DALTON
FULL PAPER

Synthesis and reactivity of sterically hindered iminopyrrolato complexes of zirconium, iron, cobalt and nickel

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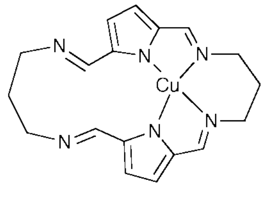
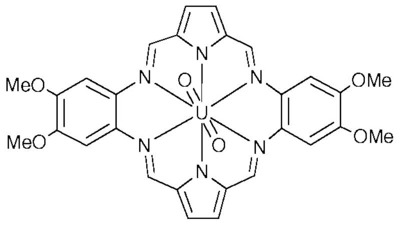
The new bis(imino)pyrrole ligand 2,5-$C_4H_2NH(CH{=}NC_6H_3Pr^i{}_2)_2$ (HL^1) reacts with $Zr(NMe_2)_4$ to give the 1 : 1 complex ($\mathbf{L}^1$)$Zr(NMe_2)_3$ (**1**), whereas the mono(imino)pyrrole 2-$C_4H_3NH(CH{=}NC_6H_3Pr^i{}_2)$ (HL^2) substitutes two amido ligands to give ($\mathbf{L}^2$)$_2Zr(NMe_2)_2$ (**2**). The lithium salt LiL^1 reacts with $ZrCl_4$ to give ($\mathbf{L}^1$)$ZrCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**), while the reaction of LiL^2 with $ZrCl_4$ or treating **2** with Me_3SiCl gives ($\mathbf{L}^2$)$_2ZrCl_2$. Iron(II) chloride reacts with LiL^1 to afford the bis(ligand) complex Fe($\mathbf{L}^1$)$_2$ (**5**), while only one pyrrolato ligand is incorporated on reacting LiL^1 with $CoCl_2$(thf) to give [Li(thf)$_4$][$CoCl_2\mathbf{L}^1$] (**6a**). On warming, **6a** readily loses thf to give [Li(thf)$_2$][$CoCl_2\mathbf{L}^1$] (**6b**). By contrast, LiL^2 reacts with $CoCl_2$ and $NiCl_2$ to give the halide-free complexes Co($\mathbf{L}^2$)$_2$ and Ni($\mathbf{L}^2$)$_2$, respectively. The crystal structures of HL^1 and complexes **1**, **2** and **5** are reported. In all cases the potentially tridentate ligand $\mathbf{L}^1$ is two-coordinate. Mixtures of the halide-free bis(ligand) complexes with methylaluminoxane do not show any activity for ethene polymerisation; however, **3** and **4** catalyse the polymerisation of ethene, while **6** has moderate activity for the oligomerisation of ethene and propene to linear and branched products.

Introduction

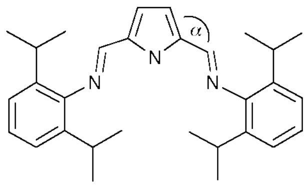
Chelating nitrogen ligands with bulky substituents are currently being explored as alternatives to cyclopentadienyl ligands for the design of olefin polymerisation catalysts based on early and late transition metal complexes.[1] Examples are bis(amido) complexes of titanium and zirconium with[2] and without[3] the ability to function as tridentate ligands *via* additional N- or O-donor functions, as well as benzamidinato complexes.[4] Late transition metal catalysts stabilised by bulky bi- and tridentate imine ligands have attracted particular attention,[5,6] while the ability of neutral nickel complexes with chelating nitrogen ligands to polymerise ethene has been known for some time.[7] We have recently reported the synthesis and catalytic activity of a series of zirconium complexes with oligodentate nitrogen ligands including iminopyrrolato derivatives.[8] Bis(imino)pyrrolato complexes of copper,[9] zinc[10] and, more recently, chromium[11] have been reported in which the ligands are bidentate, as in **A**, whereas tridentate coordination involving the pyrrole and both imino-nitrogen atoms is observed with uranium (structure **B**).[12] We describe here our studies on the coordinative behaviour of the new bis(imino)pyrrolide anion [2,5-C_4H_2N-$(CH{=}NC_6H_3Pr^i{}_2)_2]^-$ (**C**) as well as [2-$C_4H_3N(CH{=}NC_6H_3Pr^i{}_2)]^-$ as ligands towards zirconium, iron, cobalt and nickel.



A



B



C

Results and discussion

Bis(arylimino)pyrrole 2,5-$C_4H_2NH(CH{=}NR)_2$ (HL^1), where R = 2,6-$Pr^i{}_2C_6H_3$, was prepared by condensation of pyrrole-2,5-dicarbaldehyde with 2,6-diisopropylaniline in methanol as colourless crystals. The mono(arylimino)pyrrole 2-C_4H_3NH-$(CH{=}NC_6H_3Pr^i{}_2)$ (HL^2) was obtained similarly.

The crystal structure of HL^1 was determined to allow comparison with metal complexes of this ligand. The structure is shown in Fig. 1, and pertinent bond lengths and angles are given in Table 1. In the solid the compound adopts a conformation where the pyrrole core is coplanar with the two imino moieties which are oriented *cis* to each other. The imino C=N bond length of 1.265(2) Å and the C(2)–C(6) bond length of 1.448(2) Å indicate little conjugation with the pyrrole ring. The average value of the angles C(3)–C(2)–C(6) and C(4)–C(5)–C(13) of 132.57° is much wider than the value for the other exocyclic angles, N(1)–C(2)–C(6) and N(1)–C(5)–C(13) (120.40°).

The ability of the [$\mathbf{L}^1$]$^-$ anion to act as a bi- or tridentate ligand may be estimated by considering the exocyclic angle *α* (structure **C**) and the degree to which it needs to be enlarged if the ligand is to adopt a tridentate coordination mode. In the free ligand, *α* is comparatively wide, *ca.* 132.6°, and does not increase on coordination to a metal centre (see below). This behaviour contrasts for example with bis(imino)pyridines which readily form tridentate complexes, *e.g.* $FeCl_2\{C_5H_3N$-$(CMe{=}NC_6H_3Pr^i{}_2)_2$-2,6$\}$.[6] By comparison, bis(imino)pyrrolato ligands offer a more open coordination environment, where bidentate coordination is preferred.

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Table 1 Selected bond lengths (Å) and angles (°)

