Polymerisation of Ethylene and Propene using New Chiral Zirconium Derivatives. Crystal Structure of [ZrL^1Cl_2]-[H_2L^1 = (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane]†

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The chiral indene derivative (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-3-ylmethyl)-2,2-dimethyl-1,3-dioxolane has been prepared and used to synthesise the bis(η-indenyl) derivatives [ML^1Cl_2][M = Ti, Zr or Hf; H_2L^1 = (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane]. The crystal structure of the zirconium compound has been determined. Hydrogenation of the compounds [ML^1Cl_2] gives the corresponding bis(4,5,6,7-tetrahydroinden-1-ylmethyl) derivatives [ML^2Cl_2]. The ability of the new metal compounds to catalyse the polymerisation of ethylene and propene has been examined. The compounds together with methylaluminoxane [$(OAlMe)_n$] as cocatalyst are active for polymerisation of ethylene and, for M = Zr, for propene.

There has been considerable recent interest in the use of derivatives of the bent bis(η-cyclopentadienyl) system $M(\eta\text{-}C_5R_5)_2$ as catalytic components in the homogeneous isospecific Ziegler–Natta catalysed polymerisation of propene. For example, the polymerisation of propene using bis(η-cyclopentadienyl)metal(IV) derivatives (M = Ti or Zr) and methylaluminoxane [$(OAlMe)_n$] yielded atactic polymers,[1,2] or using [$Ti(\eta\text{-}C_5H_5)_2Ph_2$] gave the isotactic polymer.[3] Primary *cis* addition was shown to occur in these polymerisations and the stereochemical control was proposed to arise from the configuration of the last inserted monomer unit.

Recently, Ewen *et al.*[4] prepared highly syndiotactic polypropene using the η-fluorenylhafnium derivative [$Hf(\eta\text{-}C_5H_4\text{-}CMe_2\text{-}\eta\text{-}C_{13}H_8)Cl_2$] and methylaluminoxane. Kaminsky *et al.*[5] have reported the use of *rac*-(ethylene)bis(η-4,5,6,7-tetrahydroinden-1-yl)zirconium dichloride with methylaluminoxane to produce highly isotactic polypropene at room temperature. The activity of this system is remarkably high (> 7000 kg polymer per mol Zr per h) and approaches that obtained with industrially used supported catalyst systems.[5,6,7] The polymers have microstructures identical to those obtained from heterogeneous titanium(III) catalysts and in this case it appears that stereoregulation arises from enantiomorphic site control, *i.e.* the asymmetry of the catalyst site controls the stereoregularity. However, the use of *meso*-(ethylene)bis(indenyl)titanium dichloride at −60 °C produces only atactic polymer. We decided to attempt to prepare an analogue of the *rac*-(ethylene)bis(η-4,5,6,7-tetrahydroinden-1-yl)zirconium dichloride in which the ethylene bridge was replaced by a dioxolane group. The perceived advantage of this compound was that it would be made in only one enantiomeric form since the starting material for the dioxolane ligand is resolved tartaric acid.[8,9]

Results and Discussion

The compound (4*S*,5*S*)-*trans*-4,5-bis(1*H*-inden-3-ylmethyl)-2,2-dimethyl-1,3-dioxolane **1** was prepared, somewhat indirectly, by treatment of the previously described[8,9] optically pure 2,2-dimethyl-4,5-bis(toluene-*p*-sulphonyloxymethyl)-1,3-dioxolane **2** in diethyl ether with a suspension of indenylmagnesium bromide in toluene (Scheme 1). From this reaction a clear, pale green, viscous oil was isolated. The ^1H NMR spectrum of the oil showed the presence of two main products and ^1H–^1H correlation spectroscopy (COSY) 45 identified two sets of resonances which were assignable to 4-bromo-5-(1*H*-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane **3** and 4,5-bis(1*H*-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane **4**. Distillation of the product mixture at 145 °C (0.05 Torr, *ca.* 6.6 Pa) gave essentially pure **3**. Chromatography of the original green oil gave a second pale green oil which had a much simpler ^1H NMR spectrum and this may be assigned to the bis(inden-3-ylmethyl) compound **1**.

The analytical and spectroscopic data characterising **1**, **3** and **4**, and all the other new compounds described in this work are given in Table 1. The proposed structures are shown in Scheme 1. The ^1H NMR spectrum of the inden-1-ylmethyl derivative **4** was obtained from that of the original reaction mixture by subtraction of the resonances due to the bromo compound **3**, and the assignment of this spectrum is straightforward and comes directly from ^1H-^1H COSY 45 (see Table 1).

The process of chromatography has removed compound **3** and induced isomerisation, *via* the deprotonation and reprotonation of the inden-1-ylmethyl derivative **4** to give the thermodynamically more stable inden-3-ylmethyl derivative **1**.

The ^1H NMR spectrum of the 3-substituted indene **1** appears relatively straightforward. The higher-field 'AB'-type pattern belongs to the methylene protons attached to the dioxolane ring, while the lower-field 'AB'-type pattern arises from the methylene group in the five-membered ring of the indene moiety. The geminal coupling constants are 14.8 and 23.2 Hz respectively. The large value of the latter arises from hyperconjugative electron withdrawal from the C–H bonds into the adjacent π system, and is approximately the same as that found by Bergson[10] for free indene. Double-resonance experiments revealed long-range couplings. The assignment of the oxolane unit is straightforward, and the indene carbons were assigned by comparison with an assignment of the ^{13}C NMR spectrum of 3-methylindene by Edlund.[11]

The addition of 2 equivalents of butyllithium to a solution of compound **1** in tetrahydrofuran (thf) gives a pale green powder which we presume from the reaction described below to be the

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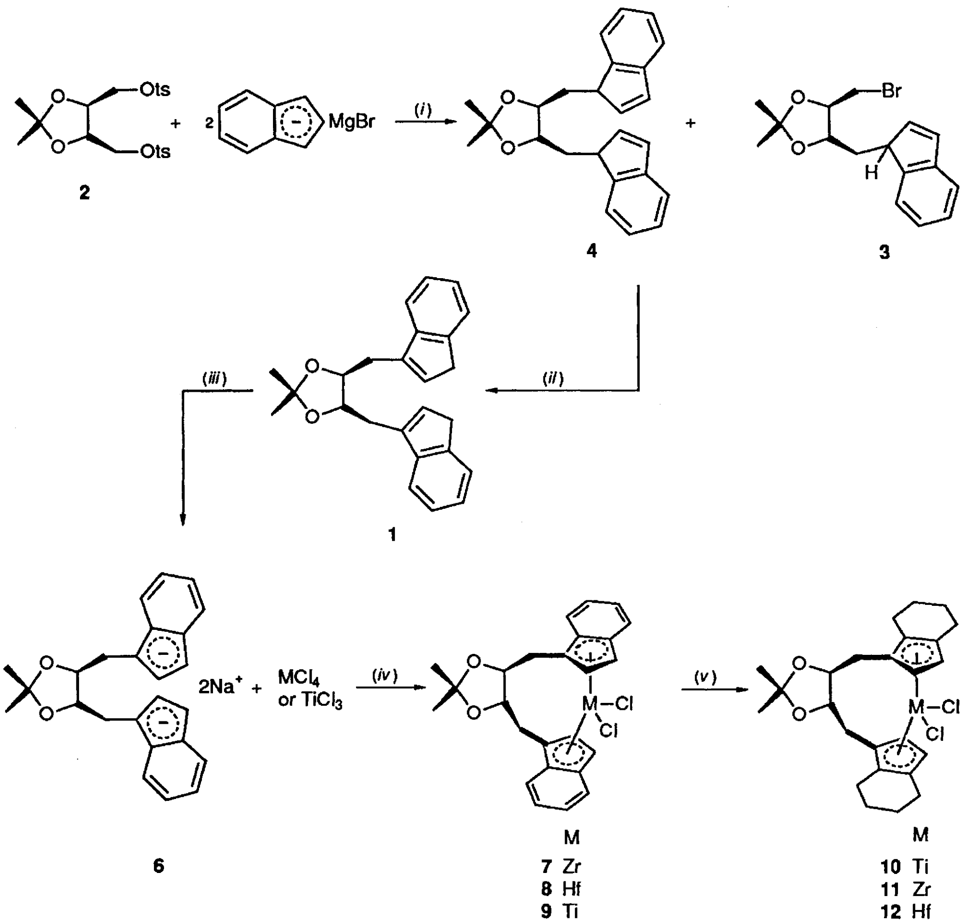
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: atm = 101 325 Pa, bar = 10^5 Pa.



Scheme 1 ts = Toluene-*p*-sulphonyl. (*i*) In toluene at 0 °C, dropwise addition over 2 h, warming to r.t.; (*ii*) In Et_2O, at chromatography on a neutral alumina column, first green band collected, yield 76%; (*iii*) Solution of compound **1** in thf added to $NaNH_2$ suspended in thf over 1 h at r.t., 74%; (*iv*) Na_2L^1 in thf added dropwise at 50 °C, 16 (M = Zr), 8 (Hf), 17% (Ti); (*v*) In CH_2Cl_2, H_2 (100 atm) with PtO_2 as catalyst at r.t. for 2 h, *ca.* 75%

dilithium salt **5**. Compound **5** is pyrophoric and very soluble in thf and hot toluene. Treatment of **1** with a suspension of 2 equivalents of freshly prepared sodium amide in thf gives an off-white powder, presumably of the disodium salt **6**, which is also pyrophoric and slightly soluble in thf. It was found necessary to dry **6** at 40 °C *in vacuo* for about 6 h to remove all the thf.

