Imine Versus Amine Donors in Iron-Based Ethylene Polymerisation Catalysts

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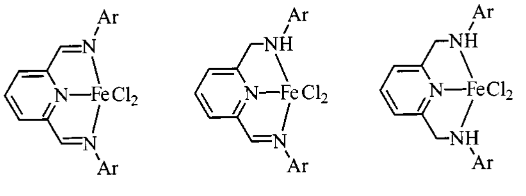
The synthesis and characterisation of iron(II) dichloro complexes containing neutral tridentate nitrogen ligands of the type 2-arylaminoalkyl-6-aryliminoalkylpyridine [2-ArNHCR(Me)-6-ArN=CR]C_5H_3N (R = H, Ar = 2,6-$i$$Pr_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$; R = Me, Ar = 2,6-$i$$Pr_2C_6H_3$)] and 2,6-bis(arylaminomethyl)pyridine [2,6-($ArNHCH_2$)$_2$]C_5H_3N (Ar = 2,6-$i$$Pr_2C_6H_3$) are described and their activity in ethylene polymerisation is compared with their 2,6-bis(aryliminoalkyl)pyridine analogues.

Introduction

Transition metal-catalyzed olefin polymerisation is currently a subject of intense academic and industrial interest. The need for greater control over the products of olefin polymerisation, combined with advances in the understanding of homogeneous polymerisation systems, have resulted in the development of highly active single-site olefin polymerisation catalysts such as Group 4 metallocenes and the "constrained geometry" catalysts'.[1−5] The development of non-metallocene early transition metal catalysts, and in particular the discovery of highly active late transition metal based systems, have signposted the way forward for further developments in catalytic olefin polymerisation.[6,7] The discovery by Brookhart and co-workers in 1995 of highly active nickel and palladium olefin polymerisation catalysts containing the α-diimine ligand frame[8] has been followed by extensive studies on variations of the α-diimine ligand.[9−11] In addition, many other non-diimine neutral bidentate ligands have been screened for olefin polymerisation activity, a large number by in situ methods.[7,12] However, to date, no other donor combinations have matched the high activities obtained with α-diimine ligands, suggesting a special feature of these systems that has yet to be fully understood.

A second family of highly active late transition metal polymerisation catalysts based on 2,6-bis(imino)pyridine complexes of iron and cobalt, was reported independently by ourselves,[13] Bennett and Brookhart in 1998.[14] The effects of ligand changes, especially at the aryl (Ar) and imino carbon (R) substituents, on the activity and product selectivity of these bis(imino)pyridine iron and cobalt catalysts (**I**) have been studied in detail,[15−17] as well as the polymerisation of propene[18−20] and applications in reactor blending.[21,22] Only a few variations on the core bis(imino)pyridine skeleton have been reported; for example, a neutral tridentate bis(oxazolinyl)pyridine ligand[23] and monoanionic tridentate bis(imino)pyrollide,[24] bis(amino)phenyl and bis(phosphanyl)amide ligands.[25] These variations have resulted in very low catalyst activities. With a view to obtaining a greater understanding of structure-activity relationships in the [N,N,N]Fe catalyst system, we have targeted alternative tridentate [N,N,N] chelate ligands. A relatively straightforward modification to the ligand frame is to replace one, or both, of the imine groups by amine donors, examples being 2-aminoalkyl-6-iminoalkylpyridine complexes of type **II** and the 2,6-bis(aminoalkyl)pyridine species of type **III** (see Figure 1). The synthesis and characterisation of complexes of type **II** and **III** are described and their ethylene polymerisation activity is discussed and compared to the parent bis(imino)pyridine system **I**.



I II III

Figure 1. Pyridyldiimine (**I**), pyridylimineamine (**II**) and pyridyldiamine (**III**) iron complexes

Results and Discussion

Synthesis of ligands and complexes

A convenient method of preparing 2-aminoalkyl-6-iminoalkylpyridines is by exploiting attack by nucleophilic reagents at the imine carbon atoms.[26] We have recently shown that $AlMe_3$ reacts with bis(imino)pyridines to give products of the type {[2-ArNCR(Me)-6-ArN=CR]-C_5H_3N}$AlMe_2$ (**1a−c**, Scheme 1) in which only one of the imino functionalities is attacked to generate an amide donor.[27] Hydrolysis of these complexes, followed by extraction with pentane and workup, affords ligands **2a−c** as pale yellow crystalline solids.

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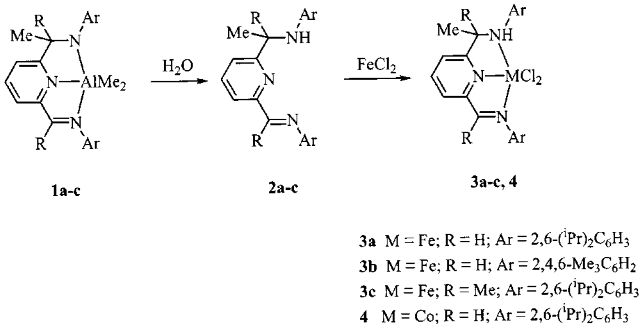


