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Synthesis and catalytic properties of *ansa*-binuclear metallocenes of the Group IV transition metals

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Abstract

The new *ansa*-bridged mono- and bi-nuclear Group IV metallocenes, $\{Zr[X(\eta\text{-}C_5H_4)_2](\eta\text{-}C_5H_5)Cl\}$ (where, $X = SiMe_2$ (1), CMe_2CMe_2 (2)), $\{[(\eta\text{-}C_5H_5)HfCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)HfCl_2]\}$ (3). $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2CH_2CH_2SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)ZrCl_2]\}$ (4), $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_9H_6][(\eta\text{-}C_5H_5)ZrCl_2]\}$ (5), $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_9H_6\text{-}(SiMe_2)\text{-}\eta\text{-}C_9H_6][(\eta\text{-}C_5H_5)ZrCl_2]\}$ (6), $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)MCl_2]\}$, $M = Hf$ (7) or Ti (8), $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5Me_5)TiCl_2]\}$ (9) and $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][TiCl_3]\}$ (10) are described. These compounds in the presence of methylaluminoxane are catalysts for the polymerisation of ethene and propene.

Keywords: Zirconium; Hafnium; Titanium; Metallocenes; Catalysis; Polyethylene; Olefin-polymerisation

1. Introduction

It was decided to attempt the synthesis of a variety of new and simple *ansa*-bridged homo- and hetero-binuclear Group IV metallocenes, and to examine their catalytic properties towards olefin polymerisation. In 1989, Petersen described the methathesis of $[\{Si\text{-}Me_2\text{-}(C_5H_4)_2\}Li_2]$ with two equivalents of $[Zr(\eta\text{-}C_5H_5)Cl_3]$ · 2THF to give the *ansa*-bridged homo-binuclear zirconocene derivative, $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)ZrCl_2]\}$ (11) [1]. It was decided extend this strategy to prepare *ansa*-bridged homo- and hetero-binuclear Group IV metallocenes. Recent independent reports have described the binuclear cyclopentadienyl titanium compounds $\{[(\eta\text{-}C_5H_5)TiCl_2]\text{-}[\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)TiCl_2]\}$ [2], $\{[TiCl_3][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][TiCl_3]\}$ [3], $\{[(\eta\text{-}C_5H_5)TiCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_5)ZrCl_2]\}$ [4], $\{[(\eta\text{-}C_5H_5)TiCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5Me_5)ZrCl_2]\}$ [4], $\{[(\eta\text{-}C_5H_5)ZrCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)ZrCl_2]\}$ [5], and $\{[M(CO)_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}CH_2\text{-}\eta\text{-}C_5H_4]\text{-}[M(CO)_2]\}$, where $M = Rh$, Ir [6], and $\{[(\eta\text{-}C_5H_5)Zr\text{-}$ $Cl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(1,4\text{-}C_6H_4)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)ZrCl_2]\}$ [7].
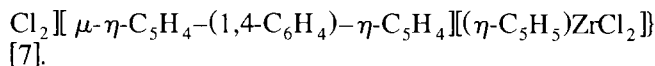
2. Results and discussion

Treatment of the previously reported compounds $Li_2[SiMe_2(C_5H_4)_2]$ [1] or $[(C_5H_4MgCl)CMe_2CMe_2\text{-}(C_5H_4MgCl)]$ · 4THF [8] with one equivalent of $[Zr(\eta\text{-}C_5H_5)Cl_3]$ · DME gave crystals of the pale yellow mononuclear *ansa*-bridged complexes, $\{Zr[X(\eta\text{-}C_5H_4)_2](\eta\text{-}C_5H_5)Cl\}$, where $X = SiMe_2$ (1) or CMe_2CMe_2 (2). The analytical and spectroscopic data characterising 1 and 2, and all other new compounds described in this work, are given in Table 1. These data will not be discussed further except where the interpretation is not straightforward.

The crystal structure of compound $\{Zr[SiMe_2(\eta\text{-}C_5H_4)_2](\eta\text{-}C_5H_5)Cl\}$ 1 has been determined. The molecular structure is shown in Fig. 1 and selected interatomic distances (Å) and angles (deg) are given in Table 2. The most significant feature of the structure is that all three C_5-rings are bound in an η^5-fashion. The Zr–C distances show large variations, ranging from 2.564 to 2.676 Å and averaging 2.61 Å. The spread of Zr–C distances is large, but a similar range is often seen

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in complexes with bulky substituted cyclopentadienyl ligands. This distance is longer than that observed in [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] (2.49 Å) [9], but is similar to that observed in [Zr(η-C$_5$H$_5$)$_3$Cl] (2.58 Å) [10], the Me$_2$C-bridged analogue, {Zr[Me$_2$C(η-C$_5$H$_4$)$_2$](η-C$_5$H$_5$)Cl} (2.58 Å) [11] and [Zr(η-C$_5$H$_5$)$_3$(η^1-C$_5$H$_5$)] (2.58 Å) [12]. The Zr–Cl distance of 2.55 Å is 0.11 Å longer than in [Zr(η-C$_5$H$_5$)$_2$Cl$_2$], but is similar to that in [Zr(η-C$_5$H$_5$)$_3$Cl] (2.53 Å) and [Zr{Me$_2$C(η-C$_5$H$_4$)$_2$}(η-

C$_5$H$_5$)Cl] (2.54 Å). The Cp-centroid–Zr–Cp centroid angles average 117.2° and the Cp-centroid–Zr–Cl angles average 99.7°. These are similar to those in [Zr(η-C$_5$H$_5$)$_3$ZrCl] (117.3° and 99.4° respectively). These results clearly indicate that, if the presence of the ansa-bridge is neglected, then the three Cp rings in compound 1 are located in a typical [M(η-C$_5$H$_5$)$_3$X] geometry with effective C_{3v} symmetry. However, the tetrahedral co-ordination environment of the Si atom is

