the low-field shift

of the phenyl hydrogen atoms, which is indicative of η coordination of the phenyl ring to the cationic zirconium center (see Scheme 3). Similar observations have been made previously.^{12,22} The complete assignment of **4a** was performed by ^1H , ^{13}C , HMQC (heteronuclear multiple quantum coherence), and NOESY (nuclear Overhauser enhancement spectroscopy) spectroscopy, and the data are collected in Table 1.

The NOESY spectrum (see Experimental Section) clearly shows a correlation between the Cp(1,2) (see Table 1 for labeling) and the Ph(12,13) hydrogen atoms with the zirconium–methyl groups, respectively (cf. Figure 1). A correlation between the CMe_2 group and the Cp(3,4) and Ph(10,11) hydrogen atoms was observed, thus enabling complete assignment of the cation **4a**.

More interesting was the reaction of **2** with 1.5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in CD_2Cl_2 at -60°C , which was monitored by NMR spectroscopy. At this temperature not only the cation **4b** was observed but also the new compound **5** (see Figure 2).

The ^{11}B NMR spectrum of **5** at -60°C indicates the presence of two distinct four-coordinate boron species, one having a chemical shift of $\delta -15$ ppm which has previously been attributed to the free $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion,¹⁴ and a second species having a chemical shift of $\delta -13$ ppm. At -40°C this second peak is no longer present, indicating that it is associated with a thermally sensitive compound. We postulate this to be the new zwitterionic–cationic complex **5** (Scheme 3).

5 can be considered to be a Lewis acid–base adduct between the 16-electron complex **4b** and the strong Lewis base $\text{B}(\text{C}_6\text{F}_5)_3$, similar to other known zwitterionic complexes such as $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Me}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^{19,20}$ and $[\text{Zr}\{\eta\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}\}_2\text{Me}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^{23}$. The proposed structure of **5** is further supported by the observation of a peak at $\delta 0.97$ ppm in the ^1H NMR spectrum, which correlates with a peak at $\delta 37.5$ ppm in the ^{13}C NMR spectrum. This peak can be assigned to a Me group bridging the Zr and B atoms. The $^1J_{\text{CH}}$ coupling constant for this bridging methyl group is 115 Hz, compared to 125 Hz for the nonbridging ZrMe group. Because of the bridging methyl group, complex **5** is chiral and all of the expected resonances are observed. Full assignment of **5** was possible using COSY, HMQC, and NOESY/EXSY (exchange spectroscopy) spectroscopy.

To investigate a possible exchange between complex **4b** and **5**, a NOESY/EXSY spectrum was recorded (see Experimental Section). The spectrum recorded at -60°C indicates an exchange not only between **4b** and **5** (see Scheme 4 and Figure 3) but also between the two sides of complex **5**.

The exchange between complexes **4b** and **5** is indicated by the cross-peak between the two different CpH, CMe_2 , and PhH signals, respectively, suggesting a reversible process (see Figure 3). This exchange is clearly seen from the cross-peak exchanging Ph(12,13) ($\delta 8.01$ ppm) of **4b** with Ph(12) ($\delta 8.57$ ppm) and Ph(13) ($\delta 8.05$ ppm, underneath Ph(12,13) peak) of **5** (see Table

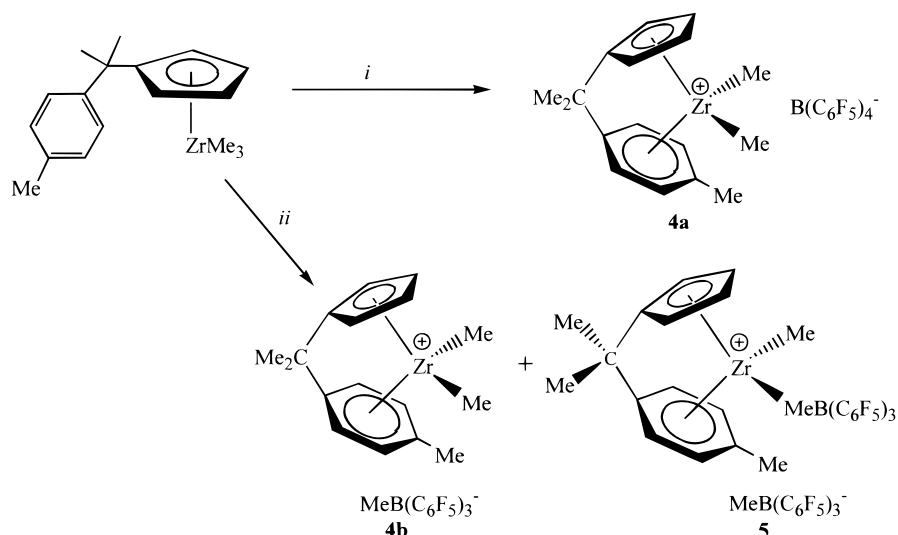
(19) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(20) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015–10033.

(21) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426–2427.

(22) Sassmannshausen, J. *New Substituted Cyclopentadienyl Complexes as 1-Alkene Polymerisation Catalysts*; University of Leeds: Leeds, U.K., 1997.

