Nitrosyl Complexes of Cobalt with Hybrid Bidentate Ligands Containing Phosphorus and Sulfur Donor Atoms

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Abstract

Nitric oxide reacts with $[Co(P{-}SR)_2](BF_4)_2$ (P–SR = 1-(thioalkyl)-2-(diphenylphosphino)ethane) to form five-coordinate mononitrosyl $\{CoNO\}^8$ complexes. On the basis of infrared and NMR data the $[Co(NO)(P{-}SR)_2]^{2+}$ cations are believed to have a trigonal–bipyramidal geometry, with a linear Co–NO linkage. The mononitrosyl derivatives disproportionate in solution giving $[Co(NO)_2(P{-}SR)_2]^+$ species, and probably Co(III) compounds. The stoichiometry of this reaction was examined in different solvents and in the presence of added halide or pseudohalide ions by NMR and IR techniques. The cobalt(III) complex $[Co(NCS)_2(P{-}SEt)_2]BF_4$ has been isolated and characterized.

Introduction

The geometry and chemical reactivity of the nitrosyl complexes of the $\{CoNO\}^8$ group** appear to be controlled by the nature of the other ligands attached to the metal. Both linear and bent Co–NO triatomic fragments have been observed in five-coordinate complexes of the type $[Co(NO)L_4]^{n+}$, depending on the donor atom set of the ligands. Thus Co–NO bond angles about 120° are found in compounds containing chelating ligands with donor sets such as N_4 (L_4 = tetraphenylporphyrin [2]); N_2O_2 (L_4 = *N,N'*-ethylenebis(acetylacetoneiminate) [3], L_4 = *N,N'*-ethylenebis(benzoylacetoneiminate) [3], L_2 = (hydroxyacetophenoneoxime)o-*O*-anion [4], L_4 = *N,N'*-ethylenebis(salicylideniminate) [5]); N_2S_2 (L_4 = *N,N'*-ethylenebis(monothioacetylacetoneiminate) [6]); and S_4 (L_2 = dimethyldithiocarbammate [7], L_2 = dithioacetylacetonate [8]).

By contrast, the nitrosyl group is coordinated in a linear fashion with Co–N–O angles about 180° in five-coordinate $[CoX_m(NO)L_{4-m}]^{n+}$ ($m = 0, 1, 2$) derivatives containing unidentate or multidentate ligands with donor atom sets such as As_4 (L_2 = *o*-phenylenebis(dimethylarsine) [9]); P_4 (L = phosphite [10], L_2 = diphosphine [11]); XL_3 (X = halide, L = phosphite [12]), and X_2L_2 (X = halide, L = phosphine [13, 14]). The P_2X_2 constitute an interesting series in which both linear and bent Co–NO moieties have been observed, in trigonal bipyramidal or square pyramidal geometries.

No example of $\{CoNO\}^8$ compounds with a P_2S_2 donor set is known. In order to determine the nature of the Co–NO linkage in nitrosyl complexes with this type of donor atom set, we have prepared some cobalt nitrosyl complexes with the ligands $Ph_2PCH_2CH_2SR$ (P–SR: R = Me, P–SMe; R = Et, P–SEt). Five-coordinate $[Co(NO)(P{-}SR)_2]^{2+}(\{Co{-}NO\}^8)$ and four-coordinate dinitrosyl $[Co(NO)_2(P{-}SR)_2]^+$-$(\{Co(NO)_2\}^{10})$ cations have been isolated, and the $\{CoNO\}^8 \rightarrow \{Co(NO)_2\}^{10}$ conversion studied by infrared and NMR spectroscopy. This work is an extension of our studies on transition metal complexes with hybrid ligands containing phosphorus and sulfur donor atoms [15].

Experimental

The ligands 1-(thioethyl)-2-(diphenylphosphino)ethane (P–SEt) and 1-(thiomethyl)-2-(diphenylphosphino)ethane (P–SMe) were prepared as previously described [16]. Infrared spectra were recorded on a Jasco DS 702 G spectrophotometer and calibrated against the absorption of polystyrene at 1601 cm^{-1}. Conductance data were obtained using a Metrohm 518 conductivity bridge. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP 80 SY Fourier transform spectrometer equipped with a variable temperature probe. NMR spectra were measured in dichloromethane solutions, using an external acetone-d_6 lock. Chemical shifts are referenced to 85% aqueous H_3PO_4, with downfield shifts considered positive. Elemental analyses were carried out by the Microanalysis Laboratory of Udine University. All solvents were reagent grade and degassed before use. The complexes $[Co(P{-}SR)_2](BF_4)_2$ (R = Me, Et) were

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**In order to avoid the ambiguities that can arise from the NO^+–NO^- formalism, Enemark and Feltham's notation $\{MNO\}^n$ is used [1].

