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Mixed-ligand iminopyrrolato-salicylaldiminato group 4 metal complexes: Optimising catalyst structure for ethylene/propylene copolymerisations

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Abstract

Treatment of $MCl_3(OC_6H_3\text{-}2\text{-}{}^t Bu\text{-}6\text{-}CH{=}NC_6F_5)(THF)$ (M = Ti, Zr) with a variety of different potassium iminopyrrolate salts ($K^+[RN{=}CHC_4H_3N]^-$), (R = phenyl, *cyclo*-hexyl, ethyl) afforded the corresponding titanium and zirconium mixed-ligand complexes MCl_2(N–O)(N–N). The molecular structures of $TiCl_2(OC_6H_3\text{-}2\text{-}{}^t Bu\text{-}6\text{-}CH{=}NC_6F_5)(C_2H_5N{=}CHC_4H_3N)$ (**1c**), $TiCl_2(OC_6H_3\text{-}2\text{-}{}^t Bu\text{-}6\text{-}CH{=}NC_6F_5)(C_6H_{11}N{=}CHC_4H_3N)$ (**1b**) and $ZrCl_2(OC_6H_3\text{-}2\text{-}{}^t Bu\text{-}6\text{-}CH{=}NC_6F_5)(C_6H_{11}N{=}CHC_4H_3N)$ (**2b**) show distorted octahedral geometries with *trans*-O^-,N^-/*cis*-Cl_2 arrangements. On activation with MAO the titanium (iminopyrrolato)(salicylaldiminato) complexes show excellent activities in ethylene polymerisation and are significantly more effective ethylene/propylene copolymerisation catalysts, both in terms of activity and propene incorporation, than either of the parent complexes. The ethylene–propylene copolymers show ca. 80% 1,2 regioselectivity and at high propylene incorporation tend towards an alternating structure.

Keywords: Titanium; Zirconium; Ethene; Copolymerization; Salicylaldiminate; Iminopyrrolate

1. Introduction

The development of new, more selective and active homogeneous polymerisation catalysts remains a driving force within organometallic chemistry. Of the non-metallocene group 4 metal complexes tested in olefin polymerisations, octahedral metal dichloride systems containing bidentate mono-anionic N,N^- or N,O^- ligands have proved to give particularly effective catalysts [1,2]. Bis(salicylaldiminato) complexes of titanium and zirconium of type **A** (Chart 1) are potent catalysts for ethylene homopolymerisations, but are inefficient copolymerisation catalyst [3–6]. They are sensitive to steric factors; for example, reducing the size of the *ortho*-substituent increases the fraction of bulky comonomer incorporated, while the activity is significantly decreased [7]. On the other hand, bis(iminopyrrolato) titanium complexes (structure **B**) give lower ethylene polymerisation productivities but achieve higher incorporation of both cyclic and terminal alkenes in the polyethylene backbone [8,9].

These limitations can be overcome with hetero-ligated group 4 metal complexes [10–14] which have been shown to combine these characteristics and are able to produce highly active catalysts capable of high levels of comonomer incorporation. The most successful systems for α-olefin co-polymerisations are the (iminopyrrolato)(salicylaldiminato)titanium complexes, which have previously been shown to combine high activity with high comonomer incorporation in copolymerisations of ethylene with 1-hexene, cyclopentene and norbornene [10]. We report here the syntheses and structures of two new titanium (N–N)(N–O)

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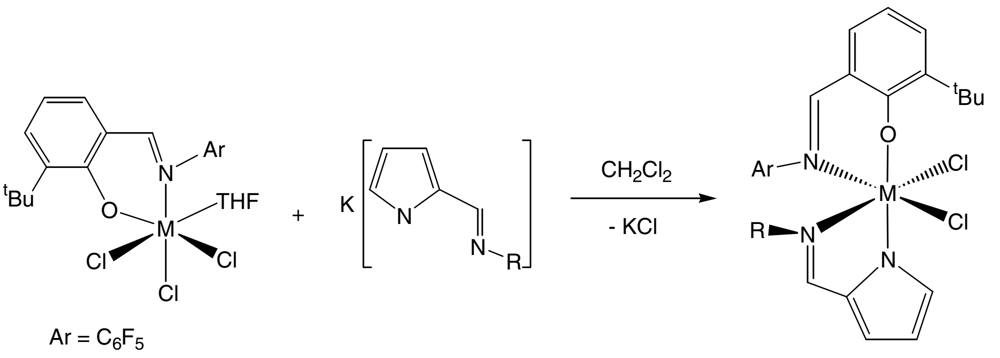


1a R = C_6H_5 (M = Ti)
1b R = cyclohexyl (M = Ti)
1c R = Et (M = Ti)
2b R = cyclohexyl (M = Zr)

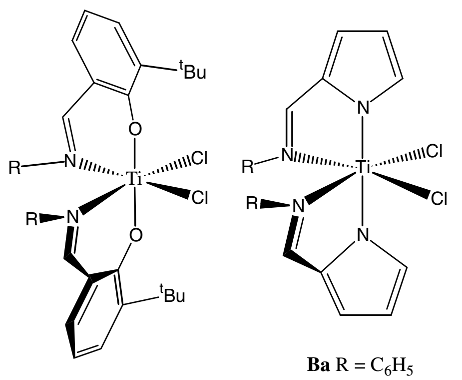
Chart 1.

mixed-ligand complexes and that of a zirconium analogue. When activated with methylaluminoxane (MAO) the titanium complexes are shown to be highly effective ethylene–propylene copolymerisation catalysts.

