

Chiral Iron(II) and Cobalt(II) Complexes with Biphenyl-Bridged Bis(pyridylimine) Ligands – Syntheses, Structures and Reactivities

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A new class of iron(II) and cobalt(II) complexes with neutral, tetradentate bis(pyridylimine) chelate ligands bridged by a chiral 6,6'-dimethylbiphenyl backbone has been synthesized. Their dihalogen derivatives gave spectral, magnetic and X-ray diffraction results in agreement with a C_2 -symmetric, approximately octahedral geometry with *cis*-positioned halide ligands and high-spin d-electron configuration. ^1H NMR signals of these paramagnetic complexes were assigned by correlating line widths with reciprocal proton-metal distances. Methyl substitution in 6-position of the pyridyl

rings lead to a different, presumably square-pyramidal coordination geometry under dissociation of one chloride ion. Fe^{II} dimethyl and diisocyanide derivatives were shown to have low-spin configuration and C_1 -symmetric geometry. With respect to MAO-activated olefin polymerization, significant catalytic activities were reproducibly obtained only under conditions, where the original complex structure was degraded.

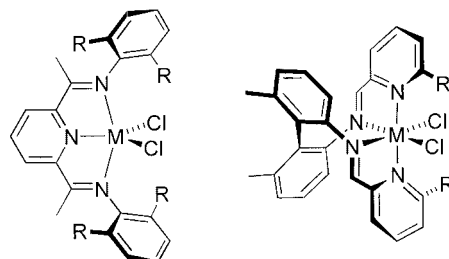
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Introduction

Complexes of late transition metals such as Pd, Ni, Fe, or Co are interesting targets for olefin polymerization catalysis,^[1,2] none the least since these catalysts are relatively tolerant towards polar substrates and might thus allow copolymerization of α -olefins with polar monomers.^[3] Iron-based catalysts in particular have shown activities for ethene polymerization which are comparable to those of the most active group(IV) metallocene catalysts. The excellent stereoselectivity of metallocene-catalyzed propene polymerization,^[4] however, is still lacking for late transition metal catalysts. Low-temperature polymerizations have afforded polypropene with only partially syndiotactic or isotactic microstructures induced by chain-end stereocontrol.^[5]

Most iron- or cobalt-based polymerization catalysts employ symmetric tridentate pyridyldiimine ligands, which form C_{2v} -symmetric bipyramidal complex species with homotopic coordination sites (Scheme 1).^[1c,2c] Enantiotopic coordination sites, as required for olefin insertion under catalytic-site control, might be obtained by use of axially chiral, tetradentate ligands, from which C_2 -symmetric octahedral complexes would be generated on coordina-

tion to MX_2 (Scheme 1). Chiral complexes with two N ligand atoms have previously been applied in enantioselective homogeneous catalysis.^[6] Here we report on the synthesis of chiral Fe^{II} and Co^{II} complexes with C_2 -symmetric, bianiline-bridged tetradentate nitrogen ligands, and on the properties of these complexes in homogeneous olefin polymerization.



Scheme 1. Pyridyldiimine complexes with C_{2v} symmetry (left) and biphenyl-bridged bis(pyridylimine) complexes with axial C_2 symmetry (right)

Results and Discussion

Ligand Syntheses

The neutral, potentially tetradentate ligands N,N' -(biphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine (**1**), and N,N' -(6,6'-dimethylbiphenyl-2,2'-diyl)bis[(6- R'' -2-pyridyl)methyl]diimine [$R'' = \text{H}$ (**2**), Me (**3**)], were prepared by condensation of the known N,N' -(biphenyl-2,2'-diyl)diamines **4** and **5**,^[7] with the appropriate heteroaromatic aldehyde in

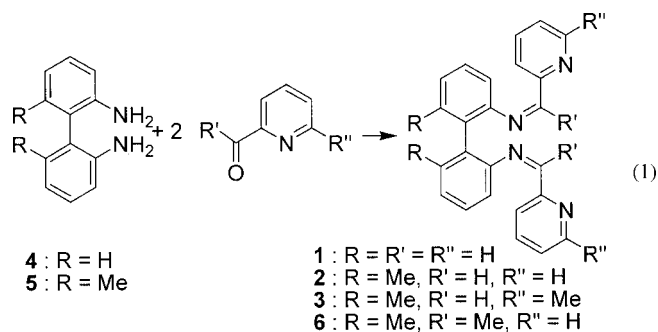
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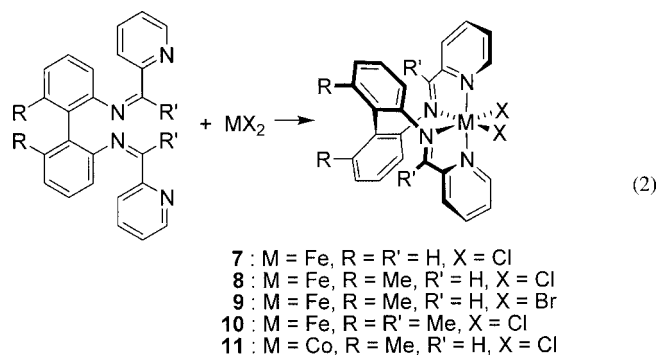
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ethanol at room temperature [Equation (1)]. Ligand **1** was reacted directly, without prior isolation, with iron(II) chloride (vide infra). Reaction of **5** with 2-acetylpyridine, be it in ethanol, methanol or dichloromethane with catalytic amounts of acetic, formic or hydrochloric acid, or in benzene over molecular sieves or in diethyl ether/pentane mixtures in the presence of excess TiCl_4 , did not afford the desired ligand **6**. Refluxing a toluene solution of **5** and 2-acetylpyridine with a catalytic amount of *p*-toluenesulfonic acid in a Dean–Stark apparatus, however, yielded after three days a mixture which contained, apart from the starting materials, *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis[1-(2-pyridyl)ethane]diimine (**6**), in ca. 45% yield as determined by ^1H NMR spectroscopy. This reaction mixture was used without purification for further complex syntheses.



Complex Syntheses, Structures, and Spectroscopic Properties

Reaction of FeCl_2 or FeBr_2 with the dipyridyldiimine ligands **1**, **2**, or **6** in THF afforded, after evaporation of solvent and extraction with CH_2Cl_2 , the blue to turquoise iron(II) complexes **7–10** [Equation (2)].^[8] Since **7–10** were found to be insoluble in non-chlorinated solvents, excess ligand (and starting materials of the ligand synthesis in the case of **6**) was removed by washing with diethyl ether and pentane to yield analytically and spectroscopically pure products. The light brown cobalt(II) complex **11** was obtained by an analogous reaction of CoCl_2 with **2**.



Single crystals of the dichloro complexes **8** and **11** were obtained by layering their dichloromethane solutions with pentane or toluene, respectively. The complexes are isostructural and crystallize in the monoclinic space group $C2/c$

with cell constants deviating by less than 0.2 Å and less than 0.5° (Figure 1, Table 1). The distorted octahedral complexes, with *cis*-positioned chlorine atoms, both possess crystallographic C_2 -symmetry. Co–N bonds are approximately 0.05 Å shorter than their Fe–N counterparts (Table 1), presumably a consequence of higher nuclear charge and more strongly contracted metal d-orbitals of cobalt. Fe–N distances are within the range generally observed in neutral, octahedral iron complexes.^[9] The bond angles $\angle\text{N1–M–Cl1}$, $\angle\text{N2–M–Cl1}$ and $\angle\text{N2–M–Cl1A}$ (M = Fe, Co) at each of the metal centers deviate by less than 2° from each other and from the value of 90° expected for octahedral coordination. The bite angles of the twisted seven-membered chelate ring, $\angle\text{N1–M–N1A} = 73–74^\circ$, and of the five-membered chelate rings, $\angle\text{N1–M–N2} = 73–74^\circ$, however, are both significantly smaller than 90° and lead to a distortion of the octahedral coordination, i.e. to an opening of the angle $\angle\text{Cl1–M–Cl1A}$ to a value of 110–112° (Table 1). Due to the twisted bianiline backbone, the planes formed by N1, N1A, and M and by M, Cl1, and Cl1A deviate from each other by 26–28°.