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TABLE I. Physical Properties, Analytical Data, and Selected IR and NMR Data for the Complexes

Complex	Color	Λ_M [a] ($cm^2\ ohm^{-1}\ mol^{-1}$)	Analysis: found (calc.) (%)			ν(NO) [b] (cm^{-1})	^{31}P NMR[c] (δ, ppm)
			C	H	N		
$[Co(NO)(P{-}SMe)_2](BF_4)_2$	light brown	171	46.01 (45.68)	4.69 (4.64)	1.79 (1.86)	1872	68.3
$[Co(NO)(P{-}SEt)_2](BF_4)_2$	olive green	162	47.38 (47.59)	4.72 (4.83)	1.73 (1.65)	1825	73.4
$[Co(NO)_2(P{-}SEt)_2]BPh_4$	red–brown	48	68.16 (68.11)	5.92 (5.93)	2.84 (2.76)	1845, 1790	34.2
$[Co(NCS)_2(P{-}SEt)_2]BF_4$	red–brown	79	50.42 (50.38)	4.72 (4.80)	3.46 (3.49)	[d]	57.6
$[CoI(P{-}SEt)_2]BPh_4$ [e]	brown	47	62.83 (63.82)	5.58 (5.55)			

[a] In nitromethane, for 10^{-3} M solutions, at 25 °C. [b] Nujol mull. [c] Relative to external 85% H_3PO_4, CH_2Cl_2 solutions. The value for $[Co(NO)(P{-}SMe)_2](BF_4)_2$ is referred to CH_3CN solution. [d] ν(CN) = 2090 cm^{-1}. [e] μ_{eff} = 2.15 BM, determined by the Gouy method.

prepared as previously described [15]. Reactions involving nitrosyl complexes were carried out under a nitrogen atmosphere. Some physical properties, spectroscopic, and analytical data of the complexes are reported in Table I.

Preparation of the Complexes

$[Co(NO)(P{-}SR)_2](BF_4)_2$

Method A. $[Co(P{-}SR)_2](BF_4)_2$ (2.0 mmol) was dissolved in acetonitrile (10 ml), and the reaction vessel was saturated with nitric oxide. The orange–red solution turned red–brown; 2-propanol (20 ml) was added, and the resulting precipitate was filtered off, washed with 2-propanol, and dried *in vacuo*. The complexes were recrystallized from acetonitrile/2-propanol (R = Me) or dichloromethane/2-propanol (R = Et).

Method B. A suspension of $Co(BF_4)_2{\cdot}6H_2O$ (2.0 mmol) and P–SR (4.0 mmol) in 2-propanol (20 ml) was gently warmed under vigorous stirring, until a clear red solution was formed. The reaction vessel was then saturated with nitric oxide. Brown products readily precipitated, which were recrystallized as described above.

The complex with P–SMe is light brown, while the P–SEt derivative was obtained as olive green pleochroic crystals.

$[Co(NO)_2(P{-}SEt)_2]BPh_4$

$[Co(NO)(P{-}SEt)_2](BF_4)_2$ (2.0 mmol) was suspended in methanol (20 ml), and the mixture refluxed for 1 h. $NaBPh_4$ (2.5 mmol) was then added to the red solution. The red–brown precipitate was recrystallized from dichloromethane/2-propanol.

trans-$[Co(NCS)_2(P{-}SEt)_2]BF_4$ and $[Co(NO)_2(P{-}SEt)_2]BPh_4$

$[Co(NO)(P{-}SEt)_2]BF_4$ (1.0 mmol) was suspended in ethanol (30 ml) and refluxed in the presence of KSCN (1.0 mmol) for 30 min, during which time a red–brown precipitate was formed. After stirring for 30 min at room temperature, the solid was filtered off and crude $[Co(NCS)_2(P{-}SEt)_2]BF_4$ was recrystallized from dichloromethane/ethanol (yield 75%).

The dinitrosyl complex separated as red–brown crystals upon addition of $NaBPh_4$ (1.0 mmol) to the filtered solution (yield 72%).

