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Zirconium indenylamido complexes: synthesis and reactivity Crystal structure of $[Zr(Ind)_2(NC_3H_6)_2]$

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Abstract

Reactions of $[ZrInd(NMe_2)_3]$ (**1**) with Me_3SiCl afforded $[ZrInd(NMe_2)_2Cl]$ (**2**), $[ZrInd(NMe_2)Cl_2]$ (**3**) and $[ZrIndCl_3]_n$ (**4**) in high yields ($\geq 90\%$). $[ZrIndCl_3(dme)]$ (**5**) was obtained either from **4** and dme or by a one-pot reaction from $[ZrInd(NMe_2)_3]$, Me_3SiCl and dme. Treatment of $[ZrInd(NMe_2)_2Cl]$ with LiMe gave $[ZrInd(NMe_2)_2Me]$ (**6**), and in similar reaction conditions $[ZrInd_2Me_2]$ (**10**) was obtained from $[ZrInd(NMe_2)Cl_2]$. Whereas the reaction of **2** with $LiN(H)^tBu$ produced $\{[ZrInd(NMe_2)_2[N(H)^tBu]\}$ (**7**), the addition of $LiN(H)^tBu$ to $[TiInd(NMe_2)_2Cl]$ afforded $[Ti(NMe_2)_2(\mu\text{-}N^tBu)]_2$ (**9**) in quantitative yield. $\{TiInd(NMe_2)_2\text{-}[N(H)^tBu]\}$ was identified by NMR as an intermediate in the synthesis of **9**, and two isomeric forms corresponding to the parallel (**8a**) and perpendicular (**8b**) orientations of the indenyl and $N(H)^tBu$ ligands were characterised. The addition of an excess of azetidine to **1** gave $[ZrInd_2(NC_3H_6)_2]$ (**11**), the molecular structure of which was determined by X-ray crystallography. Preliminary studies showed that **3**–methylaluminoxane (MAO) polymerises ethylene and propylene, whereas $[TiInd(NMe_2)Cl_2]$, **12**–MAO, only polymerises ethylene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amido ligand; Ethylene and propylene polymerisation; Half-sandwich complexes; Indenyl; Titanium; Zirconium

1. Introduction

The Lewis acidity of Group 4 metal complexes was identified as a crucial feature of efficient single-site polymerisation catalysts whose active species are electron-deficient complexes mostly containing 14 or fewer electrons [1–4]. In constrained geometry *ansa*-cyclopentadienylamido complexes, the ability of the amido ligands to tune the electronic properties of the metal centres was pointed out as a key for its high performance as olefin homo- and co-polymerisation catalysts [5–7]. This property is also most probably the origin of the high molecular weight polymers obtained with 'living' bis-amido catalysts [8–10]. Simultaneously, the different steric requirements of the amido ligands, dependent on the R groups bonded to the nitrogen, confine the active centre, leading to selectivity towards olefin substrates and control over the molecular weight parameters of the polymers [5,11].

Our study of Group 4 indenyldimethylamido complexes focuses on the synthesis, reactivity, theoretical calculations and catalytic behaviour in olefin polymerisation. The choice of indenyl, instead of cyclopentadienyl, was aimed to test whether the particular features of the indenyl ligand, the so-called 'indenyl effect', would be observed in the reactivity of these complexes, namely in the stabilisation of η^3-Ind derivatives induced by the presence of π-donor ligands as NR_2. However, this possibility was ruled out on the basis of chemical and density functional theory studies that showed a marked preference for η^5-coordination of indenyl in all $Ti(Ind)(NMe_2)_{(3-x)}Cl_x$ complexes ($x = 0$, 1, 2 and 3) [12].

We report now the synthesis and reactivity of several zirconium indenylamido complexes and the preliminary studies on the catalytic activity of $M(Ind)(NMe_2)Cl_2$ ($M = Ti$, Zr) in the polymerisation of ethylene and propylene.

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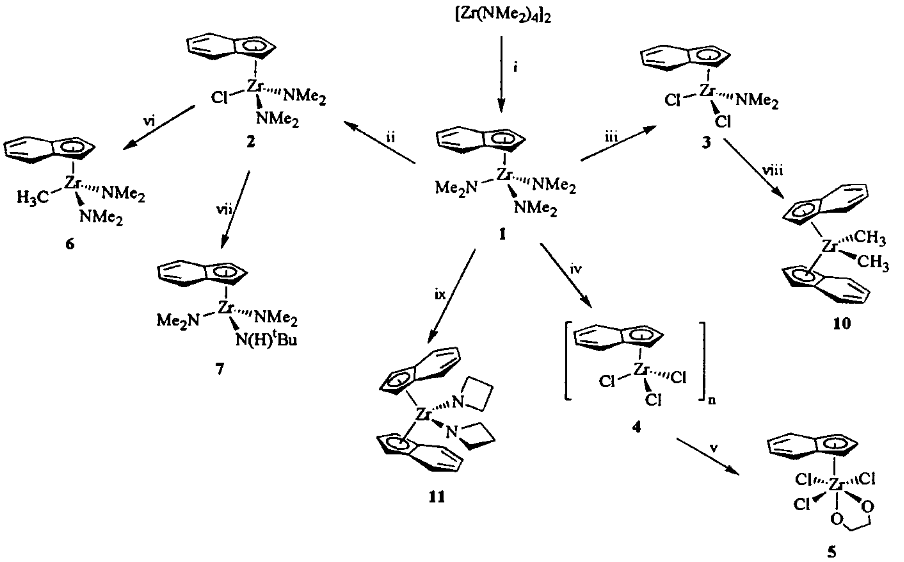
2. Results and discussion

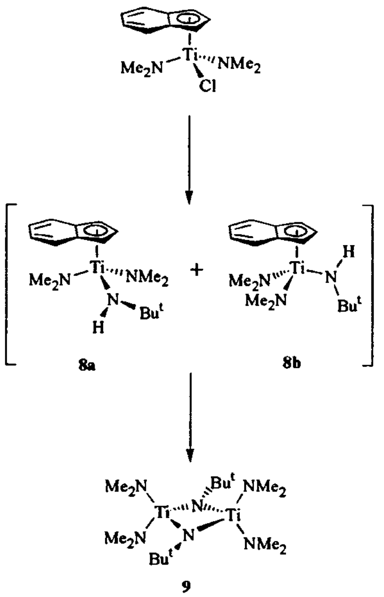
All the zirconium compounds described in this work are shown in Scheme 1. The reaction of $[Zr(NMe_2)_3(\mu\text{-}NMe_2)]_2$ [13] with indene, in toluene at 120 °C, gave $[ZrInd(NMe_2)_3]$ (**1**) quantitatively, which was previously isolated in low yield by Chandra and Lappert [14]. Complex **1** proved to be a suitable starting material for the synthesis of $[ZrInd(NMe_2)_2Cl]$ (**2**), $[ZrInd(NMe_2)Cl_2]$ (**3**) and $[ZrIndCl_3]_n$ (**4**). The metathesis of the Zr–NMe_2 bonds was accomplished in toluene with Me_3SiCl; this led to trimethylsilyldimethylamine as a by-product, which was flushed out of the reaction vessel with a slow nitrogen stream, through an oil bubbler [15–17]. In the case of complex **4**, which precipitated out of the solution as the reaction proceeded, $N(SiMe_3)Me_2$ was identified in the final product in 40% yield. The formation of $[Zr(Ind)Cl_3]_n$ through the reaction of $Sn(Ind)Cl_3$ and $ZrCl_4$ was previously reported [18] and the compound was formulated as a polymer on the basis of its low solubility. The reaction of **4** with 1,2-dimethoxyethane (dme) in CH_2Cl_2 led to the quantitative formation of $[Zr(Ind)Cl_3(dme)]$ (**5**) [18]. Alternatively, **5** was obtained in 90% yield directly from $[ZrInd(NMe_2)_3]$. The synthetic procedures to complexes **4** and **5** described in this work are very convenient alternatives to the methods previously reported in the literature, since they avoid the use of tin compounds and allow the isolation of both complexes in high yields.

