

Oligomerisation of Ethylene to Linear α -Olefins by new C_s - and C_1 -Symmetric [2,6-Bis(imino)pyridyl]iron and -cobalt Dichloride Complexes

Claudio Bianchini,^{*,[a]} Giuseppe Mantovani,^[a] Andrea Meli,^[a] Fabio Migliacci,^[a] Fabrizio Zanolini,^[a] Franco Laschi,^[b] and Anna Sommazzi^[c]

Keywords: Cobalt / Ethylene / Iron / N ligands / Oligomerisation

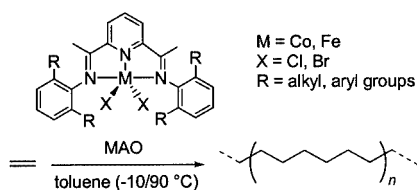
A new family of C_s - and C_1 -symmetric 2,6-bis(imino)pyridyl ligands has been synthesised. These ligands, which differ from their known counterparts in the contemporaneous presence of alkyl and aryl substituent at the ketimine nitrogen atoms, form stable, five-coordinate complexes with $FeCl_2$ and $CoCl_2$. All ligands and catalysts have been fully characterised both in the solid state and in solution. A single-crystal X-ray analysis of $[CoCl_2\{2-[CMe=N-(2,6\text{-dimethylphenyl})]-6-(CMe=N-C_6H_{11})C_5H_3N\}]\cdot H_2O$ shows the metal centre to adopt a highly distorted square-pyramidal geometry. In combination with methylaluminoxane (MAO), both iron and co-

balt compounds act as effective and selective (> 99%) catalysts for the oligomerisation of ethylene to a Schulz–Flory distribution of α -olefins, with the α factor ranging from 0.61 to 0.91. The iron catalysts exhibit TOFs as high as $7\cdot 10^5$ mol C_2H_4 (mol of cat $\times$ h) $^{-1}$ and are much more active than their cobalt analogues. Experiments at different ethylene pressures with the iron catalysts showed that both the propagation rate and the chain transfer rate are first order in ethylene pressure.

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Introduction

In 1998, Brookhart and Gibson independently discovered that [2,6-bis(arylimino)pyridyl]iron and -cobalt dihalides, when activated by MAO, are effective catalysts for the polymerisation of ethylene to high-density polyethylene (PE) with productivities as high as those of the most efficient metallocenes (Scheme 1).^[1]



Scheme 1

The advantages of these late transition metal systems over other types of single-site Ziegler–Natta catalysts (e.g.,

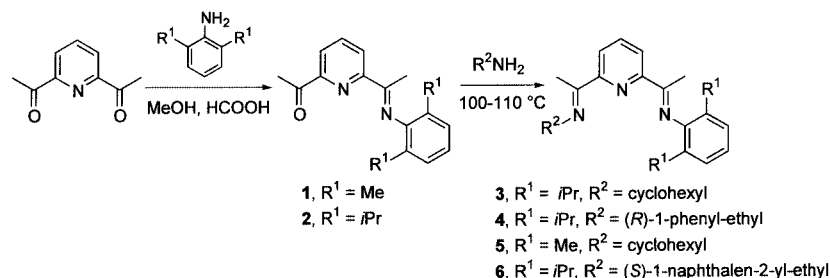
metallocenes, constrained-geometry early transition metal complexes) are multiple, ranging from their ease of preparation and handling to the use of low-cost metals with negligible environmental impact. Another intriguing feature of [bis(arylimino)pyridyl]iron and -cobalt precursors is provided by the facile tuneability of their polymerisation activity by simple modification of the ligand architecture. Indeed, previous studies have shown that the size and regiochemistry of the substituents in the iminoaryl groups are of crucial importance in controlling the polymerisation and oligomerisation of ethylene, and also the isospecific polymerisation of propene.^[1–3] In particular, the presence of substituents in both *ortho* positions on each aryl group results in the formation of high molecular weight PE with molecular weights depending upon the size of these substituents.^[1] In contrast, the presence of one *ortho* substituent generates catalysts that selectively oligomerise ethylene to Shultz–Flory distributions of α -olefins.^[2] Experimental and theoretical studies agree in identifying restricted rotation around the two nitrogen–aryl bonds as the key factor responsible for disfavoring chain transfer over chain propagation.^[1,3c,4] Only when the aryl groups are very large (e.g., naphthyl, pyrenyl, 2-benzylphenyl) does restricted rotation apparently operate without the need for two *ortho* substituents, PE being formed.^[5]

In this paper we demonstrate that the presence of two arylimino groups in the bis(imino)pyridyl backbone is not a mandatory condition to generate a ligand capable of oligomerising ethylene to α -olefins in conjunction with $FeCl_2$ /

^[a] Istituto di Chimica dei Composti Organometallici (ICCOM) – CNR, Via J. Nardi 39, 50132 Firenze, Italy
Fax: (internat.) + 39-055/2478366
E-Mail: bianchin@fi.cnr.it

^[b] Dipartimento di Chimica, Università di Siena
Via Aldo Moro, 53100 Siena, Italy

^[c] Polimeri Europa, Novara Research Centre, Istituto Guido Donegani, Via Fauser 4, 28100 Novara, Italy
Fax: (internat.) + 39-0321/447241



Scheme 2

MAO or CoCl₂/MAO. In fact, an aryl group can be replaced by an alkyl group and the resultant [2-(alkylimino)-6-(arylimino)pyridyl]Fe^{II} or -Co^{II} dichloride complexes will oligomerise ethylene as efficiently and selectively as the 2,6-bis(arylimino)pyridyl congeners. It is also shown here that the size of the alkyl group can control both the catalyst productivity and the Schulz–Flory parameters.

Results

Synthesis and Characterisation of Ligands

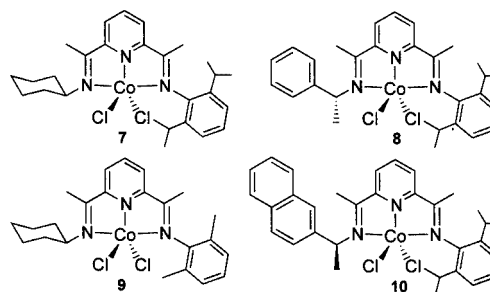
The 2-(alkylimino)-6-(arylimino)pyridyl ligands **3–6** have been synthesised via keto-imine intermediates obtained by treatment of 2,6-diacetylpyridine with the appropriate aniline (0.9 equiv.) in MeOH with formic acid as promoter (Scheme 2).

An important contribution to the selectivity of this reaction was made by the low solubility of the monoimine products, which precipitated upon formation and so suppressed further condensation with the aniline. The bis(imino)pyridine products were indeed obtained in low amounts (2–4%), however, and so the crude reaction products were purified by repeated extraction of the (imino)pyridyl ketones with boiling ethanol. Once purified, these products were treated with the appropriate neat primary amine at 100–110 °C, in the presence neither of solvent nor of acid promoter, to give the expected 2,6-bis(imine)pyridyl ligands. Under these mild conditions, the bis(imino) compounds were obtained selectively.

Synthesis and Characterisation of the Cobalt(II) Complexes

The [2,6-bis(imino)pyridyl]Co^{II} complexes illustrated in Scheme 3 were prepared in acceptable yields by heating of an *n*BuOH solution containing equimolar amounts of anhydrous CoCl₂ and ligand at reflux for ca. 10 min. Crystalline compounds were obtained upon cooling to room temperature. Complexes **7** and **9** exhibit C_s symmetry, while complexes **8** and **10** are C₁-symmetric by virtue of the sim-

ultaneous presence of 2,6-disubstituted aryl and chiral alkyl groups at the imine nitrogen atoms.



Scheme 3

All complexes are green, crystalline solids and are fairly soluble in polar organic solvents such as THF, dichloromethane, and 1,2-dichloroethane, in which they behave as non-electrolytes. Their solubilities in toluene and other hydrocarbons are very low. All compounds are reasonably thermally stable and air-stable both in the solid state and in solution. For caution's sake, however, their preparation and manipulation in solution were carried out under dry N₂.

Magnetic data at room temperature and relevant IR and UV/Vis absorptions for each complex are reported in the Exp. Sect. The IR spectra of all the compounds each show a red shift of ν(C=N) by ca. 50–60 cm^{−1} relative to the corresponding free ligand, which reflects the coordination of the imine nitrogen atoms to the cobalt atom.

