Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 665 (2003) 135–149
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Monocyclopentadienyl phenoxy-imine and phenoxy-amine complexes of titanium and zirconium and their application as catalysts for 1-alkene polymerisation

Robyn K.J. Bott, David L. Hughes, Mark Schormann, Manfred Bochmann *, Simon J. Lancaster *

Wolfson Materials and Catalysis Centre, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Received 9 September 2002; received in revised form 31 October 2002; accepted 31 October 2002

Abstract

Deprotonation of the phenol-imines 2-Bu^t-6-(RNCH)C_6H_3OH (R = 2,4,6-$Me_3C_6H_2$ (**1a**), C_6F_5 (**1b**), C_6H_{11} (**1c**) and phenol-amines 2,4-Bu^t_2-6-(R′NCH_2)C_6H_2OH (R′ = C_4H_8 (**1d**), C_5H_{10} (**1e**)) with *n*-BuLi gives the corresponding lithium phenoxides. The reaction with MCl_4 in THF solution leads to the bis(ligand) complexes {2-Bu^t-6-(RNCH)C_6H_3O}$_2MCl_2$ and {2,4-Bu^t_2-6-(R′NCH_2)C_6H_2O}$_2MCl_2$ (M = Ti: **2a**, **2d**, **2e**, Zr: **3a**, **3d** and **3e**). The cyclopentadienyl phenoxy-imine and -amine complexes Cp{2-Bu^t-6-(RNCH)C_6H_3O}MCl_2 and Cp{2,4-Bu^t_2-6-(R′NCH_2)C_6H_2O}MCl_2 (M = Ti: **4a**–**4e**, Zr: **5a**–**5e**) were prepared similarly through reaction with $CpMCl_3$. The crystal and molecular structures of **2a**, **3a**, **4a** and **4e** have been determined. **2a** and **3a** are isostructural and exhibit a distorted octahedral geometry. **4a** has a distorted square-pyramidal structure whereas **4e** is essentially tetrahedral and the nitrogen does not coordinate. All new complexes are active for the polymerisation of ethene when activated with methyaluminoxane. **4b**, **5a**, **5d** and **5e** are active for the copolymerisation of ethene and 1-hexene and the oligomerisation of 1-hexene.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Zirconium; Alkene-polymerisation; Catalysis; Cyclopentadienyl; Phenoxy-imine

1. Introduction

Research into metallocene catalysts has resulted in a good understanding of the mechanism of polymerisation by soluble Ziegler–Natta catalysts. The minimum requirement for a catalyst precursor has been established as an unreactive ancillary ligand system that provides two-coordination sites which can be activated to provide a metal alkyl *cis* to a vacant coordination site for monomer binding [1]. The quest for alternatives to the metallocene catalysts that can produce polymers with novel properties has been one of the major goals of transition metal coordination chemistry over the last decade [2].

A number of groups have explored the use of catalysts with one cyclopentadienyl and a second, bidentate, monoanionic ligand. Amongst the first examples were the cyclopentadienyl benzamidinate complexes (Plate 1, Structure **I**) [3] [4]. More recently Sita has explored the use of unsymmetrically substituted acetamidinate ligands derived from insertion of a carbodiimide into the metal methyl bond of Cp^RMMe_3 (M = Ti, Zr) to produce chiral metal complexes that are active for the living stereoselective polymerisation of 1-alkenes (Structure **II**) [5–9].

An important example of cyclopentadienyl-free N–O chelates are the bis(phenoxy-imine) complexes (Structure **III**), independently developed by Fujita and Coates [10–18]. The activity of these catalysts is highly dependent on the nature of the substituents in the *ortho*-position on the phenoxy ring and on the imine nitrogen [11–18]. We expected that the combination of a cyclopentadienyl and a phenoxy-imine or -amine ligand with a Group 4 metal would lead to a novel series of polymerisation catalysts [19,20]. More significantly,

* Corresponding authors
E-mail address: s.lancaster@uea.ac.uk (S.J. Lancaster).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)02106-X

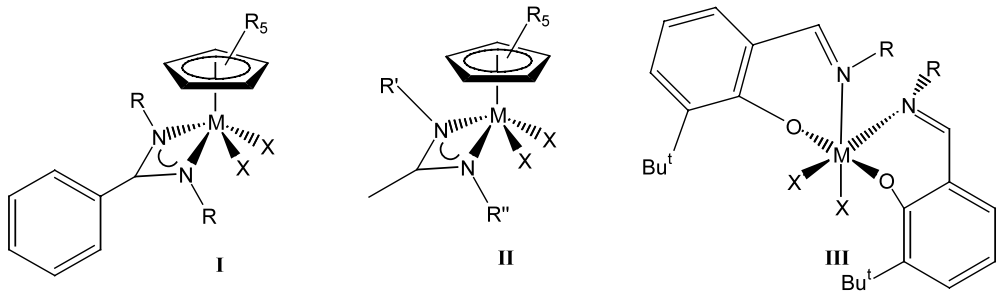


Plate 1.

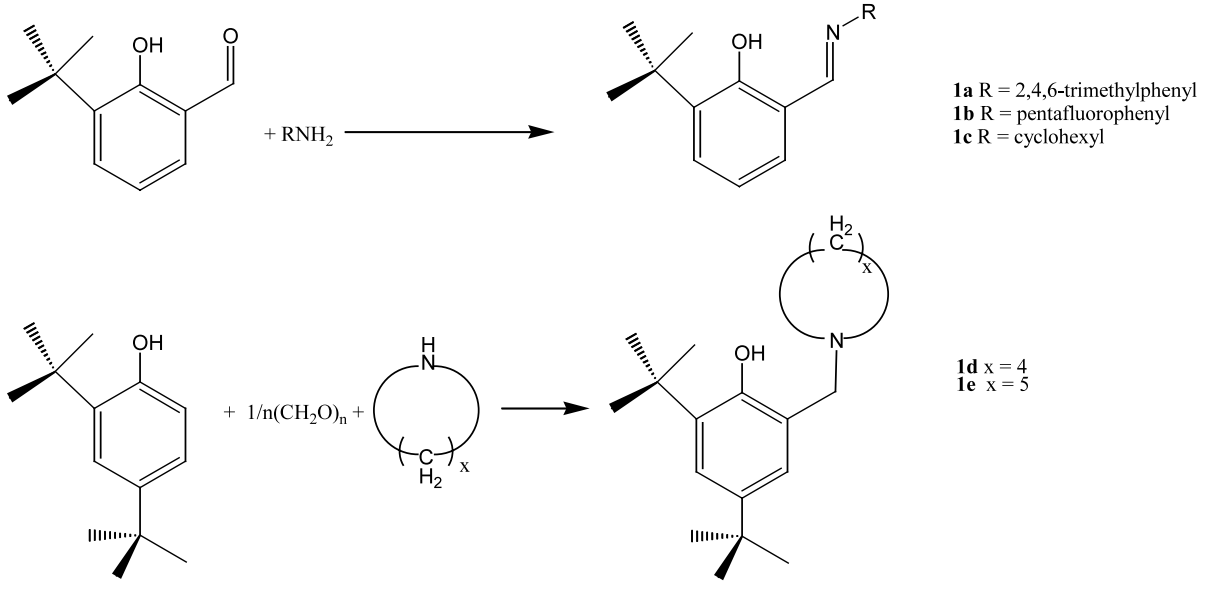
complexes of this type will by necessity be chiral-at-metal and have potential for the stereoselective polymerisation of monomers such as 1-hexene. We reasoned that the much larger bite angle of the phenoxy-imine or -amine ligand might lead to a higher barrier to racemisation and hence greater configurational stability [21,22]. Here we report the synthesis and catalytic activity of a number of novel titanium and zirconium complexes with cyclopentadienyl, phenoxy-imine and closely related phenoxy-amine ligands.

2. Results and discussion

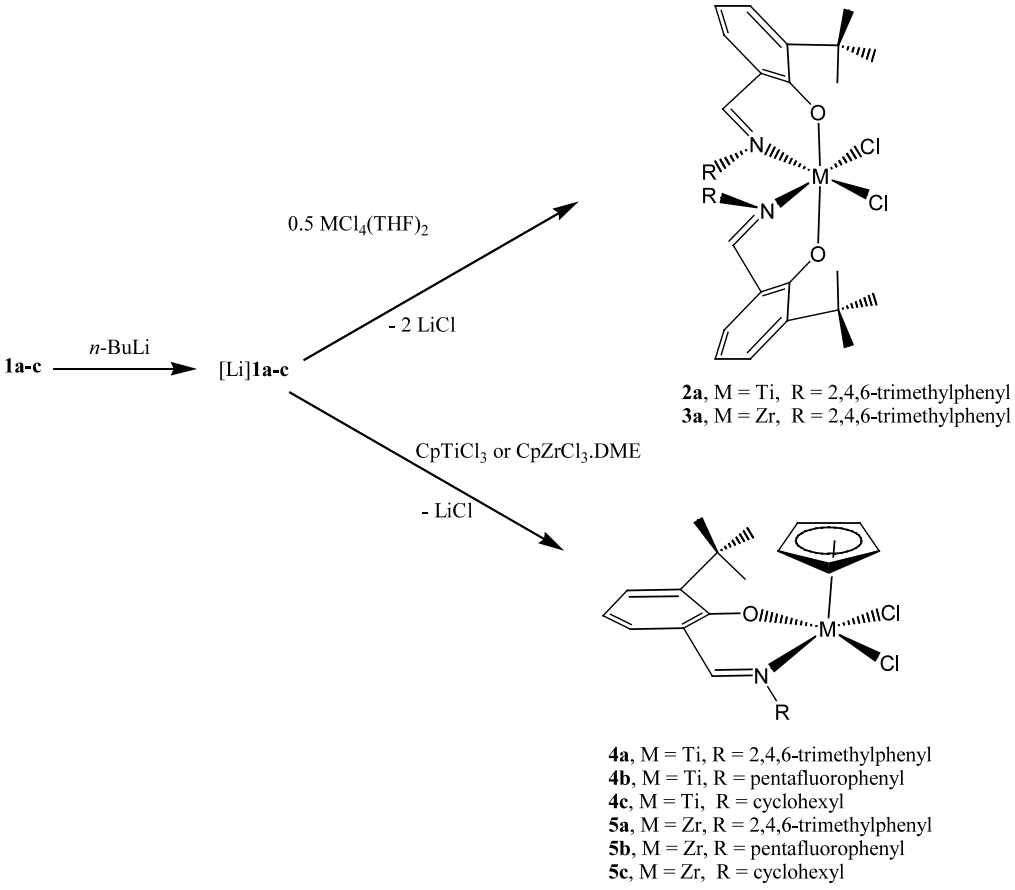
Following a modified literature procedure the phenol-imines **1a**–**c** are readily prepared through the reaction of 3-*tert*-butylsalicylaldehyde with 2,4,6-trimethylaniline, pentafluoroaniline or cyclohexylamine, respectively (Scheme 1) [12]. The phenol-amines **1d** and **1e** were prepared in a very straightforward one-pot procedure by reacting 2,4-di-*tert*-butylphenol, aqueous formaldehyde and the cyclic secondary amines pyrrolidine and piperidine. The products were easily purified by crystallisation from the reaction mixture.