Table 1
Analytical and spectroscopic data

Compound [a]			NMR data [b]
1 Pale yellow			^{1}H [c]: 6.56 [2H, pseudo q (J 2.0), C$_5$H$_4$], 6.28 [2H, pseudo q (J 2.0), C$_5$H$_4$], 5.91 [2H, pseudo q (J 2.0),
C	54.0	(58.0)	C$_5$H$_4$], 5.67 [2H, pseudo q (J 2.0), C$_5$H$_4$], 5.55 [5H, s, C$_5$H$_5$], 5.28 [3H, s, SiCH$_3$], 5.27 [3H, s, SiCH$_3$]
H	5.1	(5.1)	
Cl	9.35	(9.4)	
2 Pale yellow			^{1}H [c]: 6.16 [2H, pseudo q (J 3.0), C$_5$H$_4$], 5.90 [2H, pseudo q (J 3.0), C$_5$H$_4$], 5.74 [5H, s, C$_5$H$_5$], 5.71
C	63.4	(62.4)	[2H, pseudo q (J 3.0), C$_5$H$_4$], 1.07 [12H, s, CH$_3$ (bridge)].
H	6.2	(6.24)	^{13}C: 144.26 [s, C$_5$H$_4$ (ipso carbon)], 123.49 [d (J 173), C$_5$H$_4$], 116.66 [d (J 178), C$_5$H$_4$],
Cl	8.9	(7.7)	114.04 [d (J 173), C$_5$H$_5$], 113.66 [d (J 171), C$_5$H$_4$], 95.12 [d (J 162), C$_5$H$_4$], 41.33 [s, C(CH$_3$)$_2$
			(bridge)], 27.97 [q (J 125), CH$_3$ (bridge)], 27.81 [q (J 125), CH$_3$ (bridge)]
3 Grey			^{1}H [d]: 6.62 [4H, t (J 2.5), C$_5$H$_4$], 6.49 [4H, t (J 2.5), C$_5$H$_4$], 6.29 [10H, s, C$_5$H$_5$], 0.63 [6H, s, Si–CH$_3$].
C	32.5	(32.4)	^{13}C [c]: 124.30 [C$_5$H$_4$], 122.59 [ipso carbon, C$_5$H$_4$], 116.47 [C$_5$H$_4$], 114.94 [C$_5$H$_5$], –0.92 [Si–CH$_3$]
H	2.8	(3.0)	
Cl	17.7	(17.4)	
4 White			^{1}H [c]: 6.69 [4H, t (J 2.5), C$_5$H$_4$], 6.55 [4H, t (J 2.5), C$_5$H$_4$], 6.45 [10H, s, C$_5$H$_5$], 0.59 [4H, s,
C	42.9	(43.0)	Si–CH$_2$], 0.27 [12H, s, Si–CH$_3$]
H	4.8	(4.7)	
5 Yellow			^{1}H [c]: 7.67–7.71 [2H, m, aromatics], 7.29–7.33 [2H, m, aromatics], 6.99 [1H, d (J 3.4), C$_5$ ring
C	45.8	(45.2)	(α or β) of ind.], 6.84 [1H, d, (J 3.4), C$_5$ ring (α or β) of ind.], 6.82 [1H, pseudo q (J 2.5), C$_5$H$_4$],
H	4.0	(3.8)	6.66 [1H, pseudo q (J 2.5), C$_5$H$_4$], 6.61 [1H, pseudo q (J 2.5), C$_5$H$_4$], 6.58 [1H, pseudo q (J 2.5),
Cl	20.3	(20.55)	C$_5$H$_4$], 6.36 [5H, s, C$_5$H$_5$], 6.06 [5H, s, C$_5$H$_5$], 0.84 [3H, s, Si–CH$_3$], 0.79 [3H, s, Si–CH$_3$]
rac-6 Yellow			^{1}H [c]: 7.62 [2H, dd (J 8.3, 0.9), a or d], 7.35 [2H, dd (J 8.4, 0.9), a or d], 7.09–7.22 [4H, m, b or c],
C	49.35	(48.65)	7.14 [2H, d (J 3.3), α or β], 6.88 [2H, d (J 3.3), α or β], 6.02 [10H, s, C$_5$H$_5$], 0.97
H	3.85	(3.8)	[6H, s, Si–CH$_3$]
Cl	19.15	(19.15)	
7 Grey			^{1}H [c]: 6.71 [2H, t (J 2.5), C$_5$H$_4$], 6.63 [2H, t (J 2.5), C$_5$H$_4$], 6.59 [2H, t (J 2.5), C$_5$H$_4$], 6.50 [2H,
C	36.15	(36.3)	t (J 2.5), C$_5$H$_4$], 6.40 [5H, s, C$_5$H$_5$], 6.30 [5H, s, C$_5$H$_5$], 0.64 [6H, s, Si–CH$_3$]
H	3.3	(3.3)	
Cl	20.1	(19.5)	
8 Red			^{1}H [c]: 6.83 [2H, t (J 2.5), C$_5$H$_4$], 6.73 [2H, t (J 2.5), C$_5$H$_4$], 6.62 [2H, t, (J 2.5), C$_5$H$_4$], 6.59
C	44.2	(44.2)	[2H, t, (J 2.5), C$_5$H$_4$], 6.47 [5H, s, C$_5$H$_5$], 6.43 [5H, s, C$_5$H$_5$], 0.63 [6H, s, Si–CH$_3$]
H	4.0	(4.0)	
9 Red			^{1}H [c]: 6.73 [2H, t (J 2.5), C$_5$H$_4$], 6.54 [2H, t (J 2.5), C$_5$H$_4$], 6.43 [2H, t (J 2.5), C$_5$H$_4$], 6.37 [5H, s,
C	48.25	(48.55)	C$_5$H$_5$], 6.13 [2H, t (J 2.5), C$_5$H$_4$], 2.02 [15H, s, C$_5$(CH$_3$)$_5$], 0.62 [6H, s, Si–CH$_3$]
H	5.1	(5.15)	
10 Yellow			^{1}H [c]: 7.26 [2H, t (J 2.5), C$_5$H$_4$], 7.09 [2H, t (J 2.5), C$_5$H$_4$], 6.72 [2H, t, (J 2.5), C$_5$H$_4$], 6.60 [2H,
C	35.35	(35.95)	t (J 2.5), C$_5$H$_4$], 6.45 [5H, s, C$_5$H$_5$], 0.73 [6H, s, Si–CH$_3$]
H	3.35	(3.35)	
Cl	30.6	(31.2)	

[a] Analytical data given as: found (calculated) %. [b] ^{1}H NMR at 300 MHz, ^{13}C at 75 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (in Hz) and assignment. [c] In [^{2}H$_6$] benzene. [d] In [^{2}H$_2$] dichloromethane.
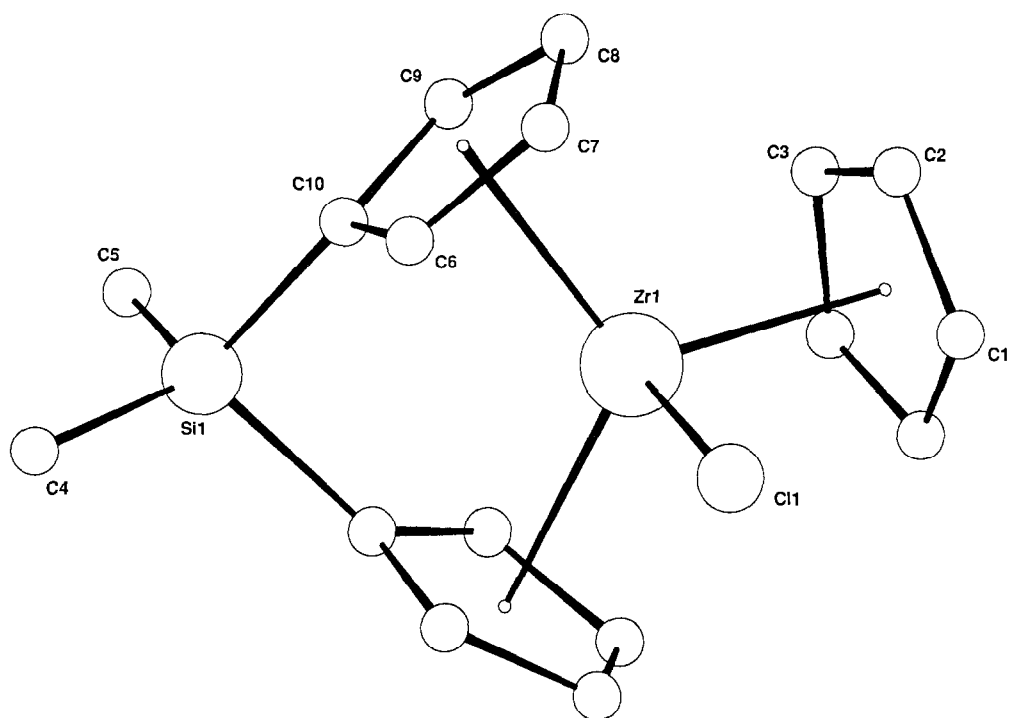
Fig. 1. Molecular structure of {Zr[SiMe$_2$(η-C$_5$H$_4$)$_2$](η-C$_5$H$_5$)Cl} **1**.
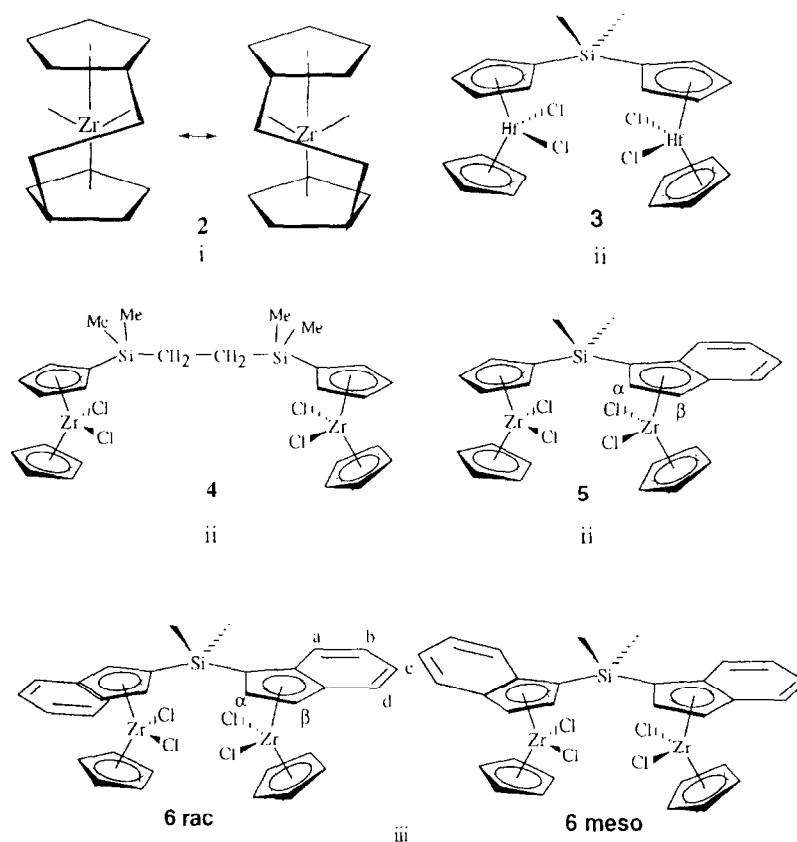
Scheme 1. (i) Showing the proposed dynamic interchange process of the *ansa*-backbone of **2**. (ii) Structures proposed for **3**, **4** and **5**. (iii) The meso and rac isomers of **6**.