(23) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Maik, K. M. A. *Organometallics* **1994**, *13*, 2235–2243.

Scheme 3^a

^a Legend: (i) $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, CD_2Cl_2 , -60°C ; (ii) 1.5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, CD_2Cl_2 , -60°C .

1 for labeling). Similarly, $\text{Ph}(10,11)$ (δ 7.22 ppm) of **4b** exchanges with $\text{Ph}(11)$ (δ 7.82 ppm) and $\text{Ph}(10)$ (δ 7.27 ppm, underneath $\text{Ph}(10,11)$ peak). The weaker cross-peak at F1 δ 8.05 ppm, F2 δ 7.22 ppm is due to COSY breakthrough; the even weaker cross-peak at F1 δ 8.57 ppm and F2 δ 7.22 ppm is due to NOESY.

Similar observations can be made for the cyclopentadienyl protons of complexes **4b** and **5**. More detailed information about the processes involved can be obtained by examining the aliphatic region of the spectrum, in particular the ZrMe and MeBX_3^- ($\text{X} = \text{C}_6\text{F}_5$) peaks.

Figure 4 shows an expansion of this region, which indicates an exchange between the free MeBX_3^- with the ZrMe_2 group of complex **4b** and with the $\text{Zr}(\mu\text{-Me})\text{BX}_3$ moieties of complex **5**. A similar ion pair dissociation/reabstraction and symmetrization has been observed previously and thoroughly investigated by Marks.^{24,25} From careful analysis of the NMR spectra of the complex $[\text{M}(\{\eta\text{-C}_5\text{H}_3\text{Me}_2\text{-1,2}\}\text{Me})[\text{MeB}(\text{C}_6\text{F}_5)_3]]$ ($\text{M} = \text{Zr}, \text{Hf}$) at various temperatures, two processes which lead to exchange of the methyl group in the metallocene wedge could be identified. The first process, more dominant in polar solvents and for $\text{M} = \text{Zr}$, cleaves the $\text{Zr}-\mu\text{-Me}$ interaction and flips the terminal $\text{Zr}-\text{Me}$ group from one side of the metallocene girdle to the other and is followed by reassociation of the anion. The second process permutes both the diastereotopic ring sites and the bridging/terminal methyl groups by an initial dissociation of $\text{B}(\text{C}_6\text{F}_5)_3$ by $\text{Me}-\text{B}$ bond cleavage and coordination to the other terminal methyl group of the zirconocene. This process is more facile when $\text{M} = \text{Hf}$, probably due to greater $\text{M}-\text{C}$ bond strength (see Scheme 5).

A similar mechanism can be suggested here: the free MeBX_3^- displaces the coordinated MeBX_3^- of complex **5**, resulting in an exchange between free and coordinated MeBX_3^- . It is known from the zwitterionic complex $[\text{Zr}\{\eta\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2\text{Me}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ that

the MeBX_3^- moiety is weakly bonded via agostic hydrogens to the cationic metal center.²³ Thus, the rather labile anion can be readily displaced by stronger Lewis bases. This displacement has been recently demonstrated by Green et al. in the formation of cationic²⁶ and dicationic²⁷ zirconocene complexes stabilized by intramolecular phenyl coordination. In these complexes the (di)cationic zirconium center is stabilized by agostic interaction of the *ortho* hydrogen of the phenyl ring (see Chart 1).

If we take this into account, the free anion MeBX_3^- of **4b** could be sufficiently Lewis basic to replace the coordinated anion MeBX_3^- in **5**.

Complex **5** can convert into **4b** by loss of BX_3 , which could recoordinate to form the inverted version of **5** (cf. Scheme 4) in a manner similar to that observed by Marks et al.^{24,25} Indeed, the ^{19}F NMR spectrum shows the presence of three compounds: $\text{B}(\text{C}_6\text{F}_5)_3$ (δ -133.4 , -149.2 , and -166.6 ppm), the solvated $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (δ -139.4 , -169.9 , and -172.7 ppm), and the chemical shift difference $\Delta\delta(m,p\text{-F})$ 2.8 ppm, indicative of a noncoordinated anion as previously described by Horton.²⁸ Values for $\Delta\delta(m,p\text{-F})$ between 3 and 6 ppm indicate coordination of the anion, while values <3 ppm indicate noncoordination of the anion. The third species in the spectrum can be assigned to be the bridging $\text{MeB}(\text{C}_6\text{F}_5)_3$ group and has absorptions centered at δ -140.7 , -163.9 , and -169.5 ppm with a value for $\Delta\delta(m,p\text{-F})$ of 5.6 ppm, indicating coordination of the anion.²⁸

The lability of **5** is demonstrated by the temperature sensitivity of the complex—warming the solution to -40°C leads to the formation of **4b** with loss of **5**.

The reaction of 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ and 1 equiv of **2** could not be monitored by NMR spectroscopy due to the very low solubility of **5** at -60°C .

The reaction of **3** with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 was monitored by NMR spectroscopy. At -40°C the

(26) Doerrer, L. H.; Häussinger, D.; Green, M. L. H.; Sassmannshausen, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2111–2118.

