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Nitrosyl Complexes of Transition Metals. II. Tertiary Phosphine Nitrosyl Cobalt Complexes[1]

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The reaction between $Co_2X_2(NO)_4$ ($X = Cl$, Br, I) and tertiary phosphines are described. Triphenylphosphine gives equilibrium mixture of $CoClPPh_3(NO)_2$ and $[Co(PPh_3)_2(NO)_2]Cl$. The equilibrium can be displaced toward the formation of the latter compound in presence of ClO_4^- and BPh_4^- anions. In presence of reducing agents the reaction yields $Co(PPh_3)_3(NO)$. The 1,2-bisdiphenylphosphinoethane (dp) yields, according to the ratio ligand/cobalt, complexes of formula $Co_2X_2dp(NO)_4$, $[Codp(NO)_2]Y$, $CoX_2dp(NO)$ ($X = Cl$, Br, I; $Y = Cl$, ClO_4, BPh_4) or $Co_2(dp)_3(NO)_2$. In solution the complex $Co_2X_2dp(NO)_4$ is in equilibrium with the ionic form $[Codp(NO)_2][CoX_2(NO)_2]$.

Introduction

In a previous paper the reaction products between the μ–dihalogenotetranitrosyldicobalt complexes and tetraalkylammonium halides, pyridine and ethylendiamine have been described.[1]

In this paper, we describe the products of the reaction between the $[CoX(NO)_2]_2$ ($X = Cl$, Br, I) and some tertiary phosphine, namely triphenylphosphine and 1,2-bisdiphenylphosphinoethane.

Although some of the compounds here described have been previously reported in literature,[2,3] the unusual behaviour reported for $Co(PPh_3)_3(NO)$[2] and the disagreement between some of the results found in our preliminary studies[4] and these already reported,[2,3], prompted re-examination of the reaction between μ-dihalogenotetranitrosyldicobalt and tertiary phosphines.

Experimental Section

All compounds were prepared and manipulated in an atmosphere of pure nitrogen. Samples for m.p. determination were contained in evacuated tubes. Infrared spectra were measured using a Perkin-Elmer mod. 337 spectrometer. The complexes $Co_2X_2(NO)_4$ ($X = Cl$, Br and I) were prepared according to the literature.[1]

Chlorotriphenylphosphinedinitrosylcobalt. $CoCl[P(C_6H_5)_3](NO)_2$. a) An ethanolic solution of triphenylphosphine (0.4 g, 1.6 mmol) was added to a solution of $Co_2Cl_2(NO)_4$ (0.5 g, 1.6 mmol) in ethanol (10 ml). The resulting dark brown precipitate was washed with ethanol and dried; d.p.; 170°C. The complex is soluble in benzene and chloroform, but insoluble in petroleum ether.

Anal. Calcd. for $C_{18}H_{15}ClN_2O_2PCo$: N, 6.7; P, 7.4; Co, 14.2; Cl, 8.5. Found: N, 6.7; P, 7.5 Co, 14.1; Cl, 8.6%.

b) A solution of potassium chloride (0.5 g, 6.7 mmol) in aqueous ethanol was added to a hot solution of $[Co\{P(C_6H_5)_3\}_2(NO)_2]ClO_4$ (0.5 g, 0.7 mmol) in 20 ml of ethanol. After filtration the complex crystallised, on cooling as dark needles; it was identified by means of its d.p. and I.R. spectrum.

Bis(triphenylphosphine)dinitrosylcobalt perchlorate. $[Co\{P(C_6H_5)_3\}_2(NO)_2]ClO_4$. An ethanolic solution of sodium perchlorate (0.6 g, 5 mmol) was added to a solution of $CoCl[P(C_6H_5)_3](NO)_2$ (0.8 g, 1.9 mmol) and triphenylphosphine (0.8 g, 3 mmol) in hot ethanol (20 ml). After filtration the complex crystallised, on cooling, as brown needles, d.p. 224°C. The complex is soluble in acetone and chloroform, but insoluble in benzene and petroleum ether.

Anal. Calcd. for $C_{36}H_{30}ClN_2O_6P_2Co$: N, 3.6; P, 8.3; Co, 7.9; Cl, 4.8. Found: N, 3.9; P, 8.2; Co, 7.8; Cl, 4.8%.

Molar conductance (10^{-3} *M* solution in nitrobenzene at 20°C), 23.9 ohm^{-1} cm^2 mol^{-1}.

