

Mixed-Ligand Complexes of Five-Coordinate Cobalt(I) with Carbonyls, Phosphines, and Isocyanides

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The preparation and characterization of five-coordinate cobalt(I) mixed-ligand complexes of the types $[\text{Co}(\text{CO})_2\text{L}_2]$, $[\text{Co}(\text{CO})_2\text{L}_3]^+$, $[\text{Co}(\text{CNR})_2\text{L}_3]^+$, and $[\text{Co}(\text{CNR})_3\text{L}_2]^+$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_2\text{OC}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, $o\text{-CH}_3\text{C}_6\text{H}_4$, $(\text{CH}_3)_2\text{C}_6\text{H}_3$, C_6H_{11} ; $\text{L} = \text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2$ or $\text{P}(\text{OCH}_3)_3$), obtained by reaction of CO or CNR with $[\text{CoXL}_4]^+$ ($\text{X} = \text{Cl}$, Br , I) cations, are described. Trigonal-bipyramidal structures with carbonyl or isocyanide ligands in equatorial positions have been deduced from infrared and pmr spectra. The $[\text{Co}(\text{CO})_2\text{L}_3]^+$ complex is nonrigid at room temperature.

Introduction

Syntheses of five-coordinate cobalt(I) complexes with π -acceptor ligands such as CO, CN^- , phosphines, and isocyanides have been accomplished by several methods including (a) disproportionation of cobalt(II)² or cobalt(0)³ compounds, (b) reduction of cobalt(II) complexes by coordinated ligands⁴ or other reducing agents (hydrazine, dithionite, or metals)⁵ (in many cases the stoichiometry of the reaction is uncertain and the nature of the reducing agent has not been determined) (c) addition of the fifth ligand to tetrahedral cobalt(I) complexes,⁶ and (d) substitution of one or more neutral ligands on other five-coordinate cobalt(I) compounds. The last method has been used to prepare carbonyl-phosphine⁷ and phosphine-isocyanide⁸ mixed-ligand cobalt(I) complexes.

Halpern, *et al.*,^{2a,4a} synthesized the complexes $[\text{Co}(\text{CN})_3(\text{CO})_2]^{2-}$, $[\text{Co}(\text{CN})_2(\text{CO})_2\text{PR}_3]^-$, $[\text{Co}(\text{CN})_2(\text{CO})(\text{PR}_3)_2]^-$, and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PR}_3)_2]$ and considerable attention has been devoted to low-spin tricarbonylbis(phosphine)cobalt(I) compounds. However, the corresponding cationic dicarbonyltriphosphine complexes have not been previously reported. Much work has also been done on the synthesis and characterization of pentakis(isocyanide)cobalt(I) compounds,⁵ but, except for a recent paper by King and Saran⁸ and brief reports by Sacco and Freni^{9a} and Boylan, *et al.*,^{9b} no published information exists on phosphine derivatives of the type $[\text{Co}(\text{CNR})_x(\text{PR}_3)_{5-x}]^+$.

In this paper we describe the reactions of $[\text{CoXL}_4]^+$ complexes ($\text{X} = \text{Cl}$, Br , I ; $\text{L} =$ diethyl phenylphosphonite) with π -acceptor ligands such as CO and isocyanides to form $[\text{Co}(\text{CO})_2\text{L}_3]^+$ and $[\text{Co}(\text{CNR})_x\text{L}_{5-x}]^+$ cations ($x = 2$ or 3 ; $\text{R} =$

ortho- or para-substituted phenyl or cyclohexyl moiety). The reduction of cobalt(II) to cobalt(I) has been investigated in order to ascertain the nature of the reducing species.

Experimental Section

Materials. Commercial reagent grade chemicals and anhydrous cobalt(II) halides were used without further purification. The solvents were purified and dried by standard methods and distilled under a current of nitrogen just prior to the use.

Diethyl phenylphosphonite, $\text{PhP}(\text{OEt})_2$, was prepared by the method of Rabinowitz and Pellon.¹⁰ The substituted phenyl and the cyclohexyl isocyanides were obtained by the phosgene method of Ugi, *et al.*¹¹ The complexes of the type $[\text{CoX}(\text{PhP}(\text{OEt})_2)_4]\text{Y}$ ($\text{X} = \text{Cl}$, Br , or I ; $\text{Y}^- = \text{ClO}_4^-$ or BPh_4^-) were prepared from diethyl phenylphosphonite and the appropriate cobalt(II) halide was prepared by published methods.¹²

CO Absorption Measurements. The apparatus and procedure used to determine the uptake of CO have been described elsewhere.¹³ Weighed samples of $[\text{CoX}(\text{PhP}(\text{OEt})_2)_4]\text{Y}$ sealed in a thin-walled glass ampoule were placed in a 100-ml reaction flask equipped with an outer jacket for thermostating. The apparatus was evacuated and a known volume of solvent (20–40 ml) was injected by a syringe through a serum cap. The solvent was left to reach thermal equilibrium (30 min), the vapor pressure was measured, and the solution was equilibrated at 1 atm with CO. Making allowance for the vapor pressure of the solvent, the constant partial pressure of CO was 420 or 580 mm when the solvent was dichloromethane or acetone, respectively. The ampoule was then allowed to drop into the solution, where it was broken by the magnetic stirrer and the volume of CO taken up at constant pressure was measured.

Apparatus. Magnetic susceptibilities in solution were measured by the method of Evans¹⁴ and corrected for diamagnetism of the ligands from tables given by Figgis and Lewis.¹⁵ Pmr measurements were made with Hitachi Perkin-Elmer R-20A and Bruker HFX-10 instruments using TMS as internal reference. The Bruker instrument was equipped with a variable-temperature probe. Conductivities of 10^{-3} M solutions of complexes in nitrobenzene at 25° were measured with an LKB bridge. Infrared spectra of KBr pellets and dichloromethane solutions were recorded on a Perkin-Elmer 621 spectrophotometer.