$[CoI(P{-}SEt)_2]BPh_4$

Stoichiometric amounts (1.0 mmol) of cobalt(II)-nitrate hexahydrate, sodium tetraphenylborate, and NaI were dissolved in 25 ml of 2-propanol. After filtering off sodium nitrate, a dichloromethane solution (10 ml) of the ligand (1.0 mmol) was added. The resulting deep red solution was warmed briefly; on cooling, it yielded brown crystals which were recrystallized from dichloromethane/2-propanol.

Results and Discussion

The $[Co(P{-}SR)_2](BF_4)_2$ derivatives react with NO at room temperature and 1 atm to give mononitrosyl complexes of the type $[Co(NO)(P{-}SR)_2](BF_4)_2$. The nitrosyl derivatives are diamagnetic, and are found to be 1:2 electrolytes in nitromethane. Their IR spectra show a strong band in the range 1875–1825 cm^{-1}. The room temperature $^{31}P\{^1H\}$ NMR spectra of the $[Co(NO)(P{-}SR)_2](BF_4)_2$ complexes show a single resonance. Though the signal slightly broadens as the temperature is lowered, it is still a singlet at 190 K (CD_2Cl_2–$CHClF_2$ solution). These NMR data are consistent with both a trigonal bipyramidal and a square pyramidal structure. However, the observed NO stretching frequencies suggest a linear Co–NO group, according to the IR rules proposed by Haymore and Ibers (ν(NO)(corrected) > 1620 cm^{-1}) [17]. Moreover, an empirical generalization has evolved, according to which the linear Co–NO groups exist in trigonal bipyramidal complexes, while the bent ones occur only in square pyramidal environments [1]. On this basis, and in agreement with Hoffman's theoretical previsions [18] we tentatively propose a trigonal bipyramidal structure with a linear Co–NO group in an equatorial position. It is possible that the $[Co(NO)(P\text{–}SR)_2]^{2+}$ species are stereochemically non-rigid in solution on the NMR time scale also at very low temperature. It should be noted that the related $[Co(NO)(diphosphine)_2]^{2+}$ cations, which are also stereochemically non-rigid at room temperature, have trigonal–bipyramidal structures, with an equatorial NO and the diphosphine ligands spanning axial and equatorial positions [11].

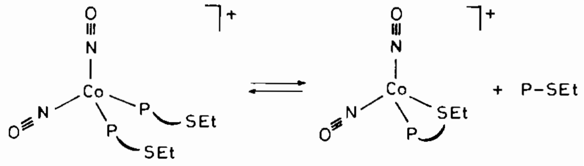
The $[Co(NO)(P\text{–}SR)_2](BF_4)_2$ complexes are air-stable in the solid state at room temperature in a dry atmosphere, while their solutions are relatively unstable, and decompose yielding $\{Co(NO)_2\}^{10}$ derivatives. Since the nature of the P–SR ligand does not affect the behaviour of the $[Co(NO)(P\text{–}SR)_2](BF_4)_2$ species, we have examined the P–SEt derivative only.

When a methanol suspension of $[Co(NO)(P\text{–}SEt)_2](BF_4)_2$ (**I**) is refluxed, a red solution is slowly formed, in which only a dinitrosyl derivative and free P–SEt (1:2 ratio) are present, as shown by ^{31}P NMR analysis. Red–brown crystals analyzing as $[Co(NO)_2(P\text{–}SEt)_2]BPh_4$ are obtained by addition of sodium tetraphenylborate to the filtered solutions. The complex $[Co(NO)_2(P\text{–}SEt)_2]BPh_4$ is diamagnetic and behaves as a 1:1 electrolyte in nitromethane; the IR spectrum shows two strong absorptions at 1845 and 1790 cm^{-1} in the solid state, and at 1854 and 1803 cm^{-1}, respectively, in freshly prepared dichloromethane solutions. These frequencies can be compared with those reported for analogous four-coordinate $\{Co(NO)_2\}^{10}$ complexes, such as $[Co(NO)_2(1,2\text{-bis(diphenylphosphino)ethane})]PF_6$ [19], $[Co(NO)_2(PPh_3)_2]PF_6$ [20], and $[Co(NO)_2(\text{dithioacetylacetonato})]$ [21], which have been shown to have a distorted tetrahedral coordination about the metal with nearly linear Co–N–O groups.

The variable temperature $^{31}P\{^1H\}$NMR spectrum of freshly prepared dichloromethane solutions show a single resonance, which can be assigned, on the basis of the coordination chemical shift (Δ = 51.1) to the P atoms of P–SEt molecules acting as monodentate ligands [22]. The IR and ^{31}P NMR data are consistent with a $\{Co(NO)_2\}^{10}$ compound having the tetrahedral structure **II**, in which both P–SEt ligands act as monodentate.

