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Tetrahedral Complexes of Cobalt(I)

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The preparation and properties of halogenotris(tertiaryphosphine)cobalt complexes, $CoXL_3$ (X = Cl, Br, I; L = PPh_3, $PBuPh_2$, $PBzPh_2$), are described. The electronic spectra and the mangetic moments of these compounds provide strong evidence for a tetrahedral configuration both in the solid state and in solution. The reaction of these compounds with carbon monoxide, which gives $CoX(CO)_2L_2$, and with carbon tetrachloride, which gives CoX_2L_2 and C_2Cl_4, are discussed.

Introduction

In the course of our studies on the products of reaction between tertiaryphosphine-complexes of cobalt and sodium borohydride,[1,2] we have found that the first product of the reaction is a tetraco-ordinated complex of the monovalent cobalt, of formula $CoXL_3$ (X = Cl, Br, I; L = PPh_3, $P(C_4H_9)Ph_2$, $P(C_6H_5CH_2)Ph_2$.

These compounds, which can be easily obtained also by reduction with powdered zinc of the corresponding cobalt(II) complexes, CoX_2L_2, are of particular interest because they provide the first example of tetrahedral cobalt(I) complexes.

Experimental Section

The compounds were manipulated in an atmosphere of nitrogen, and samples for m.p. determination were contained in evacuated tubes. Infrared spectra were measured on Nujol mulls, using the Perkin-Elmer 337 spectrometer.

Chlorotris(triphenylphospine)cobalt(I). $CoCl(PPh_3)_3$. (a) A solution of cobalt(II) chloride hexahydrate (0.6 g, 2.5 mmols) and triphenylphosphine (2.0 g, 7.6 mmols) in ethanol (70 ml) were treated under stirring with a solution of sodium borohydride (0.08 g, 2.1 mmols) in ethanol at 30-40°C. The resulting brown-green precipitate was washed several times with ethanol and water, and dried. The compound, decomp. 177°C, is soluble in benzene and methylene chloride. It is fairly stable to the air in the solid state, but not in solution. *Anal.* Calcd. for $C_{54}H_{45}ClP_3Co$: Cl, 4.0; P, 10.5; Co, 6.7. Found: Cl, 4.0; P, 10.4; Co, 6.6.

(b) A solution of cobalt(II) chloride hexahydrate (0.5 g, 2.1 mmols), triphenylphosphine (1.65 g, 6.3 mmols) and lithium chloride (3.0 g) in ethanol (100 ml) was placed in an electrolytic cell provided with a platinum anode (in a porous cup), a mercury cathode and a magnetic stirrer. After the solution was electrolyzed for several hours with a current of about 20 mA, the green precipitate was removed from the mercury by decantation, washed with ethanol and dried. *Anal.* Found: Cl, 4.1; P, 10.4; Co, 6.8.

(c) A solution of cobalt(II) chloride hexahydrate (0.5 g, 2.1 mmols) and triphenylphosphine (1.65 g, 6.3 mmols) in ethanol (70 ml) was treated with powdered zinc (0.5 g, 7.7 mmols) at room temperature under vigorous stirring for 1 hour. The resulting green precipitate was stirred in aqueous 2.5 N hydrochloric acid till complete dissolution of the zinc in excess, washed with ethanol and dried. Decomp. 188°C. *Anal.* Found: Cl, 4.0; P, 10.4; Co 6.5.

Bromotris(triphenylphosphine)cobalt(I), $CoBr(PPh_3)_3$. The compound was prepared as above from cobalt(II) bromide, triphenylphosphine and sodium borohydride (a) or zinc (b) in ethanol. Green crystals, decomp. 179°C, soluble in benzene and methylene chloride. *Anal.* Calcd. for $C_{54}H_{45}BrP_3Co$: Br, 8.6; P, 10.0; Co 6.4. Found: (a) Br, 8.7; P, 9.8; Co, 6.3. (b) Br, 8.5; P, 10.0; Co, 6.4.