The proton- and carbon-NMR spectra of complexes **1**–**3** show η^5-bonded indenyl ligands and equivalent methyl groups, denoting free rotation around the metal–nitrogen bonds as usually observed in dimethylamido complexes [19,20]. The NMR spectra of complex **4** deserve a particular comment. Two sets of resonances are observed at 23 °C, in C_6D_6 and $CDCl_3$ for the indenyl, suggesting two different environments for the ligand (^1H, δ (C_6D_6): ligand A, 7.49 ($H^{4,7}$), 7.05 ($H^{5,6}$), 6.98 (H^2), 6.68 ($H^{1,3}$); ligand B, 7.37 ($H^{4,7}$), 6.98 ($H^{5,6}$), 6.83 (H^2), 6.53 ($H^{1,3}$); ^{13}C, δ (C_6D_6): ligand A, 128.9–127.2 ($C^{5,6}$), 126.3 ($C^{4,7}$), 120.9 (C^2), 123.9 ($C^{3a,7a}$), 110.9 ($C^{1,3}$); ligand B, 128.9–127.2 ($C^{5,6}$), 126.1 ($C^{4,7}$), 124.9 (C^2), 110.4 ($C^{1,3}$)). These signals convert into a unique resonance at 70 °C when the solution is heated in toluene-d^8 from $+23$ to $+95$ °C and return to the original pattern upon cooling. The fluxional behaviour observed reveals a rapid exchange between the two types of indenyl ligand. Although we cannot exclude a higher degree of aggregation, we tentatively suggest a chloride-bridged dimeric structure for **4**, based on the NMR data and its solubility in non-coordinating and less polar solvents (benzene and toluene). The two sets of indenyl resonances would then correspond to the cis and trans isomers, which rapidly interconvert at temperatures higher than 70 °C. Similar structures were characterised by X-ray diffraction for $[Hf(Ind)Cl_3]_2$ [18] and $[Zr(C_5Me_5)Cl_3]_2$ [21]. Attempts to observe the dimeric molecular ion by FAB-MS were unfruitful. Two signals at δ 3.02 and 1.53 were assigned to the methyl protons of NMe_2SiMe_3, which nuclear Overhauser enhancement (NOE) experiments showed were not bonded to the zirconium.

Treatment of $[ZrInd(NMe_2)_2Cl]$ with LiMe gave $[ZrInd(NMe_2)_2Me]$ (**6**), and with $LiN(H)^tBu$ led to $\{ZrInd(NMe_2)_2[N(H)^tBu]\}$ (**7**). As observed for the complexes described above, the NMR spectra of **6** and **7** revealed η^5-indenyl ligands and free rotation of the amido ligands. Despite the similarities between the



Scheme 1. (i) Indene, excess; (ii) Me_3SiCl, 1.1 equivalents; (iii) Me_3SiCl, 2.2 equivalents; (iv) Me_3SiCl, 4.3 equivalents; (v) dme, excess; (vi) LiMe; (vii) $LiN(H)^tBu$; (viii) LiMe or MeMgBr; (ix) NC_3H_6, excess.



Scheme 2.

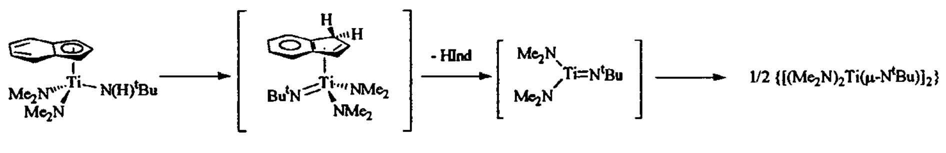
NMR spectra of [ZrInd(NMe$_2$)$_3$] and {ZrInd(NMe$_2$)$_2$-[N(H)^{t}Bu]}, the remarkable difference in the ^{1}H resonances of the dimethylamido ligands (δ 2.74 for **1** and 3.02 for **7**) is indicative that the N(H)^{t}Bu ligand behaves as a less effective π-donor than NMe$_2$. The proton chemical shift of the N(H)^{t}Bu ligand (δ 3.44) is similar to the value reported for {ZrCp*[N(H)^{t}Bu]$_3$} [22]. The stability of {ZrInd(NMe$_2$)$_2$[N(H)^{t}Bu]} contrasted markedly with that of the titanium analogue, which eliminated indene to give [Ti(NMe$_2$)$_2$(μ-N^{t}Bu)]$_2$ (**9**) [23] as the final product of the reaction of [TiInd(NMe$_2$)$_2$Cl] with LiN(H)^{t}Bu (Scheme 2). The complex {TiInd(NMe$_2$)$_2$[N(H)^{t}Bu]} (**8**) was identified by NMR as an intermediate in the formation of **9**, as represented in Scheme 2. Two isomeric forms of **8**, corresponding to the parallel (**8a**) and perpendicular (**8b**) orientations of the N(H)^{t}Bu and indenyl ligands, were observed in the NMR spectra as a consequence of the hindered rotation around the Ti–N(H)^{t}Bu bond due to the bulky *tert*-butyl group. The N(H)^{t}Bu resonances of both titanium complexes **8a** and **8b** are very deshielded (δ 6.52, 6.47) compared with the value of δ 3.44 for the same proton in the zirconium analogue. However, as expected, those values still reflect electron-richer metal centres than {TiCp[N(H)^{t}Bu]Cl$_2$}, where the amido proton resonates at δ 10.6 [24]. The C$_\alpha$ chemical shift of N(H)R ligands is a reference in the evaluation of the nitrogen sp$_2$-hybridization extent [25]. In the case of {MInd(NMe$_2$)$_2$[N(H)^{t}Bu]} these values are δ 55.4 for **7** and 46.2 and 44.9 for **8**, which, surprisingly, do not follow the same trend observed for the corresponding N(H)^{t}Bu resonances.

The high selectivity of the reaction between [TiInd(NMe$_2$)$_2$Cl] and LiN(H)^{t}Bu, (that when studied by NMR shows the dimer **9** and indene as the only products formed) and the strong trans effect of imido ligands [26] suggest that the proton migration to the indenyl most probably occurs in the coordination sphere of the titanium, as represented in Scheme 3. The different behaviour observed for complexes {MInd(NMe$_2$)$_2$[N(H)^{t}Bu]} (M = Zr, **7**; Ti, **8**) reflects the smaller size of titanium, which places bulky amido ligands in its coordination sphere at the expense of long metal–indenyl distances [12]. This reaction also points out the significant basic character of the indenyl ligand in **8**, resulting from the amido π-donation to the titanium acceptor orbitals.

