

Cationic zirconocene complexes with benzyl and Si(SiMe₃)₃ substituted cyclopentadienyl ligands

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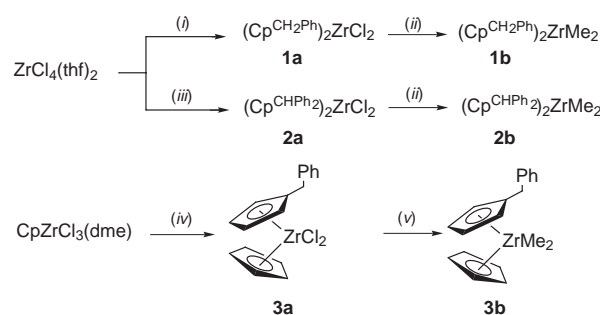
Alkyl zirconocenes [Zr(η-C₅H₄R)₂X₂] (where R = CH₂Ph, X = Cl **1a** or Me **1b**; R = CHPh₂, X = Cl **2a** or Me **2b**; R = Si(SiMe₃)₃, X = Cl **4a** or Me **4b**) and for comparison [Zr(η-C₅H₅)(η-C₅H₄CH₂Ph)Cl₂] **3a** were prepared and characterised. The reactions of these compounds with the methide abstracting reagents B(C₆F₅)₃, B(*o*-C₆F₅C₆F₄)₂ and [Ph₃C]⁺[B(C₆F₅)₄]⁻ were investigated by low temperature NMR spectroscopy. Compound **1b** reacts with [Ph₃C]⁺[B(C₆F₅)₄]⁻ to form the homodinuclear complex [{Zr(η-C₅H₄CH₂Ph)₂Me]₂(μ-Me)]⁺[B(C₆F₅)₄]⁻. The related compound [{Zr(C₅H₄CH₂Ph)₂Me]₂(μ-Me)]⁺[MeB(C₆F₅)₃]⁻ **5a** was formed from the reaction of **1b** with 0.5 equivalent of B(C₆F₅)₃. Reaction between **1b** and 1 equivalent B(C₆F₅)₃ gave [Me(η-C₅H₄CH₂Ph)₂Zr(μ-Me)B(C₆F₅)₃] **6a** and the ion pair [Zr(η-C₅H₄CH₂Ph)₂Me][MeB(C₆F₅)₃] **6b** which are in equilibrium with each other. A similar observation was made when **2b** was used instead of **1b**. The sterically more demanding **4b** does not show this behaviour. The role of the ligands in ethylene polymerisation was investigated.

Introduction

The activities and stereoselectivities of metallocene-based olefin polymerisation catalysts are known to be highly susceptible to the influence of substituents on the cyclopentadienyl ligand framework.^{1,2} The factors that affect the polymer molecular weight have, by comparison, been less well studied. The average molecular weight of a polymer chain depends on the ratio of the rate of chain propagation, *k_p*, and the rate of chain termination, *k_t*, and since this ratio is temperature dependent the modification of polymer molecular weights may within certain limits be achieved by varying the reaction temperature. Similarly, the presence of weak donor ligands such as aromatic ethers and amines can convert a polymerisation catalyst into a system for the production of oligomers, albeit not without a significant reduction in activity since donor ligands effectively compete with the olefinic substrate for the co-ordination site required for chain growth.^{3,4} Some efforts to control the polymer molecular weight of polyethylenes by substituting the Cp ligands with alkyl groups of varying degrees of steric hindrance have been reported, although the effect was not pronounced,⁵ and efforts to modify the electronic characteristics of the η-cyclopentadienyl ligands by introducing electron withdrawing or donating substituents such as CF₃ and NMe₂ appear to affect primarily the activity of the catalysts rather than the polymer molecular weight.⁶ We wished therefore to explore the possibility of controlling the *k_p*:*k_t* ratio by introducing substituents on the η-cyclopentadienyl which had the potential of acting as weakly and reversibly co-ordinating ligands to the metal centre in the catalytically active 14-electron species [Zr(η-C₅H₄R')₂R]⁺ and chose to investigate the influence of benzyl substituents. During the course of this work a related study has been reported.⁷ We report here the synthesis of cationic zirconocene alkyl species [Zr(η-C₅H₄R')₂R]⁺ where R' = CH₂Ph or CHPh₂ and, for comparison, the bulky group Si(SiMe₃)₃ and their role in ethylene polymerisation.

Results and discussion

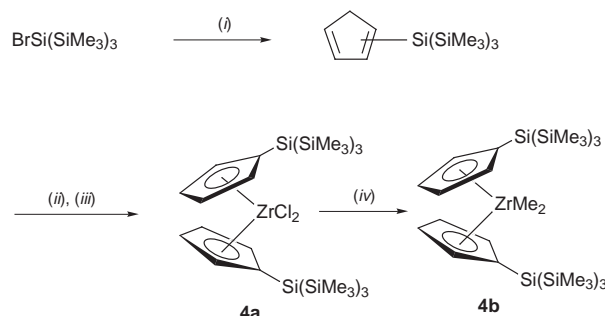
The known compound bis(benzylcyclopentadienyl)zirconium dichloride **1a** was prepared as described (Scheme 1).⁸ The



Scheme 1 (i) Li[Cp^{CH₂Ph}]; (ii) LiMe; (iii) Li[Cp^{CHPh₂}]; (iv) K[Cp^{CH₂Ph}]; (v) MgMeCl.

diphenylmethylcyclopentadienyl analogue **2a** was prepared similarly as a white solid in 35% yield. The compound [Zr(η-C₅-H₅)(η-C₅H₄CH₂Ph)Cl₂] **3a** was prepared as described as a light yellow powder.⁸

The bulky cyclopentadiene C₂H₅Si(SiMe₃)₃ was prepared in high yield from LiCp and SiBr(SiMe₃)₃ in THF as a yellow waxy material. Deprotonation of this compound with butyllithium followed by the addition of 0.5 equivalent of [ZrCl₄(thf)₂] afforded [Zr(Cp^{Si})₂Cl₂] **4a**, where Cp^{Si} = η-C₅H₄Si(SiMe₃)₃, as a yellow solid in modest yield (Scheme 2). The

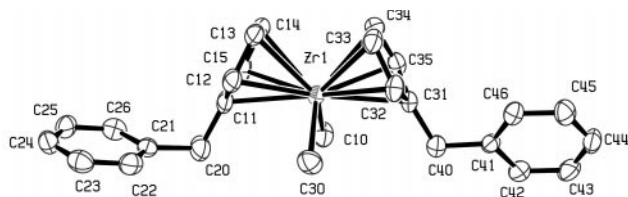


Scheme 2 (i) LiCp; (ii) LiBu, thf, -78 °C; (iii) [ZrCl₄(thf)₂], room temperature; (iv) LiMe, Et₂O.

