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Iron and Cobalt Complexes of Tridentate N-Donor Ligands in Ethylene Polymerization: Efficient Shielding of the Active Sites by Simple Phenyl Groups

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Tridentate 2,6-bis[3(5)-pyrazolyl]pyridines and 2,6-bis(4-pyrimidinyl)pyridine were synthesized and characterized spectroscopically and by single-crystal X-ray structure analysis. The derived complexes with $FeCl_2$ and $CoCl_2$ were investigated for their activity in the ethylene polymerization in the presence of methylalumoxane (MAO). Iron and cobalt catalysts bearing the ligand 2,6-bis[5-butyl-1-(4-nitrophenyl)pyrazol-3-yl]pyridine showed moderate catalytic activity and gave PE with high molecular weight, although the aryl substituents are not equipped with additional bulky side chains in the 2,6-positions to shield the metal centre. This can be explained by the geometric parameters of the pyrazole units, which provide efficient shielding of the active site, even with unsubstituted aryl groups.

Introduction

At the end of the last century, Brookhart and Gibson independently published the first members of a class of new transition metal catalysts for ethylene polymerisation,[1] obtained by coordination of iron or cobalt dichloride with 2,6-diiminopyridines. After activation with methylaluminoxane (MAO), these systems exhibit a high catalytic activity in the polymerisation of ethylene, although their structures differ fundamentally from the well-established metallocene catalysts.[2]

The role of methylaluminoxane, which is required for the activation of such 2,6-diiminopyridine complexes, is comparable to its function in traditional metallocene polymerisation catalysis: it acts as a methylating agent and as a Lewis acidic (carb)anion acceptor. This leads to the formation of a cationic 14e complex in the case of Fe^{II}, which is discussed as the active species.[3] As outlined in the Cossee–Arlmann mechanism,[4] the propagation of the polymer chain can be described by a coordination of the olefin followed by the insertion of the olefin into the metal–carbon bond. The degree of polymerisation is determined by chain propagation and chain termination reactions. Chain termination may either proceed by chain transfer onto aluminium species or by β-hydrogen transfer, either to the catalytically active site or to the coordinated monomer.[3] The latter two products can start the propagation of a new chain.

Obviously, these processes are strongly dependent on the steric demand of the ligands coordinated to the active site. For the 2,6-diiminopyridines aryl groups at the imine nitrogen atoms are required. These aryl substituents have to be functionalized in the 2- and 6-positions with alkyl groups to increase the steric demand of the whole ligand system. Otherwise only oligomers can be obtained. Starting from the basic structure of 2,6-diiminopyridine ligands, a series of new catalysts were developed including novel ligand structures.[5]

In this paper we describe the synthesis and the catalytic activity in the ethylene polymerisation of *N*-aryl-functionalized (2,6-dipyrazolylpyridine)iron(II) and -cobalt(II) complexes.

Results and Discussion

Since the mid 1990s, we have been working on the application of ligands containing pyrazolyl fragments in homogeneous catalysis. We were able to show that 2-[3(5)-pyrazolyl]pyridine and its *N*-alkylated congeners can replace the well-known 2,2′-bipyridyl ligand and additionally provide all the advantages of pyrazole chemistry such as (a) the possibility to introduce electron-donating and -withdrawing substituents in the five-membered pyrazole ring, (b) the possibility to introduce groups at various positions which enhance the solubility of the catalysts, (c) a simple protocol for the generation of chiral ligands, and (d) a simple proto-

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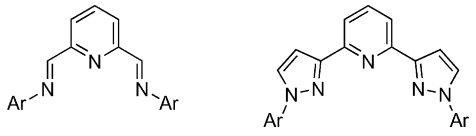
col for the heterogenization of these.[6] Aliphatic as well as aromatic[7] substitution using the N^1 atom as the nucleophilic centre provide access to further modified systems.

Expanding the bidentate 2-[3(5)-pyrazolyl]pyridine system by a further pyrazolyl substituent in the 6-position of the pyridine ring gives tridentate ligands which are structurally related to 2,2′:6′2′′-terpyridine, a ligand system that is commonly used in coordination chemistry.[8] However, 2,2′:6′2′′-terpyridine was only rarely applied in catalysis, probably due to solubility problems. By applying the synthetic routes described for the synthesis of 2-[3(5)-pyrazolyl]-pyridines and using 2,6-difunctionalized pyridines as the starting materials, 2,6-bis[3(5)-pyrazolyl]pyridines are accessible. The structure of the resulting tridentate ligands is closely related to the 2,6-diiminopyridine used for the synthesis of post-metallocene olefin polymerisation catalysts (Scheme 1). However, due to the five-membered pyrazole rings, the bond angles in the ligand backbone are different resulting in a different shielding of the active metal site (see discussion below).

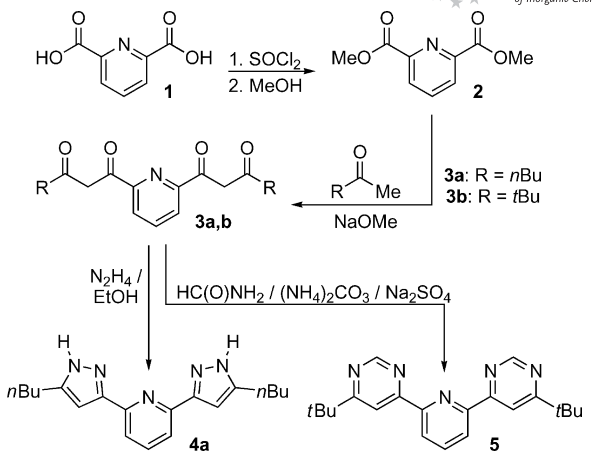


Scheme 1. Structural comparison of 2,6-diiminopyridines and 2,6-dipyrazolylpyridines.