The reaction of corresponding lithium imino- (Scheme 2) and aminophenoxides (Scheme 3) with $MCl_4(THF)_2$ in THF solution overnight produced the bis(ligand) complexes **2a**, **2d**, **2e**, (M = Ti) **3a**, **3d**, and **3e** (M = Zr) [23]. The metal complexes were separated from the LiCl by-product by extraction with dichloromethane. Analytically pure samples were obtained by layering concentrated dichloromethane solutions with light petroleum and cooling. The titanium compounds were obtained as dark red to brown and the zirconium compounds as beige to orange crystalline solids or powders in 40–60% yield. The essentially identical structures of complexes **2a** and **3a** have been confirmed by X-ray crystallography.

Following a similar procedure to that employed for the bis(ligand) complexes the monocyclopentadienyl phenoxy-imine or phenoxy-amine complexes **4a**–**e** (M = Ti) and **5a**–**e** (M = Zr) were prepared by reacting the respective lithium phenoxides with one equivalent of $CpTiCl_3$ or $CpZrCl_3 \cdot DME$ (DME = 1,2-dimethoxyethane) respectively (Scheme 2 and Table 3). The



Scheme 1.



Scheme 2.

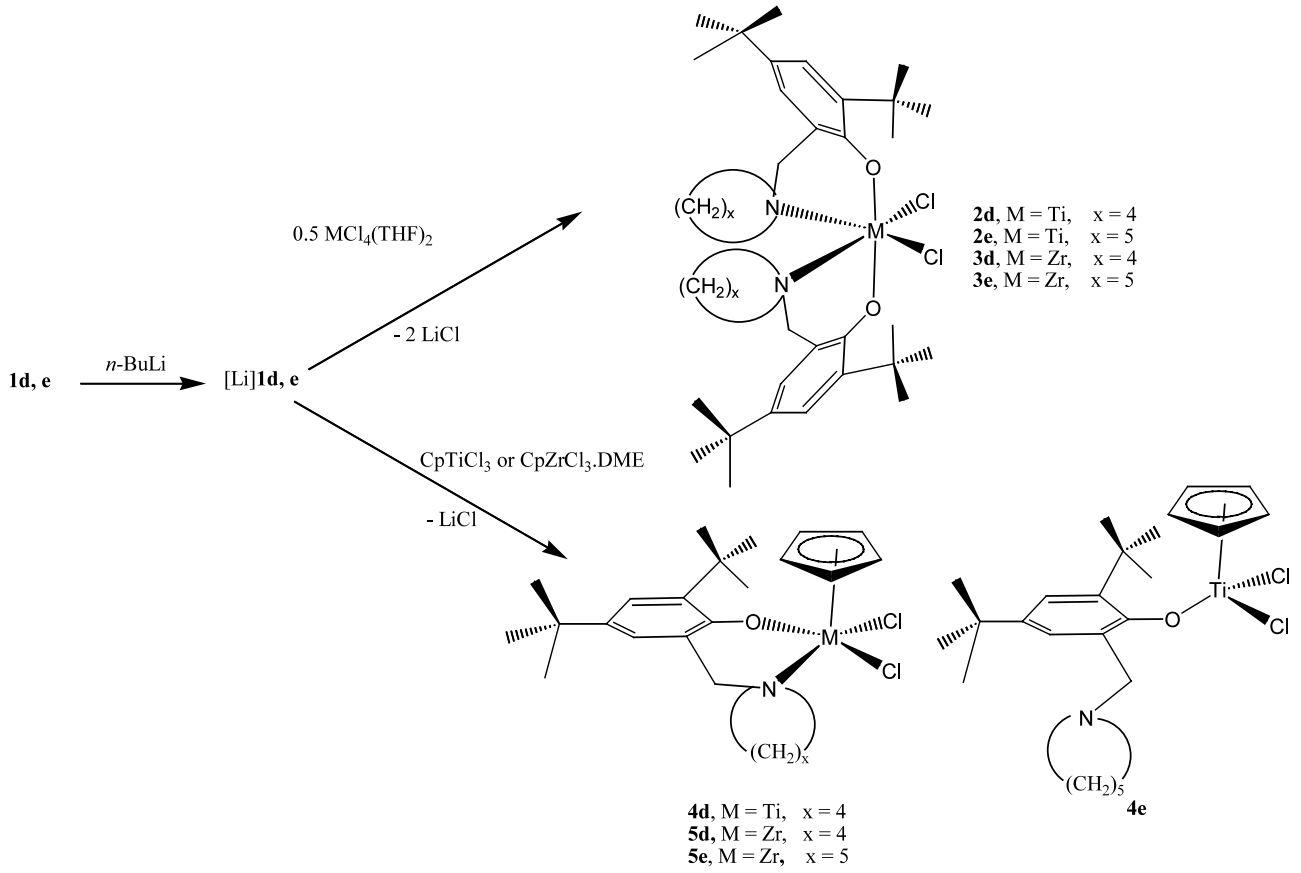
compounds were obtained as red (titanium) or beige to brown (zirconium) crystalline solids or powders in variable yield.

Integration of the ^{1}H-NMR spectra of complexes **4a**–**e** and **5a**–**e** confirms a 1:1 ratio of cyclopentadienyl to phenoxy-imine or phenoxy-amine ligand [24]. **5a** and **5b** retain one equivalent of THF even after extraction and crystallisation from dichloromethane. The ^{1}H-NMR resonances for the THF on dissolving **5b** in C_6D_6 are observed at δ 3.90 and 1.33 versus 3.56 and 1.41 for free THF in C_6D_6. Addition of further THF to a solution of **5b** gives only one set of THF resonances shifted towards free THF, suggesting a rapid exchange of free and coordinated THF on the NMR time scale. Assignment of the geometry of complexes **5a** and **5b** will require a structural determination.

The crystal data for complexes **2a**, **3a**, **4a** and **4e** are collected in Table 1. Selected bond lengths and angles are given in Tables 2–4. The titanium atom in complex **2a** (Fig. 1) has a distorted octahedral coordination with the same arrangement of *trans* oxygen atoms (O–Ti–O = 162.15(5)°) and *cis* chloride atoms (Cl–Ti–Cl = 90.24(2)°) as that previously observed for bis(phenoxy-imine)titanium dichlorides [13,15,25]. The angles appear to be governed by steric repulsion between the *ortho*-substituents on the imine mesityl substituent and the *tert*-butyl group on the phenoxide. Therefore, the structure of complex **2a** more closely resembles {2-Bu^t-6-(C_6F_5NCH)C_6H_3O}$_2$TiCl$_2$ (O–Ti–O = 163.61°, Cl–Ti–Cl = 96.42°) than the simple phenyl compound {2-Bu^t-6-(C_6H_5NCH)C_6H_3O}$_2$TiCl$_2$ (O–Ti–O = 171.6°, Cl–Ti–Cl = 103.1°) [15], Table 5.

The zirconium analogue, **3a** (Table 2), is isostructural to **2a** (Fig. 1) with similarly *trans* oxygen atoms (O–Zr–O = 157.80(5)°) and *cis* chloride atoms (Cl–Zr–Cl = 90.63(2)°). The angles differ significantly from the less bulky phenyl analogue (O–Zr–O = 165.5(1)°, Cl–Zr–Cl = 100.38(5)°) [12]. Again this is likely to be due to significantly increased steric repulsion between the *ortho*-substituents on the imine mesityl substituent and the *tert*-butyl group on the phenoxide.

For the cyclopentadienyl phenoxy-imine titanium dichloride **4a** the asymmetric unit consists of two virtually identical molecules (Fig. 2 and Table 3). In each, the Ti atom is five-coordinate with the Cp ligand in the apical site of a distorted square-pyramid. The *N*,*O*-chelating ligand forms a plane which includes the phenoxide ring, the –C=N group and two of the atoms of the *tert*-butyl group, C(61a/b) and C(64a/b); the other two methyl groups are either side of the plane. The plane



Scheme 3.

of the mesityl group is rotated almost perpendicular to the phenoxide ring, with angles between their normals of 76.18(14) and 76.05(13)° in the two molecules. The Cp ring is almost parallel with the phenoxide ring in each molecule. The Ti–Cp distance at 2.053 Å is typical for Ti(IV) Cp complexes [26]. In contrast to zirconium there are relatively few crystallographically characterised examples of $Cp(L)TiX_2$, where L is a monoanionic bidentate ligand. Two benzamidinate complexes $(C_5Me_5)\{(Me_3Si)NC(4\text{-}C_6H_4OMe)N(SiMe_3)\}TiF_2$ [27] and $Cp\{CPh(NSiMe_3)_2\}TiMe_2$ [26] have been described. In the latter complex the small Me–Ti–Me angle (84.41(7)°) was ascribed to the considerable steric bulk of the benzamidinate ligand. In **4a** the Cl–Ti–Cl angles of 87.00(4) and 87.07(4)° indicate slightly less steric congestion in the plane of the four basal ligands.

The most striking structural feature of complex **4e** (Fig. 3 and Table 4) is the pseudo tetrahedral geometry about the metal atom; the phenoxy-amine ligand is bound via the oxygen (Ti–O = 1.7932(11) Å) but the amine function is not coordinated (Ti(1)–N(1) = 4.062 Å). **4e** therefore, closely resembles the structure of other cyclopentadienyl phenoxide complexes with bulky *ortho*-substituents rather than the five-coordinate phenoxy-imine complex **4a**. For example $Cp(2\text{-Ph-}4,6\text{-}Bu^t_2C_6H_2O)TiCl_2$ has a Ti–O distance of 1.785(2) Å, Ti–Cp = 2.022(4) Å (**4e**: Ti–Cp = 2.020 Å) and Cl–Ti–Cl = 99° (**4e**: Cl–Ti–Cl = 101.26(3)°) [28].

2.1. Bonding of the phenoxy-amine ligands

The crystallographic observation that the phenoxy-amine ligand in titanium complex **4e** binds only in monodentate fashion poses the question whether the pyrrolidine and piperidine groups are bound to the metal in any of the complexes prepared. Unfortunately **4e** is the only example with these ligands to give X-ray quality crystals. It would have been particularly helpful to characterise structurally a zirconium complex where the greater size of the central metal favours higher coordination numbers.

Circumstantial evidence for the bidentate coordination of the phenoxy-amine ligand in **5d** and **5e** comes from a comparison with complex **5b**. As discussed above, **5b** not only features a bidentate phenoxy-imine ligand but also a THF molecule bound to a sixth-coordination site. Unlike **5b**, **5d** and **5e** do not retain a THF molecule, suggesting steric saturation resulting from bidentate coordination of the bulky phenoxy-amine ligands.

