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Zirconocene dichloride complexes with a 1,2-naphthylidene bridge as catalysts for the polymerisation of ethylene and propylene

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Abstract

Ansa-zirconocene dichloride complexes containing a 9-fluorenyl group at the 1-position of naphthalene and a 2-indenyl **12**, 1-indenyl **13**, or cyclopentadienyl **14** group at the 2-position of the naphthalene were synthesised and characterised. The molecular structures of the complexes have been determined by single crystal X-ray diffraction studies. After activation with excess methylalumoxane (MAO), the complexes were used as homogeneous catalysts for the homopolymerisation of ethylene and propylene.

Keywords: *Ansa*-zirconocene; 1,2-Naphthylidene bridge; Catalysis; Olefin polymerisation

1. Introduction

Zirconocene dichloride complexes activated with methylalumoxane (MAO) are established as excellent olefin polymerisation catalysts [1]. These catalysts can be very versatile because small differences in the molecular structure of the metallocene unit can cause considerable changes in the properties of the catalysts and the polyolefins produced. In many cases, such "structure–property-relationships" allow the prediction of catalyst and polyolefin features. In earlier studies we have investigated the influence of various parameters such as the nature of the aromatic ligand [2], the bridging unit [3] and ligand substituents [1(e)] in *ansa*-metallocene complexes. As a result, tailored catalysts could be prepared and applied for special purposes like "self-immobilization" processes. The design of such "multi-purpose" catalysts is a step into the direction of nanotechnology. This contribution describes the synthesis and catalytic properties of *ansa*-zirconocene complexes that possess a fluorenyl ligand that is connected over a 1,2-naphthylidene bridge with a cyclopentadienyl or a 1-indenyl or 2-indenyl ligand. The use of a 1,2-naphthylidene bridge stems from our interest in the enantiospecific synthesis of planar chiral fluorenylmetal complexes through the use of atropisomerism [4,5]. To date there have been very few examples of Group IV *ansa*-metallocenes having a $C(sp^2)$–$C(sp^2)$ bridge. Other examples reported include the etheno-bridged complexes 1,2-dimethyl- and [1,2-diphenyl-1,2-bis(cyclopentadienyl)ethene]$TiCl_2$, prepared by Burger and Brintzinger [6], and some 1,2-phenylidene-bridged complexes prepared by Halterman et al. [7,8] ([1,2-bis(tetrahydro-1-indenyl)benzene]Ti and $ZrCl_2$, and [1,2-bis(1-indenyl)benzene]Ti and $ZrCl_2$). Arts et al. [9] have also reported the preparation of [1,2-bis(2-indenyl)benzene]Zr and $HfCl_2$ (together with some indenyl-substituted complexes), and [1-(9-fluorenyl)-2-(2-indenyl)benzene]$ZrCl_2$.

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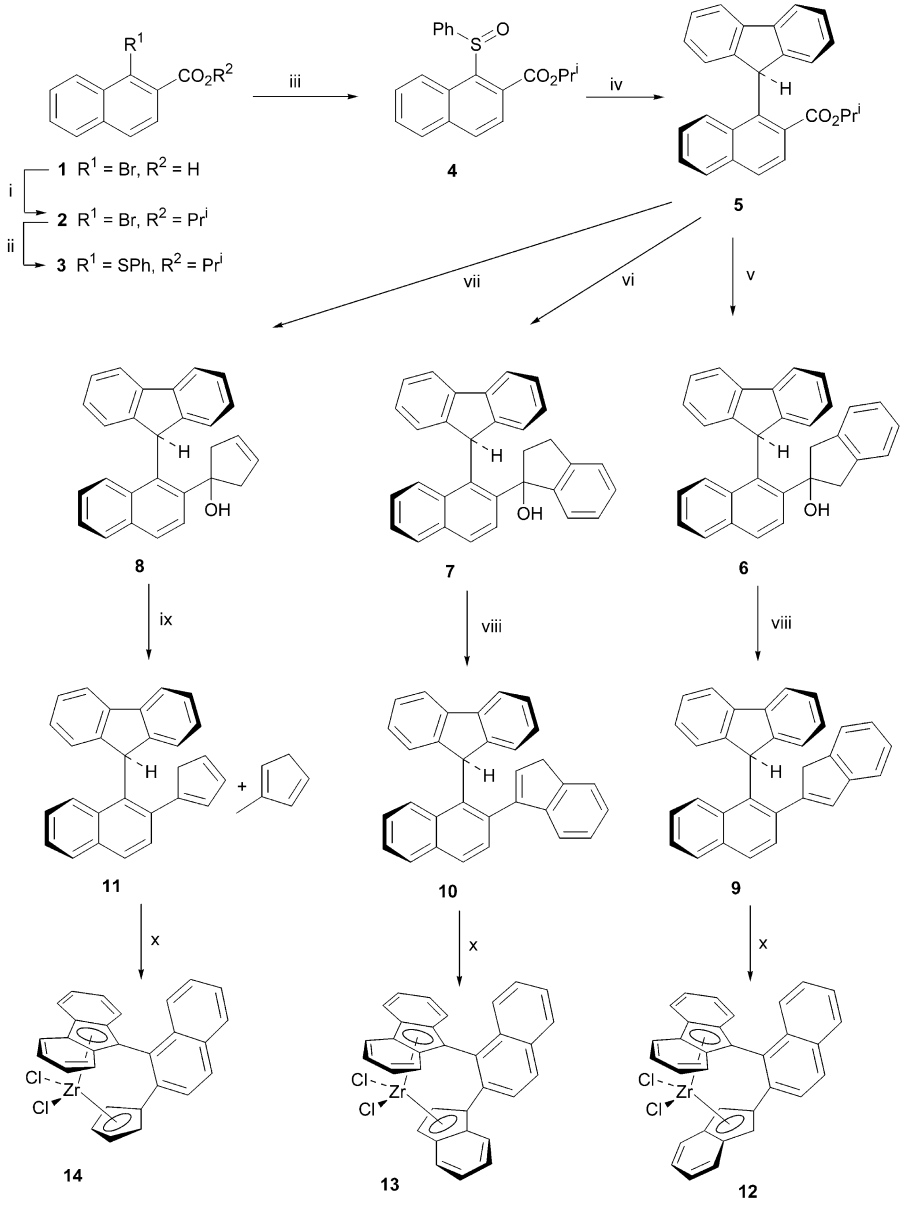
2. Results and discussion

2.1. Synthesis of complexes 12, 13 and 14

The key starting material for the synthesis of all the complexes, isopropyl *rac*-1-(phenylsulfinyl)naphthalene-2-carboxylate (**4**), was prepared in an overall yield of 73% from 1-bromo-2-naphthalenecarboxylic acid (**1**) (prepared from 2-methylnaphthalene according to the procedure of Colletti and Halterman [10]), as outlined in Scheme 1. Coupling of **4** with fluorenyllithium provides the 9-(1-naphthyl)fluorene **5** in 91% yield. A major advantage of the sulfoxide coupling methodology is that it is rotamer-specific, with **5** obtained exclusively as the rotamer where the ester moiety and the fluorene 9-H are *syn* (designated *sp*) [4]. Following the precedence of Bosnich and co-workers [11], reaction of **5** with the di-Grignard reagent derived from 1,2-bis(chloromethyl)benzene provided the 2-indanol **6** in 75% yield. Acid-catalysed dehydration of **6** provided the 2-indenyl



Scheme 1. (i) $SOCl_2$ (10 equivalents), pyridine (1 equivalents), benzene, 25 °C, 16 h, then Pr^iOH (2 equivalents), pyridine (2 equivalents), CH_2Cl_2, 25 °C, 30 min; (ii) PhSNa (1.2 equivalents), DMF, 70 °C, 16 h; (iii) OXONE® (2 equivalents), acetone (12 equivalents), MeCN/aqueous $NaHCO_3$, 25 °C, 7 h; (iv) fluorenyllithium (1.2 equivalents), THF, 0 °C, 30 min; (v) 1,2-$C_6H_4(CH_2MgCl)_2$ (1.5 equivalents), THF, −78 to 25 °C, 16 h; (vi) 2-$(XMgCH_2CH_2)C_6H_4MgX$ (X = Cl, Br; 3 equivalents), THF, −78 to 25 °C, 16 h; (vii) $BrMgCH_2CH=CHCH_2MgBr$ (2 equivalents), THF, −78 to 25 °C, 24 h; (viii) TsOH (0.05 equivalents), benzene, reflux, 20 min; (ix) $SOCl_2$ (1.2 equivalents), Pr^i_2NEt (2.9 equivalents), CH_2Cl_2, −78 °C to reflux, 20 h; (x) BuLi (2.4 equivalents), THF, 0 °C, 60 min, then $ZrCl_4$ (1.1 equivalents), benzene, 25 °C, 90 min.

derivative **9** in 93% yield. Metallation of **9** was achieved by di-lithiation with butyllithium in THF solution, followed by replacement of the solvent with benzene and reaction of the dilithio species with $ZrCl_4$. After removal of inorganic salts and concentration, the 2-indenyl *ansa*-zirconocene complex **12** crystallised in 55% yield (the synthesis and Xray crystal structure of complex **12** have been previously reported in a short communication [5]).

The synthesis of the 1-indenyl complex **13** was achieved using our recently reported di-Grignard strategy for the synthesis of 3-substituted-1*H*-indenes [12]. Reaction of **5** with the di-Grignard reagent derived from 1-bromo-2-(2-chloroethyl)benzene provided the 1-indanol **7** in 85% yield. Acid-catalysed dehydration of **7** then provided the 3-indenyl derivative **10** in 72% yield. At ambient temperature, slow rotation around the 2-napthyl–3-indenyl bond leads to inequivalence of all the fluorene carbon atoms in the ^{13}C NMR spectrum of **10**. This slow rotation also produces substantial broadening in the ^{1}H NMR spectrum of **10** for the fluorene aromatic protons and for the indene protons at the 1-position. On cooling to 260 K these signals fully resolve and sharpen. [1] Metallation of **10** was carried out using the same method described above for the preparation of **12**, with the complex **13** isolated in 55% yield.