A solution of $ZrCl_4$ in thf was treated with an equimolar quantity of salt **5** giving air-stable yellow crystals of $[ZrL^1Cl_2]$ **7** where L^1 is the dianion of compound **1**. The highest yield obtained from this reaction was 10%. Better yields of **7** were obtained when the salt **6** was used as a source of the ligand dianion. The yield could also be improved, to 16%, by adding **6** dropwise with the $ZrCl_4$ solution at reflux. Typically, the sterically demanding *ansa*-metallocene derivatives of Group 4 metals are obtained in yields of 10–30%.[12–14]

Compound **7** was found to have appreciable solubility in boiling toluene and well formed crystals could be grown overnight by allowing a hot, filtered solution to cool. The crystal structure of **7** has been determined. Two views of the molecular structure are given in Fig. 1, and selected bond angles and distances are given in Table 2. The metal–chlorine and –ring centroid distances of 2.43 and 2.23 Å, respectively, as well as the Cl–Zr–Cl and centroid–Zr–centroid angles of 97.1 and 127.2°, respectively, are in accord with those for other zirconocene dihalide derivatives.[13–15] The indene rings are more eclipsed in $[ZrL^1Cl_2]$ than in the *rac*-(ethylene)bis(tetrahydroindenyl)-titanium or -zirconium dichlorides.[13,16] The dihedral angle between the rings is 37° in the former and 131° in the latter. This arises because in $[ZrL^1Cl_2]$, the species bridging the indene rings is twisted to one side, as in *meso*-(ethylene)bis(tetrahydroindenyl)titanium dichloride,[16] where the dihedral angle is 19°.

In the ^1H NMR spectrum of compound **7** the two methine resonances occur at δ 4.2 and 4.6, while the methylene resonances occur as a series of overlapping lines at δ 3.0–3.8. The system is best described as two ABX systems where the X resonances are coupled. In the light of the crystal structure it is possible to assign the resonances due to the methine and methylene groups. Thus the lowest-field methylene resonance shows a very small coupling to its associated methine proton and so the dihedral angle between them must be approximately 90°. This is the situation for protons H_d and H_y. The shift to lower field for proton H_d arises from its proximity to the upper cyclopentadienyl ring. For the other set of three protons it is clear that the methylene proton giving the highest-field resonance is *trans* to H_x. Therefore this resonance must be associated with H_a. The assignments of H_b and H_c follow automatically from the COSY 45 spectrum; likewise, the assignments of the cyclopentadienyl protons H_{r-u}.

A refluxing solution of $HfCl_4$ in thf was treated dropwise with an equimolar quantity of salt **6** giving yellow crystals of $[HfL^1Cl_2]$ **8**, in 8% yield. The ^1H NMR spectrum closely resembles that of **7** but the methylene resonances are now clearly resolved.

When $TiCl_4$ was treated with salt **5** reduction occurred giving $[TiCl_3(thf)_3]$. However, treatment of $TiCl_3{\cdot}3thf$ with **1** equivalent of **6** gave a dark green reaction solution. Addition of 1 equivalent of $FeCl_3$ to the green solution, which presumably contains $[TiL^1Cl]$, caused the solution to become dark red and dark green crystals of $[TiL^1Cl_2]$ **9** could be isolated in 17% yield. Compound **9** was only slightly soluble in common solvents; solutions of pure **9** were red-brown. Crystals could be grown from hot *o*-dichlorobenzene, but significant decomposition also occurred. The resulting fine needles of **9** gave an elemental analysis consistent with the formulation of one

Table 1 Analytical^a and spectroscopic data

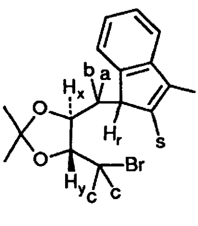
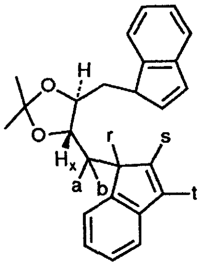
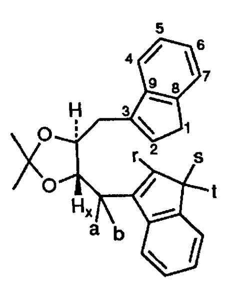
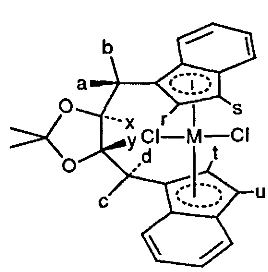
Compound	NMR data^b
3 C, 62.9 (59.45); H, 6.20 (5.9)^d 	^{1}H:^{c} 7.6–7.3 (4 H, complex bands, aromatics), 7.0 [1 H, dd, J(H$_t$–H$_s$) 5.6, J(H$_t$–H$_r$) 1.5, H$_t$], 6.8 [1 H, dd, J(H$_s$–H$_t$) 5.6, J(H$_s$–H$_r$) 1.9, H$_s$], 4.1 [1 H, ddd, J(H$_x$–H$_a$) 9.1, J(H$_x$–H$_b$) 3.2, J(H$_x$–H$_y$) 6.0, H$_x$], 4.0 [1 H, dt, J(H$_y$–H$_x$) 6.0, J(H$_y$–H$_c$) 5.3, H$_y$], 3.8 [1 H, br d, J(H$_r$–H$_s$) 1.9, J(H$_r$–H$_t$) 1.5, J(H$_r$–H$_a$) 4.7, J(H$_r$–H$_b$) 10.5, H$_r$], 3.4 [2 H, d, J(H$_c$–H$_y$) 5.3, H$_c$], 2.4 [1 H, ddd, J(H$_b$–H$_a$) 13.8, J(H$_b$–H$_r$) 10.5, J(H$_b$–H$_x$) 3.2, H$_b$], 1.7 [1 H, obscured, J(H$_a$–H$_b$) 13.8, J(H$_a$–H$_r$) 4.7, J(H$_a$–H$_x$) 9.1, H$_a$], 1.6 (3 H, s, CH$_3$), 1.55 (3 H, s, CH$_3$)
4^e 	^{1}H:^{c} 7.6–7.3 (8 H, complex bands, aromatics), 7.0 [2 H, dd, J(H$_t$–H$_s$) 5.6, J(H$_t$–H$_r$) 1.5, H$_t$], 6.8 [2 H, dd, J(H$_s$–H$_t$) 5.6, J(H$_s$–H$_r$) 1.9, H$_s$], 3.9 [2 H, dd, J(H$_x$–H$_a$) 9.2, J(H$_x$–H$_b$) 2.3, H$_x$], 3.8 [2 H, complex, J(H$_r$–H$_s$) 1.9, J(H$_r$–H$_t$) 1.5, J(H$_r$–H$_a$) 4.6, J(H$_r$–H$_b$) 11.0, H$_r$], 2.3 [2 H, ddd, J(H$_a$–H$_b$) 13.8, J(H$_a$–H$_x$) 9.2, J(H$_a$–H$_r$) 4.6, H$_a$], 1.6 (6 H, s, 2CH$_3$), 1.4 [2 H, ddd, J(H$_a$–H$_b$) 13.8, J(H$_b$–H$_x$) 2.3, J(H$_b$–H$_r$) 11.0, H$_b$]
1^f C, 82.3 (83.7); H, 7.3 (7.3) 	^{1}H:^{c} 7.4–7.1 (8 H, complex bands, aromatics), 6.3 [2 H, br s, J(H$_r$–H$_a$) 1.5, J(H$_r$–H$_b$) 1.5, J(H$_r$–H$_s$) 2.5, J(H$_r$–H$_t$) 2.5, H$_r$], 4.2 [2 H, t, J(H$_x$–H$_a$) 8.0, J(H$_x$–H$_b$) 4.5, H$_x$], 3.3 [4 H, 4 lines, J(H$_s$–H$_t$) 23.2, J(H–H$_r$) 2.5, J(H–H$_a$) 1.5, J(H–H$_b$) 1.5, H$_s$ + H$_t$], 2.9 [4 H, complex band, J(H$_a$–H$_b$) 14.8, J(H$_a$–H$_x$) 8.0, J(H$_b$–H$_x$) 4.5, J(H–H$_r$) 1.5, J(H–H$_s$) 1.5, J(H–H$_t$) 1.5, H$_a$ + H$_b$], 1.6 (6 H, s, 2CH$_3$) ^{13}C:^{g} 144.9 (s, C^9), 144.1 (s, C^8), 140.1 (s, C^3), 130.5 (d, C^2), 125.8 (d, C^5), 124.5 (d, C^6), 123.5 (d, C^7), 118.9 (d, C^4), 108.6 [s, *C*(CH$_3$)$_2$], 79.4 (d, OCH), 37.6 (t, C^1), 31.9 (t, CH$_2$), 27.5 (q, CH$_3$)
7 C, 57.8 (57.9); H, 4.9 (4.7)^i 	^{1}H:^{h} 7.6–7.1 (8 H, complex, aromatics), 6.85 [1 H, d, J(H$_r$–H$_s$) 3.1, H$_r$], 6.80 [1 H, d, J(H$_t$–H$_u$) 3.5, H$_t$], 6.30 [1 H, d, J(H$_u$–H$_t$) 3.5, H$_u$], 6.25 [1 H, d, J(H$_s$–H$_r$) 3.1, H$_s$], 4.6 [1 H, ddd, J(H$_x$–H$_y$) 7.7, J(H$_x$–H$_a$) 11.5, J(H$_x$–H$_b$) 3.5, H$_x$], 4.2 [1 H, ddd, J(H$_y$–H$_x$) 7.7, J(H$_y$–H$_c$) 10.3, J(H$_y$–H$_d$) 0.8, H$_y$], 3.7 [1 H, d, J(H$_d$–H$_c$) 15.0, J(H$_d$–H$_y$) 0.8, H$_d$], 3.36 [1 H, dd, J(H$_b$–H$_a$) 16.3, J(H$_b$–H$_x$) 3.5, H$_b$], 3.34 [1 H, dd, J(H$_c$–H$_d$) 15.0, J(H$_c$–H$_y$) 10.3, H$_c$], 3.2 [1 H, dd, J(H$_a$–H$_b$) 16.3, J(H$_a$–H$_x$) 11.5, H$_a$], 1.53 (3 H, s, CH$_3$), 1.50 (3 H, s, CH$_3$)
8 C, 49.5 (49.6); H, 3.9 (4.0)^j	^{1}H:^{h} 7.6–7.1 (8 H, complex, aromatics), 6.80 [1 H, d, J(H$_r$–H$_s$) 3.5, H$_r$], 6.75 [1 H, d, J(H$_t$–H$_u$) 3.1, H$_t$], 6.13 [1 H, d, J(H$_u$–H$_t$) 3.1, H$_u$], 6.11 [1 H, d, J(H$_s$–H$_r$) 3.5, H$_s$], 4.5 [1 H, ddd, J(H$_x$–H$_y$) 7.7, J(H$_x$–H$_a$) 11.4, J(H$_x$–H$_b$) 3.0, H$_x$], 4.2 [1 H, ddd, J(H$_y$–H$_x$) 7.7, J(H$_y$–H$_c$) 10.2, J(H$_y$–H$_d$) 1.0, H$_y$], 3.8 [1 H, d, J(H$_d$–H$_c$) 15.5, J(H$_d$–H$_y$) 1.0, H$_d$], 3.5 [1 H, dd, J(H$_b$–H$_a$) 16.0, J(H$_b$–H$_x$) 3.0, H$_b$], 3.3 [1 H, dd, J(H$_c$–H$_d$) 15.5, J(H$_c$–H$_y$) 10.2, H$_c$], 3.2 [1 H, dd, J(H$_a$–H$_b$) 16.0, J(H$_a$–H$_x$) 11.4, H$_a$], 1.53 (3 H, s, CH$_3$), 1.50 (3 H, s, CH$_3$)