Many of the metal complexes **2d**–**5d** **2e**, **3e** and **5e** exhibit complex ^1H signals for the diastereotopic

Table 1
Crystallographic data for **2a**, **3a**, **4a** and **4e**

Parameters	**2a**	**3a**	**4a**	**4e**
Empirical formula	$C_{40}H_{48}Cl_2N_2O_2Ti$	$C_{40}H_{48}Cl_2N_2O_2Zr$	$C_{25}H_{29}Cl_2NOTi$, CH_2Cl_2	$C_{25}H_{37}Cl_2NOTi$
Formula weight	707.6	750.9	563.2	486.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	*Aa* (equivalent to no. 9)	$P2_1/c$
Unit cell dimensions				
a (Å)	13.134(3)	13.208(3)	15.734(1)	6.5860(13)
b (Å)	16.878(3)	17.102(3)	14.903(2)	20.344(4)
c (Å)	17.003(3)	17.023(3)	23.180(2)	19.520(4)
β (°)	103.52(3)	103.22(3)	90.65(1)	96.95(3)
Volume (Å^3)	3664.7(13)	3743.3(13)	5435.0(9)	2596.2(9)
Z	4	4	8	4
D_{calc} (mg m^{-3})	1.283	1.332	1.377	1.244
Absorption coefficient (mm^{-1})	0.416	0.472	0.728	0.551
$F(000)$	1496	1568	2336	1032
Crystal size (mm)	0.4 × 0.3 × 0.3	0.5 × 0.2 × 0.2	0.55 × 0.25 × 0.15	0.5 × 0.3 × 0.2
θ Range for data collection (°)	1.7–25.4	2.0–25.4	2.1–25.3	2.3–25.4
Range of indices	$-15 < h < 15$, $-20 < k < 20$, $-20 < l < 20$	$-15 < h < 15$, $-20 < k < 20$, $-20 < l < 20$	$-18 < h < 18$, $-17 < k < 17$, $-27 < l < 27$	$-7 < h < 7$, $-24 < k < 24$, $-23 < l < 23$
Reflections collected	12 471	12 463	32 924	8973
Independent reflections	6706 ($R_{int} = 0.023$)	6525 ($R_{int} = 0.031$)	9480 ($R_{int} = 0.028$)	4680 ($R_{int} = 0.020$)
Data/restraints/parameters	6706/0/430	6525/0/430	9480/2/628	4680/0/271
Goodness-of-fit on F^2	1.092	1.064	1.026	1.081
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.031$, $wR_2 = 0.089$	$R_1 = 0.027$, $wR_2 = 0.073$	$R_1 = 0.045$, $wR_2 = 0.120$	$R_1 = 0.032$, $wR_2 = 0.088$
R indices (all data)	$R_1 = 0.037$, $wR_2 = 0.092$	$R_1 = 0.031$, $wR_2 = 0.075$	$R_1 = 0.051$, $wR_2 = 0.124$	$R_1 = 0.039$, $wR_2 = 0.090$
Largest difference peak and hole (e Å^{-3})	0.23 and −0.39	0.36 and −0.52	0.45 and −0.76	0.23 and −0.34

methylene groups in the heterocyclic ring adjacent to nitrogen at room temperature. Only one signal is observed for both of the free ligands and monodentate **4e**.

The chemical shift difference, $\Delta\delta$, for the methylene group Ar–CH_2N in the free ligand **1e** and complex **4e**, in which we know the nitrogen is not coordinated, is only −0.04 ppm, whereas $\Delta\delta$ for **1e** and **5e** is 0.56 ppm. (For ^{1}Hδ ArCH_2N of complexes **1**–**5d** and **1**–**5e** see Table 5.) An indication that the nitrogen atom is coordinated to the metal centre in complexes **2e**, **3e** come from even larger values for $\Delta\delta$ of 1.06 and 0.86 ppm, respectively.

The pyrrolidine derived metal complexes **2d**–**5d** also exhibit significant differences in the chemical shifts of the methylene groups adjacent to nitrogen compared with the free ligand. Here the value of $\Delta\delta$ ($\delta_{\text{free lig.}} - \delta_{\text{complex}}$) for the methylene groups in the heterocyclic ring is greater than for Ar–CH_2N.

2.2. Polymerisation studies

The ethene polymerisation productivity was determined for the new metal complexes when activated with MAO (Table 6). The results for $CpTiCl_3$, $CpZrCl_3$·DME, Cp_2ZrCl_2 and Cp_2TiCl_2 under identical conditions are included for comparison (runs 29–32). Polymerisations with the bis(phenoxy-amine) complexes of both titanium and zirconium (runs 1–3, 5 and 6) yielded only traces of polymer. The new mesityl substituted phenoxy-imine complexes also polymerised poorly, the zirconium complex **3a** giving low molecular weight polymer with a productivity of 17 kg mol^{-1} h^{-1} bar^{-1} (run 4).

The results for the new cyclopentadienyl phenoxy-imine and -amine complexes **4** and **5** were significantly better than those for the bis(ligand) complexes **2** and **3**. For titanium and zirconium the cyclopentadienyl phenoxy-imine complexes show remarkably similar productivities (runs 7–14 and 17–23) with the complexes bearing cyclohexyl and pentafluorophenyl imine substituents, giving broadly similar results and approximately ten times the productivity of the mesityl compounds.

In contrast, there is a significant difference between the cyclopentadienyl phenoxy-amine titanium and zirconium catalysts. Whereas for zirconium the amine complexes exhibit very similar productivities (runs 24–28) to the cyclohexyl and pentafluorophenyl imine catalysts at ca. 200 kg mol^{-1} h^{-1} bar^{-1}, the titanium catalysts are almost two orders of magnitude less productive (runs 15 and 16).

Table 2
Selected bond lengths (Å) and bond angles (°) for **2a** and **3a**

Complex **2a**		Complex **3a**	
Bond lengths			
Ti(1)–O(1)	1.8506(12)	Zr(1)–O(1)	1.9805(13)
Ti(1)–O(2)	1.8432(12)	Zr(1)–O(2)	1.9763(12)
Ti(1)–Cl(1)	2.3001(6)	Zr(1)–Cl(1)	2.4299(7)
Ti(1)–Cl(2)	2.3084(6)	Zr(1)–Cl(2)	2.4308(6)
Ti(1)–N(1)	2.3112(13)	Zr(1)–N(1)	2.4344(14)
Ti(1)–N(2)	2.2866(14)	Zr(1)–N(2)	2.401(2)
C(11)–N(1)	1.303(2)	C(11)–N(1)	1.308(2)
N(1)–C(12)	1.468(2)	N(1)–C(12)	1.467(2)
C(31)–N(2)	1.301(2)	C(31)–N(2)	1.306(2)
N(2)–C(32)	1.464(2)	N(2)–C(32)	1.460(2)
Bond angles			
O(2)–Ti(1)–O(1)	162.15(5)	O(2)–Zr(1)–O(1)	157.80(5)
O(2)–Ti(1)–N(2)	81.13(5)	O(2)–Zr(1)–N(2)	77.14(5)
O(1)–Ti(1)–N(2)	88.28(5)	O(1)–Zr(1)–N(2)	90.32(5)
O(2)–Ti(1)–Cl(1)	97.66(4)	O(2)–Zr(1)–Cl(1)	101.32(4)
O(1)–Ti(1)–Cl(1)	95.83(4)	O(1)–Zr(1)–Cl(1)	95.81(4)
N(2)–Ti(1)–Cl(1)	85.76(3)	N(2)–Zr(1)–Cl(1)	85.62(3)
O(2)–Ti(1)–Cl(2)	96.26(4)	O(2)–Zr(1)–Cl(2)	95.99(4)
O(1)–Ti(1)–Cl(2)	95.31(4)	O(1)–Zr(1)–Cl(2)	97.84(4)
N(2)–Ti(1)–Cl(2)	174.88(3)	N(2)–Zr(1)–Cl(2)	171.34(3)
Cl(1)–Ti(1)–Cl(2)	90.24(2)	Cl(1)–Zr(1)–Cl(2)	90.63(2)
O(2)–Ti(1)–N(1)	86.46(5)	O(2)–Zr(1)–N(1)	86.83(5)
O(1)–Ti(1)–N(1)	80.95(5)	O(1)–Zr(1)–N(1)	76.69(5)
N(2)–Ti(1)–N(1)	98.69(5)	N(2)–Zr(1)–N(1)	97.83(5)
Cl(1)–Ti(1)–N(1)	174.38(4)	Cl(1)–Zr(1)–N(1)	171.70(4)
Cl(2)–Ti(1)–N(1)	85.50(4)	Cl(2)–Zr(1)–N(1)	86.94(4)
C(1)–O(1)–Ti(1)	144.54(10)	C(1)–O(1)–Zr(1)	147.31(11)
C(21)–O(2)–Ti(1)	145.20(10)	C(21)–O(2)–Zr(1)	146.46(11)

Table 3
Selected bond lengths (Å) and bond angles (°) for **4a**

Molecule a		Molecule b	
Bond lengths			
Ti(1a)–O(1a)	1.875(3)	Ti(2b)–O(1b)	1.873(2)
Ti(1a)–N(2a)	2.268(4)	Ti(2b)–N(2b)	2.262(3)
Ti(1a)–C(31a)	2.381(4)	Ti(2b)–C(31b)	2.384(4)
Ti(1a)–C(32a)	2.388(5)	Ti(2b)–C(32b)	2.370(4)
Ti(1a)–C(33a)	2.378(4)	Ti(2b)–C(33b)	2.372(4)
Ti(1a)–C(34a)	2.374(4)	Ti(2b)–C(34b)	2.386(4)
Ti(1a)–C(35a)	2.378(4)	Ti(2b)–C(35b)	2.387(4)
Ti(1a)–Cl(4a)	2.3596(12)	Ti(2b)–Cl(4b)	2.3677(11)
Ti(1a)–Cl(5a)	2.3354(10)	Ti(2b)–Cl(5b)	2.3388(10)
Ti(1a)–C(3xa)	2.053	Ti(2b)–C(3xb)	2.055
C(12a)–N(2a)	1.305(5)	C(12b)–N(2b)	1.286(4)
N(2a)–C(21a)	1.483(5)	N(2b)–C(21b)	1.479(4)
Bond angles			
O(1a)–Ti(1a)–N(2a)	78.78(11)	O(1b)–Ti(2b)–N(2b)	78.41(10)
O(1a)–Ti(1a)–Cl(4a)	85.49(9)	O(1b)–Ti(2b)–Cl(4b)	85.14(8)
O(1a)–Ti(1a)–Cl(5a)	135.82(8)	O(1b)–Ti(2b)–Cl(5b)	137.86(8)
N(2a)–Ti(1a)–Cl(4a)	143.08(9)	N(2b)–Ti(2b)–Cl(4b)	141.73(8)
N(2a)–Ti(1a)–Cl(5a)	81.69(8)	N(2b)–Ti(2b)–Cl(5b)	82.65(7)
Cl(5a)–Ti(1a)–Cl(4a)	87.00(4)	Cl(5b)–Ti(2b)–Cl(4b)	87.07(4)
O(1a)–Ti(1a)–C(3xa)	112.30	O(1b)–Ti(2b)–C(3xb)	112.10
N(2a)–Ti(1a)–C(3xa)	107.94	N(2b)–Ti(2b)–C(3xb)	109.55
Cl(4a)–Ti(1a)–C(3xa)	108.91	Cl(4b)–Ti(2b)–C(3xb)	108.63
Cl(5a)–Ti(1a)–C(3xa)	111.33	Cl(5b)–Ti(2b)–C(3xb)	109.64
C(1a)–O(1a)–Ti(1a)	136.5(2)	C(1b)–O(1b)–Ti(2b)	137.6(2)

C(3xa) and C(3xb) are the centroids of the Cp rings in the two molecules.