All the complexes are high-spin in the solid state, with μ_{eff} at room temperature ranging from 4.6 to 4.8 BM, which is typical for high-spin cobalt(II) five-coordinate complexes with 2,6-bis(imino)pyridyl ligands.^[6] In principle, five-coordinate metal complexes may adopt either square-pyramidal or trigonal-bipyramidal geometries. In idealised C_{4v} and D_{3h} symmetries, a d⁷ metal ion may have either a low- or a high-spin configuration, according to whether the energy separation between the two highest orbitals in each symmetry is higher or lower than the spin-pairing energy. A donor atom set consisting of three nitrogen and two chlorine atoms has invariably been found to stabilise the high-spin configuration of cobalt(II).^[6] As shown by a single-crystal X-ray analysis on the cyclohexyl/2,6-dimethylphenyl

derivative **9**·H₂O (see below), the presence of the rigid chelating 2,6-bis(imino)pyridyl ligand causes important distortions from the idealised geometries. However, these are apparently not so significant as to favour spin pairing and give a doublet ground state ($S = 1/2$).

An ORTEP drawing of the molecular structure of **9**·H₂O is shown in Figure 1. Perusal of the bond angles around the metal centre shows that the coordination geometry in **9**·H₂O is greatly distorted from any idealised five-coordinate structure, and may be roughly described as a square pyramid with one chloride ion (Cl1) occupying the apical position. The presence of two chemically different imine nitrogen atoms in **9**·H₂O contributes substantially to the observed stereochemical distortions. Noticeable asymmetries affect the Co–N(imine) distances in fact: Co1–N1 is unusually short [2.185(6) Å] and Co1–N2 is exceedingly long [2.348(6) Å]. These differences are most probably due to the higher nucleophilicity of the alkyl-substituted nitrogen atom N1 relative to the aryl-substituted N2. Indeed, the N1–Co1–N2 angle of 149.3(2)° allows one to invoke *trans* influence effects. In contrast, due to the substantial departures from idealised square-pyramidal geometry, these effects cannot account for the Co–Cl distances, which (although less pronouncedly) are significantly different from one another [Co1–Cl1 2.243(2); Co1–Cl2 2.269(2) Å]. As would be expected,^{[1d–1e][2b][3c]} the M–N(pyridyl) bond [Co1–N3 2.032(6) Å] is shorter than both the M–N(imino) bonds, which have retained the imine C=N double bond character [N1–C1 1.266(10) Å, N2–C3 1.276(9) Å]. The deviation of the metal from the N₃ ligand plane is 0.06 Å. The plane of the 2,6-dimethyl-substituted aryl ring is oriented essentially orthogonally to the plane of the backbone [86.5(2)°].

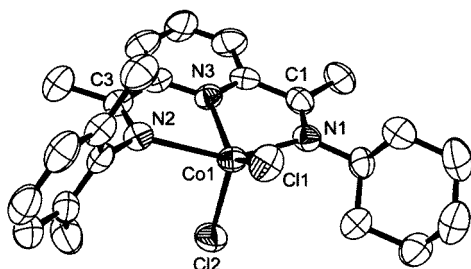


Figure 1. ORTEP drawing of **9**·H₂O (hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co1–N1 2.185(6), Co1–N2 2.348(6), Co1–N3 2.032(6), Co1–Cl1 2.243(2), Co1–Cl2 2.269(2); N3–Co1–N1 76.7(2), N3–Co1–Cl1 131.87(18), N1–Co1–Cl1 99.91(18), N3–Co1–Cl2 107.58(18), N1–Co1–Cl2 99.80(17), Cl1–Co1–Cl2 120.12(9), N3–Co1–N2 73.4(2), N1–Co1–N2 149.3(2), Cl1–Co1–N1 94.88(15), Cl2–Co1–N2 95.72(16).

The reflectance and solution UV/Vis spectra of the [2,6-bis(imino)pyridyl]Co^{II} complexes are similar to one another, indicating that the primary stereochemistry is the same both in the solid state and in solution: intermediate between the square pyramid and the trigonal bipyramid.^[6b] Although the spectra show some changes in band shape and frequency as the substituents at the imine nitrogen

atoms vary, these are not sufficient for them to be due to substantial differences in structure. Such differences are probably due to the different steric bulks of the substituents in the complexes.

The presence of three unpaired electrons ($S = 3/2$) in each complex molecule makes all the Co^{II} compounds X-band-EPR-silent at room temperature both in the solid state and in CH₂Cl₂ solution. A low-temperature EPR study of the X-band was carried out on derivative **8** in CH₂Cl₂ (Scheme 3). At 4 K the spectrum displays a broad and poorly resolved rhombic structure with $g_1 = 5.06(8) > g_2 = 3.03(8) > g_3 = 1.95(8) \neq g_{\text{elect}}$ [$\langle g \rangle = 3.35(8)$; a_1 40(8) G, a_2 80(8) G, a_3 94(8) G; $\langle a \rangle$ 71(8) G], which is typical of an “ S ” = 1/2 fictitious spin (Figure 2). Indeed, the spectrum may be interpreted in terms of an “ S ” = 1/2 effective spin Hamiltonian occasioned by large Zero Field Splitting (ZFS) effects.^[7–11] In fact, we observed a reversible temperature dependence of the signal intensity, which rules out the occurrence of a spin transition. This behaviour is not unusual for $S > 1/2$ paramagnetic metal species affected by important ZFS effects ($S = 3/2$) as well as noticeable spin-orbit coupling in highly distorted coordination geometries.^[7,8,11] All g_i regions show hyperfine structure apparently due to magnetic interaction with the ⁵⁹Co nucleus ($S = 7/2$). However, the poor resolution and the presence in each region of more than eight bands, as expected for coupling to cobalt, do not rule out either interactions with other spin-active nuclei in the molecule (e.g., ¹⁴N) or the presence of different geometric isomers.

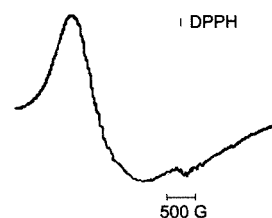


Figure 2. X-band EPR spectrum of cobalt(II) complexes **8** in CH₂Cl₂ at 4 K

The ¹H NMR spectrum of complex **7** was acquired in oxygen-free CD₂Cl₂ solution at 21 °C on a 500 MHz instrument (Figure 3). All protons resonate at chemical shifts significantly different from those of the corresponding protons in the free ligands, which is consistent with the paramagnetic nature of the compound. Analysis of the ¹H NMR resonances suggests that the isotropic shift (i.e., the difference between the observed chemical shift and the reference diamagnetic shift) is almost completely attributable to a Fermi contact contribution.^[12] Unambiguous signal assignment was achieved on this basis (Table 1). Overall, the NMR spectrum is similar to that reported by Gibson and co-workers for {2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine}cobalt dichloride.^[1d] As in the spectrum of this more symmetric complex, the 3-, 4-, and 5-hydrogen atoms of the central pyridine ring and the CHMe₂ hydrogen atom exhibit remarkable paramagnetic shifts and line

broadening as well. The strong coordination of the cyclohexyl-substituted imine arm to the cobalt atom, given in evidence in the X-ray structure, is confirmed by the large downfield shift ($\delta = 143.42$ ppm) of the *NCH* resonance as well as its broad linewidth. Similarly, the coordination of both imine nitrogen atoms is demonstrated by the chemical shifts of the *N=CMe* methyl groups. The presence of two signals for the *CHMe* protons is consistent with hindered rotation of the aryl ring about the N–C axis.^[1d]

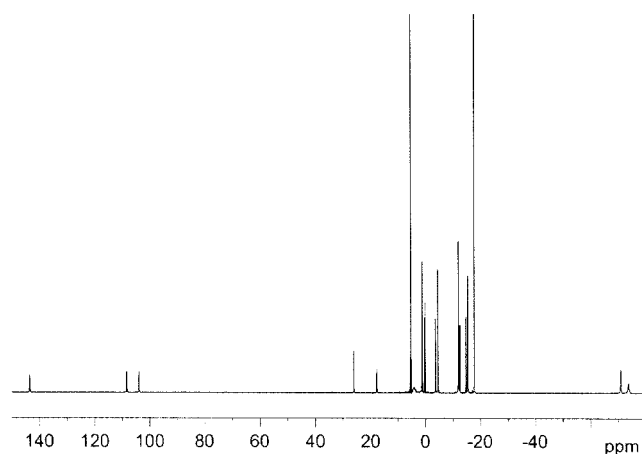


Figure 3. ¹H NMR spectrum of **7** (500.13 MHz, 21 °C, CD₂Cl₂)

Table 1. ¹H NMR assignments for **7** (CD₂Cl₂, 294 K, 500.13 MHz)

Nucleus	δ [ppm]
3/5-Py	108.18 (s, 1 H); 103.73 (s, 1 H)
4-Py	25.92 (s, 1 H)
N=CCH ₃	−4.63 (s, 3 H); −15.41 (s, 3 H)
<i>m</i> -aryl	1.15 (s, 2 H)
<i>p</i> -aryl	−12.69 (s, 1 H)
CH ₃ of <i>i</i> Pr	−12.14 (br. s, 6 H); −17.81 (s, 6 H)
CH of <i>i</i> Pr	−73.80 (br. s, 2 H)
Cy	143.42 (s, 1 H), 17.63 (s, 1 H), 4.1 (br. s, 2 H), 0.25 (s, 1 H), −3.72 (s, 2 H), −14.75 (s, 2 H), −71.05 (s, 2 H)

A cyclic voltammetry study in CH₂Cl₂ was performed on complex **9**, containing cyclohexyl and 2,6-dimethylphenyl groups on the imine nitrogen atoms (Figure 4a). The complex undergoes one irreversible one-electron oxidation at $E_p = +1.18$ V and another irreversible one-electron reduction at $E_p = -0.99$ V even at very high scan rates.