Syntheses of Complexes. All the preparative work was carried out under nitrogen. The halogenotetrakis(diethyl phenylphosphonite)cobalt(II) complexes were kept under inert atmosphere. The cobalt(I) derivatives described below are stable in the normal laboratory conditions and therefore they were manipulated without special precautions.

Dicarbonyltris(diethyl phenylphosphonite)cobalt(I) Tetraphenylborate and Iododicarbonylbis(diethyl phenylphosphonite)cobalt(I).

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Table I. Properties of Some Five-Coordinated Cobalt(I) Complexes

Compd ^a	Color	Mp, ^b °C	Molar conduct- ance ^c	% C		% H		% N		% halide		% P	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(CO) ₂ L ₃]BPh ₄	Yellow	128	15.4	65.40	65.57	6.33	6.23					9.05	8.65
[CoI(CO) ₂ L ₂]	Red	122		41.40	41.49	4.70	4.67			19.90	19.42	9.72	9.09
[Co(C ₆ H ₅ NC) ₃ L ₂]BPh ₄	Yellow	115	15.5	72.05	73.39	6.06	6.25	3.87	3.41			5.73	5.98
[Co(<i>p</i> -NO ₂ C ₆ H ₄ NC) ₂ L ₃]ClO ₄	Brown	148	23.9	50.35	50.08	3.53	3.86	5.34	5.27	3.39	3.67	8.86	8.32
[Co(C ₆ H ₅ NC) ₃ L ₂]ClO ₄	Orange	133	24.4	57.00	55.96	5.21	5.43	4.87	4.98	4.11	4.31	7.18	6.95
[Co(<i>p</i> -CH ₃ C ₆ H ₄ NC) ₃ L ₂]ClO ₄	Yellow	107	23.8	58.30	58.32	5.64	5.62	4.64	4.14	3.92	4.20	6.85	6.61
[Co(<i>p</i> -CH ₃ OC ₆ H ₄ NC) ₃ L ₂]ClO ₄	Yellow	151	24.1	55.40	54.66	5.35	5.23	4.40	4.25	3.67	4.05	6.50	6.27
[Co(<i>o</i> -CH ₃ C ₆ H ₄ NC) ₃ L ₂]ClO ₄	Yellow	117	24.7	58.30	59.13	5.64	5.97	4.64	4.69	3.92	3.98	6.85	7.00
[Co(<i>o</i> -(CH ₃) ₂ C ₆ H ₃ NC) ₃ L ₂]ClO ₄	Orange	177	25.6	59.51	59.83	6.01	6.09	4.43	4.81	3.69	4.08	6.55	6.37
[Co(C ₆ H ₁₁ NC) ₃ L ₂]ClO ₄	Yellow	103	24.7	55.85	55.24	7.15	7.16	4.77	4.76	4.03	4.15	7.03	7.06
[Co(<i>p</i> -NO ₂ C ₆ H ₄ NO) ₃ L ₂]ClO ₄	Brown	170	24.3	38.10	38.57	3.53	3.86	9.88	10.1	4.12	4.71	7.29	7.12
[Co(C ₆ H ₅ NC) ₃ L ₂]ClO ₄	Yellow	207	24.6	45.32	44.63	4.61	4.70	5.88	5.72	4.89	4.99	8.67	9.05
[Co(<i>o</i> -(CH ₃) ₂ C ₆ H ₃ NC) ₃ L ₂]ClO ₄	Orange	166	26.1	49.55	48.85	5.63	5.63	5.27	5.37	4.45	4.80	7.76	7.34

^a L = PhP(OEt)₂, L' = P(OMe)₃. ^b Melting points were determined in capillaries and uncorrected. ^c Molar conductances were determined in 10⁻³ M nitrobenzene solutions at 25°.

These two complexes were prepared simultaneously. Freshly made [CoI(PhP(OEt)₂)₄]BPh₄ (13 g, 10 mmol) (or equivalent amounts of anhydrous cobalt(II) iodide, diethyl phenylphosphonite, and sodium tetraphenylborate in the ratio 1:4:1) placed in 80 ml of anhydrous acetone or dichloromethane previously flushed out with CO was vigorously stirred for 4 hr at room temperature under an atmosphere of CO. The addition of anhydrous ethanol (100–150 ml) to the filtered and concentrated (15 ml) reaction mixture gave orange-red [CoI(CO)₂(PhP(OEt)₂)₂] which was recrystallized from ethanol. The yellow [Co(CO)₂(PhP(OEt)₂)₃]BPh₄ was obtained by reducing the mother liquor to a small volume (20 ml) and was recrystallized from ethanol-ether.

Tris(isocyanide)bis(phosphine)cobalt(I) Complexes. The complexes of the type [Co(CNR)₃L₂]Y (CNR = cyclohexyl, phenyl, *p*-methoxyphenyl, *p*-methylphenyl, *p*-nitrophenyl, *o*-methylphenyl, *o*-dimethylphenyl isocyanide; L = diethyl phenylphosphonite or trimethyl phosphite; Y⁻ = perchlorate or tetraphenylborate) were originally prepared by treating an ethanolic solution of a halogenotetrakis(diethyl phenylphosphonite)cobalt(II) tetraphenylborate with the appropriate isocyanide at room temperature, but the following general method is more simple.

Anhydrous cobalt(II) chloride (1.3 g, 10 mmol) and diethyl phenylphosphonite (7.0 g, 35 mmol, or an equivalent amount of trimethyl phosphite) were placed in 80 ml of anhydrous ethanol. Addition of the appropriate isocyanide (25 mmol) at room temperature to the magnetically stirred solution gave an exothermic reaction and the color changed from deep-green to yellow. The yellow precipitate formed immediately after the addition of lithium perchlorate (or sodium tetraphenylborate) (10 mmol) was recrystallized from anhydrous ethanol.