Table 4
Selected bond lengths (Å) and bond angles (°) for **4e**

Bond lengths	
Ti(1)–O(1)	1.7932(11)
Ti(1)–Cl(1)	2.2761(6)
Ti(1)–C(25)	2.333(2)
Ti(1)–C(21)	2.357(2)
Ti(1)–C(2x)	2.020
Ti(1)–Cl(2)	2.2688(7)
Ti(1)–C(23)	2.334(2)
Ti(1)–C(22)	2.365(2)
Ti(1)–C(24)	2.311(2)
Bond angles	
O(1)–Ti(1)–Cl(2)	103.69(4)
Cl(2)–Ti(1)–Cl(1)	101.26(3)
Cl(1)–Ti(1)–C(2x)	114.1
C(2x)–Ti(1)–O(1)	118.4
O(1)–Ti(1)–Cl(1)	104.50(4)
C(1)–O(1)–Ti(1)	163.74(10)
Cl(2)–Ti(1)–C(2x)	113.0

C(2x) is the centroid of the Cp ring.

As was the case with bis(phenoxy-imine) complexes the highest molecular weights were obtained with titanium and a pentafluorophenyl imine-substituent, i.e. complex **4b**. While many of these catalysts produce polymer samples with high M_w values, the GPC traces were abnormally complex with clearly bimodal and in some cases tetramodal distributions (for example see Fig. 4), consequently sensible values for M_n and the polydispersity could not be determined. These multimodal GPC traces are consistent with multiple catalytically active species possibly as a result of ligand dissociation and redistribution reactions under polymerisation conditions.

A number of closely related complexes, in particular asymmetric acetamidinate complexes and the zirconium aminoalkyl bis(phenolate) catalysts prepared by Kol et al. [29,30] are active for the stereoregular and living polymerisation of 1-hexene. We wished to explore whether our chiral cyclopentadienyl phenoxy-imine and phenoxy-amine complexes could also promote stereoregular polymerisation. Activating the zirconium complexes with MAO produces 1-hexene oligomers with modest productivity (Table 7). Analysis by mass spectrometry and ^{1}H-NMR of the end groups indicates an average of four to six hexene units per oligomer. The use of the alternative activator system Al(i-Bu)$_3$–[CPh$_3$][B(C$_6$F$_5$)$_4$] and carrying out the polymerisations in neat 1-hexene gave similar values for molecular weight and catalyst productivity.

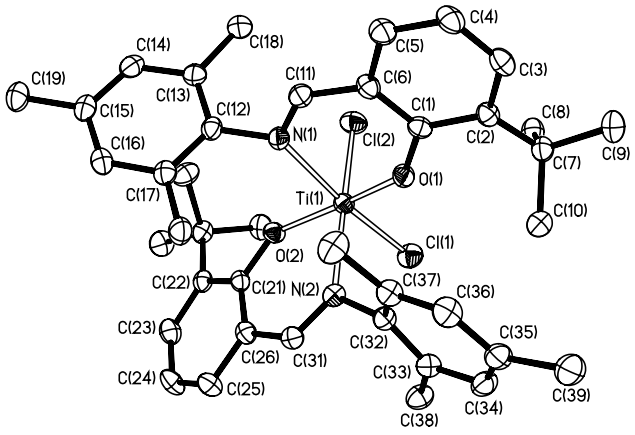


Fig. 1. Molecular structure and crystallographic numbering scheme for **2a**. **3a** is isostructural and numbered identically. Full thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table 5
^{1}H δ ArCH_2N

Complex	δ (ppm)
1d	3.77
2d	4.0
3d	4.2
4d	4.08
5d	3.8, 4.0
1e	3.64
2e	4.7
3e	4.5
4e	3.60
5e	4.20

The most effective ethene homopolymerisation catalysts were employed in preliminary ethene–1-hexene copolymerisation experiments (Table 8). 1-Hexene incorporation levels at 1–2% were significantly lower than the less bulky cyclopentadienyl phenoxy-imine titanium complexes studied by Qian [20] and much lower than

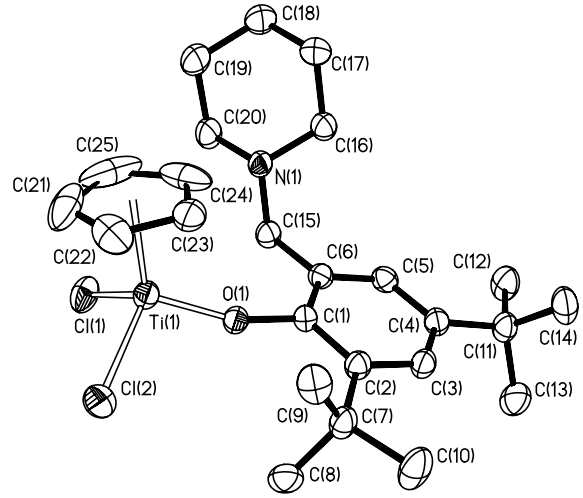


Fig. 3. Molecular structure and crystallographic numbering scheme for **4e**. Full thermal ellipsoids at 50% probability. All hydrogen atoms have been omitted.

Nomura's cyclopentadienyl phenoxide titanium catalysts [31].

2.3. Conclusion

A series of novel cyclopentadienyl phenoxy-imine and phenoxy-amine complexes of titanium and zirconium have been prepared and representative examples crystallographically characterised. For all but one example the ligands appear to be bound to the metal centre in a bidentate fashion. When activated with MAO all complexes are active for the polymerisation of ethene, but give multimodal molecular weight distributions consistent with multiple active sites. The most active systems were demonstrated to be effective for the copolymerisation of 1-hexene and ethene. In the absence of ethene, 1-hexene is oligomerised.

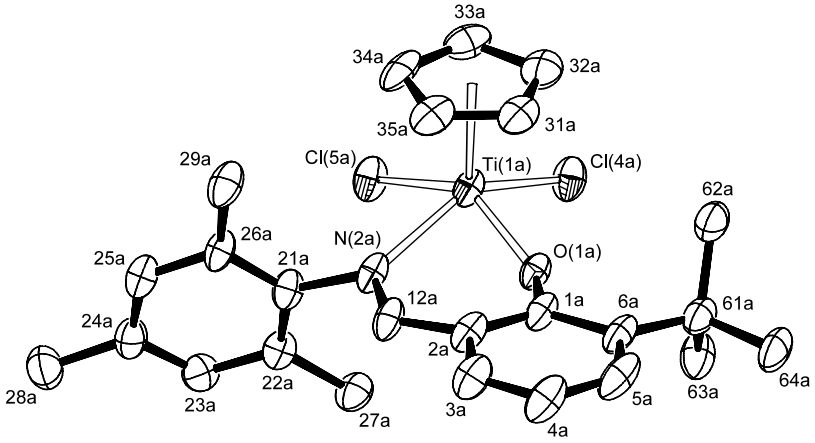


Fig. 2. One of the two virtually identical molecules in crystals of complex **4a**. Carbon atoms C(n) are shown with labels 'n'. Thermal ellipsoids of 50% probability are shown. Hydrogen atoms have been omitted for clarity.

Table 6
Selected ethene polymerisation data

Run [a]	Catalyst [b]	Co-catalyst [c] (μmol)	Temperature (°C)	Yield (g)	Productivity (g mol^{-1} h^{-1} bar^{-1})	M_w
1	**2a**	4000	25	trace		
2	**2d**	4000	25	trace		
3	**2e**	4000	25	trace		
4	**3a**	4000	25	0.087	1.7×10^4	5740
5	**3d**	4000	25	trace		
6	**3e**	4000	25	trace		
7	**4a** (40 μmol)	8000	25	0.129	1.3×10^4	328 000
8	**4b**	4000	0	0.7257	1.4×10^5	486 000
9	**4b**	4000	25	0.446	8.9×10^4	576 000
10	**4b**	20000	25	0.4914	9.8×10^4	
11	**4b**	4000	60	0.1535	3.1×10^4	627 000
12	**4c**	4000	0	0.731	1.5×10^5	587 000
13	**4c**	4000	25	0.800	1.6×10^5	
14	**4c**	4000	60	0.527	1.1×10^5	162 000
15	**4d** (40 μmol)	8000	25	0.068	6.8×10^3	343 000
16	**4e** (40 μmol)	8000	25	0.020	2.0×10^3	497 000
17	**5a**	4000	25	0.099	1.6×10^4	308 000
18	**5b**	20000	0	0.4246	8.5×10^4	142 000
19	**5b**	4000	25	0.368	7.4×10^4	513 000
20	**5b**	20000	25	0.6878	1.4×10^5	
21	**5b**	20000	60	0.9831	2.0×10^5	137 000
22	**5c**	4000	25	0.575	1.1×10^5	
23	**5c**	20000	25	0.5479	1.1×10^5	
24	**5d**	4000	0	0.1891	3.8×10^4	302 000
25	**5d**	4000	25	0.794	1.6×10^5	89 600
26	**5d**	4000	60	0.9159	1.8×10^5	39 200
27	**5e**	4000	25	0.084	1.7×10^4	173 000
28	**5e**	20000	25	1.0603	2.1×10^5	
29	$CpTiCl_3$	4000	25	0.063	1.3×10^4	
30	$CpZrCl_3 \cdot DME$	4000	25	0.027	5.5×10^3	
31	Cp_2TiCl_2 [d]	4000	25	0.42	2.1×10^6	
32	Cp_2ZrCl_2 [d]	20000	25	0.484	2.4×10^6	

[a] The polymerisations were performed in 50 ml toluene over 15 min at 1 bar ethene pressure.
[b] The catalyst loading was 20 μmol unless specified.
[c] The co-catalyst was MAO unless otherwise stated.
[d] Polymerisations were conducted for 3 min.

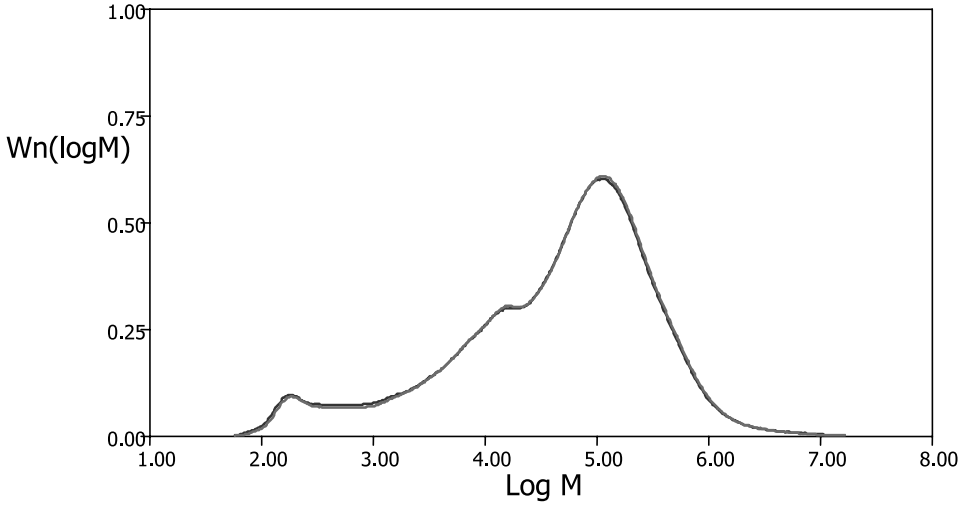


Fig. 4. Molecular weight distribution (Run 27, Table 6).