For the preparation of the cyclopentadienyl complex **14**, we sort to prepare the cyclopentadiene derivative **11** through a di-Grignard or diorganylmagnesium reaction with the ester **5**, analogous to our approach to the syntheses of **9** and **10**. The reaction of substituted butadienemagnesium complexes with carboxylate esters to yield substituted 3-cyclopentenols has been previously reported by Takase and co-workers [13], and Rieke et al. [14]. Whilst butadienemagnesium can be prepared through reaction of magnesium with butadiene in THF solution in the presence of catalytic amounts of organohalides [15], we found it more convenient to generate the complex by reacting 1,4-dibromo-2-butene with excess magnesium in THF solution at 0 °C, and then allowing the butadiene generated in situ (together with one equivalent of $MgBr_2$) to react further with the magnesium at room temperature over 18 h. Addition of the resulting pale green suspension to the ester **5** (−78 °C to room temperature over 24 h, then reflux 4 h) led to formation of a complex mixture of products, with only traces of the desired 3-cyclopentenol **8** present. It was found, however, that addition of further $MgBr_2$ (ca. 2 equivalents) to the butadienemagnesium complex suspension resulted in its complete dissolution (presumably through formation of the di-Grignard reagent), and that addition of this solution to the ester **5** (−78 °C to room temperature over 24 h) provided the desired 3-cyclopentenol **8** in 31% yield. Attempted acid-catalysed dehydration of **8** resulted in the formation of a large amount of an unidentified side-product, however, dehydration could be carried out under basic conditions ($SOCl_2$ and excess Pr^i_2NEt), affording the cyclopentadiene derivative **11** in 60% yield. The ^{1}H NMR spectrum of **11** indicated the presence of both the 1,3-cyclopentadien-1-yl and 1,3-cyclopentadien-2-yl tautomers in a ratio of 63:37 (or the reverse – the specific identity of the major/minor isomers were not determined). When out of solution, compound **11** gradually undergoes dimerisation, and so it was metallated immediately upon isolation. Metallation was carried out using the same method described above for the preparation of **12**, with the complex **14** isolated in 51% yield.

2.2. X-ray crystallographic data

The solid state molecular structures of complexes **13** and **14** have been determined by X-ray diffraction analysis. ORTEP [16] depictions of the molecules are displayed in Figs. 2 and 3, together with the structure previously determined for complex **12** [5] for comparison (Fig. 1). Table 1 summarises the crystallographic data and parameters for complexes **13** and **14**, and Table 2 presents selected bond lengths and angles for all three complexes. For all three complexes the fluorenyl ring displays typical slippage towards the 9-position {crystallographic number C(1)} [17], with the range of Zr–C distances, $\Delta = (Zr–C_{max}) - (Zr–C_{min}) = 0.307(7)$, 0.338(4) and 0.314(3) Å [18], for **12**, **13** and **14**, respectively. For complexes **12** and **13** the indenyl rings display typical slippage towards the 2-position {crystallographic number C(25)} [19], with the range of Zr–C distances $\Delta = 0.163(8)$ and 0.143(4) Å for **12** and **13**, respectively.

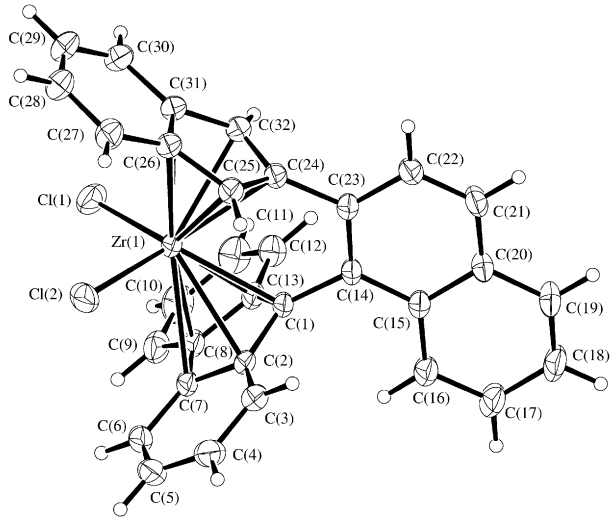


Fig. 1. ORTEP [16] depiction of complex **12** (reproduced from [5] by permission of The Royal Society of Chemistry) with crystallographic numbering; 20% displacement ellipsoids are shown for non-hydrogen atoms.

[1] Determination of the rotational barrier through DNMR methods will be described elsewhere.

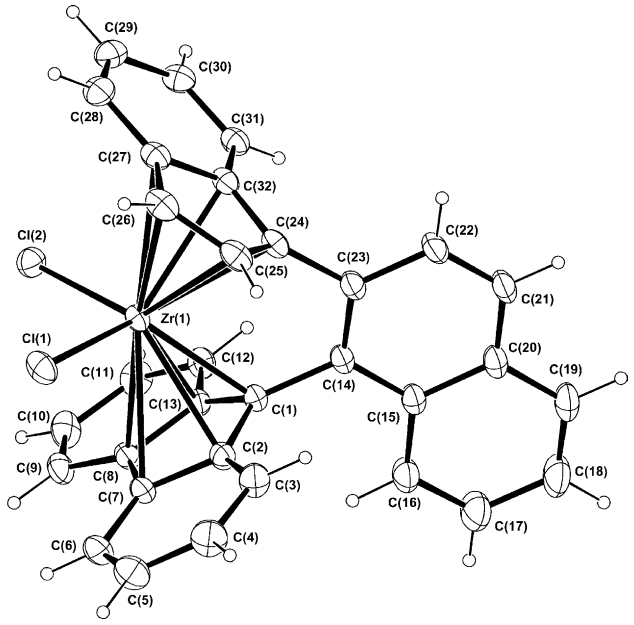


Fig. 2. ORTEP [16] depiction of complex **13**, with crystallographic numbering; 20% displacement ellipsoids are shown for non-hydrogen atoms.

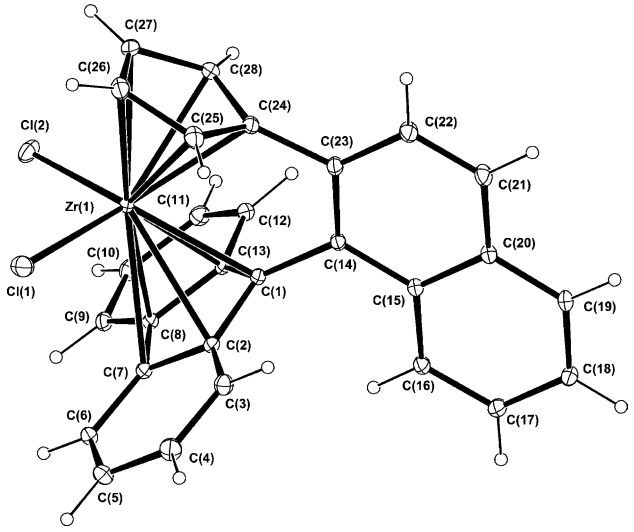


Fig. 3. ORTEP [16] depiction of complex **14**, with crystallographic numbering; 20% displacement ellipsoids are shown for non-hydrogen atoms.

In complex **14** the cyclopentadienyl ring shows relatively minor variation in the Zr–C distances, with $\Delta = 0.056(3)$ Å. There appears to be little strain associated with the 1,2-naphthylidene bridging unit, with the bonding angles associated with the bridge [i.e., C(1)–C(14)–C(23) and C(14)–C(23)–C(24)] narrowed only slightly by 2–3° for all the complexes. While the solid state molecular structure for complex **12** shows only small deviations from C_s-symmetry, complex **14** deviates significantly, with dihedral angles between the mean plane of the naphthalene the mean planes of the fluorenyl and cyclopentadienyl groups of 82.1° and 84.8°, respectively. In addition, the cyclopentadienyl moieties display consymmetric rotations [20], with respect to the $ZrCl_2$ bisector, of 3.6° and −4.8° for the fluorenyl and cyclopentadienyl groups, respectively (for the conformer illustrated in Fig. 3), and there are deviations involving the bonding angles associated with the α- and ipso-carbons of the cyclopentadienyl moieties and the naphthalene bridge carbons. In solution relatively unrestricted fluctuation between the enantiometric conformations observed in the solid state structure of complex **14** can be expected [20].

Table 1
Crystallographic data and parameters for complexes **13** and **14**

Compound	**13**	**14**
Model formula	$C_{32}H_{20}Cl_2Zr{\cdot}1.15C_6D_6$	$C_{28}H_{18}Cl_2Zr{\cdot}1.5C_6D_6$
Model molecular weight	663.37	642.76
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
A (Å)	9.4450(10)	20.864(6)
B (Å)	13.0020(10)	27.237(8)
C (Å)	26.3900(10)	11.129(3)
β (°)	95.6460(10)	114.150(4)
V (Å^3)	3225.1(4)	5771(3)
D_c (g cm^{-3})	1.366	1.480
Z	4	8
Crystal size (mm)	$0.442 \times 0.226 \times 0.138$	$0.459 \times 0.191 \times 0.176$
Crystal colour	Red	Yellow
Crystal habit	Prism	Prism
Temperature (K)	297(2)	150(2)
λ(Mo Kα) (Å)	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.532	0.592
$T_{min,max}$	0.907, 1.000[a]	0.786, 0.876[b]
$2\theta_{max}$ (°)	56.14	56.54
hkl range	−12 12, −17 17, −34 34	−27 27, −36 36, −14 14
N	33918	30511
N_{ind} (R_{merge})	7600 (0.019)	6931 (0.025)
$N_{obs}I > 2\sigma(I)$	6618	6275
N_{var}	353	361
Residuals[c] $R_1(F), wR_2(F^2)$	0.0412, 0.1253	0.0212, 0.0603
GoF(all)	1.065	1.005
Residual extrema (e Å^{-3})	−0.391, 1.017	−0.213, 0.396

[a] SADABS multi-scan.
[b] Gaussian.
[c] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma F_o$); $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (wF_c^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3$ and X and $Y = 0.0777$ and 1.218 for **13**, and 0.0384 and 2.8069 for **14**.

2.3. Complexes *12*, *13* and *14* as catalyst precursors for homogeneous α-olefin polymerisation

2.3.1. Ethylene polymerisation

After the activation of compounds **12**, **13** and **14** with MAO (30 wt% in toluene), the catalysts **12**/MAO, **13**/MAO and **14**/MAO, in combination with triisobutylal-

Table 2
Selected distances (Å) and angles (°) for complexes **12**, **13** and **14**

Compound	**12**[a]	**13**	**14**
Distances (Å)			
Zr(1)–Cl(1)	2.407(1)	2.4145(7)	2.4260(6)
Zr(1)–Cl(2)	2.412(1)	2.4071(6)	2.4273(6)
Zr(1)–Cf[b]	2.29(1)	2.30(1)	2.29(2)
Zr(1)–C(1)	2.406(3)	2.405(2)	2.4148(12)
Zr(1)–C(2)	2.580(3)	2.531(2)	2.5936(12)
Zr(1)–C(7)	2.704(4)	2.711(2)	2.7285(13)
Zr(1)–C(8)	2.713(4)	2.743(2)	2.6940(13)
Zr(1)–C(13)	2.552(3)	2.604(2)	2.5453(13)
Zr(1)–Cp[c]	2.23(1)	2.23(1)	2.19(1)
Zr(1)–C(24)	2.479(3)	2.483(2)	2.4930(13)
Zr(1)–C(25)	2.467(4)	2.475(2)	2.4753(13)
Zr(1)–C(26)	2.620(4)	2.528(3)	2.5166(15)
Zr(1)–C(β′)[d]	2.630(4)	2.618(2)	2.5313(13)
Zr(1)–C(α′)[e]	2.496(4)	2.565(2)	2.4982(13)
Angles (°)			
Cl(1)–Zr(1)–Cl(2)	99.03(5)	97.84(3)	97.16(2)
Cf–Zr(1)–Cp	127.94(4)	128.2(1)	127.70(2)
C(1)–C(14)–C(23)	117.7(3)	118.2(2)	118.31(10)
C(14)–C(23)–C(24)	117.9(3)	117.7(2)	117.09(10)
C(2)–C(1)–C(14)	126.8(3)	124.53(19)	123.80(10)
C(13)–C(1)–C(14)	124.6(3)	127.30(19)	128.30(10)
C(23)–C(24)–C(25)	125.8(3)	129.1(2)	125.02(12)
C(23)–C(24)–C(α′)	125.6(3)	124.4(2)	127.38(12)

[a] Data from [5].
[b] Centroid of C(1, 2, 7, 8, 13).
[c] Centroid of C(24, 25, 26, 31, 32) for **12**, C(24, 25, 26, 27, 32) for **13**, C(24, 25, 26, 27, 28) for **14**.
[d] C(β′) is C(31) for **12**, C(27) for **13** and **14**.
[e] C(α′) is C(32) for **12** and **13**, C(28) for **14**.