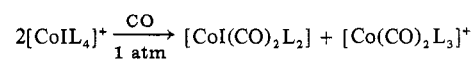
Special care must be taken to prepare the complexes with trimethyl phosphite and cyclohexyl and *o*-dimethylphenyl isocyanide. To avoid hydrolysis of the phosphite ester, methanol was used in the preparation of tris(isocyanide)bis(trimethyl phosphite)cobalt(I) perchlorate complexes. The tris(cyclohexyl isocyanide)bis(diethyl phenylphosphonite)cobalt(I) and the tris(*o*-dimethylphenyl isocyanide)-bis(phosphine)cobalt(I) perchlorate complexes are less stable and more soluble in polar and nonpolar organic solvents than the other complexes. For this reason they were recrystallized by adding a large volume (500 ml) of diethyl ether to a concentrated (20 ml) ethanolic solution.

Bis(*p*-nitrophenyl isocyanide)tris(diethyl phenylphosphonite)cobalt(I) perchlorate was obtained by the general method using the same molar ratios as for the other isocyanide derivatives, although the ratio between *p*-NO₂C₆H₄NC and PhP(OEt)₂ in this complex is different (2:3 instead of 3:2).

Results and Discussion

Products. (a) Carbonyl Complexes. Anhydrous acetone or dichloromethane solution of the halogenotetrakis(diethyl phenylphosphonite)cobalt(II) complexes [CoXL₄]Y (X = Cl, Br, or I; L = PhP(OEt)₂; Y⁻ = ClO₄⁻ or BPh₄⁻) take up CO at 1 atm and room temperature with the disappearance of the deep green color characteristic of these five-coordinate cobalt(II) compounds. Information on the stoichiometry of the reaction has been obtained using [CoIL₄]BPh₄, which reacts faster than the corresponding chloro or bromo deriva-

tives, as the starting complex. The quantitative formation of equivalent amounts of iododicarbonylbis(diethyl phenylphosphonite)cobalt(I) and dicarbonyltris(diethyl phenylphosphonite)cobalt(I) cation in accordance with the reaction



is confirmed by the recovery in quantitative yield (≥95% on the cobalt(II) complex) of the diamagnetic dicarbonyl compounds. The infrared spectrum of the final reaction mixture in the carbonyl stretching region is identical with that of a 1:1 solution of [CoI(CO)₂L₂] and [Co(CO)₂L₃]⁺ in dichloromethane. Several tricarbonylbis(phosphine)cobalt(I) complexes are reported in the literature,³ but in our case the reaction does not go beyond the absorption of two CO molecules per cobalt atom and the [Co(CO)₂L₃]⁺ complex seems to be the first monomeric dicarbonyltris(phosphine)cobalt(I) compound to have been isolated.¹⁶

In several experiments in which the CO uptake was measured, the average ratio of moles of CO absorbed per moles of cobalt(II) complex used was 2.48, and no paramagnetic products (using the Evans method¹⁴) were found in the final solution, indicating that no disproportionation of the cobalt(II) substrate occurred. This seems to suggest that CO is the reducing agent. However, the role of phosphine, the complete stoichiometry, the nature of other carbonyl intermediates, and the reduction mechanism will be the subject of a future communication.

The dicarbonyl complexes are air stable in the solid state and in solution of organic solvents such as acetone, 1,2-dichloroethane, dichloromethane, and tetrahydrofuran. The orange-red [CoI(CO)₂L₂] is nonconducting, whereas the yellow [Co(CO)₂L₃]BPh₄ is a 1:1 electrolyte (Λ_m = 15.4 ohm⁻¹ cm² mol⁻¹ in nitrobenzene at 25°). Their infrared and pmr spectra are in agreement with the formulation based on elemental analysis (Table I) and indicate the presence of the phosphine ligands and two terminal carbonyl groups in a *cis* configuration.

The values of the CO stretching frequencies reported in Table II suggest that the nature of the anionic ligand does not influence significantly the CO π-bonding ability (no. 3–5). However, other data^{2b} show that this is strictly true only for σ-bonding anions, and differences of about 10–15 cm⁻¹ can be observed in the ν(CO) frequency of [CoX(CO)₂L₂] complexes on changing X from a halide to thio-

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Table II. Ir Spectral Data for Some Complexes of the Type [CoX(CO)₂L₂] (X = Br, I, CN; L = Phosphine)

No.	Compd	cm ⁻¹		Solvent	Ref
		ν (CO) _{as}	ν (CO) _{sym}		
1	[Co(CO) ₂ (PhP(OEt) ₂) ₂] ⁺	1972	2021	CH ₂ Cl ₂	
2	[CoI(CO) ₂ (PhP(OEt) ₂) ₂]	1935	1996	CH ₂ Cl ₂	
3	[CoBr(CO) ₂ (PEt ₃) ₂]	1905	1975	CH ₂ Cl ₂	2b
4	[CoI(CO) ₂ (PEt ₃) ₂]	1905	1975	CH ₂ Cl ₂	2b
5	[CoCN(CO) ₂ (PEt ₃) ₂]	1905	1968	4a	
6	[CoI(CO) ₂ (PhPEt ₂) ₂]	1910	1975	CH ₂ Cl ₂	2b
7	[CoI(CO) ₂ (P(<i>n</i> -Bu) ₃) ₂]	1908	1973	C ₇ H ₁₆	7

