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FULL PAPER

Evidence for cationic Group 4 zirconocene complexes with intramolecular phenyl co-ordination

Linda H. Doerrer, Malcolm L. H. Green, Daniel Häußinger and Jörg Saßmannshausen

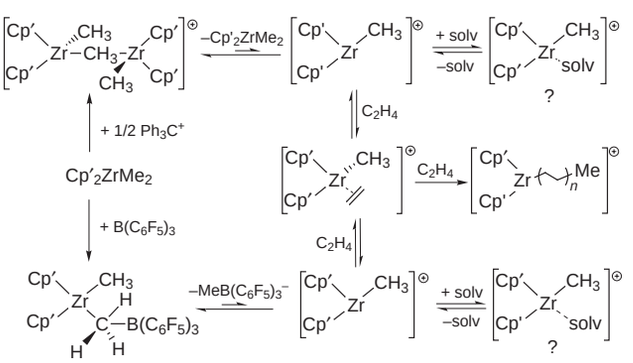
Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

Received 21st October 1998, Accepted 11th May 1999

The mono- and bis-ring substituted zirconocenes with pendant phenyl groups $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Me_2]$ **2**, $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Me_2]$ **3**, $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ **4**, and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me_2]$ **5** have been prepared. The crystal structures of **3** and **4** have been determined. Compounds **2**–**5** react with methyl abstracting reagents such as $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$ to form cationic zirconocene complexes **6**–**9** as solvent separated ion pairs as shown by low temperature NMR spectroscopy. For the cationic complexes $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Me]^+[RB(C_6F_5)_3]^-$ (R = Me **6a** or C_6F_5 **6b**) and $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Me]^+[RB(C_6F_5)_3]^-$ (R = Me **7a** or C_6F_5 **7b**) evidence for the co-ordination of a phenyl group to the zirconium centre *via* agostic C–H–M interaction was obtained by NMR spectroscopy. These cationic complexes can be considered as models for solvent adducts in Kaminsky catalysts. The cationic complexes $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me]^+[RB(C_6F_5)_3]^-$ (R = Me **8a** or C_6F_5 **8b**) (derived from **4**) and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me]^+[RB(C_6F_5)_3]^-$ (R = Me **9a** or C_6F_5 **9b**) (derived from **5**), respectively, exhibit more complex behaviour. These observations contrast with those from the previously published benzyl congener $[Zr(\eta\text{-}C_5H_4CH_2Ph)_2Me_2]$ **1** which, with methyl abstracting agent, generates both a solvent separated cation/anion pair and a tight ion pair.

Introduction

There is considerable evidence that the active centres in homogeneous Kaminsky catalyst systems are cations,[1–4] which may be represented by the general formula $[Zr(\eta\text{-}C_5H_nR_{5-n})_2R']^+$ where R may be a hydrocarbyl group, $n = 0$–4, and R′ is an alkyl group. These cations can be generated by methyl abstraction from the corresponding methyl compounds $[Zr(\eta\text{-}C_5H_nR_{5-n})_2Me_2]$ using the methyl abstracting reagent $[Ph_3C]^+[B(C_6F_5)_4]^-$ [5,6] or the Lewis acid $B(C_6F_5)_3$.[7,8] The cationic Group 4 metallocene species $[Zr(\eta\text{-}C_5H_nR_{5-n})_2Me]^+$ is a strong Lewis acid and can form Lewis acid–base binuclear adducts with the neutral precursor[9,10] when activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$ or with the anion[7,8] in the case of $B(C_6F_5)_3$ (see Scheme 1).



Scheme 1

Since most polymerisations using the cations $[Zr(\eta\text{-}C_5H_nR_{5-n})_2R']^+$ are conducted in toluene or other arenes as solvents it is possible that adducts of the general formula $[Zr(\eta\text{-}C_5H_nR_{5-n})_2R'(solv)]^+$ (solv = solvent) could serve as a resting state of the catalyst cycle (Scheme 1). These solvent adducts have been suggested before[1] but there is little direct evidence for such species. Related solvent adducts have been observed for ruthenium complexes[11] and for Group 4 half-sandwich complexes, for example $[MCp^*Me_2(arene)]^+$ ($Cp^* = C_5Me_5$; arene = benzene, toluene, *m*- and *p*-xylene, anisole, styrene or mesitylene; M = Ti, Zr or Hf)[12,13] and $[M\{\eta\text{-}C_5H_3(SiMe_3)_2\}(\eta\text{-}C_6H_5Me)Me_2]^+$ (M = Zr or Hf).[14] We previously reported[15] the synthesis and reactions of $[Zr(\eta\text{-}C_5H_4CH_2Ph)_2Me_2]$ **1** in which benzyl groups are tethered to the cyclopentadienyl ring. It was hoped that evidence for interaction between the phenyl group and the zirconium centre in the cation $[Zr(\eta\text{-}C_5H_4CH_2Ph)_2Me]^+$ would be observed. However, no direct evidence was forthcoming. Therefore, we have prepared the new monosubstituted zirconocenes $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Me_2]$ **2** and $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Me_2]$ **3** and the bis-substituted zirconocenes $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ **4** and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me_2]$ **5** in the hope that the cations derived from these compounds using methyl abstracting reagents might show evidence for phenyl–zirconium interactions.

Results and discussion

Preparation of the metallocenes 2–5

The compound $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Cl_2]$ **2a** was prepared by treating LiPh with 6,6-dimethylfulvene and subsequently quenching the reaction mixture with $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme. A mixture of desired **2a** and $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Cl_2]$ **4a** was obtained and these two compounds were separated by fractional crystallisation. Methylation of **2a** was performed with MgMeBr in order to reduce any ligand scrambling and methylation of **4a** was performed with LiMe (see Scheme 2). Crystals of **4** suitable for X-ray analysis were grown by slow cooling of a light petroleum solution to −80 °C. The crystal structure of **4** is shown in Fig. 1 and selected bond angles and distances are summarised in Table 1. The phenyl group is bent away from the zirconium and there is no evidence for intermolecular interactions.

The compound $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Cl_2]$ **3a** was prepared by treating $LiC_6H_4Me\text{-}p$ with 6,6-dimethylfulvene and quenching the resulting lithium salt with $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme. In contrast to the synthesis of **2a**, no ligand scrambling was observed and **3a** was obtained in good yields.