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Table 2
Selected interatomic distances (Å) and angles (deg) for compound 1

Zr(1)–Cl(1)	2.548	C(1)–C(2)	1.404
Zr(1)–Cp(1)cent.	2.32	C(2)–C(2)	1.411
Zr(1)–Cp(2)cent.	2.32	C(3)–C(3)	1.410 [a]
Zr(1)–C(1)	2.662	C(6)–C(7)	1.424
Zr(1)–C(2)	2.631	C(7)–C(8)	1.390
Zr(1)–C(3)	2.564	C(8)–C(9)	1.417
Zr(1)–C(6)	2.577	C(9)–C(10)	1.425
Zr(1)–C(7)	2.641	C(10)–C(6)	1.414
Zr(1)–C(8)	2.676	Si(1)–C(10)	1.859
Zr(1)–C(9)	2.571	Si(1)–C(4)	1.855
Zr(1)–C(10)	2.597	Si(1)–C(5)	1.853
Cp(1)cent.–Zr(1)–Cp(1)cent. [a]	117.80		
Cp(1)cent.–Zr(1)–Cp(2)cent.	116.92		
Cp(1)cent.–Zr(1)–Cl(1)	99.66		
Cp(2)cent.–Zr(1)–Cl(1)	99.82		
C(4)–Si(1)–C(5)	114.71		
C(4)–Si(1)–C(10)	112.32		
C(5)–Si(1)–C(10)	111.52		
C(10)–Si(1)–C(10) [a]	92.48		
Dihedral angle between:			
Cp(1) and Cp(1)	67.37		
Cp(1) and Cp(2)	61.93		

Cp refers to η-C₅-ring.
[a] The atoms marked thus are generated from the asymmetric unit using the mirror plane.

significantly distorted. For example, The C(10)–Si–C(10′) angle is 92.48°, which is 17.0° smaller than the value expected for the symmetrical tetrahedral arrangement (109.5°). The Si–C(10)–Cp(1) centroid angle is 167°, which is also distorted from the expected value (180°). This suggests Cp(1) and Cp*(1) rings are forced to be canted in order to form a typical $[M(\eta\text{-}C_5H_5)_3X]$ geometry. Compound 1 has a C_v symmetry with a mirror plane which contains the zirconium, chlorine, bridging silicon atom and C(1) of the η-C₅H₅ ring. The room temperature ¹H NMR spectra of compound 1 is consistent with this molecular structure in which the two C₅H₄ rings are equivalent but that there is fast reorientation of the η-C₅H₅ ring about the zirconium–ring centroid axis.

However, compound 2 is chiral, corresponding to C_1 point group, and can exist in two enantiomeric forms, as shown in Scheme 1. The room temperature ¹H NMR spectrum of compound 2 clearly indicates that the ligand framework structure of 2 must interconvert with its mirror image fast enough to bring about an equivalence of the two C₅H₄ rings and the two methyl groups of the CMe₂CMe₂ bridge, and that also there is fast reorientation of the η-C₅H₅ ring. This gives 2 a pseudo C_v symmetry with a pseudo mirror plane. The same interpretation applies to the ¹³C{¹H} NMR spectrum of 2.

The high resolution solid state ¹³C CP–MAS NMR spectra of {Zr[CMe₂CMe₂(η-C₅H₄)₂](η-C₅H₅)Cl} 2 have been studied. The room temperature ¹³C solid state

NMR spectrum is shown in Fig. 2. The spectrum is quite different from solution ¹³C{¹H} NMR spectra of compound 2 since there are four signals assignable to the ipso-carbons (near 145 ppm) and two sharp singlets attributed to the η-C₅H₅ rings (near 115 ppm). Taking into account degeneracies, and the presumption that there is one peak hidden underneath the η-C₅H₅ signals, there are a total of 16 signals for the C₅H₄ groups. This spectrum is consistent with the proposition that compound 2 exists in two enantiomeric forms. Variable-temperature ¹³C CP–MAS NMR spectra were recorded between 206 and 409 K. The cyclopentadienyl regions of the spectra were unchanged over the whole temperature range. However, the methyl regions of the spectra showed considerable broadening as the temperature was lowered, and at 206 K they have virtually broadened into the baseline. This observation may be understood if the reorientation of the methyl groups about their local C_3 axes slows to the point where the rate is of the order of the frequency of the H r.f. decoupling field (50–60 KHz) and also that the resonances are considerably dipolar broadened. It is interesting to note that the C₅H₅ ring reorientation occurs at a considerably greater rate than the methyl reorientation at these low temperatures, indicating just how facile η-C₅H₅ ring reorientation processes are.

The primary bonding interaction between the η-cyclopentadienyl ligands and metal involves the C₅-ring p_z orbitals. When three cyclopentadienyl ligands are
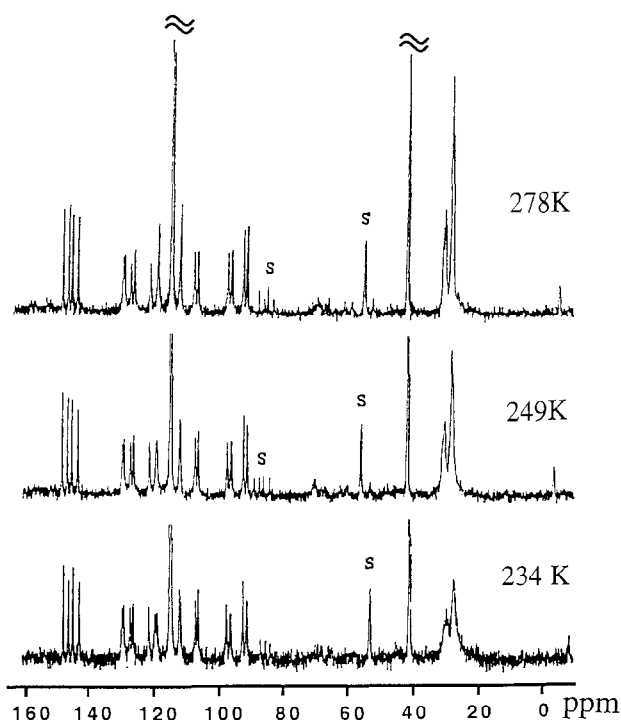

Fig. 2. Room temperature ¹³C CP–MAS solid-state NMR spectrum of compound 2.

placed around a metal atom in a typical $[M(\eta\text{-}C_5H_5)_3X]$ geometry, a large splitting of these orbitals occurs due to ligand–ligand interactions. The resulting highest energy orbital transforms as an a_2 representation under C_{3v} symmetry. However, Zr cannot stabilise the a_2 orbital, rendering it a high-energy metal–ligand non-bonding orbital [13].