Table 3
Catalyst activities and properties of the polyethylenes produced with **12**/MAO, **13**/MAO and **14**/MAO

Catalyst[a]	**12**/MAO	**13**/MAO	**14**/MAO
M_n (g/mol)	93,475	147,000	126,740
M_w (g/mol)	322,700	555,240	765,650
M_z (g/mol)	1,107,500	8,757,400	8,587,100
$D = M_w/M_n$	3.45	3.78	6.04
A (10^3 kg(PE)/g(Zr)*h)	255.4	306.9	139.5
T_m (°C)	140.6	141.8	145.4
ΔH_m (J/g)	160.1	135.3	132.8
α (%)[b]	55	47	46

[a] Polymerisation conditions: 60 °C, 250 ml pentane, 1 ml TIBA (1 M in hexane), 1 h, 10 bar ethylene pressure, MAO-Al:Zr ratio = 2500:1.
[b] Degree of crystallinity: $\alpha = \Delta H_m/\Delta H_{m,0}$ ($\Delta H_{m,0} = 290$ J/g: enthalpy of fusion for 100% crystalline PE).

uminium (TIBA), displayed good activities for ethylene polymerisation. The results are summarized in Table 3. The addition of TIBA (as a routine method) was used to increase catalyst activities [21]. This is thought to be due to bulky isobutyl substituents being transferred from TIBA to the MAO cages in the activation process. As a consequence, the generated MAO anions become more bulky and the separation of the catalyst cation and MAO anion favours higher activity [22]. An obvious influence of the catalyst precursor structure on the polymerisation activity was observed, with the indenyl derivatives **12**/MAO and **13**/MAO possessing higher activities than the catalyst containing the cyclopentadienyl ligand **14**/MAO. The reason for the increased activity of the indenyl derivatives **12**/MAO and **13**/MAO could be the so-called ring slippage reaction [17] of the indenyl ligands in addition to the ring slippage of the fluorenyl ligands. The ring slippage reaction, leading to a change of the binding mode from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$, results in a decreased electron density and an increased Lewis acidity of the central metal. Such an interpretation is reasonable when the olefin is considered as a Lewis base and as long as all the other parameters that have influence on the reaction kinetics remain constant.

The results of HT-GPC measurements show that the highest molecular weights are observed for the polyethylenes produced with the cyclopentadienyl derivative **14**/MAO and the 1-indenyl derivative **13**/MAO. The molecular weights for the polyethylene produced with the 2-indenyl derivative **12**/MAO are significantly lower. Assuming the principle chain transfer step is β-hydride elimination, this may reflect a steric influence on the growing polymer chain which favours to a greater degree the conformation required for elimination. The polydispersity of the polyethylenes grows with their molecular masses. The highest polydispersity with $D = 6.0$ is found for the polymer produced with **14**/MAO. This behaviour presumably derives from slightly different active sites generated during the polymerisation. This could be the consequence of the heterogenisation process during the polymerisation, or the formation of various ion pairs in the activation step with MAO. The melting enthalpies and the crystallinities of the polyethylenes are seen to decrease for increasing molecular weight and polydispersity, while the melting points increase. The polymers possess crystallinities between $\alpha = 46$ and 55%; these are typical values for LDPE (low density polyethylene).

The dependence of the used MAO-aluminium to zirconium ratio on the ethylene polymerisation activity was investigated in the case of **12**/MAO. MAO is a dynamic mixture of various linear and cyclic MAO oligomers [23]. The active MAO species consists of a cage type compound containing monomeric trimethylaluminium in the inside of the cage [24]. This situation explains the necessary high excess of MAO in the activation process. As illustrated in Fig. 4, a higher MAO-aluminium to zirconium ratio leads to an initial marked increase in polymerisation activity of the catalyst, which then plateaus. Similar behaviour has been observed by Herfert and Fink [25] in the polymerisation of ethylene using isopropylidene(cyclopentadienyl)(9-fluorenyl)- $ZrCl_2$/MAO; in this case activity plateaus at an Al:Zr ratio of 5100:1 and then decreases at higher ratios.

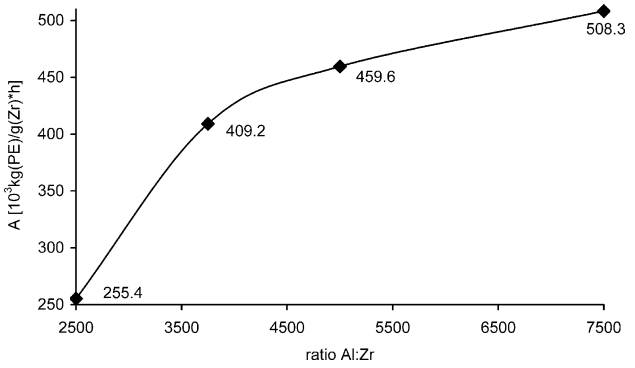


Fig. 4. Dependence of the polymerisation activity of **12**/MAO on the MAO-aluminium to zirconium ratio. Polymerisation conditions: 60 °C, 250 ml pentane, 1 ml TIBA (1 M in hexane), 1 h, 10 bar ethylene pressure, MAO-Al:Zr ratio = 2500:1 up to 7500:1.

2.3.2. Propylene polymersation

The propylene polymerisations were carried out as bulk polymerisations in neat propylene. The results are summarized in Table 4. The relative activities of **12**/MAO, **13**/MAO and **14**/MAO show an opposite behaviour to the case of ethylene polymerisation. While catalyst **13**/MAO possesses the highest activity in ethylene polymerisation, it has the lowest activity in bulk polymerisation of propylene; conversely, catalyst **14**/MAO is the least active catalyst in ethylene polymerisation, but the most active catalyst for propylene polymerisation. We interpret this result in a way that steric factors around the active centre clearly dominate electronic factors. The molecular weights of the produced polypropylenes were determined by viscometry. The trend in molecular weights of the polypropylenes was found to parallel the polymerisation activities of the catalysts.

The tacticities of the polypropylenes, determined by ^{13}C NMR spectroscopy [26], are given in Table 5, and are in accord with expectations based on the symmetry and substitution pattern of the complexes [27]. Of the two C_s-symmetric complexes, only complex **14** produces moderately syndiotactic polypropylene. The polypropylene obtained using complex **12** is substantially atactic, although with a small racemic diad excess (17.5%). Presumably the presence of substituents at all β-positions of both cyclopentadienyl moieties leads to the lack of a preferential orientation for the growing polymer chain and subsequent low enantiofacial discrimination for propylene coordination and insertion. Complex **14** produces syndiotactic polypropylene with [rrrr] = 66.0%. By way of comparison, the catalyst 1,2-ethylidene(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ (**15**)/MAO has been reported by Razavi et al. [28] to produce syndiotactic polypropylene with [rrrr] = 74.3% under bulk polymerisation conditions at 60 °C. This catalyst has also been examined by Lee et al. [29] for the polymerization of propylene at 1.2 atm pressure in toluene solution; at 25 °C, [rrrr] = 63.7%, while at 50 °C, [rrrr] = 28.4%. Consistent with the comparable stereospecificity of the complexes, the geometry around the metal in complexes **14** and **15** {Zr–Flu(centroid) = 2.28(2) Å, Zr–Cp(centroid) = 2.19(0) Å, centroid–Zr–centroid = 126.9(3)° [29]} is similar.

The C_1-symmetric complex **13** produces isotactic polypropylene with [mmmm] = 44.0% under bulk polymerisation conditions. Rieger et al. [30] have reported the polymerisation of propylene using complexes related to **13** with an ethylene bridge or substituted ethylene bridge. In the case of catalysis by 1,2-ethylidene(9-fluorenyl)(1-indenyl)$ZrCl_2$/MAO, isotactic polypropylene with [mmmm] = 68.1% was obtained at 50 °C and a propylene concentration of 0.45 mol/l in toluene; the isotacticity falls at higher propylene concentrations, with [mmmm] = 37.5% at 3.38 mol/l. For the more stereorigid catalyst (*RR,SS*)-[1-(9-fluorenyl)-1-phenyl-2-(1-indenyl)ethane]$ZrCl_2$ (**16**)/MAO, isotactic polypropylene with [mmmm] = 80.4% was obtained at 50 °C and a propylene concentration of 0.45 mol/l in toluene, and [mmmm] = 46.5% at 3.38 mol/l. The solid state structure of the substituted ethylene bridge complex **16** has been determined [30], and consistent with the comparable

Table 4
Catalyst activities and properties of the polypropylenes produced with **12**/MAO, **13**/MAO and **14**/MAO

Catalyst[a]	**12**/MAO	**13**/MAO	**14**/MAO
M_η (kg/mol)	61	29	150
A (kg(PP)/g(Zr)*h)	29.6	13.4	149.6
T_m (°C)	Amorphous	Amorphous	101.8
ΔH_m (J/g)	Amorphous	Amorphous	5.16

[a] Polymerisation conditions: bulk polymerisation, 60 °C, 500 ml propylene, 1 ml TIBA (1 M in hexane), 1 h, MAO-Al:Zr-ratio = 2500:1.

Table 5
Pentad, triad and diad distributions (in %) of the polypropylenes by ^{13}C NMR (62.9 MHz) spectroscopy[a]

Catalyst	**12**/MAO	**13**/MAO	**14**/MAO
mmmm	2.71	43.96	0.25
mmmr	7.46	18.72	0.85
rmmr	5.64	0.00	2.43
mmrr	11.55	19.94	6.40
rmrr + mmrm	25.83	5.33	7.78
mrmr	13.45	0.00	0.75
rrrr	11.34	2.00	66.03
mrrr	15.60	5.60	15.52
mrrm	6.42	4.44	0.00
mm	15.81	62.68	3.53
mr	50.83	25.27	14.93
rr	33.37	12.04	81.55
m	41.23	73.32	10.99
r	58.77	24.68	89.01

[a] Triad and diad distributions calculated from the corresponding pentad distribution.

stereospecificity of this complex with that observed with complex **13** (the concentration of propylene being ca. 10 mol/ls under bulk conditions at 60 °C [31]), the geometry around the metal in complexes **13** and **16** {Zr–Flu(centroid) = 2.259 Å, Zr–Ind(centroid) = 2.226 Å, centroid–Zr–centroid = 127.3° [30]} is similar.