Bis(triphenylphosphine)dinitrosylcobalt tetrapheylborate. $[Co\{P(C_6H_5)_3\}_2(NO)_2][B(C_6H_5)_4]$. This complex was prepared in a similar manner to the perchlorate, except that sodium tetraphenylborate was used instead of sodium perchlorate. Brown-red powder, d.p. 145°C.

Anal. Calcd. for $C_{60}H_{50}BN_2O_2P_2Co$: N, 2.9; P, 6.4; Co, 6.1. Found: N, 3.0; P, 6.3; Co, 6.1%.

Molar conductance (10^{-3} *M* solution in nitrobenzene at 20°C), 17.1 ohm^{-1} cm^2 mol^{-1}.

Tris(triphenylphosphine)nitrosylcobalt. $Co[P(C_6H_5)_3]_3(NO)$. a) A solution of $Co_2Cl_2(NO)_4$ (0.5 g, 1.6 mmol) and triphenylphoshpine (3.5 g, 13.3 mmol) in ethanol (30 ml) was treated with stirring with an ethanolic solution of sodium borohydride (0.3 g,

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(1) Part I A. Sacco, M. Rossi, and C. F. Nobile, *Ann. Chim.*, 499 (1967).
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(3) W. Hieber and G. Neumair, *Z. An. All. Chem.*, *342*, 92 (1966).
(4) A. Sacco, M. Rossi, C. F. Nobile, and L. Uva, *Chim. e Ind.* (1t), 48, 986 (1966).

7.0 mmol). The resulting dark violet precipitate was washed with ethanol and crystallised from tetrahydrofuran by adding petroleum ether. Yield 2.6 g (96%). The complex is soluble in benzene, but insoluble in ethanol and in petroleum ether; d.p. 208°C.

Anal. Calcd. for $C_{54}H_{45}NOP_3Co$: N, 1.6; P, 10.6; Co, 6.7. Found: N, 1.6; P, 10.6; Co, 6.6%.

b) A mixture of $CoCl[P(C_6H_5)_3](NO)_2$ (1.0 g, 2.4 mmol) and triphenylphosphine (1.9 g, 7.2 mmol) was finely ground with zinc powder (0.5 g, 7.6 mmol) and heated till 150°C for 10 hours.

The crude reaction product, after cooling, was dissolved in tetrahydrofuran and crystallised by adding petroleum ether. The product was identified by means of its I.R. spectrum and elemental analysis. (Found: N, 1.5; P, 10.7; Co, 6.6%).

Dichloro1,2-bisdiphenylphosphinoethanetetranitrosyldicobalt. $Co_2Cl_2\{C_2H_4(PPh_2)_2\}(NO)_4$. a) A solution of $C_2H_4(PPh_2)_2$ (1.0 g, 2.6 mmol) in hot ethanol (20 ml) was added to a solution of $Co_2Cl_2(NO)_4$ (0.8 g, 2.6 mmol) in ethanol (20 ml). The resulting dark brown precipitate was washed with ethanol and dried; d.p. 188°C.

Anal. Calcd. for $C_{26}H_{24}Cl_2N_4O_4P_2Co_2$: N, 7.9; P, 8.8; Co, 16.7; Cl, 10.0. Found: N, 8.0; P, 8.6; Co, 16.8; Cl, 10.1%.

b) A solution of $[CoCl_2(NO)_2][P(C_6H_5)_4]$ (0.6 g, 1.1 mmol) (this complex was prepared according to the literature[1]) in hot ethanol (20 ml) was added to a solution of $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]ClO_4$ (0.7 g, 1.1 mmol) in hot ethanol (20 ml). After filtration the complex crystallised, on cooling, as dark brown needles.

Anal. Found: N, 7.9; P, 8.7; Co, 16.8; Cl, 9.9%.

Dibromo1,2-bisdiphenylphosphinoethanetetranitrosyldicobalt. $Co_2Br_2\{C_2H_4(PPh_2)_2\}(NO)_4$. The compound was prepared as above from $[CoBr_2(NO)_2]P(C_6H_5)_4$ and $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]ClO_4$ in ethanol. Dark brown crystals, d.p. 162°-4°C.

Anal. Calcd. for $C_{26}H_{24}Br_2N_4O_4P_2Co_2$: N, 7.0; P, 7.8; Co, 14.8; Br, 20.1. Found: N, 6.9; P, 7.6; Co, 14.5; Br, 19.8%.