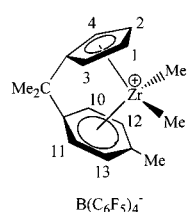
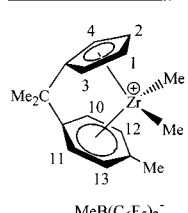
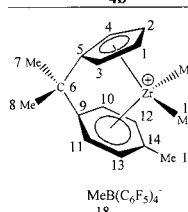
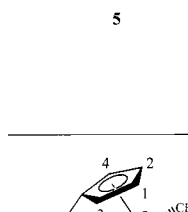
(27) Green, M. L. H.; Sassmannshausen, J. *J. Chem. Soc., Chem. Commun.* **1999**, 115–116.

(28) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, 15, 2672–2674.

(24) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, 117, 6128–6129.

(25) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, 120, 1772–1784.

Table 1. NMR Data for Cationic Complexes 4a,b, 5, and 6

Compound	¹ H NMR (ppm) ^a	assgnt	¹³ C NMR (ppm) ^b	assgnt
 B(C ₆ F ₅) ₄ ⁻ 4a	0.22 (s, 6H)	ZrMe ₂	20.5 (J _{CH} =125)	PhCH ₃
	1.71 (s, 6H)	CMe ₂	21.4 (J _{CH} =130)	CMe ₂
	2.76 (s, 3H)	PhMe	41.5	CMe ₂
	5.94 (s, 2H)	Cp ^{3,4}	42.1 (J _{CH} =116)	ZrMe ₂
	6.82 (s, 2H)	Cp ^{1,2}	108.5 (J _{CH} =175)	Cp ^{3,4}
	7.20 ^c	Ph ^{10,11}	116.3	i-C-Cp
	8.07 (d, 2H, J _{HH} =7.0)	Ph ^{12,13}	118.8 (J _{CH} =184)	Cp ^{1,2}
			125.1	Ph ^{10,11}
			131.7	i-C-Ph
			137.5 (J _{CH} =180)	Ph ^{12,13}
 MeB(C ₆ F ₅) ₃ ⁻ 4b	0.39 (br, 3H)	CH ₃ B	9.7	CH ₃ B
	0.22 (s, 6H)	ZrMe ₂	20.5	PhCH ₃
	1.72 (s, 3H)	CMe ₂	21.4	CMe ₂
	2.76 (s, 3H)	PhMe	41.5	CMe ₂
	5.95 (s, 2H)	Cp ^{3,4}	42.1 (J _{CH} =121)	ZrMe ₂
	6.82 (s, 2H)	Cp ^{1,2}	108.6 (J _{CH} =175)	Cp ^{3,4}
	7.22 (d, 2H, J _{HH} =7.0)	Ph ^{10,11}	116.3	i-C-Cp
	8.01 (d, 2H, J _{HH} =7.0)	Ph ^{12,13}	118.8 (J _{CH} =185)	Cp ^{1,2}
			125.1 (J _{CH} =180)	Ph ^{10,11}
			131.7	i-C-Ph
 MeB(C ₆ F ₅) ₄ ⁻ 5	0.43	Me ¹⁸ B	20.5	PhCH ₃
	0.97 (br, 3H)	Me ¹⁷ B	20.9	CMe ⁷
	1.30 (s, 3H)	ZrMe ¹⁶	21.1	CMe ⁸
	1.85 (s, 3H)	CMe ⁷	21.8 (J _{CH} =115)	Me ¹⁸ B
	1.91 (s, 3H)	CMe ⁸	37.5 (J _{CH} =115)	Me ¹⁷ B
	2.77 (s, 3H)	PhMe	42.8	CMe ₂
	6.15 (s, 1H)	Cp ³	58.1 (J _{CH} =125)	ZrMe ¹⁶
	6.41 (s, 1H)	Cp ¹	110.8 (J _{CH} =180)	Cp ⁴
	6.56 (s, 1H)	Cp ¹	113.6 (J _{CH} =185)	Cp ³
	7.39 (s, 1H)	Cp ²	120.2 (J _{CH} =185)	Cp ¹
 B(C ₆ F ₅) ₄ ⁻ 6	2.01 (s, 6H)	CMe ₂	20.4 (J _{CH} =131)	PhCH ₃
	2.31 (s, 2H)	CH ₂ Ph	20.8 (J _{CH} =127)	CH ₂ Ph
	2.32 (s, 2H)	CH ₂ Ph	21.9	CMe ₂
	2.68 (s, 3H)	PhMe	42.8	CMe ₂
	6.24 (s, 2H)	Cp ^{3,4}	112.7 (J _{CH} =180)	Cp ^{3,4}
	7.08 (s, 2H)	Cp ^{1,2}	124.8 (J _{CH} =180)	Ph ^{10,11}
	7.69 (d, 2H, J _{HH} =7.5)	Ph ^{10,11}	125.9 (J _{CH} =180)	Cp ^{1,2}
	8.12 (d, 2H, J _{HH} =7.5)	Ph ^{12,13}	145.7 (J _{CH} =185)	Ph ^{12,13}

^a 500 MHz. ^b 125.7 MHz. ^c Obscured by triphenylethane.