Table 1 Selected bond distances [Å] and angles [°] for complex **4**

Zr(1)–C(1)	2.5167(19)	Zr(1)–C(4)	2.5862(19)
Zr(1)–C(2)	2.4727(19)	Zr(1)–C(5)	2.6127(18)
Zr(1)–C(3)	2.5230(19)	Zr(1)–C(21)	2.2854(19)
Cp_{centr}–Zr	1.866		
C(21)–Zr(1)–C(21B)	92.3(1)	C(7)–C(6)–C(8)	109.32(17)
Cp_{centr}–Zr(1)–Cp_{centr}	131.12	C(7)–C(6)–C(11)	107.80(16)
C(5)–C(6)–C(11)	108.80(15)		

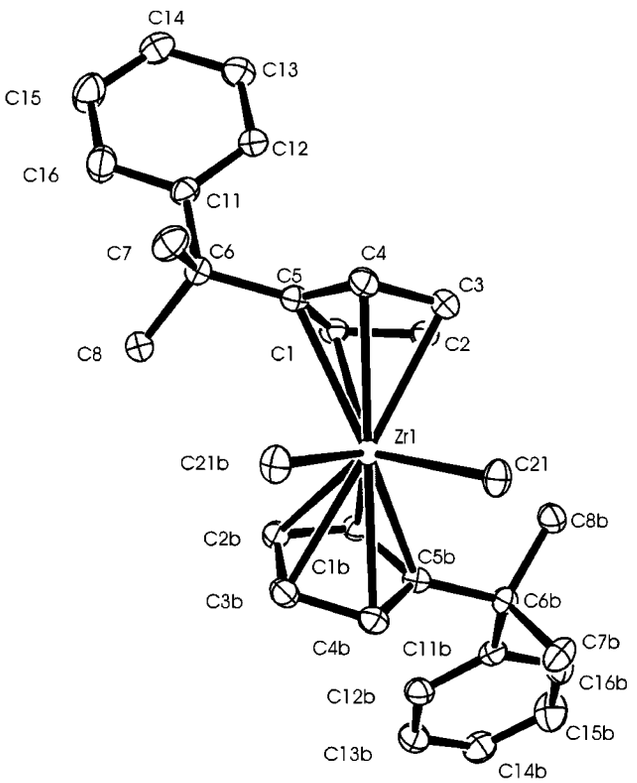
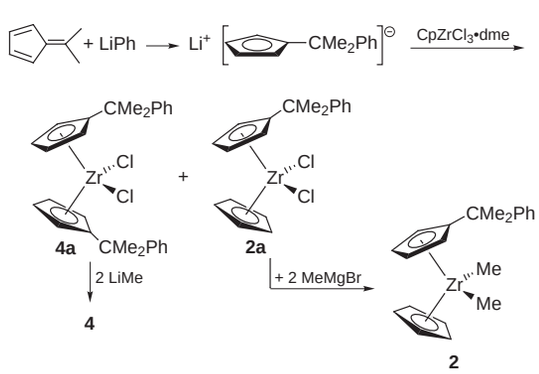


Fig. 1 Crystal structure of complex **4**.



Scheme 2

Methylation of **3a** was performed with MgMeBr in diethyl ether to afford $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Me_2]$ **3** in high yield (see Scheme 3). Crystals of **3** suitable for X-ray analysis were grown by slow cooling of a light petroleum solution to −20 °C. The crystal structure of **3** is shown in Fig. 2 and selected bond angles and distances are summarised in Table 2. Unlike the solid state structure of **1**, the phenyl groups in **3** adopt an *anti* conformation presumably to avoid repulsive interactions between the CMe_2 and the $ZrMe_2$ groups in a *syn* conformation. This is typical for substituted Group 4 metallocenes.[16] No close intermolecular contacts of phenyl groups to the zirconium centre were found.

The compound $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Cl_2]$ **5a** was prepared by the reaction between LiC_6H_4Me-*p* and 6,6-dimethylfulvene and subsequent quenching of the resulting lithium salt with 0.5 equivalent of $ZrCl_4$·2thf. Methylation with LiMe gave **5** in good yield (see Scheme 3).

Table 2 Selected bond distances [Å] and angles [°] for complex **3**

Zr(1)–C(1)	2.516(8)	Zr(1)–C(7)	2.498(8)
Zr(1)–C(2)	2.516(8)	Zr(1)–C(8)	2.53(1)
Zr(1)–C(3)	2.511(8)	Zr(1)–C(9)	2.561(9)
Zr(1)–C(4)	2.556(11)	Zr(1)–C(10)	2.596(8)
Zr(1)–C(5)	2.551(11)	Zr(1)–C(21)	2.291(6)
Zr(1)–C(6)	2.526(7)	Zr(1)–C(22)	2.289(5)
Cp'_{centr}–Zr	1.866	Cp_{centr}–Zr	1.859
C(21)–Zr(1)–C(22)	93.6(2)	C(12)–C(11)–C(13)	107.5(6)
Cp_{centr}–Zr(1)–Cp_{centr}	131.87	C(12)–C(11)–C(14)	109.1(6)
C(10)–C(11)–C(14)	106.5(6)		

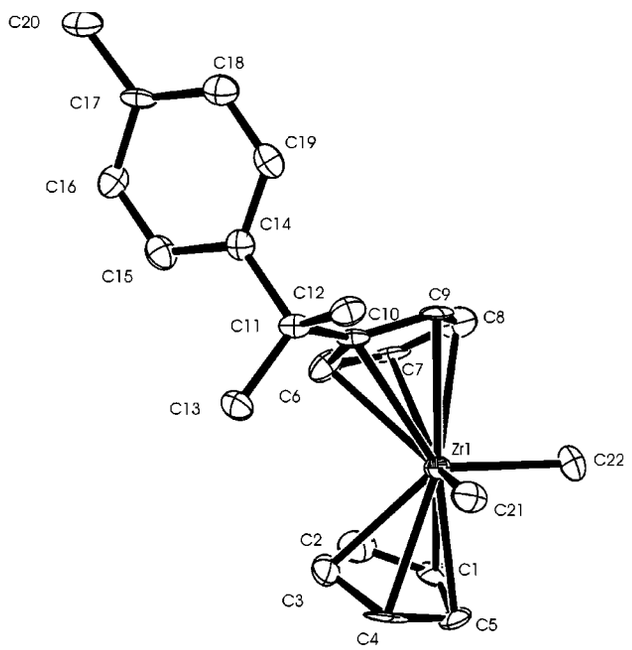
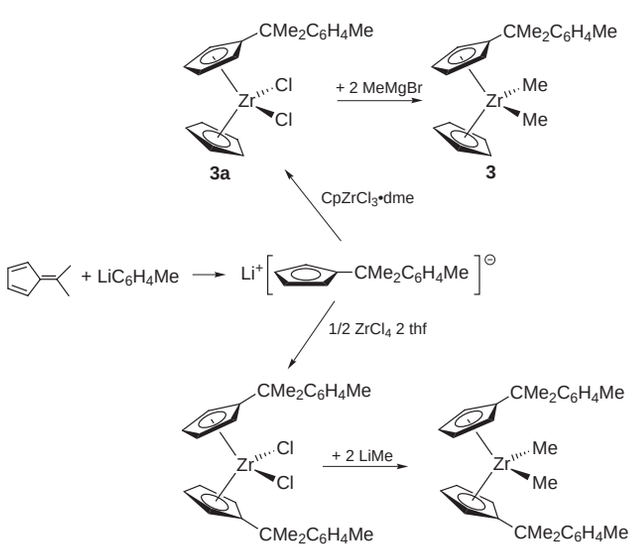


Fig. 2 Crystal structure of complex **3**.



