New *ansa*-Metallocenes of the Group 4 Transition Metals as Homogeneous Catalysts for the Polymerization of Propene and Styrene†

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The *ansa*-bridged metallocenes $[M\{CR_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$, [M = Ti, Zr or Hf; $CR_2 = CMe_2$, CPh_2 or $C(CH_2)_5$] have been prepared. The crystal structure of $[Zr\{CMe_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ has been determined. Some of these new *ansa*-metallocenes in the presence of methylaluminoxane $(AlMeO)_n$ give homogeneous catalysts, which for the polymerization of propene yield isotactic rich polypropene and of styrene yield syndiotactic polystyrene.

The homogeneous mixture of $[Ti(\eta-C_5H_5)_2Cl_2]$ and $AlEt_2Cl$ was first shown to catalyse the polymerization of ethylene by Breslow and Newburg.[1] The catalyst mixture gave polymers of relatively low molecular weights and did not polymerize propylene. The metallocene catalysts became of renewed interest when Kaminsky and co-workers[2] found that very high productivity for ethylene polymerization was obtained by using $[Zr(\eta-C_5H_5)_2Cl_2]$ together with methylaluminooxane (mao), $(AlMeO)_n$. This led to the rapid development of many zirconocene–mao systems which were found to be active towards the polymerization of propylene.[3] Some chiral metallocene–mao systems gave isotactic polymers the defect structures of which indicated that the isotactic propagation was controlled by the chiral ligand environment of the transition metal atoms. When the metallocene was $[Ti\{C_2H_4(\eta-C_9H_6)_2\}Cl_2]$ both isotactic and stereoirregular polypropylene were formed and Ewen[4] suggested that this was a consequence of the presence of a mixture of *meso* and racemic stereoisomers. Thus, the chiral racemic stereoisomers produce the isotactic polymer, whereas the achiral *meso* stereoisomer produced the stereoirregular polypropylene. Kaminsky *et al.*[5] succeeded in producing highly isotactic polypropylene, essentially free of stereoirregular polymers, using a similar catalyst consisting of mao and the pure racemic stereoisomers of either *rac*-$[Zr\{C_2H_4(\eta-C_9H_6)_2\}Cl_2]$ or *rac*-$[Zr\{C_2H_4(\eta-C_9H_{10})_2\}Cl_2]$. The optically pure $[ZrLCl_2][H_2L$ = 4*S*,5*S*,-4,5-bis(1*H*-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane] with mao also gives isotactic polypropene.[6] A further example of a catalyst which gives the stereospecific polymerization of propylene is *rac*-$[Zr(\eta-C_5H_4CHMePh)_2Cl_2]$ with mao.[7]

Recently Ewen *et al.*[8] reported that highly syndiotactic polypropylene could be obtained using $[M\{CMe_2(\eta-C_5H_4)(\eta-C_{13}H_8)\}Cl_2]$ (M = Zr or Hf) with mao over a wide range of polymerization temperatures. Thus, these metallocenes provide the opportunity to fine-tune the control of the olefin polymerization mechanism. We were therefore interested in preparing further examples of chiral metallocenes or of *ansa*-metallocenes of Group 4.

It was decided first to attempt the synthesis of new *ansa*-metallocene derivatives in the general class *ansa*-$[M\{CR_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$, M = Ti, Zr or Hf, and to study their ability to induce stereoregularity in propylene polymerizations. During the course of this work a closely related study of compounds in this class, namely *ansa*-$[M\{CHMe(\eta-C_5R_4)(\eta-C_9H_6)\}Cl_2]$ (M = Zr or Ti) has been reported.[9]

Results and Discussion

The new ligand precursors 2-cyclopentadienyl-2-indenylpropane, **I**, cyclopentadienyl(indenyl)diphenylmethane **II** and 1-cyclopentadienyl-1-indenylcyclohexane **III** have been prepared by reaction between the appropriate fulvene $C_5H_4{=}CR_2$ $[R_2 = Me_2, Ph_2$ or $(CH_2)_5]$ and lithium indenide, followed by hydrolysis of the intermediate monoanion, see Scheme 1. In a typical reaction sequence, $CMe_2(\eta-C_5H_5)(\eta-C_9H_7)$ **I** was prepared as a yellow viscous oil by addition of lithium indenide in tetrahydrofuran (thf) to 6,6-dimethylfulvene followed by hydrolysis of the reaction mixture. The ^1H NMR spectrum of the product revealed the presence of a mixture of isomers, as expected. Similarly, $CPh_2(\eta-C_5H_5)(\eta-C_9H_7)$ **II** and $C(CH_2)_5(\eta-C_5H_5)(\eta-C_9H_7)$ **III** were prepared from lithium indenide and 6,6-diphenylfulvene or 6,6-pentamethylenefulvene as red or yellow viscous oils, respectively.

The compounds **I**–**III** were then deprotonated by treatment with 2 equivalents of *n*-butyllithium giving pale yellow pyrophoric powders which were very soluble in thf. These are presumed to be the dilithio salts $Li_2[CR_2(\eta-C_5H_4)(\eta-C_9H_6)]$ since they react with the Group 4 tetrahalides MCl_4, M = Ti, Zr or Hf, to give the desired new *ansa*-metallocene derivatives $[M\{CMe_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$, $[M\{CPh_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ and $[M\{C(CH_2)_5(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$. In a typical experiment, a slurry of $ZrCl_4$ in CH_2Cl_2 was treated with an equimolar quantity of $Li_2[CMe_2(\eta-C_5H_4)(\eta-C_9H_6)]$ suspended in CH_2Cl_2. The mixture became pale yellow, turning orange overnight. When thf was used instead of CH_2Cl_2 the reaction was not successful. The resulting compound $[Zr\{CMe_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ **1** was found to have appreciable solubility in toluene and well formed crystals could be grown overnight at −20 °C giving orange, air-stable crystals in 35% yield. The compound $[Ti\{CPh_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ **3** was prepared from $TiCl_4$ in thf and $Li_2[CPh_2(\eta-C_5H_4)(\eta-C_9H_6)]$, in 80% yield. In this manner the compounds $[M\{CR_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$, where R = Me and M = Zr **1** or Hf **2**, R = Ph and M = Ti **3**, Zr **4**, or Hf **5** or $R_2 = C(CH_2)_5$ and M = Zr **6** or Hf **7** were prepared. The reactions and new compounds are shown in Scheme 1. The analytical and spectroscopic data characterizing the metallocene compounds **3**–**7** are given in Table 1 and will not be further discussed unless the interpretation is not straightforward.