HL^1			
N(1)–C(2)	1.360(2)	N(1)–C(5)	1.363(2)
C(2)–C(3)	1.379(2)	C(2)–C(6)	1.448(2)
C(3)–C(4)	1.398(2)	C(4)–C(5)	1.382(2)
C(5)–C(13)	1.446(2)	C(6)–N(6)	1.265(2)
N(6)–C(7)	1.424(2)		
C(2)–N(1)–C(5)	110.55(10)	N(1)–C(2)–C(3)	107.23(12)
N(1)–C(2)–C(6)	120.46(11)	C(3)–C(2)–C(6)	132.30(13)
C(2)–C(3)–C(4)	107.56(13)	C(5)–C(4)–C(3)	107.84(12)
N(1)–C(5)–C(4)	106.82(12)	N(1)–C(5)–C(13)	120.33(11)
C(4)–C(5)–C(13)	132.84(12)	N(6)–C(6)–C(2)	119.38(12)
C(6)–N(6)–C(7)	122.20(11)		
Compound **1**			
Zr(1)–N(6)	2.0391(11)	Zr(1)–N(5)	2.0417(11)
Zr(1)–N(7)	2.0933(11)	Zr(1)–N(1)	2.3182(10)
Zr(1)–N(4)	2.3510(10)	N(1)–C(2)	1.314(2)
N(1)–C(10)	1.449(2)	C(2)–C(3)	1.419(2)
C(3)–N(4)	1.383(2)	C(3)–C(7)	1.414(2)
N(4)–C(5)	1.367(2)	C(5)–C(6)	1.411(2)
C(5)–C(8)	1.458(2)	C(6)–C(7)	1.388(2)
C(8)–N(9)	1.280(2)	N(9)–C(22)	1.433(2)
N(5)–C(35)	1.452(2)	N(5)–C(34)	1.455(2)
N(6)–Zr(1)–N(5)	116.19(5)	N(6)–Zr(1)–N(7)	97.13(5)
N(5)–Zr(1)–N(7)	96.73(5)	N(6)–Zr(1)–N(1)	117.44(4)
N(5)–Zr(1)–N(1)	124.43(4)	N(7)–Zr(1)–N(1)	90.27(4)
N(6)–Zr(1)–N(4)	94.77(4)	N(5)–Zr(1)–N(4)	91.60(4)
N(7)–Zr(1)–N(4)	160.66(4)	N(1)–Zr(1)–N(4)	70.69(4)
C(2)–N(1)–C(10)	118.78(10)	C(2)–N(1)–Zr(1)	117.59(8)
C(10)–N(1)–Zr(1)	123.43(7)	N(1)–C(2)–C(3)	119.38(11)
N(4)–C(3)–C(7)	110.46(11)	N(4)–C(3)–C(2)	117.38(11)
C(7)–C(3)–C(2)	132.15(12)	C(5)–N(4)–C(3)	105.66(10)
C(5)–N(4)–Zr(1)	139.39(8)	C(3)–N(4)–Zr(1)	114.94(8)
N(4)–C(5)–C(8)	120.67(10)	C(6)–C(5)–C(8)	128.38(11)
N(9)–C(8)–C(5)	122.86(11)	C(8)–N(9)–C(22)	117.21(10)
C(35)–N(5)–C(34)	111.90(13)	C(35)–N(5)–Zr(1)	128.24(11)
C(34)–N(5)–Zr(1)	119.68(10)	C(36)–N(6)–C(37)	112.24(13)
C(36)–N(6)–Zr(1)	120.81(10)	C(37)–N(6)–Zr(1)	126.71(11)
C(38)–N(7)–C(39)	109.49(13)	C(38)–N(7)–Zr(1)	123.31(10)
C(39)–N(7)–Zr(1)	125.53(10)		
Compound **2**			
Zr(1)–N(18)	2.0465(14)	Zr(1)–N(15)	2.047(2)
Zr(1)–N(8)	2.2392(14)	Zr(1)–N(1)	2.2551(14)
Zr(1)–N(7)	2.4327(13)	Zr(1)–N(14)	2.5532(14)
C(6)–N(7)	1.305(2)	C(13)–N(14)	1.296(2)
N(15)–C(16)	1.462(2)	N(15)–C(17)	1.462(2)
N(18)–C(19)	1.448(2)	N(18)–C(20)	1.462(2)
N(18)–Zr(1)–N(15)	97.67(6)	N(18)–Zr(1)–N(8)	115.79(6)
N(15)–Zr(1)–N(8)	88.74(5)	N(18)–Zr(1)–N(1)	157.25(5)
N(15)–Zr(1)–N(1)	93.69(6)	N(8)–Zr(1)–N(1)	83.99(5)
N(18)–Zr(1)–N(7)	88.73(5)	N(15)–Zr(1)–N(7)	97.23(5)
N(8)–Zr(1)–N(7)	153.85(5)	N(1)–Zr(1)–N(7)	70.27(5)
N(18)–Zr(1)–N(14)	93.87(5)	N(15)–Zr(1)–N(14)	158.65(5)
N(8)–Zr(1)–N(14)	70.05(5)	N(1)–Zr(1)–N(14)	82.08(5)
C(16)–N(15)–C(17)	108.7(2)	C(16)–N(15)–Zr(1)	124.85(12)
C(17)–N(15)–Zr(1)	126.36(12)	C(19)–N(18)–C(20)	109.75(14)
C(19)–N(18)–Zr(1)	147.26(12)	C(20)–N(18)–Zr(1)	102.77(11)
N(7)–Zr(1)–N(14)	100.94(4)		
Compound **5**			
N(1)–C(1)	1.300(2)	N(1)–C(11)	1.447(2)
N(1)–Fe(1)	2.0972(13)	C(1)–C(2)	1.414(2)
C(2)–N(2)	1.373(2)	N(2)–C(3)	1.361(2)
N(2)–Fe(1)	2.0444(13)	C(3)–C(4)	1.446(2)
C(4)–N(4)	1.273(2)	N(5)–C(5)	1.294(2)
N(5)–Fe(1)	2.1347(14)	C(5)–C(6)	1.418(3)
C(6)–N(6)	1.370(2)	N(6)–C(7)	1.357(2)
N(6)–Fe(1)	2.0057(14)	C(7)–C(8)	1.442(2)
C(8)–N(8)	1.267(2)		
N(6)–Fe(1)–N(2)	106.65(6)	N(2)–Fe(1)–N(1)	82.72(5)
N(6)–Fe(1)–N(1)	153.35(6)	N(2)–Fe(1)–N(5)	115.74(6)
N(6)–Fe(1)–N(5)	81.06(6)	C(1)–N(1)–Fe(1)	108.52(10)
N(1)–Fe(1)–N(5)	117.96(6)	C(12)–C(11)–C(16)	121.6(2)
C(11)–N(1)–Fe(1)	134.06(11)	N(2)–C(2)–C(1)	117.84(14)
N(1)–C(1)–C(2)	121.50(14)	C(3)–N(2)–Fe(1)	144.56(11)
C(21)–C(2)–C(1)	131.6(2)	N(2)–C(3)–C(4)	121.2(2)
C(2)–N(2)–Fe(1)	109.42(10)	N(4)–C(4)–C(3)	121.4(2)
C(31)–C(3)–C(4)	128.5(2)	C(5)–N(5)–Fe(1)	108.94(13)
C(5)–N(5)–C(51)	118.3(2)	N(5)–C(5)–C(6)	119.8(2)
C(51)–N(5)–Fe(1)	132.73(11)	C(61)–C(6)–C(5)	133.1(2)
N(6)–C(6)–C(5)	117.2(2)	C(6)–N(6)–Fe(1)	111.18(12)
C(7)–N(6)–Fe(1)	139.64(12)	N(8)–C(8)–C(7)	121.8(2)
N(6)–C(7)–C(8)	122.1(2)		

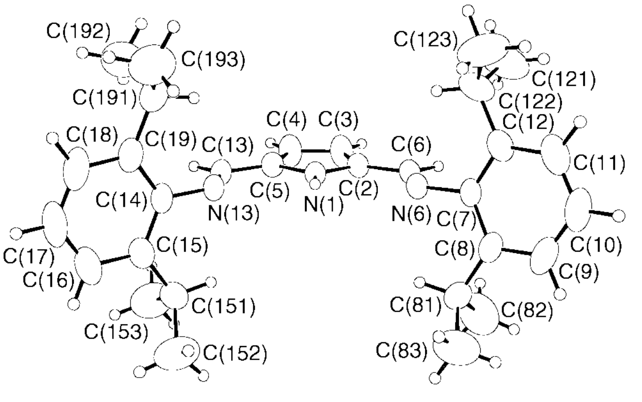
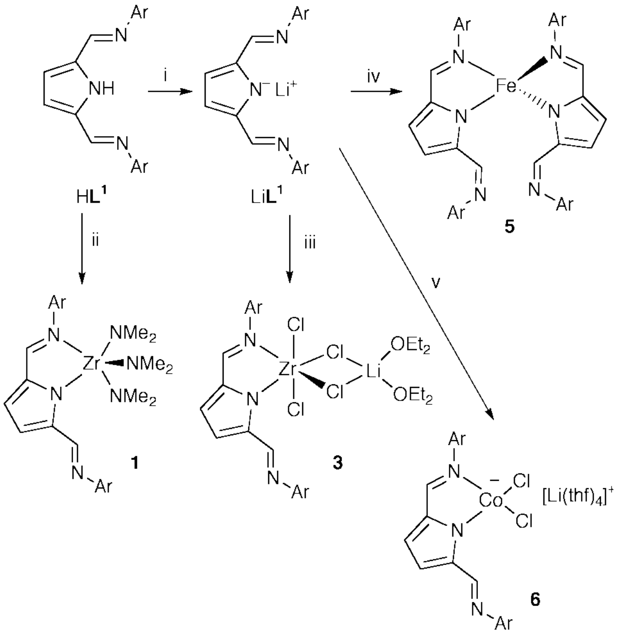


Fig. 1 Molecular structure of $HL^1 \cdot 0.5Et_2O$, showing the atomic numbering scheme. Atoms are represented by thermal ellipsoids drawn at 40% probability level.