Diiodo1,2-bisdiphenylphosphinoethanetetranitrosyldicobalt. $Co_2I_2\{C_2H_4(PPh_2)_2\}(NO)_4$. The complex was prepared analogously from $Co_2I_2(NO)_4$ and $C_2H_4(PPh_2)_2$ in ethanol (a) and from $[CoI_2(NO)_2]P(C_6H_5)_4$ and $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]ClO_4$ in ethanol (b). Dark brown crystals, d.p. 169°-70°C.

Anal. Calcd. for $C_{26}H_{24}I_2N_4O_4P_2Co_2$: N, 6.3; P, 7.0; Co, 13.2; I, 28.5. Found (a): N, 6.4; P, 7.0; Co, 13.2; I, 27.9%. Found (b): N, 6.3; P, 6.9; I, 28.1%.

1,2-bisdiphenylphosphinoethanedinitrosylcobalt chloride. $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]Cl$. a) A solution of $C_2H_4(PPh_2)_2$ (1.5 g, 3.9 mmol) in benzene (10 ml) was added to a solution of $Co_2Cl_2(NO)_4$ (0.6 g, 1.9 mmol) in benzene (15 ml). The resulting crystalline precipitate was washed with benzene and dried. Dark red plates, d.p. 117°C. The complex is soluble in ethanol and chloroform, but insoluble in petroleum ether.

Anal. Calcd. for $C_{26}H_{24}ClN_2O_2P_2Co$: N, 5.1; P, 11.2; Co, 10.7; Cl, 6.4. Found: N, 4.9; P, 11.1; Co, 10.8; Cl, 6.4%. Molar conductance (10^{-3} *M* solution in nitrobenzene at 24°C), 22.6 ohm^{-1} cm^2 mol^{-1}.

b) A solution of $C_2H_4(PPh_2)_2$ (0.7 g, 1.7 mmol) in benzene (10 ml) was added to a hot solution of $Co_2Cl_2\{C_2H_4(PPh_2)_2\}(NO)_4$ in benzene (40 ml). The complex crystallised, on cooling, as dark red plates. It was identified by means of its I.R spectrum and elemental analysis. (Found: N, 5.0; P, 11.0; Cl, 6.4%).

1,2-bisdiphenylphosphinoethanedinitrosylcobalt perchlorate. $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]ClO_4$. A solution of $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]Cl$, in ethanol was treated with an ethanolic solution of sodium perchlorate. The resulting red precipitate was washed with ethanol and dried; d.p. 206°C.

Anal. Calcd. for $C_{26}H_{24}ClN_2O_6P_2Co$: N, 4.5; P, 10.0; Co, 9.6; Cl, 5.7. Found: N, 4.5; P, 9.9; Co, 9.5; Cl, 5.6%.

Molar conductance (10^{-3} *M* solution in nitrobenzene at 20°C), 28.8 ohm^{-1} cm^2 mol^{-1}.

1,2-bisdiphenylphosphinoethanedinitrosylcobalt tetraphenylborate. $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]B(C_6H_5)_4$. a) This complex was prepared in a similar manner to the perchlorate, but using sodium tetraphenylborate instead of sodium perchlorate. It is a red powder, d.p. 188°C, soluble in acetone and chloroform, but insoluble in ethanol and benzene.

Anal. Calcd. for $C_{50}H_{44}BN_2O_2P_2Co$: N, 3.3; P, 7.4; Co, 7.1. Found: N, 3.2; P, 7.4; Co, 7.0%. Molar conductance (10^{-3} *M* solution in nitrobenzene at 20°C), 18.4 ohm^{-1} cm^2 mol^{-1}.

b) A solution of $Co_2Cl_2\{C_2H_4(PPh_2)_2\}(NO)_4$ in hot ethanol was treated with an excess of sodium tetraphenylborate. The resulting precipitate was washed with ethanol and dried. The product was identified by means of its d.p. and I.R. spectrum.

Tris{1,2-bisdiphenylphosphinoethane}dinitrosyldicobalt. $Co_2\{C_2H_4(PPh_2)_2\}_3(NO)_2$. a) A suspension of $Co_2Cl_2\{C_2H_4(PPh_2)_2\}(NO)_4$ (2.0 g, 2.8 mmol) and of $C_2H_4(PPh_2)_2$ (2.3 g, 5.8 mmol) in ethanol (30 ml) was treated, with stirring with zinc powder (1.0 g, 15 mmol) for 4 hours. The resulting residue was filtered off and crystallised from benzene by adding petroleum ether. The red crystals, d.p. 314°C, are soluble in chloroform, but insoluble in ethanol.

