have also been well characterized.[60,61] Conductivity measurements support the formulation of complexes **4** and **5** as 1:1 electrolytes ($\Lambda_M(4) = 57\ \Omega^{-1}\ cm^2\ mol^{-1}$, $\Lambda_M(5) = 47\ \Omega^{-1}\ cm^2\ mol^{-1}$). Molar conductivity values similar to these have been observed previously for other 1:1 electrolytes of this type.[62]

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Mono(aryl)cobalt(II) Compounds Stabilized by Bis Ortho Chelation

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The reaction of $Li_2[C_6H_3(CH_2NMe_2)_2\text{-}o,o']_2$ with $Co^{II}X_2L_2$ (L = py, PPh$_3$, X = Cl, Br, I; L = PEt$_3$, X = Cl) yields the air-sensitive compounds $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)$. From elemental analyses and UV and ESR spectral data it was concluded that the complexes are five-coordinate and have a square-pyramidal structure with an apical ligand L.

Introduction

The relative scarcity of organometallic compounds among the transition metals having σ metal–carbon bonds is generally recognized as a combined result of thermodynamic and kinetic instability of such complexes.[1] Reductive elimination or β-hydrogen elimination of organic groups often occurs at already low temperatures, whereas empty low-lying orbitals and the polarity of the M–C bond favor an easy chemical attack. Some of these problems have been overcome in derivatives containing an alkyl group lacking β-hydrogens or having bulky substituents. It was also found that internal coordination may have a considerable stabilizing effect.[2]

Previously we used the terdentate anionic ligand [o,o'-$(Me_2NCH_2)_2C_6H_3$] to prepare a series of stable compounds in which the ligand is bonded via at least a M–C interaction. Compounds with the same set of ligands but as monodentates are not known and probably not stable. The metals involved so far are of d^5 (Fe(III)), d^6 (Rh(III), Pt(IV)), d^7 (Ni(III)), d^8 (Ni(II), Pd(II), Pt(II), Rh(I), Ir(I)), and d^{10} (Cu(I), Hg(II), Tl(III), Sn(IV)) electronic configurations.[3–5,7,18]

The recently reported paramagnetic congeners $Ni^{III}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X_2$ with X = Cl, Br, I[4] and $Fe^{III}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']Cl_2$[5] were found to have square-pyramidal arrangements. ESR studies on the Ni(III) complexes have been a valuable tool in elucidating their electronic structure. The results were consistent with a low-spin d^7 state of Ni(III) in which the unpaired electron is located in the axial d_{z^2} orbital. As Co(II) is isoelectronic with Ni(III), the related $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']$ compounds may well have similar structural features and in this way are of dual interest in understanding the bonding in these compounds.

Therefore, a series of paramagnetic cobalt complexes having the general formula $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)$, where X = Cl, Br, I and L = pyridine, PPh$_3$, PEt$_3$, were synthesized and spectroscopically characterized.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen (99.999% pure; purchased from Hoekloos) with use of Schlenk techniques. Solvents were carefully dried and distilled prior to use. Cobalt salts of the type CoX_2L_2 were prepared according to literature procedures.[6,10] Elemental analyses were carried out at the Institute for Applied Chemistry TNO, Zeist, The Netherlands. ESR spectra were run on a Bruker ER200D-MR X-band spectrometer. UV spectra were recorded on a Cary 14 spectrophotometer.

Synthesis of $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']Cl(py)$. A solution of $Li_2[C_6H_3(CH_2NMe_2)_2\text{-}o,o']_2$ in diethyl ether (10 mL) was prepared from $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Br$ (1.45 g, 5.4 mmol) and Li.[7] The solvent was removed in vacuo. The aryllithium compound was extracted with benzene (20 mL). This extract was added at room temperature to a blue suspension of $CoCl_2(py)_2$ (1.11 g, 3.9 mmol) in benzene (30 mL). This resulted in the formation of an intensely orange solution within a few minutes. The mixture was stirred for another 2 h and filtered. The solvent was removed in vacuo. The orange-brown solid residue was washed with pentane (4 × 10 mL); yield 1.00 g (2.75 mmol, 70%). The complexes $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)$ were prepared in an analogous manner from the CoX_2L_2 complexes and $Li_2[C_6H_3(CH_2NMe_2)_2\text{-}o,o']_2$. Yields are given in parentheses: L = py, X = Br (14%), I (70%); L = PPh$_3$, X = Cl (27%), Br (55%), I (70%); L = PEt$_3$, X = Cl (50%).

