

Transition-metal complexes of phenoxy-imine ligands modified with pendant imidazolium salts: Synthesis, characterisation and testing as ethylene polymerisation catalysts

Jennifer Houghton^a, Stevan Simonovic^a, Adrian C. Whitwood^a, Richard E. Douthwaite^{a,*},
Sónia A. Carabineiro^b, Jian-Chao Yuan^b, Maria M. Marques^b, Pedro T. Gomes^{b,*}

^a Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

^b Centro de Química Estrutural, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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Abstract

Reaction between 3-((1*R*,2*R*)-2-[[1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-meth-(*E*)-ylidene]-amino]-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1a**) or the derivative 3-((1*R*,2*R*)-2-[[1-(2-hydroxy-5-nitro-phenyl)-meth-(*E*)-ylidene]-amino]-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1b**) and metal halides $MCl_x \cdot yTHF$ ($M = Zr$, $x = 4$, $y = 2$; $M = V$, $x = y = 3$; $M = Cr$, $x = y = 3$), in THF, at $-78^\circ C$ gives the metal complexes of general formula $[MCl_x(\kappa^2-N,O-OC_6H_2R^1R^2C(H)=N-C_6H_{10}-Im)_2][Br]_2$ (where $M = Zr$, $x = 2$, $R^1 = R^2 = 'Bu$, **2**; $M = Zr$, $x = 2$, $R^1 = H$, $R^2 = NO_2$, **3**; $M = V$, $x = 1$, $R^1 = R^2 = 'Bu$, **4**; $M = Cr$, $x = 1$, $R^1 = R^2 = 'Bu$, **5**; $M = Fe$, $x = 0$, $R^1 = R^2 = 'Bu$, **6**; $Im = 1$ -isopropyl-4-phenyl-3*H*-imidazol-1-ium-3-yl). 1H and ^{13}C NMR spectroscopy of **2** and **3** indicate κ^2-N,O -ligand coordination via the phenoxy-imine moiety with pendant imidazolium salt that is corroborated by a single crystal structure of **6**. Compounds **2**, **3**, **4** and **5** were tested as precatalysts for ethylene polymerisation in the presence of methylaluminumoxane (MAO) cocatalyst, showing low activity. Selected polymer samples were characterised by GPC showing multimodal molecular weight distributions.

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1. Introduction

Group 4 metallocenes and related compounds have been employed, for nearly two decades, as catalysts for α -olefin polymerisation [1] giving homo- and copolymers that could not previously be obtained using traditional heterogeneous Ziegler–Natta catalysts [2]. Recent advances in the design of transition-metal complexes have led to the discovery of several highly active non-metallocene α -olefin polymerisation catalysts [3], among which are the aluminium-free

nickel catalytic systems bearing phenoxy-imine [O^-,N] ligands [4].

Recently, as a result of systematic ligand design, Fujita and co-workers explored a new family of early-transition metal complexes (FI catalysts) containing a pair of non-symmetric phenoxy-imine ligands (Fig. 1), which are very active catalysts for α -olefin polymerisation [5–11]. Depending on the ligand design, the catalysts showed different behaviours in ethylene and propylene polymerisation, and the ligands strongly influenced catalyst parameters such as activity, polymerisation mechanism, and polymer properties including molecular weight and morphology [5]. Furthermore, FI catalysts are tolerant to a range of cocatalysts [11] and some systems are able to mediate α -olefin living polymerisation [5,9,12–17].

* Corresponding authors.

E-mail addresses: red4@york.ac.uk (R.E. Douthwaite), pedro.t.gomes@ist.utl.pt (P.T. Gomes).

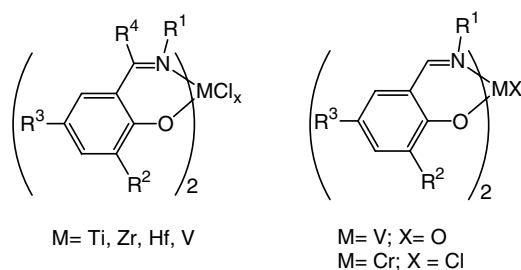


Fig. 1. Fujita's FI catalysts.