2. Syntheses

The complexes $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(R\text{–}N{=}CHC_4H_3N)$ (**1a**, R = Ph; **1b**, R = cyclohexyl; **1c**, R = Et) as well as $ZrCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(Cy\text{–}N{=}CHC_4H_3N)$ (**2b**) were synthesised following previously published procedures [8,9] by reacting the mono(salicylaldiminato) complexes $MCl_3(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(THF)$ (M = Ti, Zr) in dichloromethane with potassium salts of the corresponding iminopyrroles (Scheme 1). The products were obtained as dark red to orange crystals.

The ^1H NMR and ^{19}F NMR spectra in $CDCl_3$ of the complexes were consistent with the presence of a single stereoisomer at room temperature, with the ^1H NMR spectrum showing only two sharp imine peaks, one each for the iminopyrrolato and the salicylaldiminato ligands. The ^{19}F spectra of all the complexes indicate hindered rotation of C_6F_5 groups, rendering the *ortho*- and *meta*-fluorines inequivalent.



Aa R = C_6F_5 (M = Ti),
Ab R = C_6H_5 (M = Ti)

Ba R = C_6H_5
Bb R = Cyclohexyl
Bc R = Et

Scheme 1.

The structures of **1b, 1c** and **2b** were determined by X-ray crystallography and are shown in Figs. 1–3, respectively. Complexes **1c** and **2b** have essentially octahedral geometry, with the two anionic functions *trans* to one another while the two chloride ligands are *cis*. These structures are consistent with the most stable calculated geometry for such octahedral complexes bearing two mono-anionic ligands, and is also the geometry observed for most bis(salicylaldiminato), bis(iminopyrrolato) as well as for related mixed-ligand group 4 metal complexes [4,9–11].

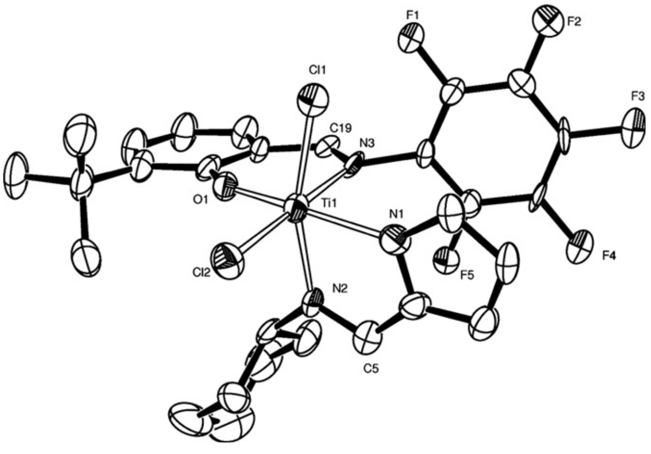


Fig. 1. ORTEP representation of the structure of **1b** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ti(1)–Cl(1) 2.282(3), Ti(1)–Cl(2) 2.282(2), Ti(1)–N(1) 2.072(6), Ti(1)–N(2) 2.119(6), Ti(1)–N(3) 2.242(6), Ti(1)–O(1) 1.820(5); Cl(1)–Ti(1)–Cl(2) 96.84(10), N(1)–Ti(1)–N(2) 76.4(2), N(2)–Ti(1)–N(3) 84.9(2), O(1)–Ti(1)–N(1) 162.7(2).

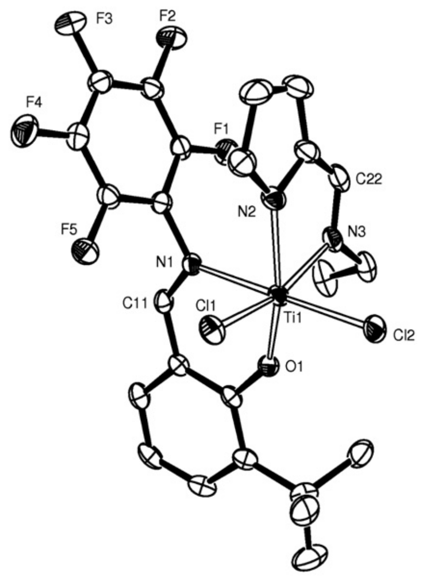


Fig. 2. ORTEP representation of the structure of **1c** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–Cl(1) 2.3031(8), Ti(1)–Cl(2) 2.2774(7), Ti(1)–N(1) 2.2837(16), Ti(1)–N(2) 2.0736(19), Ti(1)–N(3) 2.1366(18), Ti(1)–O(1) 1.8229(14); Cl(1)–Ti(1)–Cl(2) 95.52(3), N(1)–Ti(1)–N(2) 83.78(6), N(2)–Ti(1)–N(3) 76.37(7), N(1)–Ti(1)–O(1) 79.59(6).