Treatment of HL^1 with $Zr(NMe_2)_4$ leads exclusively to the monosubstitution product $(L^1)Zr(NMe_2)_3$ (**1**), even in the presence of excess HL^1 (Scheme 1). By contrast, the reaction of $Zr(NMe_2)_4$ with the less hindered mono(arylimino)pyrrole HL^2 affords cleanly the bis(pyrrolato) complex $(L^2)_2Zr(NMe_2)_2$ (**2**), independent of the $HL^2/Zr(NMe_2)_4$ ratio (Scheme 2). Both **1** and **2** were isolated as orange crystals in high yield.



Scheme 1 Synthesis of bis(imino)pyrrolato complexes (Ar = 2,6-$Pr^i_2C_6H_3$). Reagents and conditions: (i) Bu^nLi, Et_2O, 20 °C; (ii) $Zr(NMe_2)_4$, toluene, 20 °C; (iii) $ZrCl_4$, Et_2O, 0 °C; (iv) $FeCl_2$, thf, reflux; (v) $CoCl_2$, thf, −78 °C to room temperature, 3 h.

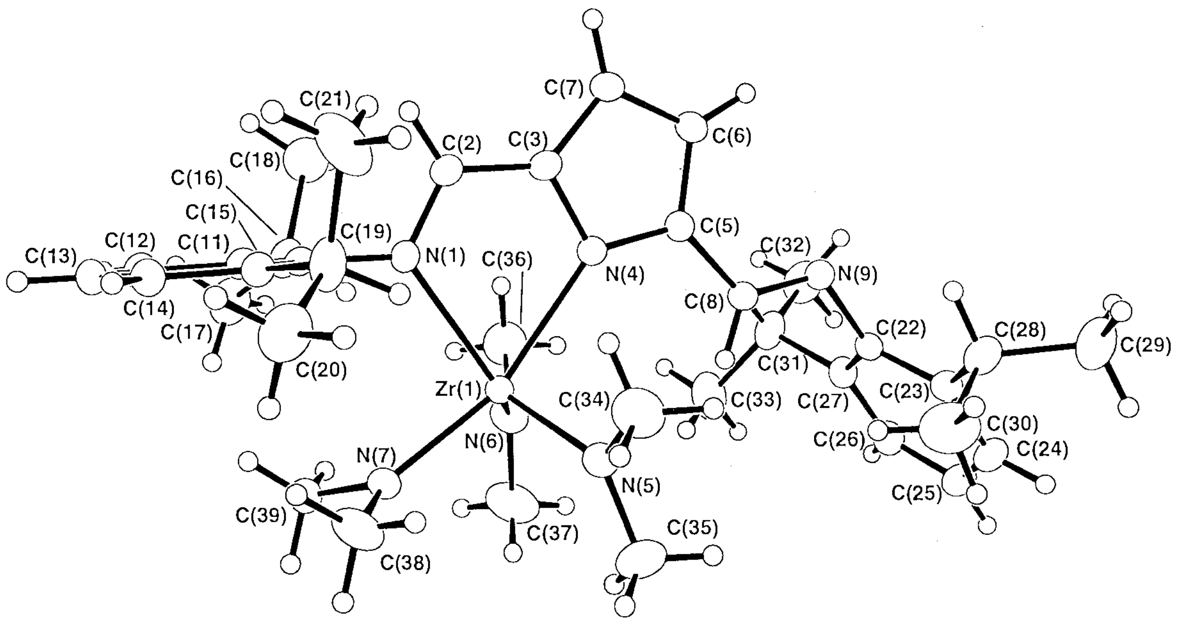
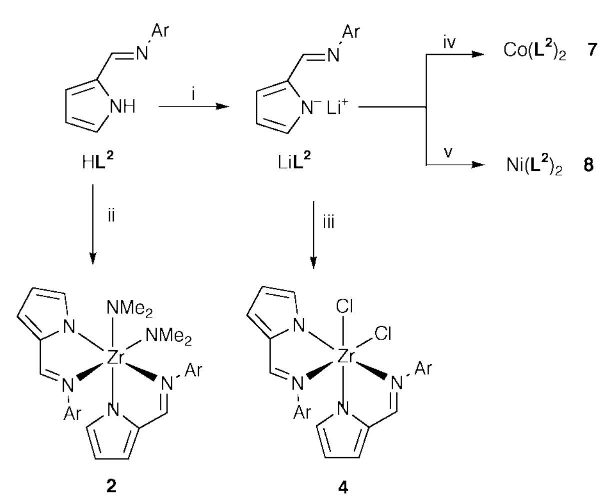
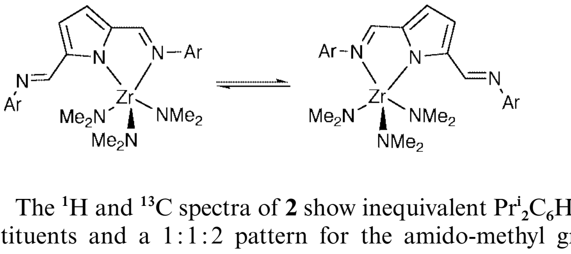


Fig. 2 Molecular structure of $(L^1)Zr(NMe_2)_3$ (**1**), showing the atomic numbering scheme.



Scheme 2 Synthesis of mono(imino)pyrrolato complexes (Ar = 2,6-$Pr^i_2C_6H_3$). Reagents and conditions: (i) Bu^nLi, Et_2O, 20 °C; (ii) $Zr(NMe_2)_4$, toluene, 20 °C; (iii) $ZrCl_4$, Et_2O, 0 °C; (iv) $CoCl_2$, Et_2O, −78 °C to ambient, 5 h; (v) $NiBr_2(dme)$, Et_2O, 0 °C, 1 h.

Complex **1** is fluxional. At −80 °C the ^1H NMR spectra show a 2 : 1 : 1 pattern for two equivalent and two inequivalent isopropyl substituents of the aryl groups; these coalesce at −21 °C. Evidently only two of the three nitrogen donors of $\mathbf{L^1}$ are bound to the metal. This is confirmed by the presence at −80 °C of two singlets for inequivalent -C*H*=N imino-hydrogen atoms which coalesce at −16 °C ($\Delta G^\ddagger = 49$ kJ mol^{-1} at 257 K) to give a single sharp resonance above 30 °C. Evidently there is an interchange of imino ligands (eqn. (1)).



(1)

The ^1H and ^{13}C spectra of **2** show inequivalent $Pr^i_2C_6H_3$ substituents and a 1 : 1 : 2 pattern for the amido-methyl groups, indicative of hindered rotation of one of the NMe_2 ligands. The data are in agreement with an octahedral structure, with the NMe_2 ligands in *cis* position to each other. Unlike the penta-coordinate complex **1**, compound **2** is stereorigid at room temperature, though significant line broadening due to the onset of exchange processes is observed on warming to 60 °C.