Scheme 1

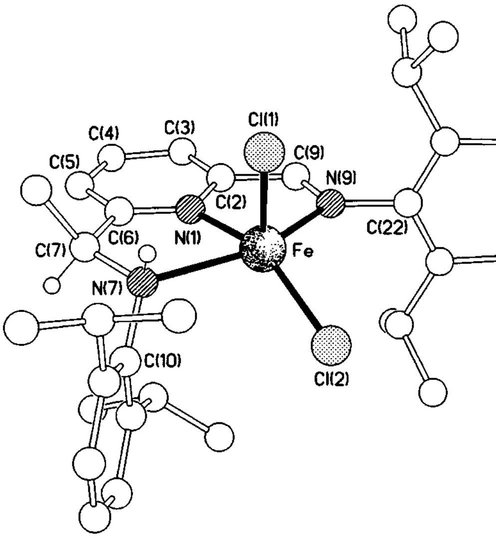


Figure 3. The molecular structure of **3a**; selected bond lengths (Å) and angles (°): Fe−N(1) 2.115(7), Fe−N(7) 2.310(8), Fe−N(9) 2.217(8), Fe−Cl(1) 2.311(3), Fe−Cl(2) 2.243(2), C(7)−N(7) 1.489(12), C(9)−N(9) 1.281(12); N(1)−Fe−N(9) 75.4(3), N(1)−Fe−Cl(2) 148.0(2), N(9)−Fe−Cl(2) 102.9(2), N(1)−Fe−N(7) 73.5(3), N(9)−Fe−N(7) 148.5(3), Cl(2)−Fe−N(7) 101.2(2), N(1)−Fe−Cl(1) 102.8(2), N(9)−Fe−Cl(1) 102.3(2), Cl(2)−Fe−Cl(1) 108.6(1), N(7)−Fe−Cl(1) 88.8(2)

The ^{1}H NMR spectra of **2a−c** confirm the presence of the amine protons as broad resonances in the range δ = 4.3−4.5, and the infrared spectra show N−H stretches in the region 3355−3365 cm^{-1}. A single crystal X-ray structure of **2a** shows the molecule to possess a *transoid* relationship between the imine and amine groups (Figure 2), a geometry that is different to the *cisoid* conformation in the metal complexes (see **3a**, Figure 3). There is only a small (ca. 7°) out-of-plane rotation of the C=N double bond relative to the pyridyl ring, whereas the 2,6-diisopropylphenyl ring system is oriented essentially orthogonally (ca. 87°). The *transoid* conformation observed here for the pyridyl imine unit is typical for such species in the solid state,[18,28,29] i.e. there has to be an approximate 180° rotation about the C(2)−C(9) bond for chelation of the pyridyl and imino nitrogen atoms to a metal centre. In contrast to the in-plane conformation of the conjugated imine group, there is a marked deviation of the saturated "amine arm" from coplanarity with the pyridyl ring, the N(1)−C(6)−C(7)−N(7) torsion angle being 65°. Centrosymmetrically related pairs of molecules pack such that the edge of ring **A** of one molecule is directed into the face of ring **B** of another; the centroid···centroid distance is 4.94 Å, and is consistent with an aromatic···aromatic edge-to-face interaction.

Treatment of **2a−c** with FeCl$_2$ in *n*BuOH at elevated temperature gives complexes **3a−c** as pale blue solids. Analogous to the bis(imino)pyridine systems, these complexes are paramagnetic, with μ_{eff} typically between 5.4 and 5.6 BM, indicating four unpaired electrons; they were further characterized by IR, MS and microanalysis. The IR spectra of **3a−c** show ν(N−H) stretches at ca. 3300 cm^{-1}. Crystals of **3a** suitable for a single crystal structure determination were grown from a concentrated acetonitrile solution. The X-ray analysis of **3a** shows[30] (Figure 3) that the partially saturated ligand (**2a**) complexes to the iron(II) centre in a similar way to its unsaturated analogue,[13,14] the N(7)−C(7)−py−C(9)−N(9) component being co-planar to within 0.07 Å, with the iron atom lying 0.07 Å out of this plane. The five-membered chelate ring containing the amino nitrogen atom N(7) is also almost planar, the torsional twist about the C(6)−C(7) bond being only ca. 6°. The geometry at iron is distorted square pyramidal with *cis* angles in the range 73.5(3) to 108.6(1)°, the iron atom lying 0.43

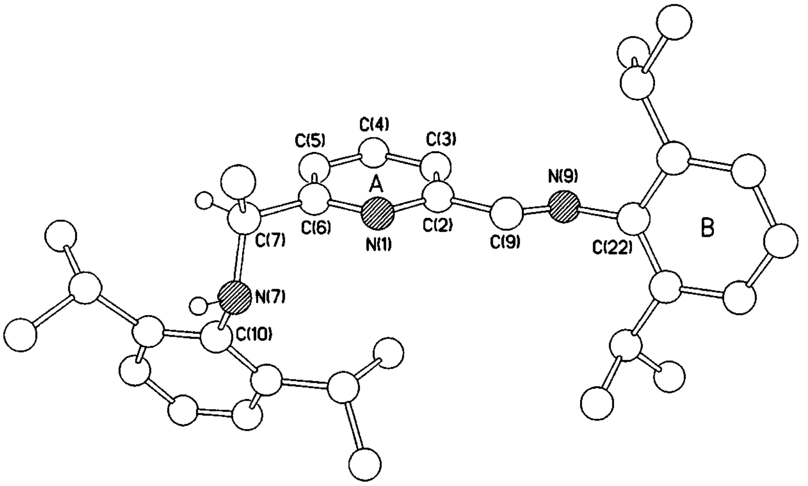
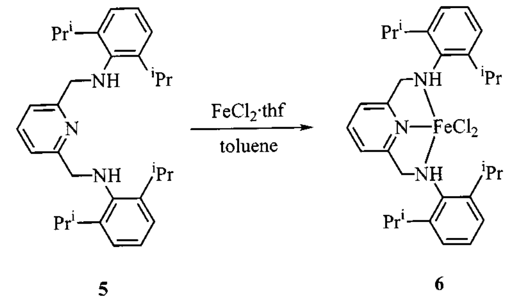


