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Synthesis of chiral and C_2-symmetric iron(II) and cobalt(II) complexes bearing a new tetradentate amine ligand system ☆

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Abstract

A synthesis for the new tetrapodal ligands [*N*,*N*′-dimethyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine (L_1) (**3a**) and [*N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine (L_2) (**3b**) and for the related octahedral complexes $(L_{1,2})FeCl_2$ (**6a** and **6b**) and $(L_{1,2})CoCl_2$ (**7a** and **7b**) is given. The solid state structures of **3b** and **6a** have been determined. Three different modes are possible for a tetradentate coordination of $L_{1,2}$ to $FeCl_2$ or $CoCl_2$. In **6a** the ligand adopts a single chiral geometry around the Cl–Fe–Cl plane.

Keywords: Iron; Cobalt; Tetradentate amine ligand; Solid state structures; Chirality

1. Introduction

In recent years a variety of chiral *ansa*-zirconocene dichlorides have been successfully utilized for the stereoselective insertion polymerization of 1-olefins [1]. However, the strong Lewis-acidic nature of the catalytically active zirconocene cations [2] allows only the use of a limited number of monomers bearing sterically hindered functional groups [3].

There is some indication in the literature that alkyl complexes of iron and cobalt can be applied for the insertion polymerization of polar monomers, such as acrylic acid derivatives [4]. Yamamoto et al. [5] used the 2,2′-bipyridyl (bipy) complex $(bipy)_2Fe(Et)_2$ for the homopolymerization of acrylonitrile. This compound gives only a moderate monomer conversion, probably owing to a labile coordination of the bipyridyl ligands which leads to a facile deactivation of the catalyst via β-H migration and reductive elimination of the growing polymer chain [6]. In addition there was also no detectable stereochemical induction in the polyacrylonitrile products [7]. This might be traced back to a dynamic equilibrium between a chiral *cis* and an achiral *trans* isomer of the $(bipy)_2Fe$ complex fragment [8].

In order to provide chiral coordination compounds which are configurationally stable we describe here the preparation and structural characterization of new tetrapodal amine ligands and some of their iron(II) and cobalt(II) complexes.

2. Results and discussion

2.1. Ligand and complex synthesis

When the secondary diamines **1a** and **1b** were treated with 2-bromomethylquinoline (**2**) in ethanol under the influence of a base (e.g. K_2CO_3), the tetrapodal ligands **3a** and **3b** are accessible with moderate to good isolated yields (Fig. 1). Alkylation of unsubstituted 1,2-ethylene diamine gave a mixture of amines which carry a variable number of 2-methylquinoline groups. The reaction of 1,2-phenylene diamine (**1c**) with the acid chloride **4** gives the amide **5** [9]. However, all attempts to reduce selectively the amide groups of **5**, using $NaBH_4$, B_2H_6 or $LiAlH_4$, resulted in mixtures of dihydroquinoline and tetrahydroquinoline products. Only traces of the desired tetramine were formed. Stirring of the ligands **3a** and **3b** with $FeCl_2$ or $CoCl_2$ in dichloromethane or ethanol

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☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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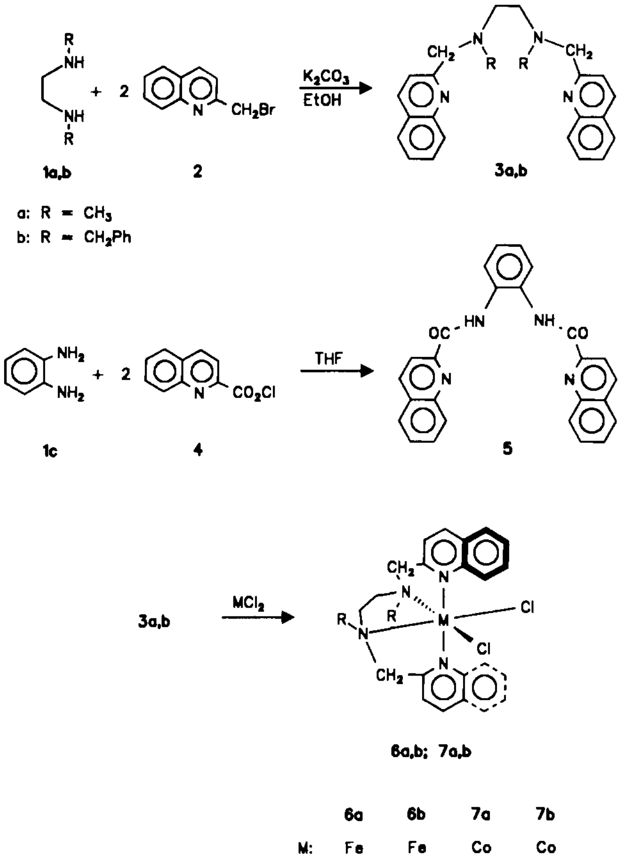