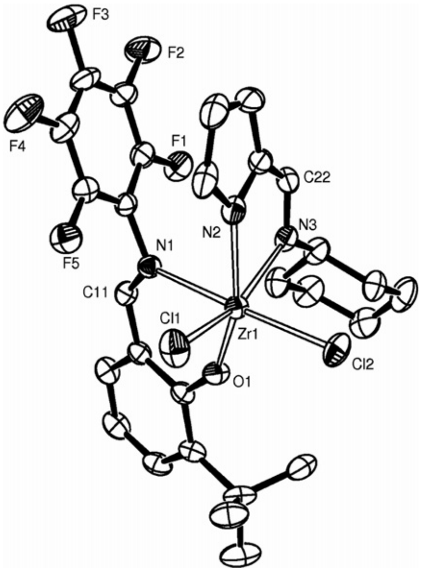


Fig. 3. ORTEP representation of the structure of **2b** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–Cl(1) 2.4132(11), Zr(1)–Cl(2) 2.3844(10), Zr(1)–N(1) 2.424(3), Zr(1)–N(2) 2.183(3), Zr(1)–N(3) 2.315(3), Zr(1)–O(1) 1.953(2); Cl(1)–Zr(1)–Cl(2) 96.79(4), N(1)–Zr(1)–N(2) 82.77(11), N(2)–Zr(1)–N(3) 73.17(12), N(1)–Zr(1)–O(1) 75.12(10).

3. Polymerisation studies

It has been shown previously that mixed-ligand (iminopyrrolato)(salicylaldiminato) titanium catalysts are more active ethylene polymerisation catalysts than their zirconium analogues [10,11]. The present studies show that the N-C_6F_5 derivatives **1a**–**c** in the presence of MAO give highly active catalysts for the homopolymerisation of ethylene and for ethylene–propene copolymerisations over a wide compositional range. On the other hand, under comparable conditions the homopolymerisation of propylene was unsuccessful; only small traces of polymer were recovered, even with long reaction times and high catalyst loadings.

3.1. Ethylene polymerisations

The effect of changing the substituent on the pyrrole-imino nitrogen atom in **1a**–**c** on the polymerisation of ethylene has been investigated. Such modification has previously been found to drastically change the catalytic performance of bis(iminopyrrolato) titanium systems (**B**), where it was shown that bulky groups such as $SiMe_3$ almost totally suppress ethylene polymerisation activities [9]. In marked contrast, all three mixed-ligand pre-catalysts **1a**–**c**, are very highly active, regardless of the nature of the substituent, whereas the productivities of the zirconium complex **2b** were an order of magnitude lower (Table 1). Complex **1a** was found to be the most effective catalyst, with an activity of 62,000 kg PE (mol metal)$^{-1}$ h^{-1} bar^{-1}, followed by **1c** and **1b**. This order of activity is rather different from that found for the bis(iminopyrrolato) titanium complexes **B** where R = cyclohexyl gave the most productive catalyst, 14,100 kg PE (mol metal)$^{-1}$ h^{-1} bar^{-1} [9].

Increasing the polymerisation temperature had very little effect on the activity of catalyst **1a**. If one considers the monomer solubility (see Supporting Information), the activity of **1b** increases twofold as the polymerisation temperature is raised from 20 to 50 °C, whilst the zirconium analogue **2b** shows a fourfold increase. Whereas catalysts **1a**, **1b** and **2b** are stable under catalytic conditions up to temperatures of 50 °C, this is not the case for the N-ethyl derivative **1c**, the activity of which is approximately halved on warming from 20 to 50 °C. The lower thermal stability of **1c** can possibly be attributed to the lower steric protection of the metal centre offered by the ethyl group.

Table 1
Ethylene homopolymerisation results for catalysts **1a**–**c** and **2b**/MAO[a]

Entry	Catalyst/ µmol	Temperature/ °C	Time/ min	Polymer/ g	Productivity[b]	M_w^c	M_w/ M_n
1	**1a**/0.5	20	1.5	0.74	62,000	158,000	2.3
2	**1a**/0.5	50	1.5	0.34	28,000	157,000	2.3
3	**1b**/0.5	20	1.5	0.26	22,000	566,000	2.5
4	**1b**/0.5	50	1.5	0.28	23,000	264,000	2.4
5	**1c**/0.5	20	1.5	0.31	26,000	275,000	2.5
6	**1c**/0.5	50	1.5	0.05	5000	269,000	2.4
7	**2b**/5	20	1.5	0.34	2800	310,000	2.5
8	**2b**/5	50	1.5	0.5	4200	212,000	2.2

[a] Conditions: total volume 250 cm^3, 1 bar ethylene, 3 mmol MAO.
[b] In kg PE (mol metal)$^{-1}$ h^{-1} bar^{-1}.
[c] Measured by gel permeation chromatography calibrated with polystyrene standards.

Gel permeation chromatography (GPC) measurements on polyethylene samples produced with **1a**–**c** showed monomodal composition, with polydispersities typical of single-site catalysts. Unlike the bis(salicylaldiminato)Ti catalyst **Aa**, catalysts **1a**–**c** are not living. Weight-average molecular weights of between 158,000 and 566,000 g mol^{-1} were found, with **1a** (R = Ph) giving the lowest and **1b** (R =Cy) the highest values.