Table 1 (*continued*)

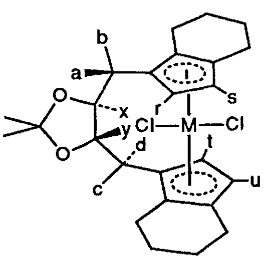
Compound	NMR data^b
9 C, 62.4 (63.2); H, 5.0 (5.1)^k	^{1}H:^{h} 7.7–7.1 (8 H, complex, aromatics), 6.90 [1 H, d, J(H$_r$–H$_s$) 3.0, H$_r$], 6.80 [1 H, d, J(H$_t$–H$_u$) 3.5, H$_t$], 6.35 [1 H, d, J(H$_u$–H$_t$) 3.5, H$_u$], 6.30 [1 H, d, J(H$_s$–H$_r$) 3.0, H$_s$], 4.5 [1 H, ddd, J(H$_x$–H$_y$) 11.2, J(H$_x$–H$_a$) 11.5, J(H$_x$–H$_b$) 3.8, H$_x$], 4.1 [1 H, ddd, J(H$_y$–H$_x$) 11.2, J(H$_y$–H$_c$) 10.2, J(H$_y$–H$_d$) 0.9, H$_y$], 3.75 [1 H, d, J(H$_d$–H$_c$) 15.3, J(H$_d$–H$_y$) 0.9, H$_d$], 3.4 [1 H, dd, J(H$_c$–H$_d$) 15.3, J(H$_c$–H$_y$) 10.2, H$_c$], 3.38 [1 H, dd, J(H$_b$–H$_a$) 17.1, J(H$_b$–H$_x$) 3.8, H$_b$], 3.3 [1 H, dd, J(H$_a$–H$_b$) 17.1, J(H$_a$–H$_x$) 11.5, H$_a$], 1.51 (3 H, s, CH$_3$), 1.45 (3 H, s, CH$_3$)
10 C, 61.7 (62.1); H, 6.4 (6.7)^l 	^{1}H:^{h} 6.53 [1 H, d, J(H$_r$–H$_s$) 2.8, H$_r$], 6.47 [1 H, d, J(H$_t$–H$_u$) 3.3, H$_t$], 5.38 [1 H, d, J(H$_u$–H$_t$) 3.3, H$_u$], 5.25 [1 H, d, J(H$_s$–H$_r$) 2.8, H$_s$], 4.1 [1 H, ddd, J(H$_x$–H$_y$) 11.2, J(H$_x$–H$_a$) 11.4, J(H$_x$–H$_b$) 3.4, H$_x$], 3.25 [1 H, ddd, J(H$_y$–H$_x$) 11.2, J(H$_y$–H$_c$) 10.5, J(H$_y$–H$_d$) 1.2, H$_y$], 3.2–2.4 (8 H, complex bands, CC*H*$_2$CH$_2$), 3.12 [1 H, d, J(H$_d$–H$_c$) 15.2, J(H$_d$–H$_y$) 1.2, H$_d$], 2.93 [1 H, dd, J(H$_c$–H$_d$) 15.2, J(H$_c$–H$_y$) 10.5, H$_c$], 2.78 [1 H, dd, J(H$_b$–H$_a$) 16.8, J(H$_b$–H$_x$) 3.4, H$_b$], 2.42 [1 H, dd, J(H$_a$–H$_b$) 16.8, J(H$_a$–H$_x$) 11.4, H$_a$], 2.1–1.6 (8 H, complex bands, CCH$_2$C*H*$_2$), 1.4 (3 H, s, CH$_3$), 1.3 (3 H, s, CH$_3$) ^{13}C:^{m} 141.9 (s, 2 × η-C), 138.2 (s, η-C), 135.2 (s, η-C), 124.8 (s, η-C), 118.5 (s, η-C), 116.6 (d, η-CH), 115.5 (d, η-CH), 110.6 (d, η-CH), 106.9 [s, *C*(CH$_3$)$_2$], 105.9 (d, η-CH), 80.1 (d, OCH), 78.3 (d, OCH), 34.2 (t, CH*C*H$_2$C), 32.7 (t, CH*C*H$_2$C), 27.2 (q, CH$_3$), 27.0 (q, CH$_3$), 26.5–21.7 (overlapping triplets, 8 × ring CH$_2$)
11 C, 57.0 (57.0); H, 6.2 (6.1)^n	^{1}H:^{h} 6.4 [1 H, d, J(H$_r$–H$_s$) 3.0, H$_r$], 6.3 [1 H, d, J(H$_t$–H$_u$) 3.3, H$_t$], 5.6 [1 H, d, J(H$_u$–H$_t$) 3.3, H$_u$], 5.4 [1 H, d, J(H$_s$–H$_r$) 3.0, H$_s$], 4.2 [1 H, ddd, J(H$_x$–H$_y$) 7.7, J(H$_x$–H$_a$) 11.5, J(H$_x$–H$_b$) 3.2, H$_x$], 3.5 [1 H, ddd, J(H$_y$–H$_x$) 7.7, J(H$_y$–H$_c$) 10.3, J(H$_y$–H$_d$) 1.0, H$_y$], 3.12 [1 H, d, J(H$_d$–H$_c$) 15.3, J(H$_d$–H$_y$) 1.0, H$_d$], 3.0–2.7 (4 H, complex bands, CC*H*$_2$CH$_2$), 2.89 [1 H, dd, J(H$_c$–H$_d$) 15.3, J(H$_c$–H$_y$) 10.3, H$_c$], 2.84 [1 H, dd, J(H$_b$–H$_a$) 16.4, J(H$_b$–H$_x$) 3.2, H$_b$], 2.6–2.3 (4 H, complex bands, CC*H*$_2$CH$_2$), 2.42 [1 H, dd, J(H$_a$–H$_b$) 16.4, J(H$_a$–H$_x$) 11.5, H$_a$], 2.1–1.5 (8 H, complex bands, CCH$_2$C*H*$_2$), 1.4 (3 H, s, CH$_3$), 1.3 (3 H, s, CH$_3$) ^{13}C:^{m} 136.4 (s, η-C), 135.8 (s, η-C), 133.1 (s, η-C), 130.2 (s, η-C), 120.1 (s, η-C), 115.3 (s, η-C), 113.0 (d, η-CH), 112.7 (d, η-CH), 108.8 (d, η-CH), 107.1 [s, *C*(CH$_3$)$_2$], 102.6 (d, η-CH), 80.7 (d, OCH), 79.9 (d, OCH), 34.4 (t, CH*C*H$_2$C), 32.6 (t, CH*C*H$_2$C), 27.1 (q, CH$_3$), 27.0 (q, CH$_3$), 25.5–22.1 (overlapping triplets, 8 × ring CH$_2$)
12 C, 48.8 (48.9); H, 5.2 (5.2)^o	^{1}H:^{h} 6.3 [1 H, d, J(H$_r$–H$_s$) 2.9, H$_r$], 6.2 [1 H, d, J(H$_t$–H$_u$) 3.3, H$_t$], 5.4 [1 H, d, J(H$_u$–H$_t$) 3.3, H$_u$], 5.3 [1 H, d, J(H$_s$–H$_r$) 2.9, H$_s$], 4.2 [1 H, ddd, J(H$_x$–H$_y$) 7.5, J(H$_x$–H$_a$) 11.5, J(H$_x$–H$_b$) 3.5, H$_x$], 3.5 [1 H, ddd, J(H$_y$–H$_x$) 7.5, J(H$_y$–H$_c$) 10.5, J(H$_y$–H$_d$) 0.9, H$_y$], 3.2 [1 H, d, J(H$_d$–H$_c$)