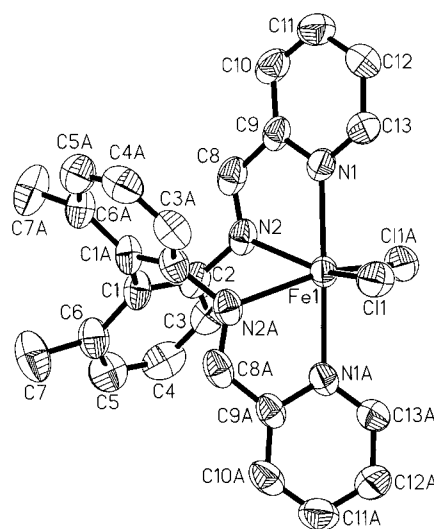


Figure 1. Crystal structures of complex **8**; hydrogen atoms omitted for clarity, thermal ellipsoids drawn at the 50% probability level

Table 1. Selected bond lengths [Å] and bond angles [°] for complexes **8** and **11**

	8 ^[a]	11 ^[b]
M–N1 (imine)	2.296(4)	2.235(2)
M–N2 (pyridine)	2.214(3)	2.175(2)
M–Cl1	2.397(2)	2.401(1)
N1–M–N1A	72.8(2)	73.8(1)
N2–M–N2A	178.6(2)	178.8(1)
X1–M–Cl1A	111.6(1)	109.8(1)
N1–M–N2	72.9(1)	74.0(1)
N1–M–N2A	106.0(1)	107.0(1)
N1–M–Cl1	91.0(1)	91.1(1)
N1–M–Cl1A	152.6(1)	154.2(1)
N2–M–Cl1	89.4(1)	88.1(1)
N2–M–Cl1A	91.4(1)	91.3(1)

[a] **8**: M = Fe, [b] **11**: M = Co.

For the magnetic moments of complexes **8** and **11**, high-spin values of $\mu_{\text{eff}} = 5.47 \mu_{\text{B}}$ and $\mu_{\text{eff}} = 4.96 \mu_{\text{B}}$, respectively, were measured by the SQUID method at 300 K. No indication for any thermally induced spin-crossover between 90 K and 300 K was obtained in either case. In this regard, complex **8** falls in line with related Fe^{II} complexes such as [bis(bipyridyl)FeCl₂] or bis(phenanthroline)FeCl₂, for which high-spin configurations have likewise been reported.^[10]

In the ¹H NMR spectrum of the paramagnetic iron(II) complex **8** in CDCl₃ solution, nine signals are detected over a range of nearly 190 ppm (Figure 2), in agreement with a time-averaged C₂-symmetric complex geometry. Based on the observed signal intensities, the resonance at $\delta = -6.72$ ppm is clearly identified as being due to the methyl groups. Since no signal above $\delta = 120$ is displayed in the NMR spectrum of complex **10**, which contains, instead of the aldimine ligand **2**, the analogous ketimine ligand **6**, we can conclude that the resonance of complex **8** at $\delta \approx 180$ ppm must be due to its aldimine protons.

Assignments of further signals are based on their relative line widths: Up to a distance of ca. 5 Å from the metal

center, relative line widths of two nuclei A and B depend reciprocally on the ratio of their distances from the metal center, $v_2(A)/v_2(B) \approx (d_B/d_A)^6$.^[11] The remaining signals can thus be assigned as shown in Figure 2 and Table 2.

¹H NMR spectra of complexes **7** and **9–11** in CDCl₃ solution, which are likewise in agreement with time-averaged C₂ symmetry, were assigned in a manner similar to that used for **8** (see Exp. Sect.). Complexes **7**, **9**, and **10**, for which crystal structure determinations are not available, could in principle adopt the C₂-symmetric geometries indicated by their ¹H NMR spectra with their two chlorine ligands either in *trans*- or in *cis*-configuration. In order to ascertain, whether these complexes have the same *cis*-halide geometry as found for **8** and **11**, we have characterized these complexes also by their far-infrared vibrational spectra.

For a C_{2v}-symmetric complex of the type [*cis*-N₄FeCl₂], four Fe–N and two Fe–Cl vibrations are expected to be IR-active. For [*trans*-N₄FeCl₂] with approximate D_{4h} symmetry, however, only one Fe–N and one Fe–Cl vibration would be IR-active, if no distinction is made between imine and pyridine N atoms.^[12] In the IR spectra of solid **8**, **9**, and **11**

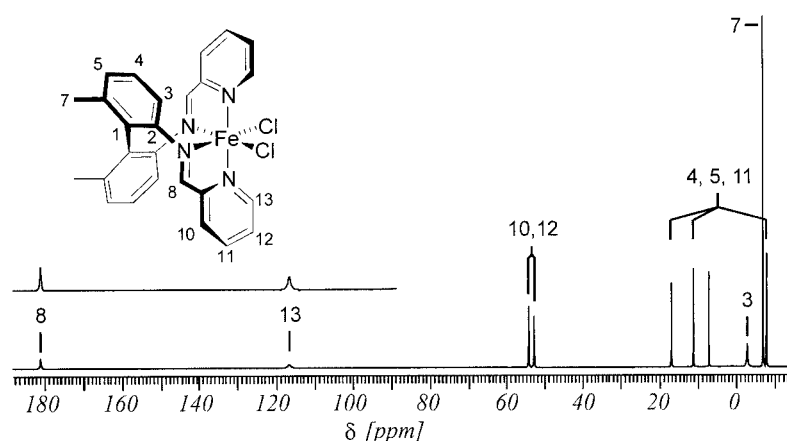


Figure 2. ¹H NMR spectrum of the paramagnetic complex **8** in CDCl₃ solution at 25 °C (600 MHz; numbering as in the crystal structure represented in Figure 1)

Table 2. Assignment of ¹H NMR resonances of complex **8**^[a]

	$d(\text{H-Fe})/\text{\AA}^{[b]}$	$d^{-6} \cdot 10^5 \cdot \text{\AA}^6$	$\nu_{\text{calc}}/\text{Hz}^{[c]}$	$\nu_{\text{exp}}/\text{Hz}$	$\delta/\text{ppm}^{[d]}$
13-H	3.250	84.86	703	520	116.2
3-H	3.977	25.27	210	149	-2.6
8-H	4.110	20.75	172	172 ^[e]	180.7
10-H	5.218	4.95	41	} 66/57	52.8/54.20
12-H	5.311	4.46	37		
4-H	5.918	2.33	19	} 42/36/30	17.1/11.4/-7.6
11-H	6.074	1.99	17		
5-H	6.678	1.13	9		
7-CH ₃	6.665	1.14	9	29 ^[e]	-6.7

[a] Numbering corresponding to that used for the crystal structure in Figure 1. [b] Taken from the crystal structure of **8**. [c] Calculated relative to 8-H. [d] For temperature dependence of these paramagnetic shift values see Supporting Information. [e] Assigned independently (see text).

(Table 3) four medium to strong vibrations are observed between ca. 180 and 350 cm^{-1} .^[13] We assign these bands, which are absent in the IR spectrum of the free ligand **2**, to metal–N vibrations.

Table 3. Far-infrared absorption bands of ligand **2** and of complexes **8**, **9**, and **11** (positions in cm^{-1})

2	8	9	11	Assignment
590 (s)	590 (w)	588 (m)	591 (m)	ligand
549 (m)	555 (m)	557 (s)	558 (m)	ligand
520 (m)	536 (w)	535 (w)	496 (m)	ligand
	515 (m)	522 (w)		
		512 (w)		
475 (s)	474 (m)	479 (s)	484 (s)	ligand
440 (w)	437 (w)	423 (w)	430 (m)	ligand
404 (s)	416 (s)	414 (m)		ligand
368 (m)	386 (w)	371 (w)	379 (w)	ligand
	337 (m)	339 (m)	341 (m)	M–N
316 (m)		318 (w)		ligand
	300 (s)	297 (s)	308 (s)	M–N
260 (m)	271 (w)	269 (m)	270 (m)	ligand
240 (m)	244 (vs)	241 (m)	242 (s)	ligand,
				M–Cl in 8 and 11
	c. f. [13]	223 (s)	225 (m)	M–N
	192 (m)	191 (s)	181 (m)	M–N
		174 (s)		Fe–Br
	144 (s)		135 (s)	M–Cl
		104 (s)		Fe–Br

Two further strong peaks are observed at 244 and 144 cm^{-1} for complex **8** and at 174 and 104 cm^{-1} for its dibromo homologue **9**. The 1.4:1 ratio of these wavenumbers, which is close to the theoretical value of 1.5 estimated from the ratio of reduced masses of Fe–Cl and Fe–Br, supports the assignment of these bands to the symmetric and asymmetric stretching modes of a *cis*-FeX₂ unit. The Co–Cl vibrations of **11** were found at 242 and 135 cm^{-1} , as expected only slightly below those of **8**. Analogous assignments hold for **7** and **10**. Complexes **7–11** thus all contain *cis*-coordinated halogen ligands in the solid state.