The crystal structure of the compound $[Zr\{CMe_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ **1** has been determined and the molecular structure is given in Fig. 1. This shows the compound to be a monomer with the expected bent metallocene structure. Selected bond angles and distances are given in Table 2 and fractional atomic coordinates in Table 7. The Cl–Zr–Cl bond angle is 100.1(1)° and the CEN(C_5H_4)–Zr–CEN(C_9H_6)

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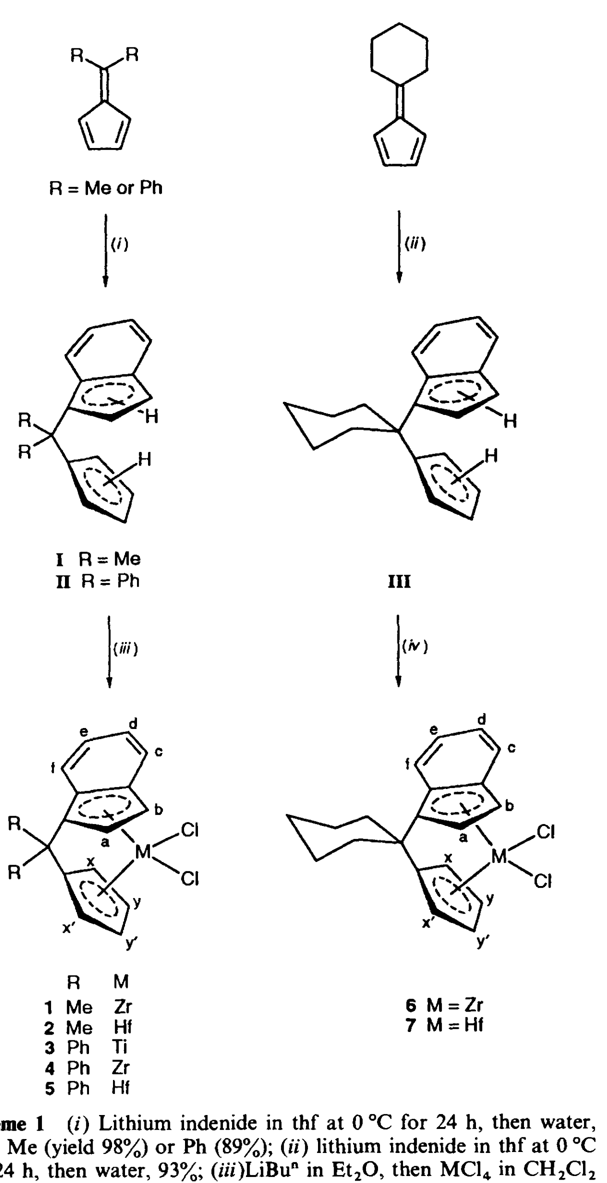
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

angle is 117.1° (CEN = ring centroid). The Zr–Cl bond distances are 2.418(1) and 2.441(1) Å. The Zr–CEN(C_5H_4) and Zr–CEN(C_9H_6) distances are 2.19 and 2.21 Å respectively. The two bonds connecting the bridgehead atoms C(5) and C(9) to the CMe_2 bridging group form an unusually acute angle of 99.5(3)°. The bridgehead C atom is bent out of the ring planes of both the η-C_5 and η-C_9 ligands towards the Zr by 0.39 and 0.26 Å respectively. Owing to the steric restrictions in a one-link bridged molecule[4] the CEN(C_5H_4)–Zr–CEN(C_9H_6) angle of 117.1° is significantly smaller whereas the Cl–Zr–Cl angle of 100.1(1)° is slightly increased compared to corresponding values of 125.0 and 98.6(3)° in *rac*-[Zr{C_2H_4(η-C_9H_6)$_2$}Cl_2].[10] The angle between the mean plane of the η-C_5H_4 ring and that of the η-indenyl ring in **1** is 106.7°. The structural features of **1** are similar to those of the recently described compound *rac-anti*-[Zr{CHMe(η-C_5H_4)(η-C_9H_6)}Cl_2].[9]

We have examined the catalytic activity of the *ansa*-metallocenes, in the presence of methylaluminoxane as the cocatalyst, for the polymerization of propylene and styrene. For convenience the new compounds have been given abbreviated names, as follows: [M{CMe_2(η-C_5H_4)(η-C_9H_6)}Cl_2] as [M(L^{Me})Cl_2], [M{CPh_2(η-C_5H_4)(η-C_9H_6)}Cl_2] as [M(L^{Ph})Cl_2], and [M{C(CH_2)$_5$(η-C_5H_4)(η-C_9H_6)}Cl_2] as [M(L^{CH_2})Cl_2], where M = Zr, Hf or Ti. The results of the propylene polymerization reactions are given in Table 3. The data show there is little difference between the activities of the three zirconium compounds. However, [Hf(L^{CH_2})Cl_2] **7** is more active than [Hf(L^{Ph})Cl_2] **5** at room temperature. The activity of [Ti(L^{Ph})Cl_2] **3** is an order of magnitude lower than those of the corresponding zirconium and hafnium compounds **4** and **5** and this may be due either to the relative ease of reduction of Ti^{IV} to Ti^{III} and/or to the smaller size of the titanium atom.



Scheme 1 (*i*) Lithium indenide in thf at 0 °C for 24 h, then water, R = Me (yield 98%) or Ph (89%); (*ii*) lithium indenide in thf at 0 °C for 24 h, then water, 93%; (*iii*)$LiBu^n$ in Et_2O, then MCl_4 in CH_2Cl_2 at 0 °C, warm to r.t. for 12 h, **1** (35), **2** (14), **3** (80), **4** (66), **5** (56%); (*iv*) $LiBu^n$ in Et_2O, then MCl_4 in CH_2Cl_2 at 0 °C, warm to r.t. for 12 h, **6** (62), **7** (27%)

The temperature dependencies of the propylene polymerization reactions for [Hf(L^{CH_2})Cl_2] **7** and [Hf(L^{Ph})Cl_2] **5** are shown in Figs 2 and 3, respectively. The data show that the polymerization activities of [Hf(L^{Ph})Cl_2] and [Hf(L^{CH_2})Cl_2] increase with increasing temperature over the range investigated, in contrast to the usual behaviour of Ziegler–Natta catalysts which normally show maximum activity within the temperature range (0–80 °C).[2] Thus it appears that the compounds described here are more thermally stable both to reduction and decomposition.

The Arrhenius plots for [Hf(L^{Ph})Cl_2] **5** and [Hf(L^{CH_2})Cl_2] **7** are shown in Fig. 4 and there is no deviation from linearity between −40 and 80 °C. The data yield the activation energies E_a = 44 kJ mol^{-1} for **5** and of 48 kJ mol^{-1} for **7**. In general, Ziegler–Natta catalyst systems which use metallocene systems