Iodotris(triphenylphosphine)cobalt(I), $CoI(PPh_3)_3$. The compound was prepared as above from cobalt(II) iodide, triphenylphosphine and sodium borohydride (a) or zinc (b) in ethanol. Because of the very low solubility of $CoI_2(PPh_3)_2$ in ethanol, the reduction of the cobalt was completed only after several hours. The product obtained by reduction with sodium borohydride was slightly impure of $CoH_3(PPh_3)_3$: it was purified by washing with a 1:1 benzene-hexane solution. Green crystals, decomp. 163°C, soluble in benzene and methylene chloride. *Anal.* Calcd. for $C_{54}H_{45}IP_3Co$: I, 13.0; P, 9.5; Co, 6.1. Found: (a) I, 13.0; P, 9.4; Co, 6.2. (b) I, 13.1; P, 9.5; Co, 6.0.

A benzene solution of the compound rapidly decomposes in a nitrogen atmosphere at 80°C, giving metallic cobalt and diiodobis(triphenylphosphine)cobalt(II), identified by means of its electronic spectrum.

Chlorotris(benzildiphenylphosphine)cobalt(I), $CoCl[P(C_6H_5CH_2)(C_6H_5)_2]_3$. The compound was obtained

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[1] A. Sacco and M. Rossi: Proceeding of the tenth International Conference on Co-ordination Chemistry, The Chemical Society of Japan, Tokyo, 1967, p. 125.
[2] A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 2, 127 (1968).

as above from cobalt(II) chloride hexahydrate (0.55 g, 2.3 mmols), benzyldiphenylphosphine (2.0 g, 7.2 mmols) and powdered zinc (0.5 g) in ethanol (40 ml). Green crystals, decomp. 162°C, soluble in benzene and methylene chloride. *Anal.* Calcd. for $C_{57}H_{51}ClP_3Co$: Cl, 3.8; P, 10.1; Co, 5.4. Found: Cl, 3.9; P, 9.6; Co, 6.2.

Bromotris(benzyldiphenylphosphine)cobalt(I), $CoBr[P(C_6H_5CH_2)(C_6H_5)_2]_3$. The compound was obtained as above from cobalt(II) bromide, benzyldiphenylphosphine and zinc in ethanol. Green crystals, decomp. 158-9C°, soluble in benzene. *Anal.* Calcd. for $C_{57}H_{51}BrP_3Co$: Br, 8.3; P, 9.6; Co, 6.1. Found: Br, 8.1; P, 9.4; Co, 6.1.

Iodotris(benzyldiphenylphosphine)cobalt(I), $CoI[P(C_6H_5CH_2)(C_6H_5)_2]_3$. The compound was obtained as above from cobalt(II) iodide, benzyldiphenylphosphine and zinc in ethanol. Green crystals, decomp. 155°C, soluble in benzene. *Anal.* Calcd. for $C_{57}H_{51}IP_3Co$: I, 12.5; P, 9.2; Co, 5.8. Found: I, 12.4; P, 8.9; Co, 5.7.

*Bromotris(*n*-butyldiphenylphosphine)cobalt(I)*, $CoBr[P(C_4H_9)(C_6H_5)_2]_3$. The compound was obtained as above from cobalt(II) bromide, n-butyldiphenylphosphine and zinc in ethanol. Green crystals, decomp. 134-5°C, soluble in benzene. *Anal.* Calcd. for $C_{48}H_{57}BrP_3Co$: Br, 9.2; P, 10.7; Co, 6.8. Found: Br, 9.1; P, 10.5; Co, 6.9.

*Iodotris(*n*-butyldiphenylphosphine)cobalt(I)*, $CoI[P(C_4H_9)(C_6H_5)_2]_3$. The compound was obtained as above from cobalt(II) iodide, n-butyldiphenylphosphine and zinc in ethanol. Green crystals, decomp. 132-3°C, soluble in benzene. *Anal.* Calcd. for $C_{48}H_{57}IP_3Co$: I, 13.9; P, 10.2; Co, 6.5. Found: I, 14.0; P, 9.9; Co, 6.3.