Table 1 (*continued*)

Compound	NMR data[b]
	15.3, $J(H_d–H_y)$ 0.9, H_d], 3.1–2.8 (4 H, complex bands, CCH_2CH_2), 2.94 [1 H, dd, $J(H_6–Ha)$ 16.2, $J(H_b–H_x)$ 3.5, H_b], 2.88 [1 H, dd, $J(H_c–H_d)$ 15.3, $J(H_c–H_y)$ 10.5, H_c], 2.6–2.4 (4 H, complex bands, CCH_2CH_2), 2.45 [1 H, dd, $J(H_a–H_b)$ 16.2, $J(H_a–H_x)$ 11.5, H_a], 2.0–1.5 (8 H, complex bands, CCH_2CH_2), 1.4 (3 H, s, CH_3), 1.3 (3 H, s, CH_3)

[a] Calculated values (%) in parentheses. [b] Given as: chemical shift (δ) [multiplicity, *J*/Hz, assignment], *etc.* [c] In [^{2}H]CHCl$_3$ at 300 MHz. [d] Br, 22.05 (24.7%); *m*/*z* (^{81}Br) 324 (P^+). [e] *m*/*z* 358 (P^+). [f] *m*/*z* 358 (P^+). [g] In [^{2}H]CHCl$_3$ at 62.9 MHz. [h] In [$^2H_2$]CH$_2$Cl$_2$. [i] Cl, 13.5 (13.7%); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +588°. [j] Cl, 11.6 (11.7%); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +429°. [k] Cl, 16.6 (14.9%); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +1000°. [l] Cl, 14.6 (14.7%); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +1100°. [m] In CD$_2$Cl$_2$ at 62.9 MHz. [n] Cl, 13.2 (13.5%); *m*/*z* (^{90}Zr) 525 (P^+); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +172°. [o] Cl, 11.8 (11.55%); *m*/*z* (^{179}Hf) 614 (P^+); α(598.3 nm, 20 °C, 10^{-3} mol dm^{-3} in CH$_2$Cl$_2$) +125°.

molecule of *o*-dichlorobenzene for every six molecules of [TiL^{1}Cl$_2$]. The ^{1}H NMR spectrum resembles that of **7** and **8** except that the degree of overlap of the methylene resonances is greater.

Compounds **9**, **7** and **8** were hydrogenated by treatment with 100 atm of hydrogen for 2 h, in the presence of PtO$_2$ as catalyst, giving the corresponding bis(4,5,6,7-tetrahydroindenyl) derivatives [ML^{2}Cl$_2$] (M = Ti, **10**; Zr, **11**; or Hf, **12**), as red, pale green or pale orange crystalline compounds, respectively (see Scheme 1). Yields for the hydrogenation reactions were between 75 and 90%. The ^{1}H NMR spectra of **10**–**12** were almost identical.

We have explored the catalytic reactivity of the compounds [ML^{1}Cl$_2$] and [ML^{2}Cl$_2$] in the presence of methylaluminoxane[17] as the cocatalyst. The results of the ethylene polymerisation experiments are given in Table 3. Plots of activity *versus* temperature are given in Fig. 2. The compound [ZrL^{1}Cl$_2$] **7** has the highest activity of the six metallocene dichlorides when used in conjunction with methylaluminoxane. The maximum activity occurs at about 35 °C and presumably catalyst decomposition occurs above this temperature, as observed for dichlorobis(η-indenyl)zirconium compounds.[18] The two titanium compounds also show maxima in their activity *vs.* temperature profile, presumably due to increasing rate of formation of titanium(III) species with increasing temperature. The low value for the activity of the [TiL^{2}Cl$_2$] system at −40 °C is due to partial precipitation of the catalyst from solution at this temperature.

The polymerisations using [ZrL^{2}Cl$_2$] **11** show an almost linear increase in activity with increasing temperature. Similar behaviour is shown by [Zr(η-C$_5$H$_5$)$_2$Cl$_2$].[19] The activities of the titanium compounds are two orders of magnitude lower than those of the corresponding zirconium compounds. The hafnium compounds are one order of magnitude less active than the zirconium compounds. This trend in activities for the Group 4 metallocene dichlorides in conjunction with aluminoxanes has previously been noted by Kaminsky *et al.*[19]

Typical rate data for the polymerisation reactions of [ZrL^{1}Cl$_2$] **7** and [ZrL^{2}Cl$_2$] **11** are shown in Fig. 3. In the case of **7** the rate rises to a maximum almost instantaneously and then decreases gradually over the duration of the experiment. The maximum rate of ethylene consumption observed is 222 mol per mol of zirconium per second. However, in the case of **11** there is a period during which no ethylene uptake is observed, followed by a gradual rise to the maximum of 170 mol per mol zirconium per second. Thereafter, the rate slowly decreases, as observed in many homogeneous Ziegler–Natta systems.[20] The Arrhenius plots for **7** and **11** are shown in Fig. 4. The values derived for E_a are 28.9 and 36.6 kJ mol^{-1}, respectively; approximately half those found for [Zr(η-C$_5$H$_5$)$_2$X$_2$] systems.[19] The greater activity of the latter system arises from the larger value of the pre-exponential factor, approximately 10^{15} for [Zr(η-C$_5$H$_5$)$_2$X$_2$] and only 10^9 for L^1-based systems. Since the pre-exponential factor is a measure of the 'steric ease' of a reaction, we can understand this result in a quantitative sense from the molecular structures of the two systems. The polyethylenes produced by the L^1-based systems are all high-density (0.96 g cm^{-3}) linear polyethylenes with melting points of 129–130 °C, indicating that they are also highly crystalline.[21] In the infrared spectrum the absence of vinyl bands at *ca.* 1640, 990 and 910 cm^{-1} indicates that the polymers have high molecular weight.[22,23]

Table 2 Selected distances (Å) and angles (°) for compound **7** *

Zr–Cl(1)	2.432(1)	Zr–C(9)	2.523(4)
Zr–Cl(2)	2.4297(9)	Zr–C(17)	2.515(4)
Zr–C(1)	2.590(3)	Zr–C(18)	2.489(4)
Zr–C(6)	2.595(4)	Zr–C(19)	2.479(4)
Zr–C(7)	2.497(4)	Zr–C(20)	2.576(3)
Zr–C(8)	2.501(4)	Zr–C(25)	2.584(4)
Cl(1)–Zr–Cl(2)	97.12(4)	CR(1)–Zr–CR(2)	127.2

* CR = Calculated η-C$_5$ ring centroid.

The polymerisation activity of compound **7** with methylaluminoxane deduced from the polyethylene is given in Table 4: the data are calculated on the assumption that every metal centre is an active site; this has been shown to be the case by a number of workers.[3,19] Consequently, the values given represent maximum or minimum values, depending upon the quantity concerned. The L^1-based systems did not polymerise propene at 1 atm pressure. However, use of compound **7** or **11** with methylaluminoxane and higher pressures of propene gave a transluscent amorphous polymer. This was extracted with pentane to dissolve any atactic or low-molecular-weight material. Data for the propene polymerisation experiments are given in Table 5. As can be seen, the activities of these zirconium systems towards propene are about two orders of magnitude lower than the corresponding activities towards ethylene. The activities of **7** and **11** are less than their ethylene-bridged counterparts, probably for steric reasons.

More interesting are the properties of the polymers produced by compound **7** (see Table 6). The yields of pentane-soluble polypropene are considerably greater than those of the pentane-insoluble solids. When the [ZrL^{2}Cl$_2$] **11** catalyst was used at 70 °C no pentane-insoluble solid was obtained and the pentane-soluble product had the appearance of a viscous liquid.