Table 7
1-Hexene hompolymerisations

Run [a]	Catalyst [b]	Co-catalyst [c] (μmol)	Temperature (°C)	Yield (g)	Conversion (%)	Productivity (g mol^{-1} h^{-1} bar^{-1})
33	**4b**	4000	25	0.95	28	2.6×10^3
34	**5a**	4000	25	2.02	60	5.6×10^3
35	**5b**	4000	25	1.05	31	2.9×10^3
36	**5d**	4000	25	1.53	45	4.3×10^3
37	**5e**	4000	25	1.45	43	4.0×10^3

[a] All polymerisations were carried out in 5 ml hexene and 3.7 ml toluene over 18 h.
[b] The catalyst loading was 20 μmol.
[c] The co-catalyst was MAO.

3. Experimental

3.1. General

Syntheses were performed under nitrogen using standard Schlenk techniques. Solvents were distilled over sodium–benzophenone (diethyl ether, THF), sodium (toluene), sodium–potassium alloy (light petroleum, b.p. 40–60 °C), or CaH_2 (dichloromethane). NMR solvents ($CDCl_3$, C_6D_6) were dried over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C), ^{19}F is relative to $CFCl_3$. Nitrogen, argon and ethene (BOC, 99.5%) were purified by passing through columns of supported P_2O_5 with moisture indicator, and activated 4 Å molecular sieves. GPC analyses were performed at UEA on a Polymer Labs PL-GPC-220 or by RAPRA Technology Ltd. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Service. Mass spectrometry was provided by the EPSRC National Mass Spectrometry Service Centre, Swansea.

Hexene, pyrrolidine, 2-*t*-butyl phenol, paraformaldehyde and pentafluoroaniline (Aldrich), piperidine and cyclohexylamine (Lancaster), formaldehyde and 2,4,6-trimethylaniline (Acros Organics) were obtained from commercial sources and used as supplied. 3-*tert*-Butyl salicylaldehyde [12], 2-*tert*-butyl-6-[(pentafluorophenylimino)-methyl]-phenol [15], $ZrCl_4(THF)_2$ [32], $CpZrCl_3 \cdot DME$ [33] and $CpTiCl_3$ [34] were prepared according to the literature procedures.

3.2. Ligand synthesis

3.2.1. 2-tert-Butyl-6-[(2,4,6-trimethylphenylimino)-methyl]-phenol (**1a**)

To a stirred solution of 2,4,6-trimethylaniline (21.2 g, 119 mmol) and 3-*tert*-butylsalicylaldehyde (16.0 g, 119 mmol) in toluene (350 ml), *p*-toluenesulfonic acid monohydrate (2.26 g, 11.86 mmol) was added. The solution was refluxed for 15 h and allowed to cool to room temperature (r.t.) before removing the volatiles under vacuum. The resulting dark yellow oil was extracted with light petroleum, and filtered to remove *p*-toluenesulfonic acid. The product was purified by column chromatography (eluent 30:1 light petroleum–diethylether) to afford 2-*tert*-butyl-6-[(2,4,6-trimethylphenylimino)-methyl]-phenol as a bright yellow oil, which crystallised from light petroleum at 5 °C as bright, lemon-yellow crystals (14.1 g, 47.6 mmol, 40%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 8.32 (s, 1H, C*H*=N), 7.40 (dd, 1H, $J = 7.8$, 1.5 Hz, Ar), 7.18 (dd, 1H, $J = 7.6$, 1.6 Hz, Ar), 6.92 (s, 2H, Ar), 6.88 (t, 1H, $J = 7.7$ Hz, Ar), 2.30 (s, 3H, CH_3), 2.19 (s, 6H, CH_3), 1.48 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 167.3 (*C*–O), 160.6 (*C*=N), 145.7 (Ar), 137.7 (Ar), 134.3 (Ar), 130.4 (Ar), 130.2 (Ar), 129.0 (Ar), 128.3 (Ar), 118.6 (Ar), 118.0 (Ar), 34.9 (*C*Me$_3$), 29.3 (C(*C*H$_3$)$_3$), 20.8 (*p*-*C*H$_3$), 18.5 (*o*-*C*H$_3$). Anal. Found: C, 81.47; H,

Table 8
Ethene–1-hexene copolymerisations

Run [a]	Catalyst [b,c]	Temperature (°C)	Yield (g)	Productivity (g mol^{-1} h^{-1} bar^{-1})	Hexene incorporation (%)	M_w
38	**4b**	25	0.0348	1.4×10^4	2.1	1 190 000
39	**5a**	25	0.0900	3.6×10^4	1.9	250 000
40	**5d**	25	0.7180	2.9×10^5	2.1	31 800
41	**5e**	25	0.1686	6.7×10^4	1.3	171 000

[a] All polymerisations were conducted in 20 ml toluene over 15 min.
[b] The catalyst loading was 20 mmol.
[c] The co-catalyst was 4000 μmol MAO.

8.53; N, 4.61. Calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74%.

3.2.2. 2-tert-Butyl-6-[(cyclohexylimino)-methyl]phenol (1c)

To a stirred mixture of 3-*tert*-butylsalicylaldehyde (9.74 g, 55 mmol) and molecular sieves 4 Å (4 g) in ethanol (50 ml), a solution of cyclohexylamine (6.00 g, 61 mmol) in ethanol (20 ml) was added dropwise at r.t. The mixture was stirred for 18 h, filtered and the molecular sieves washed with ethyl acetate (20 ml). The volatiles were removed under vacuum and the product recrystallised from light petroleum at −20 °C as a yellow solid (4.0 g, 14 mmol, 25%). ^{1}H-NMR (300 MHz, 298 K, C_6D_6): δ 8.37 (s, 1H, C*H*=N), 7.31 (d, 1H, $J = 6.5$, Ar–H), 7.10 (d, 1H, $J = 6.5$, Ar), 6.80 (t, 1H, $J = 6.5$, Ar), 3.2 (br, 1H, cyclohexyl C*H*), 1.84 (m, 4H, cyclohexyl CH_2), 1.7–1.2 (br, 6H, cyclohexyl CH_2), 1.45 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 298 K, C_6D_6): δ 162.9 (*C*H=N), 160.7 (*C*–O), 137.3 (Ar), 129.4 (Ar), 129.0 (Ar), 118.9 (Ar), 117.5 (Ar), 67.6 (cyclohexyl *C*H), 34.8 (cyclohexyl *C*H_2), 34.4 (cyclohexyl *C*H_2). 29.3 (*C*Me$_3$), 25.6 (C(*C*H$_3$)$_3$), 24.5 (cyclohexyl *C*H_2). Anal. Found: C, 78.58; H, 9.69; N, 5.12. Calc. for $C_{19}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40%. MS: 259.3 [M$^+$], 244.3, 216.2, 162.2, 134.1, 83.2, 55.3, 41.3.

3.2.3. 2,4-di-tert-Butyl-6-pyrrolidin-1-ylmethyl-phenol (1d) [35,36]

To a stirred solution of 2,4-di-*tert*-butylphenol (20.3 g, 0.1 mol) and 37% aq. formaldehyde (8.1 g, 0.1 mol) in methanol (250 ml), pyrrolidine (7.2 g, 0.1 mol) was added. The solution was then refluxed for 15 h in air and allowed to cool to r.t. The product crystallised on cooling and was separated by filtration and washing with cold methanol, affording large white crystals (27.5 g, 95 mmol, 95%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.18 (d, 1H, $J = 2.4$ Hz, Ar), 6.81 (d, 1H, $J = 2.3$ Hz, Ar), 3.77 (s, 2H, CH_2–N), 2.60 (m, 4H, pyrrolidinyl *H*), 1.81 (m, 4H, pyrrolidinyl *H*), 1.40 (s, 9H, Bu^t), 1.26 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 154.4 (*C*–O), 140.1 (Ar), 135.2 (Ar), 122.6 (Ar), 122.6 (Ar), 121.8 (Ar), 59.6 (*C*H_2N), 53.3 (pyrrolidinyl *C*H_2N), 34.8 (*C*Me$_3$), 34.1 (*C*Me$_3$), 31.7 (C(*C*H$_3$)$_3$), 29.6 (C(*C*H$_3$)$_3$), 23.7 (pyrrolidinyl *C*H_2). Anal. Found: C, 79.08; H, 10.91; N, 4.72. Calc. for $C_{19}H_{31}NO$: C, 78.83; H, 10.79; N, 4.83%. MS: 289 [M$^+$], 274, 203, 70, 57.

3.2.4. 2,4-di-tert-Butyl-6-piperidin-1-ylmethyl-phenol (1e)

Following a similar procedure to the preparation of **1d**, a mixture of 2,4-di-*tert*-butylphenol (20.3 g, 0.1 mol), formaldehyde (8.1 g, 0.1 mol, 37% aq.), piperidine (8.5 g, 0.1 mol) and methanol (175 ml) was refluxed for 15 h in air before allowing to cool to r.t. The crystals formed on cooling were filtered and washed with cold methanol to afford the desired product as colourless crystals (21.0 g, 69 mmol, 69%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 11 (br, 1H, O*H*), 7.21 (d, 1H, $J = 2.4$ Hz, Ar), 6.82 (d, 1H, $J = 2.4$ Hz, Ar), 3.64 (s, 2H, CH_2N), 2.6 (br, 4H, piperidinyl CH_2N), 1.63 (br, 4H, piperidinyl CH_2), 1.50 (br, 2H, piperidinyl CH_2), 1.45 (s, 9H, Bu^t), 1.31 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 154.4 (*C*–O), 140.1 (Ar), 135.2 (Ar), 123.3 (Ar), 121.0 (Ar), 62.9 (*C*H_2N), 53.7 (piperidinyl *C*H_2N), 34.8 (*C*(CH$_3$)$_3$), 34.1 (*C*Me$_3$), 31.7 (C(*C*H$_3$)$_3$), 29.6 (C(*C*H$_3$)$_3$), 25.8 (piperidinyl *C*H_2), 24.1 (piperidinyl *C*H_2). Anal. Found: C, 79.17; H, 10.97; N, 4.40. Calc. for $C_{20}H_{33}NO$: C, 79.15; H, 10.96; N, 4.62%. MS: 303 [M$^+$], 260, 219, 83, 57.

3.3. Complex syntheses

3.3.1. {2-Bu^t-6-(2,4,6-Me$_3$C$_6$H$_2$NCH)C$_6$H$_3$O}$_2$TiCl$_2$ (2a)

The lithium salt Li**1a** was prepared by the dropwise addition of *n*-BuLi (3.3 ml, 1.6 M in hexanes) to a stirred solution of **1a** (1.48 g, 5 mmol) in dry THF (50 ml) at −78 °C. To ensure complete deprotonation the solution was stirred for a further 30 min before warming to r.t. for 1 h. The Li**1a** solution was cooled to −78 °C and $TiCl_4$ (0.47 g, 2.5 mmol) was added. The reaction was maintained at −78 °C for 1 h before warming slowly to r.t. and stirring overnight. The volatiles were then removed under vacuum and the resulting foam extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled to 5 °C, affording dark red, cubic crystals (0.55 g, 1.15 mmol, 46%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 8.18 (s, 2H, C*H*=N), 7.53 (dd, 2H, $J = 7.7$, 1.6 Hz, Ar), 7.22 (dd, 2H, $J = 7.7$, 1.6 Hz, Ar), 6.98 (t, 2H, $J = 7.7$ Hz, Ar), 6.86 (s, 4H, Ar), 2.37 (s, 6H, Me), 2.26 (s, 6H, Me), 1.87 (s, 6H, Me), 1.17 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$), 171.6 (*C*H=N), 162.9 (*C*–O), 149.5 (Ar), 138.7 (Ar), 136.0 (Ar), 134.2 (Ar), 132.8 (Ar), 132.4 (Ar), 125.0 (Ar), 121.3 (Ar), 34.9 (*C*Me$_3$), 29.3 (C(*C*H$_3$)$_3$), 20.4 (CH$_3$), 19.7 (CH$_3$), 19.5 (CH$_3$). Anal. Found: C, 67.08; H, 6.91; N, 3.79; Cl, 11.28. Calc. for $C_{40}H_{48}N_2O_2Cl_2Ti$: C, 67.89; H, 6.84; N, 3.96; Cl, 10.02%.