Table 1 Proton and ¹³C NMR data

Compound	Data ^a (δ , J/Hz)
1a [Zr(η -C ₅ H ₄ CH ₂ Ph) ₂ Cl ₂]	¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): 3.99 (s, 4 H, CH ₂ Ph); 6.18 (t, 4 H, CpH, $J_{\text{HH}} = 1.65$); 6.21 (t, 4 H, CpH, $J_{\text{HH}} = 1.97$); 7.17–7.28 (m, 10 H, Ph) ¹³ C NMR (CDCl ₃ , 67.80 MHz, 20 °C): 36.10 (CH ₂ Ph); 112.72 (Cp); 115.71 (Cp); 126.43 (<i>p</i> -C of Ph); 128.52 (<i>m</i> -C of Ph); 128.81 (<i>o</i> -C of Ph); 133.50 (<i>ipso</i> -C of Cp); 139.71 (<i>ipso</i> -C of Ph)
2a [Zr(η -C ₅ H ₄ CHPh ₂) ₂ Cl ₂]	¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): 5.56 (s, 2 H, CHPh ₂); 5.72 (t, 4 H, $J_{\text{HH}} = 2.64$, Cp); 5.97 (t, 4 H, $J_{\text{HH}} = 2.64$, Cp); 7.02–7.04 (m, Ph) ¹³ C NMR (CDCl ₃ , 20 °C): 51.52 (CPh ₂); 115.09 (Cp); 116.09 (Cp); 126.73 (<i>p</i> -C of Ph); 128.41 (<i>m</i> -C of Ph); 129.06 (<i>o</i> -C of Ph); 136.33 (<i>ipso</i> -C of Cp); 143.48 (<i>ipso</i> -C of Ph)
4a [Zr{ η -C ₅ H ₄ Si(SiMe ₃) ₃ } ₂ Cl ₂] 1b [Zr(η -C ₅ H ₄ CH ₂ Ph) ₂ Me ₂]	¹ H NMR (CDCl ₃ , 90 MHz, 20 °C): 0.14 (s, 54 H, SiMe ₃); 6.3–6.5 (m, 8 H, Cp) ¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): -0.32 (s, 6 H, CH ₃ , $J_{\text{CH}} = 117.5$); 3.83 (s, 4 H, CH ₂ Ph); 5.81 (t, 4 H, $J_{\text{HH}} = 2.64$, Cp); 5.97 (s, 4 H, $J_{\text{HH}} = 2.64$, Cp); 7.21–7.35 (m, 10 H, Ph) ¹³ C NMR (CDCl ₃ , 20 °C): 30.05 (CH ₃); 36.08 (CH ₂ Ph); 107.84 (Cp); 111.48 (Cp); 126.13 (<i>p</i> -C of Ph); 126.47 (<i>ipso</i> -C of Cp); 128.44 (<i>m</i> -C of Ph); 128.52 (<i>o</i> -C of Ph); 141.15 (<i>ipso</i> -C of Ph)
2b [Zr(η -C ₅ H ₄ CHPh ₂) ₂ Me ₂]	¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): -0.34 (s, 6 H, CH ₃); 5.32 (s, 2 H, CHPh ₂); 5.54 (t, 4 H, $J_{\text{HH}} = 2.64$, Cp); 5.72 (t, 4 H, $J_{\text{HH}} = 2.64$, Cp); 7.12–7.28 (m, 10 H, Ph) ¹³ C NMR (CDCl ₃ , 67.80 MHz, 20 °C): 30.75 (CH ₃); 51.81 (CHPh ₂); 108.86 (Cp); 111.56 (Cp); 126.43 (<i>p</i> -C of Ph); 128.32 (<i>m</i> -C of Ph); 128.84 (<i>o</i> -C of Ph); 129.47 (<i>ipso</i> -C of Cp); 144.58 (<i>ipso</i> -C of Ph)
3b [Zr(η -C ₅ H ₅)(η -C ₅ H ₄ CH ₂ Ph)Me ₂]	¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): 0.39 (s, 6 H, ZrMe); 5.14 (d, 1 H, CH ₂ ; $J_{\text{HH}} = 1.08$); 5.41 (d, 1 H, CH ₂ ; $J_{\text{HH}} = 1.08$); 5.98 (s, 5 H, Cp); 6.04 (t, 2 H, C ₅ H ₄); 6.12 (t, 2 H, C ₅ H ₄); 7.32 (“s”, 5 H, Ph) ¹³ C NMR (CDCl ₃ , 20 °C): 31.37 (ZrMe); 109.47 (C ₅ H ₄); 109.68 (C ₅ H ₄); 110.74 (Cp); 112.79 (CCH ₂); 124.16 (CCH ₂); 127.70 (<i>p</i> -C of Ph); 128.17 (<i>o</i> -C of Ph); 128.39 (<i>m</i> -C of Ph); 141.54 (<i>ipso</i> -C of Cp'); 143.79 (<i>ipso</i> -C of Ph)
4b [Zr{ η -C ₅ H ₄ Si(SiMe ₃) ₃ } ₂ Me ₂]	¹ H NMR (CDCl ₃ , 270 MHz, 20 °C): -0.39 (s, 6 H, CH ₃); 0.0 (s, 54 H, SiCH ₃); 5.98 (t, 4 H, $J_{\text{HH}} = 2.3$, Cp); 6.01 (t, 4 H, $J_{\text{HH}} = 2.30$, Cp) ¹³ C NMR (CDCl ₃ , 67.80 MHz, 20 °C): 1.78 (SiCH ₃); 32.71 (CH ₃); 112.11 (Cp); 118.51 (Cp)

^a Cp indicates hydrogens attached to C₅-ring carbons.