While the chiral, C₂-symmetric complexes **7–11** have the *cis*-positioned homotopic sites required for enantioselective olefin insertion, substituents bigger than hydrogen would be desirable in the 6-positions of the pyridine rings, so as to transfer the axial chirality of the biphenyl backbone most effectively to the coordination sites of the complex (Figure 3).

In order to obtain a homologue of complex **8** with methyl substituents in both pyridyl 6-positions, FeCl₂ was reacted with ligand **3**. Reactions in THF yielded **12**·THF as a brown solid. The same product, without THF, was obtained from reactions in CH₂Cl₂. In contrast to complexes **7–11**, complex **12** gives a ¹H NMR spectrum with only three broad signals centered at $\delta = 3.45$, -4.91 , and -11.39 . Only two strong and one medium vibration at 367, 319, and 268 cm^{-1} , respectively, are apparent in its far-infrared spectrum, again in contrast to complexes **7–11**, where four M–N and two M–X vibrations have been observed. The C₂-symmetric geometry found for these complexes is thus unlikely to be adopted by complex **12**.

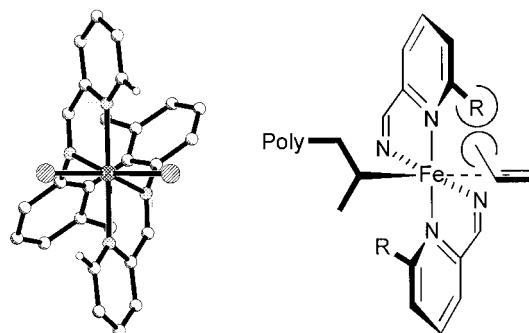


Figure 3. Front view of complex **8** (left) and of a putative Fe-poly-methyl π complex (right) with propene coordinated by its disfavored enantioface (biphenyl bridge omitted for clarity)

The only useful structural clue is derived from SQUID measurements, which yielded for complex **12** an effective magnetic moment of $\mu_{\text{eff}} = 3.41 \mu_{\text{B}}$, indicative of 2–3 unpaired electrons, i.e. of a configuration with partly paired electron spins. The ligand field separation $\Delta E = 10 Dq$ of the octahedral complexes **7–11** is clearly insufficient to induce any spin pairing, and the same holds, a fortiori, for tetrahedral or trigonal bipyramidal geometries (Figure 4). The only plausible coordination geometry, which would be in agreement with the partial spin pairing observed for **12**, is that of a square pyramidal complex, e. g. of a species [(3) FeCl]⁺Cl[−], in which one of the chloride ligands has been eliminated from the metal center due to steric repulsions by the methyl-substituted pyridyl ligands. To reach a square pyramidal geometry, at least three of the four N ligand atoms must be positioned in the square base plane of the complex (Scheme 2). Rearrangements between alternative connectivities, which are likely to occur quite rapidly, as well as chloride dissociation and re-association equilibria would plausibly explain the observed broadening of the NMR signals of **12**.^[14]

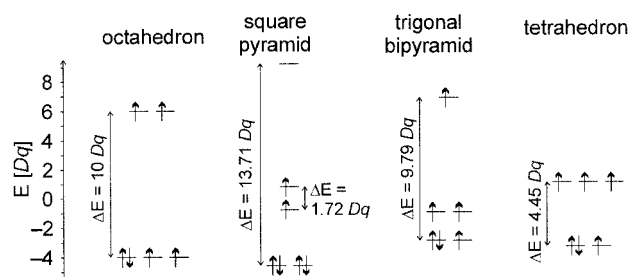
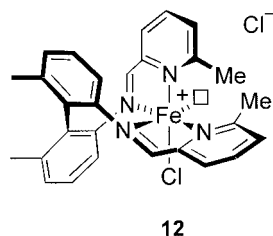
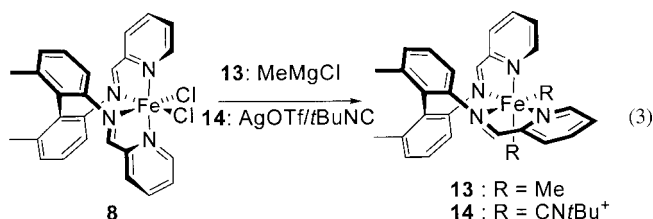


Figure 4. Effects of different complex geometries with moderately strong ligand field on d⁶ electron configurations (values taken from ref.^{[15])}

In order to obtain also bona-fide low-spin complexes with the bianiline-bridged ligand framework under consideration, complex **8** was reacted with methylmagnesium chloride [Equation (3)]. The diamagnetic dimethyl complex **13** was obtained from this reaction as a brown powder.^[16] Its ¹H NMR spectrum revealed a C₁-symmetric geometry in solution. The same geometry was also found for its counterpart with isocyanide instead of methyl ligands. This sec-

Scheme 2. Structure proposed for complex **12**

ond low-spin derivative, the orange-red complex **14** was obtained by reaction of complex **8** with two equivalents each of AgOTf and *tert*-butyl isocyanide [Equation (3)].^[17] The ¹H NMR spectrum of **14** (see Exp. Sect.) confirmed the coordination of two isocyanide ligands, and indicated, again, a C₁-symmetric geometry.



This structural assignment is supported by the results of an X-ray diffraction study (Figure 5, Table 4): In the cationic diisocyanide complex **14**, three of the four N ligand atoms reside in one meridional plane; in the second meridional plane, one of the pyridyl moieties and the two *tert*-butyl isocyanide ligands are coordinated to the iron center.^[18]

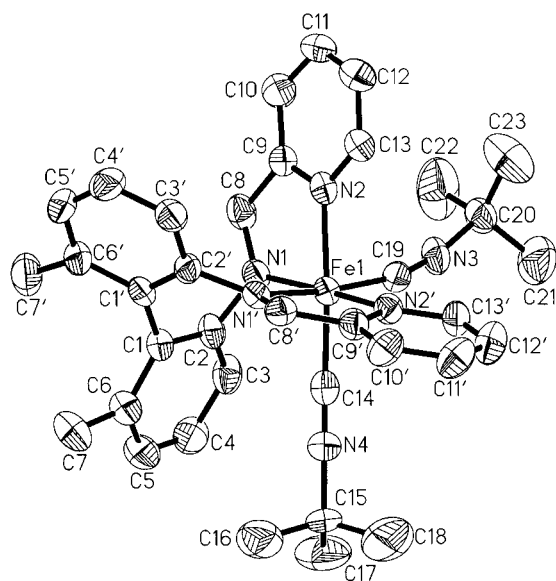


Figure 5. Crystal structure of the complex cation **14**; hydrogen atoms, triflate anions and co-crystallized solvent omitted for clarity, thermal ellipsoids drawn at the 50% probability level

The overall C₁ symmetry of this complex appears to be stabilized by one or more of the following factors: Close

Table 4. Selected bond lengths [Å] and angles [°] for complex **14**

Fe–N1 (imine)	1.940(5)	N1'–Fe–N2	89.7(2)
Fe–N1' (imine) ^[a]	2.001(4)	N1'–Fe–N2'	81.5(2)
Fe–N2 (pyridine)	2.014(4)	N1'–Fe–C14	90.1(2)
Fe–N2' (pyridine)	2.002(5)	N1'–Fe–C19	172.8(2)
^[a]			
Fe–C14	1.904(6)	N2–Fe–N2'	99.8(2)
Fe–C19	1.884(6)	N2–Fe–C14	176.0(2)
		N2–Fe–C19	84.1(2)
N1–Fe–N1A	90.0(2)	N2'–Fe–C14	84.1(2)
N1–Fe–N2	80.4(2)	N2'–Fe–C19	96.0(2)
N1–Fe–N2A	171.4(2)	C14–Fe–C19	96.4(2)
N1–Fe–C14	95.7(2)	C14–N4–C15	175.4(7)
N1–Fe–C19	92.5(2)	C19–N3–C20	167.8(5)

adherence to idealized octahedral geometry and a shortening of the Fe–N bonds, which is presumably required by the low-spin configuration of **14**, is more easily adopted by a C₁- than by a C₂-symmetric geometry, as indicated by the ligand–metal–ligand bite angles in **14** (Table 4), which are much closer to 90° than those of the C₂-symmetric complex **8** (Table 1). In addition, the pyridyl ligands are likely to prefer a *cis* over a *trans* arrangement in order to utilize different d orbitals for backdonation. A possible preference of isocyanide ligands to coordinate *trans* to pyridine, finally, can be satisfied, for at least one of the isocyanide ligands, only in the C₁-symmetric geometry shown in Figure 5.^[19]

