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# CATIONIC COBALT(I) CARBONYL COMPLEXES CONTAINING SECONDARY OR TERTIARY PHOSPHINES. A DIRECT SYNTHESIS FROM COBALT(II) SALTS

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## Summary

Cobalt(I) carbonyl complexes of formula $[Co(CO)_n(P)_{5-n}]ClO_4$ ($n = 1, 2, 3$; P = secondary or tertiary phosphine) have been prepared by reaction of CO under ambient conditions with $Co(ClO_4)_2 \cdot 6H_2O$ and phosphine in isopropyl alcohol. The chemical and spectroscopic properties of these complexes are described and the stoichiometry and mechanism of the carbonylation reaction discussed.

## Introduction

In a preliminary communication we reported that phosphine ligands react with cobalt(II) salts containing low-coordinating anions in the presence of $\pi$-acceptor ligands to give cationic cobalt(I) complexes [1]. We now report more fully on the reaction of isopropyl alcohol solutions of $Co(ClO_4)_2 \cdot 6H_2O$ and phosphines with carbon monoxide. By this route an extended series of carbonyl complexes of general formula $[Co(CO)_n(P)_{5-n}]^+$ ($n = 1, 2, 3$; P = secondary or tertiary phosphines) can be simply obtained. The previously described synthetic procedures to $[Co(CO)_n(P)_{5-n}]^+$ cations involved a disproportionation reaction of $Co_2(CO)_8$ in the presence of phosphorous ligands [2]. More recently, it has been reported [3] that the five-coordinate $[CoI(PPh(OEt)_2)_4]^+$ reacts with carbon monoxide to give equimolar amounts of $[Co(CO)_2(PPh(OEt)_2)_3]^+$ and $[CoI(CO)_2(PPh(OEt)_2)_2]$.

The present paper reports the detailed preparation and properties of a series of $[Co(CO)_n(P)_{5-n}]ClO_4$ complexes along with the results of an investigation on the stoichiometry and mechanism of the reductive carbonylation of $Co(ClO_4)_2 \cdot 6H_2O$ to cobalt(I) carbonyl complexes.

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## Results and discussion

Cobalt(II) perchlorate in isopropyl alcohol reacts under ambient conditions with carbon monoxide in the presence of secondary or tertiary phosphines (molar ratio 5:1) to give five-coordinate carbonyl complexes of cobalt(I), according to:

$$Co^{2+} \xrightarrow[CO]{P} [Co(CO)(P)_4]^+ \xrightarrow[-P]{+CO} [Co(CO)_2(P)_3]^+ \xrightarrow[-P]{+CO} [Co(CO)_3(P)_2]^+$$

With smaller secondary phosphines ($HPPh_2$, $HPEt_2$, HPEtPh, HPMePh) the reaction stops at the first step, with formation of mono-carbonyl complexes. With HPPhCy and the tertiary phosphines $PMe_2Ph$, $PMePh_2$ and $PEt_2Ph$ the reaction goes readily to bis-carbonyls and no further substitution of phosphines by carbon monoxide is observed. Under the same experimental conditions, the trialkylphosphines $PEt_3$, $PPr_3$ and $PBu_3$ yield tris-carbonyl adducts. If a large excess (30:1) of trialkylphosphine is used, the reaction can be stopped at the bis-carbonyl complex in the case of $PEt_3$, whereas with $PPr_3$ and $PBu_3$, mixture of bis- and tris-carbonyls are invariably obtained. With larger phosphines such as $PPh_3$, $HPCy_2$ and $PCy_3$, no reaction has been observed.

Mono- and bis-carbonyl complexes are yellow or orange solids, tris-carbonyl complexes are white products (Table 1). With the ligands $HPEt_2$, HPEtPh and HPMePh no crystalline products could be obtained. However, the IR spectra in tetrahydrofuran of the yellow-orange oils recovered after removal of the solvent, show a strong band in the CO stretching region at about 1925 $cm^{-1}$, which compares with the same value for the $[Co(CO)(HPPh_2)_4]ClO_4$ complex, suggesting the presence of $[Co(CO)(HPR_2)_4]^+$ species (Table 2).