Anal. Calcd. for $C_{78}H_{72}N_2O_2P_3Co_2$: N, 2.0; P, 13.5; Co, 8.6; M, 1372. Found: N, 2.0; P, 13.4; Co, 8.5%; M, 1360 (cryoscopically in benzene solution).

b) The complex was prepared in an analogous way from $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]Cl$ (0.8 g, 1.5 mmol), $C_2H_4(PPh_2)_2$ (1.2 g, 3.0 mmol) and zinc powder. The product was crystallised from benzene by adding ethanol. It was identified by means of its I.R. spectrum and elemental analysis (Found: N, 1.9; P, 13.4; Co, 8.4%).

Table I. Infrared absorption bands of triphenylphosphinenitrosyl-complexes

Compound	ν_{NO}(cm^{-1})	Solvent
$CoCl(PPh_3)(NO)_2$	1820 (s), 1765 (s), 1735 (s)	nujol
$CoCl(PPh_3)(NO)_2$	1816 (s), 1750 (s)	benzene
$CoCl(PPh_3)(NO)_2$	1835 (s), 1775 (s)	ethanol
$[Co(PPh_3)_2(NO)_2]ClO_4$	1848 (s); 1796 (vs)	nujol
$[Co(PPh_3)_2(NO)_2]ClO_4$	1850 (s), 1800 (vs)	chloroform
$[Co(PPh_3)_2(NO)_2]BPh_4$	1860 (s), 1796 (vs)	nujol
$[Co(PPh_3)_2(NO)_2]BPh_4$	1850 (s), 1800 (vs)	chloroform
$Co(PPh_3)_3(NO)$	1633 (s)	nujol
$Co(PPh_3)_3(NO)$	1670 (s)	benzene

Table II. Molar conductance of $Co_2Br_2dp(NO)_4$ and $Co_2I_2dp(NO)_4$ in 10^{-3} *M* nitrobenzene solution at 24°C under nitrogen atmosphere.

Compound	t(min)	Λ(ohm^{-1} cm^2 mol^{-1})
$Co_2Br_2dp(NO)_4$	5	10.7
	20	15.9
	30	18.2
	45	19.8
	70	20.8
	90	21.0
$Co_2I_2dp(NO)_4$	5	10.6
	30	14.0
	40	15.2
	70	19.0
	100	21.0
	120	21.2

Dichloro 1,2-bisdiphenylphosphinoethanenitrosylcobalt. $CoCl_2\{C_2H_4(PPh_2)_2\}(NO)$. A suspension of $[Co\{C_2H_4(PPh_2)_2\}(NO)_2]Cl$ (0.8 g, 1.45 mmol) in benzene (20 ml) was treated with a benzene solution (10 ml) of $C_2H_4(PPh_2)_2$ (1.1 g, 2.9 mmol) with stirring for 24 hours. The resultant mixture was filtered and the solid was washed with benzene. The benzene soluble fractions were collected and after concentration, by adding petroleum ether red crystals of $Co_2\{C_2H_4(PPh_2)_2\}_3(NO)_2$ (0.24 g, 0.17 mmol) were obtained and identified by means of I.R. spectrum and elemental analysis (Found: N, 1.8; P, 13.6; Co, 8.7%).

The solid residue left from the extraction with original mixture was treated with ethanol (5 ml), obtaining an insoluble residue and a soluble fraction. By adding sodium tetraphenylborate to the ethanolic solution the compound $[Co\{C_2H_4(PPh_2)_2\}(NO)_2][B(C_6H_5)_4]$ (0.6 g, 0.73 mmol) was obtained; it was identified by means of its d.p. and I.R. spectrum.

The solid residue left from the extraction with ethanol, crystallised from chloroform by adding methanol gave dark brown crystals of the complex (0.2 g, 0.37 mmol) d.p. 188°-9°C.

The complex is soluble in chloroform and in tetrahydrofuran, but insoluble in methanol and in petroleum ether; it is stable to the air. *Anal.* Calcd. for $C_{26}H_{24}Cl_2NOP_2Co$: N, 2.4; P, 11.1; Co, 10.6; Cl, 12.7. Found: N, 2.2; P, 11.2; Co, 10.7; Cl, 12.5%.