Figure 2. The molecular structure of **2a**; selected bond lengths (Å): C(7)−N(7) 1.473(8), C(9)−N(9) 1.255(8)

Å out of the basal plane in the direction of the apical atom Cl(1). The most noticeable feature in the pattern of bonding is the weak nature of the Fe−N(7) linkage [2.310(8) Å] — a distance equal to that to the apical chlorine centre Cl(1) [2.311(3) Å] — and a consequent shortening of the Fe−N(9) bond to 2.217(8) Å {*cf.* 2.238(4) and 2.250(4) Å in the related bis(imino)pyridine iron dichloride species[13−15]}. The Fe−N(1) bond length is, as expected, shorter at 2.115(7) Å, as is the distance to the basal chlorine [2.243(2) Å]. Both of the 2,6-diisopropylphenyl substituents are oriented approximately orthogonally to the basal coordination plane, the ca. 81° twist about the N(9)−C(22) bond facilitating characteristic C−H···N(pπ) interactions[31] between the isopropyl methine hydrogen atoms and the imine nitrogen [N(9)]; the H···N distances are 2.41 and 2.44 Å. The amine nature (i.e. sp^3 hybridisation) of the N(7) nitrogen precludes any such interaction here, and results in a distinct folding of the C(10) aryl substituent out of the N(7)−C(7)−py−C(9)−N(9) plane — the C(22) phenyl carbon atom is virtually coplanar with this plane (deviation ca. 0.03 Å) whilst C(10) lies 1.06 Å below it, such that the N−Ar bond is inclined by ca. 42° to this plane. This deviation will strongly affect the steric influence of the ligand on the remaining metal coordination sites. Finally, there are no dominant intermolecular interactions of note, although there is evidence for a weak C−H···Cl hydrogen bond between the imine C−H group [C(9)] in one molecule and the apical chorine [Cl(1)] in another; the C···Cl and H···Cl distances are 3.34 and 2.57 Å, respectively, with a C−H···Cl angle of 137°.

2,6-Bis(2,6-diisopropylphenylaminomethyl)pyridine **(5)** (see Scheme 2) was readily prepared according to a procedure by McConville and co-workers, from the reaction of 2,6-bis(bromomethyl)pyridine with LiNHAr (Ar = 2,6-diisopropylphenyl).[32] However, this potentially tridentate chelate does not react with anhydrous $FeCl_2$ in *n*BuOH, nor in THF; there is no colour change on mixing and warming to 80 °C, and after workup, only starting materials are recovered. In case this outcome may have been a consequence of the modified disposition of the large aryl groups imposed by the sp^3-hybridised nitrogen centres, we also attempted a similar reaction between 2,6-bis(diphenylaminomethyl)pyridine and $FeCl_2$ but again complexation did not occur. An alternative method, recently described by Calderazzo et al.,[33] was investigated by refluxing a mixture of pyridyldiamine ligand **5** and $FeCl_2$·thf in toluene overnight. This route leads to the desired complex **6** in high yield as blue/green crystals (Scheme 2). The compound is air stable and readily soluble in polar solvents such as dichloromethane or THF, but decomposes in acetone. Satisfactory microanalysis, IR and magnetic data (μ_{eff} = 5.08 BM) as well as X-ray crystallographic analysis confirm the structure of **6** to be the expected five-coordinate [N,N,N]$FeCl_2$ complex.



Scheme 2

Depending upon the method of crystallization, two different crystalline forms are produced, one monoclinic (**6a**, Figure 4), obtained from a hot saturated toluene solution and the other orthorhombic (**6b**, Figure 5), grown from cold (−30 °C) toluene. In the monoclinic form, the ligand is tridentate, binding to the iron centre through the pyridyl and the two amine nitrogen atoms in a fashion analogous to that seen in the imine/amine complex **3a**. The geometry at iron is still distorted square pyramidal, but with the iron atom lying 0.61 Å out of the basal plane; the *cis* angles are in the range 74.2(1) to 115.6(1)°. The two five-membered chelate rings are nonplanar, there being torsional twists of ca. 26 and 18° about the C(2)−C(7) and C(6)−C(8) bonds, respectively. Interestingly, these twists are in opposite senses, thus producing δ and λ conformations, respectively, for the two rings, whereas the configurations at the two amino centres are the same. As expected, the Fe−N(1) distance [2.118(4) Å] is significantly shorter than that to the two amine nitrogens, which are the same at 2.313(4) and 2.328(4) Å for N(7) and N(8), respectively, values essentially the same as that to the amino nitrogen in **3a**. Similarly, the Fe−Cl(axial) distance [2.313(2) Å] is longer than its basal counterpart [2.269(2) Å]. In common with **3a**, the two 2,6-diisopropylphenyl ring systems are oriented approximately orthogonally to the basal coordination plane. Although both the amine nitrogen atoms N(7) and N(8) are pyramidal, as a consequence of the different folds of the five-membered chelate rings only one of the 2,6-diisopropylphenyl rings is folded out of the basal coordination plane, the other having its N(7)−C(9) linkage virtually in plane. This results in an overall geometry very similar to that seen in the imine-amine structure **3a**. The only intermolecular packing interaction of note is a weak π-π stacking of pairs of C(21) containing 2,6-diisopropylphenyl rings of adjacent molecules; the mean interplanar separation is 3.85 Å.