Scheme 3

Low temperature NMR spectroscopy reaction studies

All spectroscopic data for these studies are given in Table 3 together with assignments, where possible. The reaction of complex **3** with $B(C_6F_5)_3$ in CD_2Cl_2 was investigated in detail by 2-D NMR spectroscopy (^1H–^{13}C-GHSQC (gradient selected

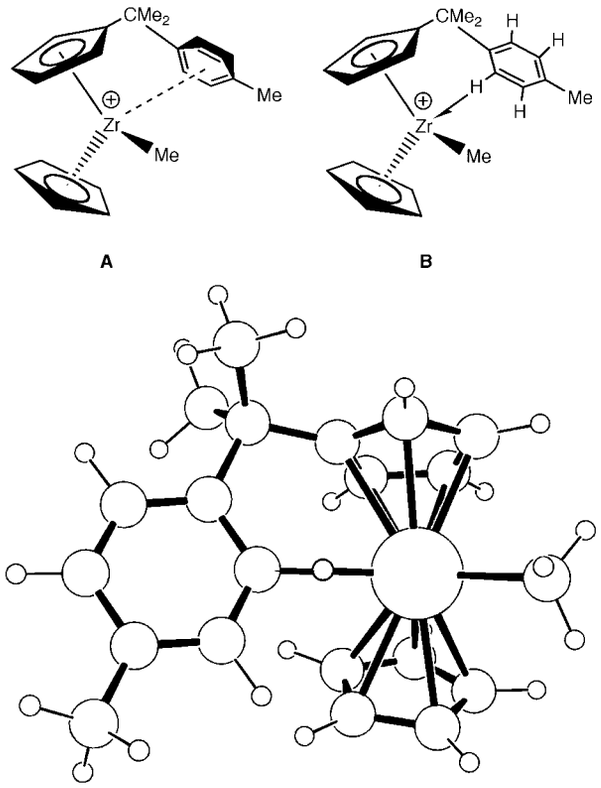


Fig. 3 (Top) proposed structures **A** and **B** for interaction of an electrophilic zirconium centre with a phenyl ring. (Bottom) proposed structure of compounds **7**.

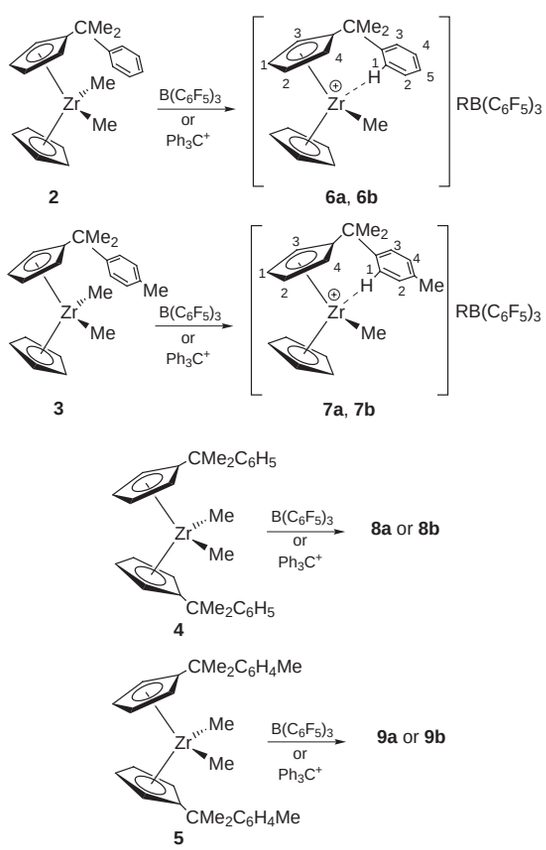
Heteronuclear Single Quantum Coherence) with and without GARP (Globally optimised Alternating-phase Rectangular Pulses)-^{13}C decoupling, ^{1}H–^{13}C-GHMBC (Gradient selected Heteronuclear Multiple Bond Correlation), ^{1}H–^{1}H NOESY, ^{1}H–^{1}H EXSY) which allowed complete assignment of the resulting cation. At −60 °C the reaction proceeds cleanly to give the solvent separated species [Zr(η-C_5H_5)(η-$C_5H_4CMe_2C_6H_4$Me-*p*)Me]$^+$[MeB(C_6F_5)$_3$]$^-$ **7a**. A solvent separated species is clearly indicated by the broad singlet at δ 0.40 in the ^{1}H NMR spectrum, which is assigned to the free anion [MeB(C_6F_5)$_3$]$^-$. In agreement with this assignment, the ^{13}C NMR spectrum shows a broad peak at δ 9.1, typical for non-co-ordinated [MeB(C_6F_5)$_3$]$^-$.[12] Further, the chemical shift difference between the *m*- and *p*-^{19}F of the anion, $\Delta\delta$, is 2.8 ppm, corresponding to a solvent separated ion pair.[17]

The cation of complex **7a** must be chiral, because in the ^{1}H NMR spectrum eight distinct aromatic signals are observed for the $C_5H_4CMe_2C_6H_4$Me-*p* ligand: four resonances for the substituted cyclopentadienyl ring and four signals for the phenyl ring. Similarly, the two methyl groups on the bridging carbon appear as two singlets. Accordingly 15 signals were observed for the $C_5H_4CMe_2C_6H_4$Me-*p* ligand in the ^{13}C-{^{1}H} NMR spectrum. The proton and carbon NMR spectra suggest an interaction of the phenyl group with the zirconium centre. The ^{1}H NMR signal for the proton labelled Ph^1 (*cf.* Table 3) is shifted 0.95 ppm upfield to δ 6.18 whereas the signals for Ph^2, Ph^3 and Ph^4 are slightly shifted downfield compared to those of the starting material **3**. A similar upfield shift is observed for Ph^1 in the ^{13}C NMR spectrum (δ 114.8). In addition, the $^{1}J_{CH}$ coupling constant for Ph^1 (148 Hz) is significantly smaller compared to the coupling constants for Ph^2 (169 Hz), Ph^3 (174 Hz) and Ph^4 (163 Hz). A reduced $^{1}J_{CH}$ coupling constant is a strong indication for an agostic C–H–M interaction.[18] Furthermore, one of the cyclopentadienyl ring protons (Cp^4) is observed at δ 6.93, which can be attributed to the magnetic anisotropy of the phenyl group, as the NOESY spectrum indicates close proximity of Cp^4 to the phenyl ring.

Two possible structures of the cation, **A** and **B** (see Fig. 3), one with the phenyl ring co-ordinated side on, the other with agostic co-ordination *via* one of the hydrogens, have been considered. However, only **B** is supported by NMR data as **A** does not explain the upfield shift of Ph^1. The NOESY spectrum as well clearly favours structure **B**, as the protons Cp^4 and Zr–CH_3 mainly interact with the protons Ph^1 and Ph^2, and only to a much smaller extent with Ph^3 and Ph^4. This small interaction is explained by the EXSY spectrum (mixing time 650 ms) that gives unambiguous proof for the following site exchanges: Ph^1 with Ph^3, Ph^2 with Ph^4, Cp^1 with Cp^2, Cp^3 with Cp^4, and Me^1 with Me^2 . Owing to these exchanges small cross peaks can be detected in the NOESY spectrum between Cp^4 and Ph^3, Ph^4 as well as Zr–CH_3 and Ph^3, Ph^4. The NOESY/EXSY spectra further show that at −60 °C a slow co-ordination/deco-ordination process takes place, in the course of which the entire η-$C_5H_4CMe_2C_6H_4$-Me-*p* moiety is free to rotate around the Zr–C_5H_4R (centroid) axis and the chiral Zr undergoes racemisation.