Fig. 1. Ligand and complex formation.

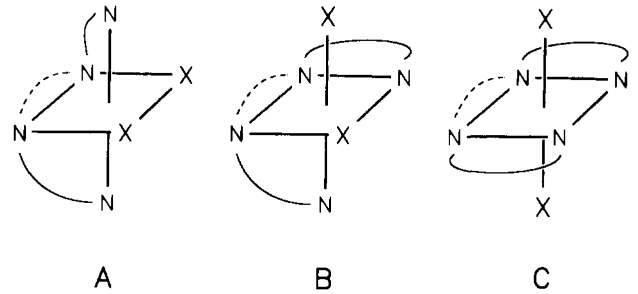

Fig. 2. Conformational isomers of tetradentate ligands in an octahedral coordination geometry: **A**, chiral, *C*2-symmetric; **B**, chiral, asymmetric; **C**, achiral.

afforded the corresponding complexes **6a** and **6b** and complexes **7a** and **7b** with up to 82% yield.

*2.2. Solid state structure of **3b** and **6a***

For octahedral complexes bearing two bidentate or one tetradentate ligand such as **3a** and **3b**, three isomers are possible (Fig. 2). An X-ray structure analysis performed on the $(bipy)_2FeEt_2$ complex of Yamamoto et al. by Lau et al. [9] showed that this complex adopts the chiral and C_2-symmetric conformation **A** [10], at least in the solid state. There was also NMR evidence that the same ligand arrangement might be preferred in solution.