Chlorodicarbonylbis(triphenylphosphine)cobalt(I), $CoCl(CO)_2(PPh_3)_2$. The chlorotris(triphenylphosphine)cobalt(I) (1.0 g, 1.13 mmols), partially dissolved in benzene (30 ml), was treated with carbon monoxide at room temperature and atmospheric pressure, under stirring, for four hours. The yellow precipitate was filtered off, and from the mother liquors a further crop of crystals was obtained by adding petroleum ether. After recrystallization from benzene by adding petroleum ether, 0.6 g of yellow crystals were obtained. The compound, decomp. 218-20°C, is soluble in benzene, tetrahydrofuran, methylene chloride, slightly soluble in acetone. *Anal.* Calcd. for $C_{38}H_{30}ClO_2P_2Co$: Cl, 5.2; P, 9.2; Co, 8.7. Found: Cl, 5.3; P, 9.3; Co, 8.7. ν_{CO}: 1920 cm^{-1} (vs), 1980 cm^{-1} (s) (in Nujol).

Bromodicarbonylbis(triphenylphosphine)cobalt(I), $CoBr(CO)_2(PPh_3)_2$. The compound was obtained as above from $CoBr(PPh_3)_3$ and CO. Yield 78%. Brown-yellow crystals, decomp. 209-10°C (106°C in open tube to the air), soluble in benzene, tetrahydrofuran, methylene chloride. *Anal.* Calcd. for $C_{38}H_{30}BrO_2P_2Co$: Br, 11,1; P, 8.6; Co, 8.2. Found: Br, 11.0; P, 8.5; Co, 8.1. ν_{CO}: 1920 cm^{-1} (vs), 1980 cm^{-1} (s) (in Nujol).

Iododicarbonylbis(triphenylphosphine)cobalt(I). $CoI(CO)_2(PPh_3)_2$. The compound was obtained as above from $CoI(PPh_3)_3$ and CO. Yield 77% Brown crystals, decomp. 206-8°C (100° in open tube to the air), soluble in benzene, tetrahydrofuran, methylene chloride. *Anal.* Calcd. for $C_{38}H_{30}IO_2P_2Co$: I, 16.6; P, 8.1; Co, 7.7. Found: I, 16.3; P, 7.9; Co, 7.6. ν_{CO}: 1920 cm^{-1} (vs), 1980 cm^{-1} (s) (in Nujol).

Reaction between $CoCl(PPh_3)_3$ and carbon tetrachloride. (a) The complex (0.8 g) was treated with carbon tetrachloride (0.7 ml) under nitrogen atmosphere at 40°C for 2 hours and then the solvent was distilled off under reduced pressure, being collected in a dry ice trap. Its I.R. spectrum was recorded, using carbon tetrachloride as reference. The presence of tetrachloroethylene was proved by the strong band at 910 cm^{-1}. The residue, washed with ethanol, was identified as $CoCl_2(PPh_3)_2$ by its electronic spectrum. The presence of triphenylphosphine oxide in the ethanolic extract was proved by the I.R. analisyys.

(b) A suspension of $CoCl(PPh_3)_3$ (0.8 g), in cyclohexene (0.7 ml) and carbon tetrachloride (0.5 ml) was treated as above. The presence of chloroform in the distillate was proved by the band at 1217 cm^{-1}, whereas the band due to the tetrachloroethylene was not detected.

Reaction between triphenylphosphine and hexachloroethane. A mixture of triphenilphosphine (0.5 g) and hexachloroethane (0.5 g) was gently heated under reduced pressure, collecting the distillate in a dry ice trap.

The presence of tetrachloroethylene was proved by means of its I.R. band at 910 cm^{-1}.

Magnetic measurements. Bulk susceptibility measurements, under a nitrogen atmosphere, for the compounds $CoCl(PPh_3)_3$, $CoBr(PPh_3)_3$ and $CoI(PPh_3)_3$ were made by the Faraday method and using the Alpha Mod. 9500 magnet, provided with the Alpha Mod. 100-20 B power supply and the Cahn Electrobalance.