Polymerization Experiments

Reaction conditions suitable for catalytic polymerization of ethene were sought in particular using complex **8** as pre-catalyst. When very finely dispersed suspensions of 10–20 mg (ca. 20–40 μmol) of turquoise **8** in 120 mL of toluene, prepared by extended exposure to an ultrasound bath, were reacted with a toluene solution of methylalumoxane (MAO) in a glass-walled reactor, with [Al]/[Fe] ratios varying between 30:1 and 1000:1, dark green solutions were obtained. Exposure of such a solution to 2–4 bar of ethene or propene yielded only miniscule flakes of polymer (if any), which escaped any isolation attempts. Neither particularly careful exclusion of air and moisture from the reaction mixture nor its deliberate exposure to the atmosphere or even addition of oxidizing reagents, such as [NO][BF₄] or Meerwein salt, which are capable of oxidizing Fe^{II} complexes,^[20] gave any more positive results, nor was this the case when the Fe^{III} complex [**8**]⁺Cl[−] was separately synthesized (see Exp. Sect.) and tested with regard to its catalytic activity after reaction with MAO or with trityl perfluorotetraphenyl borate and (*i*Bu)₃Al.^[21]

Remarkably, however, significant amounts of polymer were obtained, when 20–50 mg (ca. 40–100 μmol) of solid complex **8** in toluene were activated, *without* being finely dispersed by ultrasound treatment, by addition of a toluene solution of MAO, at [Al]/[Fe] ratios of ca. 55–85:1. When the black viscous tar, obtained from this activating procedure, was introduced into a stainless-steel reactor and then immediately exposed to 30 bar of ethene at reaction temperatures of 0–40 °C, yields of 40–160 mg polyethene

were reproducibly isolated after a reaction time of 4 hours,^[22] corresponding to productivities of ca. 160–1000 g polymer/(mol Fe≡h) (Table 5). In analogous experiments with complexes **10** and **12**, no polymer was obtained although these experiments followed a protocol which had proven successful for complex **8**.

Table 5. Conditions and results of olefin polymerization reactions^[a]

Run	Catalyst [μmol]	MAO [Al]:[Fe]	T _p [°C]	Monomer [bar]	Ultra- sound treatment	Poly- mer yield
1	8 , 38.7	30:1	20	ethene, 4	yes	traces
2	8 , 29.8	100:1	30	ethene, 2	yes	60 mg
3	8 , 27.5	300:1	40	ethene, 4	yes	traces
4	8 , 18.4	1000:1	40	ethene, 2	yes	traces
5	8 , 34.0	70:1	30	propene, 2	yes	0
6	8 , 26.3	T-FPB ^[b]	30	propene, 2	yes	0
7	8 , 94.7	100:1	25	ethene, 30	yes	traces
8	8 , 73.5	70:1	40	ethene, 30	yes	0
9	8 , 40.8	85:1	25	ethene, 30	no	160 mg
10	8 , 69.4	73:1	10	ethene, 30	no	60 mg
11	8 , 47.4	55:1	0	ethene, 30	no	100 mg
12	10 , 50.1	100:1	25	ethene, 30	no	0
13	12 , 42.2	120:1	25	ethene, 30	no	0

[a] Reaction conditions: 120 mL of toluene; reaction time, 4 hours; 1–5 min. pre-incubation with cocatalyst. [b] Trityl (perfluorotetraphenyl)borate (1 equiv.) and triisobutylaluminum (0.5 mL).

Conclusions

The results described above indicate that complex **8** undergoes some transformation upon exposure to MAO; this does not lead to an active species, capable of inducing catalytic olefin polymerization, however, when the reaction is conducted in homogeneous solution. While no direct clues indicate the nature of the green species formed under these conditions, we can surmise, in analogy to results obtained with related reaction systems,^[23] that metal alkyl cations of the type N₄FeMe⁺, most likely stabilized by uptake of a MAO-derived AlMe₃ unit, dominate in these solutions and would thus be responsible for the strongly red-shifted UV/Vis absorption of these reaction systems. If indeed present in these solutions, these species are obviously not capable of inducing chain growth by olefin insertion. Their 16-valence electron configuration is apparently not sufficiently electron-deficient to coordinate and insert an olefin substrate, in distinction to related 14-electron cations of the type N₃FeMe⁺, which are considered to be catalytically active in MAO-activated Fe^{II} pyridyldiimine systems.^[23]

The reaction of MAO with solid particles of complex **8**, on the other hand, seems to favour some other reaction paths, most likely some intermolecular ligand exchange reaction. Formation of the viscous, tarry product is likely to arise from a transfer of some of the N ligand atoms, e.g. of a pyridyl moiety, from one complex molecule to another, such that the resulting oligomeric or polymeric complex species now contains metal centers, which are coordinated to less than four N ligand atoms. More likely than not, such

a reaction would lead to a collection of different coordination patterns each with its own catalytic property, rather than to a unique complex geometry.

In accord with this assumption, a gel-permeation chromatography (GPC) analysis of the polyethene samples obtained from runs 10–12 reveals in all cases a molecular mass distribution with three distinct fractions (see Supporting Information) with *M_n* values of 130–180 (*M_w*/*M_n* ≈ 1.25), ca. 3600–7000 (*M_w*/*M_n* ≈ 1.7) and ca. 160000–320000 (*M_w*/*M_n* ≈ 6.2–7.1), respectively. Clearly, several catalytic species contribute to chain growth in these reaction systems. The component with highest *M_n* is remarkably similar, in its mean chain length as well as in its rather broad molar mass distribution, to polyethene samples obtained with typical MAO-activated iron pyridyldiimine complexes,^[1c,2d] in agreement with the assumption that some related catalyst species with reduced coordination number might be generated from complex **8** by the heterogeneous activation procedure described above. The observations presented here, in particular the lack of reactivity of any of our reaction systems vis-à-vis propene,^[21] let the probability of observing catalytic-site-controlled, stereoselective olefin polymerization by precatalyst structures of the type investigated in this report, appear rather remote.

Experimental Section

All preparations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried prior to use by refluxing over and distillation from sodium (THF, hydrocarbons) or calcium hydride (dichloromethane). Deuterated solvents were dried over 4-Å molecular sieves. All other chemicals were commercially obtained and used without further purification. Melting points were determined with a Sanyo–Gallenkamp MFB-600–010F thermometer, magnetic susceptibilities with a Quantum Design Superconducting Quantum Interference Device (SQUID) MPMS-XL5. NMR spectra were collected on Bruker AC 250 FT NMR or Bruker Avance DRX 600 spectrometers, IR spectra measured with a Perkin–Elmer 2000 FT-IR spectrometer, either as KBr or polyethene (PE) pellets, UV spectra of 1.0 mM solutions in a 1-cm cuvette with a Varian–Cary 50 and mass spectra with Finnigan MAT 312 (EI) or Finnigan AMD MAT 312/AMD 5000 (FAB) mass spectrometers. Elemental compositions were analyzed with an Elementar Vario EL device. Ligands **2** and **3** were prepared as described earlier.^[24]

N,N'-(Biphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine (1): A solution of **4** (361 mg, 1.96 mmol) in ethanol (10 mL) was stirred for 1 h with pyridine-2-carbaldehyde (373 μL, 420 mg, 3.92 mmol). After evaporation of solvent, **1** was obtained as a solid residue in almost quantitative yield. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 7.11 [d, ³J (H-H) = 7.9 Hz, 2 H; Ar-H], 7.23–7.48 (m, 8 H, Ar-H), 7.66 [t, ³J (H-H) = 7.3 Hz, 2 H; Ar-H], 7.79 [d, ³J (H-H) = 7.9 Hz, 2 H; Ar-H], 8.34 (s, 2 H, N=CH), 8.49 [d, ³J (H-H) = 4.3 Hz, 2 H; 6''-H]. Since **1** was not obtainable in powdered form, the solid residue was dissolved in THF and used for further reactions.