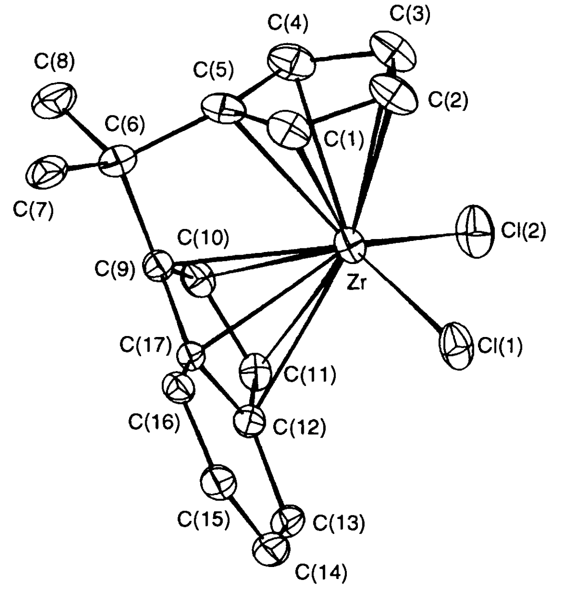


Fig. 1 Molecular structure of compound **1**

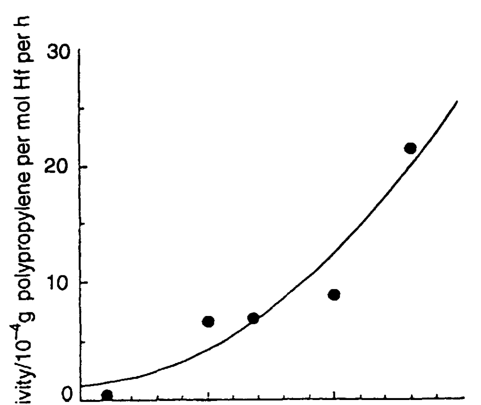


Fig. 2 Influence of the polymerization temperature on the polypropylene yields for the catalyst system [Hf(L^{CH_2})Cl_2]–mao

Table 1 Analytical and spectroscopic data^a

		Analysis			
Compound	Colour	C	H	Cl	^{1}H NMR data
1	Orange	53.7	4.30	18.7	7.68 [1 H, d, J(H$_f$–H$_e$) 9, H$_f$]
		(53.4)	(4.20)	(18.5)	7.63 [1 H, d, J(H$_c$–H$_d$) 9, H$_c$]
					7.36 [1 H, dd, J(H$_e$–H$_d$) 6, J(H$_e$–H$_f$) 9, H$_e$]
					7.05 [1 H, dd, J(H$_d$–H$_c$) 9, J(H$_d$–H$_e$) 6, H$_d$]
					6.85 [1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.53 (2 H, m, H$_{x,x'}$)
					6.14 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.84 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.72 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
					2.21 (3 H, s, Me)
					1.98 (3 H, s, Me)^b
2	Orange	43.9	3.50	15.3	7.70 [1 H, d, J(H$_f$–H$_e$) 9, H$_f$]
		(43.5)	(3.45)	(15.1)	7.60 [1 H, d, J(H$_c$–H$_d$) 9, H$_c$]
					7.31 [1 H, dd, J(H$_e$–H$_d$) 6, J(H$_e$–H$_f$) 9, H$_e$]
					7.03 [1 H, dd, J(H$_d$–H$_c$) 9, J(H$_d$–H$_e$) 6, H$_d$]
					6.74 [1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.45 (2 H, m, H$_{x,x'}$)
					6.10 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.75 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.67 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
					2.20 (3 H, s, Me)
					2.00 (3 H, s, Me)
3	Green	69.6	4.35	14.5	≈7.9 (2 H, overlapping, H$_c$ and H$_f$)
		(70.0)	(4.35)	(15.3)	7.7 [1 H, dd, J(H$_e$–H$_d$) 9, J(H$_e$–H$_f$) 14, H$_e$]
					7.5–7.2 (10 H, complex, aromatics)
					6.5–6.8 (3 H, overlapping, H$_b$, H$_d$ and H$_{x,x'}$)
					5.87 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.60 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.53 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
4	Yellow	64.3	4.00	14.2	7.91 (2 H, m, H$_c$ and H$_f$)
		(64.0)	(4.00)	(14.0)	7.69 (1 H, m, H$_e$)
					7.5–7.2 (10 H, complex, aromatics)
					6.93 [1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.59 (2 H, m, H$_{x,x'}$)
					6.27 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.90 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.74 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]^b
5	Yellow	55.2	3.45	11.2	7.92 (2 H, m, H$_c$ and H$_f$)
		(54.6)	(3.40)	(11.9)	7.67 [1 H, dd, J(H$_e$–H$_d$) 9, J(H$_e$–H$_f$) 14, H$_e$]
					7.5–7.2 (10 H, complex, aromatics)
					6.82 [1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.51 (2 H, m, H$_{x,x'}$)
					6.24 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.82 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.68 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
6	Yellow	56.2	4.60	16.9	7.7–7.6 (2 H, overlapping, H$_f$ and H$_c$)
		(56.9)	(4.75)	(16.8)	7.35 (1 H, m, H$_e$)
					7.06 (1 H, m, H$_d$)
					6.88 [1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.52 (2 H, m, H$_{x,x'}$)
					6.18 [1 H, d, J(H$_a$–H$_b$) 3, H$_a$]
					5.83 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.74 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
					3.0–2.8 (1 H, complex bands, CH$_2$)
					2.6–2.3 (3 H, complex bands, CH$_2$)
					2.0–1.4 (6 H, complex bands, CH$_2$)^b
7	Yellow	47.8	3.95	13.5	7.64 [1 H, d, J(H$_f$–H$_e$) 9, H$_f$]
		(47.1)	(3.95)	(13.9)	7.60 (1 H, d, J(H$_c$–H$_d$) 9, H$_c$]
					7.31 (1 H, dd, J(H$_e$–H$_d$) 7, J(H$_e$–H$_f$) 9, H$_e$]
					7.02 [1 H, dd, J(H$_d$–H$_c$) 9, J(H$_d$–H$_e$) 7, H$_d$]
					6.77 (1 H, d, J(H$_b$–H$_a$) 3, H$_b$]
					6.45 (2 H, m, H$_{x,x'}$)
					6.13 [1 H, d, J(H$_a$–H$_b$), 3, H$_a$]
					5.74 [1 H, q, J(H$_y$–H$_{y'}$), J(H$_y$–H$_x$), J(H$_y$–H$_{x'}$) 3, H$_y$]
					5.68 [1 H, q, J(H$_{y'}$–H$_y$), J(H$_{y'}$–H$_x$), J(H$_{y'}$–H$_{x'}$) 3, H$_{y'}$]
					3.0–2.8 (H, complex bands, CH$_2$)
					2.6–2.3 (3 H, complex bands, CH$_2$)
					2.0–1.6 (6 H, complex bands, CH$_2$)

[a] Analytical data given as found (required) %. The NMR spectra were recorded in $CDCl_3$. Data given as: chemical shift (δ) [relative intensity, multiplicity (J in Hz), assignment], *etc.* For labelling of hydrogens see Scheme 1. [b] Assignment assisted by a ^{1}H–^{1}H correlation spectroscopy at 45 °C.

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

Zr–Cl(1)	2.418(1)	Zr–C(9)	2.426(4)
Zr–Cl(2)	2.441(1)	Zr–C(10)	2.452(4)
Zr–C(1)	2.467(5)	Zr–C(11)	2.561(4)
Zr–C(2)	2.551(6)	Zr–C(12)	2.626(4)
Zr–C(3)	2.551(5)	Zr–C(17)	2.530(4)
Zr–C(4)	2.463(6)	Zr–CEN(C_5H_4)	2.188
Zr–C(5)	2.452(4)	Zr–CEN(C_9H_6)	2.209
Cl(1)–Zr–Cl(2)	100.1(1)	Cl(2)–Zr–CEN(C_9H_6)	110.5
Cl(1)–Zr–CEN(C_5H_4)	110.4	CEN(C_5H_4)–Zr–CEN(C_9H_6)	117.1
Cl(1)–Zr–CEN(C_9H_6)	108.1	C(5)–C(6)–C(9)	99.5(3)
Cl(2)–Zr–CEN(C_5H_4)	109.4		

CEN(C_5H_4) and CEN(C_9H_6) denote the centroids of the C(1)–C(5) and C(9)–C(12), C(17) rings.