Results and Discussion

Triphenylphosphinenitrosyl-complexes. Triphenylphosphine reacts under mild conditions with μ-dichlorotetranitrosyldicobalt according to the following reactions:

$$Co_2Cl_2(NO)_4 + 2PPh_3 \rightarrow \underset{\mathbf{I}}{2CoCl(PPh_3)(NO)_2} \qquad (1)$$

$$CoCl(PPh_3)(NO)_2 + PPh_3 \rightleftharpoons \underset{\mathbf{II}}{[Co(PPh_3)_2(NO)_2]^+} + Cl^- \qquad (2)$$

The compound **II** is formed in equilibrium with **I** only when a large excess of free ligand is added to an ethanolic solution of **I**. In fact, by adding triphenylphosphine to a solution of $CoCl(PPh_3)(NO)_2$ in ethanol, the conductance of the solution increases from about 4 to a maximum of 31.4 ohm^{-1} cm^2 mol^{-1} for a molar ratio PPh_3/Co of 20. Moreover, the I.R. bands of the starting complex in ethanol (1835 and 1775 cm^{-1}) are shifted in the presence of an excess of triphenylphosphine to 1855 and 1807 cm^{-1}; these values are similar to those found for the complex $[Co(dp)_2(NO)_2]Cl$ (see Table IV). The equilibrium (2) can be quantitatively displaced to the right by adding, beside an excess of ligand, a bulky anion like ClO_4^- or BPh_4^-, which give insoluble salts with the cation $[Co(PPh_3)_2(NO)_2]^+$. On the contrary, the equilibrium (2) is displaced to the left in the presence of an excess of the halide ion. Thus, starting from $[Co(PPh_3)_2(NO)_2]ClO_4$ and KCl in ethanol the compound I is obtained. Compounds **I** and **II** can be reduced in the presence of free ligand with sodium borohydride or zinc, yielding the compound of formula $Co(PPh_3)_3(NO)$. With $NaBH_4$ the reduction occurs easily at room temperature, whereas with zinc more vigorous conditions are required.

1,2-bisdiphenylphosphinoethanenitrosyl-complexes. The reaction between $Co_2X_2(NO)_4$ (X = Cl, Br and I) and the 1,2-bisdiphenylphosphinoethane (dp) in solution gives several products according to the following scheme:

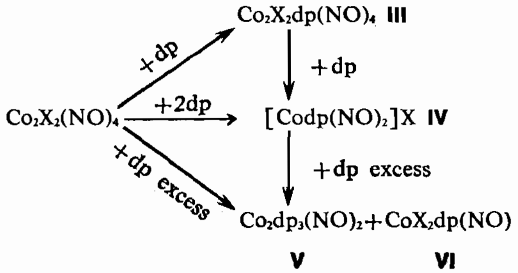


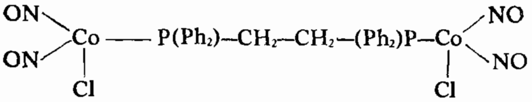
Table III. Infrared absorption bands of $Co_2X_2dp(NO)_4$ complexes

X	$\nu_{NO}(cm^{-1})$	Solvent
Cl	1815 (s), 1740 (vs), 1170 (s)	nujol
Cl	1818 (s), 1760 (vs), 1170 (m)	benzene
Cl	1850 (s), 1800 (vs), 1760 (w)	ethanol
Cl	1850 (s), 1800 (vs), 1758 (w)	nitrobenzene
Br	1818 (s), 1755 (vs), 1170 (s)	nujol
Br	1827 (s), 1765 (vs), 1170 (m)	benzene
Br	1850 (s), 1827 (m), 1800 (vs), 1765 (s)	nitrobenzene
I	1820 (s), 1833 (s), 1782 (s) 1775 (s), 1170 (s)	nujol
I	1833 (s), 1773 (vs), 1170 (m)	benzene
I	1850 (s), 1833 (s), 1800 (vs), 1773 (s)	nitrobenzene

Table IV. Infrared absorption bands of 1,2-bis(diphenylphosphine)ethanenitrosyl-complexes