Synthesis and Characterisation of the Iron(II) Complexes

Like the cobalt(II) derivatives, the iron(II) complexes could be conveniently prepared by heating of a solution containing anhydrous FeCl₂ and 1 equiv. of the ligand at reflux in *n*BuOH for ca. 10 min (Scheme 4). Crystalline compounds were obtained upon cooling to room temperature.

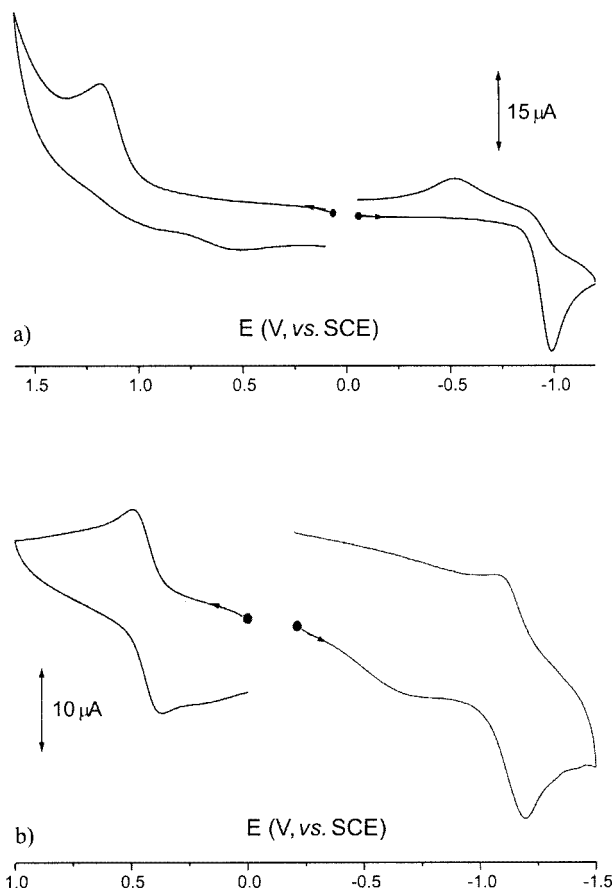
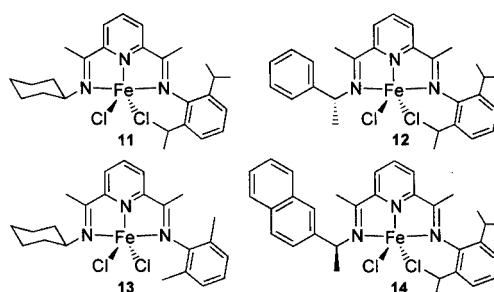


Figure 4. Cyclic voltammograms of the cobalt(II) and iron(II) complexes **9** (a) and **13** (b) in CH₂Cl₂ [$6 \cdot 10^{-4}$ M, scan rate $0.2 \text{ V} \cdot \text{s}^{-1}$; Bu₄NPF₆ (0.2 M as supporting electrolyte)]



Scheme 4

All compounds are only sparingly soluble in aromatic hydrocarbons, while dissolving fairly well in THF, MeCN, CH₂Cl₂, and 1,2-dichloroethane. In the last of these they behave as non-electrolytes. The solids are fairly air-stable, whereas they decompose in solution unless protected by dinitrogen or argon.

Magnetic data at room temperature and relevant IR absorptions for the [2,6-bis(imino)pyridyl]Fe^{II} compounds are provided in the Exp. Sect. As in the IR spectra of the Co^{II} derivatives, $\nu(\text{C}=\text{N})$ is generally red-shifted by ca. 50–60 cm^{−1} relative to the corresponding free ligand, reflecting the coordination to the metal centre.

All the compounds are dark blue and exhibit high-spin electronic configurations, as shown by their magnetic moments μ_{eff} , which range from 5.5 to 5.7 BM and are similar to those reported for several high-spin iron(II) five-coordinate complexes with quintuplet ground states.^[1,6] The quintuplet ground state makes the complexes EPR-silent even at 4 K and irrespective of the EPR frequency.

Like the [2,6-bis(imino)pyridyl]Co^{II} complexes, the Fe^{II} derivatives might adopt either square-pyramidal or trigonal-bipyramidal structures with various degrees of geometrical distortion. In either geometry, a d⁶ metal ion may assume a singlet, a triplet or a quintuplet ground state, depending on the nature of the donor atom set.^[14] A donor atom set comprising three nitrogen and two chlorine atoms generally stabilises the high-spin quintuplet configuration for iron(II), as is in fact observed for these bis(imino)pyridyl complexes.^[6,13]

None of the [2,6-bis(imino)pyridyl]Fe^{II} complexes described in this work has been studied by X-ray diffraction methods, but the molecular structures of several Fe^{II} derivatives bearing aryl substituents on the imine nitrogen atoms are available from the literature.^[1a,1d,2,3c] In most cases the geometry at the iron centre can be described as distorted trigonal-bipyramidal with the pyridyl nitrogen atom and the two chloride ligands forming the equatorial plane; only when the aryl rings on the imine nitrogen atoms bear two bulky substituents – as in {2,6-[2,6-(*i*Pr)₂C₆H₃NCMe]₂-C₅H₃N}iron dichloride – does iron tend to adopt a distorted square-pyramidal coordination geometry.^[1c]

The [2,6-bis(imino)pyridyl]Fe^{II} complexes studied here exhibit either C₁ or C_s symmetry by virtue of the simultaneous presence of substituted aryl groups and either chiral [CH(Me)Ph] or cyclic (C₆H₁₁) alkyl groups at the imine nitrogen atoms. The combined action of the ketimine group and the two *o*-alkyl substituents should lock the aryl ring in an orthogonal conformation with respect to the N₃ ligand plane both in the solid state and in solution, while the alkyl group at the other imine nitrogen atom should rotate freely about the C–N axis in solution (*vide infra*).

Trigonal-bipyramidal structures for all these iron(II) complexes are supported by the UV/Vis spectra in CH₂Cl₂ solution. Some detailed studies of the electronic spectra of five-coordinate Fe^{II} complexes with N₃Cl₂ donor atom sets were reported in the late 1960s, mainly by Ciampolini and co-workers.^[14] On the basis of these studies, a band in the 7000–8400 cm^{−1} region, common to all Fe^{II} complexes investigated in this work, can be unambiguously correlated with a spin-allowed transition in trigonal-bipyramidal high-spin Fe^{II} complexes such as [Fe(dienMe)Cl₂] or [Fe(trenMe)Cl]Cl [dienMe = bis(2-dimethylaminoethyl)methylamine; trenMe = tris(2-dimethylaminoethyl)amine].^[15] Those complexes also each showed a band at ca. 4000 cm^{−1}, not detectable for our compounds due to the measuring limit of our spectrophotometer. Unlike the trenMe and dienMe complexes, the spectra of **11**–**14** each contain a band at ca. 20000 cm^{−1} that may be attributable to a metal-to-ligand charge transfer (MLCT). Absorption bands at ca. 14500 cm^{−1} have been reported by Gibson for C_{2v}-symmetric [2,6-

bis(imino)pyridyl]Fe^{II} complexes and also attributed to MLCT.^[1d] In general, MLCT bands fall at higher energy than those observed by Gibson, but a reduction in frequency may occur for highly π -conjugated ligand systems, which may be the case for C_{2v}-symmetric 2,6-bis(imino)pyridyl ligands.^[6b]

The reflectance spectra of **11**–**14** are similar to one another and fully comparable with the solution spectra, which indicates that the primary stereochemistry of the Fe^{II} complexes is the same both in the solid state and in solution. As an example, the spectra of **12** in the solid state and in CH₂Cl₂ solution are given in Figure 5.

