Cobalt Chloride Complexes of N_3 and N_4 Donor Ligands

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A number of cobalt(II) chloride complexes of pyridine/amine N_3 and N_4 donors have been prepared and structurally characterised. Even though they are paramagnetic, assignment of the ^{1}H NMR signals was possible in several cases. With the exception of tpa, which formed a cationic monochloride complex, all new complexes have *cis*-coordinated chlorides. Nevertheless, only the relatively rigid pyp ligands gave rise to (low) ethene polymerisation activity on activation with MAO.

Introduction

Cobalt complexes with nitrogen donor ligands have been used to mimic biological systems such as vitamin B-12 coenzyme.[1] They are also of interest in the context of dioxygen activation at transition metals.[2] Recently they have attracted attention as precatalysts for olefin polymerisation.[3] Typically, the precatalysts are the cobalt(II) chloride complexes of diiminepyridine (dip) ligands (see Figure 1). Structural characterisation of these complexes requires X-ray analysis because the paramagnetic Co^{II} centre complicates NMR studies. In the hope of obtaining some insight into the optimal coordination geometries for olefin polymerisation, we decided to study a range of flexible pyridine/amine complexes and compare these with the more rigid dip complexes. The ligands are of the picolylamine type and are multidentate, with amine (N_{am}) and pyridine (N_{py}) nitrogens (Figure 1).[4]

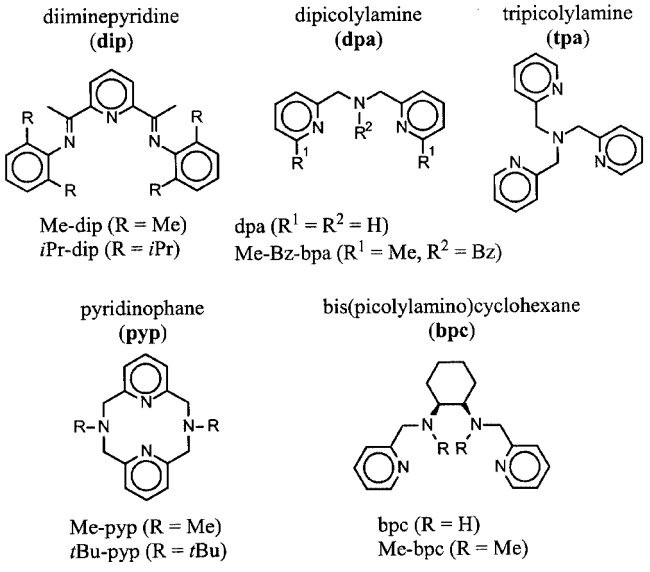

Figure 1. Pyridine/amine ligands used in this work; the dip ligand has been included for comparison

For polymerisation the two chlorides must be converted into an alkyl chain and a vacant coordination site *cis* to it. In five-coordinate complexes of dpa-type N_3 ligands, the small bite angles of the two five-membered chelate rings should disfavour equatorial coordination of all three nitrogens in a trigonal-bipyramidal coordination geometry; this leaves the *fac* and *mer* arrangements shown in Figure 2, both of which have a *cis* orientation of the remaining coordination sites (for the more rigid dip ligands, only the *mer* arrangement is accessible). Of the N_4 ligands, pyp is the least flexible one. In practice, it strongly prefers a *cis*-octahedral coordination geometry (Figure 2),[5] although other arrangements have been observed.[6,7] Six-coordinate complexes of tpa will also have a *cis*-octahedral structure; in addition, this ligands supports five-coordination, usually with an apical N_{am} donor (Figure 2). Finally, bpc-type ligands have been observed in three distinct coordination geometries shown in Figure 2: planar ("N4"), symmetric *cis*-octahedral ("N2/N2") and asymmetric *cis*-octahedral ("N3/N"). The different coordination geometries possible for the N_3 and N_4 donors also result in different patterns of N_{am} and N_{py} donors *trans* to the two sites potentially involved in polymerisation.

Results and Discussion

Synthesis

The N_3 and N_4 ligands used have all been reported previously.[8] Their $CoCl_2$ complexes were easily obtained by reaction with $CoCl_2 \cdot 6H_2O$ in the appropriate solvent.

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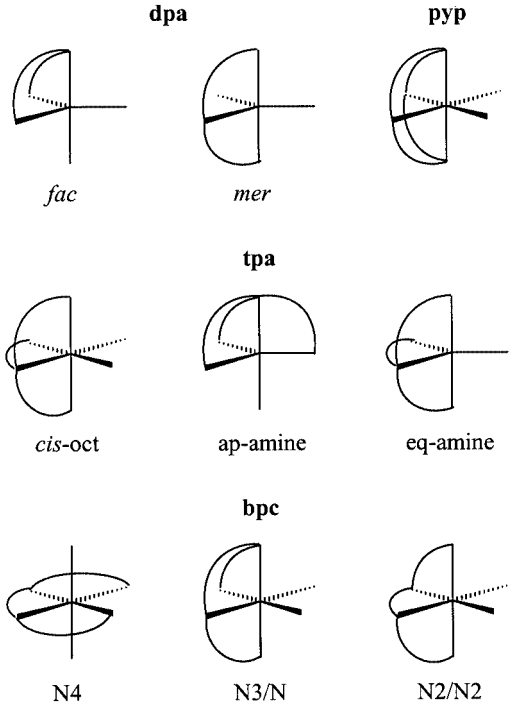


Figure 2. Coordination geometries of N_3 and N_4 ligands

Whereas most of the complexes are air stable, [(bpc)$CoCl_2$] (**5**) proved very sensitive to air and water. This complex was therefore synthesised by reaction of the ligand with dry $CoCl_2$ in anhydrous acetonitrile. The related complex [(Me-bpc)$CoCl_2$] (**6**) decomposes only very slowly in the presence of air and water.