The apparatus was calibrated with Pt, Pd, H_2O and $NiBr_2(PPh_3)_2$ at room temperature, with Pt and Pd at 77°K. For several (from 4 to 5) samples of each standard substance the force Δm exerted on the sample at constant HdH/dx and constant temperature was plotted against the weight m of the sample; straight lines were obtained according to the equation:

$$\Delta m = H\frac{dH}{dx}(\chi_g \cdot m + \chi_g^\circ m^\circ) \qquad (1)$$

where χ_g° and m° are the gram susceptibility and the weight of the Teflon container. This procedure was repeated at four different field strengths for each standard substance. All the values of $\chi_g^\circ \cdot m^\circ$, calculated from the value of m at $\Delta m = 0$ and from the known χ_g of the standard substance, were constant within the 0,5%. The susceptibilities of the cobalt-complexes were determined in a similar manner, measuring the force exerted on three samples of each complex at four different field strengths. At each field strength the value of χ_g was obtained from the above determined value of $\chi_g^\circ \cdot m^\circ$ and from the calculated value of

Table I. Magnetic data

Compound	T °K	χ_{mol} $\times 10^6$	Diam. corr. $\times 10^6$	$\mu_{eff.}$ B.M.
$CoCl(PPh_3)_3$	294	3498	−580	3.11
$CoCl(PPh_3)_3$	77	14328	−580	3.04
$CoBr(PPh_3)_3$	293	3656	−590	3.17
$CoBr(PPh_3)_3$	77	14700	−590	3.08
$CoI(PPh_3)_3$	294	4037	−604	3.32

Table II. Electronic Absorption Spectra in benzene

Compound	Absorption mμ	maxima cm^{-1}	Molar Extinc.
$CoCl(PPh_3)_3$	745	13,420	118
	~940 (sh)	~10,650	—
	1100	9,090	138
	2000	5,000	146
$CoBr(PPh_3)_3$	755	13,250	117
	~950 (sh)	~10,520	—
	1115	8,970	122
	2150	4,650	140
$CoI(PPh_3)_3$	795	12,580	—
	1160	8,620	—
	2200	4,540	—
$CoBr(PBuPh_2)_3$	710	14,090	115
	~980 sh, l)	~10,020	—
	1085	9,220	144
	—		—

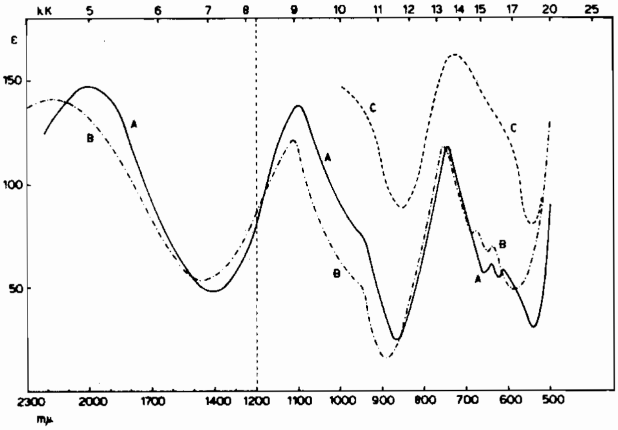

Figure 1. The electronic absorption spectra of: A, CoCl-$(PPh_3)_3$ in benzene solution; B, $CoBr(PPh_3)_3$ in benzene solution; C, $CoCl(PPh_3)_3$ by reflectance, molar absorbance scale arbitrary.

m at Δm = 0, accordingn to the equation:

$$\chi_g = -\frac{\chi_g^\circ m^\circ}{m} \qquad (2)$$

Because of the presence of some ferromagnetic impurities, most probably due to traces of metallic cobalt, the χ_g values obtained were dependent on the field strength. Clean susceptibility values were obtained by extrapolating at infinite field strength. The results of the magnetic measurements are given in Table I.

Spectral measurements. The solution spectra of the compounds were measured with an Optica Mod. CF4NI recording spectrophotometer. The benzene solutions, about 1.3×10^{-3} *M* plus an excess of free triphenylphopshine, were prepared under a nitrogen atmosphere and kept at 14°C in order to minimize the disproportionation to metallic cobalt and dihalogenobis(triphenylphosphine)cobalt(II).

The reflectance spectra of the solid $CoCl(PPh_3)_3$ was measured with the same spectrophotometer, using a standard reflectance attachment and magnesium carbonate as the reference.

The results are shown in Figure 1 and in Table II.