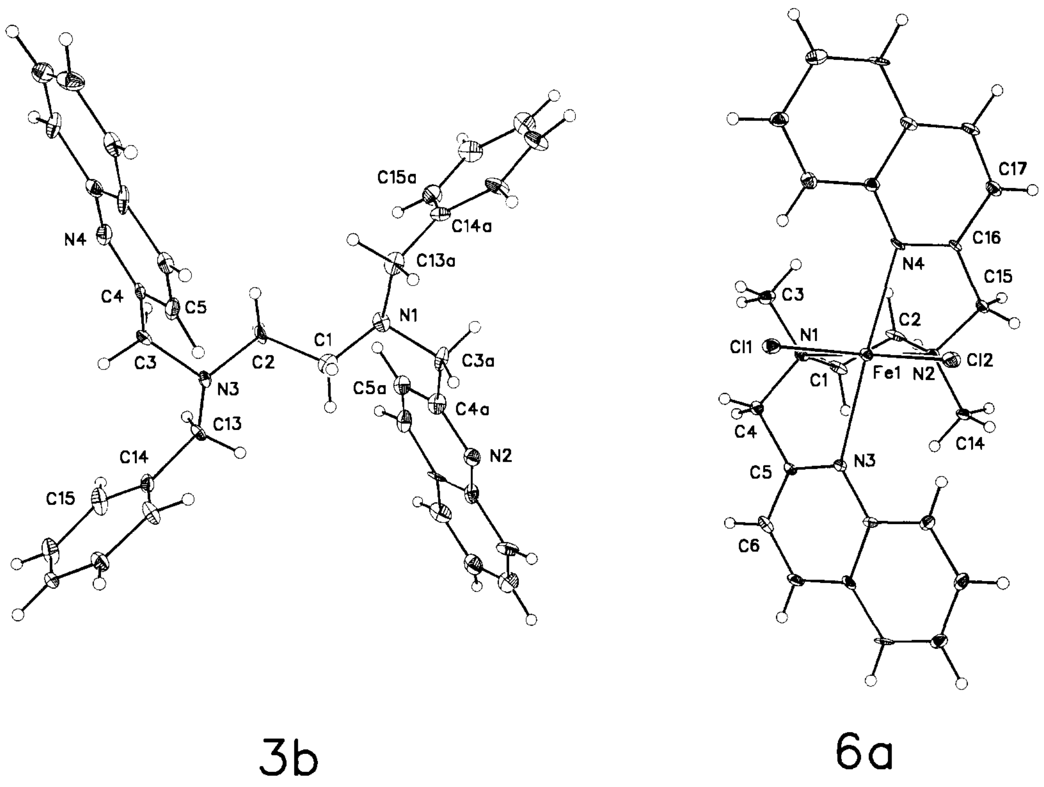

Fig. 3. Molecular structure of **3b** and **6a** at − 100°C with 20% probability thermal ellipsoids depicted.

Table 1
Selected distances (pm), angles (°) and torsion angles (°) for **3b** and **6a**

3b			
Bond distances			
C(1)–C(2)	152.5(5)	C(13a)–C(14a)	153.0(10)
C(1)–N(1)	145.3(11)	N(3)–C(3)	147.1(11)
C(2)–N(3)	148.7(11)	N(3)–C(13)	147.6(12)
N(1)–C(3a)	145.9(12)	C(3)–C(4)	152.5(13)
N(1)–C(13a)	149.9(12)	C(13)–C(14)	149.2(12)
C(3a)–C(4a)	149.7(13)		
Bond angles			
N(1)–C(1)–C(2)	112.8(5)	N(1)–C(3a)–C(4a)	117.8(8)
N(3)–C(2)–C(1)	111.1(6)	C(2)–N(3)–C(3)	110.3(8)
C(1)–N(1)–C(3a)	109.9(8)	C(4)–C(3)–N(3)	111.9(7)
6a			
Bond distances			
Fe(1)–Cl(1)	240.1(2)	C(1)–N(1)	151.3(12)
Fe(1)–Cl(2)	246.0(2)	C(2)–N(2)	148.7(12)
Fe(1)–N(1)	225.8(7)	C(1)–C(2)	147.9(12)
Fe(1)–N(2)	226.0(7)	C(4)–N(1)	150.2(10)
Fe(1)–N(3)	239.8(6)	C(15)–N(2)	148.3(10)
Fe(1)–N(4)	239.9(7)		
Bond angles			
Cl(1)–Fe(1)–Cl(2)	95.86(10)	N(1)–Fe(1)–Cl(1)	95.4(2)
N(1)–Fe(1)–N(2)	78.8(3)	N(2)–Fe(1)–Cl(2)	90.1(2)
N(3)–Fe(1)–N(4)	161.0(3)		
Torsion angle			
N(1)–C(1)–C(2)–N(2)	57.7		

However, an equilibrium between **A**, **B** and **C** in the liquid phase could not be ruled out clearly.

For **6a** and **6b** and for **7a** and **7b**, only one homogeneous fraction was isolated. On the basis of a molecular model study we expected the four complexes to exist in the chiral and C_2-symmetric geometry of the *cis* isomer **A**. An X-ray study has been performed on **3b** and **6a** in order to ascertain our structural suggestions (Fig. 3).

For **3b** the bond distances and angles are in the range expected. The results of the X-ray structure analysis of **6a** prove the desired chiral and C_2-symmetric complexation of the tetradentate ligand **3a**. The coordination geometry around Fe(II) is not ideal octahedral owing to the high ring tension of the three five-membered metallacycles (Fe, N(3), C(5), C(4), N(1); Fe, N(1), C(1), C(2), N(2); Fe, N(2), C(15), C(16), N(4)) and the chemically different nature of the two pairs of nitrogen donors (Fig. 3 and Table 1). The plane defined by the atoms (N(3), Fe, N(4)) intersects the equatorial plane (Cl(1), Cl(2), N(2), N(1)) with an angle of 74.5° instead of 90° and the Fe–N(1,2) (226 pm) and Fe–N(3,4) bonds (240 pm) have different lengths.