The reaction of complex **3** with [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ does not lead to the analogue of the well characterised and previously observed[15] homodinuclear species [{Zr(η-$C_5H_4CH_2Ph$)$_2$Me}$_2$-(μ-Me)]$^+$[B(C_6F_5)$_4$]$^-$ but to the formation of [Zr(η-C_5H_5)(η-$C_5H_4CMe_2C_6H_4$Me-*p*)Me]$^+$[B(C_6F_5)$_4$]$^-$ **7b**, which contains the *same* solvent separated cation as observed in the reaction of **3** with B(C_6F_5)$_3$, *i.e.* **7a**. This behaviour with [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ is quite unusual and has not been observed before for zirconocene complexes. It suggests that the formation of **7b** is favoured over the formation of a homodinuclear species.

The reaction of complex **2** with either B(C_6F_5)$_3$ or [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ at −60 °C in CD_2Cl_2 leads to the solvent separated complexes [Zr(η-C_5H_5)(η-$C_5H_4CMe_2$Ph)Me]$^+$[RB-(C_6F_5)$_3$]$^-$ (R = Me **6a** or C_6F_5 **6b**) with almost identical NMR data for the cation (see Scheme 4). Although in depth 2-D



Scheme 4

NMR investigations were not performed on **6a** and **6b**, the 1-D and 2-D NMR spectra recorded demonstrate the chiral nature of the cation in these two salts, and the pronounced upfield shifts for Ph^1 strongly suggest an analogous agostic C–H–M interaction as observed with **7a**.

Table 3 NMR Data (δ, J/Hz) of cationic complexes[a]

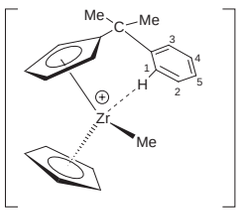
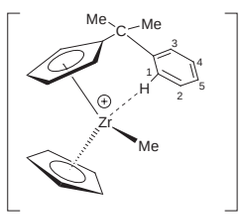
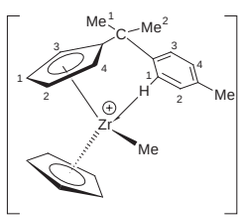
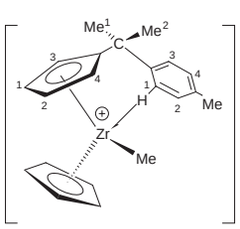
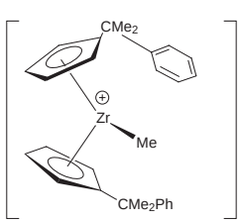
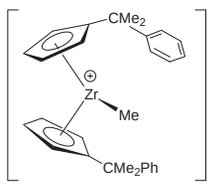
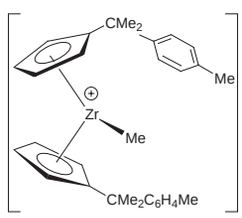
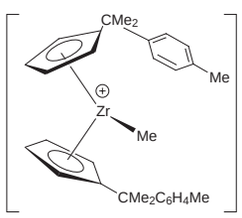
Compound	^{1}H NMR[b,c]		^{13}C NMR[b,d]	
 $MeB(C_6F_5)_3^-$ **6a**	0.43 (br, 3 H)	CH_3B	≈10	CH_3B
	0.68 (s, 3 H)	ZrMe	24.9	CCH_3
	1.68 (s, 3 H)	CCH_3	29.7	CCH_3
	1.74 (s, 3 H)	CCH_3	39.3	CMe_2
	5.84 (s, 5 H)	Cp	47.0	ZrMe
	5.90 (q, 1 H)	Cp′	103.0	Cp′
	6.16 (q, 1 H)	Cp′	112.7	Cp′
	≈6.25 (br, 1 H)	Ph H^1	114.1	Ph C^1
	6.41 (q, 1 H)	Cp′	115.3	Cp′
	6.98 (q, 1 H)	Cp′	115.9	Cp
	≈7.31 (br, 1 H)	Ph H^3	118.6	Cp′
	7.71 (t, 1 H)	Ph H^5	128.4	Ph C^3
	≈7.84 (br, 1 H)	Ph H^2	128.8	Ph C^5
	≈8.05 (br, 1 H)	Ph H^4	139.3	Ph C^2
			140.9	Ph C^4
 $B(C_6F_5)_4^-$ **6b**	0.69 (s, 3 H)	ZrMe	24.1	CCH_3
	1.70 (s, 3 H)	CCH_3	28.9	CCH_3
	1.76 (s, 3 H)	CCH_3	38.6	CMe_2
	5.84 (s, 5 H)	Cp	46.2	ZrMe
	5.89 (s, 1 H)	Cp′	102.1	Cp′
	6.15 (s, 1 H)	Cp′	111.9	Cp′
	6.26 (br, 1 H)	Ph H^1	114.1	Ph C^1
	6.42 (s, 1 H)	Cp′	114.5	Cp′
	6.99 (s, 1 H)	Cp′	115.1	Cp
	≈7.32 (br, 1 H)[e]	Ph H^3	117.8	Cp′
	7.71 (t, 1 H)	Ph H^5	128.2	Ph C^3
	≈7.84 (br, 1 H)[e]	Ph H^2	128.8	Ph C^5
	8.05 (br, 1 H)	Ph H^4	139.4	Ph C^2
			140.9	Ph C^4
 $MeB(C_6F_5)_3^-$ **7a**	0.40 (s, br, fwhs = 8.6, 3 H)	CH_3B	9.1 ($^1J_{CH}$ = 116)	CH_3B
	0.64 (s, 3 H)	ZrMe	20.2 ($^1J_{CH}$ = 127)	PhCH_3
	1.62 (s, 3 H)	CC^2H_3	23.7 ($^1J_{CH}$ = 128)	CC^1H_3
	1.69 (s, 3 H)	CC^1H_3	28.8 ($^1J_{CH}$ = 128)	CC^2H_3
	2.52 (s, 3 H)	PhCH_3	38.1	CMe_2
	5.80 (s, 5 H)	Cp	45.0 ($^1J_{CH}$ = 121)	ZrMe
	5.87 (m, 1 H)	Cp H^3	102.2 ($^1J_{CH}$ = 177)	Cp C^3
	6.12 (m, 1 H)	Cp H^1	112.4 ($^1J_{CH}$ = 179)	Cp C^1
	6.18 (d, 1 H, $^3J_{HH}$ = 6.7)	Ph H^1	114.5 ($^1J_{CH}$ = 176)	Cp C^4
	6.40 (m, 1 H)	Cp H^2	114.8 ($^1J_{CH}$ = 148)	Ph C^1
	6.93 (m, 1 H)	Cp H^4	115.2 ($^1J_{CH}$ = 179)	Cp
	7.30 (d, 1 H, $^3J_{HH}$ = 7.7)	Ph H^3	118.3 ($^1J_{CH}$ = 181)	Cp C^2
	7.59 (d, 1 H, $^3J_{HH}$ = 6.7)	Ph H^2	129.8 ($^1J_{CH}$ = 174)	Ph C^3
	7.79 (d, 1 H, $^3J_{HH}$ = 7.7)	Ph H^4	130.0	*i*-C of Cp
			130.5	*i*-C of Ph
			139.9 ($^1J_{CH}$ = 169)	Ph C^2
			140.8	*i*-C of PhCH_3
			141.7 ($^1J_{CH}$ = 163)	Ph C^4
 $B(C_6F_5)_4^-$ **7b**	0.68 (s, 3 H)	ZrMe	20.4	PhCH_3
	1.66 (s, 3 H)	CC^2H_3	24.0	CC^1H_3
	1.73 (s, 3 H)	CC^1H_3	29.0	CC^2H_3
	2.55 (s, 3 H)	PhCH_3	38.2	CMe_2
	5.81 (s, 5 H)	Cp	45.1	ZrMe
	5.87 (d, 1 H)	Cp H^3	101.8	Cp C^3
	6.11 (d, 1 H)	Cp H^1	111.9	Cp C^1
	6.20 (d, 1 H, $^3J_{HH}$ = 6.5)	Ph H^1	114.0	Cp C^4
	6.40 (d, 1 H)	Cp H^2	114.4	Ph C^1
	6.94 (d, 1 H)	Cp H^4	114.8	Cp
	7.31 (d, 1 H, $^3J_{HH}$ = 7.8)	Ph H^3	117.8	Cp C^2
	7.59 (d, 1 H, $^3J_{HH}$ = 6.5)	Ph H^2	129.1	Ph C^3
	7.80 (d, 1 H, $^3J_{HH}$ = 7.8)	Ph H^4	129.4	*i*-C of Cp
			130.0	*i*-C of Ph
			139.3	Ph C^2
			140.1	*i*-C of PhCH_3
			141.0	Ph C^4
 $MeB(C_6F_5)_3^-$ **8a**	0.44 (br, 3 H)	CH_3B	9.7	CH_3B
	0.71 (s, 3 H)	ZrMe	28.2 (br)	C(CH_3)$_2$
	1.53 (br, 12 H)	CMe_2	39.0	CMe_2
	5.01 (br, 1 H)	Cp′	47.0	ZrMe
	5.66 (br, 1 H)	Cp′	106.6 (br)	Cp′
	5.83 (br, 1 H)	Cp′	110.5 (br)	Cp′
	7.06 (br, 1 H)	Cp′	117.2 (br)	Cp′
	6.95 (d, 4 H, $^3J_{HH}$ = 7.0)	*o*-H of Ph	119.4 (br)	Cp′
	7.45 (t, 2 H, $^3J_{HH}$ = 7.5)	*p*-H of Ph	123.2 (br)	*o*-C of Ph
	7.60 (m, 4 H)	*m*-H of Ph	127.9 (br)	*p*-C of Ph
			134.4 (br)	*m*-C of Ph