The orthorhombic form of the complex **(6b)** has crystallographic C_2 symmetry about an axis passing along the Fe···N(1)···C(4) vector. The conformations of the two five-membered chelate rings are both λ relative to the *S* configurations at the amino centres (Figure 5); the torsional twists about the C(2)−C(5) bonds are ca. 17°. Accompanying this difference in the conformational/configurational relationship (*cf.* that in **6a**) is a change from a square pyramidal to a trigonal bipyramidal coordination geometry for the iron with N(1), Cl and ClA forming the equatorial plane. The angles subtended at iron by these three atoms are all, within statistical significance, 120°; the axial bonds [Fe−N(5)] subtend an angle of 153.8(2)°. The Fe−N(1) and Fe−N(5) bond lengths [2.095(5) and 2.322(4) Å, respectively] do not differ significantly from those in **6a**. In contrast to the asymmetric Fe−Cl bond lengths in **3a** and **6a**, here they are

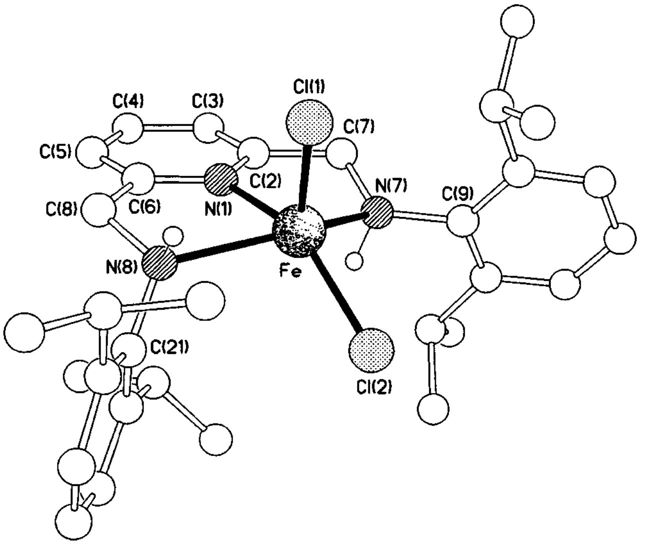


Figure 4. The molecular structure of the monoclinic form of **6** (**6a**) showing also the square pyramidal geometry at iron; selected bond lengths (Å) and angles (°): Fe−N(1) 2.118(4), Fe−N(7) 2.313(4), Fe−N(8) 2.328(4), Fe−Cl(1) 2.313(2), Fe−Cl(2) 2.269(2), C(7)−N(7) 1.445(6), C(8)−N(8) 1.507(6); N(1)−Fe−Cl(2) 142.87(12), N(1)−Fe−N(7) 74.16(14), Cl(2)−Fe−N(7) 91.09(12), N(1)−Fe−Cl(1) 103.32(12), Cl(2)−Fe−Cl(1) 113.75(7), N(7)−Fe−Cl(1) 115.61(14), N(1)−Fe−N(8) 76.48(14), Cl(2)−Fe−N(8) 101.42(11), N(7)−Fe−N(8) 145.2(2), Cl(1)−Fe−N(8) 88.94(12)

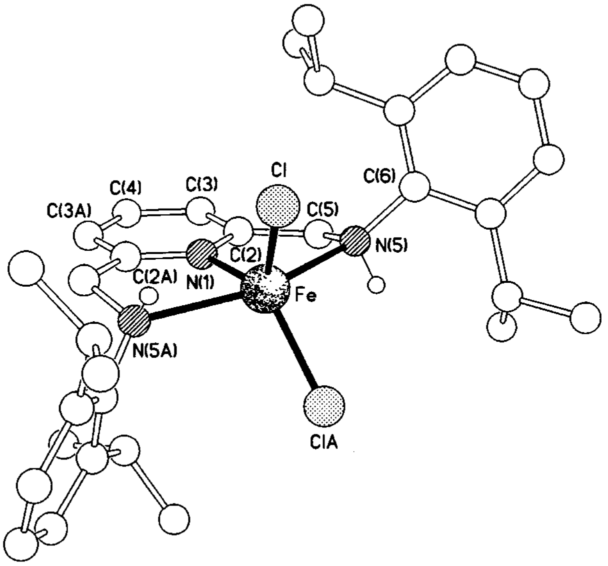


Figure 5. The molecular structure of the orthorhombic form of **6** (**6b**) showing also the trigonal bipyramidal geometry at iron; selected bond lengths (Å) and angles (°): Fe−N(1) 2.095(5), Fe−N(5) 2.322(4), Fe−Cl 2.277(2), C(5)−N(5) 1.479(6); N(1)−Fe−Cl 120.03(5), N(1)−Fe−ClA 120.03(5), Cl−Fe−ClA 119.94(9), N(1)−Fe−N(5A) 76.91(10), Cl−Fe−N(5A) 90.80(12), ClA−Fe−N(5A) 102.29(12), N(1)−Fe−N(5) 76.91(10), Cl−Fe−N(5) 102.29(12), ClA−Fe−N(5) 90.80(12), N(5A)−Fe−N(5) 153.8(2)

symmetric at 2.277(2) Å, there being no axial/basal distinction. The essentially orthogonal relationship between the 2,6-diisopropylphenyl ring systems and the N_3Fe coordination plane is retained, but in contrast to **6a**, because of the C_2 symmetry and the pyramidalisation at the amine nitrogens, one of the 2,6-diisopropylphenyl is directed “up” and the other “down”. There are no intermolecular packing interactions of consequence.