**Fig. 1** Crystal structure of complex **1b**.

spectroscopic data of all new compounds are collected in Table 1.

Treatment of the dichloride compounds **1a–4a** with either methyl lithium or methylmagnesium chloride affords the corresponding zirconocene dimethyl complexes **1b**, **2b** and **4b** as colourless solids. The compound **3b** could not be obtained pure and appears to be thermally sensitive. Slow cooling of a light petroleum solution of compound **1b** to 5 °C forms colourless plates suitable for X-ray crystallography. The molecular structure of **1b** is shown in Fig. 1 and is similar to that of the known dichloride **1a**.⁹ Selected bond distances and angles are shown in Table 2. The structure of **1b** shows that the benzyl substituent lies approximately in the plane bisecting the Me–Zr–Me angle, with the phenyl substituents bent away to occupy the sterically least encumbered position. This behaviour is similar to that of substituted titanocenes.¹⁰ The crystal packing indicates no close intermolecular contacts such as π stacking of the phenyl rings that would affect the preferential conformation of the η -C₅H₄-CH₂Ph groups.

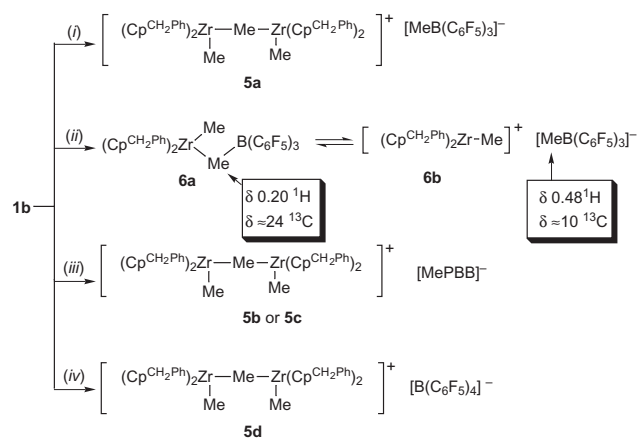
Synthesis of cationic complexes

The reaction of compound **1b** with 0.5 equivalent of B(C₆F₅)₃ in dichloromethane was monitored by NMR spectroscopy. It is slow at -78 °C but quantitative at -20 °C to give as a single product the homodinuclear complex [(Zr(η -C₅H₄CH₂Ph)₂Me)₂(μ -Me)]⁺[MeB(C₆F₅)₃]⁻ **5a**. Similar methyl-bridged zirconocenes have been observed before.^{11–14} Brintzinger and co-workers¹⁴ observed a tight ion pair [(Zr(η -C₅H₅)₂Me)₂(μ -Me)]⁺MeB(C₆F₅)₃⁻ in C₆D₆ solutions. Solutions of **5a** in CD₂Cl₂ show only solvated ion pairs (Scheme 3).

When compound **1b** was treated with 1 equivalent or a slight excess of B(C₆F₅)₃ two mononuclear products were formed

Table 2 Selected bond distances (Å) and angles (°) for compound **1b**

Zr(1)–C(10)	2.277(3)	Zr(1)–C(31)	2.587(3)
Zr(1)–C(13)	2.494(3)	Zr(1)–C(34)	2.487(3)
Zr(1)–C(30)	2.283(3)	Zr(1)–C(12)	2.526(3)
Zr(1)–C(33)	2.483(3)	Zr(1)–C(15)	2.533(3)
Zr(1)–C(11)	2.570(3)	Zr(1)–C(32)	2.546(3)
Zr(1)–C(14)	2.485(3)	Zr(1)–C(35)	2.546(3)
C(10)–Zr(1)–C(30)	98.08(13)	C(13)–Zr(1)–C(34)	86.75(10)
C(11)–Zr(1)–C(31)	171.11(8)	C(14)–Zr(1)–C(33)	94.37(11)
C(12)–Zr(1)–C(35)	150.16(10)	C(15)–Zr(1)–C(32)	159.00(10)

**Scheme 3** (i) 0.5 B(C₆F₅)₃; (ii) B(C₆F₅)₃; (iii) 0.5 PBB–C₆D₆ or PBB–CD₂Cl₂; (iv) Ph₃C⁺.

which appear to be in equilibrium. One compound is characterised by two singlets at δ 0.20 and 0.75, assigned to MeB and ZrMe groups, respectively, and the NMR data are consistent with the formulation as the zwitterionic complex [Me(η -C₅H₄-CH₂Ph)₂Zr(μ -Me)B(C₆F₅)₃] **6a**. This assignment was supported by ¹H–¹³C COSY experiments. The corresponding MeB signal for the second compound is observed at δ 0.48 and is assigned to the solvent separated isomer of **6a**, namely the ion pair [Zr(η -C₅H₄CH₂Ph)₂Me][MeB(C₆F₅)₃] **6b**. In agreement with this assignment, the ¹³C NMR spectrum of **6b** shows a broadened singlet at δ 10.2, typical for a separated, non-

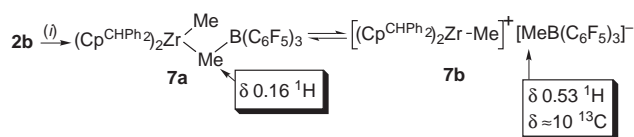
bridging $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion. The chemical shift difference between the *m*- and *p*- ^{19}F resonances of the anion¹⁵ can also be indicative of anion co-ordination. Thus values of $\Delta\delta(m,p\text{-F})$ between 3 and 6 ppm indicate co-ordination, values <3 ppm indicate non-co-ordination. We observe 2 sets of signals for the 2 different anions formed, one which has $\Delta\delta(m,p\text{-F})$ of 4.85 ppm, another which has $\Delta\delta(m,p\text{-F})$ of 2.81 ppm. However, the ZrMe signal for **6b** could not be found (Scheme 3).

It has been shown that the bulky Lewis acid $\text{B}(o\text{-C}_6\text{F}_4\text{C}_6\text{F}_5)_3$ (PBB)^{11,12} reacts with group 4 metallocene dimethyls to form cationic, dimeric complexes, even when an excess of PBB is present. Treatment of **1b** with 0.5 equivalent of PBB in C_6D_6 at room temperature gave the homodinuclear complex $[\{\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{Ph})_2\text{Me}\}_2(\mu\text{-Me})]^+[\text{MePBB}]^-$ **5b**, characterised in the ^1H NMR spectrum by two singlets at $\delta -0.1$ and -1.07 which may be assigned to the terminal and bridging Me (Scheme 3).