Table 3 (*cont'd*)

Compound	^{1}H NMR [b,c]		^{13}C NMR [b,d]	
 **8b**	0.73 (s, 3 H)	ZrMe	28.3 (br)	C(CH_3)$_2$
	1.56 (br, 12 H)	CMe_2	39.0	CMe_2
	4.99 (br, 2 H)	Cp′	47.0	ZrMe
	5.65 (br, 2 H)	Cp′	106.6 (br)	Cp′
	5.83 (br, 2 H)	Cp′	110.5 (br)	Cp′
	7.08 [e]	Cp′	117.2 (br)	Cp′
	6.98 (d, 4 H, J_{HH} = 7.0)	*o*-H of Ph	119.4 (br)	Cp′
	7.46 (t, 2 H, $^3J_{HH}$ = 7.5)	*p*-H of Ph	123.2 (br)	*o*-C of Ph
	7.61 (m, 4 H)	*m*-H of Ph	127.9 (br)	*p*-C of Ph
			134.4 (br)	*m*-C of Ph
 **9a**	0.43 (br, 3 H)	CH_3B	9.6	CH_3B
	0.73 (s, 3 H)	ZrMe	20.4	PhCH_3
	1.51 (br, 12 H)	CMe_2	28.4	C(CH_3)$_2$
	2.38 (s, 6 H)	PhCH_3	38.6	CMe_2
	4.84 (br, 2 H)	Cp′	45.9	ZrMe
	5.62 (br, 2 H)	Cp′	106.4 (br)	Cp′
	5.76 (br, 2 H)	Cp′	110.4 (br)	Cp′
	7.04 (br, 2 H)	Cp′	117.0 (br)	Cp′
	6.89 (m, 4 H)	Ph H	118.7 (br)	Cp′
	7.37 (m, 4 H)	Ph H	123.3 (br)	Ph C
			135.0 (br)	Ph C
 **9b**	0.75 (s, 3 H)	ZrMe	20.4	PhCH_3
	1.53 (br, 12 H)	CMe_2	28.4 (br)	C(CH_3)$_2$
	4.92 (br, 2 H)	Cp′	38.7	CMe_2
	5.64 (br, 2 H)	Cp′	45.9	ZrMe
	5.79 (br, 2 H)	Cp′	106.5 (br)	Cp′
	≈7.04 [e]	Cp′	110.5 (br)	Cp′
	6.91 (m, 4 H)	Ph H	117.0 (br)	Cp′
	7.40 (m, 4 H)	Ph H	118.8 (br)	Cp′
			123.3 (br)	Ph C
			134.7 [e]	Ph C

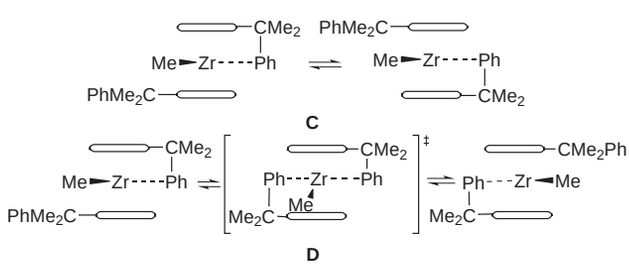
[a] The chemical shifts for the $MeB(C_6F_5)_3^-$ anion are virtually the same for all compounds and are as follows: ^{19}F NMR δ −133.6 (d, 6 F, *o*-F); −164.0 (t, 3 F, *p*-F); −166.8 (t, 6 F, *o*-F); ^{11}B NMR δ −15.2. [b] 500 MHz. [c] Cp H^n (n = 1–4) denotes hydrogens of the C_5 ring, coupled to Cp C^n (connectivity determined by C–H correlation). [d] 125.7 MHz. [e] Obscured by triphenylethane.