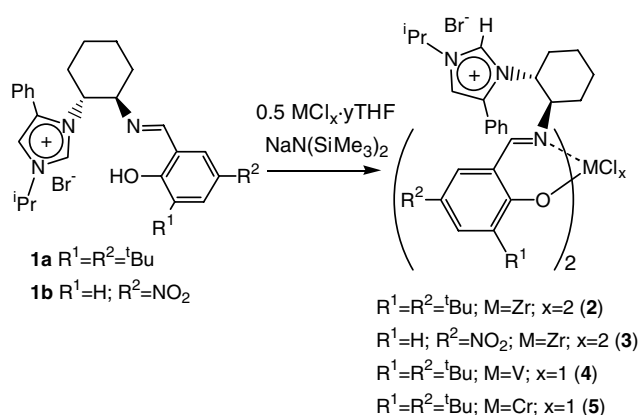
Bochmann [18], Cavallo [19], Coates [20], Pellecchia [21], Weiser [22] and others [23] have also contributed significantly to the further development of FI catalysts and related complexes, and provided useful information about the catalytic mechanism.

Here we report the synthesis and characterisation of new zirconium, vanadium and chromium complexes with modified phenoxy-imine chiral ligands containing pendant imidazolium bromide moieties and tested their activity as catalyst precursors for the polymerisation of ethylene in the presence of methylaluminoxane (MAO). The ligands used in this study are derived from compounds previously reported for the synthesis of N-heterocyclic carbenes (NHCs) that are typically prepared from imidazolium salts [24]. However, the versatility of the synthetic routes to these compounds allows other complex chemistry to be studied and our motivation for this work was to examine the effect of a pendant imidazolium salt on potential polymerisation precatalysts.

2. Results and discussion

2.1. Complex synthesis and characterisation

Reaction between 2 equiv. of 3-((1*R*,2*R*)-2-([1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-meth-(*E*)-ylidene]-amino)-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1a**) or 3-((1*R*,2*R*)-2-([1-(2-hydroxy-5-nitro-phenyl)-meth-(*E*)-ylidene]-amino)-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1b**), 2 equiv. of Na[N(SiMe₃)₂] and metal halide MCl_x · yTHF (where M = Zr, x = 4, y = 2; M = V, x = y = 3; M = Cr, x = y = 3) in tetrahydrofuran at –78 °C gave complexes **2–5** in high yield (Fig. 2). Attempts were also made to prepare complexes incorporating one phenoxy-imine ligand, however in all cases the only isolated complexes in variable yield were those shown in Fig. 2. Modifying the reagent concentration, order of addition, solvent, temperature and attempts at comproportionation gave similar results. ¹H and ¹³C NMR spectroscopy of **2** and **3** show signals that are consistent with the proposed formulation although the stereochemistry at the zirconium atom could not be unequivocally determined. However, for group 4 complexes incorporating bis-phenoxyimine dihalide ligands, *cis*-halide isomers are invariably observed and numerous examples have been structurally characterised by X-ray diffraction [15,20b,25–32]. DFT calculations

Fig. 2. Synthesis of complexes **2–5**.

support experimental evidence where the most stable isomer observed in the solid state typically exhibits *trans*-O, *cis*-N, coordination [8].

Complexes **2** and **3** exhibit similar spectra apart from the different signals attributable to the phenoxy-imine moiety. The number of observed signals indicates a single ligand environment and that significant halide exchange at zirconium does not occur during reaction. For example, for **2**, characteristic signals in the NMR spectra include imidazolium NC(H)N and NC(H)N at δ 9.00 and 131.2 in the ¹H and ¹³C NMR spectra, respectively, that do not differ significantly from **1a**. Additional evidence that imidazolium deprotonation has not occurred is provided by the diastereotopic methyl groups of the ^tPr imidazolium substituent. In related work we have found that deprotonation of the imidazolium moiety to give NHC complexes results in a significant chemical shift difference in the ¹H NMR spectrum, whereas for parent imidazolium salts the signals are barely differentiated [24]. Indeed for complexes **2** and **3** no chemical shift difference is observed. However, chemical shift differences of ca. δ 0.5 and 4 are observed for imine CH and CH signals indicative of imine nitrogen atom coordination. In addition, the phenolic OH signal observed at ca. δ 13 for **1a** and **1b** is absent in the ¹H NMR spectra of **2** and **3**.

NMR spectra of paramagnetic complexes **4** and **5** could not be determined although intense colour changes during preparation indicate reaction and elemental analysis supports the composition formulation. However, it should be noted that, for all compounds, CHN analysis gave results that are consistently low. Extractions of complexes **2–5** repeatedly give some water-soluble residue that is consistent with incorporation of salt byproduct into the product. This observation is perhaps not surprising given the ionic formulation of **2–5** and that ionic liquids based on imidazolium salts are known to be excellent solvents for a range of organic and inorganic materials [33].