Compound	$\nu_{NO}(cm^{-1})$	Solvent
$[Codp(NO)_2]Cl$	1854 (s), 1795 (vs)	nujol
$[Codp(NO)_2]Cl$	1850 (s), 1800 (vs)	chloroform
$[Codp(NO)_2]ClO_4$	1856 (s), 1795 (vs)	nujol
$[Codp(NO)_2]ClO_4$	1850 (s), 1800 (vs)	chloroform
$[Codp(NO)_2]BPh_4$	1845 (s), 1795 (vs)	nujol
$[Codp(NO)_2]BPh_4$	1850 (s), 1800 (vs)	chloroform
$Co_2(dp)_3(NO)_2$	1655 (s)	nujol
$CoCl_2dp(NO)$	1676 (s)	chloroform

The complexes **III** are obtained either by carrying out the reaction in ethanol with a molar ratio dp/Co of 0.5, or from $[CoX_2(NO)_2][PPh_4]$ and $[Codp(NO)_2]ClO_4$ in ethanol. These dark brown compounds are slight soluble in ethanol and in benzene. In a recent paper other authors have described a compound of this formula (X = Cl), assigning the following probable structure:[3]



III A

However, we found that the compounds **III** exist in two forms, according to the following equilibrium:

$$\underset{\textbf{III}}{Co_2X_2dp(NO)_4} \rightleftarrows \underset{\textbf{III B}}{[Codp(NO)_2]^+ + [CoX_2(NO)_2]^-} \quad (3)$$

In fact, the behaviour of these complexes in polar and in non polar solvents is quite different. First at all, the molar conductance of compounds III in polar solvents (nitrobenzene and ethanol), under nitrogen atmosphere, increases with the time, approaching the value of a uni-univalent electrolyte (see Table II).

Moreover, the I.R. spectra of the compounds in the same solvents agree with the ionic form. Thus three bands for the chloro derivative and four bands for the bromo and iodo derivatives are present in the region of the nitrosyl stretching frequency (see Table III).

The frequency values of these bands are comparable with those found in $[Codp(NO)_2]Cl$ (1850 and 1800 cm^{-1}) and in $[CoX_2(NO)_2][PPh_4]$ (1832-5 and 1750-63 cm^{-1}).[1]

On the contrary, the I.R. spectra of the compounds III in benzene solution are similar to those of the triphenylphosphine derivatives of formula $CoX(PPh_3)(NO)_2$, and only two bands in the region 1500-1900 cm^{-1} are present.

Thus, both I.R. spectra and molar conductance measurement strongly support the presence of the ionic form **III B** in polar solvents. The presence of a covalent form of **III** in benzene solution or in the solid state may be also reasonably supposed.

However, we have not any evidence supporting the structure **III A**. A strong band at 1170 cm^{-1} present in the I.R. spectra of the complexes **III** in nujol or in benzene solution may suggest the presence of a bridging hyponitrite group. In fact, bands in this region (1140 and 1050 cm^{-1}) have been found in the red series of the nitrosopentammine salts of cobalt[5,6,7] for which a dimeric structure involving a bridging hyponitrite group has been confirmed by X-Ray examination.[8] The compound $[Codp(NO)_2]Cl$ is formed either from $Co_2Cl_2(NO)_4$ and 1,2-bisdiphenylphosphinoethane with molar ratio dp/Co of 1 and from $Co_2Cl_2dp(NO)_4$ and dp with molar ratio dp/Co of 0.5. It behaves as an uni-univalent electrolyte in polar solvents, and it is quite stable. Both the compounds $Co_2(dp)_3(NO)_2$ and $CoCl_2dp(NO)_2$ were obtained starting from $CoCl_2(NO)_4$ and the diphosphine with a molar ratio dp/Co>3 and from $[Codp(NO)_2]Cl$ and diphosphine with a molar ratio dp/Co>1. In the last case the reaction occurs according the following equation:

$$4[Codp(NO)_2]Cl + dp = Co_2dp_3(NO)_2 + 2CoCl_2dp(NO) + 4NO$$

The reaction between $[Codp(NO)_2]Cl$ or $Co_2Cl_2dp(NO)_4$ and the diphosphine in the presence of zinc as reducing agent gives only the compound $Co_2dp_3(NO)_2$. The I.R. spectrum and the physical properties of this complex are identical to those previously reported.[3]

The compound $CoCl_2dp(NO)$, formally similar to the already described[9] derivative of formula $CoCl_2(PEt_3)_2(NO)$, is thermally more stable than this latter and it is quite stable to the air.

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