The complexes **6a**, **6b** and **7a**, **7b** are stable in CD_2Cl_2 up to −30 °C but significant broadening of the resonances is observed. Recooling the sample to −60 °C restores the original spectrum. This can be explained by the exchange processes observed in the EXSY spectrum of **7a** as discussed above.

The reactions of complexes **4** and **5** with $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ at −60 °C in CD_2Cl_2 lead to the formation of the solvent separated species $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me]^+[RB(C_6F_5)_3]^-$ (R = Me **8a** or C_6F_5 **8b**) and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me]^+[RB(C_6F_5)_3]^-$ (R = Me **9a** or C_6F_5 **9b**). However, the resulting spectra are more complex than for the cases described earlier. The reaction of **5** produces a simpler spectrum compared to that of **4** and therefore will be discussed in detail.

At −60 °C, the signals assigned for the cyclopentadienyl ring are unusually broad compared to those for complex **6** or **7**. However, the signals for the phenyl ring appear as two sharp doublets. Cooling the sample to −80 °C leads to a sharpening of *three* of the cyclopentadienyl ring signals whilst one remains broad and one of the phenyl ring signals broadens. Spin saturation experiments at this temperature reveal that the sharp signal at δ 4.84 exchanges with the broad signal at δ 5.62. Further cooling to −120 °C (in $CDCl_2F$) leads to further broadening of all of the peaks. Heating the sample leads to a coalescence of two of the cyclopentadienyl signals (δ 4.92 and 5.64) at −40 °C. The process is reversible and recooling the sample to −60 °C restores the original spectrum. This observation together with the observation of two coupled doublets for the phenyl ring (selective irradiation of one leads to the formation of a singlet in the other) indicates that more than one exchange process with different reaction rates is occurring.

In the absence of a fluxional process, four resonances for the co-ordinated and two resonances for the freely rotating phenyl ring would be expected. At −60 °C only *one* set of two signals is observed, however, therefore the two phenyl rings must be in rapid exchange with each other on the NMR timescale. This process could occur by either rapid exchange of the phenyl rings at *one* co-ordination site in a screen wiper type fashion (**C**) or by rapid exchange of the Zr–Me group between two sites (**D**, Scheme 5). Indeed, the ^{1}H NMR spectrum at −120 °C indicates



Scheme 5

two different phenyl rings and hence two different cyclopentadienyl rings but the signal assigned for the $[MeB(C_6F_5)_3]^-$ anion remains unchanged. Unfortunately we were not able to lower the temperature further and freeze out this process.

A second process is the exchange of the co-ordinated proton within the same ring, similar to the process observed for complexes **6** and **7** which is in competition with the co-ordination of the other ring.

The reaction of complex **4** or **5** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ is interesting. Unlike that of **1**, the formation of a homobinuclear complex could not be observed. Since the only difference between **1** and **4** is the substitution of the benzylic hydrogens in

1 with methyl groups, this subtle change had a significant change in the chemistry. Several reasons for this behaviour can clearly be identified: (a) the steric bulk of **4** is greater than that of **1**, as indicated by the solid state structures; (b) substitution of the benzylic hydrogens with methyl groups on the bridging carbon enhances ring closure; (c) the methyl groups have a +I effect, therefore the phenyl ring is more electron rich than in **1**. The factors (a)–(c), in addition to the *ansa* effect, enhance the co-ordination of the phenyl group to the cationic metal centre, unlike in **1**, where only the *ansa* effect is present. The introduction of a substituent in the *para* position of the phenyl ring has little, if any, influence on the chemical behaviour. However, due to a simplified spin system, the NMR spectra are easier to interpret.

Overall, the NMR data show the formation of the solvent separated species **8a**, **8b** and **9a**, **9b** similar to **6a**, **6b** and **7a**, **7b**, with the possible co-ordination of the phenyl rings, but unambiguous evidence for this could not be found in the collected data.

Conclusion

Monosubstituted zirconocene complexes with pendant phenyl rings **2** and **3** and bis-substituted zirconocene complexes **4** and **5** have been prepared and the solid state structure of one of each group has been determined. NMR Studies of the reaction of the zirconocenes **2**–**5** with either $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$ revealed the formation of discrete anions and cations **6**–**9**. These results are in marked contrast to that observed with $[Zr(\eta\text{-}C_5H_4R)_2Me_2]$ (R = H, Me, $SiMe_3$ or $Si(SiMe_3)_3$ [15]) which do not form discrete ion pairs. In the case of R = $Si(SiMe_3)_3$ the substituent is sterically more demanding than the CMe_2Ph group and should favour the formation of discrete anions and cations, taking only steric effects into account. The formation of the discrete ion pairs can be rationalised by the ability of the phenyl group to saturate the otherwise co-ordinatively unsaturated zirconium centre, therefore electronic effects are dominating in these complexes.

In the case of complexes **6** and **7**, the co-ordination of the phenyl ring *via* agostic interaction could be derived from NMR spectra. The picture for **8** and **9** is more complicated, however, because several competing dynamic processes occur preventing unambiguous assignment by NMR. The NMR studies of **6** and **7** show that the co-ordination of aromatic solvents such as toluene under standard polymerisation conditions is possible and likely. In addition, our investigations of **8** and **9** demonstrate the labile nature of the arene; rapid exchange between co-ordinated and unco-ordinated arene occurs even at −60 °C. With respect to olefin polymerisation catalysts, the arene co-ordination is labile enough to be displaced by an olefin monomer. The labile nature of the arene adduct might explain the difficulties in observing these proposed adducts. Further studies on **4** and **5** are currently being undertaken in this laboratory.

Experimental

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, 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 ampoules.

NMR Spectra were recorded at 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. The ^{13}C spectra were referenced with the solvent peak relative to TMS and were proton decoupled using a WALTZ sequence. CH Coupling constants were measured by coupled Pulsed Field Gradient-Heteronuclear Single Quantum Coherence (PFG-HSQC). ^{19}F NMR Spectra were referenced with external C_6F_6 (δ 163.0) and ^{11}B NMR spectra with $BF_3{\cdot}Et_2O$ (δ 0). Phase sensitive NOESY/EXSY spectra were performed using a standard Time Proportional Phase Increment (TPPI) pulse sequence and a mixing time of 650 ms at −60 °C. Mass spectra were determined by the EPSRC National Mass Spectrometry Service Centre by Dr. J. A. Ballantine.

The compounds $[Zr(\eta\text{-}C_5H_5)Cl_3]{\cdot}dme$ [19] and 6,6-dimethylfulvene [20] were prepared as described. The zirconocene dichlorides **2a–5a** were characterised by NMR spectroscopy and methylated without further purification.