formation of 1 equiv of Ph₃CCH₂Ph, the byproduct of the abstraction of a benzyl group, and of 1 equiv of the cationic species **6** is observed. The reaction is fairly clean, toluene resulting from hydrolysis being the only byproduct observed. The protons for the pendant phenyl ring generate signals at δ 7.69 and 8.12 ppm, while that for the attached methyl group is shifted from δ 2.29 ppm to δ 2.65 ppm, similar to that observed for **4a** at δ 2.76 ppm. The ¹J_{CH} coupling constant found for the Zr–CH₂–Ph group is 127 Hz and is typical for a benzyl group σ -coordinated to zirconium, rather than the η^2 coordination previously observed for metallocene complexes.^{23,29–35} On the basis of the evidence of NMR spectroscopy, we suggest that the structure of **6** is similar to that of **4a**; the phenyl ring is coordinated to the cationic zirconium, and the benzyl moieties are σ -bound to the zirconium. Similar cationic half-sandwich complexes have been observed before, notably by Pellecchia³⁶ for the com-

plex [Zr(η -C₅H₅)(CH₂Ph)₂]⁺[B(CH₂Ph)(C₆F₅)₃]⁻, in which the anion is η^6 -coordinated to the cationic zirconium center. The ¹J_{CH} coupling constant for this species is reported to be 122 Hz, which is very similar to that observed for **6**.

These findings explain the observed lower activity of these compounds for styrene^{12,17} and ethylene^{22,37} polymerization; the coordinated phenyl ring blocks the vacant coordination site and hinders complexation of the monomer. It also shows that coordination of a phenyl ring from the growing chain is unlikely.

Unfortunately, the triphenylethane byproduct hampered the observation of the aromatic region in the ¹H NMR spectrum.

The reaction of **3** with B(C₆F₅)₃ in CD₂Cl₂ at –60 °C did not lead to a clean product, and the ¹H NMR spectrum only consisted out of broad, featureless peaks.

Conclusion

We have prepared the half-sandwich zirconium trichloride complex **1**, which has a pendant phenyl group. Methylation of **1** leads to the formation of the trimethyl compound **2**, while treatment with PhCH₂MgCl leads to the tribenzyl compound **3**.

The reaction of **2** with 1 equiv of [Ph₃C]⁺[B(C₆F₅)₄]⁻ in CD₂Cl₂ furnishes the cationic *ansa* complex **4a** with the phenyl group η^6 -coordinated to the cationic zirconium center. The structure of **4a** could be unambiguously assigned by 2D NMR spectroscopy and NOESY experiments.

Reaction of **2** with more than 1 equiv of B(C₆F₅)₃ leads not only to the formation of **4b** but also to the formation of the novel cationic zwitterionic *ansa* zirconocene complex **5**. This complex has a methyl group bridging the zirconium and boron atoms in a manner similar to that for the zwitterionic group 4 metallocene complexes previously observed. Complexes **4a,b** are thus formally related to the neutral group 4 metallocene compounds and provide yet another example of the rich and often quite unusual chemistry of B(C₆F₅)₃.³⁸ NOESY/EXSY spectroscopy indicates that complexes **4b** and **5** are in rapid equilibrium with each other. Similar exchange processes have been observed for zwitterionic group 4 metallocene complexes.^{24,25}

The tribenzyl compound **3** reacts with [Ph₃C]⁺[B(C₆F₅)₄]⁻ in CD₂Cl₂ to yield the *ansa* complex **6**, in which the pendant phenyl ring is coordinated to the cationic zirconium center and the benzyl groups are σ -bound to the metal. These results, and those obtained by Rausch et al.¹² for styrene and by us²² for ethylene polymerization, are consistent with the lower activity of these

(30) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111–4113.

(31) Jordan, R. F.; LaPointe, R. E.; Baenzinger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

(32) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T.; Piols, A. J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 677.

(33) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511.

(34) Mintz, E. A.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4692.

(35) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(36) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473–4478.

(37) Bochmann, M. *Top. Catal.* **1999**, *7*, 9–22.

(38) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345–354.

(29) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633–640.