In the infrared spectra of the amorphous pentane-soluble fractions from compound **7** those bands associated with the helical structure of isotactic polypropene (1167, 997 and 841 cm^{-1}) are of very low intensity and indicate that the number of m (*meso*) dyads is between 50 and 65%. The ^{13}C NMR spectra of the pentane fractions show the presence of resonances associated with *n*-propyl and vinylidene chain-ends which indicates that these fractions are of very low molecular weight, and by comparing the intensities of these resonances with the total intensities of the resonances in the methyl pentad region, approximate values for the molecular weights can be obtained. These chain-ends also show that insertion is primary and chain termination proceeds by β-elimination. The methyl pentad regions of the ^{13}C NMR spectra show the presence of large numbers of rr (r = racemic) and mr triads in the polymer chain, but the relative proportion of mm triads increases with decreasing temperature, *i.e.* the pentane-soluble polymers are

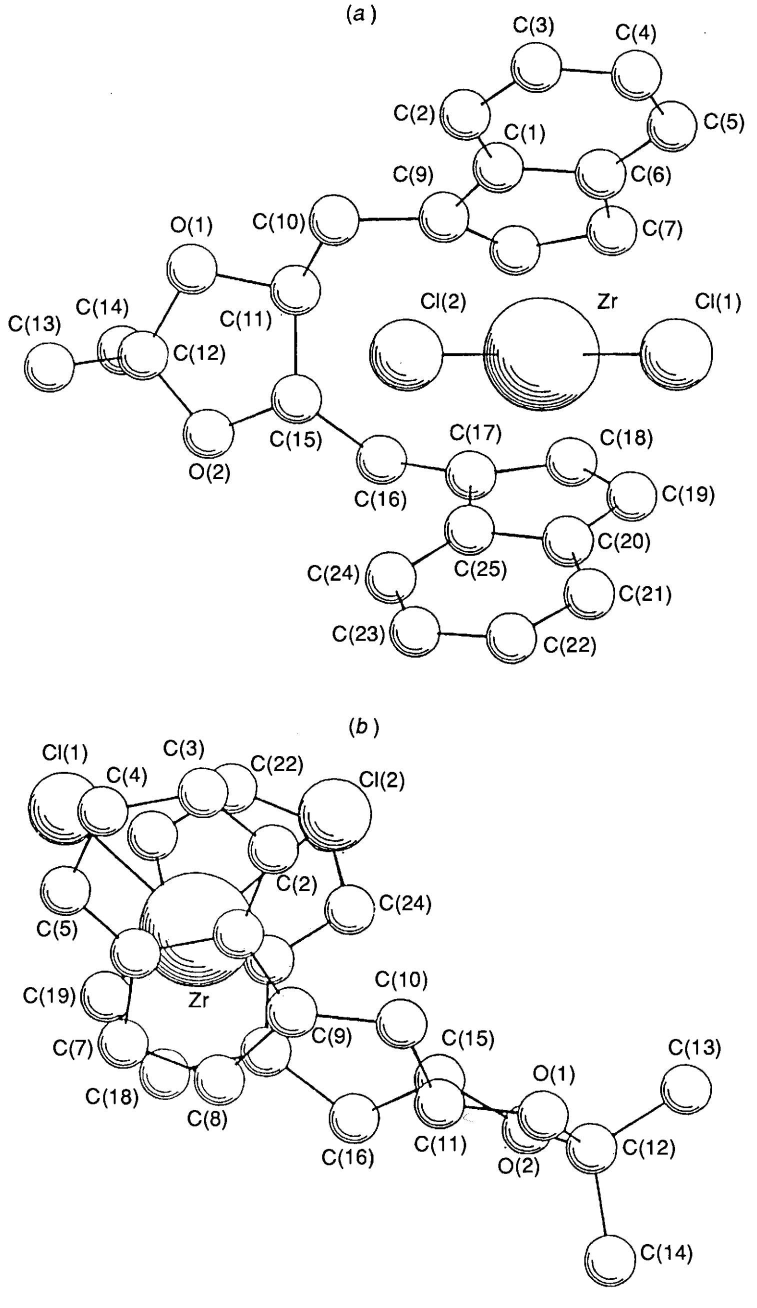


Fig. 1 Two views of the molecular structure of compound **7**. Hydrogen atoms are omitted for clarity

highly atactic, but the degree of isotacticity is greater in the polymer formed at lower temperature.

In the methyl region of the ^{13}C NMR spectra of the pentane-soluble fractions only eight bands are visible. It seems reasonable to expect that the rmmr and mmrr bands are overlapping. There are currently two probability theories that allow the calculation of the relative intensities of the methyl pentad signals. The first corresponds to a chain-end control mechanism proposed by Bovey and Tiers,[23] in which the last incorporated unit controls the stereochemistry of insertion. In the second model the asymmetry of the active site promotes co-ordination of one or other of the prochiral faces of the propene; this is the enantiomorphic-site model.[24] A simple test to determine which model is applicable is to measure the relative intensities contained within the mm, mr and rr triads (Table 7). The theoretical intensities of the lines in the methyl pentad region were calculated using both models, and the enantiomorphic-site control model gave values closer to the observed intensities.

The polypropene obtained using $[ZrL^2Cl_2]$ at 70 °C is a viscous liquid. The mass spectrum shows parent ion peaks and fragmentation patterns consistent with a mixture of straight-chain alkenes of general formula $(C_3H_6)_n$. The highest parent-ion peak observed corresponds to $C_{24}H_{48}$. The gas chromatogram confirms the multicomponent nature of the liquid and shows at least 11 separate compounds present. The broad nature of each of the peaks may suggest that each compound of formula $(C_3H_6)_n$ exists in more than one enantiomeric form. Vacuum distillation of the liquid polymer allowed separation of a fraction containing a compound for which the mass spectrum showed a parent-ion peak at m/z = 210 indicating it to be $C_{15}H_{30}$. The ^{13}C NMR spectrum of this compound supported the formulation and showed peaks assignable to terminal vinylidene groups analogous to those found in the pentane-soluble polypropenes. Comparison of the retention time of $C_{15}H_{30}$ with the chromatogram of the product polymer oil allowed each band to be assigned to a particular propene oligomer, the lowest and highest oligomers observed being $C_{12}H_{24}$ and $C_{42}H_{84}$ respectively.

Table 3 Data from ethylene polymerisation experiments

Compound	10^6 Amount/ mol	10^3 [Al]/ mol dm^{-3}	T/ °C	Yield/g	Activity/g pe per mol per h
9	4.00	5.2	0	—	—
	3.79	5.2	25	0.26	69 000
	4.73	5.2	50	0.53	112 000
	4.20	5.2	70	0.20	48 000
10	5.38	5.2	−40	0.55	102 000
	3.52	5.2	−20	0.72	205 000
	4.14	5.2	0	0.80	193 000
	4.50	5.2	25	0.70	154 000
	4.90	5.2	50	0.40	81 000
	3.73	5.2	70	0.08	20 000
7	4.83	5.5	−20	4.08	850 000
	3.86	5.5	0	12.96	3 360 000
	4.40	7.4	20	19.60	4 450 000
	3.80	6.6	35	18.40	4 800 000
	3.50	5.2	50	15.30	4 300 000
	4.05	5.2	70	15.80	3 900 000
11	4.56	5.2	−20	1.30	280 000
	5.10	5.2	0	5.75	1 100 000
	4.75	5.2	22	7.60	1 600 000
	4.80	5.2	50	11.50	2 400 000
	3.60	5.2	70	11.85	3 300 000
8	4.62	5.2	25	1.15	250 000
12	3.25	5.2	25	1.00	307 000

Conditions: in toluene (250 cm^3), 1 bar ethylene, 1 h, pe = polyethylene.

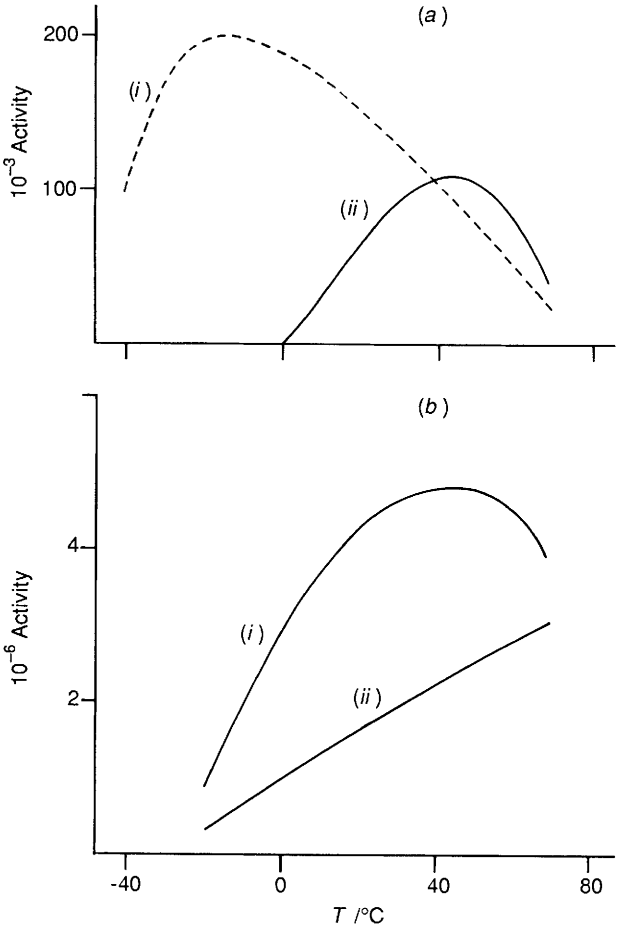


Fig. 2 Plots of activity (g pe per mol per h) *versus* temperature: (*a*) [TiL^{1}Cl$_2$] (*i*) and [TiL^{2}Cl$_2$] (*ii*); (*b*) [ZrL^{1}Cl$_2$] (*i*) and [ZrL^{2}Cl$_2$] (*ii*). Conditions: methylaluminoxane, 1 bar ethylene in toluene