The ligand synthesis starts from cheap 2,6-pyridinedicarboxylic acid (**1**) which is transformed into the corresponding diester **2** in almost quantitative yield.[9] To enhance the solubility of the derived complexes, we generally introduce alkyl chains in the ligand backbone. Condensation of **2** with *n*-butyl or *tert*-butyl methyl ketone under Claisen conditions provides the tetraketones **3a**,**b**. Due to the dynamic equilibration between the 1,3-diketone form and the oxo enol forms, the NMR spectra of the tetraketones **3a**,**b** are complex. **3a** was transformed into the dipyrazolyl derivative **4a** in high yield by ring closure with hydrazine.[10] **3b**[11] was treated with formamide in the presence of ammonium carbonate and sodium sulfate to give the dipyrimidinyl derivative **5** in moderate yield (Scheme 2). Experiments on the ring closure to pyrimidines with substituents other than *tert*-butyl resulted in very poor yields of the desired products.

The success of the syntheses was further confirmed by an X-ray structure analysis. Single crystals of compound **3b** could be obtained by recrystallisation from ethanol. Figure 1 presents the molecular structure of the tetraketone **3b** in the solid state.

Although a series of transition metal complexes containing tetraketones with structures similar to **3b** are known,[11,12] this is the first structure determination of an uncoordinated compound of this type. The 1,3-diketo moieties are both found in the enol structure. The extended delocalization of the negative charge over the whole diketo unit



Scheme 2. Synthesis of the tridentate ligands **4** and **5**.

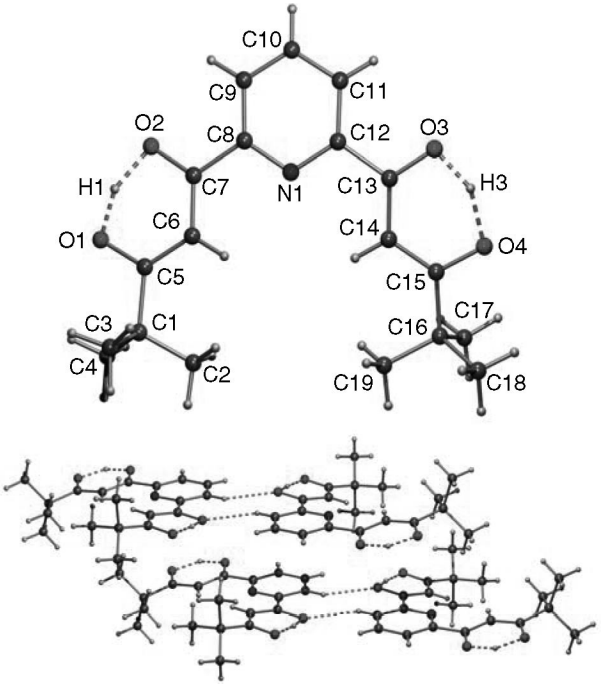
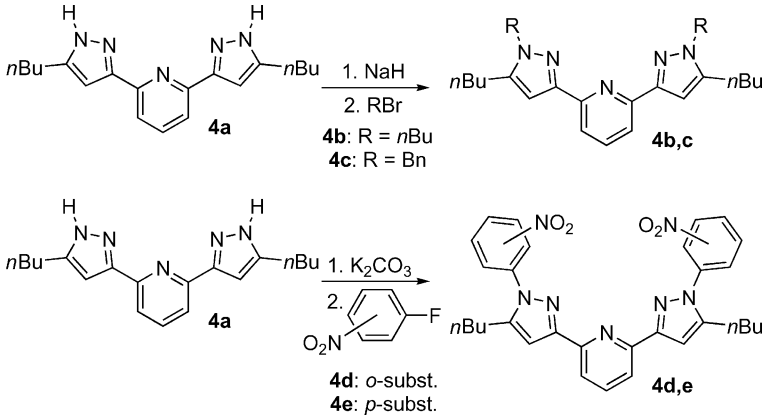


Figure 1. Molecular structure of **3b** in the solid state. Selected distances [Å], angles [°] and dihedral angles [°]: O1–C5 1.303(4), C5–C6 1.370(4), C6–C7 1.392(4), O2–C7 1.286(4), O3–C13 1.275(4), C13–C14 1.391(4), C14–C15 1.367(4), O4–C15 1.310(4), O1–H1 1.22(5), H1···O2 1.32(4), O1···O2 2.475(3), O3–H3 1.23(3), H3···O4 1.38(3), O3···O4 2.504(3), C6–H6 0.93, H6···N1 2.50, C6···N1 2.816(3), C14–H14 0.93, H14···N1 2.50, C14···N1 2.823(4), C9–H9 0.93, H9···O2′ 2.48, C9···O2′ 3.305(4); O1–H1···O2 154(4), O3–H3···O4 148(3), C6–H6···N1 100.00, C14–H14···N1 100.00, C9–H9···O2′ 148.00; C6–C7–C8–C9 –172.3(3), C11–C12–C13–C14 –172.0(3).

is confirmed by a quite small variation of the corresponding C–C and C–O bond lengths, although the O–H distances differ significantly. At a first glance it is surprising that in one of the 1,3-diketo groups, the O–H bond belonging to the oxygen atom in the 3-position is shorter than the O–H bond belonging to the oxygen atom in the 1-position, while in the other 1,3-diketo group the situation is opposite. This



Scheme 3. Alkylation and arylation of **4a**.

is due to the involvement of O2 in an intermolecular hydrogen bond, which gives rise to the formation of hydrogen-bonded dimers in the solid state. These dimers undergo π-interactions between the electron-rich diketonate group and the electron-poor pyridine ring.