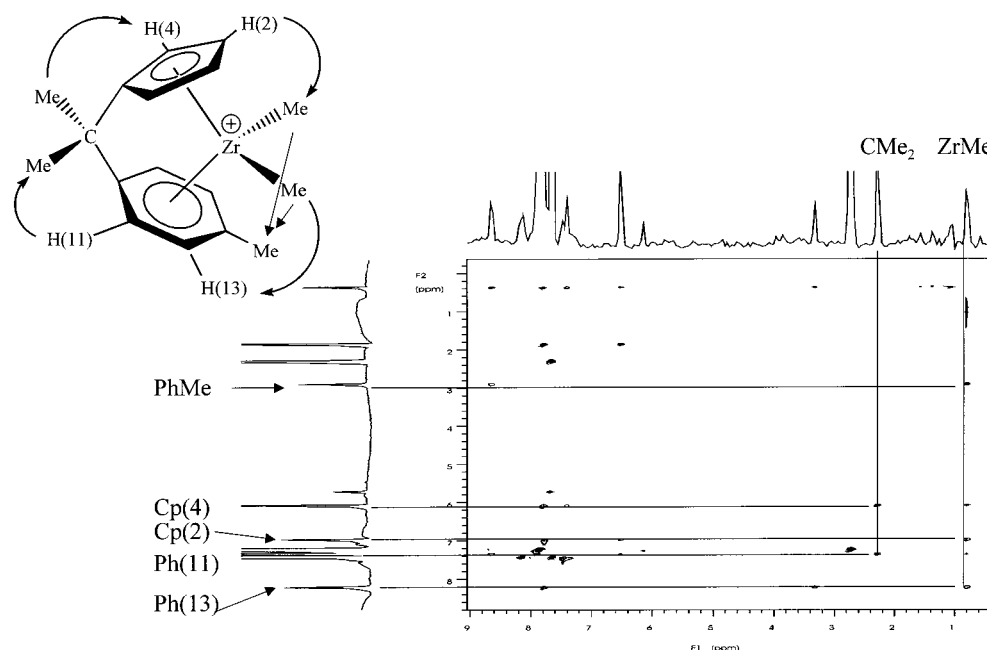


Figure 1. NOESY NMR spectrum of **4a**.

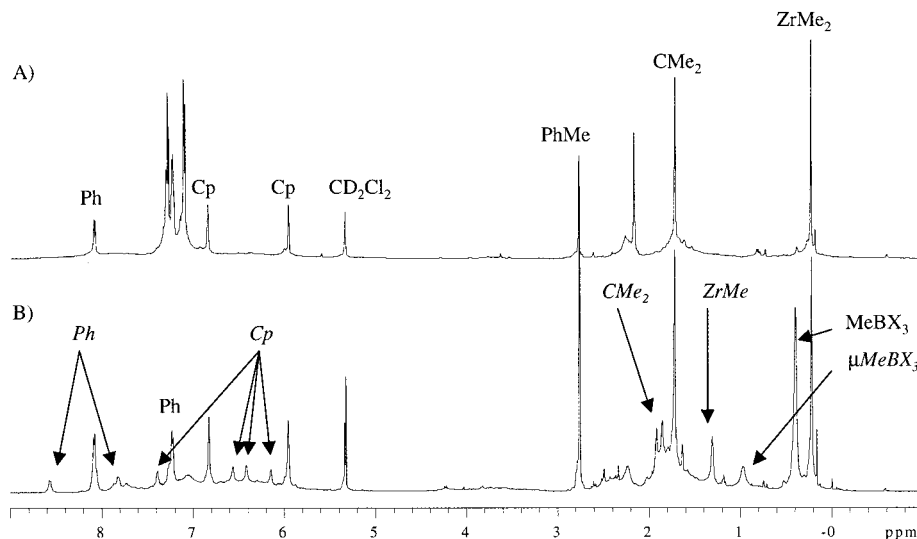


Figure 2. ^1H NMR spectra: (a) reaction of **2** with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$; (b) reaction of **2** with 1.5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$. Peaks belonging to **5** are denoted in italics.

class of compounds compared with related unsubstituted species.