The three η-cyclopentadienyl rings of the compounds 1 and 2 [14] are located in a tetrahedral $[M(\eta\text{-}C_5H_5)_3X]$ geometry, with local C_{3v} symmetry if the ansa-bridge is neglected. The electronic structures of 1 and 2 may be considered to be essentially the same as for $[M(\eta\text{-}C_5H_5)_3X]$. The compounds 1 and 2 appear to be 20-electron complexes, if the normal electron counting rules are applied in which the neutral η-cyclopentadienyl ligands are five-electron donors, the Cl radical is a one-electron donor, and the zirconium atom has four electrons. However, assuming an idealised C_{3v} symmetry, the cyclopentadienyl-based a_2 orbital cannot donate to the metal [5,6], so that the three $(\eta\text{-}C_5H_5)_3$ ligand system actually donates two electrons fewer than

the formal count of 15. This results in an electron count of 18-electrons for 1 and 2.

Treatment of the compound $Li_2[SiMe_2(C_5H_4)_2]$ [15] with two equivalents of $[Hf(\eta\text{-}C_5H_5)Cl_3] \cdot$ DME in refluxing toluene for 17 h gives the compound $\{[(\eta\text{-}C_5H_5)\text{-}HfCl_2][\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2)\text{-}\eta\text{-}C_5H_4][(\eta\text{-}C_5H_5)\text{-}HfCl_2]\}$ (3) as a grey solid. Similarly, the compound $\{[(\eta\text{-}C_5H_5)ZrCl_2]_2[\mu\text{-}\eta\text{-}C_5H_4\text{-}(SiMe_2CH_2CH_2Si\text{-}Me_2)\text{-}\eta\text{-}C_5H_4]\}$ (4) was synthesised from $Li_2[SiMe_2 CH_2\text{-}CH_2SiMe_2(C_5H_4)_2]$ and $[Zr(\eta\text{-}C_5H_5)Cl_3] \cdot$ DME.

A mixture of $Li_2[SiMe_2(C_5H_4)(C_9H_6)]$ [16] and two equivalents of $[Zr(\eta\text{-}C_5H_5)Cl_3] \cdot$ DME gave the compound $\{[(\eta\text{-}C_5H_5)ZrCl_2][(\mu\text{-}\eta\text{-}C_5H_4)\text{-}(SiMe_2)\text{-}\eta\text{-}C_9H_6][(\eta\text{-}C_5H_5)ZrCl_2]\}$ (5). The ^1H NMR spectrum shows the expected resonances of the indenyl protons, which appear as a multiplet corresponding to four aromatic protons in the region δ 7.71–7.29 ppm, and two sets of doublets (each 1H) with J values of 3.4 Hz corresponding to the α and β hydrogens of the five-membered ring of the indenyl, at δ 6.99 and 6.84 ppm. The similar assignment for the indenyl protons has been
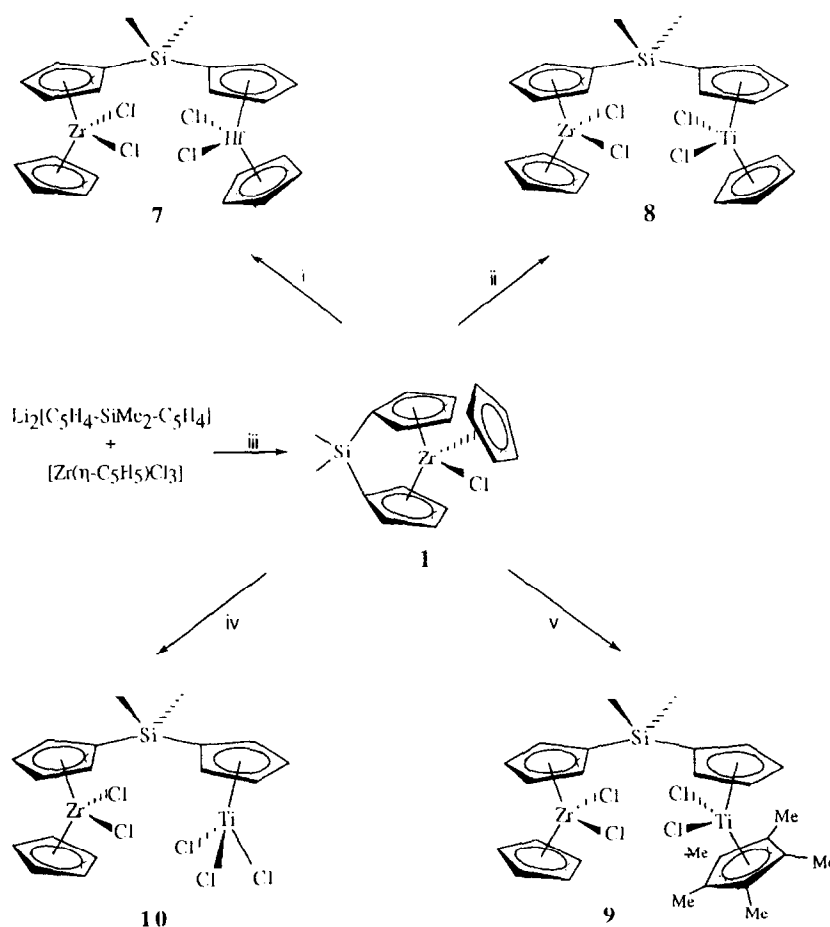

Scheme 2. (i) $[Zr(\eta\text{-}C_5H_5)Cl_3] \cdot$ DME in toluene, reflux for 17 h, yield 53%. (ii) $[Ti(\eta\text{-}C_5H_5)Cl_3]$ in toluene, reflux for 17 h, yield 53%. (iii) In toluene at r.t. for 17 h, yield 20%. (iv) $[Ti(\eta\text{-}C_5Me_5)Cl_3]$ in toluene, reflux for 17 h, yield 41%. (v) $TiCl_4$ in toluene at r.t. for 17 h, yield 40.5%.

reported for related compounds [17–20]. The structures proposed for compounds 3–5 are shown in Scheme 1.