Crystals of **1** and **2** suitable for X-ray diffraction were grown from toluene–light petroleum mixtures. Complex **1** (Fig. 2) is trigonal bipyramidal, with short Zr–NMe_2 bonds and longer distances to the pyrrole and imino-nitrogen donor atoms. The nitrogen atoms of the NMe_2 ligands are trigonal planar. Due to steric congestion the NMe_2 ligands are significantly distorted. The Me–N–Me angles vary from 109.44 to 112.24°, while the Zr–N–Me angles are much wider. The distortion is particularly pronounced for N(5), with Zr–N(5)–C(methyl) angles of 119.68 and 128.24°. Similar variations in Zr–N–Me angles have been found for example in $Zr(NMe_2)_6Li_2(thf)_2$.[13] The most notable feature, however, is the bonding of the $[\mathbf{L^1}]^-$ anion which acts as a bidentate rather than tridentate ligand, with one arylimino moiety bent away from the metal. Nevertheless, this non-bonded substituent restricts the reactivity of the complex and prevents **1** from reacting with a second equivalent of $\mathbf{HL^1}$; as a consequence, a bis(pyrrolato) complex $(\mathbf{L^1})_2Zr(NMe_2)_2$ in analogy to **2** cannot be formed, even in the presence of an excess of $\mathbf{HL^1}$ and prolonged reaction times.

Variations in the exocyclic angle *a* may be regarded as a measure of possible ring strain on coordination. As stated, in the free ligand *a* is *ca.* 132.6°. In **1**, the corresponding value for the imine involved in the metallacycle, C(2)–C(3)–C(7), is very similar, 132.15(12)°, while the angle with the non-coordinated imino moiety, C(6)–C(5)–C(8), is reduced to 128.38(11)°. While bidentate coordination of $\mathbf{L^1}$ evidently involves little strain, the moderate size of zirconium would make a tridentate bonding mode unfavourable.

The structure of **2** (Fig. 3) confirms the geometry deduced from the NMR data. All the three different types of nitrogen donors—pyrrole, imine and amide—are mutually *cis*. The Zr–N distances fall into three distinct categories and increase in the order Zr–amide (*ca.* 2.05 Å) < Zr–pyrrole (2.25 Å) < Zr–imine (2.50 Å).

One of the NMe_2 ligands, N(18), is significantly distorted, with Zr–N–Me angles of 147.26 and 102.77°, most likely due to the proximity of the bulky aryl substituent on N(7). By comparison, in the structurally related diketiminato complex $\{PhNC(Me)CHC(Me)NPh\}_2Zr(NMe_2)_2$ the amido ligands are bonded symmetrically.[14] By contrast, steric congestion has little influence on the N–Zr–N angles which are close to 90°, *e.g.* N(7)–Zr–N(18) = 88.73°.

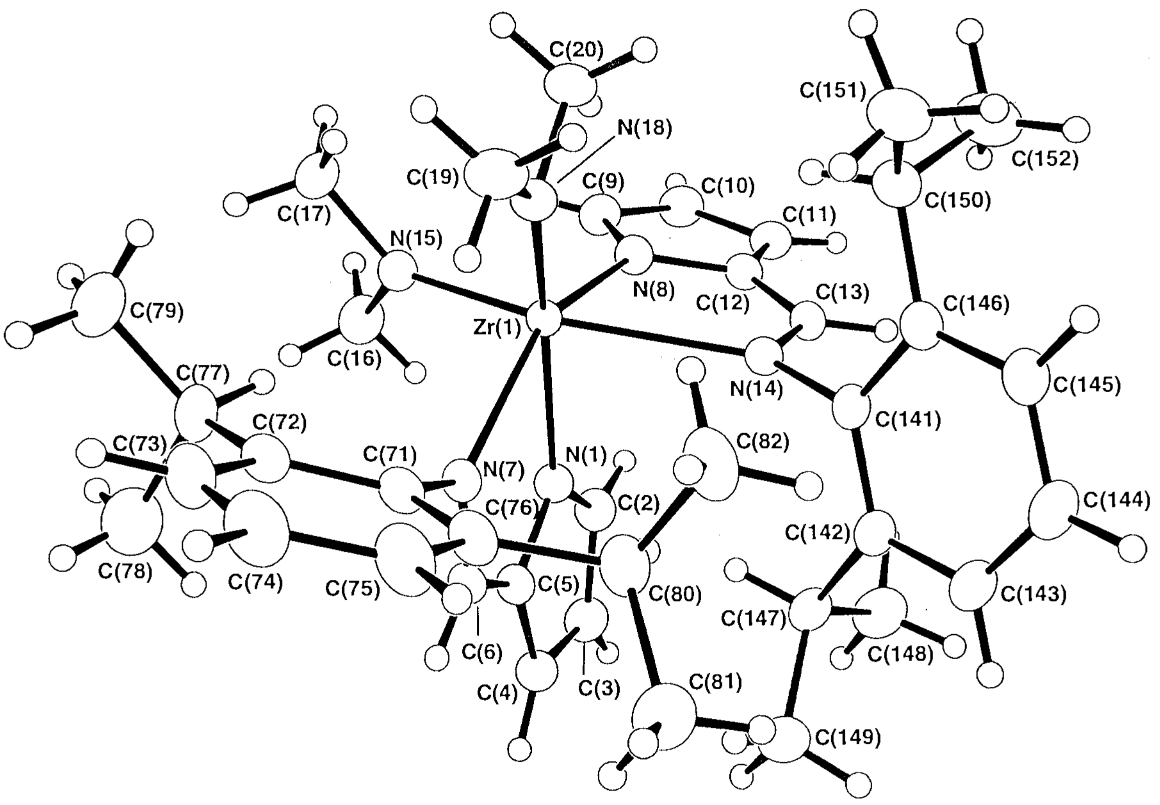


Fig. 3 Molecular structure of $(\mathbf{L}^2)_2Zr(NMe_2)_2$ (**2**), showing the atomic numbering scheme.

Warming a solution of **1** with excess trimethylchlorosilane leads to dehalosilylation and formation of a zirconium chloro complex. Although there was evidence for the formation of the expected trichloro complex $(\mathbf{L}^1)ZrCl_3$, no analytically pure product could be obtained, even after numerous recrystallisations. The reaction of $Li\mathbf{L}^1$ with $ZrCl_4$, on the other hand, gives the tetrachlorozirconate $(\mathbf{L}^1)ZrCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**) as a bright yellow crystalline solid (Scheme 1). Similarly, $Li\mathbf{L}^2$ and $ZrCl_4$ gives canary-yellow microcrystalline $(\mathbf{L}^2)_2ZrCl_2$ (**4**) (Scheme 2). The same compound is obtained from **2** and excess Me_3SiCl.

In contrast to the reaction of $Zr(NMe_2)_4$, NMR monitoring of the reaction of $H\mathbf{L}^1$ with the yttrium complex $Y[N(SiMe_3)_2]_3$ in benzene-d_6 indicates clean protolysis of two of the amido ligands to give $(\mathbf{L}^1)_2YN(SiMe_3)_2$ and $HN(SiMe_3)_2$. However, attempts to isolate a pure product from this reaction were unsuccessful.

The reaction of $Li\mathbf{L}^1$ with $FeCl_2$ in refluxing thf gives $Fe(\mathbf{L}^1)_2$ (**5**) as red, hexane soluble crystals in moderate yield. Crystalline **5** was always contaminated with variable quantities of the free ligand which has very similar solubility properties and could not be removed, even after repeated recrystallisations. A 1:1 complex of the stoichiometry $FeCl(\mathbf{L}^1)$ could not be isolated. Crystals of **5** suitable for X-ray diffraction were grown by layering a diethyl ether solution with light petroleum. The molecular structure of **5** (Fig. 4) shows that, once again, the bis(imino)-pyrrolate acts as a bidentate ligand, resulting in a strongly distorted tetrahedral geometry. The chelate ligands have bite angles of 81.06 and 82.72°, while the two exocyclic N–Fe–N angles differ significantly from one another, 115.74 and 153.35°. Although the complex is clearly sterically highly congested, the reason for such a large deviation from a tetrahedral geometry is not obvious and does not appear to arise from crystal packing.