The dipyrazolyl derivative **4a** shows a strong absorption for the N–H vibration at 3184 cm^{-1} in the IR spectrum. ^1H and ^{13}C NMR spectra recorded in $CDCl_3$ confirm the presence of only one tautomer. The ^1H NMR spectrum ($CDCl_3$) of the bright yellow dipyrimidinyl compound **5** shows one triplet at δ = 8.05 ppm and one doublet at δ = 8.59 ppm ($^3J_{HH}$ = 7.8 Hz) for the protons of the pyridine ring and two doublets at δ = 8.61 and 9.26 ppm with a small $^5J_{HH}$ coupling constant of 1.0 Hz for the pyrimidine ring protons.

Further derivatization at the N–H group of **4a** was performed by nucleophilic substitution with either halogenoalkyl or -aryl substrates (Scheme 3). Deprotonation of the pyrazole groups of **4a** with NaH in THF solution generates the corresponding pyrazolides which react with butyl or benzyl bromide to give the alkylated derivatives **4b**,**c**. Treatment of **4a** at 170 °C in dry DMSO with *ortho*- or *para*-fluoronitrobenzene results in the formation of the arylated ligands **4d**,**e**. Single crystals of compound **4d** could be obtained by recrystallization from ethanol. Figure 2 presents the molecular structure of the twofold nitroarylated dipyrazolyl derivative **4d** in the solid state.

Both *n*-butyl groups of **4d** were found to be disordered in the solid state. Due to four weak N···C–H interactions, the pyrazole rings are found in an almost coplanar arrangement with the pyridine ring. The *o*-nitrophenyl rings are twisted by 66.2 and 61.3° against the pyrazole rings, and the nitro groups are twisted by 141.4 and 43.6° against the phenyl rings.

The N^1-substituted ligands **4b**–**e** and the dipyrimidinylpyridine derivative **5** were treated with anhydrous iron or cobalt dichloride in dry methanol to give the paramagnetic complexes **6b**–**eFe**, **6b**–**eCo**, **7Fe**, and **7Co** in good yields (Scheme 4). They were characterized by elemental analysis, MALDI-TOF mass spectrometry and IR spectroscopy (in the case of the nitro-substituted derivatives).

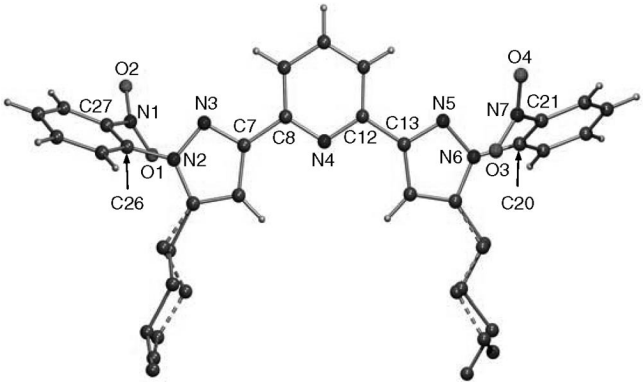
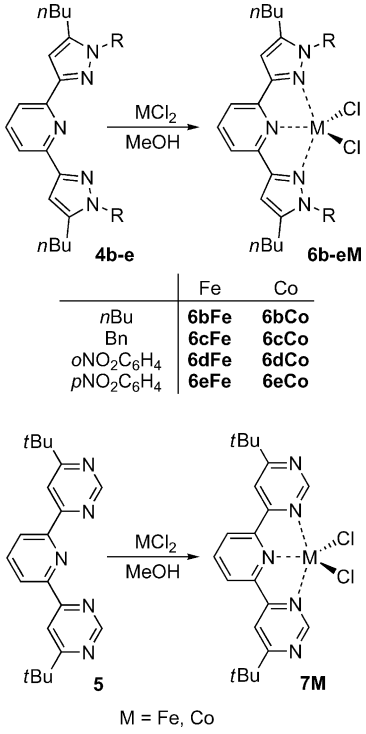


Figure 2. Molecular structure of **4d** in the solid state (the hydrogen atoms at the disordered butyl chains are omitted for clarity). Selected dihedral angles [°]: N3–C7–C8–N4 –179.54(15), N4–C12–C13–N5 –178.47(15), N3–N2–C26–C27 –66.2(2), N5–N6–C20–C21 –61.3(2), O1–N1–C27–C26 141.37(18), O3–N7–C21–C20 –43.6(3).