Crystal Structures of N_4-Ligand Complexes

[(tpa)CoCl]$_2$$CoCl_4$

We expected to prepare an octahedral complex from tpa and $CoCl_2 \cdot 6H_2O$. However, X-ray analysis showed that the five-coordinate cation [(tpa)CoCl]$^+$ (**1**$^+$) had formed (Figure 3), with $CoCl_4^{2-}$ as the counterion. The unit cell contains two crystallographically independent cations **1**$^+$. Each of these has an almost C_3-symmetric trigonal-bipyramidal coordination geometry with N_{am} and Cl^- at the two axial positions. The Co^{II} centre is displaced approximately 0.5 Å from the equatorial N_3 plane in the direction of the chloride.

The structure of **1**$^+$ is very similar to that of the dicationic complex [(tpa)Co(MeCN)]$^{2+}$ (**2**) reported by Karlin.[9] The Co−N_{py} distances of **1**$^+$ and **2**$^{2+}$ are identical within experimental error. The Co−N_{am} distance for **1**$^+$ is longer than that for **2**$^{2+}$, as expected on the basis of the larger *trans*-influence of Cl^- compared to acetonitrile.

The structures of [(*t*Bu-pyp)$CoCl_2$] (**3**)[5d] and [(Me-pyp)-$CoCl_2$] (**4**)[5a] have been reported before. Both have a *cis*-octahedral coordination; the steric bulk of the *t*Bu substituents in **3** forces the ligand to twist, lowering the symmetry from C_{2v} (as observed in **4**) to C_2.

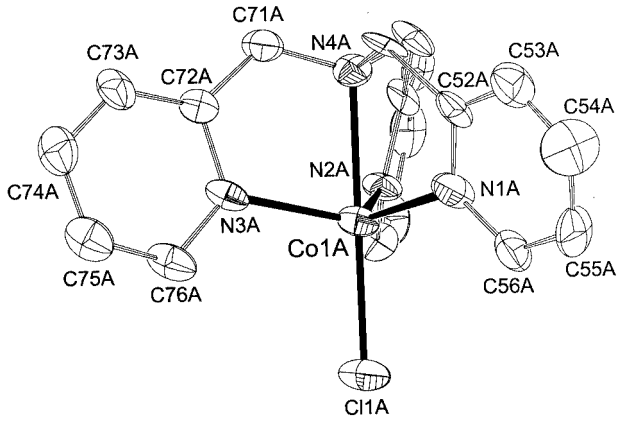


Figure 3. X-ray structure of one of the two independent cations **1**$^+$; selected bond lengths [Å] and angles [°]: Co1A−N1A 2.028(15), Co1A−N2A 2.038(14), Co1A−N3A 2.055(14), Co1A−N4A 2.240(14), Co1A−Cl1A 2.284(5), N1A−Co1A−N4A 76.3(6), N2A−Co1A−N4A 78.8(5), N3A−Co1A−N4A 76.7(5); corresponding values for the second cation: Co1B−N1B 2.072(15), Co1B−N2B 2.075(16), Co1B−N3B 2.055(14), Co1B−N4B 2.229(15), Co1B−Cl1B 2.280(6), N1B−Co1B−N4B 77.9(6), N2B−Co1B−N4B 76.2(6), N3B−Co1B−N4B 77.1(5); corresponding values for [(tpa)Co(MeCN)]$^{2+}$ (ref.[9]): Co−N1 2.041(3), Co−N2 2.037(3), Co−N3 2.053(3), Co−N4 2.177(3), Co−N5 2.046(3), N1−Co−N4 79.1(1), N2−Co−N4 78.9(1), N3−Co−N4 78.7(1)

[(bpc)$CoCl_2$] (5) and [(Me-bpc)$CoCl_2$] (6)

Both bpc complexes adopt a C_2-symmetric, *cis*-octahedral N2/N2 geometry (Figure 4). These two are the first examples of bis(picolylamino)ethylenediamine $CoCl_2$ complexes to be characterised by an X-ray structure determination. The structure of [(bpc)$CrCl_2$]$^+$ (an analogue of **5**) has been reported.[10] In addition, several metal dichloride com-

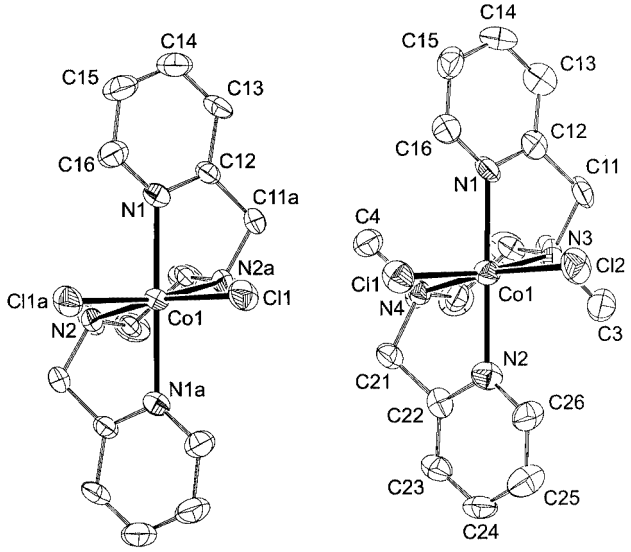
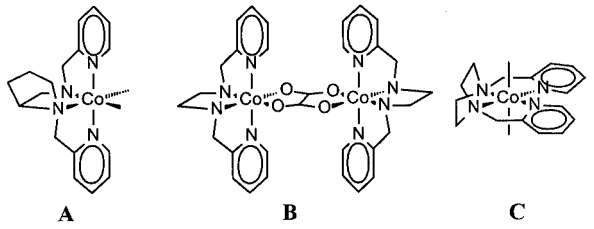


Figure 4. X-ray structures of **5** and **6**; selected bond lengths [Å] and angles [°] for **5**: Co1−N1 2.187(4), Co1−N2 2.205(4), Co1−Cl1 2.4187(14), N1−Co1−N1a 170.1(2), N2−Co1−N2a 79.8(2), Cl1−Co1−Cl1a 98.24(8) (atoms labeled a symmetry-related by $-x$, y, 1/2 − z); corresponding values for **6**: Co−N1 2.147(8), Co−N2 2.134(9), Co−N3 2.255(9), Co−N4 2.236(7), Co−Cl1 2.436(3), Co−Cl2 2.435(3), N1−Co−N2 173.1(4), N3−Co−N4 78.7(3), Cl1−Co−Cl2 98.24(13)

plexes of bis(picolylamino)ethylenediamine ligands lacking the cyclohexane ring have been structurally characterised.[11] A number of bpc and Me-bpc complexes of cobalt with counterions other than chloride have also been reported; all of these contain Co^{III}. Remarkably, all previously reported bpc cobalt complexes have the N3/N coordination geometry,[12] whereas the three Me-bpc cobalt complexes reported so far all have the N2/N2 arrangement.[13] Considering the wider class of bis(picolyl)ethylenediamine cobalt complexes, there are only a few examples of the N2/N2 arrangement: these include the more highly substituted system **A**[14] and the atypical, oxalato-bridged dimer **B**.[15]