Unlike the reaction with $FeCl_2$, $Li\mathbf{L}^1$ reacts with anhydrous $CoCl_2$ in thf to give a green crystalline ionic 1:1 complex, $[Li(thf)_4][CoCl_2(\mathbf{L}^1)]$ (**6a**) which is converted into $[Li(thf)_2][CoCl_2(\mathbf{L}^1)]$ (**6b**) on pumping *in vacuo*. A comparison of the $\nu(C{=}N)$ frequencies of **6** [1624 (m) and 1565 (s) cm^{-1}] with those of the free ligand (1622 cm^{-1}) indicates that here, too, $\mathbf{L}^1$ acts exclusively as a bidentate ligand, with one uncoordinated imino group. Layering a thf solution with light petroleum afforded green needles of **6a**. Several attempts at finding X-ray quality crystals were made. An X-ray data set was eventually collected, although the crystals deteriorated significantly during the collection process, presumably due to facile solvent loss. It was possible to identify the geometry of the compound which shows an anionic cobalt complex with a CoN_2Cl_2 core and a disordered $[Li(thf)_4]^+$ cation; the anion is illustrated in Fig. 5. However, the data were of insufficient quality for a full analysis and will therefore not be discussed further.

Table 2 Ethene polymerisation with zirconium pyrrolato complexes[a]

Run	Catalyst precursor (μmol)	T (°C)	Polyethene yield (mg)	Activity 10^3 g PE (mol Zr)$^{-1}$ bar^{-1} h^{-1}	T_m (°C)
1	**3** (25)	20	223	26.8	
2	**3** (25)	20	350	42	138.0
3	**4** (25)	20	379	45.4	
4	**4** (25)	20	532	63.8	137.6
5	**4** (25)	50	244	39.1	

[a] Conditions: 25 cm^3 toluene, 15 cm^3 MAO in toluene, Al:Zr ratio 880:1. Ethene pressure maintained at 1 bar, reaction time 15 min.

Only halide-free products were isolated when $Li\mathbf{L}^2$ was treated with either $CoCl_2$ or $NiBr_2(dme)$ in diethyl ether at 0 °C to give dark red paramagnetic $Co(\mathbf{L}^2)_2$ (**7**) ($\mu_{eff} = 2.1\ \mu_B$) and brown, diamagnetic $Ni(\mathbf{L}^2)_2$ (**8**), respectively, as microcrystalline solids. These complexes had limited solubilities, and did not produce X-ray quality crystals.

Preliminary screening tests showed the mixtures of the bis-ligand complexes **5**, **7** and **8** and methylaluminoxane (MAO, Al/metal ratio = 600:1) to be unreactive towards ethene. The zirconium complexes **3** and **4**, when activated by MAO, catalyse the polymerisation of ethene under ambient pressure (Table 2). The activities are moderate by metallocene standards but are comparable, for example, with heterogeneous $Ti/Mg/SiO_2$

Table 3 Alkene oligomerisation with cobalt complexes[a]

Run	Olefin	T/°C	t/min	Yield/g	Turnover min^{-1}	Internal olefin (%)	External olefin (%)	Branched (%)	Av. chain length, C_n
1	Ethene	20	15	0.45	21.4	72	18	10	25.1
2	Ethene	0	60	1.15	13.7	79	14	7	24.7
3	Propene	20	8	0.23	13.7	73	9	18	41
4	Propene	0	15	—	—	—	—	—	—

[a] Conditions: 40 cm^3 toluene, 30 mmol MAO (Al : Co = 600 : 1), 50 μmol Co, alkene 1 bar. Reactions were terminated by injecting 2 cm^3 methanol.

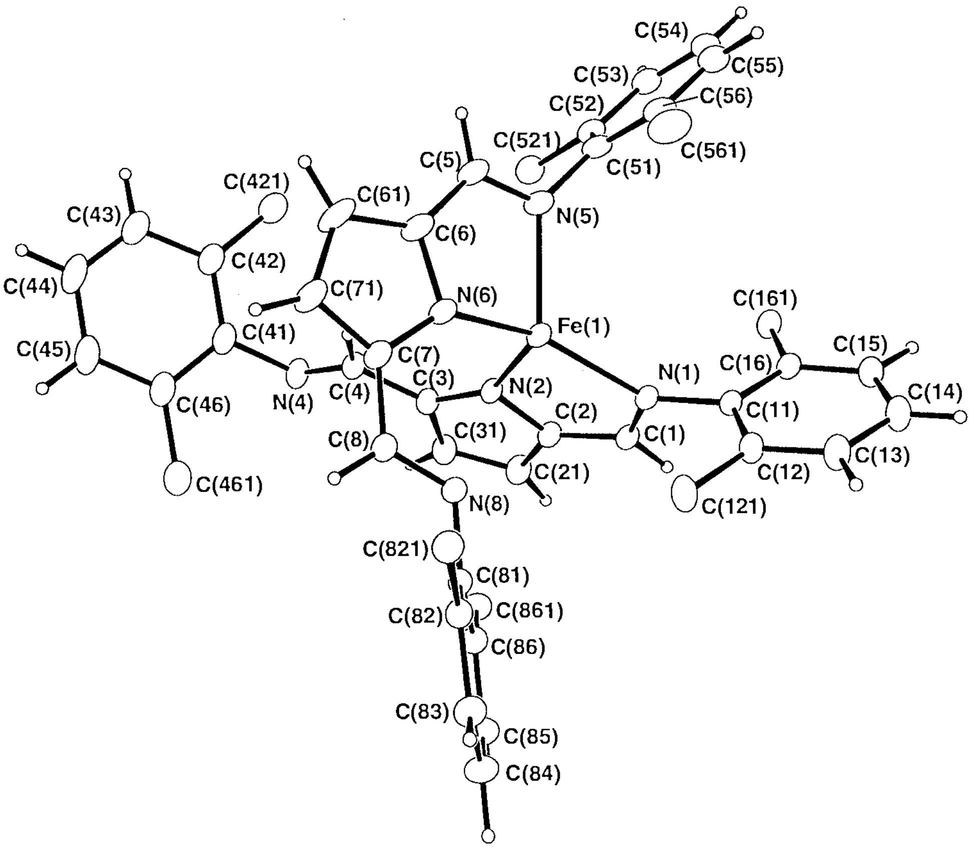


Fig. 4 Molecular structure of Fe(L^1)$_2$ (**5**), showing the atomic numbering scheme.

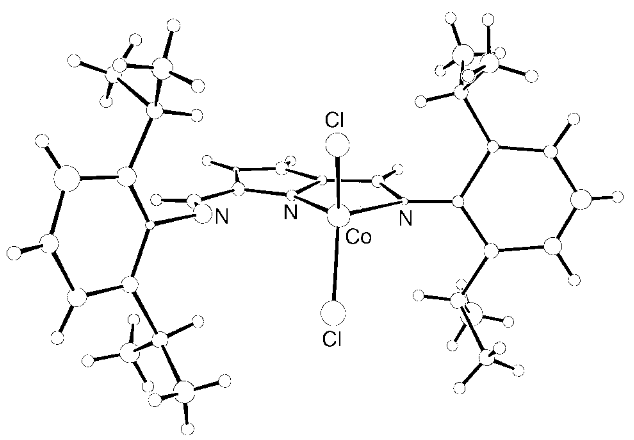
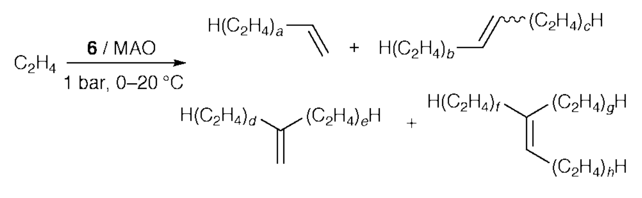


Fig. 5 Geometry of the anion [CoCl$_2$(L^1)]$^-$ in **6a**.

catalysts which are typically operated under more forcing conditions.[15] The catalysts are long lived, and while runs were usually terminated after 20 minutes, similar gas consumption rates were observed after 1 hour.