3. Conclusions

It is very difficult to predict the performance of a metallocene catalyst because too many known and unknown parameters have an influence on the polymerization kinetics such as the structure of a catalyst, the activation process with MAO, the interactions of the catalyst cation with the solvent, the monomer and the generated polymer chain. This situation justifies the investigation of "structure–property-relationships" in order to tailor catalysts. For this purpose only one parameter should be varied. In this study we could show that an indenyl moiety in a bridging ligand increases the activity in ethylene polymerization considerably compared with a cyclopentadienyl unit. Steric hindrance does not play a major role: the catalyst **13**/MAO with a 1-indenyl moiety shows only a slightly better activity than the 2-indenyl analog **12**/MAO. The situation changes in propylene polymerization: the catalyst **14**/MAO with a cyclopentadienyl unit performs much better (factor 11.2) than the 1-indenyl derivative **13**/MAO. It is tempting to speculate that steric reasons are responsible for this effect. Indeed, the bulkiness of a catalyst cannot only control the kinetics of the first step, the coordination of the olefin to the metal, but also the orientation of the growing polymer chain. The tacticity of the produced polypropylene is determined from the symmetry of the catalysts. In the case of the C_s-symmetric complexes, **12**/MAO produces atactic polypropylene, while with **14**/MAO syndiotactic polypropylene is obtained analogous to the classical example with C1-bridging, isopropylidene(cyclopentadienyl)(fluorenyl)-$ZrCl_2$ [32]. In the case of the C_1-symmetric catalyst **13**/MAO the production of isotactic polypropylene is observed, presumably through a "stationary insertion" mechanism [33].

4. Experimental

4.1. General procedures

All reactions involving moisture or air sensitive species were carried out under a nitrogen or argon atmosphere, using standard Schlenk techniques. Anhydrous THF, ether, toluene and benzene were distilled immediately prior to use from sodium-benzophenone under nitrogen. Anhydrous dichloromethane and dimethylformamide were obtained by distillation from calcium hydride. Zirconium tetrachloride was sublimed immediately prior to use at ca. 195 °C/0.3 mm Hg. The MAO used in the polymerisations was obtained from Witco, Bergkamen, Germany. Flash chromatography was performed using Merck Kieselgel 60 silica gel (particle size 0.040–0.063 mm) with the indicated solvents. Melting points of compounds were determined on a Reichert hot stage microscope and are uncorrected. Microanalyses were carried out by the Microanalytical Laboratory, University of Otago (Dunedin, New Zealand), or the Microanalytical Laboratory, University of New South Wales (Sydney, Australia). ^1H (400 MHz) and ^{13}C (100 MHz) NMR Spectra were obtained on a Bruker AMX400 spectrometer. ^1H (200 MHz) NMR Spectra were obtained on a Bruker AC200 spectrometer. Spectra were recorded in deuterochloroform, deuterodichloromethane or deuterobenzene, as stated, and were referenced to residual $CHCl_3$ at 7.26 ppm (^1H) and 77.0 ppm (^{13}C); $CHDCl_2$ at 5.35 ppm (^1H) and 53.8 ppm (^{13}C); or C_6HD_5 at 7.15 ppm (^1H) and 128.0 ppm (^{13}C) downfield from TMS, respectively. Signals are assigned as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br broad. Coupling constants, *J*, are quoted in Hertz. Mass spectra were determined on an AEI Kratos MS902 spectrometer using electron impact ionisation (70 eV) calibrated with perflourokerosene, and an MSS MASPEC data system used to obtain high resolution spectra. Infra-red spectra were recorded using a Perkin-Elmer 1600 Fourier Transform infra-red spectrometer. The determination of molecular weights (M_n, M_w and M_z) and polydispersities (*D*) of polyethylene samples was carried out by high temperature gel permeation chromatography. A Waters 150CV+ apparatus with refractive index detection was used for the measurements, with 1,2,4-trichlorbenzene as the eluting solvent at 140 °C. The column material was polystyrene of the type *Styragel HT6E*. Calibration of the instrument was carried out with polystyrene standards. The determination of M_η of polypropylene samples was carried out by dissolving the polymers in decahydronaphthalene (isomeric mixture) at 130 °C. The viscosity measurements were made using a Ubbelohde viscometer at 135 °C with the capillary No. 0c. For the measurement of the $^{13}C\{^1H\}$ NMR spectra of the polypropylenes a Bruker ARX 250 spectrometer was used. The polymers were dissolved in 1,2,4-trichlorobenzene and 1,1,2,2-dideutero-1,2-dichloroethane was added as a lock substance. The samples were measured at 70 °C. Melting points and enthalpies of fusion of the polymers were measured with a Netsch DSC-200 instrument: 3-5 mg of the polymer were sealed in a standard aluminum vessel (diameter 5 mm) and the following temperature program was used: (i) 30.0–200.0 °C at 40 °C/min, (ii) 200.0–25 °C at 30 °C/min, (iii) 30.0–180.0 °C at 10 °C/min, (iv) 180.0–25.0 °C at 30 °C/min. Melting points and

melting enthalpies were determined from the curve of program (iii). The temperature was corrected linearly to the melting point of indium (m.p. = 156.62 °C). For calibration the melting enthalpy of indium was used ($\Delta H_m = 28.45$ J/g).

4.2. Synthesis of complexes **12**, **13** and **14**

4.2.1. Isopropyl 1-bromonaphthalene-2-carboxylate **2**

Thionyl chloride (145 ml) was added to an ice-cooled solution of 1-bromo-2-naphthoic acid **1** [10] (50.0 g, 0.199 mol) in a mixture of dry benzene (200 ml), and pyridine (16 ml, 1 equivalents). The mixture was then allowed to warm to room temperature, and stirred for 18 h before dilution with an equal volume of dry benzene and evaporation in vacuo. Residual thionyl chloride was removed by azeotropic distillation with 3 further portions of dry benzene. The acid chloride thus obtained was taken up in dry dichloromethane (200 ml) and placed under a nitrogen atmosphere. Pyridine (32 ml, 0.40 mol, 2 equivalents) was added, the solution cooled in a water bath, and isopropanol (30 ml, 0.38 mol, 2 equivalents) added cautiously. The mixture began to reflux spontaneously for a short period and was stirred for 1 h. The mixture was then washed with hydrochloric acid (2 M) to remove pyridine, followed by sodium hydroxide solution (2 M) to remove any unreacted acid. Drying over sodium sulfate and evaporation in vacuo afforded the ester **2** (53 g) as a brown oil, which was used without further purification. An analytical sample was prepared by flash chromatography, eluting with 20% EtOAc-light petroleum, followed by vacuum distillation (Found: C, 57.5; H, 4.2. $C_{14}H_{13}BrO_2$ requires C, 57.4; H, 4.5%); ν_{max}(thin film)/cm^{-1} 1729 (C=O); δ_H(400 MHz, $CDCl_3$) 1.44 [6H, d, J 6.3, CH(CH_3)$_2$], 5.36 [1H, septet, J 6.3, CH(CH$_3$)$_2$], 7.56–7.67 (2H, m, 6- and 7-H), 7.63 (1H, d, $J_{3,4}$ 8.4, 3-H), 7.82 (1H, br d, $J_{4,3}$ 8.4, 4-H), 7.83 (1H, br d, $J_{5,6}$ 8.2, 5-H) and 8.44 (1H, br d, $J_{8,7}$ 8.5, 8-H); δ_C(100 MHz, $CDCl_3$) 167.8 [CO$_2$CH(CH$_3$)$_2$], 135.7, 132.94 and 132.92 (each C), 129.1, 128.9, 128.7, 128.6, 128.5 and 126.3 (each CH), 122.7 (C), 70.4 [CO$_2$$C$H(CH$_3$)$_2$] and 22.5 [CO$_2$CH($CH_3$)$_2$]; m/z 294 (M$^+$, 15%), 292 (M$^+$, 15), 252 (30), 250 (31), 235 (37), 233 (39), 207 (14), 205 (16), 127 (28), 126 (100), 76 (15), 75 (15) and 74 (17).

4.2.2. Isopropyl 1-(phenylsulfanyl)naphthalene-2-carboxylate **3**

Sodium hydride (9.6 g, 60% in paraffin oil, 0.240 mol, 1.2 equivalents) was placed under a nitrogen atmosphere, washed 4 times with dry light petroleum and dried under vacuum. The flask was cooled in an ice bath and dry dimethylformamide (125 ml) added before dropwise addition of thiophenol (24.6 ml, 0.240 mol, 1.2 equivalents) (vigorous evolution of hydrogen). The mixture was then stirred for 15 min at 0 °C, then added rapidly via cannula to a solution of the foregoing crude ester **2** in dry dimethylformamide. The temperature was raised to 70 °C and the mixture stirred for 18 h. The mixture was allowed to cool to 30 °C, then diluted with water until cloudy, seeded with crystals of sulfide **3** and cooled slowly to 5 °C. The crystallised product was filtered off, and the crystals washed with water and ethanol, affording the sulfide **3** (54.7 g, 0.170 mol, 85% from acid **1**) as light brown crystals, m.p. 70.5–72 °C (Found: C, 74.2; H, 5.4. $C_{20}H_{18}O_2S$ requires C, 74.5; H, 5.6%); ν_{max}(KBr)/cm^{-1} 1732 (C=O); δ_H(400 MHz, $CDCl_3$) 1.27 [6H, d, J 6.3, CH(CH_3)$_2$], 5.27 [1H, septet, J 6.3, CH(CH$_3$)$_2$], 7.04–7.17 (5H, m, Ph-H), 7.50–7.56 (2H, m, 6- and 7-H), 7.64 (1H, d, $J_{3,4}$ 8.4, 3-H), 7.88 (1H, br d, $J_{5,6}$ 8.0, 5-H), 7.97 (1H, br d, $J_{4,3}$ 8.4, 4-H) and 8.52 (1H, br d, $J_{8,7}$ 8.4, 8-H); δ_C(100 MHz, $CDCl_3$) 168.9 [CO$_2$CH(CH$_3$)$_2$], 139.8, 138.7, 135.3 and 135.2 (each C), 131.2 (CH), 129.5 (2 × CH), 129.2 and 128.6 (each CH), 128.2 (C), 128.1 (CH), 127.81 (2 × CH), 127.76, 126.0 and 125.1 (each CH), 70.2 ([CO$_2$$C$H(CH$_3$)$_2$] and 22.4 [CO$_2$CH($CH_3$)$_2$]; m/z 322 (M$^+$, 56%), 280 (24), 263 (24), 235 (28), 234 (75), 202 (21), 188 (11), 187 (100), 186 (41), 115 (18) and 77 (14).