Treatment of compound **1b** in dichloromethane with 1 equivalent of PBB at -60°C gave an incomplete reaction which becomes quantitative at -30°C to give the single compound **5c** (Scheme 3). The same reaction in benzene gave decomposition of the metallocene, suggesting a crucial role for the solvent in these reactions. It may be that solvent separation of the anion and the cation is enhanced in dichloromethane and whereas for benzene this separation might not occur if the reaction product is confined within a solvent cage subsequent decomposition reaction might occur more readily.

The reaction of **1b** with 1 equivalent of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 at -60°C proceeds cleanly to the homodinuclear complex $[\{\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{Ph})_2\text{Me}\}_2(\mu\text{-Me})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ **5d** (Scheme 3).

The reaction between compound **2b** and 1 equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ in dichloromethane gave rise to two compounds which are in equilibrium with each other. However, here the solvent separated compound is the dominant product, as indicated by the integration of the signals at $\delta 0.16$ and 0.53 assigned to the MeB signals of the zwitterionic complex $[\text{Me}(\eta\text{-C}_5\text{H}_4\text{CHPh}_2)_2\text{Zr}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ **7a** and the solvent separated complex $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CHPh}_2)_2\text{Me}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ **7b**, respectively (Scheme 4). The ratio between **7a** and **7b** is



Scheme 4 (i) $\text{B}(\text{C}_6\text{F}_5)_3$.

approximately 1:2 (ratio **6a**:**6b** is 3:1). The ZrMe signals were observed at $\delta 0.75$ (**7a**) and 0.84 (**7b**). The CH coupling constant of the Zr-CH_3 is around 120 Hz, and there was no indication of an α agostic interaction.

It is tempting to speculate that the formation of the ion separated compounds $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{Ph})_2\text{Me}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ **6b** and $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{CHPh}_2)_2\text{Me}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ **7b** is facilitated by co-ordination of the phenyl rings to the metal centre and thereby assisting the dissociation of the anion. This may account for the fact that other substituted zirconocenes react with $\text{B}(\text{C}_6\text{F}_5)_3$ to form only zwitterionic complexes, similar to **6a** and **7a**, under otherwise identical conditions. For example, we have studied the reaction with the sterically more encumbered **4b** with 1 equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$. The reaction proceeded cleanly in dichloromethane to give the zwitterionic complex $[\text{Me}\{\eta\text{-C}_5\text{H}_4\text{-Si}(\text{SiMe}_3)_3\}_2\text{Zr}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ **8**. The VT-NMR spectroscopic data studies are collected in Table 3.

Polymerisation of ethene with compounds **1b**, **2b** and **4b**

The ethene polymerisation reactions were performed as previously described.¹⁶ Catalyst systems were prepared by mixing **1b**

or **2b** with either $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and in the case of **4b** was mixed with methylaluminoxane (MeAlO)_n (MAO). The data for the polymerisation experiments are given in Table 4. Polydispersity values lie between 2 and 4 consistent with single-site catalysts. There is a decrease in polymer molecular weights from **4b** via **1b** to **2b**. The compound **1b** gives a more active catalyst system than **4b** or **2b**. The compounds **4b** and **2b** give catalyst systems with similar activities but the resulting polymers have different molecular weights. Assuming the same amount of active catalyst centres are formed in both cases it appears that **2b** enhances $\beta\text{-H}$ elimination without reduction of activity compared with **4b**. This implies that k_p is the same but k_t is approximately 8 times greater for **2b** than **4b**. It may be that the phenyl group acts as a weak Lewis base and enhances $\beta\text{-H}$ elimination.

Conclusion

The new zirconocenes **1a**, **2a** and **4a** and **1b**, **2b** and **4b** are described. Reaction of **1b** and **2b** with methide abstracting agents gives unusual behaviour which may reflect participation of the phenyl rings, by co-ordination to the zirconium centre. This hypothesis is strengthened by comparison with the sterically more demanding **4b**, which does not show any solvent separated species. However, the NMR data do not provide evidence for the co-ordination of the phenyl ring to the cationic metal centres of **1b** and **2b**.

Experimental

General procedures

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium-potassium alloy (diethyl ether; light petroleum, bp $40\text{--}60^\circ\text{C}$) sodium-benzophenone (thf) and calcium hydride (dichloromethane). The NMR solvents were dried over activated molecular sieves, freeze thawed and stored in Young's-Tap sealed ampoules. The spectra were recorded on a Bruker ARX250 or DPX300, a VARIAN UnityPlus 500 or a JEOL EX90FT or EX270FT machine and referenced to the residual solvent peak for ^1H . Chemical shifts are quoted in ppm relative to tetramethylsilane. The ^{13}C NMR spectra were proton decoupled using the standard program installed on the spectrometer. CH-Coupling constants were measured by INEPT (insensitive nuclei enhanced by polarisation transfer). Ethylene (BOC) was purified by passing through CaCl_2 , P_2O_5 , activated molecular sieves and AlEt_3 -silicone oil columns. The ligands $\text{C}_5\text{H}_5\text{R}$ ($\text{R} = \text{CH}_2\text{Ph}$ or CHPh_2) were prepared in moderate yields by treating the corresponding benzyl chlorides with sodium cyclopentadienide in thf.^{17,18} The known compounds bis(benzylcyclopentadienyl)-zirconium dichloride **1a** and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{CH}_2\text{Ph})\text{Cl}_2]$ **3a** were prepared essentially as described.⁸

Crystal structure determination of compound **1b**

Crystal data. $\text{C}_{26}\text{H}_{28}\text{Zr}$, $M = 431.70$, triclinic, $a = 9.857(2)$, $b = 13.365(3)$, $c = 8.244(2)$ Å, $\alpha = 103.48(2)$, $\beta = 101.19(2)$, $\gamma = 87.95(2)^\circ$, $U = 1036.0(4)$ Å³, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 2$, $\lambda = 0.71073$ Å, $\mu = 0.538$ mm⁻¹, $D_c = 1.384$ Mg m⁻³, $F(000) = 448$, crystal size $0.2 \times 0.2 \times 0.1$ mm, θ range for data collection 2.59 to 23.03° , limiting indices $0 \leq h \leq 10$, $-14 \leq k \leq 14$, $-9 \leq l \leq 9$, reflections collected 3085, independent 2888 ($R_{\text{int}} = 0.0274$). Absorption correction: none. Refinement method: full matrix least squares on F^2 , Data/restraints/parameters: 2888/0/329. Goodness-of-fit on F^2 : 1.012. Final R indices [$I > 2\sigma(I)$] $R1 = 0.0231$, $wR = 0.0568$; (all data) $R1 = 0.0331$, $wR = 0.0604$. Extinction coefficient: 0.0005(6). Largest difference peak and hole: 0.249 and -0.379 e Å⁻³.