In common with all the complexes in this study, electrospray mass spectrometry showed the largest signal consistent with the imidazolium–phenoxy-imine ligand. However, significant peaks (>25%) could be observed cor-

responding to metal complex species consistent with the proposed formulation, although for complexes **2**, **3** and **6** (vide infra) analogous peaks of significant intensity (>10%) were not observed and only a signal attributable to $[\mathbf{1b}-\text{Br}]^+$ was seen. Crystals of complexes **2–5** could be grown, however poor quality and weak diffraction prevented structural solution and elemental analysis indicated significant solvent inclusion.

Problems in obtaining structural evidence for complexes **2–5** prompted us to explore other metal complex derivatives of **1a** and reaction between 2 equiv. of **1a** and $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (Fig. 3) gave a red-orange powder that could be recrystallised from dioxane and hexane to give single crystals of **6**.

In contrast to complexes **2–5**, crystal quality was sufficient to obtain a structural solution (Fig. 4). Significant disorder in bromide position and orientation of hydrocarbyl substituents is observed, which resulted in problematic refinement, however the coordination and structural motifs present in the solid state structure of **6** can be identified. Selected bond distances (Å) and angles (°) are listed in Table 1. The asymmetric unit contains 2 equiv. of **6** where the cations primarily differ only in the orientation of hydro-

Table 1

Selected bond distances (Å) and angles (°) of complex **6** for cation containing Fe(1)

Distance (Å)	
Fe(1)–O(1)	1.905(8)
Fe(1)–N(3)	2.059(9)
O(1)–C(16)	1.310(14)
C(10)–N(3)	1.314(14)
C(11)–C(10)	1.425(17)
Fe(1)–O(2)	1.911(8)
Fe(1)–N(6)	2.077(10)
O(2)–C(49)	1.313(15)
C(43)–N(6)	1.267(15)
C(44)–C(43)	1.476(18)
Angle (°)	
N(6)–Fe(1)–O(2)	91.3(4)
N(3)–Fe(1)–O(1)	91.3(4)
N(6)–Fe(1)–O(1)	119.2(4)
N(3)–Fe(1)–O(2)	118.2(4)
Fe(1)–O(1)–C(16)	127.9(8)
O(1)–C(16)–C(11)	123.5(11)
C(16)–C(11)–C(10)	125.3(11)
C(11)–C(10)–N(3)	125.4(11)
C(10)–N(3)–Fe(1)	122.4(8)
O(1)–Fe(1)–O(2)	128.4(4)
N(3)–Fe(1)–N(6)	109.6(4)

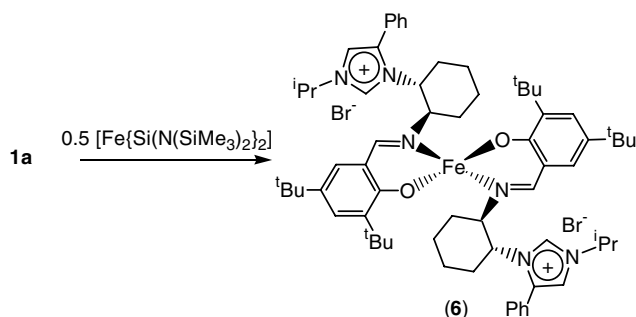
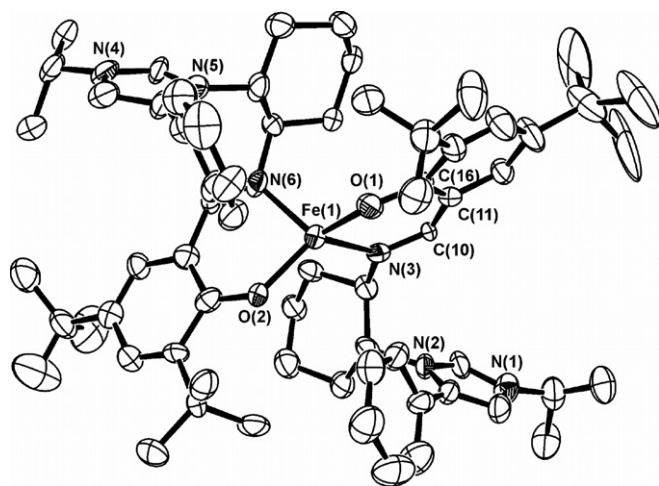
Fig. 3. Synthesis of complex **6**.