Judging from these examples, the N3/N arrangement is preferred over N2/N2 by only a small margin; substituents at the backbone may cause increased steric hindrance at the "planar" N_{am} and so promote the more extensive folding of the N2/N2 geometry. The N2/N2 geometry found in the oxalato-bridged dimer might be caused by steric hindrance between the monomer units in the N3/N geometry. Finally, only a single example of the N4 arrangement has ever been reported,[16] and in that case (**C**, above) the geometry is probably enforced by the rigid ligand backbone.

Returning to our $CoCl_2$ complexes, it seems remarkable that even bpc adopts the N2/N2 structure here. We believe that the larger size of Co^{II} (compared to Co^{III}) disfavours formation of the N3/N structure and hence is responsible for shifting the balance towards N2/N2.

In contrast to **3**, where the two enantiomeric conformations of the ligand are only slightly different and will interconvert in solution, the chiral geometry in **5** and **6** is locked through the coordination of the two pyridyl groups. On going from **5** to **6**, the introduction of the N_{am} methyl substituent results in a longer $Co-N_{am}$ distance, which is compensated for by a strengthening of the $Co-N_{py}$ interaction. In addition, the two pyridyl fragments become more nearly orthogonal (angle between planes: 121° and 104°, respectively). The rather similar Co−Cl distances in complexes **3**−**6** indicate that the *trans*-influence of N_{am} and N_{py} on the chlorides is similar.

Crystal Structures of N_3-Ligand Complexes

[(Me−Bz−dpa)$CoCl_2$] (7)

Complex **7** (Figure 5) has a pseudo trigonal-bipyramidal coordination geometry, with the two axial positions occupied by the two N_{py} atoms. The rather similar crystal structure of [(Me-dpa)$NiBr_2$] has previously been reported.[17]

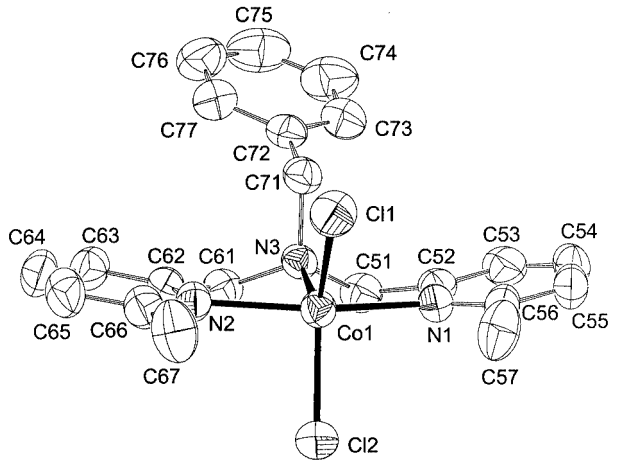


Figure 5. X-ray structure of **7**; selected bond lengths [Å] and angles [°]: Co−N1 2.178(2), Co−N2 2.182(2), Co−N3 2.124(2), Co−Cl1 2.2999(9), Co−Cl2 2.2784(9), N1−Co−N2 157.98(10), N3−Co−Cl1 111.33(6), N3−Co−Cl2 114.24(6), Cl1−Co−Cl2 134.41(4); corresponding values for (Me-dpa)$NiBr_2$ (ref.[17]): Ni−N1 2.042(10), Ni−N2 2.050(11), Ni−N3 2.007(14), Ni−Br1 2.473(3), Ni−Br2 2.494(3), N1−Ni−N2 163.6(5), N3−Ni−Br1 112.1(6), N3−Ni−Br2 98.7(5), Br1−Ni−Br2 149.2(1)

[(Me-dip)$CoCl_2$] (8)

Complex **8** (Figure 6) has a trigonal-bipyramidal geometry in the solid state, like its Fe analogue[18] and dpa complex **7**. In contrast, the $CoCl_2$ and $FeCl_2$ complexes of the isopropyl-substituted dip ligand have structures which are more nearly square pyramidal.[19] Apparently, the bulkier aryl groups promote this kind of distortion; a similar effect has been observed in a series of β-diiminate complexes.[20] In both dpa and dip complexes, the equatorial nitrogen is closer to the metal centre than the axial nitrogens. This effect is most pronounced for the dip complex, possibly due to geometric constraints of the ligand backbone.

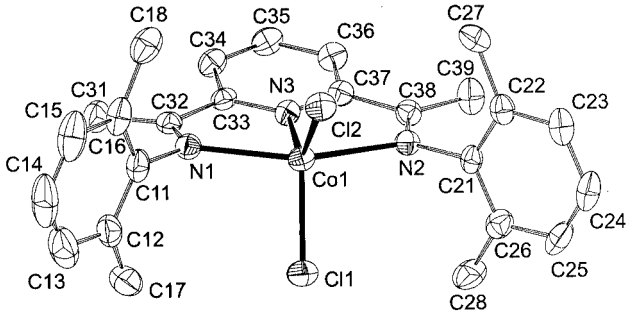


Figure 6. X-ray structure of **8**; selected bond lengths [Å] and angles [°]: Co−N1 2.247(2), Co−N2 2.265(2), Co−N3 2.0371(19), Co−Cl1 2.2578(7), Co−Cl2 2.2730(7), N1−Co−N2 150.42(7), N3−Co−Cl1 119.90(6), N3−Co−Cl2 127.14(6), Cl1−Co−Cl2 112.92(3); corresponding values for Fe analogue (ref.[18]): Fe−N1 2.271(6), Fe−N2 2.266(5), Fe−N3 2.110(6), Fe−Cl1 2.312(2), Fe−Cl2 2.278(2), N1−Fe−N2 145.5(2), N3−Fe−Cl1 118.9(2), N3−Fe−Cl2 131.3(2), Cl1−Fe−Cl2 109.9(1)