Experimental Section

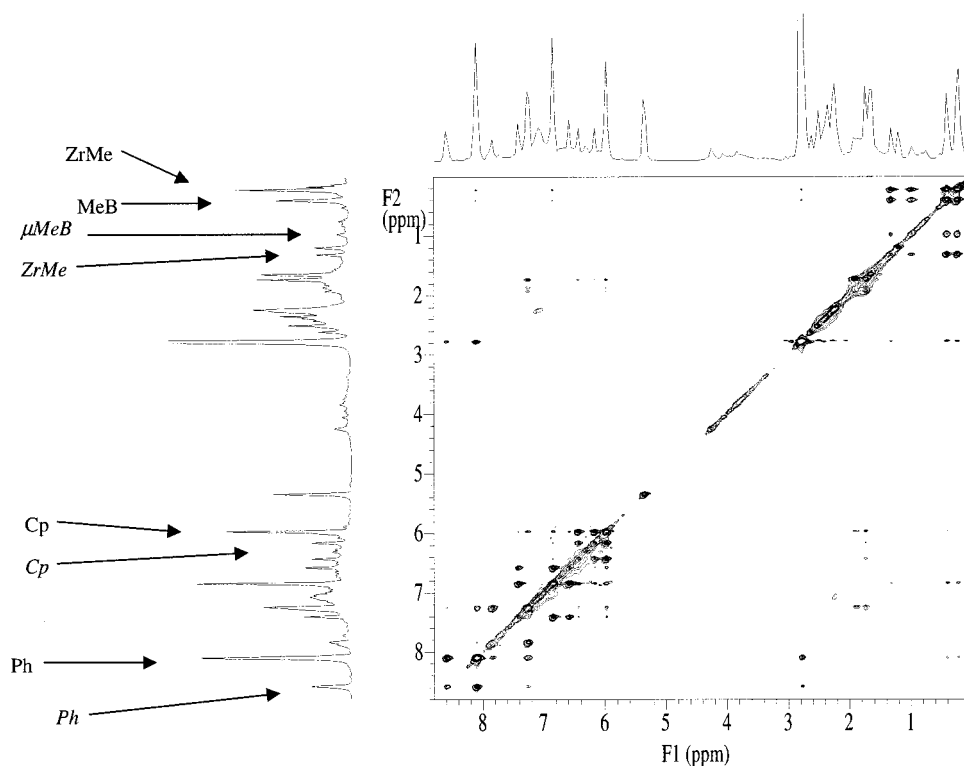
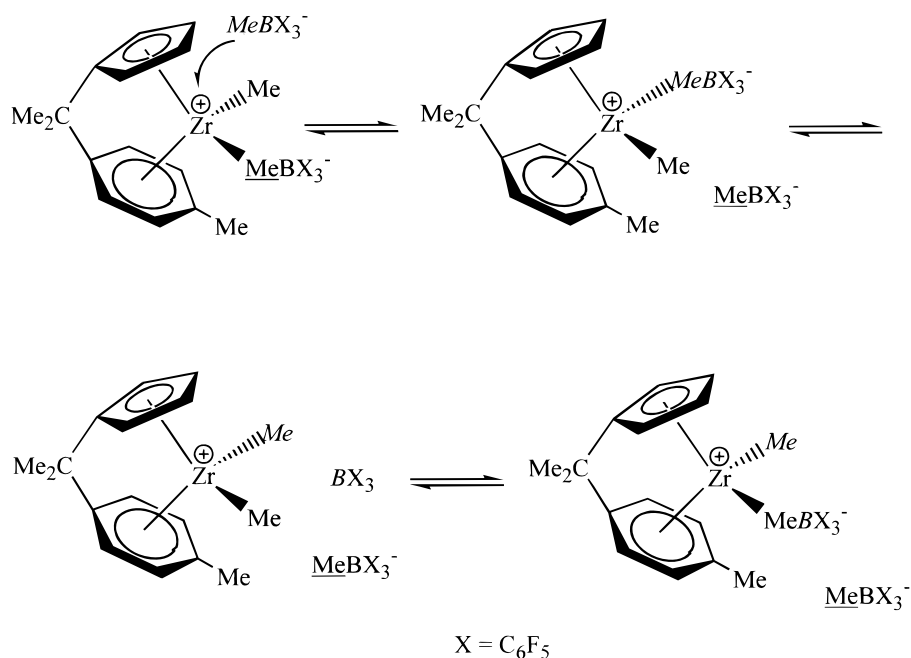
General Considerations. All experiments were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium/potassium alloy (diethyl ether, light petroleum ether, bp 40–60 °C), sodium/benzophenone (thf), and calcium hydride (dichloromethane). NMR solvents were dried over activated molecular sieves, freeze-thawed, and stored in Young's-Tap sealed ampules.

NMR spectra were recorded on a Bruker AM300 or a VARIAN UnityPlus 500 spectrometer and referenced to the residual protio solvent peak for ^1H . Chemical shifts are quoted in ppm relative to tetramethylsilane. ^{13}C NMR spectra were referenced to the solvent peak relative to TMS and were proton-decoupled using a WALTZ sequence. CH coupling constants were measured by coupled HMQC. ^{11}B NMR spectra were referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ (δ 0 ppm).

NOESY/EXSY spectra were recorded using a standard NOESY pulse program with 2K of data points for the FID, a sweep range of 4665 Hz with a 90° pulse, an initial pulse delay of 1.5 s, and a mixing time of 0.67 s. Eight scans per increment were recorded, and 512 increments were collected.

Preparation of $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me-}p)\text{Cl}_3(\text{dme})]$ (1**).** The compound $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Cl}_3(\text{dme})]$ was prepared by a modified literature procedure.²¹ The compound $\text{ZrCl}_4(\text{Me}_2\text{S})_2$, prepared from freshly sublimed ZrCl_4 (12.07 g, 51.8 mmol) and dimethyl sulfide (7.60 cm³, 103.6 mmol) in 120 cm³ of dichloromethane, was treated with $\text{C}_5\text{H}_4(\text{SiMe}_3)(\text{CMe}_2\text{-}p\text{-C}_6\text{H}_4\text{Me})$ (14.0 g, 51.8 mmol) at 0 °C. The reaction mixture was stirred for 10 days at room temperature; a white precipitate was formed. Dimethoxyethane (5.4 mL) was added, and the reaction mixture was concentrated and stored at 3 °C for 2 days. The off-white product was collected by filtration and washed with 50 cm³ of diethyl ether. The product was dried under reduced pressure and was used without further purification. Yield: 20.12 g, 41.5 mmol; 80%. Anal. Found: C, 41.2; H, 5.2; Cl, 25.2. Calcd for $\text{C}_{19}\text{H}_{27}\text{Cl}_3\text{O}_2\text{Zr}$: C, 47.1; H, 5.6; Cl, 21.9. ^1H NMR (CDCl_3 , 300 MHz, 20 °C; δ (ppm)): 1.93 (s, 6H,

Scheme 4

**Figure 3.** NOESY/EXSY NMR spectrum of **4b** and **5**. Peaks belonging to **5** are denoted in italics.

CMe₂); 2.28 (s, 3H, PhMe); 3.88 (br, 6H, dme); 4.09 (br, 4H, dme); 6.52 ("t", 2H, Cp); 6.58 ("t", 2H, Cp); 7.02 ("s", 4H, Ph). ¹³C NMR (CDCl₃, 125.7 MHz, 20 °C; δ (ppm)): 20.8 (PhMe); 27.8 (CCH₃); 40.8 (CCH₃); 118.4 (Cp'); 125.7 (Ph'); 128.7 (Ph'); 135.1 (*i*-C Cp); 145.7 (*i*-C PhMe); 148.7 (*i*-C Ph).