Table 3 Results of propylene polymerization with the new *ansa*-metallocenes

	Polymerization conditions				Activity 10^{-4} g polypropylene per mol M per h	Molecular weight		
Catalyst	10^5 catalyst/mol	T/°C	t/h	Yield/g		$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n
1 [Zr(L^{Me})Cl_2]	1.0	18	9	8.5	9.4	0.82	0.31	2.65
		−78	9	0.2	0.2			
3 [Zr(L^{Ph})Cl_2]	2.0	18	9	16.3	9.1	0.61	0.3	2.03
		−78	9	0.5	0.3			
5 [Hf(L^{Ph})Cl_2]	2.0	80	3	15.4	25.6			
		50	3	8.4	14.0			
		18	3	3.7	6.2	6.97	1.10	6.31
		0	3	1.5	2.5			
		−40	3	0.6	1.0			
2 [Ti(L^{Ph})Cl_2]	2.0	18	5	0.6	0.6			
6 [Zr(L^{CH_2})Cl_2]	2.0	18	5	9.7	9.7	0.53	0.21	2.53
		−78	9	0.6	0.3			
7 [Hf(L^{CH_2})Cl_2]	2.0	80	5	21.4	21.4	1.38	0.45	3.08
		50	5	8.8	8.8	3.86	0.97	3.97
		18	5	7.0	7.0	8.79	2.93	3.01
		0	5	6.6	6.6	21.94	1.37	16.06
		−40	5	0.4	0.4			

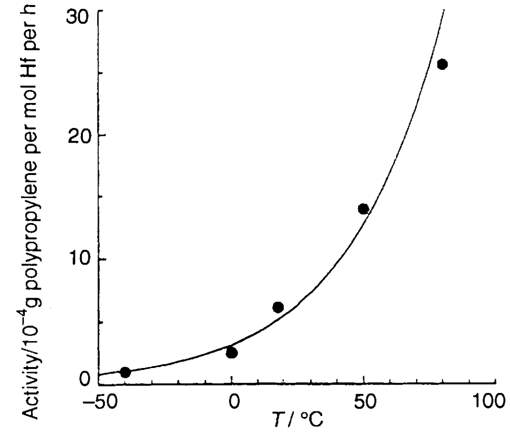


Fig. 3 Influence of the polymerization temperature on the polypropylene yields for the catalyst system [Hf(L^{CH_2})Cl_2]–mao

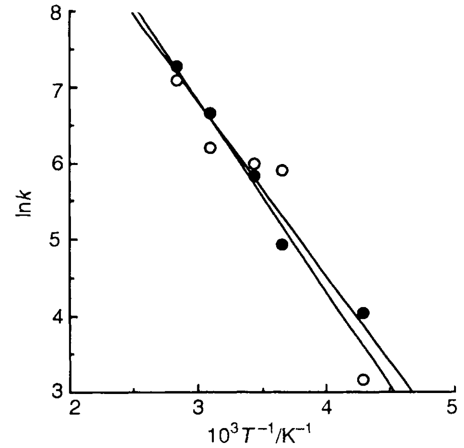


Fig. 4 Plots of ln k *vs.* $1/T$ for [Hf(L^{Ph})Cl_2] (●) and [Hf(L^{CH_2})Cl_2] (○)

in conjunction with mao show values of E_a between 9.6 and 75 kJ mol^{-1}.[2,10] The molecular weights of the polypropylenes obtained, determined by GPC analysis at 135 °C using 1,2-dichlorobenzene as solvent, are given in Table 3. The new *ansa*-metallocenes produce polypropylene waxes under conditions where appreciable yields can be obtained. The hafnium catalysts produce polypropylene with higher molecular weight relative to zirconium catalysts, presumably due to greater metal-alkyl bond strength. The average molecular weights of the polypropylene decrease with an increase of polymerization temperature presumably because of more frequent chain-transfer reactions at high temperature.

Fig. 5 shows the molecular weight distribution curves of the polymers prepared using [Zr(L^{Ph})Cl_2] **4** at 18 °C. The molecular weight distribution corresponds to the Schulz–Flory distribution, with $M_w/M_n = 2$, as is typical for homogeneous catalysts. However, the distribution curves of the polymers prepared by use of [Hf(L^{Ph})Cl_2] and [Hf(L^{CH_2})Cl_2] are

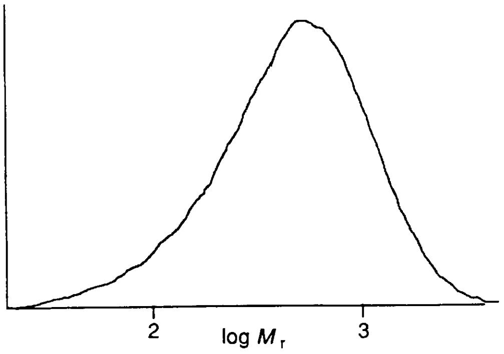


Fig. 5 Molecular weight (M_r) distribution curves of the polypropylenes prepared from $[Zr(L^{Ph})Cl_2]$–mao at 18 °C

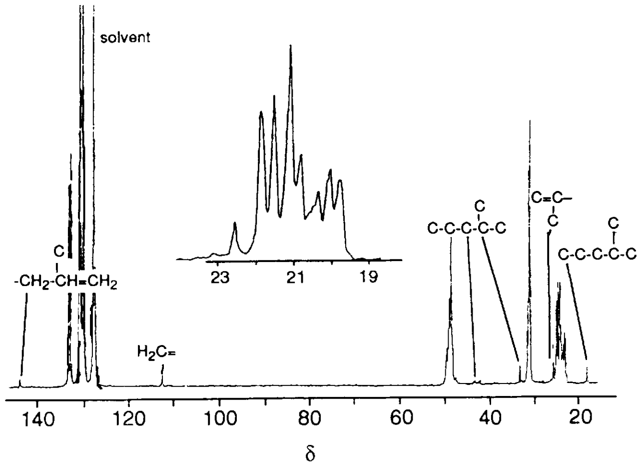


Fig. 6 The 75.5 MHz ^{13}C NMR spectrum in $CDCl_3$ of the polypropylene obtained using $[Zr(L^{Me})Cl_2]$–mao at 18 °C