Table III. ¹H Nmr Spectral Data for Some Five-Coordinated Cobalt(I) Complexes^a

Compd ^b	Phenyl protons (phosphine and/or isocyanide)	CH ₂ phosphine	CH ₂ isocyanide	CH ₃ phosphine
[CoI(CO) ₂ L ₂] ^c	2.18 br 2.59 br	5.97 m		8.71 t
[Co(CO) ₂ L ₂]BPh ₄	2.56 br 3.15 br	6.14 m		8.80 t
[Co(<i>p</i> -NO ₂ C ₆ H ₄ NC) ₂ L ₂]ClO ₄	1.70 t 2.35 br	5.98 br		8.64 q ^d
	2.45 d 2.99 d	6.10 br		
[Co(C ₆ H ₅ NC) ₃ L ₂]BPh ₄	2.70 br	5.95 m		8.70 t
[Co(C ₆ H ₅ NC) ₃ L ₂]ClO ₄	2.80 br	5.95 m		8.73 t
[Co(<i>p</i> -CH ₃ C ₆ H ₄ NC) ₃ L ₂]ClO ₄	2.50 br 2.90 br	5.80 m	7.62 s	8.62 t
[Co(<i>p</i> -CH ₃ OC ₆ H ₄ NC) ₃ L ₂]ClO ₄	2.50 br 2.98 br	5.86 m	6.16 s	8.64 t
[Co(<i>o</i> -CH ₃ C ₆ H ₄ NC) ₃ L ₂]ClO ₄	2.30 br 2.80 br	5.93	7.88 s	8.73 t
[Co(<i>o</i> -(CH ₃) ₂ C ₆ H ₃ NC) ₃ L ₂]ClO ₄	2.65 br 2.89 br	6.05 m	7.87 s	8.78 t
[Co(C ₆ H ₁₁ NC) ₃ L ₂]ClO ₄ ^e	2.30 br 2.51 br			8.67 t
[Co(<i>p</i> -NO ₂ C ₆ H ₄ NC) ₃ L ₂]ClO ₄ ^e	1.63 d 2.38 d			6.09 t
[Co(C ₆ H ₅ NC) ₃ L ₂]ClO ₄	2.59 br			6.10 t
[Co(<i>o</i> -(CH ₃) ₂ C ₆ H ₃ NC) ₃ L ₂]ClO ₄	2.87 m		7.58 s	6.20 t

^a The spectra were measured in CDCl₃ unless otherwise stated. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^b L = PhP(OEt)₂ and L' = P(OMe)₃. ^c In (CD₃)₂CO. ^d In (CD₃)₂CO and (CD₃)₂SO two triplets (1:2) (*J* = 7 Hz) at τ 8.57–8.70 and 8.64–8.77 are present, respectively. ^e The chemical shifts of methylene and methyne protons of the cyclohexyl isocyanide are at τ 8.34 and at 6.41, respectively.

cyanato or cyanide. While the highest ν (CO) of the dicarbonyltris(diethyl phenylphosphonite)cobalt(I) compound (no. 1) can be explained in terms of cationic charge which, by decreasing the Co→CO π interaction, increases the CO bond order, the higher CO stretching frequency of the iododicarbonylbis(diethyl phenylphosphonite)cobalt(I) complex (no. 2), compared to those of the other analogous compounds (4, 6, 7), must be attributed to the stronger π interaction of PhP(OEt)₂ compared to those of aryl or alkyl tertiary phosphines.

(b) **Isocyanide Complexes.** These cationic complexes were first prepared by simply adding the appropriate isocyanide to an anhydrous ethanol or acetone solution of [CoXL₄]⁺BPh₄⁻ (X = Cl, Br, or I; L = PhP(OEt)₂ at room temperature, but since the halogenotetrakis(diethyl phenylphosphonite)cobalt(II) is immediately formed, a solution of cobalt(II) halide and PhP(OEt)₂ or P(OMe)₃ in the molar ratio 1:4 can equally well be used as starting material. After the addition of the isocyanide the product can be precipitated as perchlorate or tetraphenylborate. The isocyanide derivatives are yellow or orange solids which can be handled under normal laboratory conditions. They are diamagnetic, 1:1 electrolytes in nitrobenzene at 25° (Table I), readily soluble in polar organic solvents such as acetone, 1,2-dichloroethane, and dichloromethane and slightly soluble in diethyl ether, benzene, and hydrocarbons. The yields were always good (~90%) except for complexes containing trimethyl phosphite, *o*-dimethylphenyl isocyanide, and cyclohexyl isocyanide, which undergo some decomposition in solution and are quite soluble even in nonpolar organic solvents such as diethyl ether.

Infrared and pmr spectra have been used to characterize and to confirm the formulas of the isocyanide-cobalt(I) complexes reported in this work. In the pmr spectra of [Co(CNR)₃L₂]⁺ cations (L = PhP(OEt)₂ or P(OMe)₃) there is a

1:2:1 triplet (*J* = 7 Hz) at τ 8.62–8.77 or 6.09–6.20 due to methyl protons of the diethyl phenylphosphonite or trimethyl phosphite ligands, respectively. The sharp singlet, between τ 7.62 and 7.78, is due to the protons of methyl groups in the ortho or para positions of the phenyl ring of the isocyanide ligands (the coordinated *p*-methoxyphenyl isocyanide has a singlet at τ 6.16). The ratios between the intensities of the resonance lines of the phosphine methyl protons and those of the signals of the isocyanide methyl protons have been used to establish the relative numbers of the two types of ligands in these complexes. For the complexes with

phenyl, *p*-nitrophenyl, and cyclohexyl isocyanide, the ratios of the phosphine methyl protons and the ring or methylene protons were used for the same purpose.