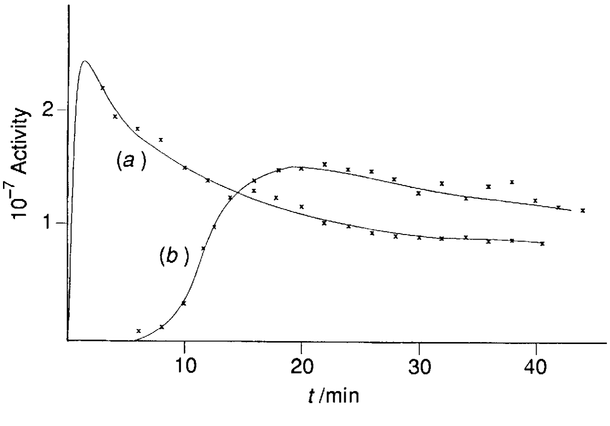


Fig. 3 Plot of rate (mol ethylene per mol Zr per s) *vs.* time for the systems: (*a*) [ZrL^{1}Cl$_2$]–methylaluminoxane–ethylene ([Zr] = 1.6 × 10^{-5} mol dm^{-3}, 30 °C) and (*b*) [ZrL^{2}Cl$_2$]–methylaluminoxane–ethylene ([Zr] = 2 × 10^{-5} mol dm^{-3}, 50 °C). Conditions: [Al] = 25 mmol dm^{-3}, 1 bar C_2H_4, in toluene

The ^{13}C NMR spectrum of the original product mixture shows a methyl pentad region with an appearance typical of atactic polypropene. From the intensities of the end-groups an average molecular weight of 350 is found.

The infrared spectra of the pentane-insoluble solids are typical of highly isotactic polypropene. Also, the ^{13}C NMR spectrum in *o*-dichlorobenzene at 130 °C of the polymer obtained from [ZrL^{1}Cl$_2$] at 50 °C, and in particular the methyl pentad region, shows an intense mmmm peak which indicates a highly isotactic nature for the polymer. The presence of mmmr, mmrr and mrrm pentads in the ratio 2:2:1 respectively points to stereoregulation errors of the type consistent with an enantiomorphic site controlling the stereochemistry of the monomer addition. The ^{13}C NMR spectrum of the polymer produced using [ZrL^{2}Cl$_2$] is closely similar except apart from bands assignable to the mmmr, mmrr and mrrm pentads, and it can be seen that other pentads are present to a significant extent. Thus the mmmr pentad band is split into a doublet, and mmrm and mrmr pentads are also present. Some element of branching may be necessary to explain the complexity of these bands.[25] The ^{13}C NMR-calculated stereoregularities are shown in Table 8. It is apparent that the molecular weights of these samples are considerably higher than those of the pentane-soluble samples. The width of the distribution is also quite narrow. The melting points of the samples are low, reflecting the relatively large number of r dyads in the chain, compared with commercial polypropene. Thus, the properties of the pentane-soluble and pentane-insoluble polypropenes produced using compound 7 are highly contrasting. The pentane-soluble products are low-molecular-weight, low-stereoregularity materials, while the pentane-insoluble polymers are high-molecular-weight, highly stereoregular materials. It may be that the catalyst decomposes to give a new zirconium species capable of polymerising propene but having no inherent asymmetry. The low molecular weight of the polymers produced by this species could be caused by an increased chain-termination rate constant.

Optically active polymers of propene have been produced from the polymerisation with catalysts obtained by treating TiCl$_4$ with the adduct tris[(*S*)-2-methylbutyl]aluminium–diethyl ether, but the specific rotatory power was low and decreased with increasing molecular weight, being undetectable for molecular weights greater than 100 000. This indicates that the observed optical activity is due only to the chiral end-groups derived from the catalyst.[26,27]

Kaminsky *et al.*[6] reported that the polypropenes produced using the ethylene-bridged zirconocene measured either as a film or in a swollen state were optically active. Similarly the polymer produced using compound 7 in decalin gave optical rotations with average value of α(589.3 nm, 20 °C) = −160°.

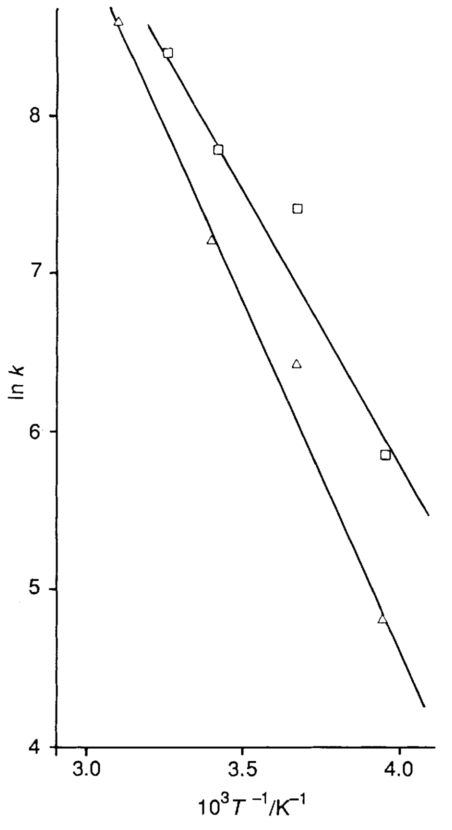


Fig. 4 Plots of ln *k* *vs.* 1/*T* for $[ZrL^1Cl_2]$ **7** (□) and $[ZrL^2Cl_2]$ **11** (△)

Table 4 Polymerisation activity of compound **7** with methylaluminoxane

T/°C	−20	25	70
10^{-6} Activity/g pe per mol Zr per h	0.85	4.5	3.9
M of polyethylene	> 500 000	200 000	130 000
Degree of polymerisation	> 17 857	7143	4643
Macromolecules per Zr per h	< 1.7	22.5	30
Chain lifetime	> 35.3 min	160 s	120s
Turnover time/s	0.12	0.022	0.025
Turnovers per second	8.3	44.6	38.7

Table 5 Data from propene polymerisation experiments

Compound	10^6 [Zr]/ mol dm^{-3}	*T*/°C	*t*/h	Yield/g	Activity/g pp per mol Zr per h
7	5.78	50	20	26.1	260 000
	5.78	20	20	6.7	58 000
	4.82	0	48	1.0	4 000
11	5.51	70	3	10.5	640 000
	4.75	20	20	12.5	130 000
	7.41	0	48	27.8	80 000

Conditions: 0.3 g Al, solvent = toluene (150 cm^3), pp = polypropene.

Table 6 Relative yields of the pentane-soluble and -insoluble polypropenes from compound **7** and methylaluminoxane

Compound	*T*/°C	Solubles/g	Insolubles/g
7	50	25.3	0.8
	20	5.7	1.0
11	70	10.5	—
	20	10.0	2.5
	0	25.0	2.8

Interestingly, a sample of polyethylene suspended in decalin also showed a rotation of approximately +50°. This suggests that the optical activity is not due to any natural rotatory power of these materials, but rather to effects such as linear dichroism[28] (the effect of an anisotropic absorption in linearly anisotropic substances) or, more likely, anisotropic light scattering[29] or birefringence.[30]

Experimental

All manipulations of air- and/or moisture-sensitive materials were carried out in an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques, or in a dry-box under an atmosphere of nitrogen. Nitrogen gas was purified by passage through a gas-drying column containing BTS catalyst and 4A molecular sieves. All solvents were thoroughly deoxygenated before use. Solvents were dried and purified by refluxing over a suitable drying agent followed by distillation under a nitrogen atmosphere. Toluene and light petroleum (b.p. 100–120 °C) were dried over molten sodium, tetrahydrofuran (thf) over molten potassium, diethyl ether and light petroleum (b.p. 30–40 and 40–60 °C) over sodium-potassium alloy (1:3 w/w) and dichloromethane by refluxing over phosphorus pentaoxide. Liquid propene was dried by stirring over magnesium sulphate in a pressure-bottle. Elemental analyses were obtained from the microanalytical department of the Inorganic Chemistry Laboratory, Oxford.