Fig. 4. Molecular structure of a cation moiety of **6**. Anions and hydrogen atoms have been removed for clarity. Thermal displacement parameters at 30% probability.

carbyl substituents but significant anion disorder is present over four of seven refined locations. The geometry about an iron atom is close to tetrahedral where, for example at Fe(1), the ligand bite angles N–Fe(1)–O are both 91.3(4)° and the acute dihedral angle between the two planes subtended at the iron atom is 88.7(8)°. The six-membered rings formed by the bidentate phenoxy-imine ligands and the Fe atom are nearly planar, where for example the six internal angles of Fe(1)–O(1)–C(16)–C(11)–C(10)–N(3) = 716°. Bond lengths Fe(1)–O(1) = 1.905(8), Fe(1)–O(2) = 1.911(8), Fe(1)–N(3) = 2.059(9), and Fe(1)–N(6) = 2.077(10) do not indicate significant distortion in the primary coordination sphere, however the imine bonds C(10)–N(3) = 1.314(14) Å and C(43)–N(6) = 1.267(15) Å suggest some distortion at the ligand periphery. Bond lengths and angles at the metal are similar to those found in two iron complexes previously reported that contain only two phenoxy-imine ligands in the primary coordination sphere [34].

2.2. Polymerisation tests

Complexes **2–5**, in the presence of methylaluminoxane (MAO), are active as catalysts for ethylene polymerisation. Except for the system **3**/MAO that was only tested in a limited number of experiments, an experimental matrix encompassing time, temperature, catalyst concentration, and cocatalyst/catalyst ratio was applied in an attempt to determine critical factors and characteristics of polymerisation reactions (Table S1 supplementary information). Table 2 lists data for selected catalytic reactions. According to the activity rating scheme suggested by Gibson et al. [3b], these results are indicative of low activity (essentially

Table 2
Ethylene polymerisation catalysed by **2–5**

Run	Cat ^a (μmol)	[Al]/[cat]	T (°C)	t (h)	Yield (mg)	Activity (kg/(mol-cat h bar))
1	[2] 10	500	0	2	140	3.50
2	[2] 10	500	22	2	154	3.85
3	[2] 10	500	50	2	127	3.18
4	[2] 10	500	75	2	88	2.20
5	[2] 10	250	22	2	116	2.90
6	[2] 10	1000	22	2	82	2.05
7	[2] 10	500	22	0.25	16	3.20
8	[2] 10	500	22	0.5	35	3.51
9	[2] 10	500	22	1	72	3.60
10	[3] 3.6	1200	25	0.67	16	2.35
11	[3] 3.6	1200	50	0.67	32	4.87
12	[3] 3.6	1200	75	0.67	28	4.25
13	[4] 10	500	0	2	39	0.98
14	[4] 10	500	22	2	72	1.80
15	[4] 10	500	50	2	52	1.30
16	[4] 10	500	75	2	7	0.18
17	[4] 10	250	22	2	52	1.30
18	[4] 10	1000	22	2	46	1.15
19	[4] 10	500	22	0.25	31	6.20
20	[4] 10	500	22	0.5	40	4.00
21	[5] 10	500	0	2	38	0.95
22	[5] 10	500	22	2	45	1.13
23	[5] 10	500	50	2	9	0.23
24	[5] 10	500	75	2	Traces	~0
25	[5] 10	250	22	2	43	1.08
26	[5] 10	1000	22	2	24	0.60

^a Catalyst loading. Reactions were conducted in 50 mL toluene with an ethylene overpressure of 2 bar for **2**, **4** and **5**, and 2.8 bar for **3**.

1–6 kg/(mol-cat h bar)), whereas the values reported by Fujita et al. for analogous catalytic systems represented in Fig. 1 can exhibit very high activity, typically 5×10^5 (Zr), 4×10^3 (V) and 10^3 kg/(mol-cat h bar) (Cr), at 25 °C [8].

Of the complexes studied here, the zirconium precatalysts **2** and **3**/MAO are generally the most active at all temperatures and [Al]/[cat] ratios studied, followed by the vanadium and chromium systems respectively (e.g. runs 2, 14 and 22). Except for precatalyst **3**, the best activities were observed at ca. 22 °C and an [Al]/[cat] = 500 (runs 2, 19 and 22), with essentially no activity observed for **4** and **5** above 80 °C (runs 16 and 24).

Selected polyethylene samples were analysed by gel permeation/size exclusion chromatography (GPC/SEC) (Table 3). Additional characterisation by ¹H and ¹³C NMR spectroscopy showed linear microstructures, with a single characteristic CH₂ resonance observed at ca. δ 30 in the ¹³C NMR spectra [35].