Preparations

$[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Cl_2]$ 2a and $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Cl_2]$ 4a. Iodobenzene (6.12 g, 30 mmol) was added to a solution of 12 ml (30 mmol) *n*-butyllithium (2.5 mol l^{-1}) in 200 ml light petroleum at room temperature. A white solid precipitated and the reaction mixture was stirred for 20 min. The mixture was cooled to 0 °C and filtered. The residue was dissolved in 150 ml diethyl ether and cooled to −78 °C. Neat 6,6-dimethylfulvene (3.19 g, 30 mmol) was added and the reaction mixture allowed to warm to room temperature yielding a white suspension which was stirred overnight. Tetrahydrofuran (50 ml) was added to dissolve the precipitate and the clear solution recooled to −78 °C. The compound $[Zr(\eta\text{-}C_5H_5)Cl_3]{\cdot}dme$ (10.6 g, 30 mmol) was added in small portions and the slurry stirred for 1 h at this temperature before being warmed to room temperature. The reaction mixture was stirred overnight to yield a yellow-orange suspension. The volatiles were removed under reduced pressure to yield a yellow solid which was extracted several times into warm (50 °C) toluene. The extract was stored at −30 °C for 4 d to yield a white solid. Yield of **2a**: 2.46 g, 5.9 mmol (20%). The mother-liquor was concentrated and recooled to −30 °C. A second crop could be obtained which was a mixture of complexes **2a** and **4a** (≈2:1 by ^1H NMR). Complex **2a**: ^1H NMR ($CDCl_3$, 300 MHz, 20 °C) δ 1.76 (s, 6 H, CMe_2); 6.27 (s, 5 H, Cp); 6.37 ("t", 2 H, Cp′); 6.48 ("t", 2 H, Cp′) and 7.2–7.3 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 125.7 MHz, 20 °C) δ 30.5 (CCH_3); 41.3 (CCH_3); 117.0 (Cp′); 117.1 (Cp); 118.2 (Cp′); 127.1 (*p*-C of Ph); 127.3 (*m*-C of Ph); 129.2 (*o*-C of Ph); 143.4 (C_q); and 150.8 (C_q). Complex **4a**: ^1H NMR ($CDCl_3$, 300 MHz, 20 °C) δ 1.78 (s, 12 H, CMe_2); 6.02 ("t", 4 H, Cp′); 6.36 ("t", 4 H, Cp′) and 7.2–7.3 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$, 125.7 MHz, 20 °C) δ 29.3 (CCH_3); 40.4 (CCH_3); 113.0 (Cp′); 117.2 (Cp′); 126.1 (*p*-C of Ph); 126.1 (*m*-C of Ph); 128.1 (*o*-C of Ph); 142.0 (C_q); and 149.8 (C_q).

$[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Cl_2]$ 3a. The compound *n*-butyllithium (12 ml, 30 mmol, 2.5 mol l^{-1} in hexanes) was added to a solution of 5.13 g (30 mmol) of 4-bromotoluene in 200 ml of diethyl ether at room temperature. The reaction mixture was stirred at 30 °C for 1 h then cooled to −78 °C and 3.19 g (30 mmol) of pure 6,6-dimethylfulvene were slowly added dropwise. The resulting yellow solution was slowly warmed to room temperature. An off-white precipitation occurred which was dissolved by addition of 30 ml of thf. The slightly yellow solution was recooled to −78 °C and 10.6 g (30 mmol) of $[Zr(\eta\text{-}C_5H_5)Cl_3(dme)]$ were added in several portions. The slurry was stirred for 30 min at this temperature before being allowed to warm to room temperature. The off-white suspension was then stirred overnight. The volatiles were removed under reduced pressure and the resultant white solid was extracted into 100 ml of toluene at 50 °C. The extract was concentrated and stored at −30 °C to yield the desired compound as a white solid. Yield: 5.79 g, 13.6 mmol (45%). ^1H NMR ($CDCl_3$, 300 MHz, 20 °C) δ 1.77 (s, 6 H, CCH_3); 2.32 (s, 3 H, $PhCH_3$); 6.28

(s, 5 H, Cp); 6.37 ("t", 2 H, Cp′); 6.49 ("t", 2 H, Cp′); and 7.16 ("d", 4 H, Ph). ^{13}C NMR ($CDCl_3$, 75.5 MHz, 20 °C) δ 20.8 (PhCH_3); 29.5 (CCH_3); 40.0 (CCH_3); 114.2 (Cp′); 116.1 (Cp); 126.1 (*o*-C of Ph); 128.7 (*m*-C of Ph) and 135.8 (C_q).

[Zr(η-$C_5H_4CMe_2C_6H_4$Me-*p*)$_2Cl_2$] 5a. The compound *n*-butyllithium (24 ml, 60 mmol, 2.5 mol l^{-1} in hexanes) was added to a solution of 10.26 g (60 mmol) of 4-bromotoluene in 250 ml of diethyl ether at room temperature. The reaction mixture was stirred at 30 °C for 1 h, then cooled to −78 °C and 6.38 g (60 mmol) of neat 6,6-dimethylfulvene were slowly added. The yellow solution was slowly warmed to room temperature. An off-white precipitation occurred which was dissolved by addition of 30 ml of thf. The slightly yellow solution was recooled to −78 °C and 11.3 g (30 mmol) of $ZrCl_4$·2thf were added in several portions. The slurry was stirred for 30 min at this temperature before being allowed to warm to room temperature. The off-white suspension was stirred overnight. The volatiles were removed under reduced pressure and the resulting white solid was extracted into 180 ml of toluene at 50 °C. The extract was concentrated and stored at −30 °C to yield the desired compound as a white solid. Yield: 5.85 g, 10.5 mmol (35%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C) δ 1.75 (s, 12 H, CCH_3); 2.28 (s, 6 H, PhCH_3); 6.15 ("t", 4 H, Cp′); 6.34 ("t", 4 H, Cp′); and 7.08 (m, 8 H, Ph). ^{13}C NMR ($CDCl_3$, 125.7 MHz, 20 °C) δ 20.8 (PhCH_3); 29.4 (CCH_3); 40.1 (CCH_3); 113.1 (Cp′); 117.1 (Cp′); 126.0 (*m*-C of Ph); 128.8 (*o*-C of Ph); 135.6 (C_q); 142.3 (C_q); and 146.9 (C_q).

[Zr(η-C_5H_5)(η-$C_5H_4CMe_2$Ph)Me_2] 2. A suspension of 2.46 g (5.9 mmol) of complex **2a** in 80 ml of diethyl ether at −78 °C was treated with 4.00 ml (11.9 mmol) of MgMeBr (3 mol l^{-1} in diethyl ether) in a dropwise manner. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. The volatiles were removed under reduced pressure to yield an off-white solid, which was extracted into 180 ml of light petroleum. The extract was concentrated and cooled to −30 °C to yield cushions of needles. Yield: 1.27 g, 3.4 mmol (58%) (Found: C, 67.7; H, 7.1. $C_{21}H_{26}Zr$ requires C, 67.6; H, 6.9%). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C) δ −0.29 (s, 6 H, $ZrMe_2$); 1.61 (s, 6 H, CMe_2); 5.99 (s, 5 H, Cp); 6.04 (m, 4 H, Cp′); and 7.19–7.30 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 125.7 MHz, 20 °C) δ 30.0 (CCH_3); 30.5 (ZrMe); 39.6 (CCH_3); 108.6 (Cp′); 110.3 (Cp′); 110.6 (Cp); 125.8 (C_q); 126.0 (*m*-C of Ph); 128.0 (*o*-C of Ph); 137.6 (C_q); and 150.5 (C_q).