All dichloridoiron and -cobalt complexes were investigated for activity in the ethylene polymerisation. It turned out that exclusively **6eFe** and **6eCo** showed activity when treated in toluene with the olefin in the presence of a large excess of MAO. All other iron and cobalt compounds were not active. This is not surprising for the alkyl-substituted systems **6b**,**cFe** and **6b**,**cCo** and for **7Fe** and **7Co** since aryl substituents are also required in the 2,6-diiminopyridine series for an efficient shielding of the metal centre. Whereas the iron and cobalt complexes **6eFe** and **6eCo** with *para*-nitrophenyl substituents at the N^1 atom of the pyrazole rings are active catalysts, their *ortho*-nitrophenyl-bearing congeners **6dFe** and **6dCo** are not active. There may be steric or electronic reasons for this behaviour. On the other hand, it is unlikely, that a nitro substituent will remain unaffected in the presence of highly alkylating (and thus reducing) MAO. This can generate amido ($Ar–NR^-$) as well as imido ($Ar–N^{2-}$) groups, which would be located in close proximity to the reactive metal site in the case of **6dFe** and **6dCo**. In the case of **6eFe** and **6eCo**, these strongly coordinating sites would only be able to bind to MAO. The reaction conditions for the polymerization tests are summarized in Table 1.



Scheme 4. Synthesis of iron and cobalt complexes.

Table 1. Summary of the polymerization experiments.

Catalyst	Amount [mg]	MAO/ catalyst	$p[C_2H_4]$ [atm]	PE yield [g]	Activity[a,b] [kg PE mmol^{-1} h^{-1}]
6eFe	13.7	500	1	0.1	0.02
6eFe	10	1000	10	12.7	0.44
6eCo	19	500	1	0.0	0.00
6eCo	10	1000	10	16.6	0.58

[a] Reaction time 110 min. [b] T = 30 °C.

At an ethylene pressure of 10 bar, the reaction started after a short induction period and had to be kept at 30 °C by external cooling. At the end of the reaction, the polymer was isolated by precipitation and analyzed by means of gel permeation chromatography. The results are summarized in Table 2.

Table 2. Characteristic properties of the obtained polymers.

Catalyst	Amount[a] [mg]	$p[C_2H_4]$ [atm]	M.p. [°C]	M_w [g/mol]	M_n [g/mol]	Q
6eFe	10	10	134	524177	155089	3.38
6eCo	10	10	135	485026	194428	2.49

[a] Al/M = 1000:1.

The catalysts do not exhibit excellent activities, at least when the PE pressure of 10 atm is taken into account. However, the molecular masses which were reached are quite interesting because there are no sterically demanding groups in the 2- and 6-positions of the aryl substituents at the pyrazole ring. In our case two simple aryl rings allow efficient shielding of the catalytically active site to prevent chain termination reactions. We assign this to the internal angles of the five-membered pyrazole rings which bring the aryl substituents much closer to the metal sites than it is the case for 2,6-diiminopyridines. This is qualitatively demonstrated in Figure 3, which shows the structures of a (2,6-diiminopyridine)- and a (2,6-dipyrazolylpyridine)-dichloridozinc complex, calculated with the semiempirical method PM3.[13]

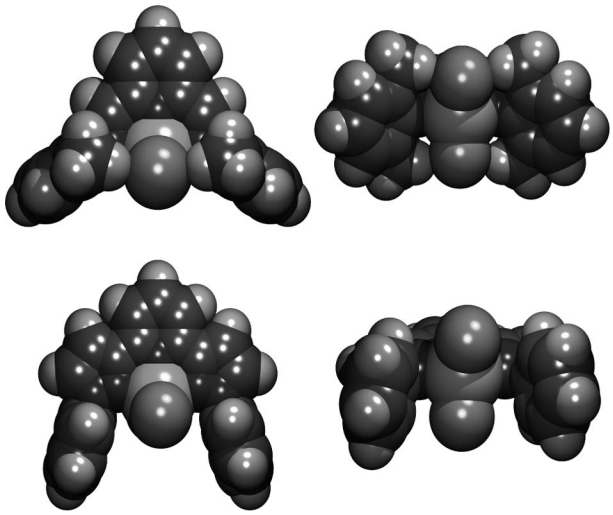


Figure 3. Shielding of the metal site in {2,6-bis[(2,6-dimethylphenyl)imino]pyridine}dichloridozinc (top) and {2,6-bis[(1-phenyl)pyrazol-3-yl]pyridine}dichloridozinc (bottom).

Conclusions

Increasing of the shielding of the active sites of post-metallocene polymerization catalysts can efficiently be achieved by implying a five-membered ring like pyrazole instead of an sp^2-hybridized imine group or a six-membered ring. This allows to use simple and cheap phenyl substituents. We are at the moment looking for other applications of this principle in catalysis.

Experimental Section

General Remarks: All manipulations were carried out under dinitrogen. Only dry solvents were used. All commercially available starting materials were used without further purification. Elemental analyses were carried out at the Departmernt of Chemistry (TU Kaiserslautern). IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 400 spectrometer.