Surprisingly, the reaction of [ZrInd(NMe$_2$)Cl$_2$] with two equivalents of LiMe or MeMgBr led to the synthesis of [ZrInd$_2$Me$_2$] (**10**) [27], which was isolated in 25% yield from hexane. Similarly, treatment of [ZrInd(NMe$_2$)$_3$] with azetidine, carried out in toluene, gave orange crystals of [ZrInd$_2$(NC$_3$H$_6$)$_2$] (**11**) in 25% yield. In their study of the reactions of *ansa*-bridged bis-indenes and Group 4 metal dialkylamides, Jordan and coworkers reported the equilibrium between mono- and bis-indenylamido complexes. The hydrolysis of metal–indenyl bonds by N(H)R$_2$ was related to the acidity of the indenyl ligands. The amide steric properties and the metal size provide stereochemical control, determining the formation of mono- or bis-indenyl products [16,28].

Crystals of complex **11**, suitable for single crystal X-ray diffraction, grew in benzene by slow diffusion of hexane. A view of the molecular structure is shown in Fig. 1, along with the atomic labelling scheme, and Table 1 presents relevant bond lengths and angles.

The coordination geometry of the zirconium centre is a distorted tetrahedron with angles N(1)–Zr(1)–N(2) and Ind(1*)–Zr(1)–Ind(2*) of 93.35(10)° and 128.21(1)° respectively (Ind(*) indicates the centroid of the indenyl five member ring). This is in good agreement with the values reported for ZrCp$_2$(NC$_4$H$_8$)$_2$ (95.68(8) and 128.5°) [29] and Zr[2-(NMe$_2$)Ind]$_2$Cl$_2$ (94.76(6) and 127.21(3)°) [30]. The distances between the metal and the indenyl five-member ring carbon atoms lie in the range typical of zirconium-(η^5-indenyl) ligands



Scheme 3.

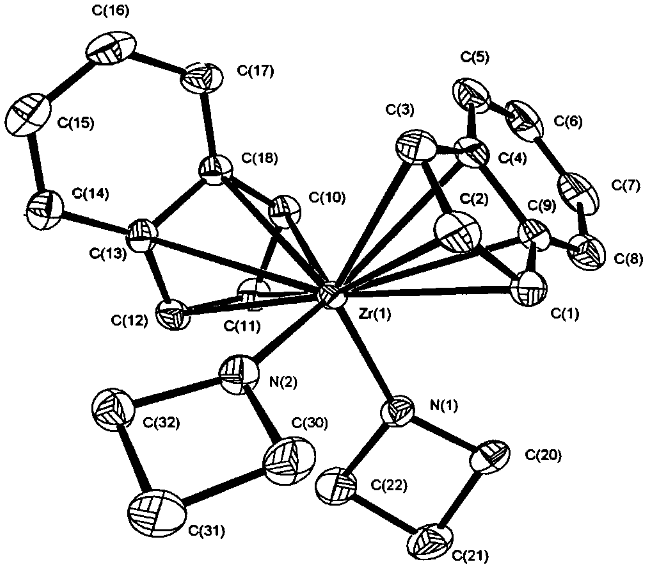


Fig. 1. Molecular structure of [$ZrInd_2(NC_3H_6)_2$] (**11**) with the atom numbering scheme. Ellipsoids are at 30% probability level.

Table 1
Selected distances (Å) and angles (°) for complex **11**

Zr(1)–N(1)	2.055(2)	Zr(1)–N(2)	2.056(2)
Zr(1)–C(10)	2.508(2)	Zr(1)–C(11)	2.515(3)
Zr(1)–C(12)	2.565(3)	Zr(1)–C(13)	2.691(3)
Zr(1)–C(18)	2.665(3)	Zr(1)–C(1)	2.565(3)
Zr(1)–C(2)	2.530(3)	Zr(1)–C(3)	2.541(3)
Zr(1)–C(4)	2.685(3)	Zr(1)–C(9)	2.671(3)
N(2)–C(30)	1.476(4)	N(2)–C(32)	1.476(4)
N(1)–C(20)	1.462(3)	N(1)–C(22)	1.482(4)
Ind(*)–Zr(1)–Ind(*)	128.21(1)	N(1)–Zr(1)–N(2)	93.35(10)
C(20)–N(1)–Zr(1)	147.01(19)	C(32)–N(2)–Zr(1)	145.22(18)
C(22)–N(1)–Zr(1)	122.75(18)	C(30)–N(2)–Zr(1)	123.7(2)
C(20)–N(1)–C(22)	90.1(2)	C(30)–N(2)–C(32)	89.8(2)

[19,31,32]; accordingly, the two indenyl ligands are planar. The fold angles [33] are 6.5(4)° for Ind(1), defined by atoms C(1) to C(9), and 9.4(3)° for the other indenyl ligand. The corresponding hinge angles are 4.7(4)° and 5.5(3)° respectively, and the zirconium atom is essentially centred on the five-member ring of the indenyl ligands ($\Delta = 0.125(4)$ and 0.141(4) Å). The Zr–N bond lengths (2.055(2) and 2.056(2) Å) denote π bonding between the two atoms. The two NC_3H_6 ligands are planar with maximum deviation 0.0688(18) Å for N(1)C(20)C(21)C(22) and 0.0499(20) Å for N(2)C(30)C(31)C(32), defining an angle of 51.05(15)° between them. The sums of the angles around N(1) and N(2) are 359.86(57)° and 358.72(58)° respectively. The amido π-donor orbitals are perpendicular to the ligand planes and compete with the same Zr π-acceptor orbital. The similarities of the N geometries and the dihedral angles N(2)–Zr(1)–N(1)–C(22) (52.5(2)°) and N(1)–Zr(1)–N(2)–C(30) (49.9(2)°) indicate that the Zr–N π-interaction is distributed over the two Zr–N bonds. Considering that the optimal Zr–N π-bond would be achieved when these dihedral angles are 90°, a significant metal–nitrogen multiple bond character is revealed by the solid-state structure. The bonding features noticed above are usually observed in d^0 Group 4 bis-amido complexes, e.g. $ZrCp_2(NC_4H_8)_2$ [29] and *ansa*-(μ-$SiMe_2$)$Ind_2Zr(NMe_2)_2$ [15], and the degree of metal–amido multiple bond order is often conditioned by steric arguments [12]. Steric crowding between the indenyl and azetidino ligands is revealed by the close non-bonded H···H contacts between hydrogen atoms on C(20) and C(1) (2.40 Å), C(32) and C(12) (2.55 Å) and C(32) and C(14) (2.58 and 2.68 Å). This circumstance is responsible for the most remarkable feature of the structure of complex **11**, i.e. the difference in the angles C(20)–N(1)–Zr(1), 147.02(19)°, C(22)–N(1)–Zr(1), 122.75(18)°, C(32)–N(2)–Zr(1), 145.22(18)° and C(30)–N(2)–Zr(1), 123.7(2)°. The asymmetry observed in the solid-state molecular structure of [$ZrInd_2(NC_3H_6)_2$] is not detected in solution, where the variable-temperature NMR spectra (−60 to 25 °C) reveal a C_{2v} symmetry resulting from metal–ligands fluxional bonds.

Compound **3** and its previously synthesised Ti analogue [$TiInd(NMe_2)Cl_2$] (**12**) [12] were tested first in the polymerisation of ethylene and propylene using methylaluminoxane (MAO) as activator (Table 2).