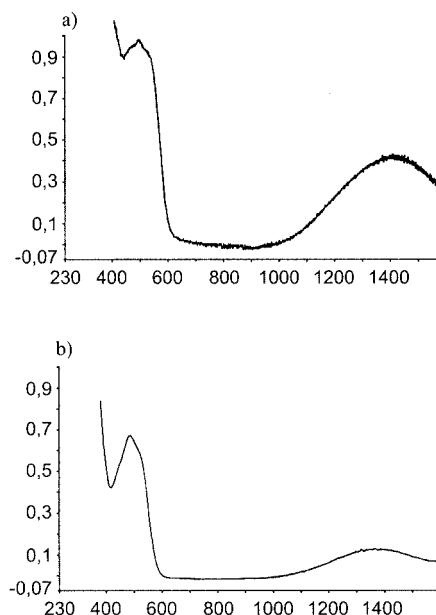
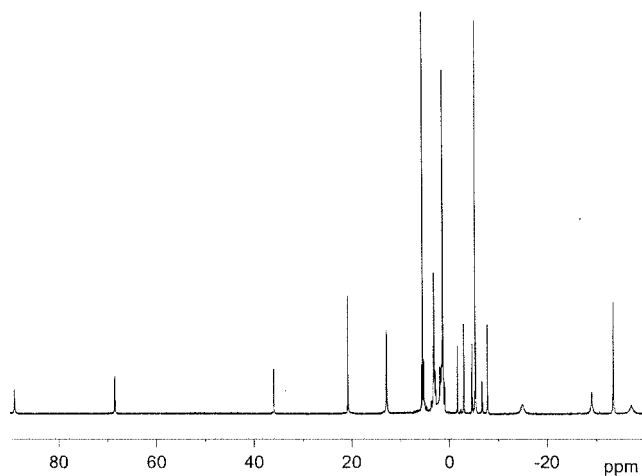


Figure 5. Reflectance spectrum of **12** (a); electronic spectrum of **12** (b) in CH₂Cl₂ solution

The ¹H NMR spectrum of **11** was acquired in deaerated CD₂Cl₂ solutions at 21 °C (Figure 6). All protons resonate at chemical shifts significantly different from the corresponding protons in the free ligands, which is consistent with the paramagnetic nature of the compounds. Band assignments are given in Table 2.

Despite the presence of the same ligand, the ¹H NMR spectrum of the iron(II) complex **11** is notably different from that of the cobalt(II) analogue **7** (Figure 3), which reflects a structural divergence in solution. In particular, the resonances of four hydrogen atoms of the cyclohexyl group are shifted to high field (ca. −30 and −37 ppm) and have very broad linewidths, which suggests that this cyclohexyl ring is spatially very close to the paramagnetic iron centre on the NMR timescale. No such linewidth broadening for the cyclohexyl resonances was observed for the Co^{II} analogue **7**. The presence of two relatively narrow signals for the *i*Pr groups confirms the hindered rotation of the aryl group.

Unlike the cobalt analogue **9**, the iron complex **13** can be reversibly oxidised ($E^{0'} = +0.43$ V) to give the yellow iron(III) derivative [FeCl₂{2-[CMe=N(2,6-dimethylphenyl)]-6-(CMe=NC₆H₁₁)C₅H₃N}]⁺, which is stable in CH₂Cl₂

Figure 6. ¹H NMR spectrum of **11** (500.13 MHz, 21 °C, CD₂Cl₂)Table 2. ¹H NMR assignments for **11** (CD₂Cl₂, 294 K, 500.13 MHz)

Nucleus	δ [ppm]
3/5-Py	89.11 (s, 1 H); 68.55 (s, 1 H)
4-Py	35.97 (s, 1 H)
N=CCH ₃	12.79 (s, 3 H); -33.57 (s, 3 H)
<i>m</i> -aryl	20.69 (s, 2 H)
<i>p</i> -aryl	-1.70 (s, 1 H)
CH ₃ of <i>i</i> Pr	3.08 (br. s, 6 H); -5.38 (s, 6 H)
CH of <i>i</i> Pr	-14.94 (br. s, 2 H)
Cy	-2.99 (s, 2 H), -7.85 (s, 2 H), -29.10 (s, 2 H), -37.18 (br. s, 2 H), 1.28 (s, 1 H), -4.72 (s, 1 H), -6.74 (s, 1 H)

solution, although no attempt was made to isolate it in the solid state (Figure 4b). Stable C₂-symmetric [2,6-bis(arylimino)pyridyl]Fe^{III} dihalide complexes have been prepared by Gibson and shown to have the same activity as the Fe^{II} precursors in the oligomerisation of ethylene, as a consequence of instantaneous Fe^{III} reduction to Fe^{II} by MAO.^[1d,16] Figure 4b also shows that the Fe^I derivative, obtained by a partially reversible one-electron reduction of **13** (at *E*^{0'} = -1.15 V), has a relatively short lifetime (*t*_{1/2} = 0.5 s).

Oligomerisation of Ethylene by the Cobalt(II) and Iron(II) Dichloride Complexes, Activated by MAO

The [bis(imino)pyridyl]cobalt (**7–10**) and -iron (**11–14**) complexes, in combination with the activator MAO, were evaluated as catalysts for the oligomerisation of ethylene in toluene.

Table 3 reports on the results of reactions carried out under a variety of experimental conditions. In all cases the addition of ethylene to the catalyst/co-catalyst mixture resulted in a rapid exothermic event, indicative of no induction period. Initially, all catalysts were tested at 4.1 bar C₂H₄ pressure and 25 °C for 15 min, with 250 equiv. of MAO as both co-catalyst and reactor scavenger. Catalyst

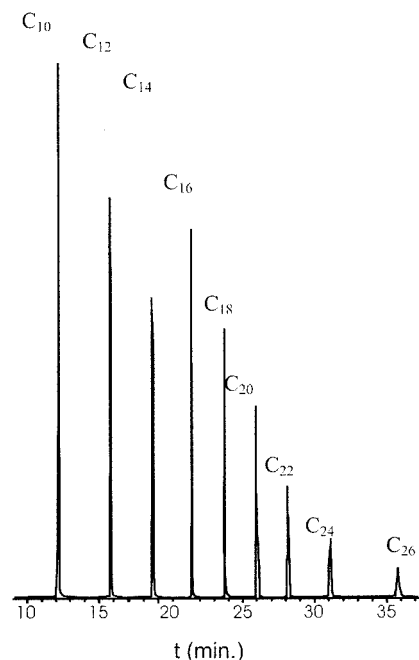
activities [mol of C₂H₄ converted (mol of M × h)⁻¹] were calculated from the GC readings, by use of extrapolated values for 1-butene.

Table 3. Ethylene oligomerisation with the iron(II) and cobalt(II) catalysts

Entry ^[a]	Pre-catalyst	Pressure [bar]	TOF [10 ⁻⁵] ^[b]	α	β
1	11	4.1	2.4	0.74	0.35
2	12	4.1	5.2	0.89	0.12
3	13	4.1	3.8	0.66	0.52
4	14	4.1	5.6	0.91	0.10
5	13	4.8	4.6	0.67	0.49
6	13	7.6	6.0	0.67	0.49
7	13	10.3	7.4	0.68	0.47
8 ^[c]	13	4.1	3.4	0.61	0.63
9	7	4.1	< 0.01 ^[d]	—	—
10	8	4.1	0.61	0.89	0.12
11	9	4.1	< 0.01 ^[d]	—	—
12	10	4.1	1.0	0.91	0.10

^[a] Reaction conditions: complex (12 μmol), toluene (100 mL), MAO (250 equiv.), 15 min, 25 °C. ^[b] TOF: mol of C₂H₄ converted (mol of M × h)⁻¹. ^[c] 80 °C. ^[d] Only butenes.

The four iron complexes **11–14** were all active catalysts for the production of α-olefins with Schulz–Flory distributions.^[17] No appreciable formation either of internal olefins or of odd carbon oligomers was observed (Figure 7).

Figure 7. GC trace relative to Entry 1 in Table 3, showing the α-olefins distribution from C₁₀ to C₂₆

The catalytic activity increased with the bulkiness of the alkyl substituent at the imine carbon atom (Entries 1, 2, 4), but decreased with the size of the substituents on the aryl ring (Entries 1, 3). The naphthyl group containing catalyst was as active as the C₂-symmetric [2,6-bis(arylimino)pyridyl]iron(II) precursors described by Brookhart and Gibson.^[2] Notably, the probability of propagation, indicated by the

Schulz–Flory parameter α ,^[17] increased steadily with the overall steric hindrance of the imine substituents.