Mixtures of **6** and MAO give yellow solutions which readily oligomerise ethene under mild conditions (1 bar, 0 °C to room temperature) with a productivity of *ca.* 3.1 × 10^4 g oligomer (mol Co)$^{-1}$ h^{-1} bar^{-1}. At room temperature the catalyst decays rapidly and becomes inactive after *ca.* 15 min, possibly due to ligand exchange with the aluminium alkyl. At 0 °C the catalyst is longer lived and produces *ca.* 2 × 10^4 g oligomer (mol Co)$^{-1}$ h^{-1} bar^{-1}. No polymerisation was observed when Et$_2$AlCl was used as the activator. The compound also shows modest activity for the oligomerisation of propene (Table 3).

The oligomerisation reactions are accompanied by extensive isomerisation, to give mixtures of terminal, internal and branched products. The branched components consist of 1,1-dialkylethenes R^{1}R^{2}C=CH$_2$, accompanied by minor amounts of trisubstituted alkenes R^{1}R^{2}C=CHR^3 which arise evidently from insertions of terminal alkenes into Co–R bonds, followed by β-H elimination (Scheme 3).



Scheme 3

Experimental

General procedures

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium–potassium alloy (diethyl ether, light petroleum, bp 40–60 °C) sodium–benzophenone (thf) and calcium hydride (dichloromethane). Methylaluminoxane (MAO, 10 wt% in toluene) was used as purchased (Witco). NMR solvents were dried over activated 4A molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded using Bruker ARX250 and DPX300 spectrometers and referenced to residual solvent peaks. Chemical shifts are quoted in ppm relative to tetramethylsilane. Ethene and propene (BOC) were passed through P_2O_5 and activated molecular sieves prior to use. The compounds 2,5-diformylpyrrole and 2-(2,6-diisopropylphenyl)-aldimino]pyrrole (HL^2) were prepared according to a literature procedure.[16]

Preparation of 2,5-bis[(2,6-diisopropylphenyl)aldimino]-pyrrole (HL^1). To a solution of 8.5 g 2,5-diformylpyrrole (6.7 mmol) in MeOH (50 cm^3) was added 23.7 g 2,6-diisopropyl-aniline (13.4 mmol). The mixture was left to stir overnight. A white precipitate began to form within 30 minutes. The white solid was collected and washed with a little cold methanol, yielding 18.8 g of the desired product. Processing of the mother liquor raised the yield to 25.0 g (85%). The compound is highly soluble in all solvents except water. Attempted recrystallisation from toluene, light petroleum or ethanol led to severe product loss; the compound is best recrystallised by allowing a methanol solution to evaporate slowly at room temperature. Anal. $C_{30}H_{39}N_3$, found (calc.) C, 81.5 (81.6); H, 8.9 (8.9); N, 9.5 (9.5)%. ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 0.96 (d, $J = 6.9$ Hz, 24H, CH*Me*$_2$), 2.9 (sept, $J = 6.9$ Hz, 4H, C*H*Me$_2$), 7.0–6.9 (m, 6H, aryl), 7.6 (s, 2H, C*H*=N), 10.3 (br, 1H, NH). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 23.0 (CH*Me*$_2$), 27.8 (*C*HMe$_2$), 115.9 (pyrrole *C*–H), 124.2, 133.6, 137.8 (aryl), 150.7 (pyrrole *C*–N), 151.5 (*C*=N). Infrared (Nujol mull, cm^{-1}): 3450 (s, ν_{N-H}), 1622 (s), 1588 (w), 1320 (w), 1160 (s), 1098 (w), 1059 (w), 815 (w), 800 (w), 766 (w) and 728 (w). Crystals for X-ray diffraction were grown from methanol containing some diethyl ether and contain 0.5 molecules of Et_2O of crystallisation, $HL^1\cdot 0.5Et_2O$.

Lithium 2,5-bis[(2,6-diisopropylphenyl)aldimino]pyrrolide, LiL^1. To a solution of 2.5 g of HL^1 (5.6 mmol) in Et_2O (20 cm^3) was added Bu^nLi in hexanes (1.6 M, 3.6 cm^3). The mixture was stirred for 2 h, giving a white precipitate. The mixture was evaporated to dryness *in vacuo* and the off-white residue washed several times with light petroleum (2 × 5 cm^3) until the product was clean by NMR. Yield 1.7 g (68%). ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 1.0 (d, 24H, CH*Me*$_2$), 3.2 (septet, 4H, C*H*Me$_2$), 7.2 (m, 6H, aryl), 8.2 (s, 2H, C*H*=N). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 24.1 (CH*Me*$_2$), 28.6 (*C*HMe$_2$), 120.7 (pyrrole C3,4), 123.8, 125.3, 140.6, 145.0 (aryl), 147.5 (pyrrole C2,5), 162.3 (*C*=N). Infrared (Nujol mull, cm^{-1}): 1621 (s), 1602 (s), 1579 (s), 1304 (w), 1160 (w), 1098 (w), 1037 (w), 1027 (w).

Lithium [2-{(2,6-diisopropylphenyl)imino}pyrrolide], LiL^2. A solution of 2-[(2,6-diisopropylphenyl)imino]pyrrole (HL^2) (2.0 g, 7.9 mmol) in diethyl ether (*ca.* 50 cm^3) was treated with n-butyllithium (4.9 cm^3, 1.6 M) at −78 °C with vigorous stirring. The solution was stirred for 2 h, affording a white solid. This solid was isolated by filtration and washed with diethyl ether. Washing was continued until the product was shown to be clean by NMR. Yield: >85%. ^1H NMR (250 MHz, 27 °C, C_6D_6): δ 8.04 (s, 1H, C*H*=N), 7.34–7.20 (m, 4H, aryl, pyrrole), 6.89 (dd, 1H, $J = 2.3$ Hz, pyrrole), 6.45 (dd, 1H, $J = 1.5$ Hz, pyrrole), 3.41 (sept, 2H, $J = 6.8$ Hz, C*H*Me$_2$), 3.03 (q, 4H, $J = 7.1$ Hz, C*H*$_2$CH$_3$), 1.29 (d, 12H, $J = 6.8$ Hz, CH*Me*$_2$), 0.79 (t, 6H, $J = 7.1$ Hz, CH$_2$C*H*$_3$). Infrared (Nujol mull, cm^{-1}): 1627 (w), 1606 (s), 1586 (m), 1395 (s), 1379 (s), 1253 (w), 1171 (m), 1108 (m), 1090 (m), 1068 (m), 1033 (m), 971 (m), 784 (w), 742 (s).

Preparation of $(L^1)Zr(NMe_2)_3$ (1). To a mixture of 1.0 g $Zr(NMe_2)_4$ (3.7 mmol) and 1.65 g HL^1 (3.7 mmol) was added toluene (10 cm^3). The solution rapidly turned an intense orange. After stirring for 2 h the volatiles were removed *in vacuo*. Crystallisation from toluene–light petroleum gave orange crystals of **1** (2.0 g, 80%). Anal. $C_{36}H_{56}N_6Zr$, found (calc.) C, 63.5 (65.1); H, 8.3 (8.5); N, 12.7 (12.1). ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 1.4 (d, $J = 6.9$ Hz, 24H, CHMe$_2$), 3.0 (s, 18H, N*Me*$_2$), 3.4 (sept, $J = 6.8$ Hz, 4H, C*H*Me$_2$), 7.3 (m, 8H, aryl), 8.2 (br, 2H, C*H*=N). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 23.7 (CH*Me*$_2$), 28.6 (*C*HMe$_2$), 42.5 (N*Me*$_2$), 123.2, 125.3, 139.4, 145.0, 161.6 (*C*H=N). Infrared (Nujol mull, cm^{-1}): 1617 (m), 1595 (m), 1575 (s), 1556 (s), 1320 (m), 1270 (m), 1170 (m), 1108 (sh), 1098 (w), 1057 (sh), 1042 (m), 935 (m), 786 (w).