Preparation of [Zr(η-C₅H₄CMe₂C₆H₄Me-*p*)Me₃] (2). The compound [Zr(η-C₅H₄CMe₂-*p*-C₆H₄Me)Cl₃(dme)] (9.52 g, 19.6 mmol) was suspended in 120 cm³ of diethyl ether and cooled to -78 °C. The Grignard reagent MgClMe (19.6 cm³, 58.9 mmol, 3 mol/L in thf) was slowly added via syringe. The reaction mixture was stirred at -78 °C for 30 min, slowly warmed to room temperature, and stirred for 2 h. The volatiles were removed under reduced pressure, and the dark brown

residue was extracted into 130 cm³ of hot light petroleum. The clear, dark yellow solution was cooled to -80 °C. The brown microcrystalline solid formed was collected by filtration. The compound is very air-sensitive and is best handled under an argon atmosphere. Yield: 1.96 g, 5.9 mmol; 30%. Anal. Found: C, 63.6; H, 7.5. Calcd for C₁₈H₂₆Zr: C, 64.8; H, 7.9. ¹H NMR (CDCl₃, 500 MHz, 20 °C; δ (ppm)): 0.25 (s, 9H, ZrMe); 1.58 (s, 6H, CMe₂); 2.29 (s, 3H, PhMe); 6.18 ("t", 2H, Cp'); 6.21 ("t", 2H, Cp); 7.07 (d, 2H, Ph'); 7.15 (d, 2H, Ph'). ¹³C NMR (CDCl₃, 125.7 MHz, 20 °C; δ (ppm)): 20.8 (PhMe); 29.8 (CCH₃); 39.0 (CCH₃); 45.3 (ZrMe); 106.8 (Cp); 110.8 (Cp'); 125.8 (Ph'); 128.8 (Ph'); 135.4 (*i*-C Cp); 142.7 (*i*-C PhMe); 147.1 (*i*-C Ph).

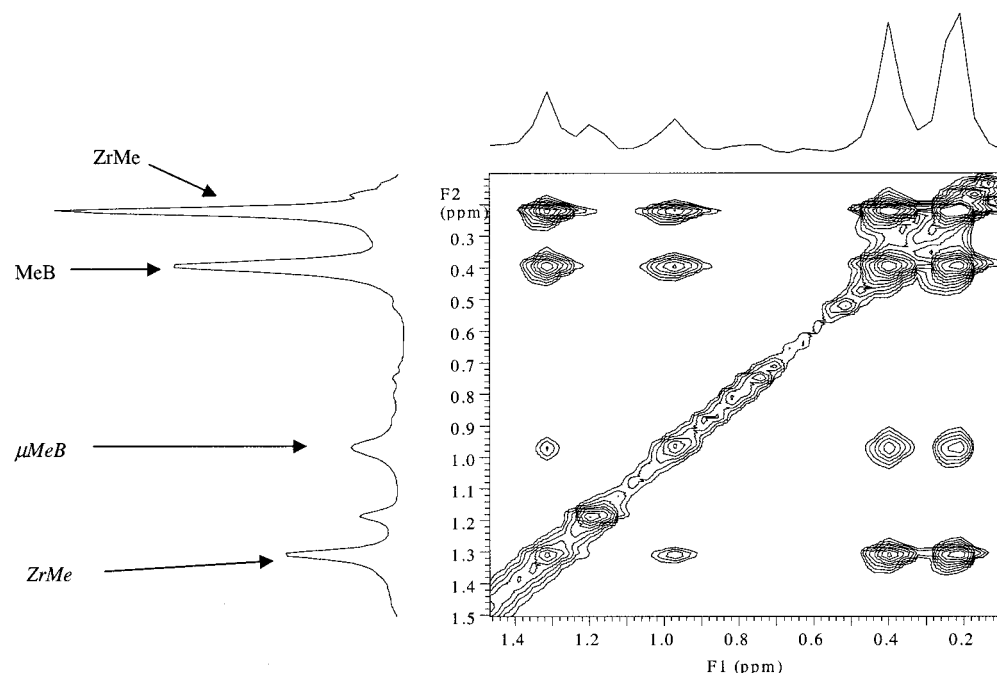


Figure 4. NOESY/EXSY spectrum of **4b** and **5**. Peaks belonging to **5** are denoted in italics.