Experiments with precursor **13** in the C₂H₄ pressure range from 4.1 to 10.3 bar showed a linear dependence of activity on the pressure, while the α factor did not vary substantially (Entries 3, 5–7). No isomeric oligomer formed either by alkene isomerisation or by reincorporation of α -olefin products into oligomers later in the reaction was observed. The absence of reincorporation mechanisms was confirmed by independent experiments in which the oligomerisation of ethylene with **13** was carried out in the presence of an excess of 1-undecene. In fact, no odd-numbered carbon oligomer was formed in the temperature range from 25 to 80 °C.^[2a] Similarly, these catalysts did not promote head-to-head dimerisation of α -olefins to internal olefins, a reaction that [2,6-bis(arylimino)pyridyl]iron complexes are able to catalyse.^[18]

Experiments at relatively high temperature (80 °C) with precursor **13** showed a slight decrease in productivity and α factor as well. Both phenomena have precedent for [2,6-bis(arylimino)pyridyl]iron precursors.^[1d] In particular, the decrease in productivity with temperature has been ascribed to the combined effects of faster catalyst degradation and lower ethylene solubility.^[1d]

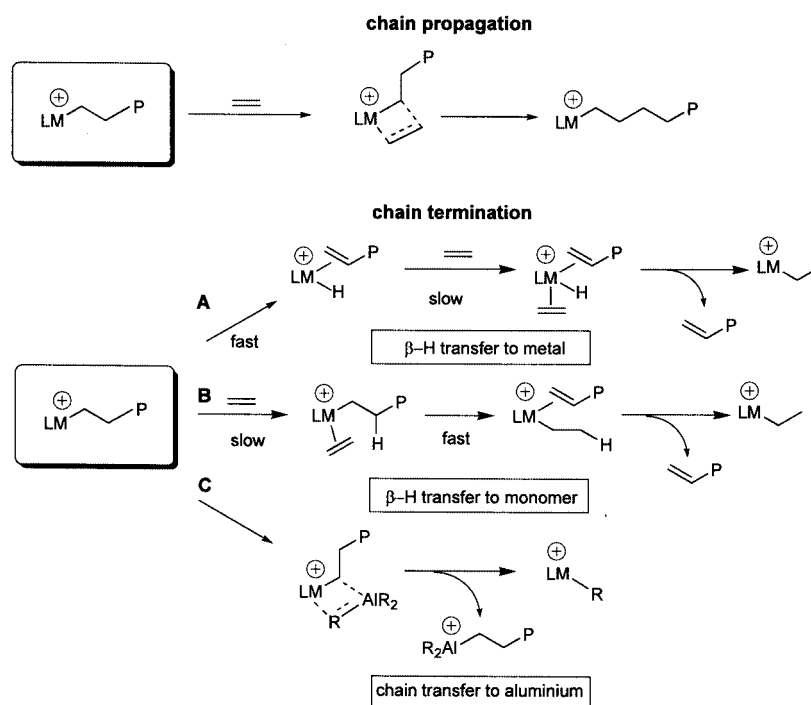
The activities of the cobalt catalysts **7–10** (Entries 9–12) were approximately one order of magnitude lower than those of the analogous iron(II) derivatives. The sensitivity to steric effects was even higher for cobalt than for iron, as shown by the catalyst precursors containing the cyclohexyl substituent (Entries 9, 11), which gave only small amounts of 1-butene, indicating a prevalence of chain transfer over chain propagation.

Discussion

The nature and statistical distribution of the α -olefins produced with the [2-(alkylimino)-6-(arylimino)pyridyl]iron and -cobalt catalysts described in this work are consistent with a mechanism involving: (i) metal–alkyl initiators produced by the action of MAO on the dichloride precursors, (ii) propagation by migratory insertion of Co(alkyl)(ethylene) (Cossee–Arlman mechanism), and (iii) termination by chain transfer (Scheme 5).^[2,19]

In line with the large majority of catalytic systems for Schulz–Flory oligomerisations of ethylene, the rates of propagation and chain transfer exhibited by the iron catalysts do not differ significantly, the β parameter ($\beta = r_{\text{transfer}}/r_{\text{propagation}}$) varying between 0.10 and 0.52. It has been found that the activity of the iron catalysts shows a linear dependence on the ethylene pressure, while α is independent of the pressure. Accordingly, both chain propagation and chain transfer are first-order in monomer concentration, as previously observed for [2,6-bis(arylimino)pyridyl]Fe^{II} and -Co^{II} oligomerisation catalysts.^[2]

Late transition metal catalysts may undergo chain transfer in ethylene polymerisation by three main mechanisms: β -hydrogen transfer to the metal atom (**A**), β -hydrogen transfer to the monomer (**B**), and chain transfer to aluminium (**C**) (this generally occurs at low pressure) (Scheme 5).^[1d,20] The last mechanism can safely be ruled out in the oligomerisation reactions reported here, as only α -olefins were produced, with no saturated hydrocarbon. It is therefore very likely that chain transfer proceeds either by path **A**, involving an associative displacement step followed by β -hydrogen transfer to the metal atom, or by path



Scheme 5. Chain propagation and chain transfer mechanisms proposed for polymerisation of ethylene by late transition metal catalysts

B, involving direct β -H transfer to the incoming monomer with no formation of metal hydride. The exclusive production of α -olefins with no appreciable formation of internal olefins might be taken as indirect evidence for the occurrence of path **B**, as it does not involve the formation of the metal hydride necessary for isomerisation. Moreover, calculations suggest its involvement in ethylene polymerisation by late transition metal systems.^[20] We wish to stress, however, that the chain transfer mechanisms **A** and **B** are kinetically indistinguishable, and so no preference is allowed; nor may one exclude their simultaneous occurrence.

Overall, the performances of these C_s- and C₁-symmetric iron and cobalt catalysts do not diverge substantially from those of the 2,6-bis(arylimino) complexes studied by Brookhart and Gibson, which means that the presence of aryl groups on both ketimine nitrogen atoms is not a necessary condition to produce an ethylene oligomerisation catalyst in conjunction with iron or cobalt dihalides and MAO. Actually, these catalysts polymerise ethylene only when the aryl rings are 2,6-substituted by alkyl groups. As a general trend, α -olefins are produced with one alkyl substituent, while the presence of two alkyl groups results in the formation of PE with molecular weight increasing with the size of these alkyl moieties.^[1,2] It has been experimentally and theoretically demonstrated that the steric interaction between the ketimine methyl group and the alkyl substituents increases the barrier to aryl rotation and effectively locks the rings in an orthogonal conformation with respect to the N₃M plane on the timescale of polymerisation.^{[1d][3c]} The steric protection provided by the orthogonal aryl rings contributes to retard the chain transfer, which – irrespective of the mechanism – requires access to the metal centre above or below the N₃M plane.^[4] Apparently, one 2,6-substituted aryl moiety is sufficient to slow down the chain-transfer rate and allow oligomer formation. The high α value (0.91) obtained with the naphthyl-substituted catalysts (Table 3, Entries 4 and 12) suggests that polymerisation to high molecular weight PE might be achieved by further increasing the size of the C=N–alkyl group. Studies in this direction are currently being carried out in our laboratory.

The thorough chemical-physical study of the catalyst precursors described in this work suggests that cobalt(II) prefers to be square-pyramidal, while iron(II) prefers to be trigonal-bipyramidal. This behaviour of cobalt(II) and iron(II) metal ions is amply recognised in the literature.^[6a,21] With no intention of minimising the importance of electronic effects related to the different d-electron count, it is possible that these structural differences (with implications on the metal spin state),^[6a] if maintained during catalysis, may contribute to rendering the cobalt catalysts less active than the iron ones. Square-pyramidal coordination, for example, generally produces less steric congestion at the metal centre than trigonal-bipyramidal coordination and requires less energy to attain the octahedral geometry that seems to feature in relevant transition states in ethylene polymerisation catalysed by five-coordinate [2,6-bis(arylimino)pyridyl]Fe^{II} and -Co^{II} complexes.^[4]

Conclusion

C₁- and C_s-symmetric 2-(alkylimino)-6-(arylimino)pyridyl ligands, readily prepared by condensation of chiral and achiral primary amines with 2-(acetyl)-6-(arylimino)pyridine intermediates, coordinate to iron(II) and cobalt(II) dichlorides to give monomeric, paramagnetic complexes. The cobalt complexes adopt distorted square-pyramidal structures both in the solid state and in solution, while the coordination geometries of the iron catalysts can be better described as trigonal-bipyramidal. All the complexes can be activated with MAO to give ethylene oligomerisation catalysts with complete selectivity for α -olefins. Unlike [2,6-bis(arylimino)pyridyl]iron precursors, no head-to-head dimerisation of α -olefins to internal olefins was observed. Iron-based catalysts can be more than one order of magnitude more active than cobalt-based systems. The catalytic activity increases with the bulkiness of the alkyl substituent and decreases with the size of the substituent on the aryl ring. The Schulz–Flory oligomer distribution factor α is not sensitive to the metal centre, but it increases with the size of the alkyl and aryl groups. Both chain propagation and chain transfer are first order in ethylene concentration, and chain transfer proceeds exclusively by β -H transfer.