Results and Discussion

Preparations. The tertiary phosphine-complexes of cobalt(I) were obtained by reduction in ethanolic solution of the corresponding cobalt(II) complexes, $CoX_2(PR_3)_2$, in presence of one mole of the free ligand. The reduction was performed with sodium borohydride, powdered zinc and electrolytically on a mercury cathode. With powdered zinc the reaction, which occurs according the following equation

$$2CoX_2(PR_3)_2 + 2PR_3 + Zn = 2CoX(PR_3)_3 + ZnX_2 \qquad (3)$$

gives the products in almost quantitative yields.

The green, crystalline cobalt(I) complexes are readily soluble in benzene, tetrahydrofuran and methylene chloride. They are fairly stable at the air in the solid state, but rapidly oxidized by the air in solution. In solution, under a nitrogen atmosphere and at room temperature, they partially decompose according to the following equation:

$$2CoX(PR_3)_3 = CoX_2(PR_3)_2 + Co + 4PR_3 \qquad (4)$$

The chloro-derivatives are more stable than the iodo-derivatives, and the rate of the decomposition increases with the temperature.

Reactions. The compounds react very easily with carbon monoxide at room temperature and atmospheric pressure to give with good yields the pentacoordinated complexes of cobalt(I) of formula $CoX(CO)_2(PR_3)_2$, which were previously obtained by different ways.[3]

Unlike the tetracoordinated planar complexes of cobalt(I), of formula $[Co(dp)_2]X$ (dp = $C_2H_4(PPh_2)_2$, X = ClO_4, BPh_4) already described,[4] these compounds do not react with hydrogen: they were recovered unaltered from the benzene solution treated with hydrogen under a pressure of 80 atmospheres.

(3) A. Sacco, *Gazz. Chim. It.*, 93, 542 (1963). W. Hieber and H. Duchatsch, *Chem. Ber.*, 98, 2530 (1965).
(4) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, 589 (1966).

The crystalline chlorotris(triphenylphosphine)cobalt(I) reacts at room temperature with carbon tetrachloride according to the equation:

$$\mathrm{2CoCl(PPh_3)_3 + 2CCl_4 = 2CoCl_2(PPh_3)_2 + Ph_3PCl_2 + Ph_3P + C_2Cl_4} \tag{5}$$

The first step of the above reaction is an oxidative addition of the carbon tetrachloride to the cobalt(I) complex to give an unstable hexacoordinated complex of cobalt(III), of formula $\mathrm{CoCl_2(CCl_3)(PPh_3)_3}$, which quickly decomposes to the stable cobalt(II) derivative $\mathrm{CoCl_2(PPh_3)_2}$ according to the equation:

$$\mathrm{[CoCl_2(CCl_3)(PPh_3)_3] \rightarrow CoCl_2(PPh_3)_2 + Ph_3P + {\cdot}CCl_3} \tag{6}$$

The following steps occur according to the equations:

$$\mathrm{2\,{\cdot}CCl_3 \rightarrow C_2Cl_6} \tag{7}$$

$$\mathrm{C_2Cl_6 + PPh_3 = C_2Cl_4 + Ph_3PCl_2} \tag{8}$$

The formation of the free trichloromethyl radical is proved by the fact that the reaction between the cobalt(I) complex and the carbon tetrachloride, carried out in presence of cyclohexane, does not give tetrachloroethylene but chloroform. Moreover, the cobalt(I) complexes react at room temperature with alkyl halides according to the equation:

$$\mathrm{2CoX(PR_3)_3 + 2R'X = 2CoX_2(PR_3)_2 + 2PR_3 + R'{-}R'} \tag{9}$$

The reaction (8) was proved to occur easily under the same experimental conditions used for the reaction between the cobalt(I) complex and the carbon tetrachloride.

Structure of the complexes. The structures of the solid complexes are deduced from their magnetic moments and their absorption spectra in the range 500 to 1000 mμ.

The structure of the complexes in benzene solution are deduced from their absorption spectra in the range 500 to 2300 mμ.

The magnetic moments of the triphenylphosphine derivatives (3.0-3.3 B.M.) are nearly the same of those found for the isoelectronic $\mathrm{NiX_2(PPh_3)_2}$ (X = Cl, Br, I), whose distorted tetrahedral structures have been determined by X-ray crystallography.[5]

The remarkable similarity of the solution and solid state spectra of the cobalt(I) complexes (see Figure 1) provides strong evidence that these compounds have the same configuration both in the crystal and in solution.