Five versus Six Coordination

The present work shows examples of both five- and six-coordinate structures. It seems that the ligand has a large influence on the preference for five- or six-coordination. The N_3 donor complexes **7** and **8** are naturally five-coordinate, but even the cobalt chloride complex of tpa prefers an ionic five-coordinate structure ($\mathbf{1}^+$). Five-coordination must be very favourable over six-coordination here (compared to pyp and bpc ligands) since even if a large excess of ligand is used, one-third of the cobalt is found as the counterion $[CoCl_4]^{2-}$ and free ligand remains. When NH_4PF_6 is then added to the reaction mixture, all cobalt is complexed by the ligand and the (presumably also five-coordinate) complex [**1**]PF_6 can be isolated. The other N_4 complexes all seem to prefer six-coordinate structures, although for complex **6** five-coordination in solution cannot be completely ruled out (see NMR section below). For **4** the coordination behaviour in solution has been described in the literature.[5a] Conductivity studies performed by Krüger showed that one chloride is exchanged for a coordinated solvent molecule in methanol, but only partial dissociation of one chloride takes place in acetonitrile. Although acetonitrile is generally considered to be a better ligand than methanol, methanol is very well suited for the solvation of chloride anions. This may be the driving force in the dissociation of chloride from **4**. The NMR spectrum of **3** shows a similar solvent dependence and suggests that this complex can also undergo chloride substitution in methanol. Clearly, complexes of pyp and bpc prefer six-coordination, although a chloride can sometimes be displaced by a polar solvent molecule. It is possible that five-coordination only occurs when the ligand can easily accommodate a trigonal-bipyramidal arrangement.

EPR Measurements

Six-coordinate [(*t*Bu-pyp)$CoCl_2$] (**3**) and five-coordinate [(Me-Bz-dpa)$CoCl_2$] (**7**) both have very broad X-band EPR spectra in the range $g = 2-6$, characteristic of high-spin ($S = 3/2$) cobalt(II) species with a large zero-field splitting ($D >> h\nu$). The EPR spectrum of **3** is shown in Figure 7.

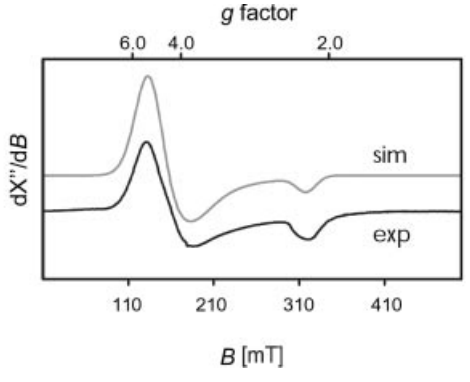


Figure 7. Experimental and simulated X-band EPR spectrum of **3**; experimental spectra in acetone/MeOH (2:3) at 6 K, 9.64 GHz. (attn. 55 dB, mod. 10 G)

Complex **3** reveals a nearly axial spectrum with no resolved hyperfine couplings, whereas the spectrum of **7** is rhombic and reveals hyperfine coupling with the cobalt nucleus at one of the *g*-tensors (Co, $I = 7/2$, 102 G). The apparent symmetry from the EPR spectra seems to correlate well with the cobalt coordination environments seen in the X-ray structures. The approximate real g values and *E*/*D* rhombicity factors derived from simulation of the experimental EPR spectra are $g_{11} = 2.17$, $g_{22} = g_{33} = 2.30$, $E/D = 0$ for complex **3** and $g_{11} = 2.03$, $g_{22} = 2.05$, $g_{33} = 2.20$, $E/D = 0.17$ for complex **7**. Apart from establishing the spin-state ($S = 3/2$) and the apparent coordination environment symmetry, these very broad EPR spectra are not very informative.

NMR Analysis

A complete interpretation of the paramagnetic ^1H NMR spectrum of $[(tpa)Co(CH_3CN)]^{2+}$ is presented in the report of Karlin,[9] and this helped us to assign all the peaks in the spectrum of $[(tpa)CoCl]^+$ ($\mathbf{1}^+$) on the basis of peak positions, linewidths and integrals. The signals from pyridine-H3, -H4, and -H5 are distinctly sharper than those of pyridine-H6 and the methylene protons. This seems to be the case for most pyridine-amine cobalt complexes studied here. Because the NMR shifts of [**1**]PF_6 and [**1**]$_2CoCl_4$ are identical, the same trigonal bipyramidal structure is assumed for both. Unfortunately, we did not succeed in growing X-ray quality crystals of [(dpa)$CoCl_2$] (**9**). However, its spectrum shows enough of a similarity to that of $[(tpa)CoCl]^+$ to allow a complete interpretation. For (Me−Bz−dpa)$CoCl_2$ (**7**), however, the extra signals from the benzyl substituent complicate the NMR spectrum too much to allow unambiguous assignments. Also, we observed no signals for the pyridine-H3 and -H5 protons between $\delta = 40$ and 60 ppm, although this is the most consistent feature of our NMR spectra. Since paramagnetic spectra are very sensitive to the environment at the metal centre, the large differences between the spectra of **7** and **9** may mean that these complexes do not have the same geometry. One possibility would be a switch to *fac* coordination of the dpa ligand in **9**. This would be inconsistent with the *decreased* tendency towards folding of bpc over Me-bpc discussed earlier. However, the two dpa complexes of Co that have been structurally characterised both have *fac*-coordinated dpa ligands.[21]

The ^1H NMR spectrum of [(bpc)$CoCl_2$] (**5**) could not be fully assigned, because all signals (apart from the NH) have approximately the same intensity and no distinct pattern could be discovered. The number of signals, however, agrees with the symmetrical structure observed in the solid state. [(Me-bpc)$CoCl_2$] (**6**) was never obtained as a single compound. A mixture of two products in a ratio of 10:6 or 10:4 was formed in the reaction of the ligand with $CoCl_2$ in CH_2Cl_2 and CH_3CN, respectively. ^1H NMR spectroscopy shows that *both* products produce twelve paramagnetic signals, the number expected for a symmetrically coordinated ligand (i.e. N4 or N2/N2, but *not* N3/N). Slow evaporation of an NMR sample resulted in crystallisation of one of the

products. This is probably the major product of the reaction, because both the crystal structure and the NMR spectrum resemble those of **5**, while the spectrum of the minor product shows no obvious similarities to that of **5**. Since the minor product also has a symmetrical ligand, one possibility would be the N4 structure, although this seems unlikely given that Co^{II} should have an even larger aversion to this arrangement than Co^{III}. Another possibility is that it is a cationic five-coordinate complex like $[(tpa)CoCl]^+$. A distinction between these two possibilities cannot be made at this stage. We were not able to obtain a ^{13}C NMR spectrum for any of the paramagnetic complexes.