Experimental Section

General Procedures: All air- and water-sensitive reactions were performed in flame-dried flasks under dinitrogen. Solid compounds were collected on sintered glass frits and washed with appropriate solvents before being dried in a stream of dinitrogen. Anhydrous THF and Et₂O were obtained by distillation from sodium/benzophenone ketyl, while CH₂Cl₂ and MeOH were distilled from CaH₂ and Mg, respectively. All the other reagents and solvents were used as purchased from commercial suppliers. Analytical TLC was performed on pre-coated silica gel 60 F₂₅₄ and/or neutral Al₂O₃ N/UV₂₅₄ plates and developed in an appropriate solvent system. The products were viewed with the aid of UV light (254 nm), I₂ vapour, 2.5% (NH₄)₆Mo₇O₂₄ + 1% (NH₄)₄Ce(SO₄)₄ in 10% H₂SO₄ and warming. Deuterated solvents for NMR measurements were dried with molecular sieves. ¹H and ¹³C{¹H} NMR spectra were obtained with a Bruker ACP 200 instrument working at 200.13 and 50.32 MHz, respectively. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (¹H and ¹³C). The multiplicity of the ¹³C{¹H} NMR spectra were determined by the DEPT 135 technique and are quoted as: CH₃, CH₂, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms, respectively. Two-dimensional ¹H and ¹³C NMR spectra were recorded at 21 °C with a Bruker Avance DRX 500 spectrometer operating at 500.132 and 125.77 MHz, respectively, and equipped with a variable-temperature control unit accurate to ± 0.1 °C. This instrument was also employed to study the paramagnetic metal complexes. Chemical shifts are relative to 0.03% (v/v) tetramethylsilane. The assignments of the signals was achieved with the aid of 1D spectra, 2D ¹H DQF-COSY, ¹H NOESY, and proton detected ¹H,¹³C correlations (HMQC and HMBC) using non-spinning samples. 2D NMR spectra were recorded with pulse sequences suitable for phase-sensitive representations by TPPI. ¹H DQF-COSY experiments^[22] were recorded with 1024 increments of size 2 K (with 16 scans each) cover-

ing the full range in both dimensions and with a relaxation delay of 1.5 s. ^1H NOESY measurements^[23] were recorded with 1024 increments of size 2 K (with 16 scans each) covering the full range in both dimensions and with mixing times of 800 ms and a relaxation delay of 1.5 s. ^1H , ^{13}C HMQC correlations^[24] were recorded by use of the standard sequence with no decoupling during acquisition, 1024 increments of size 2 K (with 16 scans each) were collected, covering the full range in both dimensions with a relaxation delay of 1 s. ^1H , ^{13}C HMBC correlations^[25] were recorded by the standard sequence with no decoupling during acquisition and a low-pass J -filter to suppress one-bond correlations, 1024 increments of size 2 K (with 32 scans each) were collected, covering the full range in both dimensions, with a relaxation delay of 0.8 s. EPR spectra were recorded for all the compounds at the X-band frequency (9.23 GHz) with a Varian ESR9 spectrometer equipped with a continuous-flow ^4He cryostat to work at 4 K. Elemental analyses were performed with a Carlo Erba Model 1106 elemental analyzer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded with a Perkin–Elmer 1600 Series FT-IR spectrophotometer with samples mullied in Nujol between KBr plates. GC analyses were performed with a Shimadzu GC-14 A gas chromatograph equipped with a flame ionisation detector and a 30-m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed with a Shimadzu QP 5000 apparatus equipped with a column identical to that used for GC analysis. Molar susceptibility analyses were performed with a Sherwood Scientific MSB AUTO balance. Materials and apparatus for electrochemistry have been described elsewhere.^[26] Potential values are referred to the Saturated Calomel Electrode (SCE). Under the adopted experimental conditions the one-electron oxidation of ferrocene occurs at $E^0 = +0.39\text{ V}$.

1-{6-[(2,6-Dimethylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (1): Formic acid (50 μL) was added by syringe at 0 $^\circ\text{C}$ to a stirred solution of 2,6-diacetylpyridine (0.490 g, 3.0 mmol) and 2,6-dimethylaniline (0.33 mL, 0.327 g, 2.7 mmol) in MeOH (7 mL). Stirring was stopped, and the resulting solution was maintained at 0 $^\circ\text{C}$ for 24 h. The desired product precipitated as large, yellow crystals, which were separated by filtration (0.447 g, 1.680 mmol). A second crop (0.148 g, 0.556 mmol) was obtained from the mother liquor after cooling to 0 $^\circ\text{C}$ for 48 h. Overall yield 75%. M.p. 117–118 $^\circ\text{C}$. IR: $\nu_{\text{C}=\text{N}}$ 1645 cm^{-1} , $\nu_{\text{C}=\text{O}}$ 1698 cm^{-1} . ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 2.02 (s, 6 H, CH_3), 2.22 [s, 3 H, $\text{C}(\text{NAr})\text{CH}_3$], 2.76 [s, 3 H, $\text{C}(\text{O})\text{CH}_3$], 6.89–6.97 (m, 1 H, CH Ar), 7.05–7.10 (m, 2H CH Ar), 7.96 (m, 1H CH Ar), 8.10 (dd, J = 7.7, 1.2 Hz, 1 H, CH Ar), 8.56 (dd, J = 7.7, 1.2 Hz, 2 H, CH Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 17.0 [1 C, $\text{C}(\text{NAr})\text{CH}_3$], 18.6 (2 C, CH_3), 26.4 [1 C, $\text{C}(\text{O})\text{CH}_3$], 123.3 (1 C, CH Ar), 123.9 (1 C, CH Ar), 125.2 (1 C, CH Ar), 126.0 (2 C, C Ar), 128.6 (2 C, CH Ar), 138.0 (1 C, CH Ar), 149.2 (1 C, C Ar), 153.1 (1 C, CH Ar), 156.2 (1 C, C Ar), 167.3 [1 C, $\text{C}(\text{NAr})\text{CH}_3$], 200.7 [1 C, $\text{C}(\text{O})\text{CH}_3$] ppm. $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$ (266.34): calcd. C 76.67, H 6.81, N 10.53; found C 76.45, H 6.54, N 10.41.

1-{6-[(2,6-Diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone (2): Formic acid (150 μL) was added by syringe at room temperature to a stirred solution of 2,6-diacetylpyridine (1.630 g, 10.0 mmol) and 2,6-diisopropylaniline (1.70 mL, 1.596 g, 9.0 mmol) in MeOH (15 mL). After 12 h, a yellow solid had formed, and this was filtered off and washed with cold (0 $^\circ\text{C}$) MeOH. The precipitate was characterised as a mixture of the expected product (97%) and the corresponding 2,6-bis(imino)pyridyl compound (3%) (^1H NMR integration). The solid was suspended

in refluxing ethanol and the resulting mixture was filtered while still hot. The solvent was removed from the filtrate under reduced pressure to give pure **1** as pale yellow crystals in 67% yield (2.17 g, 6.73 mmol). M.p. 182–184 $^\circ\text{C}$. IR: $\nu_{\text{C}=\text{N}}$ 1648 cm^{-1} , $\nu_{\text{C}=\text{O}}$ 1698 cm^{-1} . ^1H NMR (200.13 MHz, CDCl_3): δ = 1.16 [d, J = 6.9 Hz, 6 H, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 1.17 [d, J = 6.9 Hz, 6 H, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 2.28 [s, 3 H, $\text{C}(\text{NAr})\text{CH}_3$], 2.74 [sept, J = 6.9 Hz, 2 H, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 2.81 [s, 3 H, $\text{C}(\text{O})\text{CH}_3$], 7.08–7.22 (m, 3 H, CH Ar), 7.96 (t, J = 7.8 Hz, 1 H, CH Ar), 8.16 (dd, J = 7.7, 1.2 Hz, 1 H, CH Ar), 8.58 (dd, J = 7.9, 1.2 Hz, 1 H, CH Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 17.7 [1 C, $\text{C}(\text{NAr})\text{CH}_3$], 23.5 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 23.9 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 26.4 [1 C, $\text{C}(\text{O})\text{CH}_3$], 29.0 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 123.2 (1 C, CH Ar), 123.7 (2 C, CH Ar), 124.4 (1 C, CH Ar), 125.2 (1 C, CH Ar), 136.4 (2 C, C Ar), 138.4 (1 C, CH Ar), 142.9 (1 C, C Ar), 153.1 (1 C, CH Ar), 156.2 (1 C, C Ar), 167.8 [1 C, $\text{C}(\text{NAr})\text{CH}_3$], 200.8 [1 C, $\text{C}(\text{O})\text{CH}_3$] ppm. $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}$ (322.45): calcd. C 78.22, H 8.13, N 8.69; found C 78.39, H 8.17, N 8.84.