Scheme 5

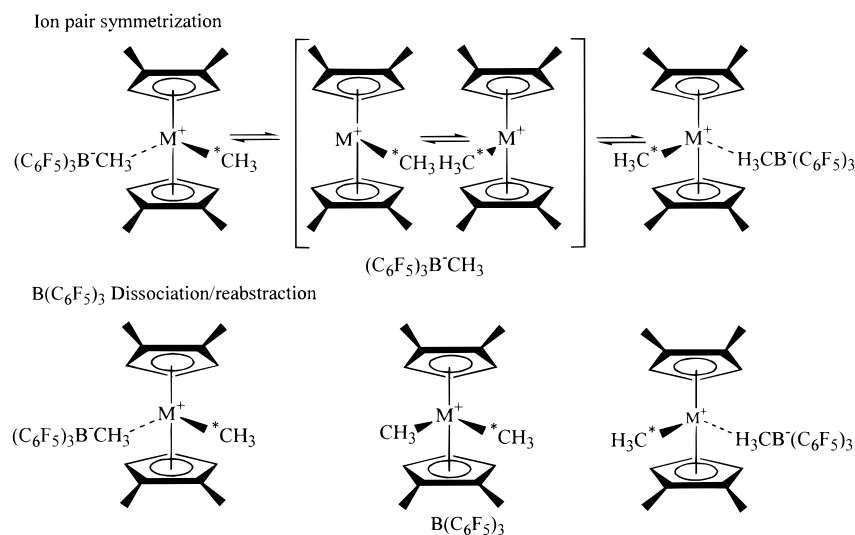
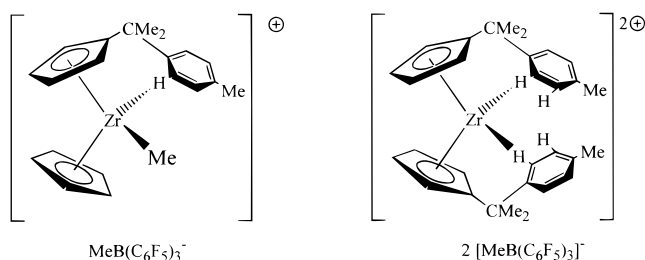


Chart 1



Preparation of $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{-}p\text{-C}_6\text{H}_4\text{Me})(\text{CH}_2\text{Ph})_3]$ (3**).** The compound $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CMe}_2\text{-}p\text{-C}_6\text{H}_4\text{Me})\text{Cl}_3(\text{dme})]$ (10.6 g, 22 mmol) was added to a solution of $\text{MgCl}(\text{CH}_2\text{Ph})$ (80 mmol) in 200 cm³ of diethyl ether at room temperature. The color changed immediately to bright yellow. The mixture was stirred for 12 h. The volatiles were removed under reduced pressure to form a dark brown solid. The solid was extracted into hot light petroleum (3 × 70 cm³). The extract was taken to dryness and extracted into hot light petroleum. Repeated extraction

into light petroleum yielded a yellow microcrystalline solid, which was pure by NMR spectroscopy. Yield: 5.58 g, 9.9 mmol; 45% Anal. Found: C, 76.7; H, 6.8. Calcd for $\text{C}_{36}\text{H}_{38}\text{Zr}$: C, 77.0; H, 6.8. ¹H NMR (CDCl_3 , 500 MHz, 20 °C; δ (ppm)): 1.54 (s, 6 H, CH_2Ph); 1.66 (s, 6H, CCH_3); 2.30 (s, 3H, PhMe); 5.25 ("t", 2H, Cp¹); 5.99 ("t", 2H, Cp²); 6.50 (d, 6H, *o*-H Bz); 7.01 (t, 3H, *p*-H Bz); 7.09 (d, 2H, Ph¹); 7.14 (t, 6H, *m*-H Bz); 7.17 (d, 2H, Ph²). ¹³C NMR (CDCl_3 , 125.7 MHz, 20 °C; δ (ppm)): 20.9 (PhCH₃); 30.3 (CCH₃); 39.7 (CCH₃); 66.6 (ZrCH₂Ph, $J_{\text{CH}} = 127$ Hz); 109.8 (Cp²); 111.5 (Cp¹); 123.2 (*p*-C Bz); 126.0 (Ph¹); 127.5 (*o*-C Bz); 128.8 (Ph²); 129.5 (*m*-C Bz); 135.5 (*i*-C PhMe); 141.0 (*i*-C Cp); 143.3 (*i*-C Bz); 147.0 (*i*-C Ph¹).

Low-Temperature NMR Studies on Cationic Compounds. Because of the sensitivity of the cationic complexes, the complexes were generated in situ, and isolation was not attempted.

The general procedure was as follows. The zirconocene compound (ca. 0.1 mmol) was dissolved in 0.25 cm³ of CD_2Cl_2 , and the solution was transferred into a precooled (−78 °C) NMR tube. The cation-generating agent $\text{B(C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}]^+[\text{B(C}_6\text{F}_5)_4]^-$ (ca. 0.11 mmol) was dissolved in 0.28 cm³ of

CD_2Cl_2 and transferred onto the zirconocene solution in the NMR tube. The tube was sealed and shaken vigorously to ensure complete mixing. The sample was placed into the precooled ($-60\text{ }^\circ\text{C}$) probe of the NMR spectrometer. 1D and 2D NMR spectra were recorded at $-60\text{ }^\circ\text{C}$, unless otherwise stated. The sample was warmed to ambient temperature at

increments of 20 K, and at each step a ^1H NMR spectrum was recorded.

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