4.2.3. Isopropyl rac-1-(phenylsulfinyl)naphthalene-2-carboxylate **4**

A solution of the sulfide **3** (50.0 g, 0.155 mol) in acetonitrile (775 ml) was cooled to 0 °C. A sodium EDTA solution (620 ml, 5×10^{-4} M) was added, followed by acetone (135 ml, 1.84 mol, 12 equivalents), sodium hydrogen carbonate (24 g, 0.286 mol) and OXONE® (48 g, 0.155 mol of $KHSO_5$). The bulk of the sulfide precipitated from solution and the liquid became bi-phasic. The suspension was stirred vigorously at 4–8 °C for 2 h, then a further equivalent of OXONE® (48 g) and sodium hydrogen carbonate (24 g) were added, and vigorous stirring continued for a further 7 h. The reaction was then quenched by addition of sufficient 2 M hydrochloric acid to dissolve the inorganic matter (~1 l). The acetonitrile was then removed in vacuo, and the precipitated product was filtered off, and washed with water. Recrystallisation from benzene afforded the pure sulfoxide **4** (45.2 g, 0.134 mol, 86%), m.p. 99.5–100.5 °C (Found: C, 70.7; H, 5.2. $C_{20}H_{18}O_3S$ requires C, 71.0; H, 5.4%); ν_{max}(KBr)/cm^{-1} 1704 (C=O), 1042 (S=O); δ_H(400 MHz, $CDCl_3$) 1.41 and 1.42 [each 3H, d, J 6.2, CH(CH_3)$_2$], 5.35 [1H, septet, J 6.2, CH(CH$_3$)$_2$], 7.36–7.46 (4H, m, 3′-, 4′-, 5′- and 7-H), 7.51 (1H, br dd, $J_{6,5}$ 8.0, $J_{6,7}$ 6.8, 6-H), 7.74 (1H, d, $J_{3,4}$ 8.5, 3-H), 7.81 (2H, m, 2′- and 6′-H), 7.86 (1H, br d, $J_{5,6}$ 8.0, 5-H), 8.00 (1H, br d, $J_{4,3}$ 8.5, 4-H) and 8.74 (1H, br d, $J_{8,7}$ 8.6, 8-H); δ_C (100 MHz, $CDCl_3$) 167.2 [CO$_2$CH(CH$_3$)$_2$], 145.0, 140.0, 136.2 and 134.1 (each C), 133.3 and 130.6 (each CH), 130.1 (C), 129.5 (3 × CH), 128.7, 128.5 and 126.3 (each CH), 125.9 (2 × CH), 124.7 (CH), 71.3 [CO$_2$$C$H(CH$_3$)$_2$] and 22.5 [CO$_2$CH($CH_3$)$_2$]; m/z 338 (M$^+$, 24%), 279 (36),

278 (31), 234 (66), 219 (29), 204 (29), 203 (100), 202 (95), 143 (46), 126 (57), 115 (56) and 77 (38).

4.2.4. Isopropyl sp-1-(9′-fluorenyl)naphthalene-2-carboxylate 5

A solution of fluorenyllithium was prepared by adding *n*-butyllithium (7.1 ml, 2.5 M in hexane, 17.8 mmol, 1.2 equivalents) to a solution of fluorene (2.95 g, 17.8 mmol, 1.2 equivalents) in dry THF (100 ml) at 0 °C under nitrogen, and stirring for 5 min. A solution of the sulfoxide **4** (5.0 g, 14.8 mmol) in dry THF (15 ml) was then added rapidly via cannula, and the mixture, which turned dark green, was stirred for 30 min before quenching with ammonium chloride solution (10%, 25 ml). The phases were separated and the aqueous phase extracted with ether. The combined organic phases were then dried over sodium sulfate and evaporated in vacuo to leave an orange oil. The product was purified by flash chromatography, eluting with 5% EtOAc-light petroleum, and afforded the pure ester **5** (5.09 g, 13.5 mmol, 91%) as a pale yellow oil which crystallised on standing, m.p. 124–125 °C (Found: C, 85.7; H, 5.85. $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.9%); ν_{max}(KBr)/cm^{-1} 1719 (C=O); δ_H(400 MHz, $CDCl_3$) 1.42 [6H, d, *J* 6.2, CH(CH_3)$_2$], 5.37 [1H, septet, *J* 6.2, C*H*(CH$_3$)$_2$], 6.20 (1H, s, 9′-H), 6.60 (1H, br d, $J_{8,7}$ 8.7, 8-H), 6.89 (1H, ddd, $J_{7,8}$ 8.7, $J_{7,6}$ 6.8, $J_{7,5}$ 1.3, 7-H), 7.21 (2H, ddd, $J_{2',1'}$ 7.4, $J_{2',3'}$ 7.4, $J_{2',4'}$ 0.9, 2′- and 7′-H), 7.27 (2H, br d, $J_{1',2'}$ 7.4, 1′- and 8′-H), 7.28 (1H, ddd, $J_{6,5}$ 8.1, $J_{6,7}$ 6.8, $J_{6,8}$ 0.8, 6-H), 7.43 (2H, br dd, $J_{3',4'}$ 7.6, $J_{3',2'}$ 7.4, 3′- and 6′-H), 7.75 (1H, br d, $J_{5,6}$ 8.1, 5-H), 7.84 and 7.85 (2H, AB, J_{AB} 8.8, 3- and 4-H) and 7.96 (2H, br d, $J_{4',3'}$ 7.6, 4′- and 5′-H); δ_C(100 MHz, $CDCl_3$) 170.1 [*C*O$_2$CH(CH$_3$)$_2$], 149.2 and 140.8 (each 2 × C), 137.2, 135.8, 133.8 and 132.0 (each C), 129.0 and 128.9 (each CH), 128.1 and 127.8 (each 2 × CH), 127.4, 127.1, 126.9 and 125.7 (each CH), 125.5 and 121.0 (each 2 × CH), 70.1 [CO$_2$*C*H(CH$_3$)$_2$], 51.7 (9′-CH) and 22.6 [CO$_2$CH(*C*H$_3$)$_2$]; *m*/*z* 378 (M$^+$, 5.5%), 336 (17) 335 (51), 319 (38), 318 (100), 290 (27), 289 (77), 288 (14), 287 (25) and 144 (12).

4.2.5. sp-2-[1′-(9″-fluorenyl)-2′-naphthyl]indan-2-ol 6

Magnesium turnings (2.92 g, 120 mmol, 4 equivalents) were activated by stirring in dry THF (20 ml) under a nitrogen atmosphere for 20 min, followed by addition of 1,2-dibromoethane (200 μl, 2.3 mmol, 0.075 equivalents) and gentle warming. After evolution of ethylene (effervescence) had ceased, a solution of α,α′-dichloro-*o*-xylene (5.25 g, 30 mmol) in dry THF (350 ml) was added slowly via cannula over 3 h at room temperature. The mixture was then stirred for 18 h, turning pale green. This solution was added slowly via cannula over 90 min to a solution of the ester **5** (7.89 g, 20.8 mmol) in dry THF (100 ml) at −78 °C under a nitrogen atmosphere. The di-Grignard reagent began to precipitate when the addition was ~2/3 complete. The mixture was stirred at −78 °C for 15 min after addition of the Grignard reagent was complete, then allowed to warm slowly to room temperature and stirred for 18 h. The reaction was quenched with ammonium chloride solution (10%, 150 ml). The phases were then separated, and the aqueous phase extracted with ether. The combined organic phases were dried over sodium sulfate and evaporated in vacuo to leave a pale yellow crystalline solid. Recrystallisation from dichloromethane-light petroleum afforded the pure alcohol **6** (6.68 g, 15.7 mmol, 75%) as colourless crystals, m.p. 199.5–201.5 °C (Found: C, 90.5; H, 5.7. $C_{32}H_{24}O$ requires C, 90.5; H, 5.7%); ν_{max}(KBr)/cm^{-1} 3531 (OH); δ_H(400 MHz, $CDCl_3$) 2.56 (1H, s, OH), 3.64 and 4.04 [each 2H, AB, J_{AB} 16.0, (1-H)$_2$ and (3-H)$_2$], 6.52 (1H, br d, $J_{8',7'}$ 8.8, 8′-H), 6.55 (1H, s, 9″-H), 6.82 (1H, ddd, $J_{7',8'}$ 8.8, $J_{7',6'}$ 6.8, $J_{7',5'}$ 1.4, 7′-H), 7.20 (1H, ddd, $J_{6',5'}$ 8.0, $J_{6',7'}$ 6.8, $J_{6',8'}$ 1.0, 6′-H), 7.19–7.24 (6H, m, 1″-, 2″-, 5-, 6-, 7″- and 8″-H), 7.28–7.32 (2H, m, 4- and 7-H), 7.40–7.45 (2H, m, 3″- and 6″-H), 7.72 (1H, br d, $J_{5',6'}$ 8.0, 5′-H), 7.81 (1H, br d, $J_{4',3'}$ 8.8, 4′-H), 7.92 (1H, d, $J_{3',4'}$ 8.8, 3′-H) and 7.98 (2H, d, $J_{4'',3''}$ 7.6, 4″- and 5″-H); δ_C(100 MHz, $CDCl_3$) 150.4 (2 × C), 143.0 (C), 141.2 and 140.7 (each 2 × C), 135.7, 134.5 and 133.5 (each C), 128.66 and 128.63 (each CH), 128.0, 127.8 and 127.4 (each 2 × CH), 126.7, 126.3 and 126.0 (each CH), 125.8 (2 × CH), 124.9 (3 × CH), 121.1 (2 × CH), 86.0 (2-COH), 51.9 (9″-CH) and 50.0 (1- and 3-CH$_2$); *m*/*z* 423 ([M−H]$^+$, 1.3%), 409 (15), 408 ([M −H$_2$O]$^+$, 63), 407 (100), 406 (37) 392 (23), 390 (20), 316 (53), 304 (57), 292 (23), 291 (68) and 165 (37).