3.3.2. {2,4-Bu$^t_2$-6-(C$_4$H$_8$NCH$_2$)C$_6$H$_2$O}$_2$TiCl$_2$ (2d)

The lithium salt Li**1d** was prepared from **1d** (1.45 g, 5 mmol) and *n*-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1d** was treated with $TiCl_4$ (0.47 g, 2.5 mmol) following the procedure used for **2a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled overnight to 5 °C, giving small brown crystals (1.02 g, 1.5 mmol, 59%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.28 (s, 2H, Ar), 6.99 (s, 2H, Ar), 4.0 (br, 4H,

CH_2N), 3.2 (br, 8H, pyrrolidinyl CH_2), 1.95 (br, 8H, pyrrolidinyl CH_2), 1.40 (s, 18H, Bu^t), 1.31 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 160.4 (C–O), 143.7 (Ar), 134.1 (Ar), 126.5 (Ar), 124.6 (Ar), 124.0 (Ar), 60.8 (CH_2–N), 53.4 (pyrrolidinyl CH_2N), 34.9 (CMe_3), 34.4 (CMe_3), 31.5 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 21.9 (pyrrolidinyl CH_2). Anal. Found: C, 60.79; H, 8.18; N, 3.51; Cl, 16.80. Calc. for $C_{38}H_{60}N_2O_2Cl_2Ti \cdot CH_2Cl_2$: C, 60.01; H, 8.01; N, 3.59; Cl, 18.17%.

3.3.3. {2,4-Bu^t_2-6-($C_5H_{10}NCH_2$)C_6H_2O}$_2TiCl_2$ (**2e**)

The lithium salt Li**1e** was prepared from **1e** (1.52 g, 5 mmol) and n-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1e** was treated with $TiCl_4$ (0.47 g, 2.5 mmol) following the procedure used for **2a**. Removal of the volatiles under vacuum gave a brown foam which was extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled overnight to 5 °C, yielding small brown crystals (0.95 g, 1.3 mmol, 52%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.28 (d, 2H, $J = 2.1$ Hz, Ar), 7.14 (d, 2H, $J = 2.1$ Hz, Ar), 4.7 (br, 4H, CH_2–N), 4.4 (br, 4H, piperidinyl CH_2–N), 3.4 (br, 4H, piperidinyl CH_2N), 1.8 (br, 8H, piperidinyl CH_2), 1.4 (br, 4H, piperidinyl CH_2), 1.42 (s, 18H, Bu^t), 1.32 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 143.9 (Ar), 134.3 (Ar), 125.0 (Ar), 123.8 (Ar), 54.5 (CH_2N), 41.3 (piperidinyl CH_2N), 34.8 (CMe_3), 34.4 (CMe_3), 31.7 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 23.2 (piperidinyl CH_2), 20.4 (piperidinyl CH_2). Anal. Found: C, 67.23; H, 9.35; N, 3.54; Cl, 9.14. Calc. for $C_{40}H_{64}N_2O_2Cl_2Ti$: C, 66.38; H, 8.91; N, 3.87; Cl, 9.80%.

3.3.4. {2-Bu^t-6-(2,4,6-$Me_3C_6H_2NCH$)C_6H_3O}$_2ZrCl_2$ (**3a**)

The reaction between Li**1a** (5 mmol) and $ZrCl_4 \cdot (THF)_2$ (0.94 g, 2.5 mmol) was performed following a similar procedure to that for the titanium analogue **2a**. The solvents were taken off and the product extracted with CH_2Cl_2. The solution was concentrated and layered with light petroleum. Pale yellow, needle-like crystals (suitable for X-ray diffraction) grew overnight at r.t. (0.56 g, 0.75 mmol, 30%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 8.32 (s, 2H, CH=N), 7.54 (dd, 2H, $J = 7.7$, 1.6 Hz, Ar), 7.23 (dd, 2H, $J = 7.7$, 1.6 Hz, Ar), 6.95 (t, 2H, $J = 7.7$ Hz, Ar), 6.89 (s, 2H, Ar), 2.33 (s, 12H, o-CH_3), 1.80 (s, 6H, p-CH_3), 1.22 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 173.9 (CH=N), 160.5 (Ar), 148.0 (Ar), 138.6 (Ar), 135.8 (Ar), 134.4 (Ar), 133.8 (Ar), 130.3 (Ar), 129.0 (Ar), 123.5 (Ar), 123.2 (Ar) 34.9 (CMe_3), 29.6 ($C(CH_3)_3$), 19.9 (o-CH_3), 19.2 (p-CH_3). Anal. Found: C, 63.88; H, 6.46; N, 3.59. Calc. for $C_{40}H_{48}N_2O_2Cl_2Zr$: C, 63.98; H, 6.44; N, 3.73%.

3.3.5. {2,4-Bu^t_2-6-($C_4H_8NCH_2$)C_6H_2O}$_2ZrCl_2$ (**3d**)

The reaction between Li**1d** (5 mmol) and $ZrCl_4 \cdot (THF)_2$ (0.94 g, 2.5 mmol) was performed following a similar procedure to that for **2a**. The product was extracted with CH_2Cl_2. The solution was concentrated, layered with light petroleum and cooled to 5 °C, yielding small, colourless crystals (1.05 g, 1.3 mmol, 52%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.30 (d, 2H, $J = 2.4$ Hz, Ar), 6.94 (d, 2H, $J = 2.4$ Hz, Ar), 4.2 (br, 4H, CH_2N), 3.7 (br, 4H, pyrrolidinyl CH_2N), 3.2 (br, 4H, pyrrolidinyl CH_2N), 2.1 (br, 8H, pyrrolidinyl CH_2), 1.45 (s, 18H, Bu^t), 1.29 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 156.2 (C–O), 142.0 (Ar), 135.6 (Ar), 124.8 (Ar), 124.6 (Ar), 124.3 (Ar), 60.0 (CH_2N), 53.4 (pyrrolidinyl CH_2N), 34.8 (CMe_3), 34.2 (CMe_3), 31.6 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$), 22.4 (pyrrolidinyl CH_2). Anal. Found: C, 56.72; H, 7.55; N, 3.14; Cl, 15.14. Calc. for $C_{38}H_{60}N_2O_2Cl_2Zr \cdot 1/2CH_2Cl_2$: C, 56.64; H, 7.47; N, 3.43; Cl, 17.37%.

3.3.6. {2,4-Bu^t_2-6-($C_5H_{10}NCH_2$)C_6H_2O}$_2ZrCl_2$ (**3e**)

The reaction between Li**1e** (5 mmol) and $ZrCl_4 \cdot (THF)_2$ (0.94 g, 2.5 mmol) was performed following a similar procedure to that for **2a**. The product was extracted with CH_2Cl_2. The solution was concentrated, layered with light petroleum and cooled to 5 °C precipitating a beige solid (1.66 g, 2.1 mmol, 82%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.29 (d, 2H, $J =$ 2.2 Hz, Ar), 7.08 (d, 2H, $J = 2.2$ Hz, Ar), 4.5 (br, 4H, CH_2N), 3.8 (br, 4H, piperidinyl CH_2N), 3.2 (br, 4H, piperidinyl CH_2N), 1.8 (br, 8H, piperidinyl CH_2), 1.5 (br, 4H, piperidinyl CH_2), 1.42 (s, 18H, Bu^t), 1.31 (s, 18H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$) δ 156.5 (Ar), 142.1 (Ar), 135.5 (Ar), 125.2 (Ar), 124.4 (Ar), 123.2 (Ar), 53.5 (CH_2–N), 34.7 (CMe_3), 34.2 (CMe_3), 31.6 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$), 23.0 (piperidinyl CH_2N), 19.1 (piperidinyl·CH_2), 18.9 (piperidinyl·CH_2). Anal. Found: C, 59.56; H, 7.83; N, 3.20; Cl, 13.70. Calc. for $C_{40}H_{64}N_2O_2Cl_2Zr \cdot LiCl$: C, 59.35; H, 7.97; N, 3.46; Cl, 13.14%.

3.3.7. Cp{2-Bu^t-6-(2,4,6-$Me_3C_6H_2NCH$)C_6H_3O}$TiCl_2$ (**4a**)

The lithium salt of **1a** was prepared by the dropwise addition of n-BuLi (3.3 ml, 1.6 M in hexanes) to a stirred solution of **1a** (1.48 g, 5 mmol) in dry THF (50 ml) at −78 °C. To ensure complete deprotonation, the solution was stirred for a further 30 min before warming to r.t. and stirring for a further 1 h. The solution of Li**1a** was cooled to −78 °C and $CpTiCl_3$ (1.09 g, 5 mmol) added. The reaction temperature was maintained for 1 h before warming to r.t. and stirring overnight. The volatiles were removed under reduced pressure and the resulting foam extracted with CH_2Cl_2. The solution was concentrated, layered with light petroleum and cooled to 5 °C, giving dark red needle-like crystals (fragments of

which were suitable for X-ray diffraction) (1.84 g, 3.9 mmol, 77%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 8.42 (s, 1 H, C*H*=N), 7.72 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.42 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.12 (t, 1H, $J = 7.7$ Hz, Ar), 6.92 (s, 2H, Ar), 6.58 (s, 5H, Cp), 2.30 (s, 3H, Me), 2.20 (s, 6H, Me), 1.56 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): 168.9 (*C*H=N), 165.6 (Ar), 154.6 (Ar), 138.3 (Ar), 135.8 (Ar), 133.7 (Ar), 131.3 (Ar), 129.2 (Ar), 122.2 (Cp), 121.8 (Ar), 121.6 (Ar), 35.2 (*C*Me$_3$), 29.4 (C(*C*H$_3$)$_3$), 20.8 (*p*-CH$_3$), 19.2 (*o*-CH$_3$). Anal. Found: C, 59.35; H, 6.07; N, 2.61. Calc. for $C_{25}H_{29}NOCl_2Ti\cdot(CH_2Cl_2)_{0.5}$: C, 58.81; H, 5.81; N, 2.69%.