The quinoline units enclose an angle of 125.3° with each other and open thus a chiral cage around the Cl–Fe–Cl plane. This arrangement resembles that of the two indenyl fragments around the Cl–Zr–Cl plane in chiral zirconocene dichloride complexes [11].

A closer investigation of bond lengths and angles of **6a** reveals that in the solid state the molecule is C_2 symmetric only in a first approximation. The Fe–Cl(1) (240.1 pm) and Fe–Cl(2) (246.0 pm) bonds differ by about 6 pm. Furthermore the angle (N(2)–Fe–Cl(2), 90.1°) is about 5° smaller than the corresponding angle (N(1)–Fe–Cl(1), 95.4°). We would like to attribute this asymmetry to packing effects in the crystal. However, in solution we can detect one set of ^{1}H NMR resonances for protons related by a C_2 axis.

3. Experimental section

All reactions were carried out under dry nitrogen using standard Schlenk tube techniques. The hydrocarbon and ether solvents were purified by distillation over $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. Quinoline-2-carboxylic acid was purchased from Aldrich, and *N,N′*-dimethyl-1,2-ethylene diamine, 1,2-ethylene diamine, $FeCl_2$ and $CoCl_2$ from Fluka. Physical measurements were performed with the equipment specified previously [1k].

*3.1. N,N′-Dibenzyl-1,2-ethylene diamine (**1b**) [12]*

A solution of benzoyl chloride (40.0 ml, 0.35 mol) in 150 mol tetrahydrofuran (THF) at 0 °C was treated with a solution of 1,2-ethylene diamine (11.5 ml, 0.17 mol) in 50 ml THF over a period of 15 min. After stirring overnight at room temperature the solvent was evaporated off and the *N,N′*-dibenzoyl-1,2-ethylene diamine was washed with ample methanol and pentane. The off-white product (40.5 g, 0.15 mol (88.5%)) was added in small portions to a suspension of $LiAlH_4$ (4.8 g, 0.13 mol) in diethyl ether at 0 °C. The suspension was heated to reflux for 1 h and then stirred at ambient temperature overnight. Hydrolysis of excess $LiAlH_4$ was performed by a careful addition of water until the gas evolution ceased. The solids were filtered off and washed several times with diethyl ether. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated in vacuo, leaving crude **1b** as a colorless oil (33.4 g). Pure **1b** was obtained after a vacuum distillation (yield, 18.7 g, 76.5 mmol (51.0%)) *N,N′*-dibenzoyl-1,2-ethylene diamine, melting point (m.p.), 259 °C. Anal. Found: C, 71.47; H, 6.44; N, 10.56. $C_{10}H_{16}N_2O_2$ (268.31) Calc.: C, 71.62; H, 6.01; N, 10.44%. Mass spectroscopy (MS) (electron impact (EI)) *m/e* (relative intensity) 269.1 (12.9%, M^+), 147 (100%, M^+-C_9H_9NO), 105.1 (86.4%, $M^+ - C_7H_5O$), 77.0 (35.7%, $M^+ - C_6H_5$). ^{1}H NMR (dimethyl sulphoxide-d_6 (DMSO-d_6), MHz: δ 7.87–78.42 (m, 10H, H_{arom}), 3.45 (s, 4H, $CH_{2,bridge}$) ppm. *N,N′*-dibenzyl-1,2-ethylene diamine (**1b**). Anal. Found: C, 80.32; H, 8.71; N, 11.21. $C_{16}H_{20}N_2$ (240.33) Calc.:

C, 79.96; H, 8.39; N, 11.66%. MS (EI): *m/e* (relative intensity) 241 (6.4%, M^+), 120 (789.6%, $M^+ - C_8H_{10}N$), 91.1 (100%, $M^+ - C_7H_7$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.28–7.09 (m, 10H, H_{arom}), 3.67 (s, 4H, $CH_{2,quinaldine}$), 2.63 (s, 4H, $CH_{2,bridge}$) ppm.