Nuclear magnetic resonance spectra were recorded on the following instruments: ^{1}H, 60 MHz, JEOL MX60, 250 MHz, Bruker AM-250, 300 MHz, Bruker WH-300, 500 MHz, Bruker AM-500; ^{13}C, 62.9 MHz, Bruker AM-250, 62.9 MHz, JEOL 270. Spectra were referenced internally using the residual protio solvent (^{1}H) or solvent (^{13}C) 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) and multiplet (m). Infrared spectra were recorded on either a Philips Analytical SP2000 grating spectrophotometer or a Perkin-Elmer 1710 FT spectrophotometer, mass spectra on an AEI MS 902 spectrometer updated by a data-handling system supplied by Mass Spectroscopy Services Ltd.

The known compounds (4*S*,5*S*)-*trans*-4,5-di(ethoxycarbonyl)-2,2-dimethyl-1,3-dioxolane, (4*S*,5*S*)-*trans*-4,5-di(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane,[31] (4*S*,5*S*)-*trans*-2,2-dimethyl-4,5-bis(toluene-*p*-sulphonyloxymethyl-1,3-dioxolane,[32] indenylmagnesium bromide[33] and methylaluminoxane[17] were prepared as described.

(4S,5S)-*trans*-4,5-*Bis*(1*H-inden*-3-*ylmethyl*)-2,2-*dimethyl*-1,3-*dioxolane* **1**.—Indenylmagnesium bromide (120 g, 0.55 mol) and toluene (300 cm^3) were stirred together at 0 °C. (4*S*,5*S*)-*trans*-2,2-Dimethyl-4,5-bis(toluene-*p*-sulphonyloxymethyl)-1,3-dioxolane (94 g, 0.2 mol) was dissolved in toluene (400 cm^3) and added dropwise to the Grignard suspension over a period of 2 h. The reaction mixture was allowed to warm to room temperature (r.t.). The solution was filtered and the solid washed with light petroleum (200 cm^3, b.p. 40–60 °C). The solvent was removed from the combined extracts under reduced pressure. The resulting green oil was extracted with light petroleum ether (200 cm^3, b.p. 40–60 °C), filtered, and the solvent removed under reduced pressure. This oil was found to be a mixture of compounds **3** and **4**. The green oil was dissolved in diethyl ether (50 cm^3) and eluted down a chromatography column containing neutral alumina in diethyl ether. The first, green band was collected and the solvent removed under reduced pressure to give the product as a viscous, pale green oil. Yield 54.4 g (76%).

Li_2L^1 **5**.—Compound **1** (22.64 g, 0.063 mol) in thf (250 cm^3) at 0 °C was treated dropwise with LiBu^n in hexane (55 cm^3 of a 2.5 mol dm^{-3} solution). The mixture became red and a solid precipitated. The solution was filtered and the solid was washed with diethyl ether (200 cm^3). Toluene (200 cm^3) was added and

Table 7 Dyad compositions, triad fractions and triad mechanistic model tests of the ^{13}C NMR spectra of the methyl region for the pentane-soluble polypropenes

Compound	Polymerisation temperature/ °C	Dyad composition [m]	Dyad composition [r]	Triad fraction [mm]	Triad fraction [mr]	Triad fraction [rr]	Triad tests* Site	Triad tests* Chain
7	50	0.48	0.52	0.24	0.48	0.27	1.13	1.13
	20	0.57	0.43	0.35	0.44	0.21	0.93	1.47
11	70	0.49	0.51	0.23	0.51	0.26	1.02	0.94
	20	0.66	0.34	0.46	0.41	0.13	0.66	1.46
	0	0.64	0.36	0.44	0.40	0.16	0.79	1.71

* $2[rr]/[mr] = 1$ for site control, $4[mm][rr]/[mr]^2 = 1$ for chain-end control.

Table 8 Properties of the pentane-insoluble polypropenes

Compound	T/°C	Stereoregularity* ^{13}C NMR	Stereoregularity* IR	M_w	M_n	M.p./°C
7	50	95	93	116 000	16 700	144
	20	96	95	—	—	—
11	20	94	92	—	—	—
	0	94	97	164 000	32 000	140

* % m dyads.

heated until the solid dissolved. Cooling of the solution produced pale green crystals which were filtered off and dried *in vacuo*. Yield 17.2 g. Titration of the solid revealed it to have four molecules of thf associated with each molecule of dilithium salt.

Na_2L^1 **6**.—Sodium metal (2.6 g, 0.11 mol) and a small crystal of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in liquid ammonia (200 cm^3) to form a deep blue solution. When all the colour had disappeared from the solution and grey sodium amide had precipitated the ammonia was allowed to evaporate. The solid was then suspended in thf (200 cm^3) and a solution of compound **1** (21.0 g, 0.059 mol) in thf (75 cm^3) was added. After a few moments a steady stream of ammonia gas was seen to flow through the bubbler and the solution became green-brown, turning green-yellow after about 10 min with formation of a precipitate. The solution was filtered and the solid washed with diethyl ether (200 cm^3) and dried *in vacuo* at 40 °C for 6 h. The filtrate was pumped to dryness, washed with diethyl ether (50 cm^3) and dried at 40 °C for 6 h. Combined yield 17.8 g (74%).

$[ZrL^1Cl_2]$ **7**.—*Method A. From* Li_2L^1 *and* $ZrCl_4$. Zirconium tetrachloride (1.2 g, 5 mmol) in thf (50 cm^3) at 50 °C was treated dropwise with Li_2L^1 (3.2 g, 4.9 mmol) in thf (100 cm^3) with stirring over 1 h. After the addition was complete the solution was stirred at 50 °C for 30 min. The solution was filtered and reduced in volume to about 50 cm^3. Diethyl ether (20 cm^3) and light petroleum (10 cm^3, b.p. 40–60 °C) were added and a yellow precipitate formed. The solution was decanted from the yellow solid and the solvent removed under reduced pressure. The resulting yellow oil was stirred with diethyl ether (100 cm^3) and methanol was added dropwise until all of the oily solid had disappeared to yield a yellow crystalline solid. The solution was decanted, the yellow solids combined and washed with methanol (30 cm^3) and diethyl ether (30 cm^3) before being dried *in vacuo*. The solid was recrystallised from boiling toluene (25 cm^3). Yield 0.27 g (10%).

Method B. From Na_2L^1 *and* $ZrCl_4$. Zirconium tetrachloride (3.8 g, 16.3 mmol) in thf (400 cm^3) at 50 °C was treated dropwise with Na_2L^1 (6.6 g, 16.4 mmol) suspended in thf (300 cm^3) over 2 h. After the addition was complete, stirring was continued for 1 h. The solution was filtered, reduced in volume to approximately 100 cm^3 and treated with diethyl ether (20 cm^3) and light petroleum (10 cm^3, b.p. 40–60 °C). The solution was decanted from the yellow solid and the solvent removed under reduced pressure. The resulting yellow oil was stirred with diethyl ether (100 cm^3) and methanol was added dropwise until all of the oily solid had disappeared to yield a yellow crystalline solid. The solution was decanted, the yellow solids combined and washed with methanol (30 cm^3) and diethyl ether (30 cm^3) before being dried *in vacuo*. The powder was recrystallised from hot toluene. Yield 1.35 g (16%).

Method C. Reaction of Na_2L^1 *with excess of* $ZrCl_4$. Zirconium tetrachloride (7.6 g, 32.6 mmol) in thf (400 cm^3) at 50 °C was treated dropwise with a suspension of Na_2L^1 (6.6 g, 16.4 mmol) in thf (300 cm^3) over 2 h. After the addition was complete, stirring was continued for 1 h. The solution was filtered, reduced in volume to approximately 100 cm^3 and treated with diethyl ether (20 cm^3) and light petroleum (10 cm^3, b.p. 40–60 °C). The solution was decanted from the yellow solid and the solvent removed under reduced pressure. The resulting yellow oil was stirred with diethyl ether (100 cm^3) and methanol was added dropwise until all of the oily solid had disappeared to yield a yellow crystalline solid. The solution was decanted, the yellow solids combined and washed with methanol (30 cm^3) and diethyl ether (30 cm^3) before being dried *in vacuo*. The powder was recrystallised from hot toluene. Yield 1.3 g (15.5%).

$[HfL^1Cl_2]$ **8**.—Hafnium tetrachloride (3.9 g, 12.0 mmol) in thf (400 cm^3) at 50 °C was treated dropwise with Na_2L^1 (5.0 g, 9.1 mmol) suspended in thf (300 cm^3) over 2 h. After the addition was complete, stirring was continued for 1 h. The solution was filtered, reduced in volume to approximately 100 cm^3 and treated with diethyl ether (20 cm^3) and light petroleum (10 cm^3, b.p. 40–60 °C). The solution was decanted from the yellow solid and the solvent removed under reduced pressure. The resulting yellow oil was stirred with diethyl ether (100 cm^3) and methanol was added dropwise until all of the oily solid had disappeared to yield a yellow crystalline solid. The solution was decanted, the yellow solids combined and washed with methanol (30 cm^3) and diethyl ether (30 cm^3) before being dried *in vacuo*. The powder was recrystallised from hot toluene. Yield 0.45 g (8%).