In addition to absorptions characteristic of the phosphine ligands, the infrared spectra of the mixed-ligand [Co(CNR)₃L₂]⁺ cations show strong absorptions in the ν (CN) frequency region which are assigned to terminal isocyanides coordinated to the cobalt atom. Unfortunately, since the compounds are ionic, it has not been possible to measure the frequencies in nonpolar solvents and the bands are usually quite broad and inadequately resolved. The general pattern of the spectra is a very weak shoulder in the region 2115–2138 cm⁻¹, a strong band between 2060 and 2090 cm⁻¹, and a shoulder at 1998–2052 cm⁻¹. A similar pattern has been previously found by Rossi¹⁷ for the [Co(*p*-CH₃C₆H₄NC)₃(PPh₃)₂]⁺ complex whose infrared spectrum is very similar to the spectra of the [Co(CNR)₃L₂]⁺ compounds reported in this work. If we assume *D*_{3h} symmetry for these cations, as verified for [Co(CH₃NC)₅]⁺¹⁸ and other five-coordinate cobalt(I) complexes,¹⁹ only the CN stretching mode (E') should be observable and this is presumably the strong band at 2060–2090 cm⁻¹. More bands than required by group theory have been found¹⁹ in both the ν (CO) the ν (CN) frequency regions for [Fe(CO)₃(CNR)₂] complexes which have been assigned *D*_{3h} symmetry and which are isoelectronic and isostructural with the [Co(CNR)₃L₂]⁺ cations. Other isocyanide derivatives such as [Cr(CNR)₆] and [Ni(CNR)₄]²⁰ show similar behavior. Cotton suggested two possible reasons for these facts. One is a combination or overtone

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Table IV. $\nu(\text{CO})$ and $\nu(\text{CN})$ Frequencies (cm^{-1}) of Cobalt(I) Complexes Discussed in this Paper

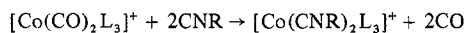
Compd	$\nu(\text{CO})$ or $\nu(\text{CN})^a$		
$[\text{Co}(\text{CO})_2\text{L}_3]\text{BPh}_4$	2021 m	1972 s	
$[\text{CoI}(\text{CO})_2\text{L}_2]$	1996 m	1935 s	
$[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	2072 sh	2050 s	2004 sh
$[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]\text{BPh}_4$	2115 sh	2069 s	1998 sh
$[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]\text{ClO}_4$	2125 sh	2069 s	2002 sh
$[\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$	2125 sh	2073 s	2035 sh
$[\text{Co}(p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$	2135 sh	2079 s	2040 sh
$[\text{Co}(o\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$	2118 sh	2066 s	2052 sh
$[\text{Co}(o\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_3\text{L}_2]\text{ClO}_4$	2116 sh	2060 s	2005 sh
$[\text{Co}(\text{C}_6\text{H}_{11}\text{NC})_3\text{L}_2]\text{ClO}_4$	2138 sh	2090 s	
$[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{ClO}_4$	2076 sh	2057 s	
$[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}'_2]\text{ClO}_4$	2136 sh	2078 s	2018 sh
$[\text{Co}(o\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_3\text{L}'_2]\text{ClO}_4$	2120 sh	2066 s	2005 sh

^a Frequencies are $\pm 0.5 \text{ cm}^{-1}$. CH_2Cl_2 solution.

band whose intensity is increased by Fermi resonance. The second is a deviation from the idealized geometry, due to the nonlinearity of the C-N-R groups, which make the totally symmetric mode (A_1') infrared active. A third reason could be the steric hindrance which would also bring about some deviation from the idealized D_{3h} geometry. It must be noted that in our case there are two bulky phosphine and three phenyl isocyanide (in some cases ortho substituted) ligands coordinated to the cobalt atom. We do not have sufficient information to decide between these alternatives and it is beyond the aims of this work. However, if we regard the two shoulders as nonfundamental absorptions, then the infrared spectra in dichloromethane are not inconsistent with the structural assignment based on pmr spectra (*vide infra*).

From Table IV one can observe that the $\nu(\text{CN})$ frequencies of the complexes in which the isocyanide ligands have one or two methyl groups in the ortho positions of the phenyl ring are lower than the corresponding frequencies of all the other $[\text{Co}(\text{CNR})_3\text{L}_2]^+$ cations. As far as polar and inductive effects are concerned $p\text{-CH}_3\text{C}_6\text{H}_4$, $o\text{-CH}_3\text{C}_6\text{H}_4$, and $o\text{-(CH}_3)_2\text{C}_6\text{H}_3$ moieties are very similar and therefore the lower $\nu(\text{CN})$ frequency for $[\text{Co}(o\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]^+$ (A) (2066 cm^{-1}) and $[\text{Co}(o\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_3\text{L}_2]^+$ (B) (2060 cm^{-1}) than for $[\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]^+$ (C) (2073 cm^{-1}) must be attributed to some other effect. The difference in the $\nu(\text{CN})$ between the ortho and para isomers (A and C) (7 cm^{-1}) is roughly half the difference between B and C (13 cm^{-1}). A possible explanation of these facts is that the steric interference of the methyl group(s) in the ortho position(s) decreases the possible rotation of the isocyanide ligands around the Co-CNR axis, thus favoring a stronger π interaction $\text{Co} \rightarrow \text{CNR}$ with a resulting lower C=N bond order.

The p -nitrophenyl isocyanide with diethyl phenylphosphonite gives only the disubstituted derivative $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]^+$ even when 6 equiv of $p\text{-NO}_2\text{C}_6\text{H}_4\text{NC}$ /equiv of $[\text{CoXL}_4]^+$ complex was used. The same product has been obtained by the reaction



($\text{CNR} = p\text{-NO}_2\text{C}_6\text{H}_4\text{NC}$; $\text{L} = \text{PhP}(\text{OEt})_2$) treating the dicarbonyltris(diethyl phenylphosphonite)cobalt(I) cation with an excess of isocyanide ligand. The analogy between $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]^+$, which is the only isocyanide derivative of the type $[\text{Co}(\text{CNR})_2\text{L}_3]^+$ obtained, and $[\text{Co}(\text{CO})_2\text{L}_3]^+$ can be understood if one considers that the presence of strong electron-withdrawing nitro group in the para position of the phenyl ring makes this isocyanide a weaker σ donor and a stronger π acceptor than all the other phenyl isocyanides we have used. Both of these effects should make