3.2. *Ethylene–propylene copolymerisations*

Complexes **1a**, **1b** and **1c**/MAO catalyse the copolymerisation of ethylene and propylene. The results are summarised in Table 2. The dependence of P incorporation on the P/E feed ratio is illustrated in Fig. 4. Complexes **1a**, **1b** and **1c** are all highly effective ethylene/propylene copolymerisation catalysts. Changing the pyrrole-imine nitrogen substituent R had very little effect on the propylene incorporation. With a gas feed of 5 L min^{-1} propylene and 0.5 L min^{-1} of ethylene at 20 °C, all three titanium catalysts incorporate up to ca. 40 mol% propylene, with activities of ca. 1000 kg polymer (mol metal)$^{-1}$ h^{-1} bar^{-1}.

The behaviour of **1a**–**c** in ethylene–propylene copolymerisations was compared with Cp_2TiCl_2/MAO (Table 2, entries 16–18) and with the well-known bis(salicylaldiminato) catalyst **Aa** (entries 19–21) [3,6,9,14–17]. Under comparable conditions catalyst **Aa** was only able to incorporate 12.5 mol% P, with an activity of 660 kg polymer (mol metal)$^{-1}$ h^{-1} bar^{-1} (Table 2, entry 20), i.e. the P incorporation is substantially lower than with the mixed-ligand systems **1a**–**c**. On the other hand, while Cp_2TiCl_2 is able to incorporate high amounts of propylene, it produces copolymers with far lower molecular weights than those obtained with **1a**–**c**. Furthermore, although the titanium bis(iminopyrrolato) catalysts **Ba** and **Bb** have previously been shown to give polymers with good P incorporation, they suffer from low catalyst activities [6]. Complexes **1a**–**1c** therefore represent a good compromise and combine high catalytic activities with excellent levels of comonomer incorporation.

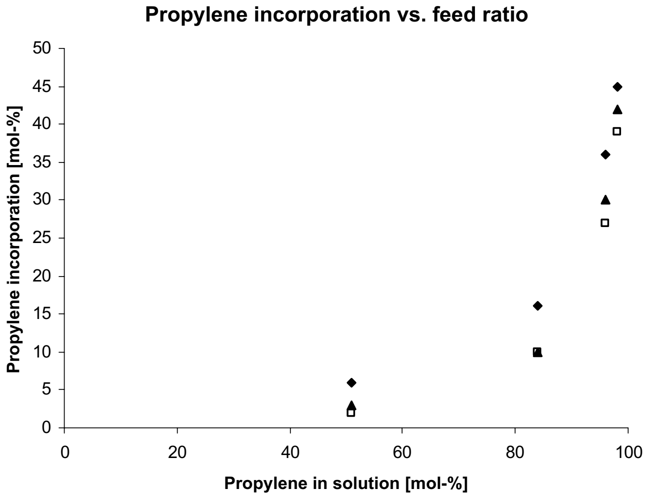


Fig. 4. Incorporation of propylene (mol%) versus propylene in toluene solution (mol%) for catalysts **1a** (◆), **1b** (□) and **1c** (▲).

Table 2
Ethylene/propylene copolymerisation results for pre-catalysts **1a**, **1b** and **1c**[a]

Entry	Catalyst/μmol	P:E[b]	Time/min	Polymer/g	Productivity[c]	% P content[d]	M_w	M_w/M_n
1	**1a**/1	1:1	3	0.1	2000	12	163,000	2.5
2	**1a**/1	5:1	10	0.12	720	36	74,000	2.6
3	**1a**/1	10:1	10	0.12	720	45	75,000	2.6
4	**1a**/1	1:5	1	0.46	29,000	6	421,000	3.4
5	**1a**/1	1:10	1	0.63	37,000	~0	452,000	3.2
6	**1b**/1	1:1	3	0.33	7000	10	200,000	2.0
7	**1b**/1	5:1	10	0.34	2000	27	172,000	2.2
8	**1b**/1	10:1	10	0.25	1500	39	127,000	2.0
9	**1b**/1	1:5	1	0.27	16,000	2	204,000	1.9
10	**1b**/1	1:10	1	0.24	14,000	~0	238,000	1.9
11	**1c**/1	1:1	3	0.25	5000	10	152,000	2.2
12	**1c**/1	5:1	10	0.31	1800	30	123,000	2.1
13	**1c**/1	10:1	10	0.23	1400	42	103,000	1.9
14	**1c**/1	1:5	1	0.37	22,000	3	158,000	2.0
15	**1c**/1	1:10	1	0.40	24,000	~0	167,000	1.9
16	Cp_2TiCl_2/1	1:1	3	0.47	9000	32	55,000	2.1
17	Cp_2TiCl_2/1	10:1	10	0.16	900	60	7700	2.6
18	Cp_2TiCl_2/1	1:10	1	0.59	34,000	~0	188,000	2.0
19	**Aa**/1	1:1	3	0.24	4800	3.0	311,000	1.8
20	**Aa**/1	10:1	10	0.12	660	12.5	258,000	2.0
21	**Aa**/1	1:10	1	0.25	15,000	~0	368,000	1.7

[a] Total volume 250 cm^3, 20 °C, 1 bar ethylene pressure, 3 mmol MAO.
[b] P:E = propylene:ethylene gas feed ratio.
[c] Productivity in kg polymer (mol metal)$^{-1}$ h^{-1} bar^{-1}.
[d] Determined by ^{13}C NMR spectroscopy.