2,6-Bis(1,3-dioxoheptyl)pyridine (3a) and 2,6-Bis(4,4-dimethyl-1,3-dioxopentyl)pyridine (3b):[11] 2-Hexanone or pinacolone (40 mmol) was added to a suspension of NaOEt (2.72 g, 40 mmol) and dimethyl 2,6-pyridinedicarboxylate (4.46 g, 20 mmol) in dry THF (100 mL). The mixture was heated to reflux for 3 h. After this time, the solvent was removed under vacuum, the resulting sodium salt was suspended in water, and the suspension was treated with HCl until pH = 4. Extraction with $CHCl_3$, drying of the solution with Na_2SO_4, and removal of the solvent in vacuo yielded the crude tetraketones in 70–80% yield as bright yellow solids, which were of sufficient purity for the following transformations. **3a**: IR (KBr): $\tilde{\nu}$ = 3103 (w), 2957 (s), 2931 (s), 2871 (m), 1711 (s), 1696 (s), 1608

(s), 1574 (s), 1444 (m), 1408 (m), 1320 (m), 1238 (m), 1149 (m), 1080 (m), 994 (m), 942 (m), 809 (m), 748 (m), 612 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 15.77 (br., 2 H, =CO*H*), 8.17 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, 3,5-H_{py}), 7.97 (t, 1 H, 4-H_{py}), 6.87 (s, 2 H, =C*H*), 2.53 (t, 4 H, CH_2), 1.71 (q, 4 H, CH_2), 1.43 (sext, 4 H, CH_2), 0.96 (t, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 198.1 (C=O), 180.8 (*C*OH), 152.2 (2,6-C_{py}), 138.2 (4-C_{py}), 124.3 (3,5-C_{py}), 96.8 (=CH), 39.3 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 13.9 (CH_3) ppm. $C_{19}H_{25}NO_4$ (331.37): calcd. C 68.86, H 7.60, N 4.23; found C 69.04, H 7.36, N 4.31. The spectroscopic data for **3b** is in complete agreement with the data given in ref.[11]

2,6-Bis(5-butylpyrazol-3-yl)pyridine (4a): This compound was synthesized according to a published procedure[10] and obtained as a colourless solid in 78% yield. Mp. 193 °C. IR (KBr): $\tilde{\nu}$ = 3184 (s), 3131 (s), 3106 (s), 2927 (s), 2858 (s), 1654 (m), 1599 (m), 1575 (s), 1505 (m), 1463 (s), 1398 (m), 1338 (m), 1297 (m), 1248 (m), 1169 (m), 1152 (m), 1094 (m), 1031 (m), 1010 (m), 963 (w), 811 (s), 792 (s), 769 (s), 727 (w), 646 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.8 (br., 2 H, NH), 7.69 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, 4-H_{py}), 7.52 (d, 2 H, 3,5-H_{py}), 6.54 (s, 2 H, 4-H_{pz}), 2.70 (t, 4 H, CH_2), 1.67 (q, 4 H, CH_2), 1.39 (sext, 4 H, CH_2), 0.92 (t, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.4 (5-C_{pz}), 148.8 (2,6-C_{py}), 144.8 (3-C_{pz}), 137.2 (4-C_{py}), 118.1 (3,5-C_{py}), 101.6 (4-C_{pz}), 31.7 (CH_2), 27.3 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. $C_{19}H_{25}N_5$ (323.43): calcd. C 70.21, H 7.57, N 21.67; found C 70.56, H 7.79, N 21.65.

2,6-Bis(6-*tert*-butylpyrimidin-4-yl)pyridine (5): A mixture of compound **3b** (5.10 g,15.4 mmol), Na_2SO_4 (6.50 g, 45.8 mmol), $(NH_4)_2CO_3$ (5.00 g, 52.0 mmol), and formamide (10 g, 222 mmol) was heated to 180 °C for 12 h. After cooling of the mixture to room temp., it was treated with 1 M NaOH (100 mL) to hydrolyze excess formamide. The crude product was extracted with diethyl ether, the organic solution was dried with $CaCl_2$, and the solvent was removed in vacuo. Purification by flash chromatography (Al_2O_3; hexane/ethyl acetate, 4:1) yielded 1.17 g (22%) of **5** as a bright yellow solid. IR (KBr): $\tilde{\nu}$ = 2961 (s), 2864 (m), 1599 (m), 1576 (s), 1528 (s), 1478 (w), 1447 (w), 1392 (w), 1355 (m), 1314 (w), 1254 (m), 1078 (w), 992 (w), 899 (m), 863 (m), 822 (m), 786 (m), 741 (m), 667 (m), 634 (m), 545 (w), 475 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.26 (d, $^5J_{HH}$ = 1.0 Hz, 2 H, 2-H_{pm}), 8.61 (d, 2 H, 5-H_{pm}), 8.59 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, 3,5-H_{py}), 8.05 (t, 1 H, 4-H_{py}), 1.47 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 179.0 (4-C_{pm}), 162.5 (6-C_{pm}), 158.4 (2-C_{pm}), 154.1 (2,6-C_{py}), 138.5 (4-C_{py}), 123.1 (3,5-C_{py}), 112.7 (5-C_{pm}), 37.9 [$C(CH_3)_3$], 29.5 [$C(CH_3)_3$] ppm. $C_{21}H_{25}N_5$ (347.44): calcd. C 72.39, H 7.51, N 18.67; found C 72.59, H 7.25, N 20.16.