Treatment of the compound $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot DME$ with $Li_2[SiMe_2(C_9H_6)_2]$ [21] gives a mixture of the compounds *rac*- and *meso*-{[$(\eta\text{-}C_5H_5)ZrCl_2$][μ-η-C_9H_6-$(SiMe_2)$-η-C_9H_6][$(\eta\text{-}C_5H_5)ZrCl_2$]} (6) as a yellow powder. The two stereoisomers, are shown in Scheme 1. However, only the *rac*-isomer is isolated. The low yield of this synthesis can be attributed in part to the difficulty in separating the stereoisomers since they have very similar solubility: the *meso*-isomer is slightly more soluble in toluene than the *rac*-isomer. The ^{1}H NMR spectrum of the rac-isomer of 6 (Table 1) may be assigned on the basis of the C_2 symmetry shown in Scheme 1. Thus the pairs of η-indenyl, η-C_5H_5 and methyl groups are equivalent. Although resonances of the indenyl protons are slightly different from those in compound 5 they are readily identified. The two sets of doublet of doublets (each 2H) with J values of 8.3 and 0.9 Hz at δ 7.62 and 7.35 ppm are assignable to protons H_a and H_d (for atom-labelling see Scheme 1). The doublet of doublets spin–spin coupling patterns are attributed to the coupling between H_a or H_d and protons in ortho- and meta-positions in the phenyl ring (H_b and H_c). The resonances for the proton H_b and H_c appear in the region of δ 7.22–7.09 ppm as a multiplet (4H) due to complex coupling within the phenyl ring. The two sets of doublets at δ 7.14 and 6.88 ppm (each 2H) are assignable to the H_α and H_β protons of the five-membered ring of the indenyl group. A similar assignment for the indenyl protons has been reported [5]. The remaining proton resonances for the methyl protons of the SiMe₂-bridge, δ 0.97 ppm, and the protons of the C_5H_5 rings (δ 6.02 ppm) are readily assignable singlets.

The compounds $\{Zr[X(\eta\text{-}C_5H_4)_2](\eta\text{-}C_5H_5)Cl\}$, where $X = SiMe_2$ (1), CMe_2CMe_2 (2), were examined as precursors for the synthesis of new *ansa*-bridged hetero-binuclear Group IV metallocenes, but only compound 1 gave the desired new *ansa*-bridged hetero-binuclear Group IV metallocenes. The metathesis reactions between compound 1 and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot DME$, $[Ti(\eta\text{-}C_5H_5)Cl_3]$, $[Ti(\eta\text{-}C_5Me_5)Cl_3]$ and $TiCl_4$ were studied.

In a typical reaction, a mixture of compound 1 and one equivalent of $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot DME$ was refluxed in toluene for 17 h affording the hetero-binuclear compound {[$(\eta\text{-}C_5H_5)ZrCl_2$][μ-η-C_5H_4-$(SiMe_2)$-η-C_5H_4][$(\eta\text{-}C_5H_5)HfCl_2$]} (7) as a grey solid. In a similar manner, the reaction between 1 and $[Ti(\eta\text{-}C_5H_5)Cl_3]$ gave the compound {[$(\eta\text{-}C_5H_5)ZrCl_2$][μ-η-C_5H_4-$(SiMe_2)$-η-C_5H_4][$(\eta\text{-}C_5H_5)TiCl_2$]} (8). During the course of this work, Nifant'ev and co-workers reported the synthesis of compound 8 using a different method [22].
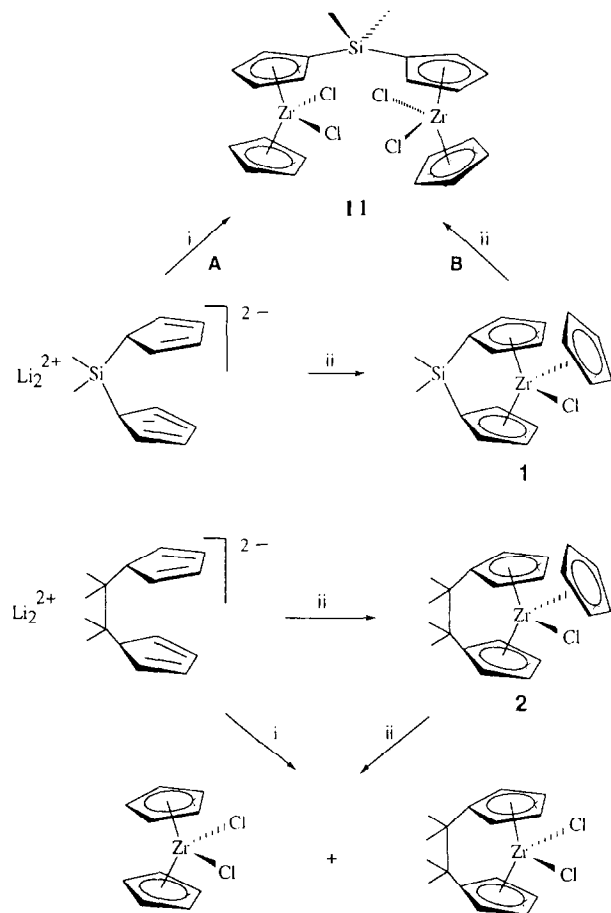
Scheme 3. Showing the different reaction pathways of the *ansa*-compounds 1 and 2. (i) Two moles of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot DME$. (ii) One mole of $[M(\eta\text{-}C_5H_5)Cl_3]\cdot DME$.

The compound {[$(\eta\text{-}C_5H_5)ZrCl_2$][μ-η-C_5H_4-$(SiMe_2)$-η-C_5H_4][$(\eta\text{-}C_5Me_5)TiCl_2$]} (9) was synthesised in a similar manner to 8 using $[Ti(\eta\text{-}C_5Me_5)Cl_3]$. Treatment of a toluene solution of compound 1 with one equivalent of $TiCl_4$ gave the hetero-binuclear compound {[$(\eta\text{-}C_5H_5)ZrCl_2$][μ-η-C_5H_4-$(SiMe_2)$-η-C_5H_4][$TiCl_3$]} (10) as a yellow powder. The structures proposed for the compounds 7–10 are shown in the Scheme 2.

The synthesis of the compounds 8–10 suggests that the compound 1 acts as an intermediate in the synthesis of binuclear *ansa*-bridged metallocene compounds, since in the direct reaction between $Li_2[SiMe_2(C_5H_4)_2]$ and two equivalents of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot DME$ giving 11 (see route A in Scheme 3). Thus it appears that it is exclusively one of the η-C_5H_4 groups of 1 which undertakes methathesis with a Zr–chlorine (route B) even though there is the possibility of methathesis between the chlorine and the η-C_5H_5 group. This latter reaction would give the mono-nuclear compounds *ansa*-$[SiMe_2(\eta\text{-}C_5H_4)_2ZrCl_2]$ and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$. It is interesting that the *ansa* compound 2 with $[M(\eta\text{-}$

Table 3
Data for ethylene polymerisation studies [a]

Compound	Time (min)	Yield (g)	Activity [b] (g PE mol M h^{-1})	T_m (°C)	M_n ($\times 10^{-5}$)	M_w/M_n
3	240	0.63	2.50×10^4	138.6	1.42	11.2
4	1	1.10	1.00×10^7	—	—	—
5	4	1.29	3.10×10^6	139.9	1.96	2.7
6	1	0.90	8.66×10^6	139.6	1.70	2.5
7	120	1.81	1.45×10^5	138.8	2.29	3.9
8	7	1.31	1.70×10^6	138.9	2.16	3.75
9	11	2.13	1.86×10^6	137.8	1.49	4.7
10	57	1.93	3.30×10^5	137.7	—	—
11	60	1.81	2.90×10^5	139.6	1.31	5.4
Cp_2ZrCl_2	5	1.86	3.57×10^6	138.3	0.99	2.5
Cp_2TiCl_2	5	1.72	3.31×10^6	139.6	1.73	2.1
Cp_2HfCl_2	30	2.80	8.95×10^5	138.7	1.64	2.5
$CpTiCl_3$	62	1.63	2.52×10^5	—	—	—

$Cp = \eta\text{-}C_5H_5$.
[a] Conditions: 2 bar absolute monomer pressure, 30°C, 210 cm^3, toluene, 0.9 g MAO, Al/M = 2500. [b] mol M: total amount of metal used (6.25 × 10^{-6} mol for each experiment).

$C_5H_5)Cl_3$] does not give binuclear *ansa*-metallocenes, but rather the η-C_5H_5 is transferred rather than one of the η-C_5H_4 ligands (see Scheme 3). This difference can be attributed to a greater strain in the *ansa*-bis-η-cyclopentadienylzirconium system in compound **1** than **2** since the former has only a single bridging atom.