Table 3 Proton and ¹³C NMR data of cationic complexes 5–10

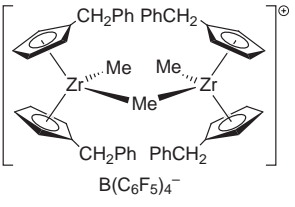
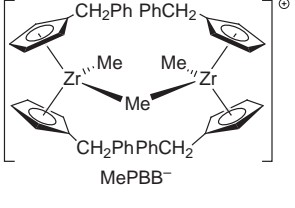
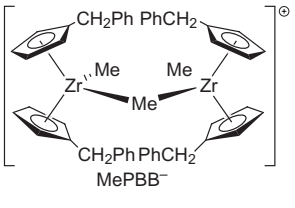
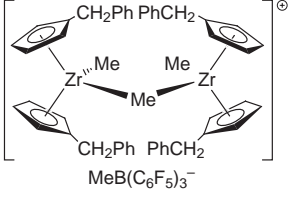
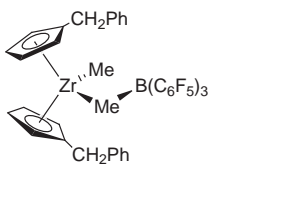
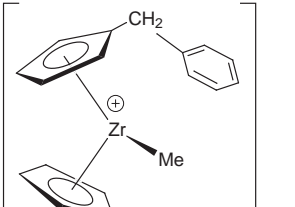
Compound	¹ H NMR (δ , J/Hz)		¹³ C NMR (δ)		¹⁹ F NMR (δ)					
5a in CD ₂ Cl ₂ , –20 °C  B(C ₆ F ₅) ₄ [–]	–0.83 (s, 3 H) ^a 0.38 (s, 6 H) 0.48 (s, 3 H) 3.74 (dd, 8 H) 5.97 (d, 4 H, <i>J</i> _{HH} = 2.5) 6.07 (d, 4 H, <i>J</i> _{HH} = 3.5) 6.08 (d, 4 H, <i>J</i> _{HH} = 2.5) 6.31 (d, 4 H, <i>J</i> _{HH} = 2.5) 7.25 (m, 20 H)	μ-Me ZrMe CH ₃ B CH ₂ Ph Cp H Cp H Cp H Cp H Cp H Ph	23.05 ^b 32.82 36.38 42.05 110.33 112.29 112.87 115.05 127.03 128.36 128.92 131.73 139.14	μ-CH ₃ CH ₃ B ZrCH ₃ CH ₂ Ph Cp Cp Cp Cp <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Cp <i>i</i> -C Ph						
	5b in C ₆ D ₆ , 20 °C  MePBB [–]	–1.07 (s, 3 H) ^a –0.88 (s, 3 H) –0.11 (s, 6 H) 3.4 (dd, 8 H) 5.38 (d, 8 H, <i>J</i> _{HH} = 2.5) 5.65 (d, 8 H, <i>J</i> _{HH} = 2.5) 7.0 (m, 20 H)	μ-CH ₃ CH ₃ B ZrCH ₃ CH ₂ Ph Cp Cp Ph			–123.58 ^c (d, 3 F, <i>J</i> _{FF} = 17.9) –139.05 (d, 3 F, <i>J</i> _{FF} = 23.5) –139.32 (d, 3 F, <i>J</i> _{FF} = 22.6) –139.40 (d, 3 F, <i>J</i> _{FF} = 21.6) –155.50 (t, 3 F, <i>J</i> _{FF} = 21.2) –159.30 (t, 3 F, <i>J</i> _{FF} = 22.8) –162.70 (t, 3 F, <i>J</i> _{FF} = 21.2) –163.30 (t, 3 F, <i>J</i> _{FF} = 22.6) –163.90 (t, 3 F, <i>J</i> _{FF} = 22.6)				
		5c in CD ₂ Cl ₂ , –30 °C  MePBB [–]	–1.63 (s, 3 H) ^a –0.81 (s, 3 H) 0.41 (s, 6 H) 3.77 (dd, 8 H) 6.01 (s, 4 H) 6.09 (s, 4 H) 6.10 (s, 4 H) 6.35 (s, 4 H) 7.19 (d, 8 H, <i>J</i> _{HH} = 7.00) 7.26 (t, 4 H, <i>J</i> _{HH} = 6.50) 7.36 (t, 8 H, <i>J</i> _{HH} = 6.50)	CH ₃ B μ-CH ₃ ZrCH ₃ CH ₂ Ph Cp H ¹ Cp H ² Cp H ³ Cp H ⁴ <i>o</i> -H Ph <i>p</i> -H Ph <i>m</i> -H Ph	≈12 ^b 23.07 (<i>J</i> _{CH} = 120) 41.53 (<i>J</i> _{CH} = 134) 35.91 110.20 112.23 112.82 115.07 126.39 128.33 128.88 131.71 139.14	CH ₃ B μ-CH ₃ ZrCH ₃ CH ₂ Cp C ³ Cp C ¹ Cp C ² Cp C ⁴ <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Cp <i>i</i> -C Ph	–130.87 ^c (s, 3 F) –145.56 (d, 3 F, <i>J</i> _{FF} = 23.04) –145.67 (d, 3 F, <i>J</i> _{FF} = 21.63) –146.85 (d, 3 F, <i>J</i> _{FF} = 15.05) –162.92 (t, 3 F, <i>J</i> _{FF} = 21.16) –165.12 (t, 3 F, <i>J</i> _{FF} = 21.63) –169.36 (t, 3 F, <i>J</i> _{FF} = 21.16) –169.87 (t, 3 F, <i>J</i> _{FF} = 21.16) –170.72 (t, 3 F, <i>J</i> _{FF} = 21.16)			
			5d in CD ₂ Cl ₂ , –60 °C  MeB(C ₆ F ₅) ₃ [–]	–0.81 (s, 3 H) ^d 0.42 (s, 6 H) 3.72 (d, 4 H) 3.90 (d, 4 H) 6.00 (d, 4 H, <i>J</i> _{HH} = 1.68) 6.07 (s, 8 H) 6.37 (d, 4 H, <i>J</i> _{HH} = 1.68) ≈7.26 ^f ≈7.30 ^f ≈7.36 ^f	μ-CH ₃ ZrCH ₃ CH ₂ Ph CH ₂ Ph Cp H ¹ Cp H ^{2,3} Cp H ⁴ <i>o</i> -H Ph <i>p</i> -H Ph <i>m</i> -H Ph	23.62 ^e (<i>J</i> _{CH} = 134.6) 35.54 (<i>J</i> _{CH} = 148.4) 41.19 (<i>J</i> _{CH} = 118.9) 109.56 111.63 112.54 114.70 126.70 128.11 128.64 131.54 139.06	μ-CH ₃ CH ₂ Ph ZrCH ₃ Cp C ³ Cp C ¹ Cp C ² Cp C ⁴ <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Cp <i>i</i> -C Ph			
				6a in CD ₂ Cl ₂ , –60 °C  B(C ₆ F ₅) ₃ [–]	0.20 (br, 3 H) ^g 0.75 (s, 3 H) 3.87 (d, d, 4 H) 6.07 (s, 2 H) 6.11 (s, 2 H) 6.28 (s, 2 H) 6.39 (s, 2 H) 7.15 (d, 4 H) ≈7.30 ^j ≈7.35 ^j	CH ₃ B ZrMe CH ₂ Ph Cp H ¹ Cp H ² Cp H ³ Cp H ⁴ <i>o</i> -H Ph <i>p</i> -H Ph <i>m</i> -H Ph	≈24 ^h 35.47 43.108 (<i>J</i> _{CH} = 123) 110.89 112.90 113.30 115.91 126.68 128.01 128.95 133.00 139.03	CH ₃ B CH ₂ Ph ZrMe Cp C ³ Cp C ² Cp C ¹ Cp C ⁴ <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Cp <i>i</i> -C Ph	–140.24 ⁱ –165.44 –170.29	
					6b in CD ₂ Cl ₂ , –60 °C  MeB(C ₆ F ₅) ₃ [–]	0.48 (br, 1.5 H) ^g ≈3.8 (2 H) ^j 5.38 6.23 6.38 6.55 ≈7.35 ≈7.27 7.48	CH ₃ B CH ₂ Ph Cp H ¹ Cp H ² Cp H ³ Cp H ⁴ <i>p</i> -H Ph <i>o</i> -H Ph <i>m</i> -H Ph	≈10 ^h 35.02 ≈113.4 114.79 115.57 117.62 127.37 128.95 129.06 129.81 138.49	CH ₃ B CH ₂ Ph Cp C ¹ Cp C ³ Cp C ² Cp C ⁴ <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Ph <i>i</i> -C Ph	–139.57 ⁱ –169.48 –172.29