4. Copolymer microstructure

Catalysts **1a**–**1c** and **Aa** all have a much higher affinity for ethylene than for propylene. ^{13}C NMR spectroscopy using peak assignments were carried out in accordance with Carman et al. [18] and Randall [19]. The labelling system for the assignments is shown in Fig. 5. Representative ^{13}C NMR spectra for copolymers with differing P content are shown in Fig. 6. E–P copolymers produced with catalyst **1b** show that P–P diads (αα methylene-carbons, Fig. 5) are highly unfavourable and only become apparent at very high propylene incorporation (Fig. 6 spectrum a). Similar results were observed for catalysts **1a** and **1c**. At high P content there is a tendency towards comonomer alternation, reminiscent of copolymers described by Zambelli et al. using vanadium catalysts [20].

The effect of changing R in pre-catalyst **1a**–**c** on the possible monomer insertions has been investigated by

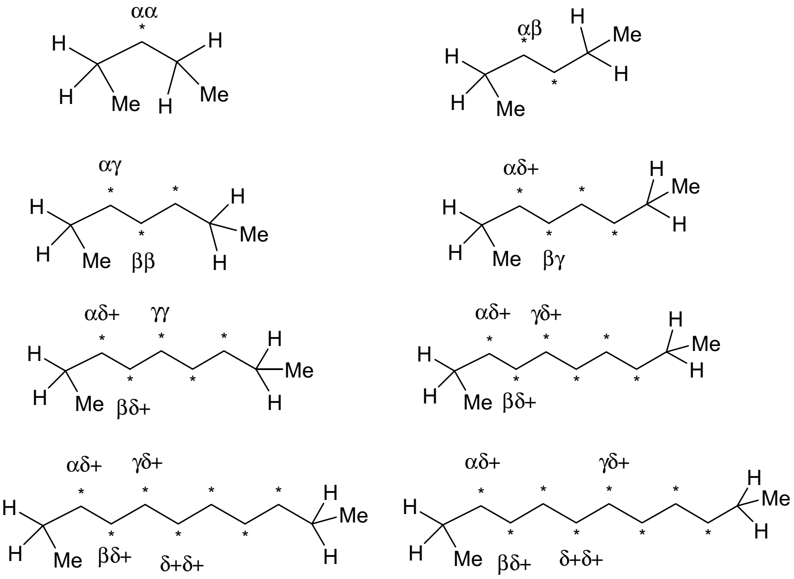


Fig. 5. Labels for methylene carbons in ^{13}C NMR spectra [16].

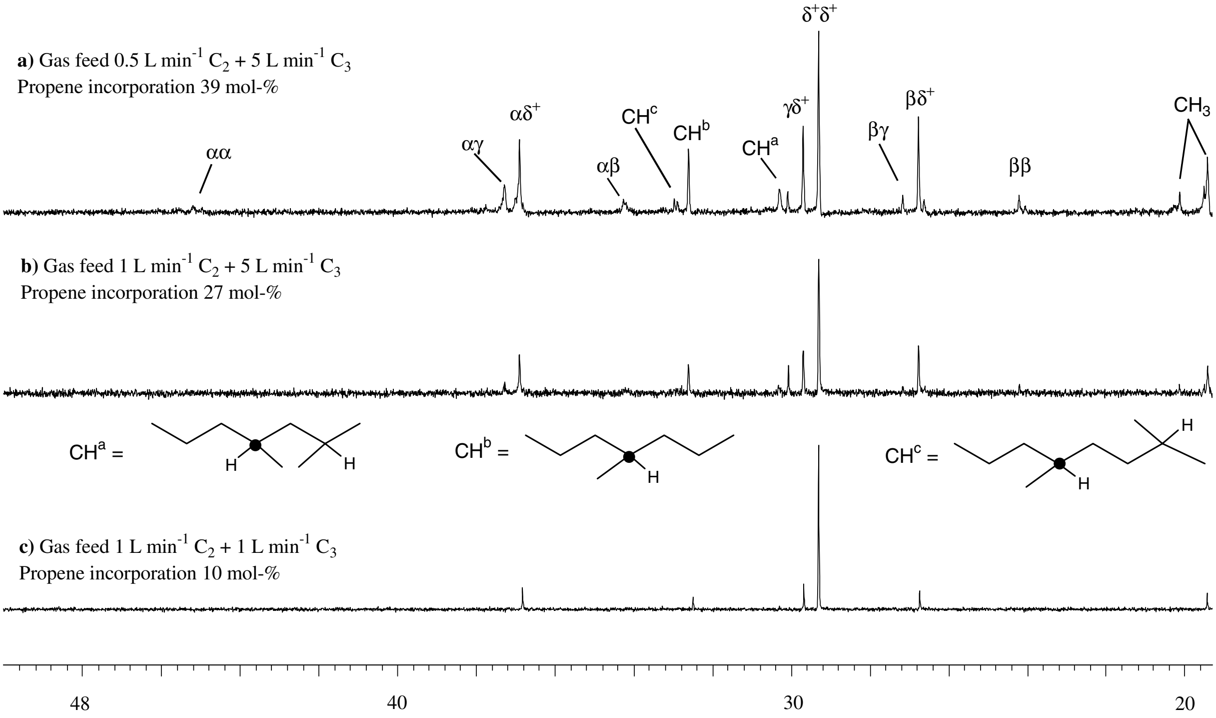


Fig. 6. ^{13}C NMR spectra of E-P copolymers prepared with catalyst **1b** MAO.