Ethene Polymerisation

All the complexes except **8** were tested for polymerisation activity by treating them with 100 equivalents of MAO in chlorobenzene under an ethene atmosphere (7 and 35 bar). Most complexes did not exhibit any polymerisation activity at all, but pyp complexes **3** and **4** produced some polymer. The *tert*-butyl-substituted complex was particularly interesting as it remained active for a very long time (35 hours), resulting in an activity of 70 $g \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$. This is a factor of 7000 less than the reported cobalt-dip system under optimised conditions.[3a,3b] GPC analysis of the polymer formed at 35 bar showed that, besides a small amount of high molecular weight polyethene, the bulk of the "polymer" had a molecular weight of approximately 1000. It was difficult to optimise the pyp system because the complex seemed to decompose when a fresh batch of MAO was used for the polymerisation experiments.

It has been suggested that the dip-cobalt and -iron complexes used by Brookhart and Gibson polymerise ethene to high molecular weight polyethene because the large aryl substituents prevent associative displacement of the growing polymer chain. $[(Me\text{-}Bz\text{-}dpa)CoCl_2]$ (**7**) has nearly the same cobalt environment as precatalyst **8**, but lacks the steric bulk above and below the active site on cobalt. Indeed, **7** is not active in ethene polymerisation (nor is **9**). If this were caused by rapid chain transfer, formation of dimers would be expected. The fact that no ethene consumption was observed indicates that the lack of steric bulk is not the only obstruction for the reactivity of our N_3 complexes. Rather, it seems likely that the electronic properties of the ligand are also important. For example, $[(dip)CoCl_2]$ is apparently activated by reduction to a low-spin Co^{I} species, although the nature of the actual active species is still unclear.[22] Our pyridine-amine ligands are much weaker π-acceptors than dip ligands and are unlikely to stabilize the Co^{I} oxidation state, let alone induce the switch to a low-spin configuration. The main problem here is could be the *formation* of the active species, rather than the activity it would have once formed.

Conclusions

Analytically pure paramagnetic cobalt(II) complexes were easily synthesised by the reaction of $Co^{II}Cl_2$ with the appropriate N_3 or N_4 ligand. Most complexes are air-stable for at least a couple of days. Different modes of coordination became apparent from the obtained crystal structures. These were correlated with the ^1H NMR spectra of the complexes and helped in their interpretation. Variation of the solvent in the NMR experiments was informative for the behaviour in solution of the pyp complexes. The pyp ligands seemed to promote six-coordination, since even when a chloride dissociates in solution, a solvent molecule occupies the free coordination site. In contrast, tpa appears to favour five-coordination. The bpc complexes **5** and **6** are both six-coordinate in the solid state, but for **6** formation of a five-coordinate complex in solution cannot be excluded. Only two of the pyridine/amine complexes prepared (**3** and **4**) showed (low) activity in ethene polymerisation.

Experimental Section

General: All procedures were carried out under N_2 using standard Schlenk techniques unless specified otherwise. Acetonitrile, THF, dichloromethane and diethyl ether were distilled under nitrogen. Ethanol and methanol were deoxygenated by bubbling a stream of N_2 through the solvent for 15 minutes. For the synthesis of **5** and **6**, $CoCl_2 \cdot 6H_2O$ was dried for 4 hours at 150 °C before use. Ligands were prepared according to literature procedures.[8] All other chemicals are commercially available and were used without further purification. NMR measurements were performed on Bruker DPX200, AMX400, and AMX500 spectrometers. X-band EPR spectra were recorded on a Bruker ER 220 spectrometer. Samples were measured in acetone/MeOH (2:3) at 6−10 K. Simulations were performed with the program WEPR (F. Neese, University of Konstanz). Chemical shifts are listed in ppm with TMS as external reference (δ = 0 ppm). NMR signals for the NH protons of paramagnetic complexes were never observed. FAB^+- and ESI^+-MS spectra were recorded on a Finnigan MAT 900XL instrument.

$[(tpa)CoCl]_2[CoCl_4]$ ($[1]_2[CoCl_4]$): $CoCl_2 \cdot 6H_2O$ (205 mg, 0.86 mmol) was added to a solution of tpa (248 mg, 0.86 mmol; 1.0 equiv.) in 20 mL of ethanol. A blue solid precipitated almost immediately. After stirring for 1 hour at room temperature, the mixture was filtered. The solid was washed with diethyl ether and dried in vacuo; yield 0.19 g (66%). Crystals suitable for X-ray diffraction were grown by vapour diffusion of THF into a saturated acetonitrile solution. The blue product is air-stable as a solid and in solution. $C_{36}H_{36}Cl_6Co_3N_8$ (970.25): calcd C 44.56, H 3.74, N 11.55; found C 44.41, H 3.79, N 11.47. ^1H NMR (200 MHz, 298 K, ppm) CD_3OD: δ = 130.1 (3 H, py-*H6*), 108.0 (6 H, NCH_2), 58.2 (3 H, py-*H5*), 49.2 (3 H, py-*H3*), −1.7 (3 H, py-*H4*). CD_3CN: δ = 134.3 (3 H, py-*H6*), 107.3 (6 H, NCH_2), 60.8 (3 H, py-*H5*), 46.2 (3 H, py-*H3*), −3.5 (3 H, py-*H4*). FAB-MS: *m/z* = 803 $[(tpa)_2Co_2Cl_3]^+$, 384 $[M]^+$, 349 $[M - Cl]^+$, 291 $[M - CH_3Py]^+$, 256 $[M - Cl, - CH_3Py]^+$. ESI-MS: *m/z* = 384 $[M]^+$, 349 $[M - Cl]^+$.