The **12**–MAO system shows moderate activity in the production of polyethylene at 20 °C (entry 1); it is slightly higher than the 70 $g_{PE}\ mmol_{metal}^{-1}\ h^{-1}\ bar^{-1}$ exhibited at 50 °C by the non-bridged cyclopentadienylamido analogue [$TiCp^*(NMe_2)Cl_2$] [34], but lower than Ti *ansa*-bridged cyclopentadienylamido-based systems working at 25 °C [35,36]. However, at 50 °C, there is a significant decrease of the **12**–MAO catalytic activity (entries 1 and 2), which is very likely due to thermal deactivation of the catalyst [37]. This behaviour is not observed for Ti (or Zr) *ansa*-bridged cyclopentadienylamido systems, which show an activity increase with temperature [6,7,35,36,38,39], and stresses the importance of the *ansa*-linkage in the catalyst precursor robustness. Also, the lack of a constrained geometry in **12** and a more pronounced steric effect of the indenyl ligand lead to the virtual inactivity of **12**–MAO towards the polymerisation of propylene at 20 °C (entry 5), contrary to what is observed in Ti *ansa*-cyclopentadienylamido-derived catalysts [38]. On the other hand, the non-bridged Zr indenylamido system **3**–MAO shows very high activities in the polymerisation of ethylene, much higher than those observed for the *ansa*-cyclopentadienylamido systems of Zr [6,7,36,39–42] or even Ti. In contrast with the Ti analogue, the **3**–MAO catalyst shows an increasing activity with temperature (entries 3 and 4) and is active in the polymerisation of propylene to polypropylene at 20 °C (entry 6).

In general, it is assumed that indenyl Group 4 derivatives are more active catalyst precursors than the corresponding cyclopentadienyl analogues, this difference being more pronounced for Zr [43]. Noteworthy is the reaction described above where, in the presence of an excess of alkylating agent (LiMe or MeMgBr), compound **3** partially gives the metallocene [$ZrInd_2Me_2$]. Further studies are in progress to ascertain whether this activity enhancement observed for **3**–MAO is intrinsically due to the Zr indenyl-amido bonding features or whether it is a consequence of the formation of the very active species [$ZrInd_2Me^+$], by reaction of **3** with excess of MAO. A more detailed report on the catalytic activities and polymer characterisation will be published elsewhere.

3. Conclusion

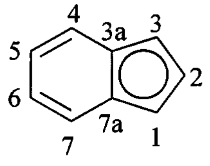
High-yield syntheses of zirconium complexes of general formula [$ZrInd(NMe_2)_xCl_{(3-x)}$] ($x = 0, 1, 2, 3$) are described. Whereas the metathesis of Zr–Cl bonds of [$ZrInd(NMe_2)_2Cl$] with LiMe and LiN(H)^{t}Bu gave the expected methyl and *tert*-butylamido derivatives, the reactions of [$ZrInd(NMe_2)Cl_2$] with LiMe or MeMgBr and of [$ZrInd(NMe_2)_3$] with azetidine led to bis-indenyl complexes. The formation of [$ZrInd_2(NC_3H_6)_2$] is reasoned to be a consequence of the smaller steric bulk of azetidino compared with dimethylamido ligands and emphasises the basic character of the indenyl ligand in zirconium dialkylamido complexes. Similar premises drive the reaction of [$TiInd(NMe_2)_2Cl$] with LiN(H)^{t}Bu, which eliminates indene giving [$Ti(NMe_2)(\mu\text{-}N^tBu)]_2$ quantitatively. Preliminary results on the catalytic activity of [$MInd(NMe_2)Cl_2$] (M = Ti, Zr) as ethylene polymerisation catalysts raise the doubt about the nature of the active species formed when [$ZrInd(NMe_2)_2Cl$] and MAO react. The formation of [$ZrInd_2Me^+$] appears as a sensible possibility.

4. Experimental

All manipulations were carried out under nitrogen, using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried over activated 4 Å molecular sieves and refluxed over sodium-benzophenone (diethyl ether, tetrahydrofuran and toluene) or calcium hydride (dichloromethane, 1,2-dichloroethane and *n*-hexane) under an atmosphere of nitrogen, and collected by distillation. Deuterated solvents were dried with molecular sieves and freeze–pump–thaw degassed prior to use. The NMR samples were prepared in Wilmad 505-PS tubes fitted with a J. Young NMR/5 valve or sealed in vacuum.

Proton- and ^{13}C-NMR spectra were recorded in a Varian Unity 300, at 298 K unless stated otherwise, referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). Assignments were supported by NOE difference spectra and one-bond ^{1}H–^{13}C heteronuclear correlation (HETCOR). Mass spectra were recorded on a Trio 2000, VG micromass quadrupole spectrometer. Elemental analyses were obtained from the Laboratório de Análises do IST (Fisons Instrument 1108).

[$Zr(NMe_2)_3(\mu\text{-}NMe_2)]_2$ and [$TiInd(NMe_2)_2Cl$] were prepared according to published procedures [12,13]. MMAO-4 was purchased from Akzo Chemical Co.



Indenyl label

4.1. Synthesis of [$ZrInd(NMe_2)_3$] (**1**)

Indene (0.13 ml, 1.12 mmol) was slowly added to a suspension of $Zr(NMe_2)_4$ (0.30 g, 1.12 mmol) in toluene

Table 2
Polymerisation of ethylene and propylene with [$MInd(NMe_2)Cl_2$] (M = Ti, **12**; Zr, **3**) activated by MAO ([Al]/[catalyst] = 2000; $P_{absolute}$ = 2 atm; solvent: toluene, 50 ml)

Entry	Catalyst precursor	[catalyst](μM)	Monomer	T (°C)	Time (min)	Yield (g)	Activity [a]
1	**12** (Ti)	83	Ethylene	20	60	0.791	92
2	**12** (Ti)	73	Ethylene	50	60	0.127	17
3	**3** (Zr)	27	Ethylene	20	30	1.994	1429
4	**3** (Zr)	25	Ethylene	50	13	1.435	2563
5	**12** (Ti)	87	Propylene	20	60	0	0
6	**3** (Zr)	25	Propylene	20	120	0.092	18

[a] Activity in grams of polymer per millimole of metal complex per hour and per bar (absolute pressure).

and the mixture was heated at 90 °C overnight under a stream of nitrogen. The orange solution formed was filtered and evaporated to dryness to give **1** as an orange oil in quantitative yield (0.37 g). Electron-impact mass spectrum: *m*/*z* 338 [M$^+$], 294 [M$^+$ − NMe$_2$], 250 [ZrC$_9$H$_7$(NMe$_2$)], 214 [M$^+$ − C$_9$H$_7$], 206 [ZrC$_9$H$_7$], 115 [C$_9$H$_7$], 91 [Zr], 44 [NMe$_2$] and 35 [Cl] with correct isotopic distributions. Anal. Found: C, 52.93; H, 7.14; N, 12.06. Calc. for C$_{15}$H$_{25}$N$_3$Zr: C, 53.21; H, 7.44; N, 12.41%. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.47 (2H, m, $^3J_{\rm H7H6}$ = 6.3 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, H^{4,7}), 6.89 (2H, m, $^3J_{\rm H7H6}$ = 6.3 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, H^{6,5}), 6.41 (1H, t, $^3J_{\rm H2H1}$ = 3.6 Hz, H^2), 6.30 (2H, d, $^3J_{\rm H1H2}$ = 3.6 Hz, H^{1,3}), 2.74 (18H, s, N(CH$_3$)$_2$); ^{13}C{^{1}H} (75.43 MHz), δ 126.3 (C^{3a,7a}), 123.0 (C^{4,7}), 122.9 (C^{5,6}), 117.0 (C^2), 98.2 (C^{1,3}), 44.2 (N(CH$_3$)$_2$).