Table 3
E/P reactivity ratios for catalysts **1a**–**1c** for copolymers with a compositional range of 0–45 mol% P

Precatalyst	Fineman-Ross			Kelen-Tüdös		
	r_e	r_p	$r_e\ r_p$	r_e	r_p	$r_e r_p$
1a	14.9	~0	~0	17.1	~0	~0
1b	50.6	0.01	~0	46.4	0.01	~0
1c	32.4	~0	~0	35.2	~0	~0

Fineman-Ross and Kelen-Tüdös statistical methods. The results are summarised in Table 3. Excellent agreement between the two methods was observed. All three catalysts show $r_e \gg r_p$, indicative of very high concentrations of isolated propylene units [21].

According to ^{13}C NMR statistical analysis (Carman method) of ethylene/propylene copolymers made using precatalyst **1b** with MAO, at 20 °C and gas feed ratios of 5 L min^{-1} of P and 0.5 L min^{-1} of E, propylene insertion with 1,2-regiochemistry was most favourable. 82 mol% of the propylene was inserted in 1,2-fashion mechanism, leaving 18% of the propylene units inserted *via* a regio-inversion (2,1 insertion) mechanism. Such behaviour is again similar to vanadium catalysts [20]. Sterically unfavourable head-to-head contacts were not detected by ^{13}C NMR spectroscopy (detection limit <0.3 mol%). The C_2 symmetric titanium bis(salicylaldiminato) catalyst **Aa** activated with MAO homo-polymerises propylene in syndiotactic fashion *via* a chain-end controlled mechanism with 2,1-regio-insertions [16]. However, when ethylene is added to the process the propylene regio-insertions become mainly 1,2 which is very similar to what is observed here for **1b**.

5. Conclusions

Titanium $(N,N^-)(N,O^-)$ mixed-ligand complexes of type **1** activated with MAO provide highly active catalysts for the homopolymerisation of ethylene and for ethylene/propylene copolymerisations. The ethylene homopolymerisation activity was found to be higher or comparable to either of the $Ti(N,O^-)_2$ and $Ti(N,N^-)_2$ parent complexes **A** and **B**. The *N*-phenyl iminopyrrolato complex **1a** showed the highest productivity for ethylene polymerisation, while changing this substituent for cyclohexyl or ethyl reduced productivity. In ethylene–propylene copolymerisations the sterically more open mixed-ligand systems show significantly enhanced comonomer incorporation accompanied by high activities and molecular weights, compared to **A**, **B** or Cp_2TiCl_2/MAO. ^{13}C NMR analysis showed that propylene is incorporated predominantly with 1,2-regiochemistry, although ca. 20% of P units show regio-inversion (2,1). The reactivity ratios indicate a predominance of isolated P units, and a tendency towards an alternating structure at high P content.

6. Experimental

6.1. General

Syntheses were carried out under nitrogen using standard Schlenk line techniques. Solvents were distilled from sodium–benzophenone (diethyl ether, THF), sodium (toluene), sodium–potassium alloy (light petroleum, b.p 40–60 °C), or CaH_2(dichloromethane). NMR solvents ($CDCl_3$, CD_2Cl_2, C_6D_6) were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded using Bruker DPX-300 spectrometer and Bruker Avance DRX-400 spectrometers with a 5 mm BBO probe. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C), ^{19}F is relative to $CFCl_3$. Nitrogen, ethylene and propylene (BOC) were purified by passing through columns of supported P_2O_5, with moisture indicator, and activated 4 Å molecular sieves. Gel permeation chromatography GPC analyses were performed by RAPRA Technology Ltd on a Polymer Laboratories PL-GPC 220 instrument equipped with two PLgel 7.5 Å MIXED B columns and calibrated with polystyrene standards. Elemental analyses were performed by London Metropolitan University. The ligands $HO(2\text{-}^tBu)C_6H_3\text{-}6\text{-}CH{=}NC_6F_5$, $C_6H_5N{=}CH\text{-}2\text{-}C_4H_3NH$ and $C_6H_{11}N{=}CH\text{-}2\text{-}C_4H_3NH$ were synthesised using standard literature procedures [22,23].

6.2. Synthesis of $C_2H_5N{=}CH\text{-}2\text{-}C_4H_3NH$

To pyrrole-2-carboxaldehyde (4.8 g, 50 mmol) was added a 70% solution of ethylamine in water (1.75 cm^3, 50 mmol). After addition of a few drops of glacial acetic acid the solution was vigorously stirred until the product precipitated. To the reaction mixture diethyl ether (40 cm^3) and a 6 N HCl (20 cm^3) solution was added at 0 °C. The organic phase was isolated, washed with saturated aqueous $NaHCO_3$ (50 cm^3), dried over $MgSO_4$ and then concentrated under vacuum to afford an orange solid. Recrystallisation from light petroleum at −25 °C gave large orange crystals (3.78 g, 35 mmol, 70%). ^1H NMR (300 MHz, 300 K, $CDCl_3$): δ 9.00 (s, 1H, C_4H_3NH), 8.07 (s, 1H, NC*H*Ar), 6.88 (br s, 1H, C_4H_3N), 6.47 (br s, 1H, C_4H_3N), 6.25–6.21 (br s, 1H, C_4H_3N), 3.59–3.51 (m, 2H, CH_2), 1.27–1.21 (m, 3H, CH_3).