3.2. 1,2-Di(quinoline-2-carboxamido)benzene (5)

Quinoline-2-carboxylic acid (10.3 g, 59.5 mmol) was suspended in $SOCl_2$. The mixture was heated under reflux until the evolution of SO_2 ceased. Excess $SOCl_2$ was distilled off and the last traces of $SOCl_2$ were removed by stirring the residue with toluene (25 ml) and then evaporating the suspension to dryness. 1,2-phenylene diamine (**1c**) (3.22 g, 29.8 mmol) was added to a solution of the acid chloride in THF (100 ml). A suspension formed immediately which was stirred overnight. The solvent was removed in vacuo and the brown residue was washed with ethanol. Compound **5** was left as a pale-yellow crystalline solid (yield, 10.4 g, 24.9 mmol (83.4%); m.p., 177–178°C). Anal. Found: C, 74.75; H, 4.64; N, 13.25. $C_{26}H_{18}N_4O_2$ (418.43) Calc.: C, 74.63; H, 4.34; N, 13.39%. MS (FD): *m/e* (relative intensity) 417.9 (100%, M^+). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.19–8.39 (m, 16 H, H_{arom}), 10.54 (s, 2H, NH) ppm.

3.3. 2-Bromomethylquinoline (2) [13]

A mixture of *N*-bromosuccinimide (62.15 g, 0.35 mol), quinaldine (45 g, 0.314 mol) and α,α'-azoisobutyronitrile (AIBN) (1.5 g) in 400 ml of CCl_4 was heated under reflux for 5 h with continuous stirring. The resulted red solution was allowed to cool to room temperature and then filtered. Removal of the solvent in vacuo left a red oil, and recrystallization from petroleum ether (300 ml) gave **2** as colorless crystals (35 g, 0.158 mol (50%)). The compound is a strong lachrymator and should be handled with care. It can be stored at −20°C without decomposition (m.p., 56°C (decomposition)). Anal. Found: C, 54.15; H, 3.79; N, 6.36. $C_{10}H_8BrN$ (222.07) Calc.: C, 54.08; H, 3.63; N, 6.31%. MS (EI): *m/e* (relative intensity) 221 (16%, M^+), 142 (100%, $M^+ - Br$), 128 (13%, $M^+ - CH_2Br$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.15–7.40 (m, 6H, H_{arom}), 4.64 (s, 2H, $CH_{2,quinaldine}$) ppm.

3.4. [N,N'-dimethyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine (3a)

A suspension of *N,N'*-dimethyl-ethylene diamine (2.27 g, 26 mmol) and K_2CO_3 (4.0 g) in ethanol (50 ml) was treated with an ice-cooled solution of 2-bromoquinoline (12.0 g, 54 mmol) in ethanol (250 ml) under vigorous stirring. The reaction mixture was heated to reflux. Stirring was continued at ambient temperature for 3 days. Subsequently, the white precipitate was filtered off (glass frit G4). A yellow oil was isolated after evaporating off the solvents in vacuo, which was dissolved in petroleum ether (300 ml). The solution was filtered and gave on cooling **3a** as colorless crystals (yield, 7.0 g, 19 mmol (73%); m.p., 59°C). Anal. Found: C, 78.13; H, 6.80; N, 14.99. $C_{24}H_{26}N_4$ (370.48) Calc.: C, 77.81; H, 7.07; N, 15.12%. MS (FD): *m/e* (relative intensity) 370 (100%, M^+). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.19–7.29 (m, 12H, H_{arom}), 3.86 (s, 4H, $CH_{2,quinaldine}$), 2.71 (s, 4H, $CH_{2,bridge}$), 2.31 (s, 6H, $N-CH_3$) ppm.