3.3.8. *Cp{2-Bu^t-6-(C$_6$F$_5$NCH)C$_6$H$_3$O}TiCl$_2$ (**4b**)*

The lithium salt Li**1b** was prepared from **1b** (1.26 g, 3.67 mmol) and *n*-BuLi (2.4 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1b** was treated with $CpTiCl_3$ (0.80 g, 3.67 mmol) following the procedure used for **4a**. The product was extracted with CH_2Cl_2 (20 ml). The resulting solution was concentrated, layered with light petroleum and cooled to −20 °C, precipitating **4b** as dark red oil. The oil was dried under vacuum and the resulting foam broken up to give an orange powder (1.64 g, 3.1 mmol, 61%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.83 (s, 1H, C*H*=N), 7.41 (dd, 1H, $J = 7.6$, 1.5 Hz, Ar), 7.02 (dd, 1H, $J = 7.6$, 1.5, Ar), 6.74 (t, 1H, $J = 7.6$, Ar), 6.16 (s, 5H, Cp), 1.44 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): 173.0 (*C*H=N), 166.7 (Ar), 139.4 (Ar), 135.2 (Ar), 132.4 (Ar), 122.4 (Cp), 121.8 (Ar), 121.4 (Ar), 35.2 (*C*Me$_3$), 29.6 (C(*C*H$_3$)$_3$). ^{19}F-NMR (282.4 MHz, 300 K, C_6D_6): δ −148.2 (br, 2F, *o*-F), −157.8 (br, 1F, *p*-F), −162.7 (br, 2F, *m*-F). Anal. Found: C, 50.68; H, 3.92; N, 2.33; Cl, 14.21. Calc. for $C_{22}H_{18}NOCl_2F_5Ti$: C, 50.22; H, 3.45; N, 2.66; Cl, 13.48%.

3.3.9. *Cp{2-Bu^t-6-(C$_6$H$_{11}$NCH)C$_6$H$_3$O}TiCl$_2$ (**4c**)*

The lithium salt Li**1c**, was prepared from **1c** (1.30 g, 5 mmol) and *n*-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1c** was treated with $CpTiCl_3$ (1.09 g, 5 mmol) following the procedure used for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (40 ml). The solution was concentrated, layered with light petroleum and cooled to 5 °C to afford the product as an orange solid (1.32 g, 3.0 mmol, 60%). ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$): δ 8.56 (s, 1H, C*H*=N), 7.59 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.37 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.05 (t, 1H, $J = 7.7$ Hz, Ar), 6.43 (s, 5H, Cp), 4.41 (m, 1H, cyclohexyl C*H*), 2.5–1.1 (br, 10H, cyclohexyl C*H*$_2$), 1.47 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 298 K, $CDCl_3$): δ 164.9 (*C*H=N), 163.7 (Ar –O), 138.3 (Ar), 132.9 (Ar), 131.8 (Ar), 121.8 (Cp), 68.8 (cyclohexyl *C*H), 35.0 (*C*Me$_3$), 29.7 (C(*C*H$_3$)$_3$), 29.3 (cyclohexyl *C*H$_2$), 25.7 (cyclohexyl *C*H$_2$), other resonances obscured. Anal. Found: C, 53.01; H, 6.45; N, 2.39; Cl, 15.96. Calc. for $C_{22}H_{29}NOCl_2Ti$: C, 54.41; H, 6.02; N, 2.88; Cl, 14.60%.

3.3.10. *Cp{2,4-Bu$^t_2$-6-(C$_4$H$_8$NCH$_2$)C$_6$H$_2$O}TiCl$_2$ (**4d**)*

The lithium salt Li**1d** was prepared from **1d** (1.45 g, 5 mmol) and *n*-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1d** was treated with $CpTiCl_3$ (1.09 g, 5 mmol) following the procedure used for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The resulting solution was concentrated, layered with light petroleum and cooled to −20 °C to afford the desired product as a brown–orange powder (1.30 g, 2.8 mmol, 55%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.26 (d, 1H, $J = 2.0$ Hz, Ar), 6.89 (d, 1H, $J = 2.0$ Hz, Ar), 6.72 (s, 5H, Cp), 4.08 (s, 2H, C*H*$_2$N), 3.32 (m, 4H, pyrrolidinyl C*H*$_2$), 1.92 (m, 4H, pyrrolidinyl C*H*$_2$), 1.42 (s, 9H, Bu^t), 1.31 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 144.7 (Ar–O), 135.7 (Ar), 123.2 (Ar), 122.4 (Ar), 121.8 (Cp), 118.2 (Ar), 61.7 (*C*H$_2$–N), 57.0 (pyrrolidinyl *C*H$_2$N), 35.0 (*C*Me$_3$), 34.5 (*C*Me$_3$), 31.5 (C(*C*H$_3$)$_3$), 29.6 (C(*C*H$_3$)$_3$), 23.5 (pyrrolidinyl *C*H$_2$). Anal. Found: C, 60.05; H, 7.62; N, 2.56; Cl, 15.50. Calc. for $C_{24}H_{35}NOCl_2Ti$: C, 61.03; H, 7.47; N, 2.97; Cl, 15.01%.

3.3.11. *Cp{2,4-Bu$^t_2$-6-(C$_5$H$_{10}$NCH$_2$)C$_6$H$_2$O}TiCl$_2$ (**4e**)*

The lithium salt Li**1e** was prepared from **1e** (1.52 g, 5 mmol) and *n*-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1e** was treated with $CpTiCl_3$ (1.09 g, 5 mmol) following the procedure used for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled to 5 °C, affording the product as large, dark orange, cubic crystals (1.48 g, 3.1 mmol, 61%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.24 (tr, 2H, $J = 2.5$ Hz, Ar), 6.85 (s, 5H, Cp), 3.60 (s, 2H, CH_2–N), 2.51 (m, 4H, piperidinyl CH_2N), 1.61 (m, 4H, piperidinyl CH_2), 1.47 (m, 2H, piperidinyl CH_2), 1.41 (s, 9H, Bu^t), 1.31 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 165.5 (Ar–O), 145.8 (Ar), 137.7 (Ar), 129.1 (Ar), 126.6 (Ar), 122.4 (Ar), 121.6 (Cp), 58.0 (CH_2N), 54.3 (piperidinyl CH_2N), 35.4 (CMe_3), 34.6 (CMe_3), 31.4 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 25.8 (piperidinyl·CH_2), 24.4 (piperidinyl CH_2). Anal. Found: C, 62.25; H, 7.75; N, 2.63; Cl, 14.44. Calc. for $C_{25}H_{37}NOCl_2Ti$: C, 61.74; H, 7.67; N, 2.88; Cl, 14.58%.

3.3.12. *Cp{2-Bu^t-6-(2,4,6-Me$_3$C$_6$H$_2$NCH)C$_6$H$_3$O}$_2$ZrCl$_2$ (**5a**)*

The reaction between Li**1a** (5 mmol) and $CpZrCl_3\cdot$(DME) (1.76 g, 5 mmol) was performed following a similar procedure to that for the titanium analogue **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and

cooled to −20 °C, precipitating the product as an orange powder (0.97 g, 1.7 mmol, 33%). ^{1}H-NMR (300.13 MHz, 300 K, $CDCl_3$): δ 8.38 (s, 1H, C*H*=N), 7.71 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.35 (dd, 1H, $J = 7.7$, 1.6, Ar), 7.05 (t, 1H, $J = 7.7$ Hz, Ar), 6.95 (s, 2H, Ar), 6.51 (s, 5H, Cp), 3.79 (m, 4H, THF), 2.32 (s, 3H, *p*-Me), 2.25 (s, 6H, *o*-Me), 1.86 (m, 4H, THF), 1.55 (s, 9 H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 172.8 (*C*H=N), 162.1 (Ar–O), 151.7 (Ar), 139.5 (Ar), 135.9 (Ar), 134.5 (Ar), 132.7 (Ar), 129.4 (Ar), 128.9 (Ar), 122.3 (Ar), 120.3 (Ar), 116.8 (Cp), 68.0 (THF), 35.1 (*C*Me$_3$), 29.3 (C(*C*H$_3$)$_3$), 25.6 (THF), 20.8 (*C*H$_3$), 19.2 (*C*H$_3$). Anal. Found: C, 58.55; H, 6.75; N, 2.03; Cl, 10.85. Calc. for $C_{25}H_{29}NOCl_2Zr \cdot C_4H_8O$: C, 58.66; H, 6.28; N, 2.36; Cl, 11.94%.

3.3.13. *Cp{2-Bu^t-6-(C$_6$F$_5$NCH)C$_6$H$_3$O}ZrCl$_2$ (**5b**)*

The reaction between Li**1b** (4 mmol) and $CpZrCl_3 \cdot$(DME) (1.42 g, 4 mmol) was performed following a similar procedure to that for **4a.** The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled to −20 °C, affording the product **5b** as yellow–green crystals (1.56 g, 2.3 mmol, 57%). ^{1}H-NMR (300 MHz, 300 K, C_6D_6): δ 7.60 (s, 1H, C*H*=N), 7.43 (dd, 1H, $J = 7.6$, 1.7 Hz, Ar), 6.85 (dd, 1H, $J = 7.6$, 1.7 Hz, Ar), 6.64 (t, 1H, $J = 7.6$ Hz, Ar), 6.34 (s, 5H, Cp), 4.25 (s, 1H, CH_2Cl_2), 3.90 (m, 4H, THF), 1.45 (s, 9H, Bu^t), 1.33 (m, 4 H, THF). ^{13}C-NMR (75.5 MHz, 300 K, C_6D_6): δ 175.8 (*C*H=N), 164.0 (Ar), 140.6 (Ar), 136.4 (Ar), 134.8 (Ar), 121.3 (Ar), 119.9 (Ar), 119.2 (Ar), 118.8 (Ar), 117.4 (Cp), 71.1 (THF), 35.1 (*C*Me$_3$), 30.0 (C(*C*H$_3$)$_3$), 25.3 (THF). ^{19}F-NMR (282 MHz, 300 K, C_6D_6): δ −150 (br, 2F, *o*-F), −157.7 (m, 1F, *p*-F), −162.9 (m, 2F, *m*-F). Anal. Found: C, 46.54; H, 4.09; N, 1.73; Cl, 15.07. Calc. for $C_{22}H_{18}NOF_5Cl_2Zr \cdot (THF)(CH_2Cl_2)_{0.5}$: C, 46.53; H, 3.98; N, 2.05; Cl, 15.55%.

3.3.14. *Cp{2-Bu^t-6-(C$_6$H$_{11}$NCH)C$_6$H$_3$O}ZrCl$_2$ (**5c**)*

The lithium salt, Li**1c**, was prepared from **1c** (1.30 g, 5 mmol) and *n*-BuLi (3.3 ml, 1.6 M) in a similar procedure to that employed for Li**1a**. Li**1c** was treated with $CpZrCl_3 \cdot$DME (1.76 g, 5 mmol) following the procedure used for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (40 ml). The solution was concentrated, layered with light petroleum and cooled to 5 °C, to afford the product as yellow crystals (0.60 g, 1.2 mmol, 25%). ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$): δ 8.47 (s, 1H, C*H*=N), 7.55 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 7.28 (dd, 1H, $J = 7.7$, 1.6 Hz, Ar), 6.96 (t, 1H, $J = 7.7$ Hz, Ar), 6.53 (s, 5H, Cp), 3.78 (m, 1H, cyclohexyl C*H*), 2.3–1.0 (br, 10H, cyclohexyl C*H*$_2$), 1.45 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 298 K, $CDCl_3$): δ 167.9 (*C*H=N), 160.4 (Ar–*C*–O), 139.6 (Ar), 133.4 (Ar), 132.8 (Ar), 121.9 (Ar), 119.9 (Ar), 116.6 (Cp), 68.6 (cyclohexyl *C*H), 34.9 (*C*Me$_3$), 34.1 (cyclohexyl *C*H$_2$), 29.6 (C(*C*H$_3$)$_3$), 25.6 (cyclohexyl *C*H$_2$), 22.3 (cyclohexyl *C*H$_2$). Anal. Found: C, 58.43; H, 6.65; N, 2.93; Cl, 17.53. Calc. for $C_{22}H_{29}NOCl_2Zr$: C, 59.75; H, 6.61; N, 3.17; Cl, 16.03%.