Also dichloromethane solutions of $[Co(NO)(P\text{–}SEt)_2]^{2+}$ are unstable and slowly decompose giving complex **II**, with a molar ratio $\{Co(NO)_2\}^{10}$:$\{CoNO\}^8$ of 0.5. The decomposition can conveniently be followed by IR and ^{31}P NMR spectroscopies. The diamagnetism of the final mixture indicates the absence of Co(II) products. Moreover, infrared measurements show that also complex **II** is not stable in dichloromethane solution. The IR bands at 1854 and 1803 cm^{-1} are gradually replaced by two new absorptions at 1872 and 1815 cm^{-1}. When an excess of P–SEt ligand is added to the reaction mixture, the bands at 1872 and 1815 cm^{-1} disappear, and are replaced by the characteristic absorptions of complex **II**.

These observations are consistent with equilibrium (1), which involves the reversible elimination of one P–SEt molecule from complex **II**. The formation of complex **III**, containing only one chelating P–SEt ligand, is furthermore supported by the ^{31}P NMR spectra of aged solutions of **II**, in which the singlet at 34.2 ppm (complex **II**) has almost disappeared, and two new peaks at 55.8 and –16.9 ppm are observed. The lower field singlet (Δ = 72.7 ppm) is attributed to complex **III**, while the higher field signal is relative to the free ligand.



II **III** (1)

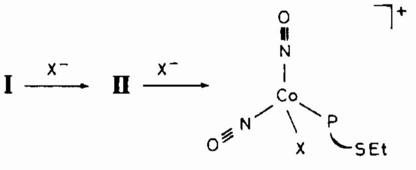
The five-coordinate $[Co(NO)(P\text{–}SEt)_2]^{2+}$ cation readily reacts with pseudohalide or halide ions to yield $\{Co(NO)_2\}^{10}$ derivatives. In the presence of thiocyanate ions (dichloromethane solution), complex **I** disproportionates to produce complex **II** and the cobalt(III) species $[Co(NCS)_2(P\text{–}SEt)_2]^+$, according to the stoichiometry

$$2[Co(NO)(P\text{–}SEt)_2]^{2+} + 2NCS^- \longrightarrow$$

$$[Co(NO)_2(P\text{–}SEt)_2]^+ + \textit{trans}\text{-}[Co(NCS)_2(P\text{–}SEt)_2]^+$$

The formation of the cobalt(III) complex and of the dinitrosyl derivative is deduced from the IR spectra of the solution, which show bands at 2095 cm^{-1} (ν(CN)) and at 1854 and 1803 cm^{-1} (ν(NO)). Moreover, the Co(I) and Co(III) products are isolated in 1:1 ratio, and in almost quantitative yield when potassium thiocyanate and $[Co(NO)(P\text{–}SEt)_2](BF_4)_2$ are mixed in ethanol. The insoluble $[Co(NCS)_2(P\text{–}SEt)_2]BF_4$ separates as red–brown crystals, while the more soluble $[Co(NO)_2(P\text{–}SEt)]^+$ can be obtained as a red–brown product by addition of sodium tetraphenylborate to the filtered solution.

When Bu_4NX (X = Br, I) is added (1:1) to dichloromethane solutions of **I**, the band at 1818 cm^{-1} is replaced by the peaks at 1854 and 1803 cm^{-1} (typical of complex **II**) over a few minutes. The dinitrosyl derivative slowly reacts further with X$^-$, according to the overall scheme



X = Br
ν(NO) = 1846, 1772 cm^{-1}

X = I
ν(NO) = 1838, 1778 cm^{-1}

The IR data of the iodo-derivative agrees with those reported for the analogous $CoI(NO)_2(PPh_3)$ [23]. The ^{31}P NMR spectra of the reaction mixture (X = I) shows the presence of free phosphine, and a signal at 29.3 ppm ($\Delta = 46.2$ ppm), which can be attributed to a P–SEt molecule bonded to the cobalt through the phosphorus atom only [22]. It is likely that also in the case of halide ions, the formation of complex **II** occurs via a disproportionation reaction, but the resulting cobalt(III) complex is probably unstable, and decomposes giving free P–SEt and X$^-$, which reacts further with **II**.