2,6-Bis(1,5-dibutylpyrazol-3-yl)pyridine (4b) and 2,6-Bis(1-benzyl-5-butylpyrazol-3-yl)pyridine (4c): NaH (0.74 g, 31 mmol) was suspended in dry THF (150 mL). Solid **4a** (4.85 g, 15 mmol) was added slowly, and the resulting mixture was stirred at room temp. until the evolution of H_2 had ceased. Then of either butyl or benzyl bromide (33 mmol) was added, and the solution was heated under reflux for 8 h. After filtration of NaBr, the solvent was removed in vacuo, and the crude product was purified by column chromatography (**4b**: SiO_2; ethyl acetate; **4c**: Al_2O_3; hexane/ethyl acetate, 1:1). Yields: 4.20 g (64%) of **4b**, bright brown solid; 3.20 g (41%) of **4c**, colourless oil. **4b:** IR (KBr): $\tilde{\nu}$ = 2957 (s), 2931 (s), 2871 (s), 1594 (m), 1573 (m), 1545 (m), 1503 (m), 1464 (m), 1402 (m), 1381 (m), 1346 (m), 1315 (m), 1283 (m), 1254 (m), 1194 (m), 1151 (w), 1078 (m), 991 (w), 960 (m), 800 (m), 743 (m), 649 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.81 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, 3,5-H_{py}), 7.67 (t, 1 H, 4-H_{py}), 6.77 (s, 2 H, 4-H_{pz}), 4.06 (t, 4 H, NCH_2), 2.61 (t, 4 H, CCH_2), 1.84 (q, 4 H, CH_2), 1.72 (q, 4 H, CH_2), 1.45 (sext, 4 H, CH_2), 1.37 (sext, 4 H, CH_2), 0.94 (m, 12 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.0 (5-C_{pz}), 150.5 (2,6-C_{py}), 143.8 (3-C_{pz}), 136.5 (4-C_{py}), 117.80 (3,5-C_{py}), 102.77 (4-C_{pz}), 48.8 (NCH_2), 32.4 (CCH_2), 30.5 (CH_2), 25.1 (CH_2), 22.2 (CH_2), 19.8 (CH_2), 13.6 (CH_3), 13.5 (CH_3) ppm. $C_{27}H_{41}N_5$ (435.66): calcd. C 74.44, H 9.49, N 16.08; found C 73.17, H 9.79, N 14.51. **4c:** IR (KBr): $\tilde{\nu}$ = 3064 (w), 3031 (w), 2955 (s), 2928 (s), 2855 (m), 1594 (w), 1573 (m), 1546 (w), 1498 (m), 1455 (m), 1402 (m), 1380 (m), 1355 (m), 1316 (m), 1254 (m), 1192 (m), 1151 (w), 1078 (w), 1030 (w), 1003 (w), 991 (w), 959 (w), 803 (m), 726 (m), 695 (m), 580 (w), 456 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.94 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, 3,5-H_{py}), 7.76 (t, 1 H, 4-H_{py}), 7.31 (m, 6 H, *m*-H_{ph}, *p*-H_{ph}), 7.13 (d, $^3J_{HH}$ = 7.1 Hz, 4 H, *o*-H_{ph}), 6.94 (s, 2 H, 4-H_{pz}), 5.41 (s, 4 H, CH_2Ph), 2.56 (t, 4 H, CH_2), 1.64 (quint, 4 H, CH_2), 1.38 (sext, 4 H, CH_2), 0.91 (t, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.1 (5-C_{pz}), 151.1 (2,6-C_{py}), 144.9 (3-C_{pz}), 137.3 (1-C_{ph}), 129.8 (4-C_{py}), 128.7, 126.56 (*o*-C_{ph}, *m*-C_{ph}), 127.49 (4-C_{ph}), 118.4 (3,5-C_{py}), 103.9 (4-C_{pz}), 53.2 (CH_2Ph), 30.45 (CH_2), 25.4 (CH_2), 22.3 (CH_2), 13.8 (CH_3) ppm. $C_{33}H_{37}N_5$ (503.66): calcd. C 78.69, H 7.40, N 13.91; found C 78.58, H 7.20, N 13.02.