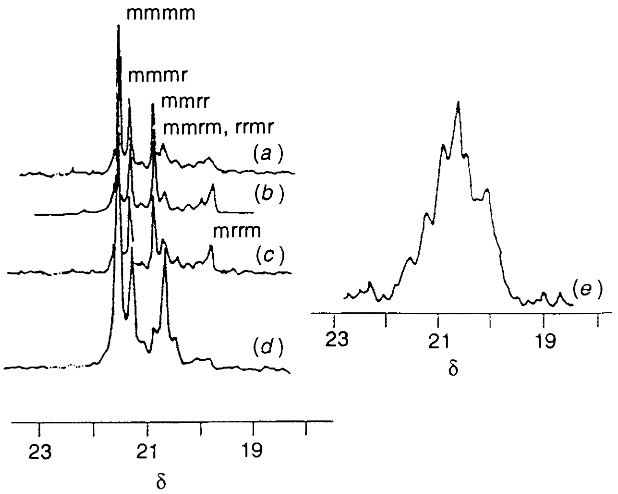


Fig. 7 The methyl region of the 75.5 MHz ^{13}C NMR spectra in 1,2,4-trichlorobenzene–C_6D_6 of the polypropylenes obtained using (*a*) $[Hf(L^{Ph})Cl_2]$ **5**–mao at 18 °C, (*b*) $[Hf(L^{CH_2})Cl_2]$ **7**–mao at 18 °C, (*c*) $[Ti(L^{Ph})Cl_2]$ **3**–mao at 18 °C, (*d*) $[Zr(L^{Ph})Cl_2]$ **4**–mao at 18 °C and (*e*) $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$–mao at −78 °C

broader than those expected for homogeneous catalysts, indicating that local heatings arising from viscous polymerization reactions occur leading to a larger number of lower-molecular-weight polymers than normally expected for homogeneous catalysts.

The microstructure of the polypropylenes obtained using $[Zr(L^{Me})Cl_2]$ **1**, $[Zr(L^{Ph})Cl_2]$ **4** and $[Zr(L^{CH_2})Cl_2]$ **6** with mao at 18 °C have been investigated by ^{13}C NMR spectroscopy. The spectra are almost identical and a typical one, for **1**, is shown in Fig. 6 in which the methyl region has been expanded. All of these polymers were highly viscous liquids, indicating that chain-transfer reactions took place frequently in the polymerizations. The resonances associated with the chain-end structures in these low-molecular-weight polymers could be observed.[10] Thus, in Fig. 6 the resonances at δ 40, 30 and 14.7 can be attributed to the presence of Pr^n at the chain-end, and those at δ 144, 111.8 and 22.4 to the presence of vinylidene at the chain-end.[11] The resonances at δ 24.5, 23.2–23.8 and 22.2–22.7 may be assigned to the methine and two methyl carbons of the isopropyl group at the chain-end.[11] The observation of vinylidene and *n*-propyl chain-end structures in almost equal amount shows that the main chain-transfer process involves β-hydrogen elimination from a regioregular monomer unit followed by initiation of a new polymer chain at a metal–hydrogen bond *via* primary insertion. In addition, the absence of detectable amounts of vicinal group at the chain-end shows that the propylene polymerization proceeds only by primary insertion of the propylene monomer at the metal centre. The observation of isopropyl group at the chain-end suggests that the first propagation step would be by primary insertion of propylene into the Zr–CH_3 active centre which arises from the methylation of the zirconium compound by the mao.

In addition, the smaller intensity of isopropyl chain-end structures relative to the amount of *n*-propyl and vinylidene chain-end structures suggests that most of the polymer chains are reinitiated at Zr–H bonds arising from β-hydrogen elimination, and that chain ends are produced by the very frequent repetition of the chain-transfer reaction. The ^{13}C NMR spectra also show the presence of large numbers of mr and rr dyads (m = *meso*, r = racemic) in the polymer chain which indicates the presence of atactic polypropylenes. The ^{13}C NMR spectra also show that the regiochemistry of the propagation reaction proceeds by enantiomorphic-site control.

The microstructures of the polypropylenes obtained from $[Hf(L^{Ph})Cl_2]$ **5**, $[Hf(L^{CH_2})Cl_2]$ **7** and $[Ti(L^{Ph})Cl_2]$ **3** with mao have also been determined using ^{13}C NMR spectroscopy.[12] The spectra show that the resonances assignable to chain-end groups have a smaller intensity for the polymers formed by the hafnium catalysts than those formed by the zirconium catalysts. It seems that chain-transfer reactions of the hafnium catalyst systems occur less readily in comparison with the zirconium catalyst systems and this may be due to a greater metal–carbon bond strength for hafnium. The ^{13}C NMR spectra of the methyl region of the product polypropylene mixtures from the catalyst precursors **5**, **7**, **3** and **4** are isotactic in nature although the spectra also show the presence of the stereoblock junctures (mmmr, mmrr, mmrm, mrrm). We note that the degree of isotacticities is only about 70% compared to the isotactic polypropylenes obtained using the *rac*-ethylenebis(indenyl)zirconium dichloride–mao system (> 99%). It is also the case that the average molecular weights of the polymers from the above catalysts (M_w = 10^3–10^4) are lower than those from the isotactic polypropylenes obtained using the *rac*-ethylenebis(indenyl)zirconium dichloride–mao system (10^4–10^5).[5]

The spectra of compounds **5**, **7** and **3** (Fig. 7) show a remarkably high intensity of the pentad mmrr relative to the mmrm pentad. From the mmmr : mmrr : mrrm = 2 : 2 : 1 ratio,[13] it appears that these polymers are formed by enantiomorphic-site control. The isotactic polypropylenes obtained using catalysts prepared from chiral *ansa*-metallocenes are also formed under enantiomorphic-site control.[4,5] Relatively few such examples exist and it appears that the chiral transition-metal centre is controlling the stereoselectivity. The crystal structure determination of the compound $[Zr\{CMe_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **1** shows that it is chiral, as expected from the

Table 4 Dyad compositions, triad fractions and triad mechanistic model tests of the ^{13}C NMR spectra of the methyl region of the polypropylenes

	Dyad fraction		Triad fraction			Triad test	
Catalyst	[m]	[r]	[mm]	[mr]	[rr]	$4[mr][rr]/[mr]^2$	2[rr]/[mr]
3 $[Ti(L^{Ph})Cl_2]$	0.72	0.28	0.57	0.29	0.14	3.9	1.0
4 $[Zr(L^{Ph})Cl_2]$	0.46	0.54	0.19	0.53	0.28	0.8	1.1
5 $[Hf(L^{Ph})Cl_2]$	0.65	0.35	0.52	0.27	0.21	6.0	1.6
6 $[Hf(L^{CH_2})Cl_2]$	0.68	0.32	0.53	0.29	0.18	4.5	1.2
$[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ at −78 °C	0.8	0.2	0.63	0.32	0.05	1.3	0.3