It should be noted that the transformation of **I** into **II** in dichloromethane solution is also accelerated by addition (1:1) of bases such as NEt_3 or pyridine. The effect follows the order of increasing basicity, $NEt_3 >$ 2-methyl-pyridine $\simeq$ pyridine; in the presence of 4-cyano-pyridine, no appreciable effect on the rate of the reaction has been observed. The production of the $\{Co(NO)_2\}^{10}$ unit formally implies an intermolecular transfer of a nitrosyl ligand as NO$^-$ from a $\{CoNO\}^8$ unit to another one. This type of nitrosyl transfer is currently presumed to occur through the formation of a μ-bridged nitrosyl species [24, 25]. If such a mechanism is operative also in this case, then the dependence of the rate of formation of **II** on the presence of X$^-$ or bases can be understood assuming the formation of a six-coordinate intermediate $[L\text{–}Co(NO)(P\text{–}SEt)_2]^{2+}$ (L = X$^-$, base), in which the Co–NO moiety is bent and susceptible of electrophilic attack [9]. This species may react rapidly with **I** to give a bridging nitrosyl intermediate, Co(μ-NO)Co, prerequisite to NO transfer. Some support to this hypothesis comes from the observation that the low-spin five-coordinate $[CoI(P\text{–}SEt)_2]$-BPh_4 complex reacts in n-hexane suspension with NO to give a nitrosyl derivative, which shows ν(NO) at 1610 cm^{-1}, in the range expected for bent Co–NO. This red product, probably $[CoI(NO)(P\text{–}SEt)_2]BPh_4$ (not isolated in a pure form), in solution immediately yields $[Co(NO)_2(P\text{–}SEt)_2]^+$. However, in the absence of a kinetic investigation, a nitric oxide dissociative mechanism as proposed in nitrosyl transfer from cobaltnitrosyl complexes to hemoglobine cannot be excluded [26].

The cobalt(III) complex $[Co(NCS)_2(P\text{–}SEt)_2]BF_4$ obtained by the disproportionation reaction is a red–brown diamagnetic solid which is fairly stable both in the solid and in solution. This compound is a 1:1 electrolyte in nitromethane solution, and its IR spectrum shows a strong broad band at 2090 cm^{-1}, which can be assigned to the CN stretching vibration of a terminal NCS group [27]. Only one sharp ν(CN) is present at 2095 cm^{-1} in dichloromethane solution. In addition, absorption peaks appear at 816 and 490 cm^{-1}, due to ν(CS) and δ(NCS), respectively. The IR data are consistent with the N-bonded nature of the thiocyanato group, and with the presence of a *trans*-$Co(NCS)_2$ moiety [27]. The ^{31}P NMR spectrum shows a single resonance, which would indicate that a single isomer is present, having equivalent phosphorus atoms in *cis* or *trans* positions. The electronic spectrum of *trans*-$[Co(NCS)_2(P\text{–}SEt)_2]BF_4$ contains a weak band at about 16 500 cm^{-1}, which blends into a much stronger band at 23 530 cm^{-1}, with $\epsilon_{mol} =$ 12 800 l cm^{-1} mol^{-1}. A further absorption at 29 800 cm^{-1} has $\epsilon_{mol} = 18\,000$ l cm^{-1} mol^{-1}. Analogous cobalt(III) complexes with the phosphine–thioether ligand *o*-$C_6H_4(PPh_2)(SMe)$ have been recently reported by Levason [28].

Conclusions

Nitric oxide promotes the dismutation of the $[Co(P\text{–}SR)_2]^{2+}$ complexes through the formation of $[Co(NO)(P\text{–}SR)_2]^{2+}$ as unstable intermediates. The decomposition reaction of these mononitrosyl derivatives is spontaneous in solution, and is accelerated by the presence of bases or X$^-$ ions. In the case of NCS$^-$, cobalt(I) and cobalt(III) complexes are formed in a 1:1 molar ratio. The mechanism of the reaction is probably similar to the one observed in other NO promoted dismutations of cobalt complexes [8, 29, 30], and appears to be related to the rearrangement of the electron distribution within the CoNO group which occurs when a sixth ligand is added to the metal. The thiocyanate ion appears to be particularly able in stabilizing the cobalt(III) derivatives, as previously observed in the disproportionation reactions of other cobalt compounds [29, 30]. Our results with cobalt complexes of P–SR ligands, as well as previous reports on phosphites [29] and phosphine derivatives [30] seem to indicate that NO promoted dismutation provides a useful synthetic route to cobalt(III) complexes containing a variety of ligands.

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