Table 3 (Contd.)

Compound	¹ H NMR (δ , J/Hz)		¹³ C NMR (δ)	¹⁹ F NMR (δ)
7a in CD ₂ Cl ₂ , -60 °C	0.16 (br, 1.5 H) ^g 0.75 (s, 1.5 H)	CH ₃ B ZrMe	41.99 ^h ($J_{\text{CH}} = 121$)	ZrMe
7b in CD ₂ Cl ₂ , -60 °C	0.53 (br, 5 H) ^g 0.84 (q, 3 H) 5.03 (s, 2 H) 5.81 (s, 2 H) 5.92 (s, 2 H) 6.04 (s, 2 H) 6.20 (s, 2 H) 6.8–7.6 (m, 20 H)	CH ₃ B ZrMe CHPh Cp H ¹ Cp H ² Cp H ³ Cp H ⁴ Ph	≈ 10 ^h 49.19 ($J_{\text{CH}} = 118$) 53.39 112.13 113.13 115.15 116.57 127.1 127.9 128.7 134.2	CH ₃ B ZrMe CHPh ₂ Cp C ² Cp C ¹ Cp C ³ Cp C ⁴ <i>p</i> -C Ph <i>o</i> -C Ph <i>m</i> -C Ph <i>i</i> -C Cp
8 in CD ₂ Cl ₂ , -60 °C	0.10 (m, 54 H) ^g 0.68 (s, 3 H) 5.80 (s, 2 H) 6.19 (s, 2 H) 6.43 (s, 2 H) 6.60 (s, 2 H)	SiCH ₃ ZrMe Cp H ¹ Cp H ⁴ Cp H ³ Cp H	0.84 ^h ≈ 23 45.97 ($J_{\text{CH}} = 122$) 115.47 119.80 120.29 120.75 127.38	SiCH ₃ CH ₃ B ZrMe Cp C ² Cp C ¹ Cp C ³ Cp C ⁴ <i>i</i> -C Cp

Cp Hⁿ ($n = 1-4$) denotes hydrogens of the C₅ ring, coupled to Cp Cⁿ (connectivity determined by CH correlation). ^a 500 MHz. ^b 125.7 MHz. ^c 470 MHz. ^d 300 MHz. ^e 75.5 MHz. ^f Obscured by triphenylethane. ^g 270 MHz. ^h 67.8 MHz. ⁱ 470 MHz, -90 °C. ^j Peaks not resolved.

CCDC reference number 186/1237.

See <http://www.rsc.org/suppdata/dt/1999/43/> for crystallographic files in .cif format.

Preparations

Diphenylmethylcyclopentadiene. Chlorodiphenylmethane (100 g, 500 mmol) in 200 cm³ thf at -78 °C was treated with a solution of NaCp (500 mmol) in 200 cm³ thf by slow addition. The reaction mixture was warmed to room temperature and stirred for 30 min before pouring onto ice-water/NH₄Cl. The organic phase was separated and the aqueous phase was washed with light petroleum. The combined organic phases were dried over MgSO₄ and the volatiles removed under reduced pressure. The oily residue was vacuum distilled [bp (0.01 mmHg) 125–145 °C] giving an orange liquid. Yield: 30 g, 129 mmol, 25.8%.