3.5. [N,N'-dibenzyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine (3b)

To an ice-cooled solution of 2-bromoquinaldine (12.0 g, 54 mmol) in ethanol (200 ml) was added a solution of *N,N'*-dibenzyl-ethylene diamine (6.18 g, 26 mmol) in ethanol (50 ml) and K_2CO_3 (4.0 g) under continuous stirring. The reaction mixture was heated at reflux temperature; then stirring was continued at ambient temperature for 2 days. The resulting white precipitate was filtered off, washed with water, ethanol, petroleum ether and dried in vacuo to give pure **3b** (yield, 8.0 g, 15.3 mmol (59%); m.p., 192°C. Anal. Found: C, 81.48; H, 6.46; N, 10.59. $C_{36}H_{34}N_4$ (522.69) Calc.: C, 82.72; H, 6.55; N, 10.72%. MS (EI): *m/e* (relative intensity) 522.4 (4%, M^+), 431.3 (5%, $M^+ - C_7H_7$), 380.3 (91%, $M^+ - C_{10}H_8N$), 239 (91%, $M^+ - C_{20}H_{16}N_2$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.06–7.19 (m, 22H, H_{arom}), 3.86 (s, 4H, $CH_{2,quinaldine}$), 3.68 (s, 4H, $CH_{2,benzyl}$), 2.75 (s, 4H, $CH_{2,bridge}$) ppm.

3.6. Dichloro{[N,N'-dimethyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine}iron(II) (6a) and dichloro{[N,N'-dibenzyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine}iron(II) (6b)

To a stirred yellow suspension of $FeCl_2$ (0.81 g, 6.38 mmol) in CH_2Cl_2 (50 ml) was added a solution of the ligand (7.02 mmol) in CH_2Cl_2 (50 ml). Stirring was continued for 24 h, during which an orange precipitate was formed. The solid was filtered, washed with diethyl ether and dried in vacuo.

3.6.1. 6a

Yield, 2.07 g, 4.17 mmol (65%). Anal. Found: C, 58.15; H, 5.58; N, 11.26. $C_{24}H_{26}Cl_2N_4Fe$ (497.25) [14] Calc.: C, 57.97; H, 5.27; N, 11.26%. MS (fast atom bombardment (FAB)): *m/e* (relative intensity) 461 (100%, $M^+ - Cl$). ^{1}H NMR (D_2O, 250 MHz): δ 8.13–7.32 (m, 12 H, H_{arom}), 4.18 (s, 4H, $CH_{2,quinaldine}$), 3.27 (s, 4H, $CH_{2,bridge}$), 2.65 (s, 6H, $N-CH_3$) ppm.

3.6.2. *6b*

Yield, 3.4 g, 5.24 mmol (82%). Anal. Found: C, 65.97; H, 5.35; N, 8.39 $C_{36}H_{34}Cl_2N_4Fe$ (649.36) Calc.: C, 66.58; H, 5.23; N, 8.63%. MS (FD): *m/e* (relative intensity) 613 (100%, $M^+ - Cl$) [15].

3.7. *Dichloro{[N,N′-dimethyl-N,N′-di(quinoline-2-methyl)]-1,2-ethylene diamine}cobalt(II) (7a) and dichloro{[N,N′-dibenzyl-N,N′-di(quinoline-2-methyl)]-1,2-ethylene diamine}cobalt(II) (7b)*

To a stirred solution of $CoCl_2$ (0.64 g, 4.91 mmol) in ethanol (50 ml) was added a clear solution of the ligand (5.39 mmol) in ethanol (50 ml). Stirring was continued for 24 h, during which a light-blue precipitate was formed. The solid was filtered, washed with ethanol, petroleum ether, and dried in vacuo.

3.7.1. *7a*

Yield, 1.30 g, 2.6 mmol (53%). Anal. Found: C, 57.84; H, 5.82; N, 11.02. $C_{24}H_{26}Cl_2N_4Co$ (500.34) Calc.: C, 57.61; H, 5.24; N, 11.19%. MS (FAB): *m/e* (relative intensity) 464 (100%, $M^+ - Cl$), 429 (13%, $M^+ - 2Cl$).

3.7.2. *7b*

Yield, 1.92 g, 2.94 mmol (60%). Anal. Found: C, 65.67; H, 5.44; N, 8.58. $C_{36}H_{34}Cl_2N_4Co$ (652.53) Calc.: C, 66.26; H, 5.25; N, 8.59%. MS (FAB): *m/e* (relative intensity) 616.3 (51%, $M^+ - Cl$), 581 (5%, $M^+ - 2Cl$).