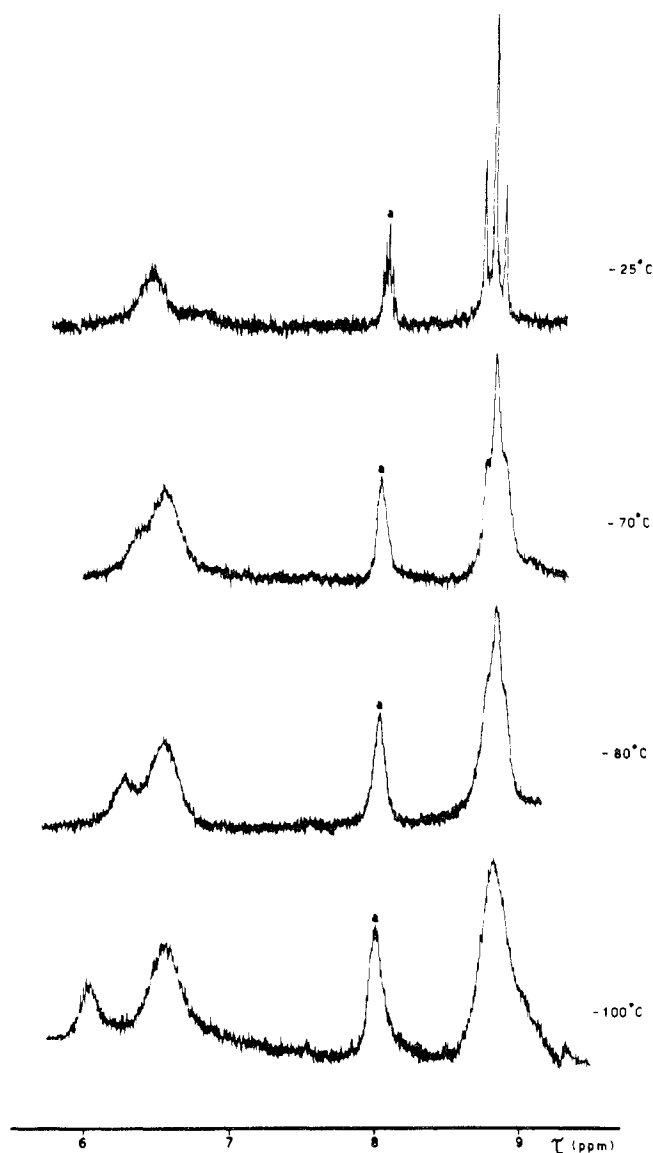


Figure 1. Pmr spectrum of $[\text{Co}(\text{CO})_2(\text{PhP}(\text{OEt})_2)_3]\text{BPh}_4$ at different temperatures in 1:1 acetone-Freon solution. The resonance line is due to $\text{CHD}_2\text{COCH}_3$.

the Co-CNR bond in the bis(p -nitrophenyl isocyanide)tris(diethyl phenylphosphonite)cobalt(I) complex more similar to the Co-CO bond of the dicarbonyltris(diethyl phenylphosphonite)cobalt(I) derivative. In accord with this idea the $\nu(\text{CN})$ frequency of $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2\text{PhP}(\text{OEt})_2)_3]^+$ is the lowest and therefore the π back bond is the strongest (Table IV).

The $\nu(\text{CN})$ frequencies of the E' mode of the $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]^+$ and $[\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]^+$ cations (2069 and 2073 cm^{-1} , respectively) are some 40 cm^{-1} lower than those for the analogous $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_5]^+$ and $[\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_5]^+$ complexes (2120 and 2105 cm^{-1} , respectively^{17,19}) in the same solvent. A decrease in the CO or CN bond order is expected when strong π -acceptor ligands such as CO or CNR are replaced by weaker π -acceptor and stronger σ -donor phosphine ligands, because electronic charge transfer to the empty antibonding π^* orbitals of the remaining isocyanide or carbonyl groups is enhanced. For this reason the susceptibility to nucleophilic attack of the carbon atom directly bonded to cobalt in the $[\text{Co}(\text{CNR})_3\text{L}_2]^+$ cations should be low.

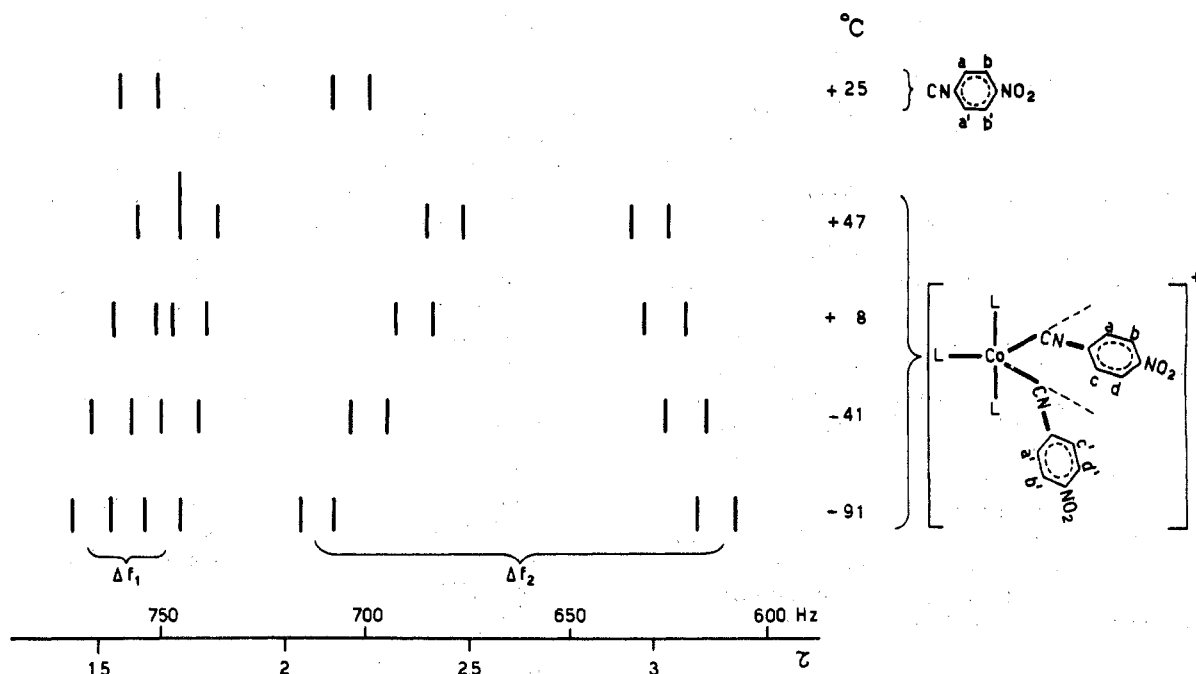
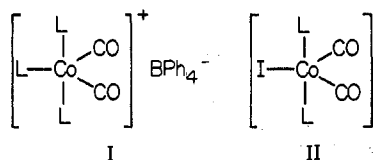