Bromotris(trimethylsilyl)silane. The compound (Me₃Si)₄-Si¹⁹⁻²¹ (19.0 g, 59.2 mmol) was dissolved in 250 cm³ thf. Methyl-lithium in diethyl ether (42 cm³, 59.2 mmol, 1.4 mol l⁻¹) was slowly added. The solution changed to red. The reaction mixture was stirred overnight, changing to orange, and some white, fluffy material was observed. This mixture was added slowly to a solution of 3.0 cm³ (59.2 mmol) Br₂ in 50 cm³ thf at -78 °C. The red colour of the bromine slowly changed to yellow, indicating consumption of the bromine. A precipitate was formed, which later dissolved again. After complete addition the reaction mixture was warmed to room temperature and stirred for 1 h. The volatiles were removed under vacuum at room temperature to yield an orange oil, which was extracted with hot light petroleum and the solvent was removed

under vacuum to yield a yellow oil. This was extracted again with 100 cm³ CH₂Cl₂ and the solvent removed under vacuum to yield a yellow oil. Yield: 19.4 g, 59.2 mmol, 100%.

Tris(trimethylsilyl)silylcyclopentadiene. Freshly distilled C₅H₆ (3.91 g, 59.2 mmol) was diluted with 150 cm³ thf and 23.7 cm³ (59.2 mmol) butyllithium (2.5 mol l⁻¹) were added at -78 °C. After complete addition the reaction mixture was warmed to room temperature and stirred for 30 min. This mixture was added to a solution of 19.4 g (59.2 mmol) of SiBr(SiMe₃)₃ in 100 cm³ thf at -78 °C. After complete addition the reaction mixture was allowed to warm up and stirred at room temperature for 1 h. The volatiles were removed under vacuum to yield a yellow oil which was extracted with 200 cm³ light petroleum. The filtrate was concentrated to dryness to yield a yellow, waxy material. The ¹H NMR spectrum indicated a strong (≈27 H) signal for the SiMe₃ protons at around δ 0 and a weaker signal (≈4 H) for the Cp protons. Yield 18.3 g, 58 mmol, 98%.

[Zr(η -C₅H₄CH₂Ph)₂Cl₂] 1a. Benzylcyclopentadiene (7.2 g, 46 mmol) in thf (100 cm³) at -78 °C was treated with butyllithium (18.4 cm³, 46 mmol) at -78 °C. The mixture changed to red. It was slowly warmed to room temperature and stirred for 1 h. The compound [ZrCl₄(thf)₂] [8.86 g (23 mmol)] was slowly added. The mixture changed to a darker red and finally to a rust brown. After stirring overnight, the solvent was removed under reduced pressure and the red-brown solid residue extracted with 150 cm³ toluene. The extract was stored at -78 °C for 2 d and an off-white solid formed which was collected by filtration, washed and dried. Yield: 4.6 g, 9.7 mmol, 48.7%. A satisfactory elemental analysis could not be obtained.

Table 4 Data for ethylene polymerisation with zirconocenes **1b**, **2b** and **4b**^a

Run	Zr/CGA	T/°C	t/min	PE yield/mg	Productivity ^b	10 ⁻³ M _w	10 ⁻³ M _n	M _w /M _n
1	1b /Ph ₃ C ⁺	60	1	68.3	409.8			
2	1b /Ph ₃ C ⁺	60	1	88.8	532.8	26.7	7.4	3.6
3	1b /Ph ₃ C ⁺	20	1	123.0	738.0			
4	1b /Ph ₃ C ⁺	20	1	112.5	675.0	36.4	9.1	4.1
5	1b /Ph ₃ C ⁺	0	1	163.5	981.0			
6	1b /Ph ₃ C ⁺	0	1	154.5	927.0	54.3	18.9	2.9
7	1b /B(C ₆ F ₅) ₃	60	1	60.5	363.0	25.8	8.3	3.2
8	1b /B(C ₆ F ₅) ₃	60	1	75.2	451.2			
9	1b /B(C ₆ F ₅) ₃	20	1	133.1	798.6	22.4	8.8	2.5
10	1b /B(C ₆ F ₅) ₃	20	1	137.2	823.2			
11	1b /B(C ₆ F ₅) ₃	0	1	96.6	579.6	47.5	21.8	2.2
12	1b /B(C ₆ F ₅) ₃	0	1	137.8	826.8			
13	2b /Ph ₃ C ⁺	60	1	75.0	450.0	3.3	1.1	3
14	2b /Ph ₃ C ⁺	60	1	12.7	76.2			
15	2b /Ph ₃ C ⁺	20	1	57.8	346.8	6.4	2.5	2.5
16	2b /Ph ₃ C ⁺	20	1	56.7	340.2			
17	2b /Ph ₃ C ⁺	0	1	78.8	472.8	11.2	4.6	2.4
18	2b /Ph ₃ C ⁺	0	1	64.5	387.0			
19	2b /B(C ₆ F ₅) ₃	60	1	27.4	164.4	4.4	1.0	4.4
20	2b /B(C ₆ F ₅) ₃	60	1	97.0	582.0			
21	2b /B(C ₆ F ₅) ₃	20	1	52.9	317.4	6.3	2.8	2.2
22	2b /B(C ₆ F ₅) ₃	20	1	53.6	321.6			
23	2b /B(C ₆ F ₅) ₃	0	1	80.3	481.8	15.4	6.7	2.2
24	2b /B(C ₆ F ₅) ₃	0	1	69.5	417.0			
25	4b /MAO	60	2	59.1	177.3	12.6	3.2	3.9
26	4b /MAO	60	2	42.3	126.9	13.1	3.4	3.7
27	4b /MAO	23	1	96.1	576.6	40.2	8.8	4.5
28	4b /MAO	20	1	112.1	672.6	44.8	10.4	4.3
29	4b /MAO	0	1	71.2	427.2	122.5	40.4	3.0
30	4b /MAO	0	1	58.8	532.8	126.0	51.8	2.4

^a Conditions: 20 cm³ toluene, 1 bar ethylene, 10 mmol [Zr], 10 mmol CGA {cationic generating agent, *i.e.* [Ph₃C]⁺[B(C₆F₅)₄]⁻ or B(C₆F₅)₃}; 2 cm³ MAO (10% in toluene, WITCO). ^b In 10³ g PE (mol Zr h bar)⁻¹.