Table 5 Polystyrene obtained using various stereorigid metallocenes with mao

	Polymerization conditions				
Compound	10^5 cat/mole	T/°C	*t*/h	Yield (%)	Stereospecificity
3 $[Ti(L^{Ph})Cl_2]$	3.0	18	20	1.8[a]	Syndiotactic
4 $[Zr(L^{Ph})Cl_2]$	3.0	18	20	<0.1[a]	Atactic
5 $[Hf(L^{Ph})Cl_2]$	3.0	18	20	<0.1[a]	Atactic
1 $[Zr(L^{Me})Cl_2]$	3.0	18	48	<0.1[a]	Atactic
$[TiL'Cl_2]$[b]	1.5	18	19	0.8[c]	Syndiotactic
$[ZrL'Cl_2]$	1.5	50	168	0.5[c]	Atactic
$[TiLCl_2]$	2.5	50	24	1.6[d]	Syndiotactic
$[ZrLCl_2]$	2.5	50	7	1.3[d]	Atactic
$[HfLCl_2]$	2.5	50	7	2.1[d]	Atactic
$[TiL''Cl_2]$[e]	2.5	50	4	0.6[d]	Syndiotactic

[a] In toluene (30 cm^3)–styrene (30 cm^3), [mao] = 18 mmol dm^{-3}. [b] Ref. 14. [c] [mao] = 9 mmol dm^{-3}. [d] In toluene (10 cm^3)–styrene (50 cm^3), [mao] = 15 mmol dm^{-3}. [e] H_2L'' = 4*S*,5*S* – 4,5-bis(1*H*-indan-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane.

Table 6 Relationships between the metallocene catalysts and the stereoregularities of the polypropylene and polystyrene products

	Stereoregularity	
Catalyst	Polypropylene	Polystyrene
$[Ti(\eta\text{-}C_5H_5)_2Cl_2]$	Atactic	Syndiotactic
$[Ti(\eta\text{-}C_5H_5)Cl_3]$	Atactic	Syndiotactic
4 $[Zr(L^{Ph})Cl_2]$	Atactic	Atactic
3 $[Ti(L^{Ph})Cl_2]$	Isotactic	Syndiotactic
5 $[Hf(L^{Ph})Cl_2]$	Isotactic	Atactic
$[TiLCl_2]$		Syndiotactic
$[ZrLCl_2]$	Isotactic	Atactic
$[TiL'Cl_2]$[a]	Atactic	Syndiotactic

[a] Ref. 13.

position of the CMe_2 bridge at the indenyl ring. The compounds with the ligands $CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)$ and $C_6H_{10}(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)$ are also chiral, for the same reason. The NMR spectra of the polypropylenes provide triad intensity data and triad mechanistic model tests using these data are summarized in Table 4. They show that the polymers have an isotactic microstructure produced according to the enantiomorphic-site control model. These conclusions accord very well with those drawn from the methyl region of the ^{13}C NMR spectra.

The ^1H NMR spectrum of polypropylenes obtained from $[Hf\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$[12] **5** showed resonances at δ 4.6 assignable to the presence of a vinylidene chain-end structure but no detectable amount of vicinal chain-end structures was seen. The polypropylenes formed using compounds **3** and **7** under the same conditions as for **5** had very similar end-group analyses.

We conclude that the catalyst systems using $[Zr\{CMe_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **1**, $[Zr\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **4** and $[Zr\{C_6H_{10}(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **6** with mao produced an atactic polypropylene with low molecular weight, but that $[Hf\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **5**, $[Hf\{C_6H_{10}(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **7** and $[Ti\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **3** with mao give isotactic polypropylenes with low molecular weight. Thus, the zirconium compounds produce an aspecific polymer and the hafnium and titanium compounds produce an isospecific polymer. Also, the results suggest that an effective stereoregular catalyst is not simply one having a chiral metal site, rather one of tighter steric control of the ligand system.

The new metallocenes, $[M(L^{Ph})Cl_2]$ (M = Ti **3**, Zr **4** and Hf **5**) and $[Zr(L^{Me})Cl_2]$ **1**, the chiral stereorigid metallocenes, $[MLCl_2]$, M = Ti or Zr[6] and the achiral stereorigid metallocenes $[ML'Cl_2]$ [M = Ti or Zr; L' = $(CH_2)_5(\eta\text{-}C_5H_4)_2$] have been tested as catalysts for the polymerization of styrene towards the syndiotactic polymer. The data are given in Table 5 and show that all these bridged metallocene catalysts have lower activity than has been reported for the related unbridged catalysts.[15]

The ^{13}C NMR spectra of the phenyl C^1 carbon of the polymers obtained using the chiral stereorigid catalysts of Ti, Zr and Hf **3**–**5** and the achiral stereorigid catalyst show that both chiral and achiral stereorigid titanium catalysts polymerize styrene to an extremely highly syndiotactic polymer. However, the catalysts of Zr and Hf had very low activity and produced atactic polystyrene, presumably by simple thermal polymerization. A comparison of the stereoregularities of the polypropylene and the polystyrene polymers formed by various metallocene catalyst precursors is given in Table 6. This shows that most of the catalysts which produced atactic polypropylenes also polymerized styrene to the syndiotactic polymer and the catalysts which produced isotactic-rich polypropylenes were mostly inactive towards styrene. However, the $[Ti\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$–mao system produced both isotactic and syndiotactic polymer.

Experimental

All manipulations of air- and/or moisture-sensitive materials were carried out in an inert atmosphere using a dual vacuum/dinitrogen (or argon) line and standard Schlenk techniques, or in a dry-box under an atmosphere of dinitrogen (< 10 ppm oxygen, < 20 ppm water). Nitrogen gas was purified by passage through a column containing BTS catalyst and 4A molecular sieves. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless-steel cannulae (diameter 0.5–2.0 mm) and mixtures were filtered in a similar way using modified cannulae which could be fitted with either filter-paper or glass-fibre filter discs (Whatman GFC).

Chromatography was performed on columns of neutral alumina (Fluka or Aldrich) deactivated with 6% w/w water, or silica (Fluka) made up in light petroleum.

All solvents were thoroughly deoxygenated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, tetrahydrofuran over molten potassium. Diethyl ether, light petroleum and pentane (b.p. 35, 30–40 and 40–60 °C) were dried over sodium–potassium alloy (1:3 w/w), dichloromethane by refluxing over phosphorus pentaoxide. Propene was used without further purification. Styrene was dried over CaH_2 and distilled under vacuum.

Nuclear magnetic resonance spectra were recorded on the following instruments: ^1H, 250 MHz, Bruker AM-250; 270, 300 MHz, Bruker WH-300 or AM-300; ^{13}C, 75.6 MHz, Bruker AM-300. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ 0). All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m). The ^{13}C NMR spectra of polymers were recorded in 1,2,4-trichlorobenzene–C_6D_6 (80:20 v/v) as the solvent, at 100–130 °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. Infrared spectra were recorded on a Perkin Elmer 1510 Fourier-transform spectrometer or on a Mattson Polaris Fourier-transform spectrometer. Mass spectra were recorded on an AEI MS 902 spectrometer updated by a data-handling system supplied by Mass Spectroscopy Services Ltd. Gas chromatograms were recorded on a Shimazu GC-MINI 3(PF) gas chromatograph equipped with a hydrogen-flame ionization detector for the qualitative analyses of the reaction products. Gel-permeation chromatograms of the polymers were obtained at 135 °C by using a Waters model 150C instrument at Idemitsu Kosan Co. (Japan). The solvent was 1,2,4-trichlorobenzene, and the flow rate was 1.0 $cm^3 min^{-1}$. Elemental analyses were obtained by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford.