$[(tpa)CoCl]PF_6$ ($[1]PF_6$): $CoCl_2 \cdot 6H_2O$ (330 mg, 1.39 mmol) was added to a solution of tpa (424 mg, 1.46 mmol; 1.05 equiv) in 25 mL of methanol. After addition of NH_4PF_6 (1.2 g, 7.2 mmol, 5.2 equiv.) a green microcrystalline solid precipitated. This solid was filtered off, washed three times with diethyl ether and dried under vacuum; yield 676 mg (92%). The product is air-stable as a solid and in solution. $C_{18}H_{18}ClCoF_6N_4P$ (529.72): calcd C 40.81, H 3.43, N 10.58; found C 40.64, H 3.42, N 10.44. ^1H NMR (200 MHz, 298 K, ppm): CD_3OD δ = 129.8 (3 H, py-*H6*), 107.6 (6 H, NCH_2),

57.91 (3 H, py-*H5*), 49.1 (3 H, py-*H3*), −1.44 (3 H, py-*H4*). CD_3CN: δ = 134.4 (3 H, py-*H6*), 107.1 (6 H, NCH_2), 60.8 (3 H, py-*H5*), 46.2 (3 H, py-*H3*), −3.6 (3 H, py-*H4*).

[(*t*Bu-pyp)$CoCl_2$] (3):[5d] $CoCl_2·6H_2O$ (172 mg, 0.72 mmol) was added to a warm solution (40 °C) of *t*Bu-pyp (256 mg, 0.72 mmol; 1.00 equiv.) in 35 mL of THF. After refluxing for 30 min a light-blue solid precipitated. The mixture was cooled to room temperature and filtered. The residue was washed twice with small portions of THF and dried under vacuum; yield 275 mg (79%). $C_{22}H_{32}Cl_2CoN_4$ (483.26): calcd C 54.78, H 6.69, N 11.62; found C 54.66, H 7.78, N 11.55. ^{1}H NMR (200 MHz, 298 K, ppm) CD_2Cl_2: δ = 81.4 (4 H, py-*H3*), 26.2 (2 H, py-*H4*), 3.1 (?), −9.4 (4 H, NCH_2), −35.8 (4 H, NCH_2), −43.5, −76.3 (*t*Bu?). CD_3OD: δ = 73.8 (4 H, py-*H3*), 28.3 (4 H, NCH_2), 18.8 (2 H, py-*H4*), −4.7 (4 H, NCH_2), −38.6 (*t*Bu). FAB-MS: *m*/*z* = 446 [M − Cl]$^+$, 411 [M − 2Cl]$^+$, 353 [M − 2Cl, − *t*BuH]$^+$.

[(Me-pyp)$CoCl_2$]·H_2O (4·H_2O): This compound was synthesised according to a literature procedure.[5a] ^{1}H NMR (200 MHz, 298 K, ppm) CD_2Cl_2: δ = 48.0 (4 H, NCH_2), 46.4 (4 H, py-*H3*), 24.0 (6 H, NCH_3), 14.2 (4 H, NCH_2), 7.2 (2 H, py-*H4*). CD_3OD: δ = 117.7 (6 H, NCH_3), 88.8 (4 H, NCH_2), 46.9 (4 H, py-*H3*), 31.5 (4 H, NCH_2).

[(bpc)$CoCl_2$] (5): A solution of dried $CoCl_2$ (106 mg, 0.82 mmol) in 10 mL of CH_3CN was added to a solution of bpc (239 mg, 0.81 mmol; 0.99 equiv.) in 7 mL of CH_3CN. The mixture immediately turned bright red. Evaporation of the solvent yielded a bright pink compound, which was washed twice with THF and dried under vacuum; yield 237 mg (68%). Single crystals suitable for X-ray diffraction were grown from a saturated CD_3CN solution. The product is highly air-sensitive as a solid and in solution. ^{1}H NMR (200 MHz, CD_3CN, 298 K, ppm): δ = 195.1 (2 H), 88.9 (2 H), 52.4 (2 H), 26.0 (2 H), 22.0 (4 H), 16.2 (2 H), 9.2 (2 H), 5.6 (2 H), 4.2 (2 H), 0.4 (2 H).

[(Me-bpc)$CoCl_2$] (6): Dried $CoCl_2$ (115 mg, 0.88 mmol) was added to a solution of Me-bpc (296 mg, 0.91 mmol; 1.03 equiv.) in 12 mL of CH_3CN. A purple solid precipitated immediately. After 2 hours the mixture was filtered and the dark pink residue was dried in vacuo; yield 244 mg (61%). Additional product precipitated from the mother liquor on standing at −20 °C. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CD_2Cl_2 solution. The product is air-stable as a solid and in solution, although it is very poorly soluble in most organic solvents. $C_{20}H_{28}Cl_2CoN_4$ (454.31): calcd C 52.88, H 6.21, N 12.33; found C 51.66, H 6.22, N 12.00. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K, ppm): δ = 164.9 (2H), 104.3 (2H), 102.6 (1.2 H), 89.4 (1.2 H), 83.0 (3.6 H, NCH_3), 61.1 (6 H, NCH_3), 51.8 (2 H), 47.5 (1.2 H), 29.7 (1.2 H), 24.7 (1.2 H), 24.4 (1.2 H), 23.9 (2H), 21.8 (0.8 H), 21.1 (2 H), 20.5 (2 H), 18.6 (2 H), 17.4 (1.2 H), 15.9 (1.2 H), 9.3 (1.2 H), 8.1 (2 H), 6.6 (2 H), 5.8 (2 H), 3.3 (1.2 H), −16.93 (2 H). FAB-MS: *m*/*z* = 418 [M − Cl]$^+$, 383 [M − 2Cl]$^+$.