At 22 °C, precatalysts **2** and **3** give rise to a narrow monomodal distribution of an oligomeric polyethylene fraction ($M_n = 390$ –450) and an extremely broad and multimodal higher molecular weight fraction that are essentially invariant with the reaction time (runs 1 and 7–9; Fig. S6a, supplementary information). When the reaction temperature increases from 0 to 75 °C (runs 1–4), there is a decrease in the low molecular weight fraction and a concomitant increase of the higher fraction. A similar

Table 3
Polyethylene molecular weight characteristics obtained by GPC/SEC

Run ^a	Cat	$M_w \times 10^{-3}$ ^b	M_w/M_n ^b	Area (%) ^c
1	2	0.54	1.3	62
		171	270	38
2	2	0.55	1.3	59
		223	300	41
3	2	0.45	1.3	12
		284	110	88
4	2	0.60	1.3	4
		341	50	96
7	2	0.59	1.4	44
		158	180	56
8	2	0.52	1.3	59
		123	190	41
9	2	0.51	1.3	63
		160	240	37
11	3	0.63	1.3	8
		692	140	92
13	4	1060	19	
14	4	904	13	
15	4	966	6.2	
21	5	367	57	
22	5	307	55	
25	5	319	44	

^a Runs from Table 2.

^b For runs 1–11, details are given for the lower and higher molecular weight distributions.

^c Peak area percentage of low and high molecular weight distributions from the GPC/SEC chromatograms.

molecular weight distribution is observed for precatalyst **3** at 50 °C (run 11). Precatalyst **4** gives significantly less low molecular weight product (runs 13–15; Fig. S7, supplementary information) and a multimodal distribution with the M_n approximately invariant with the reaction temperature. In contrast, for **5** a wide multimodal distribution is observed (runs 21 and 22; Fig. S8, supplementary information), that is also insensitive to reaction temperature.

The trend in molecular weight is reflected in the FI catalysts with ca. $M_v = 10^4$ (Zr), 10^5 (Cr) and 6×10^5 (V) respectively [8], however in contrast to the results shown here, monomodal distributions are observed. Clearly **2–5** either upon reaction with MAO, or inherent instability of intermediates, give molecular weight distributions indicative of multiple catalytic species. One possibility is that in the presence of MAO deprotonation of the imidazolium moiety to an NHC is likely to form an aluminium adduct

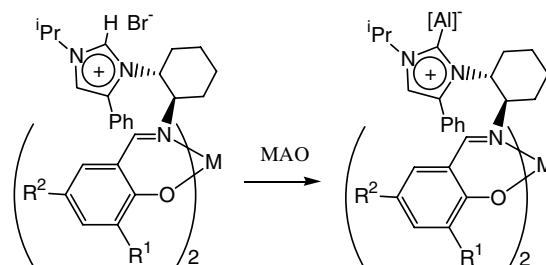


Fig. 5. Potential phenoxymine–aluminum motif.

analogous to those isolated from reaction between an NHC and trialkylaluminium compounds [36], giving transition metal complexes containing an imidazolium–aluminate zwitterion substituent (Fig. 5).

However, further work is required to examine the reactivity of the pendant imidazolium moiety in complexes such as 2–6.

3. Conclusions

Early metal complexes incorporating chiral phenoxy-imine ligands with pendant imidazolium salt moieties can be prepared. Complexes containing two phenoxy-imine ligand moieties are kinetically and probably thermodynamically stable in comparison to complexes containing one phenoxy-imine ligand. A screening study examining complexes 2–5 as precatalysts shows that in these complexes pendant imidazolium salts appear not to be beneficial giving low activity and multimodal molecular weight distributions.