4.2.6. sp-1-[1′-(9″-fluorenyl)-2′-naphthyl]indan-1-ol 7

1,2-Dibromoethane (100 μl, 1.2 mmol) was added dropwise to a stirred suspension of magnesium granules [20 mesh (Aldrich), 480 mg, 19.6 mmol] in dry THF (5 ml) under an argon atmosphere. Upon cessation of effervescence a solution of 1-bromo-2-(2-chloroethyl)benzene [12] (1.0 g, 4.6 mmol) in dry THF (15 ml) was added dropwise over 30 min at room temperature. After stirring overnight, the di-Grignard solution was added dropwise via cannula over 1 h to a solution of the ester **5** (500 mg, 1.32 mmol) in dry THF (5 ml) at −78 °C under an argon atmosphere. The mixture was then allowed to warm slowly to room temperature over 18 h before quenching with ammonium chloride solution (10%, 10 ml). The phases were separated and the aqueous phase extracted with ether. The combined organic phases were then dried over sodium sulfate and evaporated in vacuo to leave a pale yellow oil. Flash chromatography eluting with 1:9:11 EtOAc–CH_2Cl_2–light petroleum afforded the alcohol **7** (474 mg, 1.12 mmol, 85%) as a colourless solid, m.p. 247.5–249.5 °C; (Found: C, 90.55; H, 5.5. $C_{32}H_{24}O$ requires C, 90.5; H, 5.7%); ν_{max}(KBr)/cm^{-1} 3538 (OH); δ_H(400 MHz, $CDCl_3$) 2.37 (1H, s, OH), 2.70–2.77 (1H, m, 2-H), 2.95–3.03 (1H, m, 2-H), 3.12–3.21 [2H, m, (3-H)$_2$], 6.51 (1H, br d, $J_{8',7'}$ 8.7,

8′-H), 6.56 (1H, s, 9″-H), 6.81 (1H, ddd, $J_{7',8'}$ 8.7, $J_{7',6'}$ 6.7, $J_{7',5'}$ 1.3, 7′-H), 7.07 (1H, br d, $J_{8'',7''}$ 7.5, 8″-H), 7.15 (1H, ddd, $J_{7'',6''}$ 7.5, $J_{7'',8''}$ 7.5, $J_{7'',5''}$ 0.9, 7″-H), 7.18 (1H, ddd, $J_{6',5'}$ 8.2, $J_{6',7'}$ 6.7, $J_{6',8'}$ 0.9, 6′-H), 7.24 (1H, ddd, $J_{2'',1''}$ 7.5, $J_{2'',3''}$ 7.5, $J_{2'',4''}$ 1.1, 2″-H), 7.25 (1H, d, $J_{3',4'}$ 8.6, 3′-H), 7.36–7.44 (5H, m, 3″-, 4-, 5-, 6- and 6″-H), 7.45 (1H, br d, $J_{1'',2''}$ 7.5, 1″-H), 7.52–7.56 (1H, m, 7-H), 7.64 (1H, br d, $J_{4',3'}$ 8.6, 4′-H), 7.68 (1H, br d, $J_{5',6'}$ 8.2, 5′-H), 7.95 (1H, br d, $J_{5'',6''}$ 7.5, 5″-H) and 7.96 (1H, br d, $J_{4'',3''}$ 7.5, 4″-H); δ_C(100 MHz, $CDCl_3$) 149.7 (2 × C), 148.7, 143.8, 143.6, 140.03, 139.96, 134.4, 133.7 and 132.8 (each C), 128.7, 128.0, 127.4, 127.3, 127.1, 127.0, 126.7, 126.6, 125.9, 125.5, 125.4, 125.3, 125.2, 124.9, 124.8, 124.0, 120.3 and 120.2 (each CH), 87.5 (1-COH), 51.4 (9″-CH), 45.3 (3-CH_2) and 30.1 (2-CH_2); *m/z* 406 ([M−H_2O]$^+$, 100%), 405 (57), 404 (19), 389 (24), 318 (22), 315 (41), 289 (22), 278 (25), 241 (28), 228 (20) and 165 (23).

4.2.7. *sp-1-[1′-(9″-fluorenyl)-2′-naphthyl]-3-cyclopentenol* **8**

1,2-Dibromoethane (90 μl, 1.0 mmol) was added dropwise to a stirred suspension of magnesium powder [50 mesh (Aldrich), 540 mg, 22.2 mmol] in dry THF (5 ml) under an argon atmosphere. Upon cessation of effervescence the reaction was cooled to 0 °C and a solution of 1,4-dibromo-2-butene (1.13 g, 5.28 mmol) in dry THF (100 ml) was added dropwise over 1 h. The mixture was then allowed to warm slowly to room temperature over 18 h, affording a pale green suspension. A solution of $MgBr_2$ in THF was prepared by adding 1,2-dibromoethane (1.04 ml, 12.1 mmol) dropwise to a stirred suspension of magnesium powder [50 mesh (Aldrich), 580 mg, 23.9 mmol] in dry THF (100 ml) under an argon atmosphere. After stirring 1 h at room temperature, this solution was added via cannula to the pale green suspension, resulting in dissolution of the suspension and formation of a pale green solution. This solution was then added dropwise via cannula over 1.5 h to a solution of the ester **5** (1.00 g, 2.65 mmol) in dry THF (10 ml) at −78 °C under an argon atmosphere. The mixture was then allowed to warm slowly to room temperature over 24 h before quenching with ammonium chloride solution (10%, 50 ml). The phases were separated and the aqueous phase extracted with ether. The combined organic phases were then dried over sodium sulfate and evaporated in vacuo to leave a pale yellow oil. Flash chromatography eluting with 20% EtOAc-light petroleum afforded the alcohol **8** (310 mg, 0.83 mmol, 31%) as a colourless solid, m.p. 138–139 °C (Found: M$^+$, 374.1663. $^{12}C_{28}{}^{1}H_{22}{}^{16}O$ requires M$^+$, 374.1671); ν_{max}(KBr)/cm^{-1} 3429 (OH); δ_H(400 MHz, $CDCl_3$) 1.69 (1H, s, OH), 3.02 and 3.51 [each 2H, AB, J_{AB} 16.3, (2-H)$_2$ and (5-H)$_2$], 5.81 (2H, s, 3- and 4-H), 5.82 (1H, br s, 9″-H), 6.40 (1H, br d, $J_{8',7'}$ 8.7, 8′-H), 6.78 (1H, ddd, $J_{7',8'}$ 8.7, $J_{7',6'}$ 6.8, $J_{7',5'}$ 1.2, 7′-H), 7.12–7.20 (5H, m, 6′-, 1″-, 2″-, 7″- and 8″-H), 7.40 (2H, br dd, $J_{3'',2''}$ 7.5, $J_{3'',4''}$ 7.5, 3″- and 6″-H), 7.71 (1H, br d, $J_{5',6'}$ 8.1, 5′-H), 7.82 (1H, br d, $J_{4',3'}$ 8.9, 4′-H), 7.95 (2H, d, $J_{4'',3''}$ 7.5, 4″- and 5″-H) and 8.09 (1H, d, $J_{3',4'}$ 8.9, 3′-H); δ_C(100 MHz, $CDCl_3$) 150.0 (2 × C), 145.2 (C), 140.7 (2 × C), 134.4, 133.9 and 133.2 (each C), 129.4 (2 × CH), 128.7 and 128.5 (each CH), 128.0 and 127.5 (each 2 × CH), 126.4, 126.2 and 125.8 (each CH), 124.9 (2 × CH), 124.5 (CH), 121.2 (2 × CH), 83.6 (1-COH), 52.2 (2- and 5-CH_2) and 51.4 (9″-CH); *m/z* 374 (M$^+$, 1.4%), 372 (2), 356 (100), 341 (12), 339 (12), 328 (33), 315 (54), 302 (13), 289 (35), 178 (16) and 165 (23).

4.2.8. *sp-9-[2′-(2″-indenyl)-1′-naphthyl]fluorene* **9**

A solution of the alcohol **6** (7.33 g, 17.3 mmol) and *p*-toluenesulfonic acid (150 mg, 0.79 mmol, 5 mol%) in benzene (250 ml) was refluxed for 20 min in a Dean-Stark apparatus for azeotropic removal of water. The solution was allowed to cool, then the solvent was removed in vacuo and replaced with dichloromethane (200 ml). The solution was then washed with water, dried over sodium sulfate, and evaporated in vacuo to leave an off-white crystalline solid. Recrystallisation from benzene afforded the pure hydrocarbon **9** (6.53 g, 16.6 mmol, 93%) as colourless crystals, m.p. 263.5–264.5 °C; (Found: C, 94.3; H, 5.4. $C_{32}H_{22}$ requires C, 94.5; H, 5.5%); δ_H(400 MHz, $CDCl_3$) 3.96 [2H, s, (1″-H)$_2$], 5.96 (1H, s, 9-H), 6.48 (1H, dd, $J_{8',7'}$ 8.7, $J_{8',6'}$ 1.1, 8′-H), 6.86 (1H, ddd, $J_{7',8'}$ 8.7, $J_{7',6'}$ 6.8, $J_{7',5'}$ 1.3, 7′-H), 7.13 (1H, br s, 3″-H), 7.18 (1H, ddd, $J_{5'',4''}$ 7.4, $J_{5'',6''}$ 7.4, $J_{5'',7''}$ 1.1, 5″-H), 7.18–7.23 (4H, m, 1-, 2-, 7- and 8-H), 7.22 (1H, ddd, $J_{6',5'}$ 8.0, $J_{6',7'}$ 6.8, $J_{6',8'}$ 1.1, 6′-H), 7.27 (1H, br dd, $J_{6'',5''}$ 7.4, $J_{6'',5''}$ 7.3, 6″-H), 7.38 (1H, br d, $J_{4'',5''}$ 7.4, 4″-H), 7.36–7.42 (2H, m, 3- and 6-H), 7.48 (1H, br d, $J_{7'',6''}$ 7.3, 7″-H), 7.57 (1H, d, $J_{3',4'}$ 8.5, 3′-H), 7.74 (1H, br d, $J_{5',6'}$ 8.0, 5′-H), 7.81 (1H, d, $J_{4',3'}$ 8.5, 4′-H) and 7.91 (2H, br d, $J_{4,3}$ 7.6, $J_{5,6}$ 7.6, 4- and 5-H); δ_C(100 MHz, $CDCl_3$) 149.6 (2 × C), 148.9, 145.6 and 144.1 (each C), 140.8 (2 × C), 139.0, 134.4, 133.8 and 132.2 (each C), 131.7, 129.0 and 128.4 (each CH), 128.0 and 127.65 (each 2 × CH), 127.58, 127.4, 126.7, 126.5, 126.1 and 125.5 (each CH), 124.8 (2 × CH), 124.3 and 121.9 (each CH), 52.2 (9-CH) and 45.2 (1″-CH_2); *m/z* 406 (M$^+$, 100%), 405 (28), 390 (19), 315 (50), 302 (36), 278 (21), 241 (25), 239 (20) and 165 (43).