[(Me-Bz-dpa)$CoCl_2$] (7): A solution of $CoCl_2·6H_2O$ (88 mg, 0.37 mmol) in 10 mL of acetonitrile was added to a solution of Me-Bz-dpa (111 mg, 0.35 mmol; 0.95 equiv.) in 5 mL of acetonitrile. The colour of the mixture immediately changed to blue/purple. After stirring for 7 hours at room temperature the volume was reduced by half under reduced pressure and a purple precipitate formed. The solid was collected by filtration, washed three times with diethyl ether and dried under vacuum; yield 85 mg (54%). The purple product is air-stable as a solid and in solution. Crystals of **7** suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution. **7**·CH_3CN, $C_{23}H_{26}Cl_2CoN_4$ (488.32): calcd C 56.57, H 5.37, N 11.47; found C 56.48, H 5.32, N 11.41. ^{1}H NMR (200 MHz, CD_3CN, 298 K, ppm): δ = 152.0 (2 H), 28.0 (2H), 15.6 (2 H), 14.6 (2 H), 14.2 (2 H), 12.1 (2 H), 7.7 (1 H, bz-*p*), −12.0 (2 H), −61.1 (6 H, py-CH_3). FAB-MS: *m*/*z* = 446 [M]$^+$, 411 [M − Cl]$^+$.

[(Me-dip)$CoCl_2$] (8):[3a] Me-dip (564 mg, 1.53 mmol) and $CoCl_2·6H_2O$ (363 mg, 1.53 mmol, 1.00 equiv.) were dissolved in 40 mL of THF. A colour change could be observed almost immediately and a green solid precipitated. After stirring for an additional hour at room temperature, this solid was filtered off, washed with THF (2×) and hexane (2×), and recrystallised from a layered methanol/hexane (1:1) solution, giving 266 mg (0.53 mmol, 35%) of the product as green air-stable crystals. ^{1}H NMR (200 MHz, 298 K, ppm) CD_2Cl_2: δ = 112.0 (2 H, py-*H3*), 36.1 (1 H, py-*H4*), 6.1 (4 H, Ar-*Hm*), −1.2 (6 H, N=C*Me*), −12.1 (2 H, Ar-*Hp*), −28.2 (12 H, Ar-*Me*). CD_3OD: δ = 111.9 (2 H, py-*H3*), 36.2 (1 H, py-*H4*), 6.2 (4 H, Ar-*Hm*), −1.1 (6 H, N=C*Me*), −12.0 (2 H, Ar-*Hp*), −28.1 (12 H, Ar-*Me*). FAB-MS: *m*/*z* = 463 [M − Cl]$^+$.

[(dpa)$CoCl_2$] (9): A solution of $CoCl_2·6H_2O$ (136 mg, 0.57 mmol) in 5 mL of ethanol was added to a solution of dpa (102 mg, 0.52 mmol; 0.91 equiv.) in 5 mL of ethanol. The colour of the mixture changed from light purple to dark-blue after stirring for 5 minutes at room temperature. After stirring for 16 hours at room temperature, the product was precipitated by adding diethyl ether. The mixture was filtered and the residue washed with diethyl ether and dried in vacuo; yield 73 mg (42%). The purple product is air-stable as a solid, however it decomposed in solution after being exposed to air for one day. ^{1}H NMR (200 MHz, 298 K, ppm) CD_3CN: δ = 126.1 (2 H, py-*H6*), 120.8 (2 H, NCH_2), 113.5 (2 H, NCH_2), 55.9 (2 H, py-*H5*), 44.0 (2 H, py-*H3*), −1.1 (2 H, py-*H4*). CD_2Cl_2: δ = 127.0 (2 H, py-*H6*), 113.6 (2 H, NCH_2), 110.3 (2 H, NCH_2), 55.7 (2 H, py-*H5*), 44.6 (2 H, py-*H3*), −0.80 (2 H, py-*H4*). $CDCl_3$: δ = 126.4 (2 H, py-*H6*), 112.9 (4 H, NCH_2), 55.1 (2 H, py-*H5*), 45.2 (2 H, py-*H3*), −0.7 (2 H, py-*H4*). FAB-MS: *m*/*z* = 293 [M − Cl]$^+$, 258 [M − 2Cl]$^+$.

Polymerisation Experiments: Chlorobenzene was distilled from a small amount of sodium. MAO was purchased as a solution in toluene (4.96% Al) and used as such. Polymerisation reactions under 7 bar of ethene were performed in a glass autoclave; reactions under 35 bar of ethene were done in a steel vessel (Hastelloy C).

A suspension of 33 μmol of the precatalyst in 10 mL of chlorobenzene was transferred under nitrogen into a 100 mL autoclave. Under nitrogen-flow 2 mL of MAO (100 equiv.) was transferred into a steel tube connected to the top of the pressure vessel. The complete system was put under ethylene pressure (7 or 35 bar), the MAO was added to the reaction mixture and the autoclave was closed. When ethylene consumption had stopped, or after about 6 hours if no reaction was observed, the autoclave was opened and the reaction mixture was neutralised by adding a mixture of methanol and aqueous HCl (5:1). The mixture was filtered and the polyethylene − if formed − was washed several times with methanol and dried under vacuum.

X-ray Structure Determinations: Single crystals were mounted in air on glass fibres. Intensity data were collected at room temperature on an Enraf−Nonius CAD4 diffractometer. Unit cell dimensions were determined from the angular setting of a limited number of reference reflections. Intensity data were corrected for Lorentz and polarisation effects, and for absorption using a semi-empirical ψ-scan correction.[23] Structures were solved by the program system DIRDIF[24] using the program PATTY[25] to locate all non-hydrogen atoms and refined with standard methods (refinement against

F^2 of all reflections) using SHELXL-97.[26] All non-hydrogen atoms were refined anisotropically; hydrogens were placed at calculated positions and refined isotropically in a riding mode, unless otherwise noted. Geometrical calculations (PLATON[27]) revealed neither unusual geometric features, nor unusual short intermolecular contacts, no higher symmetry and no (further) solvent-accessible areas. Details of the data collection and structure determinations are collected in Table 1.