2,6-Bis[5-butyl-1-(2-nitrophenyl)pyrazol-3-yl]pyridine (4d) and 2,6-Bis[5-butyl-1-(4-nitrophenyl)pyrazol-3-yl]pyridine (4e): A mixture of **4a** (4.00 g, 12.4 mmol), K_2CO_3 (10.00 g, 70 mmol), 1-fluoro-2-nitrobenzene or 1-fluoro-4-nitrobenzene (4.23 g, 30.0 mmol), and DMSO (150 mL) was heated to 170 °C for 4 h. After pouring on ice, addition of HCl until pH = 3, and warming to room temp., the crude products could be separated by filtration. They were washed with water and dried at 50 °C under vacuum. The crude products were purified by column chromatography (SiO_2), first by elution of residual 1-fluoronitrobenzene with pentane followed by elution of the product with diethyl ether/acetone (1:1). Yields: 4.30 g (61%) of **4d**, dark brown solid; 4.60 g (65%) of **4e**, yellow solid. **4d:** Mp. 164 °C. IR (KBr): $\tilde{\nu}$ = 2962 (m), 2933 (m), 2860 (m), 1608 (m), 1587 (m), 1572 (m), 1535 [s, $\nu(NO_2)$], 1494 (s), 1456 (m), 1398 (w), 1376 (s), 1358 [s, $\nu(NO_2)$], 1301 (m), 1253 (m), 1196 (w), 1152 (m), 1138 (m), 1102 (w), 1039 (w), 1019 (w), 957 (m), 852 (m), 814 (m), 780 (m), 750 (m), 703 (m), 645 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.06 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{ph}), 7.92 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, 3,5-H_{py}), 7.75 (m, 3 H, 4-H_{py}, H_{ph}), 7.64 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{ph}), 7.59 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{ph}), 7.23 (s, 2 H, 4-H_{pz}), 2.59 (t, 4 H, CH_2), 1.68 (q, 4 H, CH_2), 1.39 (sext, 4 H, CH_2), 0.89 (t, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 153.3 (5-C_{pz}), 151.3 (2,6-C_{py}), 146.8, 146.7, 137.4, 133.4, 133.3, 129.8, 129.8, 125.4, 119.51, 105.1 (4-C_{pz}), 30.7 (CH_2), 25.70 (CH_2), 22.35 (CH_2), 13.79 (CH_3) ppm. $C_{31}H_{31}N_7O_4$ (565.60): calcd. C 65.83, H 5.52, N 17.34; found C 65.73, H 5.65, N 17.33. **4e:** Mp. 214 °C. IR (KBr): $\tilde{\nu}$ = 2954 (m), 2932 (m), 2871 (m), 1596 (s), 1574 (m), 1520 [s, $\nu(NO_2)$], 1497 (s), 1452 (m), 1378 (m), 1339 [s, $\nu(NO_2)$], 1259 (m), 1198 (m), 1153 (m), 1131 (m), 1109 (m), 1082 (m), 1025 (m), 1008 (m), 955 (w), 853 (m), 802 (m), 788 (m), 750 (m), 730 (w), 689 (w), 644 (w), 534 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.38 (m, 4 H, *m*-H_{ph}), 8.05 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, 3,5-H_{py}), 7.85 (t, 1 H, 4-H_{py}), 7.77 (m, 4 H, *o*-H_{ph}), 7.21 (s, 2 H, 4-H_{pz}), 2.81 (t, 4 H, CH_2), 1.74 (q, 4 H, CH_2), 1.42 (sext, 4 H, CH_2), 0.93 (t, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.9 (5-C_{pz}), 151.2 (2,6-C_{py}), 146.6 (3-C_{pz}), 146.1, 145.2 (*i*-C_{ph}, *p*-C_{ph}), 137.9 (4-C_{py}), 125.1 (*m*-C_{ph}), 124.9 (*o*-C_{ph}), 119.9 (3,5-C_{py}), 106.8 (4-C_{pz}), 31.1 (CH_2), 26.8 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. $C_{31}H_{31}N_7O_4$ (565.60): calcd. C 65.83, H 5.52, N 17.34; found C 65.55, H 5.30, N 16.98.

Synthesis of the Dichloridoiron and -cobalt Complexes 6b–eFe, 6b–eCo, 7Fe, and 7Co: $FeCl_2$ or $CoCl_2$ (1 equiv., ca. 1.00 g) was added to a solution of the tridentate ligand **4b–e** or **5** (1 equiv.) in dry and degassed methanol (50 mL). The solution was heated to reflux for 4 h. After cooling to room temp., about 80% of the solvent was removed in vacuo, and the precipitated products were isolated by filtration and dried in vacuo.

[2,6-Bis(1,5-dibutylpyrazol-3-yl)pyridine]dichloridoiron(II) (6bFe): Yield: 33%, orange yellow solid. MALDI-TOF MS: *m/z* (%) = 561.17 (23) $[M]^+$, 526.25 (100) $[M - Cl]^+$. $C_{27}H_{41}Cl_2FeN_5$ (562.41): calcd. C 57.66, H 7.35, N 12.45; found C 57.74, H 7.31, N 12.59.

[2,6-Bis(1,5-dibutylpyrazol-3-yl)pyridine]dichloridocobalt(II) (6bCo): Yield: 52%, green solid. MALDI-TOF MS: *m/z* (%) = 529.19 (100) $[M - Cl]^+$. $C_{27}H_{41}Cl_2CoN_5$ (565.50): calcd. C 57.35, H 7.31, N 12.38; found C 56.70, H 7.08, N 12.28.

[2,6-Bis(1-benzyl-5-butylpyrazol-3-yl)pyridine]dichloridoiron(II) (6cFe): Yield: 67%, bright brown solid. MALDI-TOF MS: *m/z* (%) = 594.11 (100) $[M - Cl]^+$. $C_{33}H_{37}Cl_2FeN_5$ (630.40): calcd. C 62.87, H 5.92, N 11.10; found C 62.75, H 6.04, N 10.96.

[2,6-Bis(1-benzyl-5-butylpyrazol-3-yl)pyridine]dichloridocobalt(II) (6cCo): Yield: 58%, green solid. MALDI-TOF MS: *m/z* (%) = 597.29 (100) $[M - Cl]^+$. $C_{33}H_{37}Cl_2CoN_5$ (633.49): calcd. C 62.56, H 5.89, N 11.11; found C 62.71, H 5.70, N 11.10.

{2,6-Bis[5-butyl-1-(2-nitrophenyl)pyrazol-3-yl]pyridine}dichloridoiron(II) (6dFe): Yield: 72%, bright brown solid. IR (KBr): $\tilde{\nu}$ = 1531 (s), 1342 [s, 2 $\nu(NO_2)$] cm^{-1}. MALDI-TOF MS: *m/z* (%) = 690.99 (100) $[M]^+$, 656.05 (90) $[M - Cl]^+$, 566.22 (16) $[M - FeCl_2]^+$. $C_{31}H_{31}Cl_2FeN_7O_4$ (692.34): calcd. C 53.78, H 4.51, N 14.16; found C 53.53, H 4.38, N 13.81.