Preparation of $(L^2)_2Zr(NMe_2)_2$ (2). Toluene (10 cm^3) was added to a mixture of $Zr(NMe_2)_4$ (1.2 g, 4.5 mmol) and 2-(2,6-diisopropylphenyl)iminopyrrole (2.28 g, 9.0 mmol). The solution rapidly became deep orange. After stirring for 2 h the volatiles were removed *in vacuo*. Crystallisation from toluene–light petroleum gave orange crystals (2.75 g, 89%). Anal. $C_{38}H_{54}N_6Zr$, found (calc.) C, 65.3 (66.5); H, 7.3 (7.9); N, 12.3 (12.3). ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 0.48 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 0.70 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 0.71 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 0.81 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 0.86 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 0.94 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$), 1.03 (d, $J = 6.8$ Hz, 3H, CH*Me*$_2$), 1.18 (d, $J = 6.6$ Hz, 3H, CH*Me*$_2$), 1.77 (sept, $J = 6.9$ Hz, 1H, C*H*Me$_2$), 2.30 (sept, $J = 6.9$ Hz, 1H, C*H*Me$_2$), 2.41 (s, 6H, N*Me*$_2$), 2.87 (br, 3H, N*Me*$_2$), 2.93 (sept, $J = 6.8$ Hz, 1H, C*H*Me$_2$), 3.00 (br, 3H, N*Me*$_2$), 3.46 (sept, $J = 7.0$ Hz, 1H, C*H*Me$_2$), 6.06 (dd, $J = 3.4$ and 1.6 Hz, 1H, pyrrole), 6.29 (s, 1H, pyrrole), 6.46 (s, 2H, pyrrole), 6.65 (dd, $J = 3.5$ and 1.0 Hz, 1H, pyrrole), 7.05–6.85 (m, 8H, aryl), 7.36 (s, 1H, pyrrole), 7.42 (s, 1H, C*H*=N), 7.47 (s, 1H, C*H*=N). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 21.1, 22.6, 23.4, 23.8, 26.0, 26.1, 26.3, 26.6, 26.8, 26.9, 27.0, 28.1 (all *C*H*Me*$_2$), 39.2, 45.7, 47.3 (all N*Me*$_2$), 113.1, 114.0, 119.5, 121.2 (pyr), 123.5, 123.6, 125.3, 125.8, 126.4, 136.8, 137.4, 139.4, 141.6, 142.0, 142.6, 142.7 (aryl), 147.6 (pyr), 149.6 (pyr), 162.1 (C=N), 163.5 (C=N). Infrared (Nujol mull, cm^{-1}): 1627 (s), 1595 (s), 1578 (s), 1488 (m), 1429 (s), 1362 (w), 1343 (w), 1323 (m), 1310 (m), 1294 (s), 1255 (m), 1190 (w), 1167 (m), 1133 (m), 1092 (m), 1035 (s), 993 (m), 952 (m), 933 (w), 907 (m), 885 (w), 747 (s), 695 (w).

Preparation of $(L^1)ZrCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (3). A suspension of $ZrCl_4$ (0.36 g, 1.6 mmol) in diethyl ether (*ca.* 50 cm^3) was treated with LiL^1 (0.70 g, 1.6 mmol) at 0 °C with vigorous stirring. The mixture was stirred for 2 h and then filtered to remove residual solids. The solvent was removed from the filtrate *in vacuo*, affording a bright yellow powder. Bright yellow crystals were obtained from a diethyl ether solution at −20 °C. Yield 0.87 g (1.05 mmol, 85%). Anal. $C_{38}H_{58}Cl_4LiN_3O_2Zr$, found (calc.) C, 55.3 (55.1); H, 7.0 (7.0); N, 4.8 (5.1); Cl, 17.1 (17.1). NMR ^1H (300 MHz, 25 °C, C_6D_6): δ 8.09 (s, 2H, C*H*=N), 7.17–7.12 (m, 6H, aryl), 6.38 (br, 2H, pyrrole), 3.99 (sept, 4H, $J = 6.7$ Hz, C*H*Me$_2$), 3.16 (q, 8H, $J = 7.1$ Hz, -C*H*$_2$CH$_3$), 1.49 (d, 12H, $J = 6.7$ Hz, CH*Me*$_2$), 1.16 (d, 12H, $J = 6.7$ Hz, CH*Me*$_2$), 0.85 (t, 12H, $J = 7.1$ Hz, -CH$_2$C*H*$_3$). ^{13}C (75.4 MHz, 25 °C, C_6D_6): δ 163.11 (*C*H=N), 148.93 (pyrrole, C–N), 142.46 (C_6H_3, *o*-C), 141.99 (C_6H_3, *p*-C), 126.70 (C_6H_3, *ipso*-C), 123.25 (C_6H_3, *m*-C), 117.41 (pyrrole, C–H), 65.33 (-*C*H$_2$CH$_3$), 28.63 (*C*HMe$_2$), 25.11 (CH*Me*$_2$), 23.71 (CH*Me*$_2$), 14.36 (-CH$_2$*C*H$_3$). Infrared (Nujol mull, cm^{-1}): 1594 (s), 1581 (s), 1568 (s), 1417 (s), 1378 (s), 1357 (s), 1335 (s), 1096 (s), 1069 (vs), 806 (m), 780 (m), 741 (m).

Table 4 Crystal data of iminopyrrole compounds

Compounds	$HL^1\cdot 0.5Et_2O$	**1**	**2**	**5**
Formula	$C_{30}H_{39}N_3\cdot 0.5Et_2O$	$C_{36}H_{56}N_6Zr$	$C_{38}H_{54}N_6Zr$	$C_{60}H_{76}FeN_6$
M	478.70	664.09	686.09	937.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	6.07990(10)	13.5477(1)	14.7035(2)	10.6498(1)
b/Å	18.1845(5)	16.453(1)	11.3266(1)	21.2477(2)
c/Å	27.3900(7)	18.0523(1)	22.2836(3)	24.3318(3)
β/°	91.7080(14)	109.5360(4)	97.8130(6)	97.2920(5)
U/Å^3	3026.89(12)	3792.98	3676.68(8)	5461.36
D_c/g cm^{-3}	1.050	1.163	1.239	1.140
Z	4	4	4	4
μ/mm^{-1}	0.062	0.320	0.333	0.318
Reflections collected/unique	11599/5903	14177/7244	13383/7069	20488/10540
R_{int}[a]	0.0209	0.0120	0.0511	0.0146
R_1 [$I > 2\sigma(I)$][b]	0.0600	0.0240	0.0355	0.0407
wR_2 (all data)[c]	0.2051	0.0632	0.0953	0.1151