For bis(imino)pyridine iron complexes we have shown previously that, depending on the aryl substituents of the ligand (e.g. 2,6-diisopropylphenyl versus mesityl), either square based pyramidal or trigonal bipyramidal geometries are observed in the solid state.[15] Here we see that, in the case of complex **6**, different geometries (**6a** and **6b**) are obtained depending on the method of crystallisation. These results suggest a small energy difference between the two geometries, indicating stereochemical nonrigidity of $[N,N,N]FeCl_2$ complexes, a behaviour that is not uncommon for five-coordinate complexes.[34]

Ethylene Polymerisation Results

The results of ethylene polymerization tests at 1 bar and 10 bar with precatalysts **3a−c**, **4** and **6** with methylaluminoxane (MAO) as activator are collected in Table 1. For comparison, the polymerisation results of the previously reported pyridyldiimine iron precatalysts **7** and **8** are also included (Figure 6). Two sets of polymerisation tests are shown in Table 1. Tests at 1 bar were carried out in a Schlenk flask at room temperature, with no scavenger and toluene as the solvent. High pressure tests (10 bar) were performed in a 1 litre autoclave at 35 °C, with triisobutylaluminium as a scavenger and isobutane as the solvent.

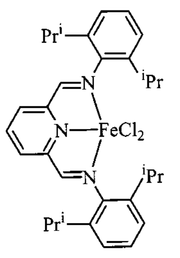
The results collected in Table 1 show that all of the new pyridylimine amine (**3a−c**) and pyridyldiamine (**6**) iron complexes are active ethylene polymerisation catalysts under these conditions. However, it is also apparent that the activities of these new precatalysts are dramatically reduced relative to the pyridyldiimine catalysts **7** and **8** (run 10 and 11). The highest activities of 90−110 g/mmol·h·bar are obtained with complex **3c**, which is derived from the pyridyldiketimine ligand (as in complex **8**). The precatalysts **3a** and **3b**, derived from aldimine precursors, generally show lower activities, around 20 g/mmol·h·bar. This difference in activity parallels the trends observed for aldimine (**7**) versus ketimine (**8**) precatalysts based on pyridyldiimine ligands (runs 10 and 11).[15] The very low activity observed for the pyridylimine amine cobalt precursor **4** (run 7) compared to the iron analogue **3a** (run 1) is equally not surprising, bearing in mind that, in general, for pyridyldiimine systems, cobalt precatalysts are an order of magnitude less active than their iron counterparts. Substitution of both imine donors for amine donors as in precatalyst **6** leads to a further decrease in activity, typically to around 10 g/mmol·h·bar. A similar behaviour of diimine versus diamine donors is observed in nickel ethylene polymerisation systems, where the saturated bis(2,6-diisopropylphenyl)ethylene diamine ligand showed only very low activity relative to the α-diimine analogue.[12]

Previously we have shown for pyridyldiimine iron polymerisation catalyst **8**, that the rate of propagation is first order in ethylene, resulting in a linear increase of the yield of polyethylene with pressure.[15] Although we have not carried out a systematic study of the effect of pressure on these new pyridylimine amine systems, the results in Table 1 show

Table 1. Results of ethylene polymerization runs using precatalysts **3a**−**c**, **4**, **6**−**8**

Run	Precatalyst (µmol)	Activator (mmol/equiv.)	T (°C)	P (bar)	Yield (g)	Activity (g $mmol^{-1}$ h^{-1} bar^{-1})	M_n	M_w	M_w/M_n
1[a]	**3a** (20)	MAO (8/400)	25	1	0.4	20			
2[b]	**3a** (25)	MAO (10/400)	35	10	5.2	21	30000	210000	7.1
3[a]	**3b** (20)	MAO (8/400)	25	1	0.4	18			
4[b]	**3b** (27)	MAO (10/400)	35	10	3.7	14	21000	177000	8.4
5[a]	**3c** (20)	MAO (8/400)	25	1	2.1	90			
6[b]	**3c** (25)	MAO (10/400)	35	10	27.8	110	161000	896000	5.5
7[a]	**4** (20)	MAO (8/400)	25	1	0.06	3			
8[a]	**6** (20)	MAO (8/400)	25	1	0.21	11			
9[b]	**6** (25)	MAO (10/400)	35	10	0.70	3	3000	63000	21.1
10[c]	**7** (6)	MAO (1.2/200)	35	10	18.2	305	3400	132000	38.9
11[c]	**8** (0.5)	MAO (0.5/1000)	50	10	26.9	5340	64000	611000	9.5

[a] Schlenk-test conditions: Toluene solvent (40 mL), reaction time 1 hour. − [b] High pressure reactor conditions: Isobutane solvent (0.5 L), reaction time 1 hour, $AliBu_3$ scavenger (2 mL of a 1 M solution). − [c] Results for precatalysts **7** and **8** taken from ref.[15]



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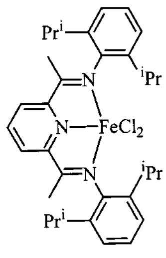

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Figure 6. 2,6-Bis(imino)pyridine iron precatalysts **7** and **8**

the difference between 1 bar and 10 bar tests. With a tenfold increase in pressure (similar amount of catalyst in each case) an approximate tenfold increase in polymer yield is observed, suggesting that for these systems the rate of propagation is also first order in ethylene.