*4.2. Synthesis of [ZrInd(NMe$_2$)$_2$Cl] (**2**)*

Me$_3$SiCl (0.6 ml, 4.74 mmol) was added to a solution of [ZrInd(NMe$_2$)$_3$] (1.46 g, 4.31 mmol) in 50 ml of toluene. The solution was heated at 45 °C for 18 h and was then filtered and the solvent evaporated to dryness. Complex **2** was obtained as an orange oil in 95% yield (1.35 g). Electron-impact mass spectrum: *m*/*z* 329 [M$^+$ − H], 294 [M$^+$ − Cl], 285 [M$^+$ − NMe$_2$], 250 [M$^+$ − 2NMe$_2$], 223 [M$^+$ − C$_9$H$_7$], 206 [ZrC$_9$H$_7$], 115 [C$_9$H$_7$], 91 [Zr] and 44 [NMe$_2$] with correct isotopic distributions. Anal. Found: C, 47.01; H, 5.66; N, 8.01. Calc. for C$_{13}$H$_{19}$ClN$_2$Zr: C, 47.32; H, 5.80; N, 8.49%. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.49 (2H, m, $^3J_{\rm H7H6}$ = 6.6 Hz, $^4J_{\rm H7H5}$ = 3.3 Hz, H^{4,7}), 6.92 (2H, m, $^3J_{\rm H7H6}$ = 6.6 Hz, $^4J_{\rm H7H5}$ = 3.3 Hz, H^{6,5}), 6.22–6.21 (3H, m, H^{1,3}, H^2), 2.68 (12H, s, N(CH$_3$)$_2$); ^{13}C{^{1}H} (75.43 MHz), δ 126.4 (C^{3a,7a}), 124.4 (C^{4,7}), 123.6 (C^{5,6}), 116.8 (C^2), 100.6 (C^{1,3}), 42.9 (N(CH$_3$)$_2$).

*4.3. Synthesis of [ZrInd(NMe$_2$)Cl$_2$] (**3**)*

Me$_3$SiCl (0.6 ml, 4.74 mmol) and [ZrInd(NMe$_2$)$_3$] (1.46 g, 4.31 mmol) dissolved in 25 ml of toluene were heated at 40 °C for 17 h. The solution was then filtered, concentrated until one-third of its initial volume and cooled to − 20 °C to afford yellow crystals of **3**. Yield: 1.36 g (98%). Electron-impact mass spectrum: *m*/*z* 276 [M$^+$ − NMe$_2$], 241 [ZrC$_9$H$_7$Cl], 206 [ZrC$_9$H$_7$], 205 [M$^+$ − C$_9$H$_7$], 170 [Zr(NMe$_2$)Cl], 161 [ZrCl$_2$], 126 [ZrCl], 115 [C$_9$H$_7$] and 44 [NMe$_2$] with correct isotopic distributions. Anal. Found: C, 40.14; H, 4.40; N, 4.15. Calc. for C$_{11}$H$_{13}$Cl$_2$NZr: C, 41.11; H, 4.08; N, 4.38%. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.36 (2H, m, $^3J_{\rm H7H6}$ = 6.6 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, H^{4,7}), 6.92 (2H, m, $^3J_{\rm H7H6}$ = 6.6 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, H^{6,5}), 6.23 (2H, d, $^3J_{\rm H1H2}$ = 3.0 Hz, H^{1,3}), 6.18 (1H, t, $^3J_{\rm H2H1}$ = 3.0 Hz, H^2), 2.78 (6H, s, N(CH$_3$)); ^{13}C{^{1}H} (75.43 MHz), δ 126.6 (C^{5,6}), 125.6 (C^{3a,7a}), 124.5 (C^{4,7}), 118.4 (C^2), 100.6 (C^{1,3}), 43.8 (N(CH$_3$)$_2$).

*4.4. Synthesis of [ZrIndCl$_3$]$_n$(NMe$_2$SiMe$_3$)$_{0.4}$ (**4**)*

The addition of Me$_3$SiCl (3.04 ml, 23.87 mmol) to a solution of [ZrInd(NMe$_2$)$_3$] (1.87 g, 5.55 mmol) in toluene (25 ml) led to the formation of a yellow solid that was separated by filtration after 22 h of reaction. The solid was repeatedly washed with hexane and dried. Yield: 1.74 g (87%). Electron-impact mass spectrum: *m*/*z* 346 [ZrC$_9$H$_7$Cl$_4^+$], 311 [ZrC$_9$H$_7$Cl$_3^+$], 276 [ZrC$_9$H$_7$Cl$_2^+$], 241 [ZrC$_9$H$_7$Cl$^+$], 117 [NMe$_2$SiMe$_3$], 115 [C$_9$H$_7$], 73 [SiMe$_3$] and 44 [NMe$_2$] with correct isotopic distributions. Anal. Found: C, 36.65; H, 3.66; N, 1.72. Calc. for C$_5$H$_{15}$Cl$_3$Zr(C$_7$H$_{21}$NSi)$_{0.4}$: C, 36.74; H, 3.23; N, 1.38%. NMR (C$_6$D$_6$): ^{1}H (300 MHz), δ 7.49 (2H, m, $^3J_{\rm H7H6}$ = 6.5 Hz, $^4J_{\rm H7H5}$ = 3.3 Hz, H^{4,7} ligand A), 7.37 (2H, m, $^3J_{\rm H7H6}$ = 6.3 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, H^{4,7} ligand B), 7.05 (2H, m, $^3J_{\rm H7H6}$ = 6.5 Hz, $^4J_{\rm H7H5}$ = 3.3 Hz, H^{6,5} ligand A), 6.98 (3H, m, $^3J_{\rm H7H6}$ = 6.3 Hz, $^4J_{\rm H7H5}$ = 3.0 Hz, $^3J_{\rm H2H1}$ = 3.3, H^{6,5} ligand B + H^2 ligand A), 6.83 (1H, t, $^3J_{\rm H2H1}$ = 3.4 Hz, H^2 ligand B), 6.68 (2H, d, $^3J_{\rm H1H2}$ = 3.3 Hz, H^{1,3} ligand A), 6.53 (2H, d, $^3J_{\rm H1H2}$ = 3.34 Hz, H^{1,3} ligand B), 3.2 (6H, s, N(CH$_3$)), 1.53 (9H, s, Si(CH$_3$)$_3$); ^{13}C{^{1}H} (75.43 MHz), δ 128.9–127.2 (C^{5,6} ligand A + ligand B), 126.3 (C^{4,7} ligand A), 126.1 (C^{4,7} ligand B), 125.5 (C^{3a,7a} ligand B), 124.9 (C^2 ligand B), 123.6 (C^{3a,7a} ligand A), 120.9 (C^2 ligand A) 110.9 (C^{1,3} ligand A), 110.4 (C^{1,3} ligand B), 34.4 (N(CH$_3$)$_2$), 3.0 (Si(CH$_3$)$_3$).