4.2.9. *sp-9-[2′-(3″-indenyl)-1′-naphthyl]fluorene* **10**

The alcohol **7** (2.09 g, 4.93 mmol) was dehydrated using the procedure described for the preparation of **9**. Recrystallisation from benzene–heptane afforded the pure hydrocarbon **10** (1.44 g, 3.55 mmol, 72%) as fine colourless crystals, m.p. 208–209.5 °C; (Found: C, 94.45; H, 5.5. $C_{32}H_{22}$ requires C, 94.5; H, 5.5%); δ_H(400 MHz, $CDCl_3$, 260 K) 3.61 (1H, A part of ABX, J_{AB} 23.7, $J_{1'',2''}$ 1.9, 1″-H), 3.70 (1H, B part of ABX, J_{AB} 23.7, $J_{1'',2''}$ 1.9, 1″-H), 5.94 (1H, s, 9-H), 6.61 (1H, br d, $J_{8',7'}$ 8.4, 8′-H),

6.88 (1H, apparent t, $J_{2'',2''}$ 1.9, 2″-H), 6.98 (1H, ddd, $J_{7',8'}$ 8.4, $J_{7',6'}$ 6.9, $J_{7',5'}$ 1.3, 7′-H), 7.17–7.22 (2H, m, 1- and 2-H), 7.31–7.38 (3H, m, 7-, 6′- and 6″-H), 7.40–7.47 (3H, m, 3-, 8- and 5″-H), 7.48–7.52 (2H, m, 6- and 4″-H), 7.63 (1H, br d, $J_{7'',6''}$ 7.3, 7″-H), 7.67 (1H, d, $J_{3',4'}$ 8.4, 3′-H), 7.88 (1H, br d, $J_{5',6'}$ 7.8, 5′-H), 7.970 (1H, br d, $J_{4,3}$ 7.6, 4-H), 7.971 (1H, d, $J_{4',3'}$ 8.4, 4′-H) and 8.01 (1H, br d, $J_{5,6}$ 7.6, 5-H); δ_C(100 MHz, $CDCl_3$, 295 K) 149.0, 148.7, 146.2, 145.5, 143.9, 140.2, 139.9, 136.2, 134.00 and 133.94 (each C), 132.3 (CH), 131.6 (C), 128.3 and 127.8 (each CH), 127.3 (2 × CH), 127.2, 126.9, 126.8, 126.5, 126.3, 125.7, 125.4, 125.1, 124.4, 124.2, 123.9 and 120.4 (each CH), 120.2 (2 × CH), 51.4 (9-CH), and 38.6 (1″-CH_2); *m/z* 406 (M^+, 100%), 405 (31), 389 (14), 315 (24), 278 (13), 241 (16), 228 (10), 165 (10), 78 (14).

4.2.10. *sp-9-[2′-(1″,3″-cyclopentadien-1″-yl)-1′-naphthyl]-fluorene and sp-9-[2′-(1″,3″-cyclopentadien-2″-yl)-1′-naphthyl]fluorene* ***11***

A solution of the alcohol **8** (590 mg, 1.58 mmol) in dry dichloromethane (15 ml) was added dropwise to a solution of *N*,*N*-diisopropylethylamine (800 μl, 4.6 mmol) and thionyl chloride (140 μl, 1.9 mmol) dry dichloromethane (15 ml) at −78 °C under an Ar atmosphere. The mixture was then allowed to warm to room temperature and then heated at reflux for 19 h. The solution was then diluted with dichloromethane and washed with dilute HCl (2 M) and water. The organic phase was dried over sodium sulfate and evaporated in vacuo to leave a pale yellow oil. The product was purified by flash chromatography, eluting with 8% EtOAc-light petroleum, and afforded the pure ligand **11** (338 mg, 0.95 mmol, 60%) as a pale yellow foam; (Found: M^+, 356.1560. $^{12}C_{28}{}^{1}H_{20}$ requires M^+, 356.1565); the ^{1}H NMR spectrum indicated two tautomers were present in a ratio of 63:37, δ_H(200 MHz, C_6D_6, * denotes signal for the minor tautomer) 2.77 and 3.30* [2H, each apparent q, *J* 1.4, (5″-$H)_2$], 6.05* and 6.16 (1H, each s, 9-H), 6.25–6.32 and 6.34–6.39* (1H, each m, vinyl-H), 6.48–6.52 and 6.73–6.77* (1H, each m, vinyl-H), 6.54–6.65 (1H, m, 7′-H), 6.82–7.26 (9H, m, vinyl-H and Ar-H), 7.38–7.62 (3H, m, Ar-H) and 7.76 (2H, d, $J_{4,3}$ 7.6, 4- and 5-H); *m/z* 356 (M^+, 100%), 339 (22), 328 (43), 315 (53),178 (20) and 165 (23).

4.2.11. *[1′-(9-fluorenyl)-2′-(2″-indenyl)naphthalene]zirconium dichloride* ***12***

n-Butyllithium (1.23 ml, 2.48 M in hexanes, 3.0 mmol, 2.4 equivalents) was added to a solution of the ligand **9** (508 mg, 1.25 mmol) in dry THF (15 ml) at 0 °C under argon, and the mixture stirred for 30 min to form the dark red/burgundy dianion. The solvent was removed under vacuum, then the residue was redissolved in dry benzene (15 ml), and the solvent removed once more under vacuum. The residue was then taken up in dry benzene (15 ml) and the dark red solution (at r.t.) added via cannula to a suspension of zirconium tetrachloride (325 mg, 1.39 mmol, 1.1 equivalents) in dry benzene (5 ml) at r.t. The mixture, which turned orange and cloudy, was then stirred for 1 h. The mixture was filtered through Celite under argon and washed through with dry benzene (10 ml), to give a clear orange solution. The volume was reduced to 15 ml under vacuum, while maintaining the temperature near r.t. The solution was then allowed to stand overnight to allow the complex to crystallise. The supernatant solution was then removed via cannula and the remaining crystals dried under vacuum. This afforded orange prisms of the complex (393 mg, 0.694 mmol, 55%), m.p. dec. >175 °C; (Found: C, 67.4; H, 3.5; Cl, 12.55. $C_{32}H_{20}Cl_2Zr$ requires C, 67.8; H, 3.6; Cl, 12.5%); (Found: M^+, 564.0003. $^{12}C_{32}{}^{1}H_{20}{}^{35}Cl_2{}^{90}Zr$ requires M^+, 563.9989); δ_H(400 MHz, C_6D_6) 6.03 (2H, s, 1″- and 3″-H), 6.86–6.96 (5H, m, 1-, 5″-, 6″-, 7′- and 8-H), 6.96–7.05 (3H, m, 2-, 7- and 8′-H), 7.23 (1H, br dd, $J_{6',5'}$ 8.2, $J_{6',7'}$ 6.5, 6′-H), 7.30–7.35 (5H, m, 3-, 3′-, 4″-, 6- and 7″-H) and 7.74–7.79 (4H, m, 4-, 4′-, 5- and 5′-H); δ_C(100 MHz, C_6D_6) 139.4 (2′-C), 137.6 (2″-C), 134.3 (1′-C), 134.0 (8a′-C), 133.6 (4a′-C), 129.6 (2- and 7-CH), 129.3 (4′-CH), 128.59 (5′-CH), 128.53 (3a″- and 7a″-C), 127.9 (7′-CH), 127.4 (6′-CH), 127.1 (8a- and 9a-C), 127.0 (3C, 3′-, and 3- and 6-, or 5″ and 6″-CH), 126.7 (5″- and 6″-, or 3- and 6-CH), 125.8 (4″- and 7″-CH), 124.97 (4- and 5-CH), 124.90 (8′-CH), 124.87 (4a- and 4b-C), 122.2 (1- and 8-CH), 102.1 (1″- and 3″-CH) and 100.9 (9-C); *m/z* 574 (2.1%), 573 (6.6), 572 (18), 571 (27), 570 (58), 569 (61), 568 (85), 567 (84), 566 (100), 565 (90) and 564 (92, each M^+), 563 (26), 529 (29), 528 (22), 527 (35), 526 (22), 525 (28), 523 (24), 400 (23) and 263 (20).

4.2.12. *[1′-(9-fluorenyl)-2′-(1″-indenyl)naphthalene]zirconium dichloride* ***13***

The ligand **10** (500 mg, 1.23 mmol) was metallated using the procedure described for the preparation of complex **12**. Crystallisation from 15 ml of dry benzene afforded bright orange/pink microfine crystals of the complex **13** (380 mg, 0.671 mmol, 55%), m.p. dec. >175 °C; (Found: M^+, 563.9959. $^{12}C_{32}{}^{1}H_{20}{}^{35}Cl_2{}^{90}Zr$ requires M^+, 563.9989); δ_H(400 MHz, C_6D_6) 6.04 (1H, d, $J_{2'',3''}$ 3.1, 2″-H), 6.54 (1H, d, $J_{3'',2''}$ 3.1, 3″-H), 6.73 (1H, br dd, $J_{6'',7''}$ 8.6, $J_{6'',5''}$ 7.4, 6″-H), 6.82 (1H, br d, $J_{1,2}$ 8.6, 1-H), 6.87–6.92 (2H, m, 7- and 8-H), 6.99 (1H, br dd, $J_{5'',4''}$ 8.2 $J_{5'',6''}$ 7.4, 5″-H), 6.99–7.06 (2H, m, 2- and 7′-H), 7.07 (1H, br d, $J_{7'',6''}$ 8.6, 7″-H), 7.16 (1H, br d, $J_{8',7'}$ 8.6, 8′-H), 7.26 (1H, br dd, $J_{6,5}$ 8.6, $J_{6,7}$ 7.4, 6-H), 7.27 (1H, br d, $J_{4'',5''}$ 8.2, 4″-H), 7.34 (1H, br dd, $J_{6',7'}$ 6.7, $J_{6',5'}$ 8.2, 6′-H), 7.41 (1H, br d, $J_{3',4'}$ 8.6, 3′-H), 7.51 (1H, br dd, $J_{3,4}$ 8.2, $J_{3,2}$ 7.4, 3-H), 7.82 (1H, br d, $J_{5,6}$ 8.6, 5-H), 7.88 (1H, br d, $J_{5',6'}$ 8.2, 5′-H), 7.90 (1H, br d, $J_{4',3'}$ 8.6, 4′-H) and 7.95 (1H, br d, $J_{4,3}$ 8.2, 4-H); δ_C(100 MHz, C_6D_6): [2]

[2] Two quaternary carbon signals, which are probably obscured by the solvent peak, could not be located

138.6, 137.3, 135.4 and 134.7 (each C), 130.2 (CH), 129.9(C), 129.81(CH), 129.5 (C), 129.0, 128.8, 128.6, 128.0, 127.8 and 127.5 (each CH), 127.3 (2 × CH), 126.7 and 126.3 (each CH), 125.69 (C), 125.63, 125.4 and 125.2 (each CH), 124.8 (C), 123.5, 122.8 and 122.1 (each CH), 121.6 (C), 113.2 and 109.4 (each CH) and 100.4 (9-C); *m/z* 573 (2.1%), 572 (7.4), 571 (12), 570 (34), 569 (26), 568 (68), 567 (61), 566 (98), 565 (70) and 564 (100, each M^+), 563 (16), 562 (16), 527 (18), 405 (33), 404 (49), 403 (28), 402 (19), 401 (19) and 400 (21).