***N*-{[(*E*)-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene]-2,6-diisopropylaniline (3):** A mixture of **1** (0.170 g, 0.53 mmol) and cyclohexylamine (0.910 mL, 0.789 g, 7.95 mmol) was heated at 100 $^\circ\text{C}$ without stirring for 20 h. Elimination of excess cyclohexylamine by distillation under reduced pressure gave an oily material that was dissolved in 3–4 mL of MeOH and cooled to 0 $^\circ\text{C}$. After 6 h, yellow crystals of the desired product were isolated by filtration (0.153 g, 0.38 mmol, yield 72%). M.p. 186–188 $^\circ\text{C}$. IR: $\nu_{\text{C}=\text{N}}$ 1636 cm^{-1} . ^1H NMR: (200.13 MHz, CD_2Cl_2): δ = 1.16 [d, J = 6.9 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 1.25–1.95 (m, 10 H, CH_2), 2.26 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.77 [sept, 2 H, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$], 3.55–3.66 (m, 1 H, CH), 7.05–7.25 (m, 3 H), 7.81 (t, J = 7.8 Hz, 1 H, CH Ar), 8.21 (dd, J = 7.8, 1.1 Hz, 1 H, CH Ar), 8.36 (dd, J = 7.8, 1.1 Hz, 2 H, CH Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 14.1 [1 C, $\text{C}(\text{N-alkyl})\text{CH}_3$], 17.8 [1 C, $\text{C}(\text{N-Ar})\text{CH}_3$], 23.6 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 23.9 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 25.48 (2 C, CH_2), 25.49 (1 C, CH_2), 28.50 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 34.1 (2 C, CH_2), 61.0 (1 C, CH), 121.9 (1 C, CH Ar), 122.7 (1 C, CH Ar), 123.7 (2 C, CH Ar), 124.1 (1 C, CH Ar), 136.5 (2 C, C Ar), 147.2 (1 C, CH Ar), 155.4 (1 C, CH Ar), 157.8 (1 C, C Ar), 164.4 [1 C, $\text{C}(\text{N-alkyl})\text{CH}_3$], 167.8 [1 C, $\text{C}(\text{N-Ar})\text{CH}_3$] ppm. $\text{C}_{27}\text{H}_{37}\text{N}_3$ (403.61): calcd. C 80.34, H 9.24, N 10.41; found C 80.54, H 9.37, N 10.39.

2,6-Diisopropyl-*N*-{[(*E*)-1-(6-[(1*R*)-1-phenylethyl]ethanimidoyl)-2-pyridinyl]ethylidene]aniline (4): A mixture of **1** (0.170 g, 0.53 mmol) and (*R*)-(+)-(1-phenylethyl)amine (0.473 mL, 0.450 g, 3.71 mmol) was heated at 100 $^\circ\text{C}$ without stirring for 18 h. Elimination of the excess of amine by distillation under reduced pressure gave an oily material that was dissolved in 3–4 mL of MeOH and cooled to 0 $^\circ\text{C}$. After 2 d, yellow microcrystals of the product were isolated by filtration (0.153 g, 0.36 mmol, yield 68%). M.p. 91–93 $^\circ\text{C}$. IR: $\nu_{\text{C}=\text{N}}$ 1633, 1644 cm^{-1} . ^1H NMR (200.13 MHz, CDCl_3): δ = 1.14–1.19 [m, 12 H, $\text{CH}(\text{CH}_3)_2$], 1.58 (d, J = 6.6 Hz, 3 H, CHCH_3), 2.26 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 2.73 (m, 2 H, CH), 4.97 (q, J = 6.6 Hz, 1 H, CHCH_3), 7.07–7.77 (m, 8 H, CH Ar), 7.85 (m, 1 H, CH Ar), 8.36–8.39 (m, 2 H, CH Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ = 14.4 [1 C, $\text{C}(\text{N-alkyl})\text{CH}_3$], 17.9 [1 C, $\text{C}(\text{N-Ar})\text{CH}_3$], 23.6 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 23.9 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 25.5 (1 C, CH_3), 29.0 [2 C, $\text{CH}(\text{CH}_3)(\text{CH}_3)$], 61.0 (1 C, CH), 122.2 (1 C, CH Ar), 122.9 (1 C, CH Ar), 123.7 (2 C, CH Ar), 124.2 (1 C, CH Ar), 127.4 (1 C, CH Ar), 127.4 (2 C, CH Ar), 129.1 (2 C, CH Ar), 136.5 (2 C, C Ar), 137.4 (2 C, CH Ar), 146.7 (1 C, CH Ar), 147.3 (1 C, CH Ar), 155.4 (1 C, CH Ar), 157.5 (1 C, C Ar), 165.4 [1 C, $\text{C}(\text{N-alkyl})\text{CH}_3$], 167.8

[1 C, C(N-Ar)CH₃] ppm. C₂₉H₃₅N₃ (425.62): calcd. C 81.83, H 8.29, N 9.87; found C 82.04, H 8.47, N 9.85.

***N*-(*(E)*-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene)-2,6-dimethylaniline (5):** A mixture of **2** (0.131 g, 0.49 mmol) and cyclohexylamine (0.485 g, 4.9 mmol) was heated at 100 °C without stirring for 24 h. Elimination of the excess of cyclohexylamine by distillation under reduced pressure gave an oily material that was dissolved in 2 mL of MeOH and cooled to −24 °C. After 3 d, small yellow needles of the product were isolated by filtration (0.13 g, 0.38 mmol, yield 78%). M.p. 98–100 °C. IR: $\nu_{(C=N)}$ 1634 cm^{−1}. ¹H NMR (200.13 MHz, CD₂Cl₂): δ = 1.25–1.95 (m, 10 H, CH₂), 2.01 (s, 6 H, CH₃), 2.20 (s, 3 H, CH₃), 2.42 (s, 3 H, CH₃), 3.55–3.66 (m, 1 H, CH), 6.88–7.08 (m, 3 H, CH Ar), 7.81 (m, 1 H, CH Ar), 8.18 (dd, *J* = 7.7, 1.1 Hz, 1 H, CH Ar), 8.34 (dd, *J* = 7.7, 1.1 Hz, 1 H, CH Ar) ppm. ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = 14.1 [1 C, C(N-alkyl)CH₃], 17.8 [1 C, C(N-Ar)CH₃], 18.6 (2 C, CH₃), 25.5 (2 C, CH₂), 26.5 (1 C, CH₂), 34.2 (2 C, CH₂), 61.0 (1 C, CH), 121.9 (1 C, CH Ar), 122.8 (1 C, CH Ar), 123.6 (1 C, CH Ar), 126.1 (2 C, C Ar), 128.5 (2 C, CH Ar), 137.3 (1 C, CH Ar), 149.5 (1 C, C Ar), 155.3 (1 C, CH Ar), 157.8 (1 C, C Ar), 164.4 [1 C, C(N-alkyl)CH₃], 168.1 [1 C, C(N-Ar)CH₃] ppm. C₂₃H₂₉N₃ (347.50): calcd. C 79.50, H 8.41, N 12.09; found C 79.78, H 8.65, N 12.15.

2,6-Diisopropyl-*N*-(*(E)*-1-[6-((1*S*)-1-(2-naphthyl)ethyl)ethanimidoyl]-2-pyridinyl]ethylidene)aniline (6): A mixture of **1** (0.170 g, 0.53 mmol) and (*S*)-(−)-(1-naphthalenylethyl)amine (0.33 mL, 0.350 g, 2.04 mmol) was heated at 100 °C without stirring for 17 h. The resulting mixture was diluted with 2–3 mL of MeOH and cooled to 0 °C. After 5 h, pale yellow microcrystals of the product were isolated by filtration (0.118 g, 0.36 mmol, yield 69%). M.p. 66–69 °C. IR: $\nu_{(C=N)}$ 1643 cm^{−1}. ¹H NMR (200.13 MHz, CD₂Cl₂): δ = 1.10–1.17 [m, 12 H, CH(CH₃)₂], 1.72 (d, *J* = 6.5 Hz, 3 H, CHCH₃), 2.26 (s, 3 H, CH₃), 2.50 (s, 3 H, CH₃), 2.73 [m, 2 H, CH(CH₃)₂], 5.67 (q, *J* = 6.5 Hz, 1 H, CHCH₃) 7.03–7.20 (m, 3 H, CH Ar), 7.45–7.77 (m, 7 H, CH Ar), 7.88 (m, 1 H, CH Ar), 8.32–8.43 (m, 2 H, CH Ar) ppm. C₃₃H₃₇N₃ (475.68): calcd. C 83.32, H 7.84, N 8.83; found C 83.64, H 7.82, N 8.77.

Synthesis of Metal Complexes: All iron(II) and cobalt(II) complexes with the 2,6-bis(imino)pyridyl ligands were prepared by the following procedure. The ligand (1.0 equiv.) was added under nitrogen to a solution of the metal halide (1.2 equiv.) in *n*BuOH and the resulting mixture was heated at reflux for 10 min. After the mixture had cooled to room temperature, a crystalline solid was obtained within 30–60 min. This was filtered through a sintered-glass frit, washed with *n*BuOH and petroleum ether and then dried in a stream of nitrogen.