N,N'-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis[1-(2-pyridyl)ethyl]diimine (6): To a solution of **5** (4.45 g, 21.0 mmol) in toluene (100 mL) was added 2-acetylpyridine (4.70 mL, 5.08 g, 41.9 mmol) and *para*-toluenesulfonic acid hydrate (797 mg, 4.19 mmol). After refluxing the reaction mixture in a Dean–Stark apparatus for 3 days, the solvent

was evaporated. The residue was suspended in 200 mL of diethyl ether, freed from solids by filtration and the solids washed with diethyl ether. The combined ether fractions were extracted with diluted sodium hydroxide solution (200 mL) and subsequently dried with MgSO₄. After evaporation of solvent, a brown crude product was obtained (6.97 g), which contained, according to its ¹H NMR, 24% toluene, 6% **5**, 12% 2-acetylpyridine, 21% of the mono condensation product, and 37% of **6**. Attempted purification by column chromatography on silica gel lead to decomposition of **6** to the starting materials. Since this crude ligand was suitable for complex formation, no further attempts were undertaken to purify it. Yield (calculated on ¹H NMR basis) 2.58 g (6.16 mmol, 29%). ¹H NMR (250 MHz, CDCl₃, ppm): δ = 2.14 (s, 6 H, 6-CH₃/6'-CH₃), 2.28 (s, 6 H, N=C-CH₃), 6.57 [d, ³J (H-H) = 7.9 Hz, 2 H; 3-H/3'-H], 7.03 [d, ³J (H-H) = 7.3 Hz, 2 H; 5-H/5'-H], 7.15–7.30 (m, 4 H, 4-H/4'-H, 5''-H), 7.56–7.67 (m, 4 H, 3''-H, 4''-H), 8.55 [d, ³J (H-H) = 4.9 Hz, 2 H; 6''-H].

General Procedure for the Synthesis of Dihalogeno Metal(II) Complexes 7–11: To a stirred suspension of the metal halide in THF (10 mL/mmol), a solution of 1.02 equiv. of the ligand in THF (10 mL/mmol) was slowly added. After stirring overnight, the solvent was evaporated and the residue extracted four times with CH₂Cl₂ (4 × 20 mL/mmol). The combined extracts were evaporated to dryness and the remaining solids suspended in diethyl ether (15 mL/mmol). The complex was collected by filtration, washed with diethyl ether (3 × 5 mL/mmol), once with pentane (5 mL/mmol), and finally dried in vacuo.

Dichloro[N,N'-(biphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(II)·0.5CH₂Cl₂ (7·0.5CH₂Cl₂): A solution of **1**, obtained from **4** (361 mg, 1.96 mmol) and pyridine-2-carbaldehyde (373 μL, 420 mg, 3.92 mmol), in THF (20 mL) was reacted, following the general procedure, with FeCl₂ (246 mg, 1.94 mmol) to yield blue 7·0.5CH₂Cl₂ (858 mg, 1.61 mmol, 83%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = −8.29 (s, Δν_{1/2} = 72.3 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), −4.20 (s, Δν_{1/2} = 179 Hz, 2 H; 3-H/3'-H), 5.34 (s, Δν_{1/2} = 61.5 Hz, 1 H; CH₂Cl₂), 6.42 (s, Δν_{1/2} = 78.8 Hz, 2 H; 6-H/6'-H), 11.07 (s, Δν_{1/2} = 76.9 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 17.61 (s, Δν_{1/2} = 94.9 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 55.12 (s, Δν_{1/2} = 119 Hz, 2 H; 3''-H or 5''-H), 56.01 (s, Δν_{1/2} = 113 Hz, 2 H; 3''-H or 5''-H), 116.53 (s, Δν_{1/2} = 575 Hz, 2 H), 180.40 (s, Δν_{1/2} = 230 Hz, 2 H; N=CH). ¹³C NMR (151 MHz, CDCl₃, ppm): δ = 14.59, 71.37 (C-6/C-6'), 160.91 (C-4/C-4' or C-5/C-5' or C-4''), 193.84, 193.95, 198.96, 218.13 (C-4/C-4' or C-5/C-5' or C-4''), 244.74, 421.96 (C-3'' or C-5''), 544.79 (C-3'' or C-5''), other expected ¹³C signals were not observable due to the low solubility and the low intensity of the broad ¹³C signals. IR (KBr, cm^{−1}): ν̃ = 3054, 3045, 3019 (m, m, w, Ar-H), 2978, 2964 (m, w, C-H), 1632, 1593, 1564 (s, s, m, C=N, C=C), 1471 (m, C-H_{def}), 1304 (m), 1011 (m). IR (PE, cm^{−1}): ν̃ = 560 (m), 542 (m), 503 (m), 495 (m), 451 (m), 419 (m), 397 (w), 328 (w, Fe-N), 295 (m, Fe-N_{imine}), 251 (vs, Fe-Cl), 214 (w), 202 (w), 146 (m, Fe-Cl). Further ν̃(Fe-N) bands could not be identified. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 653 (1290). C_{24.5}H₁₉Cl₃FeN₄ (531.65): calcd. C 55.35, H 3.60, N 10.54; found C 55.24, H 3.75, N 10.58 (%).

Dichloro[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(II) (8): Following the general procedure, **2** (2.10 g, 5.38 mmol) and FeCl₂ (668 mg, 5.27 mmol) yielded turquoise **8** (2.54 g, 4.91 mmol, 93%). SQUID: μ_{eff} = 5.47 μ_B. ¹H NMR (600 MHz, CDCl₃, ppm): δ = −7.62 (s, Δν_{1/2} = 30.3 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), −6.72 (s, Δν_{1/2} = 28.7 Hz, 6 H; CH₃), −2.65 (s, Δν_{1/2} = 149 Hz, 2 H; 3-H/3'-H), 11.35 (s, Δν_{1/2} = 36.3 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 17.08 (s, Δν_{1/2} = 42.1 Hz, 2

H; 4-H/4'-H or 5-H/5'-H or 4''-H), 52.77 (s, Δν_{1/2} = 66.4 Hz, 2 H; 3''-H or 5''-H), 54.20 (s, Δν_{1/2} = 56.6 Hz, 2 H; 3''-H or 5''-H), 116.21 (s, Δν_{1/2} = 520 Hz, 2 H; 6''-H), 180.74 (s, Δν_{1/2} = 172 Hz, 2 H; N=CH). ¹³C NMR (151 MHz, CDCl₃, ppm): δ = −181.44, 0.41, 39.30 (CH₃), 71.79 (C-4/C-4' or C-5/C-5' or C-4''), 80.22, 157.30 (C-4/C-4' or C-5/C-5' or C-4''), 194.91 (C-4/C-4' or C-5/C-5' or C-4''), 195.76, 199.13, 232.31, 418.95, 533.17, 908.63 (C=N). IR (KBr, cm^{−1}): ν̃ = 3065, 3012 (w, w, Ar-H), 2962, 2916, 2850 (w, w, w, C-H), 1627, 1594, 1563 (m, s, m, C=N, C=C), 1475, 1450 (m, m, C-H_{def}), 1012 (m). IR (PE, cm^{−1}): ν̃ = 590 (w), 555 (m), 536 (w), 515 (m), 488 (m), 474 (m), 437 (w), 416 (s), 386 (w), 337 (m, Fe-N), 300 (s, Fe-N_{imine}), 271 (w), 244 (vs, Fe-Cl), 192 (m, Fe-N), 144 (s, Fe-Cl), one ν̃(Fe-N) was probably hidden by ν̃ = 244 cm^{−1}. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 641 (1140). MS (FAB): m/z (%): 516/518/520 (11/8/2) [M⁺], 481/483 (100/43) [M⁺ − Cl], 446 (22) [481/483 − Cl]; for C₂₆H₂₂Cl₂FeN₄ (517.24): calcd. C 60.38, H 4.29, N 10.83; found C 60.37, H 4.38, N 10.95 (%).

Dibromo[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(II) (9): Following the general procedure, **2** (506 mg, 1.30 mmol) and FeBr₂ (274 mg, 1.27 mmol) yielded blue **9** (398 mg, 657 μmol, 52%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = −9.14 (s, Δν_{1/2} = 16.4 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), −7.09 (s, Δν_{1/2} = 20.1 Hz, 6 H; CH₃), −6.55 (s, Δν_{1/2} = 110 Hz, 2 H; 3-H/3'-H), 11.15 (s, Δν_{1/2} = 20.9 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 17.43 (s, Δν_{1/2} = 22.0 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 53.48 (s, Δν_{1/2} = 37.3 Hz, 2 H; 3''-H or 5''-H), 57.97 (s, Δν_{1/2} = 34.2 Hz, 2 H; 3''-H or 5''-H), 119.70 (s, Δν_{1/2} = 425 Hz, 2 H; 6''-H), 191.20 (s, Δν_{1/2} = 128 Hz, 2 H; N=CH); due to the very low solubility no signals were observed in the ¹³C NMR spectrum. IR (KBr, cm^{−1}): ν̃ = 3089, 3057, 3015 (w, m, m, Ar-H), 1636, 1598, 1564 (m, m, m, m, m, C=N, C=C), 1476, 1448 (m, m, C-H_{def}), 1306 (m), 1217 (m), 1013 (m). IR (PE_{THF}, cm^{−1}): ν̃ = 588 (m), 557 (s), 535 (w), 522 (w), 512 (w), 479 (s), 423 (w), 414 (m), 371 (w), 339 (m, Fe-N), 318 (w), 297 (s, Fe-N_{imine}), 269 (m), 241 (m), 223, 191 (s, s, Fe-N), 174 (s, Fe-Br), 104 (s, Fe-Br). UV/Vis (CH₂Cl₂): λ_{max} (ε) = 630 (1000). C₂₆H₂₂Br₂FeN₄ (606.14): calcd. C 51.52, H 3.66, N 9.24; found C 52.07, H 3.63, N 9.19 (%).