*4.5. Synthesis of [ZrIndCl$_3$(dme)] (**5**)*

A toluene solution of [ZrInd(NMe$_2$)$_3$] (0.51 g, 1.50 mmol) and Me$_3$SiCl (0.82 ml, 6.45 mmol) was heated at 45 °C for 4 h. Excess of 1,2-dimethoxyethane (1.56 ml, 15 mmol) was added to the solution, which was kept at that temperature for 12 h. The yellow solution was filtered and cooled to −15 °C. Complex **5** precipitated out in 90% yield (0.54 g). Anal. Found: C, 38.65; H, 4.14. Calc. for C$_{13}$H$_{17}$Cl$_3$O$_2$Zr: C, 38.76; H, 4.25%. NMR (CDCl$_3$): ^{1}H (300 MHz), δ 7.68 (2H, m, $^3J_{\rm H7H6}$ = 6.5 Hz, $^4J_{\rm H7H5}$ = 2.9 Hz, H^{4,7}), 7.33 (2H, m, $^3J_{\rm H7H6}$ = 6.65 Hz, $^4J_{\rm H7H5}$ = 2.9 Hz, H^{6,5}), 6.85 (1H, t, $^3J_{\rm H2H1}$ = 3.3 Hz, H^2), 6.74 (2H, d, $^3J_{\rm H1H2}$ = 3.3 Hz, H^{1,3}), 3.99 (4H, br., (H$_3$COCH_2)$_2$), 3.81 (6H, br., (H_3COCH$_2$)$_2$); ^{13}C{^{1}H} (75.43 MHz), δ 127.5 (C^{5,6}), 125.7 (C^{3a,7a}), 122.4 (C^{4,7}), 116.2 (C^2), 109.4 (C^{1,3}), 73.8 ((H$_3$COCH$_2$)$_2$), 59.2 ((H$_3C$OCH$_2$)$_2$).

*4.6. Synthesis of [ZrInd(NMe$_2$)$_2$Me] (**6**)*

The dropwise addition of a 1.6 M solution of LiMe in diethyl ether (3.31 ml, 5.30 mmol) to a solution of [ZrInd(NMe$_2$)$_2$Cl] (1.75 g, 5.30 mmol) in Et$_2$O led to the immediate formation of a precipitate and the darkening of the solution. The mixture was allowed to react for 15 min and the precipitate was removed by filtration. The solvent was evaporated to dryness and the residue was extracted with hexane, which, after removal in vacuum, gave a dark-yellow oil. Yield: 1.1 g (67%). Electron-impact mass spectrum: *m/z* 294 [$M^+ - Me$], 265 [$M^+ - NMe_2$], 250 [$ZrC_9H_7(NMe_2)$], 194 [$Zr(NMe_2)_2Me$], 179 [$Zr(NMe_2)_2$], 150 [$Zr(NMe_2)_2Me$], 115 [C_9H_7] and 44 [NMe_2] with correct isotopic distributions. Anal. Found: C, 53.93; H, 7.03; N, 8.68. Calc. for $C_{14}H_{22}N_2Zr$: C, 54.32; H, 7.16; N, 9.05%. NMR (C_6D_6): ^1H (300 MHz), δ 7.41 (2H, m, $^3J_{H7H6} = 6.6$ Hz, $^4J_{H7H5} = 3.3$ Hz, $H^{4,7}$), 6.94 (2H, m, $^3J_{H7H6} = 6.6$ Hz, $^4J_{H7H5} = 3.3$ Hz, $H^{6,5}$), 6.23 (1H, t, $^3J_{H2H1} = 3.3$ Hz, H^2), 6.17 (2H, d, $^3J_{H2H1} = 3.3$ Hz, $H^{1,3}$), 2.71 (12H, s, $N(CH_3)_2$), -0.30 (3H, s, CH_3); $^{13}C\{^1H\}$ (75.43 MHz), δ 125.2 ($C^{3a,7a}$), 123.6 ($C^{4,7}$), 123.5 ($C^{5,6}$), 115.2 (C^2), 99.0 ($C^{1,3}$), 41.8 ($N(CH_3)_2$), 25.9 (CH_3).

4.7. Synthesis of {ZrInd(NMe$_2$)$_2$[N(H)^{t}Bu]} (7)

LiN(H)^{t}Bu (0.23 g, 2.88 mmol) in suspension in toluene was added to a solution of [ZrInd(NMe$_2$)$_2$Cl] (0.95 g, 2.88 mmol) in toluene at -50 °C. The mixture was allowed to warm to room temperature and stirred for ca. 14 h. The precipitate was filtered off and the solvent was evaporated to dryness. Extraction in hexane gave an orange solution that upon evaporation of the solvent led to **7** as an oil. Yield: 0.88 g (83%). Electron-impact mass spectrum: *m/z* 365 [$M^+ - H$], 350 [$M^+ - Me - H$], 322 [$ZrC_9H_7(NMe_2)(NBu)$], 277 [$ZrC_9H_7(NBu)$], 249 [$Zr(NMe_2)_2(NBu) - H$], 234 [$ZrC_9H_7N_2$], 220 [ZrC_9H_7N], 205 [ZrC_9H_6] and 115 [C_9H_7]. Anal. Found: C, 55.39; H, 7.70; N, 11.33. Calc. for $C_{17}H_{29}N_3Zr$: C, 55.69; H, 7.97; N, 11.46%. IR(KBr), cm^{-1}: 3388 (ν_{N-H}). NMR (C_6D_6): ^1H (300 MHz), δ 7.39 (2H, m, $^3J_{H7H6} = 6.4$ Hz, $^4J_{H7H5} = 2.8$ Hz, $H^{4,7}$), 6.94 (2H, m, $^3J_{H7H6} = 6.4$ Hz, $^4J_{H7H5} = 2.8$ Hz, $H^{6,5}$), 6.39 (1H, t, $^3J_{H2H1} = 3.3$ Hz, H^2), 6.20 (2H, d, $^3J_{H1H2} = 3.3$ Hz, $H^{1,3}$), 3.44 (1H, br., NH), 2.88 (12H, s, $N(CH_3)$), 1.06 (9H, s, $C(CH_3)_3$); $^{13}C\{^1H\}$ (75.43 MHz), δ 126.5 ($C^{3a,7a}$), 123.5 ($C^{4,7}$), 122.8 ($C^{5,6}$), 115.4 (C^2), 97.8 ($C^{1,3}$), 55.4 ($\mathit{C}(CH_3)_3$), 45.2 ($N(CH_3)_2$), 34.2 ($C(\mathit{C}H_3)_3$).