4.2.13. [1′-(9-fluorenyl)-2′(cyclopentadienyl)naphthalene]zirconium dichloride **14**

The ligand **11** (255 mg, 0.72 mmol) was metallated using the procedure described for the preparation of complex **12**. Crystallisation from 10 ml of dry benzene afforded bright yellow/orange microfine crystals of the complex **14** (190 mg, 0.37 mmol, 51%), m.p. dec. >175 °C; (Found: C, 65.5; H, 3.85%. $C_{28}H_{18}Cl_2Zr$ requires C, 65.1; H, 3.5%); δ_H(400 MHz, CD_2Cl_2) 6.05 and 6.44 (each 2H, apparent t, *J* 2.6, Cp-H), 7.04 (1H, d, $J_{8',7'}$ 8.5, 8′-H), 7.17 (2H, d, $J_{1,2}$ 8.6, 1- and 8-H), 7.31–7.36 (3H, m, 2-, 7- and 7′-H), 7.58 (1H, dd, $J_{6',5'}$ 8.3, $J_{6',7'}$ 6.8, 6′-H), 7.66 (1H, d, $J_{3',4'}$ 8.4, 3′-H), 7.72 (2H, dd, $J_{3,2}$ 6.9, $J_{3,4}$ 8.5, 3- and 6-H), 8.09 (1H, d, $J_{5',6'}$ 8.3, 5′-H), 8.14 (1H, d, $J_{4',3'}$ 8.4, 4′-H) and 8.21 (2H, d, $J_{4,3}$ 8.5, 4- and 5-H); δ_C(100 MHz, CD_2Cl_2) 138.8, 135.7, 134.6, 134.3 and 134.1 (each C), 129.8 (2 × CH), 129.7, 128.8 and 127.5 (each CH), 127.4 (2 × C), 127.2 and 127.10 (each CH), 127.06 (2 × CH), 125.4 (2 × C), 125.0 (2 × CH), 124.5 (CH), 122.2, 120.2 and 109.5 (each 2 × CH) and 100.1 (9-C); *m/z* 522 (7.7%), 521 (9.1), 520 (31), 519 (22), 518 (68), 517 (42), 516 (100), 515 (49) and 514 (92, each M^+), 481 (13), 480 (10), 479 (22), 478 (13), 477 (25), 475 (15) and 239 (13).

4.3. Polymerisation reactions

4.3.1. Homogeneous polymerisation of ethylene

A quantity of 0.5–10.0 mg of the catalyst precursor was dissolved or suspended in 5–10 ml of toluene and activated with the corresponding amount of MAO solution (30 wt% in toluene) to give the desired ratio of MAO-aluminium to zirconium. A solution of TIBA (1 ml of a 1 M solution in hexane) was added, and the solution of the activated catalyst then dissolved in pentane (250 ml). The pentane solution was then transferred into a 1 l Büchi autoclave and warmed up to 60 °C. Ethylene (99.98% purified with aluminium oxide) was then polymerised under a constant pressure of 10 bar. After 1 h the ethylene supply was stopped and the reaction mixture cooled to room temperature. The formed suspension was filtered and the polymer was dried in vacuo.

4.3.2. Homogeneous polymerisation of propylene

The polymerisation of propylene was carried out as a bulk polymerisation in neat propylene. A quantity of 5–10 mg of the catalyst precursor was dissolved or suspended in 5–10 ml of toluene and activated with the corresponding amount of MAO solution (30 wt% in toluene) to give a ratio of MAO-aluminium to zirconium of 2500:1. A solution of TIBA (1 ml of a 1 M solution in hexane) was added, and the solvent then removed in vacuo. The catalyst was transferred into a 1 l Büchi autoclave and propylene (500 ml) condensed into the autoclave. The reaction mixture was then stirred for 1 h at 60 °C. The remaining propylene was then allowed to expand and the formed polymer was dried in vacuo.

4.4. X-ray structure determinations for complexes **13** and **14**

Suitable crystals of compounds **13** and **14** were grown from C_6D_6 solution at room temperature. Diffraction data for compounds **13** and **14** were obtained from a Bruker SMART 1000 diffractometer using graphite monochromated Mo Kα radiation generated from a sealed tube. Room temperature data were collected for **13** by attaching a crystal to a thin glass fibre. Data for **14** were collected at 150(2) K by attaching, with Exxon Paratone N, a single crystal to a short length of suture fibre supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. The data integration and reduction were undertaken with SAINT and XPREP [34]. The data for compound **13** were corrected for absorption using a multi-scan correction determined with SADABS [35], and the data for **14** were corrected with a Gaussian absorption correction [34,36]. Data reduction included the application of Lorentz and polarisation corrections. Subsequent computations were carried out with the teXsan [37], WinGX [38] and XTAL [39] graphical user interfaces. Solutions for **13** and **14** were obtained with SIR 97 [40], and were extended and refined with SHELXL 97 [41].

The asymmetric unit of **13** contains a complex molecule and 1.5 deuterated benzene molecules, with one of the solvate molecules being centred on an inversion site. The benzene molecules have high thermal motion and, or, unresolved disorder and the solvate molecule C(33)–C(38) was constrained to planarity. The populations of the solvates were refined to convergence and then fixed at the first decimal place, with an occupancy of 0.7 for C(33)–C(38) and 0.9 for C(39)–C(41). The benzene molecules were modeled with isotropic thermal parameters, and the remaining non-hydrogen atoms were modeled with anisotropic thermal parameters. The asymmetric unit of **14** contains the complex molecule and three deuterated benzene molecules, each of which

is centred on a twofold axis. A riding atom model was used for the hydrogen and deuterium atoms for both of the structures.

5. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 231233 and 231234 for compounds **13** and **14**, respectively. Copies of this information (but not including the thermal parameters) may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(b) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255;
(c) F. Küber, Chem. Unserer Zeit 28 (1994) 197;
(d) W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413;
(e) H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.

[2] (a) K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63;
(b) H.G. Alt, R. Zenk, W. Milius, J. Organomet. Chem. 514 (1996) 257;
(c) H.G. Alt, R. Zenk, J. Organomet. Chem. 522 (1996) 177;
(d) H.G. Alt, M. Jung, W. Milius, J. Organomet. Chem. 558 (1998) 111.

[3] (a) H.G. Alt, R. Zenk, J. Organomet. Chem. 518 (1996) 7;
(b) H.G. Alt, R. Zenk, J. Organomet. Chem. 522 (1996) 39;
(c) H.G. Alt, M. Jung, G. Kehr, J. Organomet. Chem. 562 (1998) 153;
(d) H.G. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 127.

[4] R.W. Baker, M.A. Foulkes, J.A. Taylor, J. Chem. Soc. Perkin Trans. 1 (1998) 1047.

[5] R.W. Baker, M.A. Foulkes, P. Turner, J. Chem. Soc. Dalton Trans. (2000) 431.

[6] P. Burger, H.H. Brintzinger, J. Organomet. Chem. 407 (1991) 207.

[7] R.L. Halterman, T.M. Ramsey, N.A. Pailes, M.A. Khan, J. Organomet. Chem. 497 (1995) 43.

[8] R.L. Halterman, A. Tretyakov, M.A. Khan, J. Organomet. Chem. 568 (1998) 41.

[9] H.J. Arts, M. Kranenburg, R.H.A.M. Meijers, E.G. Ijpeij, G.J.M. Gruter, F.H. Beijer, Eur. Pat. Appl. 1059300, 2000.

[10] S.L. Colletti, R.L. Halterman, Organometallics 10 (1991) 3428.

[11] W.E. Ellis, T.K. Hollis, W. Odenkirk, J. Whelan, R. Ostrander, A.L. Reingold, B. Bosnich, Organometallics 12 (1993) 4391.

[12] R.W. Baker, M.A. Foulkes, M. Griggs, B.N. Nguyen, Tetrahedron Lett. 43 (2002) 9319.

[13] M. Yang, M. Ando, K. Takase, Tetrahedron Lett. 12 (1971) 3529.

[14] R.D. Rieke, M.S. Sell, H. Xiong, J. Am. Chem. Soc. 117 (1995) 5429.

[15] K. Fujita, Y. Ohnuma, H. Yasuda, H. Tani, J. Organomet. Chem. 113 (1976) 201.

[16] C.K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.

[17] H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323.

[18] J.L. Atwood, W.E. Hunter, D.C. Hrncir, E. Samuel, H. Alt, M.D. Rausch, Inorg. Chem. 14 (1975) 1757.

[19] J.W. Faller, R.H. Crabtree, A. Habib, Organometallics 4 (1985) 929.

[20] P. Burger, J. Diebold, S. Gutmann, H.U. Hund, H.H. Brintzinger, Organometallics 11 (1992) 1319.

[21] A.H. Tullo, Chem. Eng. News Oct. 22 (2001) 38.

[22] C.E. Denner, H.G. Alt, J. Appl. Polym. Sci. 89 (2003) 1336.

[23] (a) J.F. van Baar, M. Galimberti, K.L. von Hebel, A.D. Horton, G.M.M. van Kessel, P.A. Schut, T. Dall'Occo, PCT Int. Appl. WO 9921896, 1999;
(b) A.D. Horton, J.F. van Baar, P.A. Schut, G.M.M. van Kessel, K.L. von Hebel, PCT Int. Appl. WO 9921899, 1999;
(c) J.F. van Baar, P.A. Schut, A.D. Horton, T. Dall'Occo, G.M.M. van Kessel, PCT Int. Appl. WO 0035974, 2000.

[24] (a) M.R. Mason, J.M. Smith, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 115 (1993) 4971;
(b) C.J. Harlan, M.R. Mason, A.R. Barron, Organometallics 13 (1994) 2957;
(c) C.J. Harlan, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 117 (1995) 6465.

[25] N. Herfert, G. Fink, Makromol. Chem. 193 (1992) 1359.

[26] (a) A. Zambelli, P. Locatelli, G. Bajo, F.A. Bovey, Macromolecules 8 (1975) 687;
(b) V. Busico, R. Cipullo, G. Monaco, M. Vacatello, A.L. Segre, Macromolecules 30 (1997) 6251;
(c) M.D. Bruce, R.M. Waymouth, Macromolecules 31 (1998) 2707.

[27] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.

[28] A. Razavi, D. Vereecke, L. Peters, K. Den Dauw, L. Nafpliotis, J.L. Atwwod, in: G. Fink, R. Mülhaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Springer-Verlag, Berlin, 1995, pp. 111–147.

[29] M.H. Lee, J.-W. Park, C.S. Hong, S.I. Woo, Y. Do, J. Organomet. Chem. 561 (1998) 37.

[30] B. Rieger, G. Jany, R. Fawzi, M. Steimann, Organometallics 13 (1994) 647.

[31] Wm.R. Parrish, J. Chem. Eng. Data 32 (1987) 311.

[32] J.A. Ewen, R.L. Jones, A. Razavi, J. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255.

[33] A. Razavi, L. Peters, L. Nafpliotis, D. Vereecke, K. Den Dauw, J.L. Atwood, U. Thewald, Macromol. Symp. 89 (1995) 345.

[34] Bruker, SMART, SAINT and XPREP: area detector control and data integration and reduction software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1995.

[35] G.M. Sheldrick, SADABS: Empirical absorption correction program for area detector data, University of Göttingen, Germany, 1996.

[36] P. Coppens, L. Leiserowitz, D. Rabinovich, Acta Crystallogr. 18 (1965) 1035.

[37] Molecular Structure Corporation, teXsan for Windows: Single Crystal Structure Analysis Software, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1997–1998.

[38] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[39] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), Xtal 3.6 System, University of Western Australia, 1999.

[40] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[41] G.M. Sheldrick, SHELX 97: Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1998.