Preparations.—Methylaluminoxane, mao. (*a*) *Using* $CuSO_4\cdot 5H_2O$. The reported procedure was used.[13]

(*b*) *Using* $Al_2(SO_4)_3\cdot 16H_2O$. Powdered $Al_2(SO_4)_3\cdot 16H_2O$ (12.3 g, 0.020 mol) and toluene (100 cm^3) were placed in a three-necked round-bottom flask (300 cm^3) under nitrogen gas and immersed in a water-bath. Trimethylaluminium (20 cm^3, 0.209 mol) was added very slowly dropwise at 10 °C using a cannula. The reaction was allowed to continue for 24 h. The mixture was filtered using a filter cannula with glass filter-paper. A clear toluene solution was obtained. The filtrate was concentrated and dried *in vacuo* at 50 °C. A white glassy solid was obtained in 28.9% yield (3.50 g).

$CMe_2(C_5H_5)(C_9H_7)$ **I**. Lithium indenide (5.0 g, 0.041 mol) was dissolved in thf (200 cm^3). A solution of 6,6-dimethylfulvene (4.35 g, 0.041 mol) in thf (50 cm^3) was added dropwise at 0 °C. When the addition was complete the solution was warmed to room temperature (r.t.). Then stirring was continued overnight. The reaction mixture was quenched at 0 °C by addition of water (20 cm^3). The resulting two-phase mixture was diluted with Et_2O (200 cm^3) and the organic layer washed well (three times) with water and then with concentrated NaCl solution. The organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure to produce a yellow viscous oil. The product was purified by chromatography on alumina. Elution with light petroleum (b.p. 40–60 °C) gave, upon removal of the solvent, 8.9 g (98%) of a yellow viscous oil. Proton NMR studies showed this to be an isomeric mixture of products.

$CPh_2(\eta-C_5H_5)(\eta-C_9H_7)$ **II**. Lithium indenide (6.0 g, 0.049 mol) was dissolved in thf (200 cm^3). A solution of 6,6-diphenylfulvene (11.32 g, 0.049 mol) in thf (100 cm^3) was added dropwise at 0 °C. When the addition was complete, the solution was warmed to r.t. Then stirring was continued overnight. The reaction mixture was quenched at 0 °C by addition of water (20 cm^3). The two-phase mixture was diluted with Et_2O (200 cm^3) and the organic layer washed well (three times) with water and then with concentrated NaCl solution. The organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide a yellow viscous oil. The product was purified by chromatography on alumina. Elution with light petroleum (b.p. 40–60 °C) gave, upon removal of solvent, 15.2 g (89.4%) of a red viscous oil. Proton NMR studies showed this to be an isomeric mixture of products.

$C(CH_2)_5(\eta-C_5H_5)(\eta-C_9H_7)$ **III**. Lithium indenide (6.0 g, 0.049 mol) was dissolved in thf (200 cm^3). A solution of 6,6-pentamethylenefulvene (7.2 g, 0.049 mol) in thf (50 cm^3) was added dropwise at 0 °C with stirring. When the addition was complete the solution was warmed to r.t. and stirring was continued overnight. The reaction mixture was quenched at 0 °C by addition of water (20 cm^3). The two-phase mixture was diluted with Et_2O (200 cm^3) and the organic layer washed well (three times) with water and then with concentrated NaCl solution. The organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide a yellow viscous oil. The product was purified by chromatography on alumina. Elution with light petroleum (b.p. 40–60 °C) gave, upon removal of the solvent, 12.8 g (93%) of a pale orange viscous oil. Proton NMR studies showed this to be an isomeric mixture of products.

$Li_2[CMe_2(\eta-C_5H_4)(\eta-C_9H_6)]$. 2-Cyclopentadienyl-2-indenylpropane (10.68 g, 0.049 mol) was dissolved in Et_2O (250 cm^3) and cooled to 0 °C. *n*-Butyllithium in Et_2O (39.1 cm^3 of a 2.5 mol dm^{-3} solution) was added dropwise causing the solution to turn yellow with eventual precipitation of a solid. The solution was then filtered and washed with Et_2O (100 cm^3 × 2). Removal of solvent *in vacuo* gave 9.89 g (86%) of a pale yellow powder.

$Li_2[CPh_2(\eta-C_5H_4)(\eta-C_9H_6)]$. Cyclopentadienyl(indenyl)diphenylmethane (17.69 g, 0.05 mol) was dissolved in Et_2O (250 cm^3) and cooled to 0 °C. *n*-Butyllithium in Et_2O (40.8 cm^3 of a 2.5 mol dm^{-3} solution) was added dropwise whereupon the solution turned red with eventual precipitation of a solid. The solution was then filtered and washed with Et_2O (100 cm^3 × 2). Removal of solvent *in vacuo* gave 11.9 g (63%) of an orange powder.

$Li_2[C(CH_2)_5(\eta-C_5H_4)(\eta-C_9H_6)]$. 1-Cyclopentadienyl-1-indenylcyclohexane (13.14 g, 0.050 mol) was dissolved in Et_2O (250 cm^3) and cooled to 0 °C. *n*-Butyllithium in Et_2O (40.1 cm^3 of a 2.5 mol dm^{-3} solution) was added dropwise whereupon the solution turned red with eventual precipitation of a solid. The solution was then filtered and washed with Et_2O (100 cm^3) twice. Removal of solvent *in vacuo* gave 12.3 g (90%) of a pale yellow powder.

$[Zr\{CMe_2(\eta-C_5H_4)(\eta-C_9H_6)\}Cl_2]$ **1**. Zirconium(IV) chloride (1.49 g, 6.4 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[CMe_2(\eta-C_5H_4)(\eta-C_9H_6)]$ (1.5 g, 6.4 mmol) in CH_2Cl_2 (50 cm^3) was added slowly at 0 °C. After the addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield an orange solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave orange crystals which were filtered off and dried *in vacuo* (0.85 g, 35%).

Two recrystallizations from CH_2Cl_2 yielded a pure sample. One of these was used for the crystal structure determination.

$[Hf\{CMe_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **2**. Hafnium chloride (1.46 g, 4.6 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[CMe_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ (1.07 g, 4.6 mmol) in CH_2Cl_2 (50 cm^3) was added slowly at 0 °C. After addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave yellow crystals which were filtered off and dried *in vacuo* (0.3 g, 14%).

$[Ti\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **3**. Titanium(IV) chloride (1.02 g, 5.39 mmol) was treated at −98 °C with thf (50 cm^3). The solution $Li_2[CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ (2.0 g, 5.39 mmol) was dissolved in thf (50 cm^3) and added dropwise to the $TiCl_4$ solution at 0 °C. The solution darkened and a green precipitate formed. After HCl gas was bubbled through the solution for 2 min the precipitate disappeared. The solvent was removed under reduced pressure and the residue washed on a Buchner funnel with several portions of Et_2O until the filtrate was essentially colourless. The solid was then washed with 10% aqueous HCl, water, ethanol and Et_2O. After drying *in vacuo*, 2.0 g (80%) of a green powder were obtained.