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Table I. ESR Parameters of $Co[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)^a$

L	X	g_{xx}^f	g_{yy}^f	g_{zz}	g_{iso}^b	$A_{xx}(Co)$	$A_{yy}(Co)$	$A_{zz}(Co)$	$A(L)$
py	Cl	2.401	2.258	2.019	2.226	c	~27	72	9^d
py	Br	2.405	2.254	2.016	2.225	c	~25	71	c
py	I	2.412	2.256	2.017	2.228	c	c	68	c
PPh$_3$	Cl	2.16	2.01	2.37	2.18	~25	34	59	e
PPh$_3$	Br	2.15	2.01	2.37	2.18	~25	27	56	e
PPh$_3$	I	2.13	2.04	2.36	2.18	25	28	58	e
PEt$_3$	Cl	2.10	2.01	2.36	2.16	c	~25	74	e

^{a} Measured between 130 and 150 K in toluene glass; A expressed in gauss (estimated error 3 G). ^{b} Calculated as $g_{iso} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$. ^{c} Not resolved. ^{d} On g_{zz}. ^{e} ^{31}P couplings were observed on all tensors but were poorly resolved. ^{f} x and y may be interchanged.

Table II. Electronic Spectral Data of $Co[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)^a$

L	X	UV	vis			near-IR	
py	Cl	b	410 (650)	540 (900)	660 (150)	800 (10)	1370 (70)
py	Br	285 (4000)	420 (250)	560 (350)	675 (50)	805 (5)	1380 (50)
py	I	b	395 (500)	460 (850)	605 (100)		1385 (40)
PPh$_3$	Cl	300 (5000)			630 (300)	1160 (120)	1750 (25) sh
PPh$_3$	Br	320 (4000)		490 (110) sh	645 (250)	1150 (130)	1710 (15) sh
PEt$_3$	Cl	285 (4000)	345 (1000)	465 (300)	660 (350)	1020 (250)	1600 (20) sh

^{a} Spectra were measured in benzene at room temperature. Absorption maxima are expressed in nm. Concentrations were in the range 0.1–1 mol/L. ϵ values are expressed in L mol^{-1} cm^{-1} and are shown in parentheses (estimated error 25%). sh = shoulder. ^{b} Not measured.

Results and Discussion

The chemistry of organometallic compounds of cobalt having an alkyl– or aryl–cobalt bond is mainly confined to compounds having several π-acceptor ligands as in carbonyl, cyanide, and cyclopentadienyl complexes and cobalamins.[8] The discovery of the organometallic nature of vitamin B$_{12}$ and its role in oxygen and electron transport in living systems has led to the development of an extensive series of model compounds that have a cobalt–carbon bond.[15]

Bis(aryl) compounds of the type Co^{II}R$_2$L$_2$ with L = phosphine or aromatic amine have been synthesized and their properties studied in detail.[10,11] Cope et al.[9] used aryl ligands with a substituent containing a donor atom that can coordinate to the cobalt atom. By using the bidentate monoanion [C$_6$H$_4$(CH$_2$NMe$_2$)-o], they prepared the tris(aryl)cobalt compound Co^{III}[C$_6$H$_4$-(CH$_2$NMe$_2$)-o]$_3$. Recently we found that treatment of a suspension of CoX$_2$L$_2$ in benzene (L = py, PPh$_3$, X = Cl, Br, I; L = PEt$_3$, X = Cl) with $^1/_2$ equiv of the aryllithium compound Li$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']$_2$ at room temperature resulted in the formation of the mono(aryl) species Co^{II}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']X(L) (see eq 1).

$$^1/_2Li_2[C_6H_3(CH_2NMe_2)_2\text{-}o,o']_2 + CoX_2L_2 \rightarrow$$
$$Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L) + LiX + L \quad (1)$$
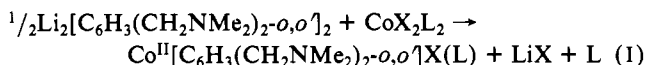
The complexes are highly colored (L = py, orange; L = phosphine, blue-green) and very air sensitive. They rapidly turn blue on exposure to the atmosphere with formation of the free arene m-(Me$_2$NCH$_2$)$_2$C$_6$H$_4$. Although this extreme sensitivity precluded the attainment of accurate analytical data, they were fair enough to establish the overall stoichiometry as indicated for the complexes in eq 1. It was observed that the ligand L:cobalt ratio is 1:1, which indicates that the aryl moiety is coordinated in a terdentate fashion to cobalt. We are therefore dealing with a 5-coordinate 17-electron cobalt complex.