[Zr(η-C₅H₄CHPh)₂Cl₂] 2a. Diphenylmethylcyclopentadiene (9.3 g, 40 mmol) in 250 cm³ thf at -78 °C was treated with butyllithium (16 cm³, 40 mmol) at -78 °C in a dropwise manner. The mixture changed to red. It was warmed to room temperature and stirred for 1.5 h. To this was added 6 g (20 mmol) [ZrCl₄(thf)₂] and stirred overnight. The solvent was removed under vacuum and the residue extracted with 200 cm³ toluene. The filtrate was stored in a freezer for 3 d to obtain white crystals, which were collected by filtration. Yield: 4.9 g, 7.9 mmol, 35%. A satisfactory elemental analysis could not be obtained.

[Zr(η-C₅H₄CH₂Ph)₂Me₂] 1b. To a suspension of compound **1a** (4.60 g, 9.7 mmol) in 200 cm³ diethyl ether at -78 °C was added slowly methyllithium (13.8 cm³, 19.4 mmol). The reaction mixture was stirred for 10 min at -78 °C, slowly warmed to room temperature and stirred for 1 h. The volatiles were removed under reduced pressure and the residue was extracted with 300 cm³ of warm light petroleum. The extract was filtered and the filtrate stored at 5 °C for 3 d which yielded white crystals suitable for X-ray crystallography. A second crop of crystals was obtained from the concentrated mother-liquor after 6 d at 5 °C. Yield: 2.50 g, 5.8 mmol 59.8%. (Found: C, 72.3; H, 6.5. Calc.: C, 72.32; H, 6.54%).

[Zr(η-C₅H₄CHPh)₂Me₂] 2b. Compound **2a** (4.9 g, 7.9 mmol) was suspended in 250 cm³ diethyl ether at -78 °C. Methyllithium (11.3 cm³, 16.8 mmol) was slowly added. The mixture was stirred for 4 min at -78 °C, slowly warmed to room temperature, and stirred for 1 h. The volatiles were removed under vacuum to yield a white solid which was extracted with 200 cm³ light petroleum. The extract was stored at -30 °C for 1 day to yield white crystals. The residue was repeatedly extracted with warm light petroleum and the combined extracts were stored at -78 °C to yield further product. The fractions were combined and recrystallised from 400 cm³ warm light petroleum and slowly cooled to -30 °C to yield a white solid. (2.1 g, 3.6

mmol 45.6%) (Found: C, 77.87; H, 6.45. Calc.: C, 78.16; H, 6.21%).

Attempted synthesis of [Zr(η-C₅H₃)(η-C₅H₄CH₂Ph)Me₂] 3b. A suspension of the compound [Zr(η-C₅H₃)(η-C₅H₄CH₂Ph)Cl₂] (573.5 mg, 1.7 mmol) in diethyl ether at -78 °C was treated with LiMe·LiBr (2.0 cm³, 3 mmol) in Et₂O. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. A white precipitate formed. The volatiles were removed under reduced pressure and the residue was extracted with light petroleum. The extract was filtered, concentrated and stored at -78 °C for 1 d to yield a white solid. After filtration, the solid turned into a brown liquid at room temperature and gas evolution was observed. The NMR data indicate the formation of the product **3b** as well as intractable side products.

[Zr{η-C₅H₄Si(SiMe₃)₃}₂Cl₂] 4a. The compound C₅H₅Si(SiMe₃)₃ (18.3 g, 50 mmol) in 200 cm³ thf at -78 °C was treated with *n*-butyllithium (20 cm³, 50 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. To this was slowly added [ZrCl₄(thf)₂] (9.6 g, 25 mmol), changing to dark red. The reaction mixture was stirred overnight. The volatiles were removed under vacuum and the residue was extracted with 100 cm³ toluene and stored at -78 °C for 2 d. A light yellow solid was obtained which was collected by filtration. Yield: 3.5 g, 4.5 mmol 18%. (Found: C, 42.04, H, 7.76. Calc.: C, 42.81; H, 7.95%).

[Zr{η-C₅H₄Si(SiMe₃)₃}₂Me₂] 4b. To a suspension of compound **4a** (3.5 g, 4.5 mmol) suspended in 250 cm³ diethyl ether at -78 °C was added methyllithium (6.3 cm³, 9 mmol), and the reaction mixture was stirred at low temperature for 30 min before being allowed to warm slowly to room temperature. Stirring was continued for 1 h. The mixture changed from pale yellow to colourless, became clear, and a new precipitate was formed. The volatiles were removed under reduced pressure and the residue was extracted with 200 cm³ light petroleum, and

stored at $-40\text{ }^{\circ}\text{C}$ for 3 d. The resulting crystals were collected by filtration and the mother-liquor was cooled to $-78\text{ }^{\circ}\text{C}$ to yield another crop. Yield: 1.5 g, 2.0 mmol, 45% (Found: C, 45.99; H, 9.36. Calc.: C, 48.38; H, 9.20%). The low carbon content may be due to the formation of SiC.

Low temperature NMR studies on cationic compounds

Owing to the sensitivity of the cationic complexes, they 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 $0.25\text{ cm}^3\text{ CD}_2\text{Cl}_2$ and the solution transferred to a precooled ($-78\text{ }^{\circ}\text{C}$) NMR tube. The cation generating agent, such as $\text{B}(\text{C}_6\text{F}_5)_3$, $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or PBB (*ca.* 0.11 mmol), was dissolved in $0.28\text{ cm}^3\text{ CD}_2\text{Cl}_2$ and transferred to the zirconocene solution in the NMR tube. The tube was sealed and shaken vigorously to ensure complete mixing. The reaction mixture became yellow. The sample was placed in the precooled ($-60\text{ }^{\circ}\text{C}$) probe of the NMR spectrometer and ^1H , ^{13}C , H-COSY and CH-COSY spectra were recorded at $-60\text{ }^{\circ}\text{C}$. 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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