[*N*-(*(E)*-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene)-2,6-diisopropylaniline]cobalt Dichloride (7): This complex was obtained as green microcrystals. Yield 70%. IR: $\nu_{(C=N)}$ 1590, 1587 cm^{−1}. μ_{eff} = 4.82 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 25000 sh, 17000 sh, 15600, 10500, 8200, 5700. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 25000 sh, 17000 sh, 14950 (ε 830), 11100 (ε 67), 7800 (ε 100). C₂₇H₃₇Cl₂CoN₃ (533.45): calcd. C 60.79, H 6.99, N 7.88; found C 60.55, H 7.01, N 8.72.

[2,6-Diisopropyl-*N*-(*(E)*-1-[6-((1*R*)-1-phenylethyl)ethanimidoyl]-2-pyridinyl]ethylidene)aniline]cobalt Dichloride (8): This complex was obtained as green crystals. Yield 85%. IR: $\nu_{(C=N)}$ 1590 cm^{−1}. μ_{eff} = 4.95 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 25000 sh, 17200 sh, 15500, 10500, 8300, 5600. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 25000 sh, 17100 sh, 14800 (ε 710), 10500 (ε 40), 8000 (ε 75). C₂₉H₃₅Cl₂CoN₃ (555.46): calcd. C 62.71, H 6.35, N 7.57; found C 62.80, H 6.29, N 7.60.

[*N*-(*(E)*-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene)-2,6-dimethylaniline]cobalt Dichloride (9): This complex was obtained as green crystals. Yield 84%. IR: $\nu_{(C=N)}$ 1590 cm^{−1}. μ_{eff} = 4.85 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 25000 sh, 16950, 15400, 10500, 8150, 5700. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 25000 sh, 17000 (ε 460), 15450 (ε 740), 11000 (ε 42), 7800 (ε 90). C₂₃H₂₉Cl₂CoN₃ (477.34): calcd. C 57.87, H 6.12, N 8.80; found C 57.61, H 6.25, N 8.61.

[2,6-Diisopropyl-*N*-(*(E)*-1-[6-((1*S*)-1-(2-naphthyl)ethyl)ethanimidoyl]-2-pyridinyl]ethylidene)aniline]cobalt Dichloride (10): This complex was obtained as green crystals. Yield 88%. IR: $\nu_{(C=N)}$ 1592 cm^{−1}. μ_{eff} = 4.87 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 25100 sh, 17400 sh, 15600, 10300, 8000, 5650. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 25000 sh, 17300 sh, 14900 (ε 700), 10350 (ε 40), 7800 (ε 90). C₃₃H₃₇Cl₂CoN₃ (477.34): calcd. C 65.46, H 6.16, N 6.90; found C 65.58, H 6.03, N 6.93.

[*N*-(*(E)*-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene)-2,6-diisopropylaniline]iron Dichloride (11): This complex was obtained as dark blue microcrystals. Yield 81%. IR: $\nu_{(C=N)}$ 1589, 1580 cm^{−1}. μ_{eff} = 5.72 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 18200 sh, 7400. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 20230 (ε 240), 7170 (ε 6). C₂₇H₃₇Cl₂FeN₃ (530.36): calcd. C 61.15, H 7.03, N 7.92; found C 60.97, H 6.91, N 7.88.

[2,6-Diisopropyl-*N*-(*(E)*-1-[6-((1*R*)-1-phenylethyl)ethanimidoyl]-2-pyridinyl]ethylidene)aniline]iron Dichloride (12): This complex was obtained as a blue powder. Yield 87%. IR: $\nu_{(C=N)}$ 1584 cm^{−1}. μ_{eff} = 5.56 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 18000 sh, 14600, 8100. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 20300 (ε 250), 7700 (ε 8). C₂₉H₃₅Cl₂FeN₃ (552.37): calcd. C 63.06, H 6.39, N 7.61; found C 62.68, H 6.28, N 7.59.

[*N*-(*(E)*-1-[6-(Cyclohexylethanimidoyl)-2-pyridinyl]ethylidene)-2,6-dimethylaniline]iron Dichloride (13): This complex was obtained as dark blue crystals. Yield 81%. IR: $\nu_{(C=N)}$ 1589 cm^{−1}. μ_{eff} = 5.68 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 18800 sh, 8330 cm^{−1}. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 19050 (ε 230), 8350 (ε 12). C₂₃H₂₉Cl₂FeN₃ (474.26): calcd. C 58.25, H 6.16, N 8.86; found C 58.13, H 6.29, N 8.88.

[2,6-Diisopropyl-*N*-(*(E)*-1-[6-((1*S*)-1-(2-naphthyl)ethyl)ethanimidoyl]-2-pyridinyl]ethylidene)aniline]iron Dichloride (14): This complex was obtained as blue microcrystals. Yield 79%. IR: $\nu_{(C=N)}$ 1590 cm^{−1}. μ_{eff} = 5.77 BM (25 °C). Diffuse reflectance spectra (40000–5550 cm^{−1}): 18300 sh, 8000. Solution spectra (CH₂Cl₂, 28500–6250 cm^{−1}): 20000 (ε 240), 7900 (ε 8). C₃₃H₃₇Cl₂FeN₃ (602.43): calcd. C 65.79, H 6.19, N 6.98; found C 65.90, H 6.10, N 6.84.

Oligomerisation Reactions: A 0.5-L stainless steel reactor was heated at 100 °C under vacuum for 3 h, solid precatalyst (12 μmol) was introduced into the autoclave at room temperature, and the system was evacuated. A solution of oxygen-free toluene (100 mL) and MAO (sol. 10% w/w, 1.6 mL) was then introduced into the reactor and the mixture was stirred at room temperature for 10 min. The system was then heated or thermostatted to the desired temperature, pressurised with ethylene, and stirred at 1500 rpm. The reaction was terminated by cooling to 5 °C and slow depressurisation, followed by addition of MeOH (2 mL) and *n*-heptane (internal standard, 200 μL).

X-ray Structure Determination of 9·H₂O: Single crystals of 9·H₂O were grown by slow diffusion of *n*-hexane into a CH₂Cl₂ solution of **9**. A summary of crystal and intensity data is presented in Table 4.

Experimental data were recorded at 20 °C with an Enraf–Nonius CAD4. A set of 25 carefully centred reflections in the range $8^\circ \leq \theta \leq 10.25^\circ$ was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections were measured periodically every 200 reflections for orientation and intensity control. This procedure did not reveal any appreciable decay in intensities. The data were corrected for Lorentz and polarisation effects. Atomic scattering factors were those tabulated by Cromer and Waber,^[27] with anomalous dispersion corrections taken from ref.^[28] An empirical absorption correction was applied by use of the program XABS with correction factors in the range 1.3518–0.394. The computational work was carried out by intensive use of the program WINGX. Final atomic coordinates of all atoms and structure factors are available on request from the authors and are provided. A dark green parallelepiped crystal with dimensions $0.375 \times 0.300 \times 0.225$ mm was used for the data collection. The structure was solved by direct methods by use of the SIR97 program.^[29] Refinement was performed by full-matrix, least-squares calculations, initially with isotropic thermal parameters and then with anisotropic thermal parameters for all the atoms other than the oxygen atoms. In the final stage of the refinement, two atoms were detected and were assigned as oxygen of solvent molecules and successfully refined. The phenyl ring was treated as a rigid body with D_{6h} symmetry, and the hydrogen atoms were allowed to ride on the attached carbon atoms. Hydrogen atoms were introduced at calculated positions. CCDC-195274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Selected crystallographic data for $9 \cdot \text{H}_2\text{O}$

Empirical formula	$\text{C}_{23}\text{H}_{31}\text{Cl}_2\text{CoN}_3\text{O}$
Formula mass	495.36
T [K]	293(2)
Crystal system	orthorhombic
Space group	$Pcab$ (No. 61)
a [Å]	8.5557(10)
b [Å]	22.0942(17)
c [Å]	27.468(8)
V [Å ³]	5192(2)
Z	8
$\rho_{\text{calcd.}}$ [g·cm ^{−3}]	1.262
Absorption coefficient [mm ^{−1}]	0.884
Crystal size [mm]	$0.38 \times 0.30 \times 0.22$
Transmission, min./max.	0.8258/0.7327
2θ range [°]	2.66–24.97
Data/restraints/parameters	4546/0/265
Reflections collected	4546
Independent reflections	4546
R [a], wR 2	7.75; 23.09

[a] $I > 2\sigma(I)$.

Acknowledgments

Polimeri Europa and the European Commission (contract no. HPRN-CT-2000-00010, COST Action D17 Working Group 0003/2000) are thanked for financial support. We are grateful to Mr. Dante Masi (ICCOM-CNR) for technical assistance in X-ray data collection and to Prof. Piero Zanello (University of Siena) for CV measurements.

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Received November 25, 2002
[I02624]