3. Polymerisation studies

One aim of this research was to find interesting Ziegler–Natta catalysts and their polymers and, possibly, a 'living' catalyst system. A characteristic property of a living catalyst system is that the molecular weight

distribution (M_w/M_n) of the resulting polymer is unity [23].

Ethene polymerisations were performed in toluene at 30°C with a monomer pressure of 2 bar. The new metallocenes used as catalysts were **3**–*rac*-**6**, **7**–**10**, {[(η-C_5H_5)ZrCl$_2$][μ-η-C_5H_4–(SiMe$_2$)–η-C_5H_4][(η-C_5H_5)ZrCl$_2$]} (**11**) [1], and, for the purposes of comparison, the compounds [M(η-C_5H_5)$_2$Cl$_2$], where M = Ti, Zr, or Hf and [M(η-C_5H_5)Cl$_3$].

The characterising data for the polymers formed in the ethene polymerisation experiments are given in Tables 3 and 4. The data show that the compounds **4** and *rac*-**6** have an activity (greater than 8.5 × 10^6 g PE mol^{-1} M h^{-1}) which is greater than that of the [M(η-C_5H_5)$_2$Cl$_2$] catalyst system (3.6 × 10^6 g PE mol^{-1} M h^{-1}), first described by Kaminsky and

Table 4
Data for propylene polymerisation studies [a]

Compound	Time (min)	Yield (g)	Activity [b] (g PP mol M h^{-1})	M_n [c]	mm [d]	mr [d]	rr [d]
3	1828	7.0	7.3×10^3	—	0.42	0.43	0.14
4	210	30.7	2.8×10^5	2239	—	—	—
5	362	60.3	3.2×10^5	1121	0.26	0.52	0.22
6	360	46.7	2.5×10^5	—	0.39	0.43	0.18
7	622	5.7	1.8×10^4	2940	—	—	—
8	360	13.8	7.3×10^4	2226	—	—	—
9	404	7.3	3.5×10^4	592	0.22	0.48	0.30
10	192	18.8	1.9×10^5	1873	—	—	—
11	600	2.6	8.4×10^3	1428	—	—	—
Cp_2ZrCl_2	360	49.8	2.7×10^5	840	0.19	0.47	0.34
Cp_2TiCl_2	360	1.8	9.7×10^3	—	—	—	—
Cp_2HfCl_2	360	22.8	1.2×10^5	3272	—	—	—
$CpTiCl_3$	1131	1.1	1.8×10^3	2218	—	—	—

$Cp = \eta\text{-}C_5H_5$.
[a] Conditions: 2 bar absolute monomer pressure, 30°C, 210 cm^3, toluene, 4.5 g MAO, Al/M = 2500. [b] mol M: total amount of metal used (3.13 × 10^{-5} mol for each experiment). [c] Determined by end-group analysis by ^{1}H NMR spectroscopy. [d] From triad analysis by ^{13}C NMR spectroscopy.

co-workers [24]. The compounds **5, 8** and **9** have similar activity $((1.8–3.1) \times 10^6$ g PE mol^{-1} M h^{-1}) whilst the four compounds **11, 3, 7** and **10**, show remarkably low activities (less than 3.3×10^5 g PE mol^{-1} M h^{-1}). The lower activity of the hafnium compound **3** compared with its zirconium analogue **11** may reflect differences in the concentration of active centres and/or a greater carbon–metal bond strength for hafnium [25–28].

The polyethylenes produced by the binuclear Group IV metallocene–MAO catalysts show melting points in the range 137–140°C, indicating that they are highly linear and highly crystalline [29]. The molecular weights and molecular weight distributions (M_w/M_n) were measured by GPC analysis and the data are given in Table 3. The molecular weight distributions for the polyethylenes produced by compounds **11** and **3** are unusually broad $(M_w/M_n > 5.4)$ compared with the molecular weight distributions of the polyethylene produced by mononuclear compounds, for example [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] $(M_w/M_n = 2.5)$. There was no evidence for a bimodal distribution. These results may indicate that the interaction between two metals creates more than one kind of active species during the polymerisation [30]. The molecular weight distribution of the polyethylene produced by compounds **5** and *rac*-**6** gives values for $M_w/M_n \simeq 2$, indicating that only one or two very similar active species exists in these systems. The slightly broad molecular weight distributions of the polyethylene produced by hetero-binuclear compounds **7–10**, $(M_w/M_n = 3.8–4.7)$ is not unexpected since the molecules have two different centres, both of which are active. Finally, the molecular weight distribution shows the binuclear Group IV metallocenes are not living catalysts.

The data for propene polymerisation studies are given in Table 4. The order of activity is similar to that of ethylene polymerisations, except for compounds **8** and **9** which contain titanium and which are about an order of magnitude lower than that of [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] [31]. This may reflect the relative ease of reduction of Ti(IV) to Ti(III) [32].

All of the polypropylenes produced in this work were soluble in toluene, and IR spectroscopy showed them to be atactic polypropylenes [33,34]. The microstructures of some polypropylenes were further characterised by triad analysis, using ^{13}C NMR spectroscopy [35–37]. However, even the polypropylene produced by chiral compound **6** shows an isotacticity (mm) of only 0.39, which is at least 0.5 lower than that of the isotactic polypropylenes produced by Ti-based heterogeneous Ziegler–Natta catalysts (mm > 0.90) [38].

The molecular weights and molecular weight distributions of the polypropylenes were measured by GPC analysis. It is clear that all the polypropylenes show molecular weight distributions $M_w/M_n > 2$. The chain-end structures of the polypropylenes were determined

by ^{1}H and ^{13}C NMR spectroscopy [39] and it was found that, in all cases, the chain-end groups of the polypropylenes consisted solely of *n*-propyl and vinylidene groups in a 1:1 ratio. This observation is consistent with a specific regioregular 1,2 insertion of a propylene monomer into the active species (M$^+$–H), with exclusive chain transfer by β-hydrogen elimination. The vinylidene end-group was readily detected by ^{1}H NMR studies as two sharp singlets in the region of δ 4–5 ppm [39]. By comparing the integration of the vinylidene protons with that of remaining protons (δ 0–2 ppm), it was possible to calculate the number-average molecular weight (M_n) of the polymer, and the data, shown in Table 4, indicates that the polymers have comparatively low molecular weights.

4. Experimental

All manipulations of air- and moisture-sensitive materials were carried out in an inert atmosphere, using either a dual vacuum/nitrogen line and standard Schlenk techniques, or in an inert atmosphere dry box containing nitrogen. In each case the nitrogen was purified by passage over 4 Å molecular sieves, and either BASF catalyst or MnO. Solvent and solutions were transferred, using a positive pressure of nitrogen, through stainless steel cannulae. Filtrations were generally performed using modified stainless steel cannulae which could be fitted with glass fibre filter discs (Whatman GFC). All glassware and cannulae were dried overnight at 200°C before use. Solvents were pre-dried by standing over 4 Å molecular sieves and then refluxed and distilled under a nitrogen atmosphere from: sodium–potassium alloy (1:3 w/w) (pentane, petroleum ether (b.p. 40–60°C, diethyl ether); sodium (1,2-bis(methoxy)ethane, toluene); potassium (tetrahydrofuran); phosphorus pentoxide (dichloromethane). All solvents were thoroughly deoxygenated before use by bubbling dinitrogen through the solvent for at least 30 min. Deuterated solvents for NMR studies were stored in Young's ampoules over 4 Å molecular sieves under a nitrogen atmosphere (C$_6$D$_6$, CD$_2$Cl$_2$).