The electronic spectra of the benzene solutions show three absorption bands, due to d–d transitions, in quite good agreement with the theoretical prediction for d^8 complexes with pseudo-tetrahedral (actually C_{3v}) symmetry. The weak bands which appear in the 600-700 mμ region are due to the presence of slight amounts of cobalt(II) complexes arising from some decomposition of the cobalt(I) complexes, according to the equation (4). In fact, the absorption maxima of these bands are identical, for the bromo- and the iodo-derivatives, to those observed for the corresponding cobalt(II) complexes in benzene solution. For the chloro-derivatives the weak bands observed at 605 and 635 mμ do not correspond to those previously reported for $\mathrm{CoCl_2(PPh_3)_2}$ in ethyl methyl ketone.[6] However, we have found that $\mathrm{CoCl_2(PPh_3)_2}$ undergoes a remarkable solvolysis in ethyl methyl ketone solution. In fact, the electronic spectrum of this solution is quite different from that of the solid compounds. Moreover, the dichlorobis(triphenylphosphine)cobalt(II), unlike the corresponding bromo- and iodo-derivatives, dissolves in benzene only in presence of an excess of free ligand and the electronic spectrum of this solution is quite similar to that of the solid compound (see Figure 2). This behaviour suggests for the chloro-derivative the formation of insoluble polimeric species, according to the equation:

$$\mathrm{nCoCl_2(PPh_3)_2 \rightleftharpoons [CoCl_2(PPh_3)_x]_n + n(2{-}x)PPh_3} \tag{10}$$

The above equilibrium is quantitatively displaced to the left in presence of an excess of free ligand. The absorption maxima and the molar extinction coefficients of $\mathrm{CoCl_2(PPh_3)_2}$ in benzene solution are shown in Table III.

Table III. Electronic absorption spectra of $\mathrm{CoCl_2(PPh_3)_2}$ in benzene.

Absorption maxima (mμ)	Molar extinc.
605 (581) [a]	515 (235) [a]
635 (638) [a]	675 (290) [a]
745 (682) [a]	405 (310) [a]

[a] Values found in methyl ethyl ketone solution.

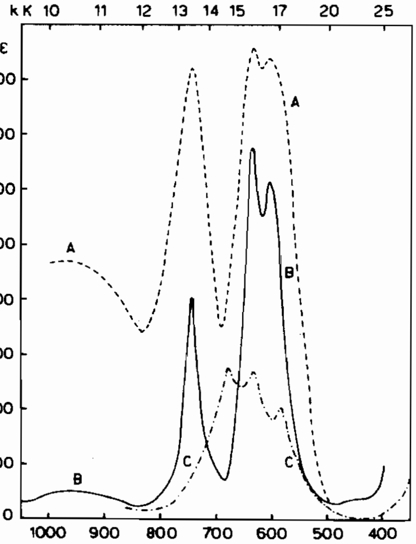

Figure 2. The electronic absorption spectra of $\mathrm{CoCl_2(PPh_3)_2}$: (A) by reflectance, molar absorbance scale arbitrary; (B) in benzene solution, in presence of an excess of free ligand; (C) in $\mathrm{CH_3COC_2H_5}$.

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[5] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

[6] F. A. Cotton, O. D. Faut, D. M. Goodgame and R. H. Holm, *J. Amer. Chem. Soc.*, *83*, 1780 (1961).

Conclusions

Both the electronic spectra and the magnetic moments of the cobalt(I) complxes point consistently to a tetrahedral configuration of these compounds. It is well known that effects which weaken the ligand field around the metal atom will tend to favour the tetrahedral, paramagnetic form relative to the square-planar, diamagnetic form. Thus, it is not surprising that, passing from $[Co\{C_2H_4(PPh_2)_2\}_2]^+$ to $CoX(PR_3)_3$, the structure changes from square-planar to tetrahedral, in agreement with the lesser ligand field strength of the halide in respect of that of the tertiary phosphine.

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