3.3.15. *Cp{2,4-Bu$^t_2$-6-(C$_4$H$_8$NCH$_2$)C$_6$H$_2$O}ZrCl$_2$ (**5d**)*

The reaction between Li**1d** (5 mmol) and $CpZrCl_3 \cdot$(DME) (1.76 g, 5 mmol) was performed following a similar procedure to that for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled to 5 °C, precipitating **5d** as a pale brown powder (1.16 g, 2.3 mmol, 45%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.28 (d, 1H, $J = 2.4$ Hz, Ar), 6.84 (d, 1H, $J = 2.2$ Hz, Ar), 6.66 (s, 5H, Cp), 4.0 (br, 1H, C*H*$_2$N), 3.8 (br, 1H, C*H*$_2$N), 3.5 (br, 2H, pyrrolidinyl C*H*$_2$N), 2.9 (br, 2H, pyrrolidinyl C*H*$_2$N), 2.0 (br, 4H, pyrrolidinyl C*H*$_2$), 1.41 (s, 9H, Bu^t), 1.30 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 156.4 (Ar), 142.7 (Ar), 137.4 (Ar), 124.1 (Ar), 123.7 (Ar), 121.4 (Ar), 116.8 (Cp), 61.1 (*C*H$_2$N), 41.3 (pyrrolidinyl *C*H$_2$N), 34.8 (*C*Me$_3$), 34.3 (*C*Me$_3$), 31.6 (C(*C*H$_3$)$_3$), 29.4 (C(*C*H$_3$)$_3$), 22.9 (pyrrolidinyl *C*H$_2$). Anal. Found: 56.05; H, 7.13; N, 2.60; Cl, 12.58. Calc. for $C_{24}H_{35}NOCl_2Zr$: C, 55.90; H, 6.84; N, 2.72; Cl, 13.75%.

3.3.16. *Cp{2,4-Bu$^t_2$-6-(C$_5$H$_{10}$NCH$_2$)C$_6$H$_2$O}ZrCl$_2$ (**5e**)*

The reaction between Li**1e** (5 mmol) and $CpZrCl_3 \cdot$(DME) (1.76 g, 5 mmol) was performed following a similar procedure to that for **4a**. The solvents were removed under vacuum and the product extracted with CH_2Cl_2 (20 ml). The solution was concentrated, layered with light petroleum and cooled overnight to 5 °C, precipitating the product as a beige powder (0.85 g, 1.6 mmol, 32%). ^{1}H-NMR (300 MHz, 300 K, $CDCl_3$): δ 7.30 (d, 1H, $J = 2.3$Hz, Ar), 6.98 (d, 1H, $J = 2.2$ Hz, Ar), 6.64 (s, 5H, Cp), 4.20 (s, 2H, C*H*$_2$N), 3.0–2.7 (br, 4H, piperidinyl C*H*$_2$N), 2.0–1.7 (br, 4H, piperidinyl C*H*$_2$), 1.50 (m, 2H, piperidinyl C*H*$_2$), 1.41 (s, 9H, Bu^t), 1.32 (s, 9H, Bu^t). ^{13}C-NMR (75.5 MHz, 300 K, $CDCl_3$): δ 156.8 (Ar–O), 142.9 (Ar), 137.2 (Ar), 124.2 (Ar), 120.8 (Ar), 118.2 (Ar), 117.1 (Cp), 54.1 (*C*H$_2$N), 41.3 (piperidinyl *C*H$_2$N), 34.8 (*C*Me$_3$), 34.4 (*C*Me$_3$), 31.6 (C(*C*H$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$), 22.6 (piperidinyl *C*H$_2$), 20.4 (piperidinyl *C*H$_2$). Anal. Found: C, 55.94; H, 7.54; N, 2.26; Cl, 13.65. Calc. for $C_{25}H_{37}NOCl_2Zr$: C, 56.69; H, 7.04; N, 2.64; Cl, 13.39.

3.4. X-ray crystallography

Crystal data for **2a**, **3a**, **4a** and **4e** are collected in Table 1. Crystals were selected from samples under perfluoropolyether oil, mounted on glass fibres and fixed in the cold nitrogen stream. They were mounted on a Rigaku R-Axis IIc image plate diffractometer

equipped with a rotating anode X-ray source (Mo–K_α radiation) and graphite monochromator. Using 4° oscillations, 48 exposures of 30 min each (40 min for **3a**) were made. Data were processed using the DENZO/SCALEPACK programs [37].

The structures of all the complexes were determined by the direct methods routines in the XS program and refined by full-matrix least-squares methods, on F^2's, in XL [38] or SHELXL [39]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms were taken from the literature [40].

In **4a**, there are two, virtually identical Ti-complex molecules in the asymmetric unit, in quite different orientations; these were well-resolved and refined with anisotropic thermal parameters. There are also (probably) two CH_2Cl_2 solvent molecules in the asymmetric unit; these were not satisfactorily resolved and were disordered over several orientations. There was a persistent difference peak between the two principal solvent regions; this, we suspect, was occupied as the methylene carbon atom (spanning chlorine atoms in the two regions) when there was only one solvent molecule in the asymmetric unit.

It was noted that in assigning the space group as *Aa*, there were many 'observed' reflections, weak but certainly having $I > 2\sigma(I)$, amongst the 'systematic absences'. We suspect that the disorder in the solvent regions is not totally random. Preliminary refinement in the corresponding primitive cell, with space group *Pn*, did not clarify the solvent situation but nor did the four Ti-complexes show the normal distortions of dimension when refined in the lower space group.

Computer programs used in this analysis have been noted above or in Table 4 of reference [41], and were run on a Silicon Graphics Indy at the University of East Anglia, or a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

3.5. Ethene polymerisation

A solution of MAO in toluene (50 ml) was saturated with ethene at 1 bar at a given temperature. Polymerisation was initiated by addition of a toluene solution of pre-catalyst into the reactor under vigorous stirring (1000 rpm). Methanol (1 ml) was added to terminate the polymerisation. The polymer was precipitated and separated from aluminium residues by addition of methanol (~300 ml) and 2 M HCl (~5 ml). The polymer was collected by filtration, washed with methanol, 2 M HCl, distilled water and again with methanol before drying overnight at 80 °C.

4. Supplimentary material

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms are available upon quoting the CCDC deposition numbers 192841–192844 for **2a**, **3a**, **4a** and **4e**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

The support of the Engineering and Physical Sciences Research Council and the University of East Anglia are gratefully acknowledged. We thank Dr. Shaun Garratt for assistance with GPC measurements.

References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(b) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255;
(c) E.Y.X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.
[2] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428;
(b) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[3] R. Gómez, R. Duchateau, A.N. Chernega, J.H. Teuben, F.T. Edelmann, M.L.H. Green, J. Organomet. Chem. 491 (1995) 153.
[4] For related β-diketiminate complexes see: R. Vollmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N.J. Taylor, S. Collins, Organometallics 19 (2000) 2161.
[5] L.R. Sita, J.R. Babcock, Organometallics 17 (1998) 5228.
[6] L.A. Koterwas, J.C. Fettinger, L.R. Sita, Organometallics 18 (1999) 4183.
[7] K.C. Jayaratne, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 958.
[8] K.C. Jayaratne, R.J. Keaton, D.A. Henningsen, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 10490.
[9] R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L.R. Sita, J. Am. Chem. Soc. 123 (2001) 6197.
[10] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, T. Fujita, Chem. Lett. (1999) 1065.
[11] J. Tian, G.W. Coates, Angew. Chem. Int. Ed. 39 (2000) 3626.
[12] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.
[13] J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134.
[14] J. Saito, M. Mitani, J. Mohri, S. Ishii, Y. Yoshida, T. Matsugi, S. Kojoh, N. Kashiwa, T. Fujita, Chem. Lett. (2001) 576.
[15] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 3327.

[16] S. Ishii, J. Saito, M. Mitani, J. Mohri, N. Matsukawa, Y. Tohi, S. Matsui, N. Kashiwa, T. Fujita, J. Molec. Catal. A: Chem. 179 (2002) 11.
[17] S. Matsui, T. Fujita, Catal. Today 66 (2001) 63.
[18] P.D. Hustad, J. Tian, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 3614.
[19] While this manuscript was in preparation Qian et al. reported the syntheses and polymerisation activities of some titanium monocyclopentadienyl phenoxy-imine complexes without bulky *ortho*-substituents: see reference [20].
[20] J. Huang, B. Lian, Y. Qian, W. Zhou, W. Chen, G. Zheng, Macromolecules 35 (2002) 4871.
[21] D.L. Kepert, Inorganic Stereochemistry, Springer-Verlag, New York, 1982.
[22] J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219.
[23] Complexes **2b**,**c** and **3b**,**c** have been described previously. See reference [12].
[24] This contrasts with the difficulties encountered by Qian et al. in preparing *ortho*-substituent free analogues, see reference [20].
[25] S. Saito, M. Mitani, S. Matsui, N. Kashiwa, T. Fujita, Macromol. Rapid. Commun. 21 (2000) 1333.
[26] R. Gómez, R. Duchateau, A.N. Chernega, A. Meetsma, F.T. Edelmann, J.H. Teuben, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1995) 217.
[27] J.K. Buijink, M. Noltemeyer, F.T. Edelmann, Z. Naturforsch. Teil. B 46b (1991) 1328.
[28] M.G. Thorn, J.S. Vilardo, J. Lee, B. Hanna, P.E. Fanwick, I.P. Rothwell, Organometallics 19 (2000) 5636.
[29] E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, Organometallics 20 (2001) 3017.
[30] E.Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, Organometallics 21 (2002) 662.
[31] K. Nomura, K. Oya, Y. Imanishi, J. Molec. Catal.: Chem. 174 (2001) 127.
[32] L.E. Manzer, Inorg. Synth. (1982) 136.
[33] E.C. Lund, T. Livinghouse, Organometallics 9 (1990) 2426.
[34] R.B. King, Organomet. Synth. 1 (1965) 78.
[35] During the preparation of this manuscript we became aware of an independent report of **1d**, see reference [36].
[36] T. Maki, Y. Araki, Y. Ishida, O. Onomura, Y. Matsumura, J. Am. Chem. Soc. 123 (2001) 3371.
[37] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, 1997.
[38] G.M. Sheldrick, SHELXTL Package, Including xs for Structure Determination, XL for Refinement and XP for Molecular Graphics, Siemens Analytical, 1995.
[39] G.M. Sheldrick, SHELXL-Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[40] International Tables for X-ray Crystallography Vol. C., Kluwer Academic Publishers, 1992.
[41] S.N. Anderson, R.L. Richards, D.L. Hughes, J. Chem. Soc., Dalton Trans. (1986) 245.