Solution NMR spectra were recorded on the following instruments: ^{1}H NMR 300 MHz Bruker AM-300; ^{13}C NMR 75.43 MHz Bruker AM-300: spectra were referenced internally using the residual protio solvent or solvent resonance relative to tetramethylsilane ($\delta = 0$ ppm). All chemical shifts are quoted in δ (ppm) and coupling constants are given in hertz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublets (dd). ^{13}C NMR spectra of polypropylenes were recorded by using 1,2-trichlorobenzene and benzene-d_6 (v/v = 80/20) at 100°C. The variable-temperature unit of the NMR

spectrometer was calibrated by use of a thermocouple immersed in toluene within an NMR tube: temperatures were accurate to ± 1 K.

Solid-state ^{13}C CP–MAS NMR spectra were recorded on a Bruker MSL200 spectrometer operating at a field strength of 4.7 T with consequent resonance frequencies of 50.32 MHz for ^{13}C and 200.13 MHz for ^{1}H. All ^{13}C chemical shifts were referenced externally to TMS using adamantane, as a secondary standard; for adamantane the upfield methine resonance was taken as δ 29.5 ppm [40]. The magic angle was set by maximising the intensity of the rotational echoes on the ^{79}Br FID derived from a small amount of KBr mixed with adamantane standard [41]. Spectral assignment was aided by NQS and TOSS spectra. Infrared spectra were recorded on a Perkin–Elmer 1510 Fourier transform spectrometer. Elemental analyses were obtained from the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford.

Gel-permeation chromatograms of the polymer were obtained at 135°C by using a Waters model 150C in the laboratories of the Chisso Petrochemical Corporation (Japan). The solvent was o-dichlorobenzene and the flow rate was 1.0 cm^3 min^{-1}. The melting points (T_m) of the polymers were determined with a Seiko SSC-5500 system at a heating rate of 20°C min^{-1}. The polymer was first melted and cooled before the actual measurement to obtain reproducible T_m.

The following dilithium or Grignard salts were prepared by literature methods, Li$_2$[SiMe$_2$(C$_5$H$_4$)$_2$] [1], [CMe$_2$CMe$_2$(C$_5$H$_4$MgCl)$_2$] · 4THF [8], Li$_2$[SiMe$_2$CH$_2$-CH$_2$SiMe$_2$(C$_5$H$_4$)$_2$] [15], Li$_2$[SiMe$_2$(C$_5$H$_4$)(C$_9$H$_6$)] [16] Li$_2$[SiMe$_2$(C$_9$H$_6$)$_2$] [21]. The compounds [M(η-C$_5$H$_5$)C$_3$] · DME (M = Ti, Zr, Hf) were prepared by literature methods [42].

4.1. Synthesis of {Zr[SiMe₂(η-C₅H₄)₂](η-C₅H₅)Cl} 1

A mixture of Li$_2$[SiMe$_2$(C$_5$H$_4$)$_2$] (3.0 g, 15 mmol) and [Zr(η-C$_5$H$_5$)Cl$_3$] · DME (5.28 g, 15 mmol) in toluene (200 cm^3) was stirred at room temperature (r.t.) for 17 h. The resulting yellow solution was then filtered from solid residues, which were extracted with more toluene (50 cm^3). The combined toluene extracts were concentrated under reduced pressure and cooled to −20°C to give pale yellow crystals of compound 1. Yield, 1.14 g (20.1%).

4.2. Synthesis of {Zr[CMe₂CMe₂(η-C₅H₄)₂](η-C₅H₅)Cl} 2

A mixture of [CMe$_2$CMe$_2$(C$_5$H$_4$MgCl)$_2$] · 4THF (3.56 g, 5.6 mmol) and [Zr(η-C$_5$H$_5$)Cl$_3$] · DME (1.97 g, 5.6 mmol) in toluene (150 cm^3) was kept at r.t. for 17 h. The resulting yellow solution was then filtered from solid residues, which were extracted with more toluene.

The combined toluene solutions were concentrated under reduced pressure and cooled −20°C to give pale yellow crystals of compound 2. Yield, 1.0 g (44.5%).

4.3. Synthesis of [{[(η-C₅H₅)HfCl₂][μ-η-C₅H₄-(SiMe₂)-η-C₅H₄][(η-C₅H₅)HfCl₂]} 3

A mixture of Li$_2$[SiMe$_2$(C$_5$H$_4$)$_2$] (1.0 g, 5 mmol) and [Hf(η-C$_5$H$_5$)Cl$_3$] · DME (4.4 g, 10 mmol) was refluxed in toluene (100 cm^3) for 17 h. The volatiles were removed under reduced pressure and the resulting solid was extracted with CH$_2$Cl$_2$. The solution was concentrated and cooled to −20°C, affording compound 3 as a grey solid. Yield, 2.3 g (56.4%).

4.4. Synthesis of {[(η-C₅H₅)ZrCl₂][μ-η-C₅H₄-(SiMe₂CH₂CH₂SiMe₂)-η-C₅H₄][(η-C₅H₅)ZrCl₂]} 4

A mixture of Li$_2$[SiMe$_2$CH$_2$CH$_2$SiMe$_2$(C$_5$H$_4$)$_2$] (0.16 g, 0.56 mmol) and [Zr(η-C$_5$H$_5$)Cl$_3$] · DME (0.4 g, 1.12 mmol) was refluxed in toluene (30 cm^3) for 17 h. The volatiles were removed under reduced pressure and the residual solid was extracted with CH$_2$Cl$_2$. The solution was concentrated and cooled to −20°C, affording compound 4 as a white solid. Yield, 0.19 g (46.7%).

4.5. Synthesis of {[(η-C₅H₅)ZrCl₂][η-C₅H₄-(SiMe₂)-η-C₉H₆][(η-C₅H₅)ZrCl₂]} 5

A mixture of Li$_2$[SiMe$_2$(C$_5$H$_4$)(C$_9$H$_6$)] · 0.6Et$_2$O (1.5 g, 5.1 mmol) and [Zr(η-C$_5$H$_5$)Cl$_3$] · DME (3.62 g, 10.3 mmol) in toluene (70 cm^3) was refluxed for 17 h. The reaction mixture was filtered and the volatiles were removed under reduced pressure. Subsequent recrystallization from CH$_2$Cl$_2$–petroleum ether (b.p. 40–60°C) at −80°C gave compound 5. Yield, 1.5 g (42.6%).

4.6. Synthesis of rac-{[(η-C₅H₅)ZrCl₂]{μ-η-C₉H₆-(SiMe₂)-η-C₉H₆][(η-C₅H₅)ZrCl₂]} rac-6

A mixture of Li$_2$[SiMe$_2$(C$_9$H$_6$)$_2$] · 0.5Et$_2$O (2.0 g, 5.93 mmol) and [Zr(η-C$_5$H$_5$)Cl$_3$] · DME (4.2 g, 11.9 mmol) was refluxed in toluene (70 cm^3) 17 h. The reaction mixture was filtered and the volatiles were removed under reduced pressure. The resulting yellow powder was washed with hot toluene (80°C) and dried in vacuo to afford the rac-isomer of compound 6 as a yellow powder. The toluene washings were concentrated and cooled to −20°C to give further quantities of compound rac-6. Yield, 0.85 g (19.5%).

4.7. Synthesis of {[(η-C₅H₅)ZrCl₂][μ-η-C₅H₄-(SiMe₂)-η-C₅H₄][(η-C₅H₅)HfCl₂]} 7

A mixture of compound 1 (0.345 g, 0.91 mmol) and [Hf(η-C$_5$H$_5$)Cl$_3$] · DME (0.4 g, 0.91 mmol) was refluxed in toluene (100 cm^3) for 17 h. The volatiles were

removed under reduced pressure and the resulting solid extracted with CH_2Cl_2. The solution was concentrated and cooled to $-20°C$, affording compound **7** as a grey solid. Yield, 0.35 g (52.7%).