Molecular weight data have only been obtained for the pyridyl imine amine systems which showed moderate activity (Table 1). The M_w value for the polyethylene obtained with the ketimine-derived imine amine catalyst **3c** is comparable to the parent pyridyl diimine catalyst **8**. The aldimine-derived analogue **3a** gives a lower value for M_n and M_w than for **3c**, but follows the same trend as seen for pyridyl diimine systems (cf. Runs 2 and 6 versus 10 and 11), including a negligible difference between 2,6-diisopropyl and mesityl substituents (**3a** versus **3b**, runs 2 and 4).

In conclusion, we have synthesized and characterized a series of complexes containing neutral tridentate [N,N,N] ligands. The 2-aminoalkyl-6-iminoalkyl-pyridine iron complexes of type **II** (Figure 1) show moderate activity in ethylene polymerisation, whereas a 2,6-bis(alkylamino)pyridyl iron complex of type **III** shows only low activity. Interestingly, although the activities are significantly lower than the related pyridyldiimine catalysts, similar trends upon ligand variation, both in activity as well as in polymer properties, are observed. A possible reason for the lower activity relative to bis(imino)pyridine systems is the weakness of the amino-iron interaction, which may lead to dissociation of the amine arm in these catalysts. However, the lack of conjugation through the ligand backbone may also be significant, as may the orientation of the amino aryl substituent in hindering access of monomer to the active site or growth of the polymer chain.

Experimental Section

General: All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College, Medac Ltd. or SACS at the University of North London. NMR spectra were recorded on a Bruker spectrometer at 250 MHz (^1H), and 62.9 MHz (^{13}C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent; coupling constants are quoted in Hz. Mass spectra were obtained using either Fast Atom Bombardment (FAB), Electron Impact (EI) or Chemical Ionization (CI). Magnetic susceptibility studies were performed using an Evans balance or the Evans NMR method (solvent CD_2Cl_2; reference: cyclohexane).

Materials: The ligands 2,6-bis[(2,6-diisopropylphenylimino)methyl-]pyridine,[15] and 2,6-bis[(2,6-diisopropylphenylamino)methyl]pyridine (**5**),[32] as well as pyridinedicarboxaldehyde,[35] $FeCl_2$·thf[33] and the aluminium complexes **1a**−**c**[27] were prepared according to established procedures while 2,6-diacetylpyridine, MAO (10% solution in toluene) and all anilines were purchased from Aldrich Chemical Co. All other chemicals were obtained commercially and used as received unless stated otherwise.

Synthesis of Ligands and Complexes

6-[(2,6-Diisopropylphenylamino)-1-ethyl]-2-[(2,6-diisopropylphenylimino)methyl]pyridine (2a): Pentane (40 mL) was added to $[C_5NH_3\{CH{=}N(2,6\text{-}iPr_2\text{-}C_6H_3)\}\{CHMeN(2,6\text{-}iPr_2\text{-}C_6H_3)\}]AlMe_2$ (**1a**; 5.79 g, 11.0 mmol) followed by slow addition of an equal volume of water. After stirring for a further 3 h the pentane was stripped off. The aqueous phase was then extracted into chloroform (3 × 30 mL), filtered, dried over $MgSO_4$ and taken to dryness to give analytically pure $[C_5NH_3\{CH{=}N(2,6\text{-}iPr_2\text{-}C_6H_3)\}\text{-}\{CHMeNH(2,6\text{-}iPr_2\text{-}C_6H_3)\}]$ (**2a**; 4.14 g, 80%). − ^1H NMR ($CDCl_3$, 293 K): δ = 8.38 (s, 1 H, N=CH), 8.17 [d, $^3J(HH)$ = 7.7, 1 H, Py-H_m], 7.73 [app. t, $^3J(HH)$ = 7.7, 1 H, Py-H_p], 7.3−7.0 (m, 7 H, Ar-H, Py-H_m), 4.48 [d, $^3J(HH)$ = 10.4, 1 H, N-H], 4.3−4.4 (m, 1 H, N−CHMe), 3.31 [sept, $^3J(HH)$ = 6.8, 2 H, $CHMe_2$], 3.02 [sept, $^3J(HH)$ = 6.8, 2 H, $CHMe_2$], 1.49 [d, $^3J(HH)$ = 6.6, 3 H, N−CHMe], 1.3−1.2 (m, 18 H, $CHMe_2$), 1.09 (d, 6 H, $CHMe_2$). − CI MS: *m*/*z* = 470 [(M + H)$^+$]. − IR (Nujol mull): ṽ = 3356 cm^{-1} [ν(N−H)]. − $C_{32}H_{43}N_3$ (469.71): calcd. C 81.88, H 9.17, N 8.96; found C 82.21, H 9.30, N 8.71.