[a] $\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Preparation of $(L^2)_2ZrCl_2$ (4). A suspension of $ZrCl_4$ (0.28 g, 1.2 mmol) in diethyl ether (*ca.* 50 cm^3) was treated with Li**L**^{2} (0.80 g, 2.4 mmol) at 0 °C with vigorous stirring. The mixture was stirred for 2 h and then filtered to remove residual solids. The solvent was removed from the filtrate *in vacuo*, affording a yellow solid, yield 0.68 g (1.01 mmol, 84%). Anal. $C_{34}H_{42}Cl_2N_4Zr$, found (calc.) C, 62.5 (61.1); H, 6.6 (6.3); N, 8.2 (8.4); Cl, 6.7 (10.6). ^{1}H NMR (300 MHz, 27 °C, C_6D_6): δ 7.60 (s, 2H, CH=N), 7.18–7.05 (m, 8H, aryl, pyrrole), 6.57 (dd, 2H, $J = 1.1$ and 1.1 Hz, pyrrole), 6.12 (dd, 2H, $J = 2.1$ and 2.0 Hz, pyrrole), 3.02 (sept, 2H, $J = 6.6$ Hz, C*H*Me$_2$), 2.85 (sept, 2H, $J = 6.6$ Hz, C*H*Me$_2$), 1.21 (d, 6H, $J = 6.6$ Hz, CH*Me*$_2$), 1.07 (d, 6H, $J = 6.6$ Hz, CH*Me*$_2$), 0.88 (d, 6H, $J = 6.6$ Hz, CH*Me*$_2$), 0.84 (d, 6H, $J = 6.6$ Hz, CH*Me*$_2$). ^{13}C NMR (75.4 MHz, 27 °C, C_6D_6): δ 163.59 (CH=N), 146.38 (pyrrole, C–N), 144.19 (aryl, C–H), 143.51 (aryl), 142.55 (aryl), 137.85 (aryl), 124.75 (aryl, C–H), 123.80 (pyrrole, C–H), 123.43 (aryl, C–H), 115.26 (pyrrole, C–H), 29.26 (*C*HMe$_2$), 28.18 (*C*HMe$_2$), 27.14 (CH*Me*$_2$), 26.67 (CH*Me*$_2$), 23.68 (CH*Me*$_2$), 22.74 (CH*Me*$_2$). Infrared (Nujol mull, cm^{-1}) 1627 (m), 1594 (s), 1580 (s), 1398 (m), 1379 (m), 1298 (m), 1282 (m), 1252 (w), 1164 (m), 1106 (w), 1039 (s), 994 (w), 896 (w), 802 (w), 762 (m), 753 (m).

Preparation of $Fe(L^1)_2$ (5). To a suspension of $FeCl_2$ (0.35 g, 2.77 mmol) in thf (40 cm^3) was added lithium 2,5-bis-(2,6-diisopropylphenyl)iminopyrrollide (2.28 g, 9.0 mmol). The solution was refluxed for 16 h. The deep red solution was evaporated to dryness and extracted with diethyl ether (20 cm^3). This extract was concentrated and left to crystallise at −20 °C. A mixture of crystals of the iron complex **5** and the free ligand formed. Crystals of **5** were selected manually. Solid **5** shows a magnetic moment $\mu_{eff} = 3.43$ μ_B. The compound was identified by X-ray diffraction. Anal. $C_{60}H_{76}FeN_6$, found (calc.) C, 75.6 (76.9); H, 8.2 (8.2); N, 8.2 (9.0)%. Infrared (Nujol mull, cm^{-1}): 1621 (s), 1564 (s), 1401 (m), 1379 (m), 1359 (m), 1318 (s), 1282 (m), 1205 (w), 1098 (m), 1061 (m), 1045 (m), 933 (w), 857 (m), 803 (m), 773 (m), 757 (m), 735 (m), 687 (w).

Preparation of $[Li(thf)_n]^+[CoCl_2(L^1)]^-$ (6). To a solution of $CoCl_2$(thf) (0.65 g, 5 mmol) in thf (25 cm^3) at −78 °C was added dropwise a solution of Li[**L**^{1}] (2.25 g, 5 mmol) in thf (25 cm^3). The mixture was warmed to room temperature and stirred for 3 h. The solvent was removed *in vacuo*, giving a deep green glassy solid (yield 3.2 g, 90%). This crude product was used for polymerisation reactions. Extraction with diethyl ether followed by concentration to dryness *in vacuo*, redissolving in 5 cm^3 of thf and layering with light petroleum gave fine green needles of **6a** ($n = 4$) suitable for X-ray diffraction analysis (0.22 g). The compound is paramagnetic. Drying the compound *in vacuo* at room temperature gave a material which analysed for $[Li(thf)_2][CoCl_2(L^1)]$ (**6b**). Anal. $C_{38}H_{54}N_3Cl_2CoLiO_2$, found (calc.) C, 61.0 (63.3); H, 7.6 (7.5); N, 5.8 (5.8); Cl, 10.2 (9.8)%. Infrared (Nujol mull, cm^{-1}): 1624 (m), 1565 (s), 1407 (m), 1363 (m), 1322 (s), 1256 (w), 1214 (w), 1165 (m), 1098 (m), 1046 (m), 933 (w), 890 (w), 859 (w), 801 (w), 773 (w), 754 (w), 735 (w).

Preparation of $Co(L^2)_2$ (7). To H**L**^{2} (1.54 g, 6 mmol) in Et_2O (40 cm^3) was added dropwise Bu^{n}Li (3.8 cm^3, 1.6 M) at −78 °C. The mixture was allowed to warm to room temperature and added to a cold (0 °C) slurry of $CoCl_2$ (0.80 g, 6 mmol) in Et_2O (20 cm^3). Stirring was continued for 5 h. The mixture was filtered and concentrated to afford a dark-red halide-free paramagnetic solid, yield 0.85 g (25%). Anal. $C_{34}H_{42}CoN_4$, found (calc.): C, 71.7 (72.2); H, 7.8 (7.5); N, 10.0 (9.9); EI-MS: *m*/*z* 565 (M$^+$).

Preparation of $Ni(L^2)_2$ (8). To H**L**^{2} (1.59 g, 6 mmol) in Et_2O (40 cm^3) was added dropwise Bu^{n}Li (3.9 cm^3, 1.6 M) at −78 °C. The mixture was allowed to warm to room temperature and added to a cold (0 °C) slurry of $NiBr_2$(dme) (2.0 g, 6.5 mmol) in Et_2O (20 cm^3). Stirring was continued for 1 h. The solvent was removed and the brown residue extracted with toluene and filtered. Removal of the solvent left a brown halide-free solid, yield 0.54 g (15%). Anal. $C_{34}H_{42}NiN_4$, found (calc.) C, 71.5 (72.2); H, 7.6 (7.5); N, 9.6 (9.9). ^{1}H NMR (250 MHz, 25 °C, C_6D_6): δ 1.23 (d, 12H, CH*Me*$_2$), 1.31 (d, 12H, CH*Me*$_2$), 4.53 (sept, 4H, C*H*Me$_2$), 5.15 (m, 2H, pyrrole), 5.99 (m, 2H, pyrrole), 6.61 (m, 2H, pyrrole), 6.64 (s, 2H, CH=N), 7.06–7.25 (m, 6H, aryl).

Ethene polymerisations

A toluene solution of methylaluminoxane (10 wt%, 15 cm^3) was diluted with 25 cm^3 toluene and saturated with 1 bar ethene at room temperature, with vigorous stirring. A solution of the catalyst precursor (25 μmol Zr) was added. Reactions were terminated after 20 min by injecting 5 cm^3 methanol. The contents of the reaction vessel was poured into methanol, washed with HCl and methanol and dried.

Alkene oligomerisation

For a typical polymerisation experiment, 20 cm^3 of a toluene solution of MAO (10 wt%) was diluted with 20 cm^3 of toluene and saturated with ethene at 1 bar at 20 °C. The catalyst was injected as a 0.5 M solution in toluene (0.1 cm^3, 50 μmol). Once feed gas uptake had ceased, the reaction was quenched by the addition of 1 cm^3 of dilute HCl. The organic phase was separated and the solvent removed by distillation. The sample was analysed by NMR spectroscopy.

X-Ray crystallography

In each case a suitable crystal was coated in an inert perfluoropolyether oil and mounted in a nitrogen stream at 150 K on a Nonius Kappa CCD area-detector diffractometer. Data collection was performed using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the CCD detector placed 30 mm from the sample *via* a mixture of 1° φ and ω scans at different θ and κ settings using the program COLLECT.[17] The raw data were processed to produce conventional data using the program DENZO-SMN.[18] The data sets were corrected for absorption using the program SORTAV.[19] All structures were solved by heavy-atom methods using SHELXS-97[20] and were refined by full-matrix least squares refinement (on F^2) using SHELXL-97.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised positions. Crystallographic data for compounds **HL**^{1}, **1**, **2** and **5** are summarised in Table 4.

CCDC reference number 186/1804.

See http://www.rsc.org/suppdata/dt/a9/a909125d/ for crystallographic files in .cif format.

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