3.8. *X-ray structure determinations [16]*

Suitable crystals of **3b** and **6a** were obtained by crystallization from $CHCl_3$ and CH_3OH respectively. Samples of **3b** and **6a** were mounted on glass fibers. Graphite-monochromated Mo Kα radiation was used. Two check reflections were monitored after every 58 intensity measurements. The structures were solved by direct methods (program SHELXTL-PC). Hydrogen atoms are placed in calculated position (riding model) and phenyls were treated as rigid groups. All attempts to solve the structure of **3b** in space group *C*2/*c* failed. The crystals of **6a** were only of minor quality. Here a

Table 2
Crystallographic data for **3b** and **6a**

	3b	**6a**
Formula	$C_{36}H_{34}N_4$	$C_{24}H_{26}Cl_2FeN_4 * 0.5\ H_2O$
Formula weight	522.7	505.2
Crystal color; crystal form	Colorless; needle	Orange; cubic
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc* [c]	*Pbcn*
a (pm)	3083.4(6)	1652.4(10)
b (pm)	636.1(1)	820.8(3)
c (pm)	1728.3(3)	3362.2(12)
α (°)	90	90
β (°)	123.26(3)	90
γ (°)	90	90
V ($\times 10^6$ pm^3)	2834.5(9)	4560(4)
d_{calc} (g cm^{-3})	1.225	1.472
Z	4	8
Crystal dimensions (mm)	0.10 × 0.10 × 0.45	0.10 × 0.25 × 0.25
Absorption coefficient μ (mm^{-1})	0.072	0.918
T (K)	173	173
Scan mode	ω	Wyckoff
Scan range (°)	2.0	1.5
2θ range (°)	4–50	4–50
Scan speed (° min^{-1})	8.37–29.30	8.37–29.30
Number of data collected	9520	26318
Number of independent data	5013	4023
Number of unique data	2452	2381
Observed criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$
Number of parameters	362	286
R [a]	0.0531	0.0953
wR_2 [b]	0.1299	0.2011
Residual density ($\times 10^{-6}$ electrons pm^{-3})	+0.22, −0.19	+0.86, −1.37

Conditions: Siemens P4 four cycle diffractometer; Mo Kα radiation; 71.073 pm; graphite monochromator. Solution: direct methods; all non-hydrogen atoms were refined anisotropically.

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

[c] The use of the space group *C*2/*c* was unsuccessful.

Table 3
Atomic coordinates and equivalent isotropic displacement coefficents for the ligand **3b**

Atom	x $(\times 10^{-4})$	y $(\times 10^{-4})$	z $(\times 10^{-4})$	U_{eq} $(\times 10^{-1}\ pm^2)$
N(1)	4697(3)	1589(12)	4386(6)	30(2)
N(2)	5856(3)	1661(14)	6715(6)	31(2)
N(3)	3660(3)	−1531(12)	4414(5)	27(2)
N(4)	2512(3)	−1706(13)	2098(6)	30(2)
C(1)	4376(4)	839(17)	4706(7)	31(2)
C(2)	3998(3)	−880(17)	4089(7)	32(2)
C(3)	3186(3)	−2542(14)	3657(6)	35(2)
C(4)	2811(3)	−952(16)	2940(7)	34(2)
C(5)	2789(4)	1093(17)	3225(8)	32(2)
C(6)	2405(4)	2437(16)	2576(7)	31(2)
C(7)	2074(3)	1749(15)	1661(7)	34(2)
C(8)	1683(4)	3137(20)	959(8)	43(3)
C(9)	1367(4)	2203(25)	66(9)	55(3)
C(10)	1428(4)	183(19)	−149(8)	44(3)
C(11)	1814(4)	−1092(21)	524(8)	41(3)
C(12)	2136(3)	−332(17)	1447(7)	32(2)
C(13)	3935(3)	−3005(14)	5199(7)	32(2)
C(14)	3644(3)	−3507(15)	5637(6)	35(2)
C(15)	3555(4)	−5580(19)	5806(9)	47(3)
C(16)	3315(5)	−5958(18)	6244(9)	57(3)
C(17)	3069(4)	−4339(17)	6437(8)	41(3)
C(18)	3153(4)	−2312(17)	6251(7)	51(3)
C(19)	3428(4)	−1865(14)	5881(7)	45(3)
C(3A)	5168(3)	2556(15)	5152(6)	31(2)
C(4A)	5549(3)	1015(15)	5589(8)	26(2)
C(5A)	5594(4)	−1084(18)	6234(8)	34(2)
C(6A)	5946(4)	−2411(16)	7151(7)	37(2)
C(7A)	6282(4)	−1729(17)	7865(8)	31(2)
C(8A)	6673(4)	−2972(17)	8742(8)	36(2)
C(9A)	6987(4)	−2356(19)	8949(7)	39(2)
C(10A)	6925(4)	−260(22)	8277(7)	48(3)
C(11A)	6558(4)	1066(19)	7369(6)	36(2)
C(12A)	6221(4)	363(16)	3569(6)	30(2)
C(13A)	4415(4)	3003(17)	3172(5)	36(2)
C(14A)	4729(3)	3463(14)	2939(6)	26(2)
C(15A)	4934(4)	1922(15)	3264(8)	36(2)
C(16A)	5213(3)	2302(15)	2523(6)	37(2)
C(17A)	5266(4)	43878(18)	2349(7)	39(2)
C(18A)	5084(4)	5944(17)	2588(8)	41(3)
C(19A)	4787(4)	5488(18)	2985(9)	41(3)