4. Experimental

4.1. General procedures

All manipulations were performed under argon using standard Schlenk techniques or in a glove-box (MBraun) under nitrogen unless stated otherwise. Solvents were dried over the appropriate drying agent and distilled under nitrogen: sodium benzophenone ketyl (tetrahydrofuran, diethyl ether, toluene, *n*-hexane), calcium hydride (acetonitrile, benzene, dichloromethane) [37]. Unless stated, all reagents were purchased from Acros, Aldrich, Avocado or Lancaster and used as supplied. Potassium carbonate (K₂CO₃) sodium carbonate (Na₂CO₃) and magnesium sulphate (MgSO₄) were purchased in their anhydrous form and dried at least 24 h at 120 °C before use. Transition metal precursors ZrCl₄ · 2THF [38], VCl₃ · 3THF [39], CrCl₃ · 3THF [40], [Fe{N(Si(CH₃)₃)₂}₂] [41], were prepared using literature procedures. Compounds 1a–b were prepared using a modified literature procedure [24]. Flash chromatography was performed according to the method of Still et al. using Fluka Silica gel 60 (35–70 μm mesh) [42]. Analytical thin layer chromatography was carried out on 0.25 mm precoated silica gel plates (Merck, Silica gel 60 F₂₅₄, aluminium backing) and compounds were visualized using UV fluorescence. NMR spectra were recorded on a Jeol EX 270 (¹H, 270 MHz; ¹³C, 67.9 MHz) at probe temperature. Chemical shifts are described in parts per million (ppm) downfield shift from Si(CH₃)₄ and are reported consecutively as position (δH or δC), relative integral, multiplicity (s = singlet, d = doublet, sep = septet, m = multiplet), coupling constant (*J*/Hz) and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals (C₄D₇HO δ 1.73 and CD₂H₂CN δ 1.94). Carbon spectra were referenced to a ¹³C resonance of the solvent (C₄D₈O δ 24.4 and CD₃CN δ 118.26). ¹³C{¹H},

HSQC, PENDANT, DEPT and Gradient HMBC experiments were performed using standard Bruker pulse sequences. Fast Atom Bombardment (FAB+) mass spectra were recorded on a Micromass Autospec spectrometer, using 3-nitrobenzyl alcohol as the matrix. Electrospray ionisation (ESI) mass spectra were recorded on a Micromass LCT using dichloromethane as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Elemental Analyses were performed at the University of North London or University of Manchester.

4.2. Syntheses of complexes

4.2.1. Zirconium dichloro-bis-[3-((1*R*,2*R*)-2-{[1-(3,5-Di-*tert*-butyl-2-*oxy*-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide], [ZrCl₂(κ²-*N*,*O*-OC₆H₂-3,5-^{*t*}Bu₂-C(*H*)=N-C₆H₁₀-Im)₂][Br]₂ (2)

At –78 °C a tetrahydrofuran (10 mL) solution of sodium bis(trimethylsilylamide) (157 mg, 0.86 mmol) was added dropwise to a tetrahydrofuran (30 mL) solution of 1a (500 mg, 0.86 mmol), and stirred for 30 min and subsequently added dropwise to a tetrahydrofuran (10 mL) suspension of ZrCl₄ · 2THF (162 mg, 0.43 mmol) cooled to –78 °C. The mixture was allowed to warm to 25 °C, and the reaction stirred for a further 2 h. The mixture was filtered through a Celite plug and the volatiles removed from the filtrate to give a yellow solid that was washed with hexane (2 × 10 mL) to give 2 as a pale yellow powder. Yield: 478 mg, 84%. ¹H NMR (CD₃CN, 270 MHz): δ 1.29 (9H s, C(CH₃)₃), 1.40 (9H, s, C(CH₃)₃), 1.59 (6H, d, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 1.10–2.50 (8H, m, ^{*c*}-hexCH₂), 4.65 (1H, sep, ³J_{H-H} = 6.7 Hz, CH(CH₃)₂), 4.67 (1H, m, ^{*c*}-hexCHN_{imid}), 5.26 (1H, m, ^{*c*}-hexCHN_{imine}), 6.65 (1H, s, NCHC), 7.19–7.86 (8H, m, ^{Ph}CH + imineCH), 9.00 (1H, s, NCHN). ¹³C{¹H} NMR (CD₃CN, 67.9 MHz): δ 21.2, 21.8 (CH(CH₃)₂), 25.0, 25.2 (^{*c*}-hexCH₂), 28.7, 30.5 (C(CH₃)₃), 33.9, 34.1 (^{*c*}-hexCH₂), 34.5, 34.6 (C(CH₃)₃), 53.6 (CH(CH₃)₂), 57.9 (^{*c*}-hexCHN_{imid}), 67.2 (^{*c*}-hexCHN_{imine}), 117.9 (NCHC), 123.4, 125.2 (C_{ipso}), 129.4, 129.6, 130.0, 130.1, 130.3, (PhCH), 131.2 (NCHN), 134.0, 134.9, 137.6 (C_{ipso}), 156.2 (OC_{ipso}), 169.0 (imineCH). MS (ESI); *m/z*: 500 [1a-Br]⁺ (100%). Anal. Calc. for C₆₆H₉₀Br₂Cl₂N₆O₂Zr: C, 59.99; H, 6.86; N, 6.36. Found: C, 58.07; H, 6.62; N, 6.25%.