4.8. Synthesis of {[(η-C₅H₅)ZrCl₂][μ-η-C₅H₄-(SiMe₂)-η-C₅H₄][(η-C₅H₅)TiCl₂]} 8

A mixture of compound **1** (0.36 g, 0.95 mmol) and $[Ti(\eta-C_5H_5)Cl_3]$ (0.21 g, 0.95 mmol) was refluxed in toluene (100 cm^3) for 17 h. The volatiles were removed under reduced pressure and the resulting solid extracted with CH_2Cl_2. The solution was concentrated and cooled to $-20°C$, affording compound **8** as a red solid. Yield, 0.3 g (53.0%).

4.9. Synthesis of {[(η-C₅H₅)ZrCl₂][μ-η-C₅H₄-(SiMe₂)-η-C₅H₄][(η-C₅Me₅)TiCl₂]} 9

A mixture of compound **1** (0.57 g, 1.51 mmol) and $[Ti(\eta-C_5H_5)Cl_3]$ (0.44 g, 1.51 mmol) was refluxed in toluene (100 cm^3) for 17 h. The volatiles were removed under reduced pressure and the residual solid was extracted with CH_2Cl_2. The solution was concentrated and cooled to $-20°C$, giving compound **9** as a red solid. Yield, 0.42 g (41.7%).

4.10. Synthesis of {[(η-C₅H₅)ZrCl₂][μ-η-C₅H₄-(SiMe₂)-η-C₅H₄][TiCl₃]} 10

One equivalent of $TiCl_4$ (1.0 cm^3 of a 1.0 M toluene solution) was added to compound **1** (0.39 g, 1.0 mmol) in toluene (100 cm^3) at 0°C. The resulting solution was stirred for 17 h at r.t. The volatiles were removed under reduced pressure and the residual solid was extracted with CH_2Cl_2. The solution was concentrated and cooled to $-20°C$, affording compound **10** as a yellow solid. Yield, 0.29 g (49.5%).

4.11. Polymerisation studies

Ethylene and propylene (pure grade) were purified by passage through 4 Å molecular sieves and then over finely divided potassium metal supported on glass wool. Polymerisations were carried out in a Fischer–Porter reactor placed in a thermostatically heated bath and equipped with a magnetic stirrer. The polymerisation reactions for ethene were carried out under conditions similar to those employed by Kaminsky et al. [43]. Methylaluminoxane (MAO) (850 mg) was placed into the Fischer–Porter bottle, which was then connected to the ethylene supply via a computer-controlled gas supply system and filled with ethylene. Toluene (200 cm^3) was then added, the ethylene pressure increased to 2 bar (absolute pressure) and the mixture was stirred at 30°C until saturated with ethylene. Meanwhile, metallocene

$(6.25 \times 10^{-6}$ mol of transition metal in total) in 10 cm^3 of toluene was added to 50 mg of MAO and stirred for 15 min pre-activation. The metallocene–MAO mixture was added quickly to the reactor. The reaction mixture was stirred vigorously at 30°C under 2 bar pressure of ethylene. The polymerisation was quenched by venting the ethylene and adding a small amount of ethanol. The contents of the reactor were transferred to a conical flask and 250 cm^3 of 20% (by volume) solution of conc. HCl in ethanol was added and the mixture stirred overnight. The polymer was then separated from the solution using a sintered glass funnel (on a Buchner flask, connected to a water aspirator) and was washed with water and ethanol then dried in vacuo at 60°C to constant weight.

The polymerisation reactions for propene were performed under the same conditions as used for ethene (2 bar monomer pressure, 30°C) except: (i) 4.25 g of MAO and 160 cm^3 of toluene were pre-saturated with propylene at 2 bar and 30°C, (ii) metallocene (3.13×10^{-5} mol of transition metal in total) in 50 cm^3 was added to 250 mg of MAO for a 15 min period of pre-activation. The polymerisation was quenched by venting the propylene and adding a small amount of ethanol. The contents of the reactor were transferred to a conical flask and 250 cm^3 of 20% (by volume) solution of conc. HCl in ethanol was added and the mixture stirred overnight. The polypropylene was soluble in toluene, so the toluene layer was separated, washed with water (300 cm^3) then stirred with $MgSO_4$ drying agent. After filtration, the toluene was removed under reduced pressure leaving the polypropylene, typically a highly viscous liquid, which was dried to constant weight in vacuo at 60°C.

4.12. Crystal data for compound 1

$C_{17}H_{19}Cl_1Si_1Zr_1$, $M = 378.1$, monoclinic, $a = 7.1736(6)$, $b = 9.8089(4)$, $c = 11.0823(4)$ Å, $\beta = 92.571(5)°$, space group $P2_1/m$, $V = 779$ Å^3, $Z = 2$, $F(000) = 384$, $D_c = 1.61$ g cm^{-3}. Yellow blocks. Crystal dimensions: $16 \times 31 \times 0.65$ mm, $\mu(Mo\ K\alpha) = 9.28$ cm^{-1}. Data were collected on an Enraf–Nonius CAD4 diffractometer at room temperature using graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and an ω–2θ scan mode. Data were corrected for Lorentz and polarisation effects and an empirical absorption coefficient correction based on azimuthal scan data applied. A total of 2860 reflections were measured ($1 \geq \theta \geq 30°$, $-10 \geq h \geq 10, -1 \geq l \geq 15$) of which 2343 were unique (merging $R = 0.022$) and 2178 were observed ($I \geq 3\sigma(I)$).

The structure was solved by direct methods and refined by full matrix least squares. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were located from successive difference Fourier syntheses and were refined with isotropic

Table 5
Fractional atomic co-ordinates for compound **1**

Atom	x	y	z
Zr(1)	0.29484(2)	0.2500	0.29997(1)
Si(1)	0.10015(6)	0.2500	0.00452(4)
Cl(1)	0.64985(5)	0.2500	0.32224(5)
C(1)	0.3831(3)	0.2500	0.5358(2)
C(2)	0.2731(2)	0.3663(1)	0.5128(1)
C(3)	0.0931(2)	0.3219(1)	0.4743(1)
C(4)	0.2233(3)	0.2500	−0.1391(2)
C(5)	−0.1579(2)	0.2500	−0.0139(2)
C(6)	0.3748(2)	0.4208(1)	0.1334(1)
C(7)	0.3887(2)	0.5007(1)	0.2406(1)
C(8)	0.2103(2)	0.5152(1)	0.2831(1)
C(9)	0.0849(2)	0.4388(1)	0.2073(1)
C(10)	0.1852(1)	0.3869(1)	0.10915(9)
H(1)	0.513(4)	0.2500	0.557(3)
H(2)	0.308(2)	0.457(2)	0.521(2)
H(3)	−0.003(3)	0.379(2)	0.452(2)
H(6)	0.477(2)	0.398(2)	0.083(1)
H(7)	0.499(3)	0.537(2)	0.274(2)
H(8)	0.167(3)	0.565(2)	0.353(2)
H(9)	−0.052(2)	0.430(2)	0.219(1)
H(41)	0.213(5)	0.328(4)	−0.182(3)
H(42)	0.360(5)	0.2500	−0.129(3)
H(51)	−0.201(4)	0.332(3)	−0.054(2)
H(52)	−0.213(5)	0.2500	0.064(3)

temperature factors. A three term Chebyshev weighting scheme [44] was applied which gave satisfactory agreement analyses. At convergence $R = 0.020$ and $R_w = 0.022$ for 141 parameters (observations/variables = 15.5). Selected distances and angles are given in Table 2 and fractional atomic co-ordinates are given in Table 5.

All crystallographic calculations were carried out using the CRYSTALS [45] program package on a 486 personal computer. Atomic scattering factors were taken from the usual sources [46]. Anisotropic thermal parameters and a complete list of band lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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