$[TiL^1Cl_2]$ **9**.—The compound $TiCl_3 \cdot 3thf$ (3.68 g, 10 mmol) in thf (300 cm^3) at reflux was treated dropwise with a suspension of Na_2L^1 (4.0 g, 10 mmol) in thf (100 cm^3) over 1 h. The solution became dark green and was refluxed for 1 h. Iron(III) chloride (1.73 g, 10.6 mmol) in thf (50 cm^3) was added and the solution became dark red. Refluxing was continued for 15 min. The reaction was allowed to cool and the solvent removed under reduced pressure. The residue was washed with methanol (50 cm^3), water (50 cm^3), methanol (50 cm^3), and diethyl ether (50 cm^3) and finally dried *in vacuo*. Yield of dark green solid 0.8 g (17%).

$[TiL^2Cl_2]$ **10**.—The compound $[TiL^1Cl_2]$ (300 mg), amorphous PtO_2 (75 mg) and dichloromethane (50 cm^3) in a Parr hydrogenation autoclave (300 cm^3) were treated with H_2 (100 atm) at r.t. for 2 h. The solution was filtered and the solvent removed under reduced pressure to give a dark red solid which

Table 9 Crystallographic data for [ZrL^{1}Cl$_2$] **7**

Formula	$C_{25}H_{24}Cl_2O_2Zr$
M	518.591
Crystal size/mm	0.75 × 0.3 × 0.25
T/K	295
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	12.177(3)
b/Å	12.791(2)
c/Å	14.548(3)
α,β,γ/°	90
U/Å^3	2265.9
Z	4
D_c/g cm^{-3}	1.520
μ/cm^{-1}	7.33
F(000)	1056
Data collection	
Minimum, maximum θ/°	1, 28
Scan mode:	ω–2θ ω(scan angle) = 1.15 + 0.35tan θ aperture width = 3.5 mm
Minimum, maximum scan speed/° min^{-1}	1.8, 5.5
Total data	3730
Total unique data	3066
Observed data: [$I > 3\sigma(I)$]	2509
Minimum, maximum absorption correction	1.0, 1.05
Sheldrick merging R factor (%)	2.21
Structure refinement	
No. of parameters	295
No. of restraints	20
Observations/parameters	8.51
Weighting scheme and coefficients	Three-term Chebyshev (7.770, −4.172, 5.763)
Extinction parameter:	0.0
Maximum residual electron density/ e Å^{-3}	0.6

was recrystallised from hot toluene (10 cm^3) to give the product as a dark red crystalline solid. Yield 235 mg (77%).

[ZrL^{2}Cl$_2$] **11**.—The compound [ZrL^{1}Cl$_2$] (1.0 g), amorphous PtO$_2$ (75 mg) and dichloromethane (50 cm^3) in a Parr hydrogenation autoclave (300 cm^3) were treated with H$_2$ (100 atm) at r.t. for 2 h. The solution was filtered and the solvent removed under reduced pressure to give a pale brown solid. This was recrystallised from hot toluene (5 cm^3) to give very pale green crystals. Yield 0.89 g (87%).

[HfL^{2}Cl$_2$] **12**.—The compound [HfL^{1}Cl$_2$] (1.0 g), amorphous PtO$_2$ (75 mg) and dichloromethane (50 cm^3) in a Parr hydrogenation autoclave (300 cm^3) were treated with H$_2$ (100 atm) at r.t. for 2 h. The reaction mixture was filtered and the solvent removed under reduced pressure to give a pale brown solid. This was recrystallised from hot toluene (5 cm^3) to give the product as very pale orange crystals. Yield 0.76 g (75%).

Table 10 Fractional atomic coordinates for [ZrL^{1}Cl$_2$] **7** with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Zr	0.162 38(3)	0.330 06(3)	−0.008 72(2)
Cl(1)	0.100 8(1)	0.149 60(8)	−0.019 81(9)
Cl(2)	−0.018 26(7)	0.409 89(8)	0.001 54(7)
C(1)	0.153 7(4)	0.356 4(3)	0.167 6(2)
C(2)	0.053 4(4)	0.346 9(4)	0.218 3(3)
C(3)	0.030 1(5)	0.250 5(5)	0.255 7(4)
C(4)	0.095 5(5)	0.163 7(5)	0.240 7(4)
C(5)	0.191 4(5)	0.167 9(4)	0.191 5(4)
C(6)	0.220 8(4)	0.267 1(4)	0.153 6(3)
C(7)	0.315 5(3)	0.299 5(4)	0.101 2(3)
C(8)	0.307 5(3)	0.408 9(4)	0.091 2(3)
C(9)	0.206 4(3)	0.445 5(3)	0.126 9(2)
C(10)	0.167 5(4)	0.555 6(3)	0.133 5(2)
C(11)	0.228 3(4)	0.632 6(4)	0.072 4(3)
C(12)	0.201 0(5)	0.802 6(4)	0.024 4(4)
C(13)	0.097 2(8)	0.867 9(6)	0.020 7(6)
C(14)	0.303 4(8)	0.868 2(7)	0.031 4(6)
C(15)	0.200 1(4)	0.631 7(4)	−0.030 0(3)
C(16)	0.276 7(4)	0.572 1(4)	−0.094 1(3)
C(17)	0.249 3(4)	0.460 0(4)	−0.116 2(3)
C(18)	0.319 5(4)	0.372 1(4)	−0.111 7(3)
C(19)	0.266 9(4)	0.285 0(4)	−0.149 4(3)
C(20)	0.162 6(4)	0.319 3(4)	−0.185 5(2)
C(21)	0.079 4(5)	0.265 7(5)	−0.235 3(3)
C(22)	−0.007 0(5)	0.323 8(6)	−0.269 2(4)
C(23)	−0.012 1(5)	0.432 1(6)	−0.255 5(4)
C(24)	0.063 6(4)	0.485 9(4)	−0.204 4(3)
C(25)	0.153 7(4)	0.427 3(3)	−0.167 5(2)
O(1)	0.193 4(3)	0.734 7(2)	0.100 7(2)
O(2)	0.208 6(5)	0.739 8(3)	−0.055 0(2)

Polymerisation using the [ML^{1}Cl$_2$]– *and* [ML^{2}Cl$_2$]–(OAlMe)$_n$ *Systems* (M = Ti, Zr *or* Hf).—(*a*) *Ethylene*. Polymerisations were performed in a three-necked round-bottom flask (500 cm^3) containing a Teflon stirrer bar and fitted with a tap; the remaining necks were sealed with Suba-seals. The temperature was controlled by means of a thermostatted water-bath for temperatures greater than 0 °C, or by using a solid CO$_2$–acetone bath for temperatures below 0 °C. Typically, a solution of 5 × 10^{-6} mol of the metallocene dichloride and 5 × 10^{-3} mol of methylaluminoxane in toluene (10 cm^3) was added to toluene (300 cm^3) contained in the reaction vessel. After equilibration for 10 min the nitrogen atmosphere was removed and replaced with ethylene at 1.0 atm. After 1 h, methanol (20 cm^3) was added and the contents of the flask filtered. The product was washed with dilute hydrochloric acid, water and acetone before being dried in an oven at 70 °C.

(*b*) *Propene*. Polymerisations were performed in a Parr hydrogenation apparatus (300 cm^3) equipped with a mechanical stirrer and thermostat bath. Typically, a solution of 5 × 10^{-6} mol of the metallocene dichloride and 5 × 10^{-3} mol of methylaluminoxane in toluene (10 cm^3) was added to toluene (150 cm^3) contained in the reaction vessel. After equilibration for 20 min the nitrogen atmosphere was removed and propene (25–35 g), predried as a liquid over magnesium sulphate in a Fischer–Porter bottle, was distilled in. The reaction was allowed to continue until either (*a*) the pressure in the vessel dropped to atmospheric, or (*b*) the pressure in the vessel did not appear to change over a period of 8 h. The vessel was opened, the contents transferred to a round-bottom flask (500 cm^3) and treated with methanol (20 cm^3) before removing all volatile components under reduced pressure. The remaining material was extracted with a total of 1 l of pentane and the solid so obtained was washed with dilute hydrochloric acid, water, acetone and diethyl ether before being dried *in vacuo*. The pentane extracts were pumped to dryness to yield an opaque material which varied typically from a viscous liquid to a waxy solid. The exact form of this material was dependent upon both the metallocene dichloride and the polymerisation temperature.

Crystal Structure Determination of [ZrL^{1}Cl$_2$] **7**.—The crystal structure was determined on an Enraf-Nonius CAD4F four-circle diffractometer using graphite-monochromated MoKα radiation (λ = 0.710 69 Å). The structure was solved and refined using the CRYSTALS[34] package and plotted using the CHEMGRAF[35] program on a VAX 11/750 computer. Scattering factor data were taken from ref. 36.

The zirconium and chlorine atomic coordinates were determined using Patterson and direct methods; subsequent electron-density difference syntheses revealed the location of all non-hydrogen atoms, which were refined by full-matrix least squares with isotropic thermal parameters. Hydrogen atoms were included in calculated positions (C–H 1.0 Å) which were modified between successive cycles of refinement. Refinement converged at $R = 0.0323$ ($R' = 0.0357$). Crystal data, data collection and processing parameters are given in Table 9; final fractional atomic coordinates in Table 10.

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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