4.2.2. Zirconium dichloro-bis-[3-((1*R*,2*R*)-2-{[1-(2-*oxy*-5-*nitro*-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide], [ZrCl₂(κ²-*N*,*O*-OC₆H₃-5-NO₂-C(*H*)=N-C₆H₁₀-Im)₂][Br]₂ (3)

Complex 3 was prepared via an analogous method to 2 using 1b (500 mg, 0.97 mmol), sodium bis(trimethylsilylamide) (178 mg, 0.97 mmol) and ZrCl₄ · 2THF (183 mg, 0.48 mmol) to give 3 as a yellow powder. Yield: 523 mg, 83%. ¹H NMR (d₈THF, 270 MHz): δ 1.38 (6H, d, ³J_{H-H} =

6.7 Hz, CH(CH₃)₂), 1.28–2.71 (8H, m, ^{c-hex}CH₂), 4.65 (1H, sep, ³J_{H-H} = 6.7 Hz, CH(CH₃)₂), 4.67 (1H, m, ^{c-hex}CHN_{imid}), 5.37 (1H, m, ^{c-hex}CHN_{imine}), 6.64 (1H, d, ³J_{H-H} = 9.2 Hz, ^{OC}CH_{CH}), 7.29–7.87 (8H, m, NCHC + ^{Ar}CH + ^{imine}CH), 8.15 (1H, d, ³J_{H-H} = 9.2 Hz, ^{ON}CH_{CH}) 9.52 (1H, s, NCHN). ¹³C{¹H} NMR (d₈THF, 67.9 MHz): δ 22.4, 23.2 (CH(CH₃)₂), 25.1, 25.6, 35.4, 36.0 (^{c-hex}CH₂), 54.7 (CH(CH₃)₂), 59.4 (^{c-hex}CHN_{imid}), 68.9 (^{c-hex}CHN_{imine}), 119.0 (NCHC), 121.0 (^{Ph}CH), 123.7, 127.0 (*C*_{ipso}), 129.0, 129.1, 130.5, 131.6, 132.4 (^{Ph}CH), 135.8 (NCHN), 136.4, 139.1 (*C*_{ipso}), 166.9 (^{imine}CH), 168.6 (*OC*_{ipso}). MS (ESI); *m/z*: 500 [1a–Br]⁺ (100%). Anal. Calc. for C₅₀H₅₆Br₂Cl₂N₈O₆Zr: C, 50.59; H, 4.76; N, 9.44. Found: C, 49.21; H, 4.56; N, 9.09%.

4.2.3. Vanadium chloro-bis-[3-((1*R*,2*R*)-2-{[1-(3,5-di-tert-butyl-2-oxy-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide], [VCl(κ²-N,O-OC₆H₂-3,5-^tBu₂-C(H)=N-C₆H₁₀-Im)₂][Br]₂ (4)

Complex **4** was prepared via an analogous method to **2** using **1a** (500 mg, 0.86 mmol), sodium bis(trimethylsilylamide) (316 mg, 1.72 mmol) and VCl₃·3THF (160 mg, 0.43 mmol) to give **4** as a dark red powder. Yield: 491 mg, 92%. MS (ESI); *m/z*: 500 [1a–Br]⁺ (100%), 1132 [M–BrCl]⁺ (35%). Anal. Calc. for C₆₆H₉₀Br₂ClN₆O₂V: C, 63.64; H, 7.28; N, 6.75. Found: C, 62.90; H, 7.12; N, 6.47%.

4.2.4. Chromium chloro-bis-[3-((1*R*,2*R*)-2-{[1-(3,5-di-tert-butyl-2-oxy-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide], [CrCl(κ²-N,O-OC₆H₂-3,5-^tBu₂-C(H)=N-C₆H₁₀-Im)₂][Br]₂ (5)

Complex **5** was prepared via an analogous method to **2** using **1a** (500 mg, 0.86 mmol), sodium bis(trimethylsilylamide) (316 mg, 1.72 mmol) and CrCl₃·3THF (162 mg, 0.43 mmol) to give **5** as a dark green powder. Yield: 433 mg, 81%. MS (ESI); *m/z*: 500 [1a–Br]⁺ (100%), 1122 [M–2Br+Cl]⁺ (25%). Anal. Calc. for C₆₆H₉₀Br₂ClCrN₆O₂: C, 63.58; H, 7.28; N, 6.74. Found: C, 61.79; H, 7.02; N, 6.50%.