CCDC-186122−186127 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Notes on Individual Structures

[1]$_2$[CoCl$_4$]: One molecule of water and one molecule of acetonitrile were located and refined (hydrogen atoms for the water molecule were not included in the refinement). Hydrogen atoms were placed at calculated positions and were subsequently refined freely. Some anisotropic thermal displacement parameters showed physically unacceptable values when determined using default least-squares refinement parameters. The SQUEEZE procedure[27] was used to account for the residual electron density in a solvent area of 50 Å^3, resulting in a total electron count for this void of 44 electrons in the unit cell. This electron density should probably also be attributed to water molecules. Next the DIFABS procedure[28] was used, lowering the anisotropic *R*-value from 8.3% to 7.9%, resulting in considerably improved anisotropic thermal displacement parameters. The DELU and SIMU options still had to be applied to all atoms, however, and the ISOR option specifically to N2A, C51A, C55A, C62A, C51B, C65B, C72B, C76B, and O1.

5: One molecule of acetonitrile was located and refined. The refinement was hampered by the severe deterioration of the crystal during the data collection. A correction of almost 50% for crystal decay was necessary during the data reduction process.

6: One molecule of water was located and refined; hydrogen atoms for this water molecule were not included in the refinement. Based solely on donor-acceptor distances hydrogen bonds could probably be formed between O1 and Cl1 and between O1 and Cl2.

Table 1. Details of crystal structure determinations

Compound	[**1**]$_2$[CoCl$_4$]	**5**	**6**	**7**	**8**
Crystal colour	dark green	transparent red-brown	transparent purple-red	purple	green
Crystal shape	regular fragment	very irregular fragment	rather regular fragment	regular fragment	small, regular fragment
Crystal size [mm	0.24×0.18×0.15	0.52×0.48×0.28	0.29×0.17×0.10	0.42×0.24×0.12	0.13×0.11×0.08
Empirical formula	$C_{19}H_{20.5}Cl_3Co_{1.5}N_{4.5}O_{0.5}$	$C_{22}H_{30}Cl_2CoN_6$	$C_{20}H_{30}Cl_2CoN_4O$	$C_{23}H_{26}Cl_2CoN_4$	$C_{26}H_{31}Cl_2CoN_3O$
Molecular weight	514.64	508.35	472.31	488.31	531.37
Temperature [K]	293(2)	298(2)	293(2)	293(2)	150(2)
Crystal system, space group	Monoclinic, *Cc*	Monoclinic, *C*2/*c*	Orthorhombic, *Pna*2$_1$	Monoclinic, *P*2$_1$/*c*	Monoclinic, *P*2$_1$/*n*
Unit cell det. #, θ range	15, 6.504···11.817	25, 19.293···22.715	25, 11.961···14.468	25, 10.488···20.064	13258, 1.830···25.350
a [Å]	12.095(3)	12.9525(6)	16.3169(11)	8.9564(12)	14.1667(12)
b [Å]	27.587(9)	12.1804(10)	14.7110(10)	20.817(5)	14.6541(8)
c [Å]	14.074(3)	16.3098(10)	8.8110(6)	13.1776(19)	13.1684(11)
α [°]	90	90	90	90	90
β [°]	93.967(17)	103.698(4)	90	106.227(10)	109.558(4)
γ [°]	90	90	90	90	90
Volume [Å^3]	4685(2)	2499.9(3)	2115.0(2)	2359.0(7)	2576.0(3)
Z, d_{calc} [g·cm^{-3}]	8, 1.459	4, 1.351	4, 1.483	4, 1.375	4, 1.370[a]
Abs. coeff. [mm^{-1}	1.432	0.921	1.083	0.971	0.897[a]
Scan	ω	ω/2θ	ω/2θ	ω/2θ	Area det. θ, ω
F(000)	2092	1060	988	1012	1108[a]
θ range [°]	2.78···23.25	2.57···27.46	2.85···27.46	2.56···25.61	1.83···25.35
Index ranges	$0 \le h \le 13$ $-30 \le k \le 0$ $-15 \le l \le 15$	$-16 \le h \le 0$ $0 \le k \le 15$ $-20 \le l \le 21$	$0 \le h \le 21$ $0 \le k \le 19$ $0 \le l \le 11$	$0 \le h \le 10$ $0 \le k \le 25$ $-16 \le l \le 15$	$-17 \le h \le 15$ $-17 \le k \le 16$ $-15 \le l \le 12$
Collected/unique [R_{int}]	3546/3546	2985/2863 [0.0320]	2576/2576	4722/4431 [0.0242]	13258/4707 [0.0501]
Observed [$I_o > 2\sigma(I_o)$]	1888	2210	1314	3067	3265
Abs struct par	0.02(4)		0.00(5)		
DIFABS used?	yes	no	no	no	no
Relat. transm. fact.	1.052···0.962	1.051···0.916	1.021···0.965	1.069···0.961	
Data/restraints/pars	3546/531/515	2863/0/142	2576/1/250	4431/0/375	4707/0/286
Goodness−of−fit on F^2	1.004	1.332	1.053	1.084	0.960
SHELXL-97 wt pars	0.0692	0.2000	0.0361, 1.3080	0.0403, 0.6266	0.0402
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0733, 0.1365	0.0995, 0.2789	0.0705, 0.1074	0.0405, 0.0846	0.0400, 0.0802
*R*1, *wR*2 (all data)	0.1635, 0.1608	0.1207, 0.3140	0.1700, 0.1331	0.0741, 0.0963	0.0689, 0.0869
Diff. peak, hole [e·Å^{-3}]	0.629, −0.537	2.084, −1.124	0.402, −0.501	0.278, −0.224	0.309, −0.371

[a] Excluding contents of a "void" of 165 Å^3; see text for details.

7: One molecule of acetonitrile was located and refined. Hydrogen atoms were refined freely.

8: Calculations[27] showed a void of 165 Å^3, containing 32 electrons, resulting in a large volume of about 35 Å^3 per atom. Hexane and methanol were used in the synthetic route but no reasonable guess could be made about the nature of the solvent moiety or moieties present, nor was it possible to assign any physically meaningful parameters to the electron density. Therefore the SQUEEZE procedure was applied to account for this electron density. As a consequence this electron density could not be taken into account while calculating the physical·molecular properties as given in Table 1.

Acknowledgments

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