4.8. {TiInd(NMe$_2$)$_2$[N(H)^{t}Bu]} (8a,b)

LiN(H)^{t}Bu (0.02 g, 0.30 mmol) was transferred to a 5 mm NMR tube equipped with a J-Young valve and a solution of [TiInd(NMe$_2$)$_2$Cl] (0.9 g, 0.30 mmol) in 0.5 ml of toluene-d^8, cooled at -40 °C, was added. The tube was sealed in vacuum and then the temperature was allowed to rise slowly to room temperature. NMR spectra of the mixture were ran periodically. Complexes **8a** and **8b** were detected after 4 h and the reaction was allowed to proceed until completion. After 10 days, [Ti(NMe$_2$)$_2$(μ-N^{t}Bu)]$_2$, **9**, and indene were the only products present. NMR (toluene-d^8, -20 °C): ^1H (300 MHz), δ 7.51, 7.30 (4H, m, $^3J_{H7H6} = 6.3$ Hz, $^4J_{H7H5} = 3.0$ Hz, $H^{4,7}$ 8a, 8b), 6.95 (4H, m, $^3J_{H7H6} = 6.3$ Hz, $^4J_{H7H5} = 3.0$ Hz, $H^{6,5}$ 8a + 8b), 6.52, 6.47 (2H, br., N(H) 8a, 8b), 6.29, 6.24 (2H, t, $^3J_{H2H1} = 3.2$ Hz, H^2 8a, 8b), 6.08 (4H, d, $^3J_{H1H2} = 3.2$ Hz, $H^{1,3}$ 8a + 8b), 3.13 (6H, s, $N(CH_3)$ 8a), 3.09 (12H, s, $N(CH_3)$ 8b), 2.95 (6H, s, $N(CH_3)$ 8a), 1.40–1.10 (18H, s, br., $C(CH_3)_3$ 8a + 8b); $^{13}C\{^1H\}$ (75.43 MHz), δ 126.5, 125.8 ($C^{3a,7a}$ 8a, 8b), 123.8, 123.3 ($C^{4,7}$ 8a, 8b), 122.8 ($C^{5,6}$ 8a + 8b), 117.3, 113.9 (C^2 8a, 8b), 98.9, 98.4 ($C^{1,3}$ 8a, 8b), 50.8 ($N(CH_3)_2$ 8a), 49.0 ($N(CH_3)_2$ 8b), 48.0 ($N(CH_3)_2$ 8a), 46.2, 44.9 ($\mathit{C}(CH_3)_3$ 8a, 8b), 35.3, 32.5 ($C(\mathit{C}H_3)_3$ 8a, 8b).

4.9. Synthesis of [Ti(NMe$_2$)(μ-N^{t}Bu)]$_2$ (9)

A suspension of LiN(H)^{t}Bu (0.13 g, 1.64 mmol) in toluene (15 ml) was added to a solution of [TiInd(NMe$_2$)$_2$Cl] (0.47 g, 1.64 mmol) in 20 ml of the same solvent cooled at -55 °C. The temperature was allowed to increase until room temperature and then was heated at 60 °C for 4 h. The solvent was evaporated to dryness and the residue was extracted in hexane. Complex **9** was isolated in quantitative yield from hexane by concentrating and cooling the solution. Anal. Found: C, 46.02; H, 9.98; N, 19.99. Calc. for $C_{16}H_{42}N_6Ti_2$: C, 46.39; H, 10.22; N, 20.29%. NMR (C_6D_6): ^1H (300 MHz), δ 3.39 (12H, s, NMe_2), 1.20 (9H, s, ^{t}Bu).

4.10. Synthesis of [ZrInd$_2$Me$_2$] (10)

A 1.6 M solution of LiMe in diethyl ether (2.79 ml, 4.41 mmol) was slowly added to a solution of [ZrInd(NMe$_2$)Cl$_2$] (0.63 g, 1.96 mmol) in 20 ml of toluene, and led to the immediate formation of a precipitate. The mixture was allowed to react for 1.5 h and the volatiles were then evaporated to dryness. The resulting solid was extracted in hexane and filtered. Evaporation of the solvent led to the formation of [Zr(Ind)$_2$Me$_2$] in 25% yield (0.17 g). Electron-impact mass spectrum: *m/z* 335 [$M^+ - Me - H$], 320 [$M^+ - 2Me - H$], 205 [$ZrC_9H_7 - H$], 115 [C_9H_7]. Anal. Found: C, 67.83; H, 5.75. Calc. for $C_{20}H_{20}Zr$: C, 68.32; H, 5.73%. NMR (C_6D_6): ^1H (300 MHz), δ 7.21 (2H, m, $^3J_{H7H6} = 6.4$ Hz,

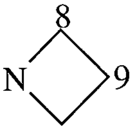


Table 3
Crystal data and structure refinement for **11**

Empirical formula	$C_{24}H_{26}N_2Zr$
Formula weight	433.69
Temperature (K)	293(2)
Wavelength (Å)	0.71 069
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.3806(7)
b (Å)	12.8118(12)
c (Å)	16.5192(15)
α (°)	90
β (°)	100.724(7)
γ (°)	90
Volume (Å^3)	1950.6(3)
Z	4
Density (calc.) (Mg m^{-3})	1.477
Absorption coefficient (mm^{-1})	0.574
F(000)	896
Crystal size (mm^3)	$0.45 \times 0.35 \times 0.23$
θ range for data collection (°)	2.02 to 25.99
Index ranges	$-1 \leq h \leq 11$; $-1 \leq k \leq 15$; $-20 \leq l \leq 20$
Reflections collected	4980
Independent reflections	3825 ($R_{int} = 0.0135$)
Reflections observed ($>2\sigma$)	3257
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3825/0/244
Goodness-of-fit on F^2	0.878
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0931$
R indices (all data)	$R_1 = 0.0412$, $wR_2 = 0.1080$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.352 and -0.974

${}^4J_{H7H5} = 3.0$ Hz, $H^{4,7}$), 6.90 (2H, m, ${}^3J_{H7H6} = 6.4$ Hz, ${}^4J_{H7H5} = 3.0$ Hz, $H^{6,5}$), 5.79 (2H, d, ${}^3J_{H2H1} = 3.3$ Hz, $H^{1,3}$), 5.62 (1H, t, ${}^3J_{H2H1} = 3.3$ Hz, H^2), -0.78 (6H, s, CH_3); ${}^{13}C\{{}^1H\}$ (75.43 MHz), δ 125.0 ($C^{3a,7a}$), 124.8 ($C^{5,6}$), 124.1 ($C^{4,7}$), 114.8 (C^2), 99.8 ($C^{1,3}$), 35.6 (CH_3).

*4.11. Synthesis of [ZrInd$_2$(NC$_3$H$_6$)$_2$] (**11**)*

Azetidine, NC_3H_6 (0.40 ml, 5.90 mmol), was added dropwise, at room temperature, to a solution of [ZrInd(NMe$_2$)$_3$] (0.62 g, 1.84 mmol) in 20 ml of toluene. The colour of the solution darkened immediately. The reaction was stirred for 14 h and the volatiles were evaporated. The bright-red residue was washed with hexane and extracted in benzene. Yellow crystals of **11** formed upon slow diffusion of hexane in the benzene solution. Yield: 25% (0.20 g). Anal. Found: C, 66.38; H, 6.16; N, 6.43. Calc. for $C_{24}H_{26}N_2Zr$: C, 66.46; H, 6.04; N, 6.46%. NMR (C_6D_6): ${}^1H$ (300 MHz), δ 7.55 (4H, m, ${}^3J_{H7H6} = 6.3$ Hz, ${}^4J_{H7H5} = 3.0$ Hz, $H^{4,7}$), 6.99 (4H, m, ${}^3J_{H7H6} = 6.3$ Hz, ${}^4J_{H7H5} = 3.0$ Hz, $H^{6,5}$), 5.94 (2H, t, ${}^3J_{H2H1} = 3.4$ Hz, H^2), 5.61 (4H, d, ${}^3J_{H2H1} = 3.4$ Hz, $H^{1,3}$), 4.03 (8H, t, ${}^3J_{H8H9} = 7.2$ Hz, H^8), 4.03 (4H, t, ${}^3J_{H8H9} = 7.2$ Hz, H^9); ${}^{13}C\{{}^1H\}$ (75.43 MHz), δ 126.1 ($C^{3a,7a}$), 123.5 ($C^{4,7}$), 122.8 ($C^{5,6}$), 119.2 (C^2), 97.7 ($C^{1,3}$), 59.4 (C^8), 23.3 (C^9).