Crystal Data for 2a: $C_{32}H_{43}N_3$, M = 469.7, monoclinic, space group $P2_1/c$ (no. 14), a = 16.208(2), b = 10.364(1), c = 17.664(3) Å, β = 100.67(1)°, V = 2916.1(6) Å^3, Z = 4, D_c = 1.070 g cm^{-3}, μ(Cu-K_α) = 4.70 cm^{-1}, F(000) = 1024, T = 293 K; clear plates, 0.23 × 0.07 × 0.02 mm, Siemens P4/RA diffractometer, ω-scans, 4065 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.096, wR_2 = 0.191 for 1619 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 116°$] and 317 parameters.
Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149266. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

6-[(2,4,6-Trimethylphenylamino)-1-ethyl]-2-[(2,4,6-trimethylphenylimino)methyl]pyridine (2b): Prepared in the same way as described for compound **2a**, from Al complex **1b**. Yield 75%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.28 (s, 1 H, N=CH), 8.07 [d, ^3J(HH) = 7.8, 1 H, Py-H_m], 7.64 [app. t, ^3J(HH) = 7.8, 1 H, Py-H_p], 7.14 (d, 1 H, Py-H_m), 6.84 (s, 2 H, Ar-H), 6.70 (s, 2 H, Ar-H), 4.43 [br, q, ^3J(HH) = 6.5, 1 H, N−CHMe], 4.31 (s, br, 1 H, N−H), 2.23 (s, 3 H, Ar-Me_p), 2.18 (s, 6 H, Ar-Me_o), 2.13 (s, 3 H, Ar-Me_p), 2.07 (s, 6 H, Ar-Me_o), 1.36 (d, 3 H, NCHMe). − CI MS: *m*/*z* = 385 [(M + H)$^+$]. − IR (Nujol mull): ṽ = 3359 cm^{-1} [ν(N−H)]. − $C_{26}H_{31}N_3$ (385.55): calcd. C 81.04, H 8.05, N 10.91; found C 81.44, H 8.39, N 10.79.

6-[2-(2,6-Diisopropylphenylamino)-2-isopropyl]-2-[(2,6-diisopropylphenylimino)ethyl]pyridine (2c): Prepared in the same way as described for compound **2a**, from Al complex **1c**. Yield 71%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.25 [d, ^3J(HH) = 7.7, 1 H, Py−H_m], 7.79 (app. t, ^3J(HH) = 7.7, 1 H, Py-H_p), 7.59 (d, 1 H, Py-H_m), 7.2−7.0 (m, 6 H, Ar-H), 4.47 (s, br, 1 H, N−H), 3.31 [sept, ^3J(HH) = 6.7, 2 H, $CHMe_2$], 2.77 [sept, ^3J(HH) = 6.7, 2 H, $CHMe_2$], 2.24 (s, 3 H, N=CMe), 1.51 (s, 6 H, N−CMe_2), 1.17 (d, 12 H, $CHMe_2$), 1.07 (d, 12 H, $CHMe_2$). − EI MS: *m*/*z* = 497 [M$^+$]. − IR (Nujol mull): ṽ = 3362 cm^{-1} [ν(N−H)]. − $C_{34}H_{47}N_3$ (497.77): calcd. C 82.09, H 9.46, N 8.45; found C 82.39, H 9.71, N 8.30.

{6-[(2,6-Diisopropylphenylamino)-1-ethyl]-2-[(2,6-diisopropylphenylimino)methyl]pyridine}iron(II) Dichloride (3a): $FeCl_2$ (0.20 g, 1.57 mmol) was dissolved in hot *n*-butyl alcohol (10 mL) at 80 °C. A suspension of **2a** (0.72 g, 1.62 mmol) in *n*-butyl alcohol was added dropwise at 80 °C. The reaction mixture turned blue. After stirring at 80 °C for 15 minutes the reaction was allowed to cool to room temperature. The reaction volume was then reduced to a few millilitres and diethyl ether added to precipitate [C_5NH_3{CH=N(2,6-*i*Pr_2-C_6H_3)}{CHMeNH(2,6-*i*Pr_2-C_6H_3)}]$FeCl_2$ (**3a**; 0.76 g, 83%) as a blue powder, which was subsequently washed three times with diethyl ether (10 mL). − μ_{eff} (Evans Balance): 5.6 BM. − IR (Nujol): ṽ = 3303 cm^{-1} [ν(N−H)]. − FAB MS: *m*/*z* = 596 [M$^+$], 560 [M$^+$ − Cl]. − $C_{32}H_{43}N_3FeCl_2$ (596.46): calcd. C 64.43, H 7.21, N 7.05; found C 64.70, H 7.19, N 6.99.

Crystal Data for 3a: $C_{32}H_{43}Cl_2N_3Fe$, M = 596.4, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.433(2), b = 13.449(3), c = 18.624(3) Å, V = 3365(1) Å^3, Z = 4, D_c = 1.177 g cm^{-3}, μ(Mo-K_α) = 6.30 cm^{-1}, F(000) = 1264, T = 293 K; deep red blocks, 0.57 × 0.40 × 0.23 mm, Siemens P4/PC diffractometer, ω-scans, 3302 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.065, wR_2 = 0.113 for 1968 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 347 parameters. The absolute chirality of **3a** (which undergoes spontaneous resolution upon crystallisation) was determined by an *R*-factor test [R_1^+ = 0.0648, R_1^- = 0.0666].
Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149267. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

{6-[(2,4,6-Trimethylphenylamino)-1-ethyl]-2-[(2,4,6-trimethylphenylimino)methyl]pyridine}iron(II) Dichloride (3b): Complex **3b** was prepared by an analogous route to that outlined for complex **3a** from $FeCl_2$ (0.15 g, 1.18 mmol) and ligand **2b** (0.44 g, 1.18 mmol). Yield: 0.46 g, 80%. − μ_{eff} (Evans Balance): 5.4 BM. − IR (Nujol): ṽ = 3307 cm^{-1} [ν(N−H)]. − FAB MS: *m*/*z* = 511 [M$^+$], 476 [M$^+$ − Cl]. − $C_{26}H_{31}Cl_2N_3Fe$ (512.30): calcd. C 60.94, H 6.05, N 8.20; found C 60.11, H 6.12, N 7.98.