Figure 2. Schematic representation of the temperature dependence of the phenyl proton resonances of $p\text{-NO}_2\text{C}_6\text{H}_4\text{NC}$ ligands in $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]\text{ClO}_4$.

Structures. The structure of $[\text{Co}(\text{CH}_3\text{NC})_5]^+$ cation has been shown by single-crystal X-ray analysis to be trigonal bipyramidal.¹⁸ Previously, by examination of the infrared spectrum, Cotton¹⁹ proposed the same structure for the $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_5]^+$ complex. By analogy one can assume that both the carbonyl-phosphine- and the isocyanide-phosphine-cobalt(I) complexes will also be trigonal bipyramidal.

The average ratio between the intensities of the antisymmetric and the symmetric $\nu(\text{CO})$ frequencies of $[\text{Co}(\text{CO})_2\text{L}_3]^+$ and $[\text{Co}(\text{CO})_2\text{L}_2]$ complexes is 2.54 and 2.76, respectively (Figure 1). From the equation $I_{\text{antisym}}/I_{\text{sym}} = (1 - \cos \delta)/(1 + \cos \delta)$ proposed by Reckziegel and Bigorgne²¹ for the iso-electronic and isostructural $[\text{Fe}(\text{CO})_x\text{L}_{5-x}]$ complexes, the OC-Co-CO bond angle δ is found to be 116° for the dicarbonyltris(phosphine)cobalt(I) and 118° for the iododicarbonylbis(phosphine)cobalt(I) derivatives. These results suggest the structures

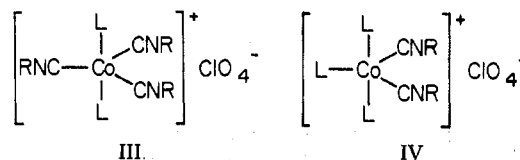


Further support is given by the pmr spectra (Table III). The $[\text{Co}(\text{CO})_2\text{L}_2]$ complexes exhibit, in the temperature range $40\text{--}80^\circ$, a 1:2:1 triplet ($J = 7$ Hz) centered at τ 8.71 due to the resonance of methyl protons of diethyl phenylphosphonite split by methylene protons, suggesting that the two phosphine ligands are magnetically, and hence stereochemically, equivalent. A 1:2:1 triplet ($J = 7$ Hz) centered at τ 8.80 can also be observed at room temperature for the $[\text{Co}(\text{CO})_2\text{L}_3]^+$ cation (Figure 1). However, cooling the acetone-Freon (1:1) solution caused this signal to become broad and the multiplet at τ 6.14 of the methylene protons splits into two peaks with a chemical shift difference of 0.3 ppm at

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-80° and 0.6 ppm at -100° and with an intensity ratio of 1:2. These facts seem to indicate that $[\text{Co}(\text{CO})_2\text{L}_3]^+$ is a nonrigid molecule at room temperature on the nmr time scale and that the equatorial and the two apical phosphine ligands become nonequivalent at low temperature. Non-rigidity has been previously observed for other iron(0)²² and cobalt(I)²³ five-coordinate complexes.

The sharp singlet which appears in the pmr spectra of $[\text{Co}(\text{CNR})_3\text{L}_2]^+$ complexes, assigned to the protons of methyl groups in the ortho or para positions of the phenyl ring of the isocyanides, indicates that these three ligands are magnetically equivalent. Similar conclusions can be inferred, for the two phosphine ligands, from the triplet due to their methyl protons (Table III). The molecular structure III can



therefore attributed to these compounds. Further support has been found by the syntheses of the corresponding tris(isocyanide)bis(trimethyl phosphite)cobalt(I) derivatives. The resonance lines of the phosphite methyl protons appear as a 1:2:1 triplet ($J = 6$ Hz) at τ 6.09–6.20 because of strong "virtual" coupling²⁴ between the two phosphorus nuclei. As found in other cases²⁵ this indicates that the two phosphine ligands are in trans positions.

Quite different behavior is shown by the $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]^+$ complex.

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$\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]^+$ cation. Its pmr spectrum in deuteriochloroform exhibits a 1:4:5:2 quartet ($J = 7$ Hz) centered at τ 8.64, assigned to the methyl protons, which become two (1:2:1, 2:4:2) triplets in hexadeuterioacetone and in hexadeuteriodimethyl sulfoxide with a difference in the chemical shift of 0.10 and 0.13 ppm, respectively. This means that two magnetically equivalent phosphine ligands are different from the third. Although the structure with two equatorial and one apical phosphine cannot be excluded completely for this complex, we prefer structure IV because of the analogy with structure III.