As efforts to obtain crystals suitable for X-ray diffraction work have as yet failed, we are dependent on spectroscopic data to establish the structural features of these complexes. Clear information comes from ESR and electronic spectra, of which the data are given in Tables I and II. ESR spectra recorded at room temperature in toluene solution show a broad featureless isotropic signal at $g \simeq 2.2$. This value suggests a low-spin d^7 spin state ($S = ^1/_2$) in which the unpaired electron is mainly located in a metal orbital. When the solutions are frozen, the g tensor splits
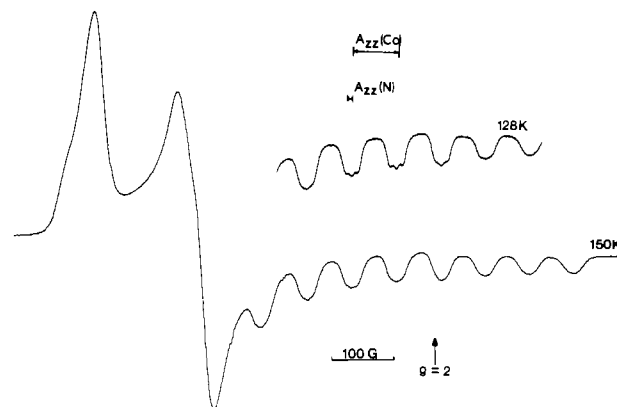
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Figure 1. ESR spectrum of Co[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']Cl(py) in toluene glass.
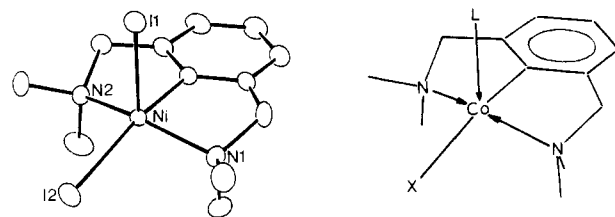
Figure 2. Crystal structure of Ni[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']I$_2$[4] and proposed structure of Co[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']X(L).

into its three principal components g_{xx}, g_{yy}, and g_{zz} (see Figure 1) for Co^{II}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']Cl(py)). Hyperfine coupling with the ^{59}Co nucleus ($I = ^7/_2$, 100% abundance) becomes obvious then in all complexes. Superhyperfine coupling with the monodentate ligands is found in Co^{II}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']Cl(py) with ^{14}N ($I = 1$, $A_{zz} = 9$ G) and on all hyperfine components in the phosphine complexes with ^{31}P ($I = ^1/_2$), although the latter are poorly resolved ($A_{zz} \simeq 75$ G). Coupling with the nitrogen atoms of the CH$_2$NMe$_2$ arms of the terdentate ligand was never observed. It must be noted that when the solutions are heated the signal at $g \simeq 2.2$ disappears irreversibly in favor of a high-spin signal at $g \simeq 4.2$. As this is accompanied by some turbidity and color change, it probably indicates the formation of decomposition products.

The ESR patterns of the Co^{II}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']X(py) complexes show a marked resemblance to those of the isoelectronic five-coordinate Ni(III) complexes Ni^{III}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o']X$_2$ with X = Cl and Br.[4] We have shown that the Ni(III) complexes

have a square-pyramidal configuration (see Figure 2). Both compounds have $g_{zz} \simeq 2.0$ and $g_{xx}, g_{yy} > g_{zz}$. The Ni(III) complexes show a splitting of the g_{zz} component due to a coupling of the unpaired electron with the apical halogen. The absence of additional couplings with the other N and halogen nuclei pointed to the conclusion that the unpaired electron is in a metal orbital with d_{z^2} symmetry. Accordingly the ESR data of the present Co(II)–pyridine complexes suggest a similar five-coordinate square-pyramidal structure as has been established for the Ni(III) compounds (see figure 2). The pyridine acts as the apical ligand as can be deduced from the superhyperfine coupling on g_{zz} with one ^{14}N nucleus in $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']Cl(py)$ (see figure 1). A similar coupling with a single ^{14}N nucleus is also observed in several tetradentate Schiff base and porphyrin cobalt complexes having an axial coordinated pyridine ($A_{zz} \simeq 15$ G).[12]

As the anisotropy observed at low temperatures in the ESR spectra of transition-metal complexes is mainly due to a removal of degeneracy of d orbitals, it should be possible to correlate the ESR and electronic data. Maki et al.[13] and McGarvey[14] derived a set of relationships that accounts for the experimental parameters observed in low-spin d^7 systems. As the $d_{x^2-y^2}$ orbital (x, y toward the ligands) is highest in energy and empty, four possible ground-state configurations remain. For the suggested $(d_{xz})^2\text{-}(d_{yz})^2(d_{xy})^2(d_{z^2})^1$ configuration the following equations have been derived:

$$g_{xx} = 2.002 - 6b_1 \qquad g_{yy} = 2.002 - 6b_2 \qquad g_{zz} = 2.002$$

$$A_{xx} = P[-\kappa - \tfrac{2}{7} - 6b_1 - \tfrac{3}{7}b_2]$$

$$A_{yy} = P[-\kappa - \tfrac{2}{7} - 6b_2 - \tfrac{3}{7}b_1]$$

$$A_{zz} = P[-\kappa + \tfrac{4}{7} + \tfrac{3}{7}(b_1 + b_2)]$$

where $b_1 = \lambda/\Delta E_{yz \to z^2}$, $b_2 = \lambda/\Delta E_{xz \to z^2}$, and λ is the spin–orbit coupling parameter (515 cm^{-1} for the free Co(II) ion[13]). The constants κ and P usually are in the ranges 0.10–0.30[14] and 150–300 G,[14] respectively. P is calculated to have the value of 245 G in the free Co(II) ion.[16] Taking $A_{xx} = 0$, $A_{yy} = -25$ G, and $A_{zz} = 70$ G, we find an excellent fit for the three pyridine complexes. The parameters κ and P were calculated to have values of 0.14 and 185 G. Reducing the spin–orbit coupling parameter λ by the same amount from its free-ion value (25%) as P, we further find $\Delta E_{yz \to z^2} = 6000$ cm^{-1} ($\hateq 1650$ nm) and $\Delta E_{xz \to z^2} = 9000$ cm^{-1} ($\hateq 1100$ nm). These calculated energy separations could not be unambiguously assigned in the electronic spectra (see Table II), but it should be realized that the intensities of such d–d transitions usually are very weak and may well be hidden under other absorptions found in the near-infrared region. Changing the halogen (X) has hardly any effect on the data. This is not surprising since this change of a ligand in the xy plane would mainly influence the $d_{x^2-y^2}$ orbital, which is supposed to be empty. Interpretation of the ESR data for the phosphine complexes in terms of structural features is less straightforward than for the

pyridine complexes. The largest couplings due to both the ^{59}Co and ^{31}P nuclei were found on the principal component appearing at $g = 2.37$ and is assigned to g_{zz}. The substantial shift however of this value from $g = 2$ indicates that the unpaired electron is no longer in an orbital of a discrete d_{z^2} symmetry. A substantial mixing of orbitals lying in the xy plane seems to have occurred, and in fact they predominate. The electronic configuration of the phosphine complexes is therefore primarily of the form $(d_{xz})^2\text{-}(d_{yz})^2(d_{xy})^2(d_{x^2-y^2})^1$. This is explained as being a result of the stronger σ-donor/π-acceptor behavior of the phosphines compared with the only σ-donor pyridine, which destabilizes the d_{z^2} orbital. It is argued that the coupling that is observed in the z direction in spite of the suggested $(d_{x^2-y^2})^1$ ground state is due to a strong spin polarization. It is possible to derive a set of relationships between g and A values for this spin state[17] analogous to the ones mentioned earlier. If one takes $A_{xx} = 25$ G, $A_{yy} = 30$ G, and $A_{zz} = -58$ G for the three triphenylphosphine complexes and uses κ and P as calculated for the pyridine complexes, one finds a reasonable fit. Two d–d transitions were calculated to occur in the near-infrared region, i.e. $\Delta E_{x^2-y^2 \to yz} = 5200$ cm^{-1} ($\hateq 1900$ nm) and $\Delta E_{x^2-y^2 \to xy} = 8500$ cm^{-1} ($\hateq 1200$ nm). They may well correspond to the weak transitions observed at ca. 1730 and 1150 nm in the triphenylphosphine complexes (see Table II). The $(d_{x^2-y^2})^1$ electronic configuration suggested for the phosphine complexes is not commonly met with in five- or six-coordinate Co(II) complexes,[12,14] but there are some precedents in isoelectronic Ni(III) complexes.[17]

In our earlier work on the organometallic chemistry of the terdentate ligand $[o,o'\text{-}(Me_2NCH_2)_2C_6H_3]$ it was noticed that due to the hard nature of the ligand the oxidation potential of the complexed metals is for example drastically lowered in the case of Ni (Ni(II) to Ni(III))[4] and Pt (Pt(II) to Pt(IV)).[18] However, attempts to oxidize $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']X(L)$ to a Co(III) complex with a variety of reagents ($^1/_2$ X$_2$, Cu^{II}Cl$_2$, Fe^{III}Cl$_3$, AgOAc) have been unsuccessful so far; products arising from metal–carbon bond cleavage were observed instead. Stirring a solution of $Co^{II}[C_6H_3(CH_2NMe_2)_2\text{-}o,o']Cl(py)$ in benzene with a slight excess of PPh$_3$ for several days resulted in the displacement of pyridine and formation of the corresponding phosphine complex as was evidenced by UV/visible spectroscopy. This corroborates the observation made earlier that the phosphines are much better ligands in these complexes than is pyridine.

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