*4.12. Ethylene and propylene polymerisation tests with **2**–, **3**–, **12**– or **13**–MAO systems*

All polymerisations were performed in thermostatic and magnetically stirred 250 ml crimp-top bottles equipped with Neoprene rubber septa. The typical procedure for a polymerisation test is as follows. The solvent (toluene, freshly distilled over Na–K alloy) was transferred to the previously degassed and heat-dried bottles, thermostatically controlled to the reaction temperature and allowed to equilibrate with the gaseous monomer at 2 atm (absolute pressure). A solution of MAO in toluene was then added by means of a syringe and the system was again allowed to equilibrate. A toluene solution (1 ml) containing the required amount of the catalyst precursor was transferred into the reaction vessel with a canula and the pressure maintained constant at 2 atm throughout the polymerisation reaction. After a typical reaction time the monomer feed was stopped, the excess of ethylene was vented and the contents of the reactor treated overnight with 200 ml of a 2% HCl solution in methanol. The polymers were filtered, further washed with pure methanol and dried under reduced pressure in a vacuum-oven for 24 h at 50 °C.

4.13. X-ray crystallography

Crystal data for compound **11** were collected in a MACH3 (Enraf Nonius) diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.710\,69$ Å) in the ω–2θ scan mode. Unit cell dimensions were determined from the setting angles of 25 reflections ($18 < \theta < 20°$). Data were corrected for Lorentz polarisation effects and for absorption, using ψ scans and MOLEN software [44]. The molecular and crystal structure was solved by a combination of direct methods and Fourier difference synthesis. Refinement was based on F^2. All non-hydrogen atoms were allowed to refine with anisotropic thermal parameters with no restraints. Hydrogen atoms were inserted in idealised positions, riding in the parent carbon atom. All remaining crystal data and refinement parameters are presented in Table 3. Calculations were done using SHELXS-97 [45] and SHELXL-97 [46] and molecular drawing was done with ORTEP III [47]. Experimental details, atomic fractional coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 157349. Copies of data can be obtained free of charge upon application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

[2] S. Tinkler, R.J. Deeth, D.J. Duncalf, A. McCamley, Chem. Commun. (1996) 2623.

[3] A.D. Horton, J. de With, Chem. Commun. (1996) 1375.

[4] E.T.X. Chen, T.J. Marks, Chem. Rev. 100 (2001) 391.

[5] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[6] J.M. Canich, G.C. Hlatky, H.W. Turner, WO 92/0333, 1992.

[7] J.C. Stevens, F.J. Timmers, R.D. Wilson, G.F. Schmidt, P.N. Nicklas, R.K. Rosen, G.W. Knight, Eur. Patent Appl. EP 416815-A2, 1991.

[8] J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10 008.

[9] J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, Macromolecules 29 (1996) 5241.

[10] J.M. Canich, H.W. Turner, WO 92/121, 1992.

[11] V.C. Gibson, B.S. Kimberly, A.J.P. White, D.J. Williams, P. Howard, Chem. Commun. (1998) 313.

[12] A.M. Martins, J.R. Ascenso, C.G. Azevedo, M.J. Calhorda, A.R. Dias, S.S. Rodrigues, L. Toupet, P. Leonardis, L.F. Veiros, J. Chem. Soc. Dalton Trans. 23 (2000) 4332.

[13] M.H. Chisholm, C.E. Hammond, J.C. Huffman, Polyhedron 7 (1988) 2515.

[14] G. Chandra, M.F. Lappert, J. Chem. Soc. A (1968) 1940.

[15] J.N. Christopher, G.M. Diamond, R.F. Jordan, Organometallics 15 (1996) 4038.

[16] G.M. Diamond, R.F. Jordan, Organometallics 15 (1996) 4030.

[17] D.W. Carpenetti, L. Kloppenburg, J. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[18] S.L. Shaw, R.J. Morris, J.C. Huffman, J. Organomet. Chem. 489 (1995) C4.

[19] A. Vogel, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 527 (1997) 297.

[20] A. Martín, M. Mena, C. Yélamos, R. Serrano, J. Organomet. Chem. 467 (1994) 79.

[21] A. Martín, M. Mena, F. Palacios, J. Organomet. Chem. 480 (1994) C10.

[22] Y. Bai, H.W. Roesky, M. Noltemeyer, M. Witt, Chem. Ber. 125 (1992) 825.

[23] W.A. Nugent, R.L. Harlow, Inorg. Chem. 18 (1979) 2030.

[24] D.M. Giolando, K. Kirschbaum, L.J. Graves, U. Bolle, Inorg. Chem. 31 (1992) 3887.

[25] C.T. Jekel-Vroegop, J.H. Teuben, J. Organomet. Chem. 286 (1985) 309.

[26] W.A. Nugent, B.L. Haymore, Coord. Chem. Rev. 31 (2001) 123.

[27] E. Samuel, M.D. Rausch, J. Am. Chem. Soc. 95 (1973) 6263.

[28] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.

[29] R.V. Bynum, H.-M. Zhang, W.E. Hunter, J.L. Atwood, Can. J. Chem. 64 (1986) 1304.

[30] H.J.G. Luttikhedde, R.P. Leino, C.-E. Wilén, J.H. Näsman, Organometallics 15 (1996) 3092.

[31] R. Wartchow, S. Doye, J. Organomet. Chem. 566 (1998) 287.

[32] M.D. Rausch, K.J. Moriatty, J.L. Atwood, W.E. Hunter, E. Samuel, J. Organomet. Chem. 327 (1987) 39.

[33] S.A. Westcott, A.K. Kakkar, G. Stringer, N.J. Taylor, T.B. Marder, J. Organomet. Chem. 394 (1990) 777.

[34] P.-J. Sinneme, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 598 (2000) 179.

[35] T. Eberle, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. (1998) 237.

[36] J. Okuda, T. Eberle, T.P. Spaniol, V. Piquet-Fauré, J. Organomet. Chem. 591 (1999) 127.

[37] W.A. Nugent, D.W. Overnall, S.J. Holmes, Organometallics 2 (1983) 161.

[38] Y.-X. Chen, T.J. Marks, Organometallics 16 (1997) 3649.

[39] P.-J. Sinneme, K. Liekelema, O.K.B. Staal, B. Hessen, J.H. Teuben, J. Mol. Catal. A 128 (1998) 143.

[40] L. Duda, G. Erker, R. Fröhlich, F. Zippel, Eur. J. Inorg. Chem. (1998) 1153.

[41] H. Juvaste, T.T. Pakkanen, Organometallics 19 (2001) 1729.

[42] P.T. Gomes, M.L.H. Green, A.M. Martins, J. Organomet. Chem. 551 (1998) 133.

[43] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.

[44] C.K. Fair, MOLEN. An interactive intelligent system for crystal structure analysis, Enraf Nonius, 1990.

[45] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[46] G.M. Sheldrick, SHELXL-97, a computer program for refinement of crystal structures, University of Göttingen, 1997.

[47] M.N. Burnett, C.K. Johnson, ORTEP III: Oak Ridge thermal ellipsoid plot program for crystal structure illustration, Oak Ridge National Laboratory Report ORNL-6895, 1996.