4.2.5. Iron-bis-[3-((1*R*,2*R*)-2-{[1-(3,5-di-tert-butyl-2-oxy-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide], [Fe(κ²-N,O-OC₆H₂-3,5-^tBu₂-C(H)=N-C₆H₁₀-Im)₂][Br]₂ (6)

At –78 °C a tetrahydrofuran suspension (30 mL) of **1a** (300 mg, 0.52 mmol) was added dropwise to a tetrahydrofuran solution (30 mL) of [Fe(N(Si(CH₃)₃)₂)₂] (82 mg, 0.22 mmol) precooled to –78 °C and the mixture allowed to warm with stirring to 25 °C over 12 h. The mixture was filtered through a Celite plug and the volatiles removed from the filtrate to give a red-orange solid that was washed with hexane (2 × 10 mL) to give **6** as an orange powder. Yield: 256 mg, 93%. Attempts at elemental analysis of single crystalline **6** did not give repeatable satisfactory results. MS (ESI); *m/z*: 500 [1a–Br]⁺ (100%).

4.3. Crystallographic details

Single crystals of **6** were grown from a 1,4-dioxane and hexane solution cooled to –40 °C. Crystals were mounted on a glass fiber with STP oil and immediately cooled to 110 K in a dinitrogen gas stream on the diffractometer. Data was collected on a Bruker Smart 6000 diffractometer equipped with a molybdenum source with a CCD detector. Structures were solved and refined by full-matrix least squares on *F*² using SHELX programs [43]. *Crystal data* for **6**: C₆₀H₉₀N₆O₂Br₂Fe, dimensions 0.20 × 0.20 × 0.015 mm, *M*_r = 1215.11, cubic *I*23, *a* = *b* = *c* = 46.3083(9) Å, α = β = γ = 90°, *V* = 99306(3) Å³, *Z* = 48, λ(Mo Kα) = 0.71073 Å, ρ_{calc} = 0.975 g cm^{–3}, *T* = 100(2) K, *F*(000) = 30,723, θ range for data collection 0.62–20.01°, limiting indices –44 ≤ *h* ≤ 44, –44 ≤ *k* ≤ 44, –44 ≤ *l* ≤ 44, 15,406/12,725 collected/unique reflections (*R*_{int} = 0.0988), absolute structure parameter –0.016(15), goodness of fit on *F*² = 1.291, Δρ_{max/min} = 1.512/–0.688 e Å^{–3}, final *R* indices (*I* > 2σ(*I*)) *R*₁ = 0.0945, *wR*₂ = 0.2585.

4.4. Polymerisation details

Polymerisations were carried out in 250 mL crown capped pressure bottles sealed with neoprene septum and pump filled with nitrogen atmosphere (the bottles were previously dried in the oven at 140 °C for several days). Fifty mL of (freshly distilled, dried over Na/K alloy) toluene were added to each polymerisation bottle and the resulting solvent was then saturated at a monomer relative pressure of 2 bar, which was maintained throughout the polymerisation reactions. Then the co-catalyst (MAO) was added in the proper Al/metal ratio via a glass syringe. Solutions were then brought to the desired temperatures (0, 22, 50 or 75 °C) and allowed to equilibrate for 15 min. After this, the corresponding amount of a toluene solution of the desired catalyst was added to the polymerisation reactors with a glass syringe. The polymerisations were terminated after 15, 30, 60 or 120 min by quenching the mixture with 150 mL of an acidic methanol (1% HCl) solution. The obtained polymers were then filtered, washed several times with methanol and dried in a vacuum oven at 60 °C for 3 days.

Molecular weight distributions of selected polyethylene samples were analysed at RAPRA Technology, Shrewsbury, UK, using a Polymer Laboratories GPC220 Instrument gel permeation chromatography apparatus, equipped with PLgel guard plus 2 × mixed bed-B columns (30 cm, 10 μm), using 1,2,4-trichlorobenzene with anti-oxidant as a solvent and a flow-rate of 1.0 mL/min (nominal) at 160 °C (nominal). Differential refractometer and differential pressure viscometer online detectors were used, the GPC system being calibrated with polystyrene standards. The resulting calibration curve was corrected to polyethylene values by the application of the corresponding viscometric Mark–Howink–Sakurada parameters.

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Appendix A. Supplementary material

CCDC 662969 contains the supplementary crystallographic data for **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.060](https://doi.org/10.1016/j.jorganchem.2007.11.060).

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