{2,6-Bis[5-butyl-1-(2-nitrophenyl)pyrazol-3-yl]pyridine}dichloridocobalt(II) (6dCo): Yield: 67%, green solid. IR (KBr): $\tilde{\nu}$ = 1531 (s), 1342 [s, 2 $\nu(NO_2)$] cm^{-1}. MALDI-TOF MS: *m/z* (%) = 658.81 (100) $[M - Cl]^+$, 563.89 (10) $[M - CoCl_2]^+$. $C_{31}H_{31}Cl_2CoN_7O_4$ (695.47): calcd. C 53.59, H 4.50, N 14.12; found C 53.68, H 4.54, N 13.93.

{2,6-Bis[5-butyl-1-(4-nitrophenyl)pyrazol-3-yl]pyridine}dichloridoiron(II) (6eFe): Yield: 65%, bright brown solid. IR (KBr): $\tilde{\nu}$ = 1528 (s), 1344 [s, 2 $\nu(NO_2)$] cm^{-1}. MALDI-TOF MS: *m/z* (%) = 656.31 (100) $[M - Cl]^+$, 642.43 (25) $[M - Cl - CH_3]^+$, 629.32 (25) $[M - Cl - 2\ CH_3]^+$, 566.43 (29) $[M - FeCl_2]^+$, 535.33 (38) $[M - FeCl_2 - 2\ CH_3]^+$. $C_{31}H_{31}Cl_2FeN_7O_4$ (692.38): calcd. C 53.78, H 4.51, N 14.16; found C 53.67, H 4.59, N 14.15.

{2,6-Bis[5-butyl-1-(4-nitrophenyl)pyrazol-3-yl]pyridine}dichloridocobalt(II) (6eCo): Yield: 76%, green solid. IR (KBr): $\tilde{\nu}$ = 1526 (s), 1344 [s, 2 $\nu(NO_2)$] cm^{-1}. MALDI-TOF MS: *m/z* (%) = 659.44 (100) $[M - Cl]^+$, 643.43 (34) $[M - Cl - CH_3]^+$, 630.43 (44) $[M - Cl - 2\ CH_3]^+$, 566.53 (14) $[M - CoCl_2]^+$. $C_{31}H_{31}Cl_2CoN_7O_4$ (695.43): calcd. C 53.54, H 4.49, N 14.09; found C 53.68, H 4.61, N 14.16.

[2,6-Bis(6-*tert*-butylpyrimidin-4-yl)pyridine]dichoridoiron(II) (7Fe): Yield: 87%, dark blue solid. MALDI-TOF MS: *m/z* (%) = 473.25 (100) $[M]^+$, 438.29 (90) $[M - Cl]^+$. $C_{21}H_{25}Cl_2FeN_5$ (474.22): calcd. C 53.19, H 5.31, N 14.95; found C 52.19, H 5.32, N 14.12.

[2,6-Bis(6-*tert*-butylpyrimidin-4-yl)pyridine]dichloridocobalt(II) (7Co): Yield: 89%, bright green solid. MALDI-TOF MS: *m/z* (%) = 441.27 (100) $[M]^+$. $C_{21}H_{25}Cl_2CoN_5$ (477.30): calcd. C 52.85, H 5.28, N 14.67; found C 52.76, H 5.33, N 14.42.

X-ray Structure Analyses of Compounds 3b and 4d: The crystal data of compounds **3b** and **4d** were obtained with a Stoe IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[14] Table 3 summarizes the crystallographic and refinement data. The structure was solved by direct methods.[15] The hydrogen atoms were localized geometrically, a riding model was taken for refinement.[16] CCDC-692307 (**3b**) and CCDC-692308 (**4d**) 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.

Table 3. Crystal data and structural refinement for compounds **3b** and **4d**.

	3b	**4d**
Empirical formula	$C_{19}H_{25}NO_4$	$C_{31}H_{31}N_7O_4$
Formula mass	331.40	565.63
Crystal size [mm]^3	0.42×0.32×0.09	0.45×0.38×0.27
Scan mode	Φ-oscillation	Φ-oscillation
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
T [K]	293(2)	193(2)
a [Å]	15.698(3)	9.5267(8)
b [Å]	6.2374(6)	10.8174(9)
c [Å]	19.935(3)	15.0455(13)
α [°]	90	105.179(10)
β [°]	100.235(19)	97.332(10)
γ [°]	90	98.290(10)
V [Å^3]	1920.9(5)	1458.4(2)
Z	4	2
$\rho_{calcd.}$ [g cm^{-1}]	1.146	1.288
μ [mm^{-1}]	0.080	0.088
$F(000)$	712	596
θ_{min}–θ_{max} [°]	2.1 to 24.0	2.7 to 26.7
h, k, l	–17/17, –6/6 –22/22	–12/12, –13/13 –19/19
Total data	14517	15595
Unique data	2942	5706
Observed data [$I > 2.0\sigma(I)$]	1269	4123
N_{ref}, N_{par}	2942, 229	5706, 457
R (all data)	0.1136	0.0698
wR_2 (all data)	0.1328	0.1468
R [$I > 2.0\sigma(I)$]	0.0533	0.0503
wR_2 [$I > 2.0\sigma(I)$]	0.1179	0.1343
GooF	0.859	1.043
Min/max residual density [e Å^{-3}]	0.160/–0.134	–0.212/0.188

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