{6-[2-(2,6-Diisopropylphenylamino)-2-isopropyl]-2-[(2,6-diisopropylphenylimino)ethyl]pyridine}iron(II) Dichloride (3c): Complex **3c** was prepared by an analogous route to that outlined for **3a** from $FeCl_2$ (0.15 g, 1.18 mmol) and **2c** (0.59 g, 1.18 mmol). Yield: 0.46 g, 62%. − μ_{eff} (Evans Balance): 5.6 BM. − IR (Nujol): ṽ = 3301 cm^{-1} [ν(N−H)]. − FAB MS: *m*/*z* = 623 [M$^+$], 588 [M$^+$ − Cl]. − $C_{34}H_{47}Cl_2N_3Fe$ (624.52): calcd. C 65.38, H 7.53, N 6.73; found C 65.31, H 7.89, N 7.31.

{6-[(2,6-Diisopropylphenylamino)-1-ethyl]-2-[(2,6-diisopropylphenylimino)methyl]pyridine}cobalt(II) Dichloride (4): Complex **4**[30] was prepared by an analogous route to that outlined for **3a** from $CoCl_2$ (0.15 g, 1.15 mmol) and **2a** (0.54 g, 1.15 mmol). Yield: 0.48 g, 70%. − μ_{eff}(Evans Balance): 4.6 BM. − IR (Nujol mull): ṽ = 3304 cm^{-1} [ν(N−H)]. − FAB MS: *m*/*z* = 599 [M$^+$], 563 [M$^+$ − Cl], 528 [M$^+$ −2Cl].

[2,6-Bis(2,6-diisopropylphenylaminomethyl)pyridine]iron(II) Dichloride (6): A suspension of the pyridyldiamine ligand **5** (0.45 g; 1.0 mmol) and $FeCl_2$·thf (1 equiv.) in toluene (50 mL) was refluxed overnight. Upon cooling to room temperature, the product precipitated as blue/green crystals (**6a**), which were washed with toluene and pentane and dried in vacuo. Another batch of crystals were grown from a saturated toluene solution at −30 °C (**6b**). Yield: 0.51 g (87%). − μ_{eff} (Evans NMR method): 5.08 BM. − $C_{31}H_{43}N_3FeCl_2$·0.5thf (620.51): calcd. C 63.88, H 7.63, N 6.77; found C 64.07, H 7.77, N 6.52.

Crystal Data for 6a (monoclinic form): $C_{31}H_{43}N_3Cl_2Fe$·$0.5C_7H_8$, M = 630.5, monoclinic, space group $P2_1/n$ (no. 14), a = 9.789(2), b = 14.750(4), c = 24.757(3) Å, β = 95.79(1)°, V = 3556(1) Å^3, Z = 4, D_c = 1.178 g cm^{-3}, μ(Mo-K_α) = 6.00 cm^{-1}, F(000) = 1340, T = 293 K; blue/straw dichroic needles, 0.77 × 0.17 × 0.17 mm, Siemens P4/PC diffractometer, ω-scans, 6268 independent reflections. The structure was solved by the heavy atom method and all the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.066, wR_2 = 0.137 for 3276 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 438 parameters.

Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149268. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Crystal Data for 6b (orthorhombic form): $C_{31}H_{43}N_3Cl_2Fe\cdot 3C_7H_8$, $M = 860.8$, orthorhombic, space group $Pccn$ (no. 56), $a = 25.815(2)$, $b = 10.106(1)$, $c = 18.516(1)$ Å, $V = 4830.6(5)$ Å^3, $Z = 4$ (the complex has crystallographic C_2 symmetry), $D_c = 1.184$ g cm^{-3}, μ(Cu-K_α) = 37.9 cm^{-1}, $F(000) = 1840$, $T = 183$ K; pale yellow plates, 0.53 × 0.47 × 0.07 mm, Siemens P4/RA diffractometer, ω-scans, 3564 independent reflections. The structure was solved by direct methods and all the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.068$, $wR_2 = 0.168$ for 2253 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 124°$] and 288 parameters.
Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149269. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

General Polymerization Procedures: (a) *High Pressure Tests*: A 1 litre stainless steel reactor was baked out under a nitrogen flow for at least 1 h at >85 °C and subsequently cooled to the temperature of polymerization. Isobutane (0.5 L) and trialkylaluminum (triisobutylaluminum) were introduced into the reactor and stirred at the reaction temperature for at least 1 hour. Ethylene was introduced by over-pressure and the difference between the total pressure and the initial pressure (isobutane and nitrogen: ca. 10 bar) is the pressure quoted in Table 1. The catalyst solution in toluene was then injected under nitrogen. The reactor pressure was maintained constant throughout the polymerization run by computer controlled addition of ethylene. The polymerization time was 60 minutes. Runs were terminated by venting off volatiles and the reactor contents were isolated, washed with aqueous HCl, methanol and dried in a vacuum oven at 50 °C.

(b) *Schlenk-line 1 bar ethylene Tests*: The precatalyst was dissolved in toluene (40 mL) and MAO (10 wt% in toluene) added to produce an orange solution. The Schlenk tube was placed in a water bath, purged with ethylene and the contents magnetically stirred and maintained under ethylene (1 bar) for the duration of the polymerization (60 minutes). The polymerization was terminated by the addition of aqueous hydrogen chloride. The solid PE was recovered by filtration, washed with methanol (50 mL) and dried (vacuum oven at 50 °C).

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