6.3. Synthesis of $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(PhN{=}CHC_4H_3N)$ (**1a**)

In a modification of a literature procedure [10,11], to a stirred solution of $TiCl_3(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)$-(THF) (2.31 g, 5 mmol) in dichloromethane (15 cm^3) at −78 °C was slowly added by syringe a suspension of $K^+[PhN{=}CH(C_4H_3N]^-$ (1.04 g, 5 mmol) in dichloromethane (15 cm^3). The resulting solution was allowed to warm to room temperature and stirred for 6 h. The volatiles were removed under vacuum and the resulting red-black solid was extracted with diethyl ether (4×60 cm^3) and washed with light petroleum (6×25 cm^3). The resulting dark red solid was recrystallised from dichloromethane/light petroleum at −30 °C to give very dark red-black needle-shaped crystals (1.2 g, 40%). ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 8.41 (s, 1H, *CH*=N, FI), 7.75 (d, 1H, $J = 7.2$ Hz, Ar), 7.74 (s, 1H, *CH*=N, PI), 7.65 (d, 1H, $J = 7.7$ Hz, Ar), 7.34 (d, 1H, $J = 7.6$ Hz, Ar), 7.15–7.05 (m, 6H, Ar), 6.68 (d, 1H, $J = 7.6$ Hz, Ar), 6.15 (m, 1H, Ar), 1.34 (s, 9H, ^{t}Bu) (FI = phenoxy-imine, PI = pyrrole-imine). ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 174.4 (*C*=N), 160.9 (*C*=N, 156.8, 150.2, 144.4, 139.1, 137.8, 136.5, 134.6, 129.3, 127.1, 125.2, 124.0, 123.5, 122.9, 121.0, 34.1, 29.7. ^{19}F NMR (282.4 MHz, 300 K, CDCl$_3$): δ 141.0 (d, 1F, *o*-F), 149.3 (d, 1F, *o*-F), 157.1 (t, 1F, *p*-F), 161.5, (m, 1F, *m*-F), 162.6 (m, 1F, *m*-F). Anal. Calc.: C, 53.36; H, 3.52; N, 6.67; Cl, 11.25. Found: C, 53.14; H, 3.55; N, 6.65; Cl, 11.58%.

6.4. *Synthesis of* $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)\text{-}(C_6H_{11}N{=}CHC_4H_3N)$ *(**1b**)*

The complex was synthesised in an analogous way to **1a**, using the appropriate potassium iminopyrrolate salt. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 8.30 (s, 1H, *CH*=N, FI), 7.77 (s, 1H, *CH*=N, PI), 7.76 (d, 1H, $J = 7.9$ Hz, Ar), 7.58 (m, 1H, Ar), 7.36 (d, 1H, $J = 8.7$ Hz, Ar), 7.18 (t, 1H, $J = 8.6$ Hz, Ar), 6.46 (m, 1H, Ar), 6.01 (m, 1H, Ar), 3.74 (m, *cyclo*-hexyl *p*-H), 1.85 (s, 9H, ^{t}Bu), 1.76–1.34 (m, 11 H cyclo-hexyl). (FI = phenoxy-imine, PI = pyrrole imine). ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 174.4 (*C*=N), 170.0 (*C*=N), 155.5, 154.0, 142.8, 139.8, 139.5, 137.8, 136.4, 124.7, 125.1, 123.8, 118.1, 112.6, 65.3, 38.5, 35.7, 34.6, 33.9, 32.9, 31.6, 26.2, 25.8, 24.9. ^{19}F NMR (282.4 MHz, 300 K, CDCl$_3$): δ 142.0 (d, 1F, *o*-F), δ 149.6 (d, 1F, *o*-F), δ 157.6 (t, 1F, *p*-F), δ 161.5, (m, 1F, *m*-F), δ 163.3 (m, 1F, *m*-F). Anal. Calc.: C, 52.85; H, 4.44; N, 6.60. Found: C, 52.96; H, 4.42; N, 6.63%.

6.5. *Synthesis of* $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)\text{-}(EtN{=}CHC_4H_3N)$ *(**1c**)*

The complex was synthesised in an analogous way to **1a**, using the appropriate potassium iminopyrrolate salt. The product was isolated as very dark orange plate-like crystals suitable for X-ray diffraction. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 8.37 (s, 1H, *CH*=N, FI), 7.82 (dd, 1H, $J = 8.5$ Hz, Ar), 7.80 (s, 1H, *CH*=N, PI), 7.72 (m, 1H, Ar), 7.41 (m, 1H, Ar), 7.19 (t, 1H, $J = 7.0$ Hz, Ar), 6.47 (m, 1H, Ar), 6.07 (m, 1H, Ar), 3.70 (m, 2H, CH$_2$), 1.63 (s, 9H, ^{t}Bu), 1.25 (m, 3H, CH$_3$). (FI = phenoxy-imine, PI = pyrrole imine). ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 174.7, 161.0, 156.7, 150.2, 142.7, 139.6, 137.8, 137.5, 136.5, 134.9, 125.3, 124.0, 118.2, 112.3, 35.5, 30.1, 15.1. ^{19}F NMR (282.4 MHz, 300 K, CDCl$_3$): 139.9 (d, 1F, *o*-F), 152.1 (d, 1F, *o*-F), 157.2 (t, 1F, *p*-F), 161.4 (m, 1F, *m*-F), 163.1 (m, 1F, *m*-F). Anal. Calc.: C, 49.51; H, 3.81; N, 7.22. Found: C, 49.49; H, 3.90; N, 7.33%.