Table 4
Atomic coordinates and equivalent isotropic displacement coefficents for **6a**

Atom	x $(\times 10^{-4})$	y $(\times 10^{-4})$	z $(\times 10^{-4})$	U_{eq} $(\times 10^{-1}\ pm^2)$
Fe(1)	5031(1)	−3002(2)	6220(1)	20(1)
Cl(1)	4400(1)	−1308(3)	5727(1)	33(1)
Cl(2)	5422(1)	−762(3)	6666(1)	27(1)
N(1)	4714(4)	−5383(8)	5922(2)	20(2)
N(2)	5639(4)	−4810(9)	6629(2)	20(1)
N(3)	3692(4)	−3730(9)	6431(2)	23(2)
N(4)	6409(4)	−3238(8)	6002(2)	19(1)
C(1)	4860(5)	−6714(11)	6225(3)	30(2)
C(2)	5636(5)	−6434(11)	6433(3)	27(2)
C(3)	5170(5)	−5713(14)	5549(3)	34(2)
C(4)	3834(5)	−5295(14)	5812(3)	33(2)
C(5)	3339(4)	−4581(12)	6143(3)	24(2)
C(6)	2479(5)	−4896(12)	6131(3)	28(2)
C(7)	2012(5)	−4297(12)	6431(3)	26(2)
C(8)	1920(5)	−2797(12)	7072(3)	31(2)
C(9)	2286(6)	−2014(14)	7379(3)	39(2)
C(10)	3147(5)	−1724(12)	7367(3)	30(2)
C(11)	3585(5)	−2296(11)	7052(3)	26(2)
C(12)	3228(5)	−3151(11)	6739(2)	22(2)
C(13)	2365(5)	−3407(11)	6746(3)	26(2)
C(14)	5258(5)	−4941(13)	7023(3)	30(2)
C(15)	6489(5)	−4273(12)	6678(2)	25(2)
C(16)	6875(4)	−3887(11)	6278(2)	19(2)
C(17)	7705(5)	−4257(11)	6228(3)	28(2)
C(18)	8058(5)	−3922(11)	5869(3)	26(2)
C(19)	7917(5)	−2820(12)	5177(3)	30(2)
C(20)	7440(6)	−2146(12)	4897(3)	30(2)
C(21)	6618(6)	−1762(12)	4975(2)	28(2)
C(22)	6289(5)	−2138(11)	5338(2)	23(2)
C(23)	6760(4)	−2888(11)	5640(2)	20(2)
C(24)	7594(5)	−3187(11)	5559(3)	24(2)
O(1)	5000	1223(14)	7500	48(3)

water molecule was located in the asymmetric unit. The final cell parameters and specific data collection parameters are summarized in Table 2. The final atomic positional data can be found in Table 3 (**3b**) and Table 4 (**6a**).

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[16] Further details on the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58756, the names of the authors and the journal citation.