$[Zr\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **4**. Zirconium(IV) chloride (0.63 g, 2.69 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ (1.0 g, 2.69 mmol) in CH_2Cl_2 (50 cm$_3$) was added slowly at 0 °C. After addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield an orange solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave orange crystals which were filtered off and dried *in vacuo* (0.9 g, 66%).

$[Hf\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **5**. Hafnium(IV) chloride (1.73 g, 5.39 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ in CH_2Cl_2 was added slowly at 0 °C. After addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave yellow crystals which were filtered off and dried *in vacuo* (1.8 g, 56%).

$[Zr\{C(CH_2)_5(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **6**. Zirconium(IV) chloride (0.85 g, 3.65 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[C(CH_2)_5(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ (1.0 g, 3.65 mmol) in CH_2Cl_2 (50 cm^3) was added slowly at 0 °C. After addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield an orange solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave orange crystals which were filtered off and dried *in vacuo* (0.95 g, 62%).

$[Zr\{C(CH_2)_5(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ **7**. Hafnium(IV) chloride (1.17 g, 3.65 mmol) was placed in a Schlenk vessel (300 cm^3) and CH_2Cl_2 (50 cm^3) added at −98 °C. A suspension of $Li_2[C(CH_2)_5(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)]$ (1.0 g, 3.65 mmol) in CH_2Cl_2 (50 cm^3) was added slowly at 0 °C. After addition was complete the mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The extract was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C overnight gave yellow crystals which were filtered off and dried *in vacuo* (0.47 g, 27%).

Polymerization of Propylene using the $[M\{CR_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$*–mao Systems* [M = Ti, Zr *or* Hf; R_2 = Me_2, Ph_2, *or* $(CH_2)_5$].—Polymerizations were performed in a Fischer–Porter apparatus (100 cm^3) equipped with a magnetic stirrer and thermostatted bath. Typically, 0.02 mmol of the metallocene dichloride and 20 mmol of mao were weighed into the reaction vessel in a glove-box and then toluene (10 cm^3) was added. After 5 min of equilibration, the nitrogen atmosphere was removed and propylene gas was introduced at 2 kg cm^{-2} for 5–9 h, whilst the polymerization reaction continued. Then excess of propylene was vented and the contents of the reaction vessel treated with dilute hydrochloric acid (100 cm^3) to destroy the catalyst. The toluene layer was separated from the aqueous layer and dried over $MgSO_4$. The toluene solvent was removed under reduced pressure giving a low-melting solid which was dried *in vacuo*.

Polymerization of Styrene using the $[M\{CR_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$*–mao Systems* [M = Ti, Zr *or* Hf, R_2 = Me_2, Ph_2, *or* $(CH_2)_5$].—Polymerizations were performed in a Schlenk vessel (300 cm^3) equipped with a magnetic stirrer and thermostatted bath. A typical experiment is described. The vessel was charged with toluene (40 cm^3), $[Zr\{CPh_2(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ (10 mg) and mao (1.2 g). Typically, 27 g of styrene monomer were then added. The temperature of the polymerization was controlled by means of a thermostatted bath. The reaction mixture was stirred variously for 5 h to 10 d. After polymerization, polymers were coagulated with acidified methanol (200 cm^3), recovered by filtration, washed with fresh methanol and dried *in vacuo*. Polymer samples were extracted with boiling ethyl methyl ketone.

Crystal Structure Determination of Compound **1**.—*Crystal data.* $C_{17}H_{16}Cl_2Zr$, M = 382.4, orthorhombic, space group $Pna2_1$, a = 9.813(2), b = 12.214(2), c = 12.806(4) Å, U = 1534.9 Å^3 (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, λ = 0.71069 Å), Z = 4, D_c = 1.66 g cm^{-3}, $F(000)$ = 768, μ = 10.4 cm^{-1}. Crystal dimensions 0.3 × 0.3 × 0.4 mm.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω-scan width = 0.80 + tanθ, ω-scan speed = 0.9–6.7° min^{-1}, graphite-monochromated Mo-Kα radiation, 2824 reflections measured ($1.5 \leqslant \theta \leqslant 25°, 0 \leqslant h \leqslant 11, 0 \leqslant k \leqslant 14; 0 \leqslant l \leqslant 12$), 1407 unique (merging R = 0.036), giving 1185 with $I > 3\sigma(I)$.

Structure analysis and refinement. Direct methods were employed and full-matrix least-squares refinement with all non-hydrogen atoms in anisotropic approximation (181 variables, observations/variables = 6.5). All hydrogen atoms were located in the Fourier difference maps and included in the final refinement with fixed positional and thermal parameters. A Chebyshev weighting scheme[16] was applied with parameters 4.98, −2.04 and 3.96. Corrections for Lorentz and polarization effects were applied; the anomalous-dispersion contributions were included in the calculated structure factors. The final R and R' values are 0.022 and 0.026. The maximum and minimum peaks in the final difference synthesis were 0.30 and −0.27 e Å^{-3}. The Flack test[17] was applied for the absolute configuration (the enantiopole parameter was refined to 0.03 using 1806 reflections with non-averaged Friedel equivalents). Crystallographic calculations were carried out using the CRYSTALS[18] program package on a Micro VAX 3800 computer. Fractional atomic coordinates are listed in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 7 Fractional atomic coordinates for compound **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	−0.906 17(4)	−0.065 32(3)	−0.266 23(7)
Cl(1)	−0.859 4(2)	−0.181 0(1)	−0.415 2(1)
Cl(2)	−0.930 5(2)	−0.204 1(1)	−0.130 4(1)
C(1)	−1.062 3(6)	0.047 9(5)	−0.371 7(4)
C(2)	−1.141 0(6)	−0.046 7(5)	−0.349 9(5)
C(3)	−1.163 2(5)	−0.048 5(5)	−0.240 8(5)
C(4)	−1.098 2(5)	0.041 7(6)	−0.196 2(5)
C(5)	−1.037 2(4)	0.105 2(4)	−0.276 0(4)
C(6)	−0.925 3(4)	0.190 4(3)	−0.259 5(5)
C(7)	−0.911 6(5)	0.269 7(5)	−0.351 3(5)
C(8)	−0.949 7(7)	0.257 1(5)	−0.159 3(5)
C(9)	−0.802 6(4)	0.113 9(3)	−0.247 5(3)
C(10)	−0.772 6(5)	0.056 7(4)	−0.153 7(4)
C(11)	−0.679 2(5)	−0.027 9(4)	−0.174 2(4)
C(12)	−0.644 5(4)	−0.022 9(3)	−0.280 2(4)
C(13)	−0.548 5(5)	−0.084 3(3)	−0.339 7(4)
C(14)	−0.536 0(5)	−0.062 0(4)	−0.443 4(4)
C(15)	−0.616 6(4)	0.019 0(4)	−0.491 7(4)
C(16)	−0.707 9(4)	0.081 2(3)	−0.437 6(4)
C(17)	−0.722 3(4)	0.063 9(3)	−0.329 6(3)

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