[Zr(η-C_5H_5)(η-$C_5H_4CMe_2C_6H_4$Me-*p*)Me_2] 3. The preparation was carried out in a manner similar to that for complex **2**. The crystals obtained were suitable for X-ray analysis. Yield: 3.66 g, 9.5 mmol (70%) (Found: C, 68.2; H, 7.3. $C_{22}H_{28}Zr$ requires C, 68.8; H, 7.4%). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C) δ −0.28 (s, 6 H, $ZrCH_3$); 1.60 (s, 6 H, CCH_3); 2.37 (s, 3 H, PhCH_3); 6.00 (s, 5 H, Cp); 6.04 (m, 4 H, Cp′); and 7.13 (m, 4 H, Ph). ^{13}C NMR ($CDCl_3$, 75.5 MHz, 20 °C) δ 20.8 (PhCH_3); 30.1 (CCH_3); 30.5 ($ZrCH_3$); 39.4 (CCH_3); 108.7 (Cp′); 110.2 (Cp′); 110.6 (Cp); 126.0 (*o*-C of Ph); 128.7 (*m*-C of Ph); 135.3 (C_q); 137.9 (C_q); and 147.6 (C_q).

[Zr(η-$C_5H_4CMe_2$Ph)$_2Me_2$] 4. To a suspension of 4.32 g (10.5 mmol) of complex **4a** (second fraction obtained from the preparation of **2a**) in diethyl ether, 14 ml (21 mmol) of LiMe (1.5 mol l^{-1}) in diethyl ether were added at −78 °C. After the addition was complete the reaction mixture was slowly warmed to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the off white residue was extracted into warm light petroleum. The extract was stored at 5 °C for 3 d to yield **4** as the only product. Crystals suitable for X-ray analysis were grown by slowly cooling a light petroleum solution to −80 °C. Yield: 0.54 g, 0.8 mmol (8%) (Found: C, 73.5; H, 7.6. $C_{30}H_{36}Zr$ requires C, 73.9; H, 7.4%). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C) δ −0.24 (s, 6 H, ZrMe); 1.58 (s, 12 H, CCH_3); 5.90 ("t", 4 H, Cp′); 5.98 ("t", 4 H, Cp′); and 7.19–7.27 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$, 75.5 MHz, 20 °C) δ 29.9 (CCH_3); 31.1 (ZrMe); 39.8 (CCH_3); 109.7 (Cp′); 110.8 (Cp′); 125.8 (*p*-C of Ph); 126.0 (*m*-C of Ph); 128.0 (*o*-C of Ph); 137.2 (C_q); and 150.6 (C_q).

Table 4 Crystallographic data of complexes **3** and **4**

	3	**4**
Formula	$C_{22}H_{28}Zr$	$C_{15}H_{18}Zr_{0.5}$
M	383.69	243.92
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*C*2/*c*
a/Å	7.009(3)	18.8890(8)
b/Å	11.633(4)	6.8630(3)
c/Å	12.838(4)	19.0360(5)
α/°	109.01(2)	
β/°	94.91(2)	101.401(3)
γ/°	106.07(2)	
V/Å^3	933.0	2419.0
Z	2	8
D_c/g cm^{-3}	1.37	1.34
T/K	110	125
μ(Mo-Kα)/mm^{-1}	0.58	0.46
Transmission coefficients	0.68–0.75	0.86–0.91
F(000)	400	1024
Total data	5648	6627
No. unique data	1144	2502
No. observed data [$I > 3\sigma(I)$]	1021	2463
No. parameters	209	141
R	0.0407	0.0403
R′	0.0501	0.0395
R(int)	0.049	0.029
Goodness of fit	1.0860	0.9832
Largest peak/e Å^{-3}	0.31	0.47

[Zr(η-$C_5H_4CMe_2C_6H_4$Me-*p*)$_2Me_2$] 5. The preparation was conducted in a similar manner to that of complex **4** but **5a** was used as starting material. Yield: 1.73 g, 3.3 mmol (31%) (Found: C, 73.9; H, 7.8. $C_{32}H_{40}Zr$ requires C, 73.9; H, 7.85%). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C) δ −0.21 (s, 6 H, ZrMe); 1.56 (s, 12 H, CCH_3); 2.31 (s, 6 H, Ph*Me*); 5.91 ("t", 4 H, Cp′); 5.98 ("t", 4 H, Cp′); and 7.10 ("s", 8 H, Ph). ^{13}C NMR ($CDCl_3$, 75.5 MHz, 20 °C) δ 20.8 (PhCH_3); 29.9 (CCH_3); 31.1 (ZrMe); 39.4 (CCH_3); 109.6 (Cp′); 110.1 (Cp′); 125.9 (*m*-C of Ph); 128.6 (*o*-C of Ph); 135.2 (C_q); 137.4 (C_q); and 147.7 (C_q).

Low temperature NMR studies on cationic compounds: general procedure

The zirconocene complex (0.1 mmol) was dissolved in 0.25 ml of CD_2Cl_2 and transferred to a precooled (−78 °C) NMR tube. The cation generating agent (0.11 mmol) such as $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$ was dissolved in 0.28 ml of CD_2Cl_2 and transferred to the top of the zirconocene solution in the NMR tube. The tube was sealed with a Suba Seal and shaken vigorously to ensure complete mixing. The colour changed to yellow and the sample was inserted into a precooled (−60 °C) spectrometer. The ^{1}H, ^{13}C-{^{1}H}, H–H COSY and C–H COSY spectra were recorded at −60 °C. The sample was warmed to ambient temperature in steps of 20 K and at each temperature a ^{1}H NMR spectrum was recorded.

Crystal structure determination

Data collection and processing. Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) as summarised in Table 4. The images were processed with the DENZO and SCALEPACK programs.[21] Corrections for Lorentz-polarisation effects were performed.

Structure solution and refinement. All solution, refinement, and graphical calculations were performed using the CRYSTALS[22] and CAMERON[23] software packages. Figs. 1 and 2 were generated with ORTEP,[24] Fig. 3 with CAChe.[25] The crystal structure was solved by direct methods using the SIR 92 program[26] and refined by full-matrix least squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme was applied as well as an empirical absorption correction.[27]

For compound **3** the crystal was of moderate quality, thus giving a relatively low ratio of data to refined parameters. We have processed the data for two different mosaicities and obtained $R(\text{int}) = 0.049$ at low mosaicity and 0.033 at higher mosaicity. The final R factors shift from 0.0407 ($R' = 0.0501$) to 0.0448 (0.0542) for processing with higher mosaicity leading us to believe the data processed with a lower mosaicity better represent the molecular structure which is unambiguous in either case.

CCDC reference number 186/1459.

See http://www.rsc.org/suppdata/dt/1999/2111/ for crystallographic files in .cif format.

Acknowledgements

D. H. wishes to thank the Deutsche Forschungsgemeinschaft for financial support and L. H. D. thanks St. John's College (Oxford) for a Junior Research Fellowship.

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