Dichloro[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(1-(2-pyridyl)ethane)diimine]iron(II) (10): Following the general procedure, crude **6** (1.59 g, 1.41 mmol, based on ¹H NMR) and FeCl₂ (157 mg, 1.24 mmol) yielded blue **10** (608 mg, 1.12 mmol, 90%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = −10.43 (s, Δν_{1/2} = 16.8 Hz (2 signals), 4 H; 3-H/3'-H and 4-H/4'-H or 5-H/5'-H or 4''-H), −7.45 (s, Δν_{1/2} = 12.6 Hz, 6 H; 6-CH₃/6'-CH₃), 0.07 (s, Δν_{1/2} = 43.1 Hz, 6 H; N=C-CH₃), 10.13 (s, Δν_{1/2} = 21.4 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 17.19 (s, Δν_{1/2} = 22.9 Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 52.32 (s, Δν_{1/2} = 38.0 Hz, 2 H; 3''-H or 5''-H), 71.49 (s, Δν_{1/2} = 48.0 Hz, 2 H; 3''-H or 5''-H), 112.82 (s, Δν_{1/2} = 552 Hz, 2 H; 6''-H). ¹³C NMR (151 MHz, CDCl₃, ppm): δ = −344.57 (N=C-CH₃), −169.06, −10.31, 30.66, 58.11, 66.02 (C-3'' or C-5''), 163.12, 185.37, 194.82, 198.83 (C-4/C-4' or C-5/C-5' or C-4''), 207.07, 347.97, 449.81, 522.34. IR (KBr, cm^{−1}): ν̃ = 3091, 3057, 3021 (m, m, m, Ar-H), 2985, 2965, 2946, 2921, 2860 (w, w, w, m, w, C-H), 1629, 1593, 1565 (m, m, m, C=N, C=C), 1436 (m, C-H_{def}), 1366 (m), 1318 (m), 1258 (m), 1009 (m). IR (PE, cm^{−1}): ν̃ = 595 (w), 590 (m), 575 (m), 569 (m), 559 (m), 537 (m), 420 (m), 372 (w), 345 (m, Fe-N), 245, 235 (s, s, Fe-N, Fe-Cl), 192 (w), 179 (m, Fe-N), 150 (w), 141 (m, Fe-Cl), one (Fe-N) signal was probably hidden by peaks at ν̃ = 245 and 235 cm^{−1}. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 625 (1430). C₂₈H₂₆Cl₂FeN₄ (545.29): calcd. C 61.67, H 4.81, N 10.27; found C 61.78, H 4.95, N 10.23 (%).

Dichloro[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]cobalt(II) (11): Following the general procedure, **2** (512 mg,

1.31 mmol) and CoCl_2 (167 mg, 1.29 mmol) yielded light brown **11** (542 mg, 1.04 mmol, 81%). SQUID: $\mu_{\text{eff}} = 4.96 \mu_{\text{B}}$. ^1H NMR (600 MHz, CDCl_3 , ppm): $\delta = -16.17$ (s, $\Delta\nu_{1/2} = 137$ Hz, 2 H; 3-H/3'-H), -10.57 (s, $\Delta\nu_{1/2} = 14.1$ Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), -2.17 (s, $\Delta\nu_{1/2} = 11.5$ Hz, 6 H; CH_3), 6.46 (s, $\Delta\nu_{1/2} = 18.7$ Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 12.94 (s, $\Delta\nu_{1/2} = 22.8$ Hz, 2 H; 4-H/4'-H or 5-H/5'-H or 4''-H), 38.15 (s, $\Delta\nu_{1/2} = 39.8$ Hz, 2 H; 3''-H or 5''-H), 54.23 (s, $\Delta\nu_{1/2} = 54.2$ Hz, 2 H; 3''-H or 5''-H), 70.38 (s, $\Delta\nu_{1/2} = 472$ Hz, 2 H; 6''-H), 230.67 (s, $\Delta\nu_{1/2} = 215$ Hz, 2 H; $\text{N}=\text{CH}$). ^{13}C NMR (151 MHz, CDCl_3 , ppm): $\delta = 15.75$, 51.37 (C-4/C-4' or C-5/C-5' or C-4''), 53.44 (CH_3), 73.51 , 130.72 (C-4/C-4' or C-5/C-5' or C-4''), 219.72 (C-4/C-4' or C-5/C-5' or C-4''), 225.22 , 258.22 , 296.55 , 411.81 , other expected ^{13}C signals were not detectable due to the low solubility and the low intensity of the broad ^{13}C signals. IR (KBr, cm^{-1}): $\tilde{\nu} = 3093$, 3061 , 3042 , 3013 (w, m, w, m, Ar-H), 1639 , 1598 , 1568 (s, s, m, C=N, C=C), 1479 , 1448 (m, s, C-H_{def}), 1307 (s), 1219 (s), 1014 (s). IR (PE, cm^{-1}): $\tilde{\nu} = 591$ (m), 558 (m), 496 (m), 484 (s), 430 (m), 379 (w), 341 , 308 (m, s, Co-N), 270 (m), 242 (s, Co-Cl), 225 , 181 (m, Co-N), 135 (s, Co-Cl). UV/Vis (CH_2Cl_2): no maxima observed. $\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{CoN}_4$ (520.33): calcd. C 60.02, H 4.26, N 10.77; found C 59.32, H 4.47, N 10.64 (%).

Dichloro{[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(6-methyl-2-pyridyl)methyl]diimine}iron(II)·THF (12)·THF (**12**·THF): According to the general procedure for complexes **7–11**, ligand **3** (1.04 g, 2.48 mmol) and FeCl_2 (308 mg, 2.43 mmol) yielded brown **15**·THF (891 mg, 1.44 mmol, 59%). ^1H NMR (250 MHz, CDCl_3 , ppm): $\delta = -11.39$ (s, $\Delta\nu_{1/2} = 325$ Hz), -4.91 (s, $\Delta\nu_{1/2} = 75.3$ Hz), 3.45 (s, $\Delta\nu_{1/2} = 94.2$ Hz). MS (FAB): m/z (%): 509/511 (100/50) [$\text{M}^+ - \text{THF} - \text{Cl}$], 474 (38) [509/511 – Cl], 406 (77), 371 (71); $\text{C}_{32}\text{H}_{34}\text{Cl}_2\text{FeN}_4\text{O}$ (617.40): calcd. C 62.25, H 5.55, N 9.07; found: C 62.42, H 5.41, N 8.99 (%).

Dichloro{[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(6-methyl-2-pyridyl)methyl]diimine}iron(II) (12): A solution of ligand **3** (1.01 g, 2.42 mmol) in CH_2Cl_2 (30 mL) was added to a suspension of FeCl_2 (301 mg, 2.37 mmol) in CH_2Cl_2 (30 mL). After 2 days, the reaction mixture was filtered, the filtrate evaporated to dryness and the residue suspended in diethyl ether (20 mL). The solid was collected by filtration, washed with diethyl ether (3 × 5 mL) and dried in vacuo. Yield 872 mg (1.60 mmol, 68%) of brown **15**. SQUID (CH_2Cl_2): $\mu_{\text{eff}} = 3.41 \mu_{\text{B}}$; SQUID (diethyl ether): $\mu_{\text{eff}} = 5.23 \mu_{\text{B}}$. IR (PE, diethyl ether, cm^{-1}): $\tilde{\nu} = 595$ (w), 580 (m), 568 (w), 560 (m), 550 (w), 541 (m), 526 (m), 488 (w), 477 (m), 444 (m), 435 (w), 362 (m), 327 (s), 307 (m), 269 (m), 202 (m). IR (PE, CH_2Cl_2 , cm^{-1}): $\tilde{\nu} = 586$ (m), 565 (m), 541 (m), 528 (m), 512 (m), 448 (m), 431 (w), 408 (w), 367 (vs), 319 (vs), 268 (m). $\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{FeN}_4$ (545.29): calcd. C 61.67, H 4.81, N 10.27; found C 61.82, H 5.01, N 10.31 (%).^[a]