The pmr spectra of all the isocyanide-phosphine derivatives show no changes in the +30 to -80° temperature range except minor, but significant, changes in the spectrum of the $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2(\text{PhP}(\text{OEt})_2)_3]^+$ complex. While two 1:1 doublets ($J = 9$ Hz) at τ 1.61 and 2.18 assignable to the phenyl ring protons (AA'BB' spectrum which approximates to AB) can be observed for the free *p*-nitrophenyl isocyanide (Figure 2), a set of four 1:1 doublets ($J = 9$ Hz) at τ 1.48, 1.67, 2.09, and 3.17 due to the corresponding protons is present in the spectrum of the bis(*p*-nitrophenyl isocyanide)-tris(diethyl phenylphosphonite)cobalt(I) cation at -91° in acetone-Freon (1:1) solution. The downfield doublets can be assigned to the protons in the ortho positions with respect to the nitro group (bb' and dd') and the two upfield doublets to the other protons (aa' and cc'). As shown in Figure 2 an increase in temperature causes a decrease in Δf_1 and Δf_2 ²⁶ and at $+47^\circ$ the two downfield doublets collapse in a 1:2:1

(26) Δf_1 and Δf_2 are the differences in chemical shifts of the two downfield and the two upfield doublets, respectively, as shown in Figure 2.

pseudotriplet. These facts can be rationalized in terms of an increase of the internal rotation of the two isocyanide ligands. There are two rotational modes which will tend to make these pairs of protons equivalent. One is rotation about the Co-CN axis and the other is rotation about the CN-Ph axis. Presumably at sufficiently high temperatures total equivalence of the protons ortho to the nitro group and those ortho to the isocyanide function will be observed and two 1:1 doublets, as for the free ligand, should be observed. Two 1:1 doublets at τ 1.63 and 2.38 are in fact observed in the pmr spectrum of the $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_3(\text{P}(\text{OME})_3)_2]^+$ cation at 25° . In this case the apical trimethyl phosphite ligand, whose steric influence is minor relative to that of $\text{PhP}(\text{OEt})_2$, allows a complete rotation of the isocyanide ligands even at room temperature.

Acknowledgments. This research was supported by the Consiglio Nazionale delle Ricerche. We thank Dr. Gyorgy Bor and Professor Peter R. Welles for valuable suggestions and discussions on infrared and pmr spectra. Thanks are also due to Mr. Adriano Berton and to Mrs. Adriana Lucchiari for elemental analysis.

Registry No. $[\text{Co}(\text{CO})_2\text{L}_3]\text{BPh}_4$, 42294-95-1; $[\text{CoI}(\text{CO})_2\text{L}_2]$, 42294-96-2; $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]\text{BPh}_4$, 42294-97-3; $[\text{Co}(p\text{-NO}_2\text{-C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$, 42422-51-5; $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]\text{ClO}_4$, 42294-98-4; $[\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$, 42294-99-5; $[\text{Co}(p\text{-CH}_3\text{O-C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$, 42295-00-1; $[\text{Co}(o\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}_2]\text{ClO}_4$, 42295-01-2; $[\text{Co}(o\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_3\text{L}_2]\text{ClO}_4$, 42295-02-3; $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_2]\text{ClO}_4$, 42295-03-4; $[\text{Co}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{ClO}_4$, 42295-04-5; $[\text{Co}(\text{C}_6\text{H}_5\text{NC})_3\text{L}'_2]\text{ClO}_4$, 42295-05-6; $[\text{Co}(o\text{-(CH}_3)_2\text{-C}_6\text{H}_3\text{NC})_3\text{L}'_2]\text{ClO}_4$, 42388-31-8; $[\text{CoI}(\text{PhP}(\text{OEt})_2)_4]\text{BPh}_4$, 38798-28-6. (L = $\text{PhP}(\text{OEt})_2$; L' = $\text{P}(\text{OME})_3$.)

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Stereochemical Studies of the Radiocobalt Exchange in Solids Containing the $\text{Co}(\text{pn})_2\text{Cl}_2^+$ Ion¹

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Received July 5, 1973

The solid-phase radiocobalt exchange reactions between labeled CoCl_2 and the complexes *trans*- $[\text{Co}(\text{pn})_2\text{Cl}_2]\text{Cl}$, *trans*- $[\text{Co}(\text{pn})_2\text{Cl}_2](\text{H}_2\text{O})_2\text{Cl}_2$, and *cis*- $[\text{Co}(\text{pn})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ (pn = 1,2-diaminopropane) were studied in static air at 100, 120, and 150° . Although isomerization occurs during dehydration, cobalt exchange takes place mainly after dehydration and occurs with complete retention of configuration. In some cases, however, $\text{Co}(\text{pn})_3^{3+}$ forms. The results are compared with those obtained in transfer annealing and postradiation annealing studies of related complexes.

Introduction

When complexes of cobalt(III) and chromium(III) are irradiated with neutrons in the solid state, Szilard-Chalmers recoil occurs causing bond rupture. If the solid is subsequently heated, the recoil fragments recombine, a process known as thermal annealing. A striking feature of this post-radiation annealing of cobalt(III) and chromium(III) complexes is that it generally occurs with retention of configuration. This has been reported in studies of *d*- $[\text{Co}(\text{en})_3](\text{NO}_3)_3$ ² and *cis*- and *trans*- $[\text{M}(\text{en})_2\text{Cl}_2]\text{X}$, where M = Cr^{3,4}

or Co^{5,6} and X = Cl or NO₃. The only cases where significant stereochemical changes have been reported are *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$.⁷

Stereochemical retention is also observed in the solid-phase isotopic metal exchange reactions of *cis*- and *trans*- $[\text{M}(\text{en})_2\text{-}$

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