6.6. *Synthesis of* $ZrCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)\text{-}(C_6H_{11}N{=}CHC_4H_3N)$ *(**2b**)*

The complex was synthesised in an analogous way to **1a**, using the appropriate potassium iminopyrrolate salt and the zirconium mono(salicylaldiminato) complex as opposed to the titanium one. The product was isolated as large block-like orange crystals suitable for X-ray crystallography. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 8.31 (s, 1 H, *CH*=N, FI), 7.95 (s, 1H, *CH*=N, PI), 7.79 (d, 1H, $J = 6.0$ Hz, Ar), 7.29 (m, 1H, Ar), 7.26 (d, 1H, $J = 8.1$ Hz, Ar), 7.11 (t, 1H, $J = 7.8$ Hz, Ar), 6.54 (m, 1H, Ar), 6.04 (m, 1H, Ar), 3.44 (m, cyclohexyl *p*-H), 1.61 (s, 1H, ^{t}Bu), 1.22–0.96 (m, 11H, cyclohexyl). (FI = phenoxy-imine, PI = pyrrole imine). ^{19}F NMR (282.4 MHz, 300 K, CDCl$_3$): δ 143.0 (d, 1F, *o*-F), δ 149.6 (d, 1F, *o*-F), δ 157.5 (t, 1F, *p*-F), δ 162.0, (1F, *m*-F), δ 163.1 (1F, *m*-F). Anal. Calc.: C, 49.48; H, 4.15; N, 6.18. Found: C, 49.38; H, 4.10; N, 6.35%.

6.7. *Polymerisation of ethylene*

A solution of MAO in toluene (250 cm^3) was saturated with ethylene (1 bar), with vigorous stirring (1000 rpm). Polymerisation was initiated by charging a toluene (1 cm^3) solution of the appropriate pre-catalyst. After polymerisation had occurred methanol (3 cm^3) was added to terminate the run. The polymer was precipitated with methanol (300 cm^3) and aluminium residues were dissolved by further addition of 2 M HCl (5 cm^3). The polymer was separated by filtration and washed with methanol (100 cm^3), 2 M HCl (5 cm^3), water (20 cm^3) and then again methanol (10 cm^3). The resulting polymer was then dried in a vacuum oven at 60 °C to constant mass.

6.8. *Ethylene–propylene copolymerisations*

Runs were carried out in the same way as ethylene homopolymerisations, with the exception that an ethylene/propylene gas mix was varied using a dual gas flow meter.

6.9. *X-ray crystallography*

Intensity data for **1c** and **2b** were recorded on an Oxford Diffraction Xcalibur Sapphire 3 diffractometer equipped with a Spellman DF3 molybdenum sealed-tube source operating at −50 kV, and fitted with Enhance X-ray optics. Data for **1b** were collected on a Bruker SMART APEX2 CCD diffractometer at Daresbury SRS station 16.2smx. In all cases, crystals were mounted on glass fibres in perfluorinated polyether oil, and held in place by the nitrogen cold-stream of the instrument. Data collection and reduction were carried out using either CRYSALIS CCD and RED

Table 4
Crystal data for compounds **1b**, **1c** and **2b**

Compound	**1b**	**1c**	**2b**
Formula	$C_{28}H_{28}Cl_2F_5N_3OTi$	$C_{24}H_{22}Cl_2F_5N_3OTi$	$C_{28}H_{28}Cl_2F_5N_3OZr$
Formula weight	636.33	582.25	679.65
Crystal description	Colourless block	Orange plate	Yellow block
Crystal dimensions/mm	0.01 × 0.01 × 0.01	0.45 × 0.12 × 0.04	0.40 × 0.20 × 0.15
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	17.992(10)	7.6548(7)	18.507(2)
b/Å	12.198(6)	10.5818(18)	8.2301(8)
c/Å	14.103(7)	15.8130(19)	20.480(2)
α/°	90	94.628(12)	90
β/°	108.222(5)	95.744(9)	112.495(10)
γ/°	90	97.746(10)	90
V/Å^3	2940(3)	1257.0(3)	2882.1(5)
Z	4	2	4
T/K	120(2)	140(2)	180(1)
μ/mm^{-1}	0.531	0.613	0.627
θ range/°	3.8–29.7	3.5–34.1	3.4–25.0
Number of data collected	11,075	22,750	35,618
Number of unique data	4131	9016	5050
Number of 'observed' data	2060	3681	4077
R_{int}	0.1401	0.0739	0.0690
R_1 [$I > 2\sigma(I)$], R_1 (all data)	0.0728, 0.1681	0.0448, 0.1534	0.0556, 0.0695
wR_2 (all data)	0.1843	0.0779	0.0954

programs (**1c**, **2b**) [24] or APEX2 and SAINT (**1b**) [25]. Structure determination was by direct methods in SHELXS-97 [26], and refinement was by full-matrix least-squares methods using SHELXL-97 [26] within the WINGX program suite [27]. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were added using a riding model. The crystal and refinement data are collected in Table 4.

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Appendix A. Supplementary material

CCDC 641426, 641427 and 641428 contain the supplementary crystallographic data for **1b**, **1c** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.047.

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