Dimethyl{[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridyl)methyl]diimine}iron(II) (13): Complex **8** (700 mg, 1.35 mmol) was suspended in THF (20 mL) and cooled to -78°C . At this temperature MeMgCl (451 μL of a 3.0 M solution in THF, 1.35 mmol) was added and the reaction mixture was allowed to warm to room temperature within 3 h. After stirring overnight, solvent was removed by distillation and the residue extracted with toluene (40 mL). Evaporating the solvent yielded complex **13** as a brown powder (289 mg, 607 μmol , 45%). ^1H NMR (600 MHz, CD_2Cl_2 , ppm): $\delta = -0.47$ (s, 3 H, $\text{Fe}-\text{CH}_3$,_{ax}), 1.15 (s, 3 H, $\text{Fe}-\text{CH}_3$,_{eq}), 2.04 (s, 3 H, 6- CH_3), 2.09 (s, 3 H, 6'- CH_3), 6.70 [d, 3J (H-H) = 7.6 Hz, 1 H; 3'-H], 6.72 [d, 3J (H-H) = 7.9 Hz, 1 H; 3-H], 6.88 [t, 3J (H-H) = 6.5 Hz, 1 H; 5'''-H], 6.99 [t, 3J (H-H) = 7.6 Hz, 1 H; 4-H], 7.03 [d, 3J (H-H) = 7.6 Hz, 1 H; 5'-H], 7.05 [d, 3J (H-H) = 5.6 Hz, 1 H; 6'''-H], 7.09 [d, 3J (H-H) = 7.3 Hz, 1 H; 5-H], 7.19 [t, 3J (H-H) =

7.6 Hz, 1 H; 4'-H], 7.30 [t, 3J (H-H) = 7.9 Hz, 1 H; 4'''-H], 7.40 [t, 3J (H-H) = 6.3 Hz, 1 H; 5''-H], 7.47 [t, 3J (H-H) = 7.5 Hz, 1 H; 4''-H], 7.51 [d, 3J (H-H) = 7.9 Hz, 1 H; 3'''-H], 7.70 [d, 3J (H-H) = 8.2 Hz, 1 H; 3''-H], 8.63 (s, 1 H, 2'-N=CH), 8.87 [d, 3J (H-H) = 5.9 Hz, 1 H; 6''-H], 9.68 (s, 1 H, 2-N=CH). ^{13}C NMR (151 MHz, CD_2Cl_2 , ppm): $\delta = 18.13$ ($\text{Fe}-\text{CH}_3$,_{ax}), 19.75 (6'- CH_3), 20.43 (6- CH_3), 22.22 ($\text{Fe}-\text{CH}_3$,_{eq}), 115.18 (C-3'), 115.87 (C-5'''), 118.90 (C-5'''), 121.84 (C-3), 123.57 (C-3'), 124.80 (C-3'''), 126.61 (C-5'), 126.66 (C-5, C-4'), 128.25 , 128.27 (C-4, C-4'), 128.52 (C-1), 129.17 (C-1'), 130.28 (C-4'''), 137.19 (C-6'), 139.04 (C-6), 148.28 (C-6'''), 148.54 (2-N=C), 149.90 (2'-N=C), 151.85 (C-6''), 152.27 (C-2), 154.41 (C-2'), 157.48 (C-2'''), 157.92 (C-2''). IR (KBr, cm^{-1}): $\tilde{\nu} = 3054$, 3008 (m, w, Ar-H), 2963 , 2916 , 2856 (w, w, m, C-H), 1584 , 1567 (s, s, C=N, C=C), 1467 , 1441 (s, s, C-H_{def}), 1407 (s), 997 (m), 991 (m). IR (PE, cm^{-1}): $\tilde{\nu} = 588$ (m), 551 (w), 539 (w), 520 (s), 476 (s), 452 (m), 405 (m). UV/Vis (THF): λ_{max} (ϵ) = 834 (3200). $\text{C}_{28}\text{H}_{28}\text{FeN}_4$ (476.40): calcd. C 70.59, H 5.92, N 11.76; found C 67.48, H 5.49, N 11.15 (%).

Di(tert-butylisocyanato)[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(II)-bis(trifluoromethanesulfonate) (14): To a suspension of **8** (300 mg, 580 μmol) in THF (20 mL) was added *tert*-butylisocyanide (131 μL , 96.4 mg, 1.16 mmol) and a solution of AgOTf (298 mg, 1.16 mmol) in THF (15 mL). A red suspension formed immediately. After stirring overnight the solvent was evaporated and the residue dissolved in CH_2Cl_2 (40 mL). The solution was filtered via cannula and the solvents evaporated to dryness and the solid residue suspended in diethyl ether (20 mL). The solid was collected by filtration and washed with diethyl ether (3 × 5 mL). Yield 407 mg (447 μmol , 77%) orange **14**. ^1H NMR (600 MHz, CDCl_3 , ppm): $\delta = 1.04$ [s, 9 H; $\text{C}(\text{CH}_3)_3$,_{ax}], 1.57 [s, 9 H; $\text{C}(\text{CH}_3)_3$,_{eq}], 2.03 (s, 3 H, 6- CH_3), 2.22 (s, 3 H, 6'- CH_3), 6.85 [d, 3J (H-H) = 7.9 Hz, 1 H; 3-H], 7.05 [d, 3J (H-H) = 7.9 Hz, 1 H; 3'-H], 7.14 [t, 3J (H-H) = 7.9 Hz, 1 H; 4-H], 7.34 [d, 3J (H-H) = 7.9 Hz, 2 H; 5-H, 5'-H], 7.45 [t, 3J (H-H) = 7.8 Hz, 1 H; 4'-H], 7.58 [t, 3J (H-H) = 6.2 Hz, 1 H; 5'''-H], 7.83 [d, 3J (H-H) = 5.3 Hz, 1 H; 6'''-H], 7.89 [t, 3J (H-H) = 6.5 Hz, 1 H; 5''-H], 7.98 [t, 3J (H-H) = 7.3 Hz, 1 H; 4'''-H], 8.15 [t, 3J (H-H) = 7.3 Hz, 1 H; 4''-H], 8.23 [d, 3J (H-H) = 7.6 Hz, 1 H; 3'''-H], 8.50 (s, 1 H, 2'-N=CH), 8.58 [d, 3J (H-H) = 7.6 Hz, 1 H; 3''-H], 8.89 [d, 3J (H-H) = 5.0 Hz, 1 H; 6''-H], 9.37 (s, 1 H, 2-N=CH). ^{13}C NMR (151 MHz, CDCl_3 , ppm): $\delta = 20.03$ (6'- CH_3), 20.29 (6- CH_3), 30.06 [$\text{C}(\text{CH}_3)_3$,_{ax}], 30.54 [$\text{C}(\text{CH}_3)_3,_{eq}], 58.91 , 60.70 [$\text{C}(\text{CH}_3)_3$], 115.37 (C-3'), 122.56 (C-3), 126.54 (C-1'), 129.03 (C-4', C-5'''), 129.58 (C-1), 129.81 (C-3'''), 129.95 (C-5''), 130.00 (C-5'), 130.04 (C-4), 131.47 (C-3''), 132.74 (C-5), 139.18 (C-4'''), 139.27 (C-4''), 140.00 (C-6'), 140.26 (C-6), 143.79 (C-2), 151.44 (C-2'), 153.09 (C-6''), 156.03 (C-2''), 156.19 (C-6''), 157.01 (C-2''), 169.08 (2-N=C), 171.86 (2'-N=C), the CF_3 and $\text{C}\equiv\text{N}$ signals could not be detected. ^{19}F NMR (376 MHz, CDCl_3 , ppm): $\delta = -77.44$. IR (KBr, cm^{-1}): $\tilde{\nu} = 3075$, 3033 (w, w, Ar-H), 2984 , 2939 , 2879 (m, w, w, C-H), 2184 , 2160 (s, s, $\text{C}\equiv\text{N}$), 1619 , 1603 , 1594 , 1569 (m, m, m, m, C=N, C=C), 1477 , 1462 , 1451 (m, w, m, C-H_{def}), 1276 , 1262 , 1223 , 1149 (s, s, s, s, S=O, C-F), 1031 (s), 636 (s). IR (PE, cm^{-1}): $\tilde{\nu} = 571$ (s), 550 (m), 516 (s), 464 (m), 445 (m), 394 (m), 348 (m), 320 (m), 293 (m), 270 (m), 227 (w), 209 (m), 188 (w), 177 (w). UV/Vis (CH_2Cl_2): no maxima observed. MS (FAB): m/z (%): 761 (5) [$\text{M}^+ - \text{OSO}_2\text{CF}_3$], 595 (100) [761 – 2 $\text{CNC}(\text{CH}_3)_3$], 529 (10) [761 – OSO_2CF_3 – $\text{CNC}(\text{CH}_3)_3$], 446 (63) [529 – $\text{CNC}(\text{CH}_3)_3$]. $\text{C}_{38}\text{H}_{40}\text{F}_6\text{FeN}_6\text{O}_6\text{S}_2$ (910.79): calcd. C 50.11, H 4.43, N 9.23; found C 50.29, H 4.60, N 9.27 (%).$

Bis(trifluoromethanesulfonato)[N,N'-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(II): A solution of AgOTf (289 mg, 1.12 mmol) in THF (15 mL) was added to complex **8** (0.55 mmol) suspended in THF (15 mL). After stirring overnight,

Table 6. Details of crystal structure determinations

	8	11	14 ^[a]
Empirical formula	C ₂₆ H ₂₂ Cl ₂ FeN ₄	C ₂₆ H ₂₂ Cl ₂ CoN ₄	[C ₃₆ H ₄₀ N ₆ Fe] [CF ₃ O ₃ S] ₂ ·C ₇ H ₈
CCDC number ^[b]	229184	229186	229185
<i>M</i> _w (g/mol); <i>F</i> (000)	517.23; 1064	520.31; 1068	1002.77; 1040
Crystal color and form	blue plate	red prism	red prism
Crystal size (mm)	0.5 × 0.3 × 0.3	0.5 × 0.5 × 0.4	0.4 × 0.4 × 0.3
<i>T</i> (K); <i>d</i> _{calcd.} (g/cm ³)	243; 1.380	238; 0.933	243; 1.351
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
Unit cell: <i>a</i> [Å]	14.598(4)	14.396(2)	12.564(7)
<i>b</i> [Å]	10.657(2)	10.6835(15)	13.497(6)
<i>c</i> [Å]	17.304(6)	17.3013(18)	15.876(8)
<i>α</i> [°]	90	90	97.95(3)
<i>β</i> [°]	112.40(3)	111.955(7)	101.67(5)
<i>γ</i> [°]	90	90	106.93(3)
<i>V</i> [Å ³]; <i>Z</i>	2488.8(11); 4	2468.0(6); 4	2465.9(22); 2
<i>θ</i> range [°]	2.44–25.00	2.44–26.99	1.34–25.00
Reflections: collected	2375	3262	9284
independent	1874	2700	7860
<i>R</i> _{int}	4.90%	1.67%	6.12%
<i>μ</i> (mm ⁻¹); absorption corr.	0.842; <i>ψ</i> -scan	0.933; <i>ψ</i> -scan	0.464; <i>ψ</i> -scan
<i>R</i> 1(<i>F</i>); <i>wR</i> (<i>F</i> ²) [<i>I</i> > 2σ(<i>I</i>)]	5.54%; 12.44%	3.39%; 8.31%	7.19%; 18.57%
<i>R</i> 1(<i>F</i>); <i>wR</i> (<i>F</i> ²) (all data)	8.55%; 13.98%	4.30%; 8.79%	11.57%; 23.16%
<i>GoF</i> (<i>F</i> ²)	1.086	1.052	1.051
Residual electron density	0.406 e ⁻ ·Å ⁻³	0.352 e ⁻ ·Å ⁻³	0.644 e ⁻ ·Å ⁻³

[a] One disordered triflate anion was refined with geometrical restraints applied; occupation factors were refined to 0.66 and 0.34, respectively. [b] CCDC-229184 to -229186 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

the solvent was evaporated to dryness and the residue extracted with CH₂Cl₂ (6 × 40 mL). The combined extracts were evaporated to dryness, the solids suspended in diethyl ether (20 mL), collected by filtration and washed with diethyl ether (10 mL). Yield 318 mg (427 μmol, 76%) of violet product. ¹H NMR (250 MHz, CDCl₃): no signals detected. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3109, 3084, 3062, 3034 (m, w, m, w, Ar-H), 2963, 2928, 2854 (m, m, w, C-H), 1640, 1602, 1571 (s, s, m, C=N, C=C), 1477, 1453 (m, s, C-H_{def}), 1315, 1306, 1237, 1220, 1184, 1172, 1158 (s, m, s, s, s, m, s, S=O, C-F), 1029 (s), 1016 (s), 780 (s), 628 (s). IR (PE, cm⁻¹): $\tilde{\nu}$ = 584 (s), 571 (m), 558 (m), 515 (s), 473 (m), 435 (m), 418 (s), 358 (m), 349 (w), 336 (m), 315 (m), 292 (s), 249 (m), 235 (m), 212 (m), 187 (m), 171 (m), 139 (w), 123 (w). UV/Vis (CH₂Cl₂): λ_{max} = 492. C₂₈H₂₂F₆FeN₄O₆S₂ (744.48): calcd. C 45.17, H 2.98, N 7.53; found C 45.37, H 3.31, N 7.53 (%). For crystal structure data see CCSD no 229183.

Dichloro[*N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine]iron(III) chloride·CH₂Cl₂ (8Cl·CH₂Cl₂): A solution of ligand **2** (894 mg, 2.29 mmol) in THF (20 mL) was added to FeCl₃ (364 mg, 2.24 mmol) in THF (30 mL). After stirring overnight, the solution was evaporated to dryness, the residue dissolved in CH₂Cl₂ (20 mL), filtered via cannula, and the solvent removed by evaporation again. The solid residue was suspended in diethyl ether (20 mL), collected by filtration, washed with diethyl ether (3 × 10 mL) and dried in vacuo. Yield 865 mg (1.36 mmol, 61%) of dark violet 8Cl·CH₂Cl₂. SQUID: μ_{eff} = 6.69 μ_{B} . ¹H NMR (250 MHz, CDCl₃): no signals detected. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3062, 3014 (m, m, Ar-H), 2964, 2924, 2863 (m, w, m, C-H), 1631, 1595, 1567 (m, s, m, C=N, C=C), 1467, 1449 (m, s, C-H_{def}), 1017 (s). IR (PE, cm⁻¹): $\tilde{\nu}$ = 591 (m), 557 (m), 518 (m), 483 (m), 460 (m), 416 (w), 379 (s), 331 (w), 278 (m), 236 (m), 136 (m). UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 591 (1980). MS (FAB): *m/z* (%): 483/481 (64/33) [M⁺ - CH₂Cl₂ - 2 Cl], 446 (93) [481/483 - Cl], 391 (100) [446 - Fe + H]. C₂₇H₂₄Cl₅FeN₄ (637.63): calcd. C 50.86, H 3.79, N 8.79; found C 50.87, H 3.94, N 8.88 (%).

Diffraction Structure Determination: Diffraction data for complexes **8**, **11**, and **14** were collected on a Siemens P4 diffractometer by using graphite-monochromatized Mo-*K* α radiation with λ = 0.71073 Å (Table 6). Three check reflections were measured every 97 reflections. The structures were solved by direct methods (SHELXS97).^[25] All non-hydrogen atoms were refined based on *F*_{obs}² (SHELXL97).^[25] while hydrogen atoms were refined on calculated positions with fixed isotropic *U*, using riding model techniques.

Supporting Information: Far-infrared spectra of compounds **2**, **8**, **9**, **12**, and **12b**, temperature dependence of paramagnetic NMR shifts for complex **8**, GPC elution diagrams of polyethylene samples obtained from entries 9–11 in Table 5.

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- [14] When brown **12** or **12**·THF was stirred overnight in an apolar solvent such as toluene or diethyl ether, it was transformed to a pink-colored solid (**12b**). Stirring **12b** in THF or CH_2Cl_2 regenerates brown **12**. Complex **12b** has a high-spin value of $\mu_{\text{eff}} = 5.23 \mu_{\text{B}}$. Formation of **12b** in non-polar solvents indicates that both chloride ligands are coordinated, but **12b** differs from the C_2 -symmetric complexes **7–11** in its FIR bands at 327 (s), 269 (m) and 202 (m) cm^{-1} . In the absence of suitable single crystals, its coordination geometry cannot be reliably assigned.
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- [17] Reactions of **8** with 2 equiv. of silver triflate gave the analytically pure bistriflate derivative (see Exp. Sect.). A diffractometric structure determination revealed a C_2 -symmetric geometry rather similar to that of **8** (for details see CCDC-229183).
- [18] Vibrations of the isocyanide ligands were observed at 2160 and 2184 cm^{-1} , significantly higher than $\nu_{\text{CN}} = 2138 \text{ cm}^{-1}$ measured for free isocyanide. Back-bonding from the metal to the isocyanide ligand thus appears negligible.
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