As previously found [2,3], the IR spectra of the bis-carbonyl derivatives show two CO stretching absorptions, consistent with the presence of two carbonyl groups in non-equivalent positions. The methyl resonance in the $^1H$ NMR spectra of $[Co(CO)_2(PR_3)_3]^+$ (PR = $PPhMe_2$, $PPh_2Me$) appears as a broad featureless multiplet (at 8.2-8.3 $\tau$ in $CH_2Cl_2$), and so a definite structure cannot be assigned. A temperature dependence was observed, but at —80°C, the lowest tem-

TABLE 1

PROPERTIES AND ANALYTICAL DATA FOR SOME CARBONYL COMPLEXES

| Compound | Colour | M.p. (°C) | Analyses (%) | | | | | | Time of reaction (h) |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | | H | | Cl | | |
| | | | Found | Calcd. | Found | Calcd. | Found | Calcd. | |
| $[Co(CO)(HPPh_2)_4]ClO_4$ | orange | 177 | 62.92 | 63.20 | 4.82 | 4.76 | 3.85 | 3.81 | 24 |
| $[Co(CO)_2(HPPhCy)_3]ClO_4$ | yellow | 159 | 57.35 | 57.69 | 6.58 | 6.49 | 4.54 | 4.48 | 96 |
| $[Co(CO)_2(PPhMe_2)_3]ClO_4$ | yellow | 152 | 49.22 | 49.66 | 5.29 | 5.29 | 5.70 | 5.63 | 1 |
| $[Co(CO)_2(PPh_2Me)_3]ClO_4$ | orange | 133 | 60.85 | 60.42 | 5.01 | 4.82 | 4.40 | 4.35 | 36 |
| $[Co(CO)_2(PPhEt_2)_3]ClO_4$ | orange | 147 | 53.13 | 53.96 | 6.44 | 6.36 | 5.17 | 4.97 | 15 |
| $[Co(CO)_2(PEt_3)_3]ClO_4$ | yellow | 99 | 41.84 | 42.25 | 8.02 | 7.98 | 7.14 | 6.95 | 3 |
| $[Co(CO)_3(PEt_3)_2]ClO_4$ | white | 196 | 37.59 | 37.75 | 6.50 | 6.50 | 7.65 | 7.41 | 12 |
| $[Co(CO)_3(PPr_3)_2]ClO_4$ | white | 213 | 44.79 | 44.87 | 7.69 | 7.52 | 6.39 | 6.29 | 12 |
| $[Co(CO)_3(PBu_3)_2]ClO_4$ | white | 196 | 50.75 | 50.15 | 8.65 | 8.35 | 5.58 | 5.47 | 48 |

TABLE 2

CONDUCTIVITY DATA AND CO STRETCHING FREQUENCIES FOR COBALT(I) CARBONYL COMPLEXES

| Complex | P | ν(CO) (cm$^{-1}$) [a] | $\Lambda_M$ (S cm$^2$ mol$^{-1}$) [b] |
|---|---|---|---|
| $[Co(CO)(P)_4]ClO_4$ | HPPhMe | 1924vs [c] | [d] |
| | $HPEt_2$ | 1927vs [c] | [d] |
| | HPPhEt | 1924vs [c] | [d] |
| | $HPPh_2$ | 1925vs [c] | 80 |
| $[Co(CO)_2(P)_3]ClO_4$ | HPPhCy | 2002m, 1945vs | 103 |
| | $PPhMe_2$ | 2000m, 1950vs | 99 |
| | $PPh_2Me$ | 2000m, 1950vs | 93 |
| | $PPhEt_2$ | 2000m, 1945vs | 91 |
| | $PEt_3$ | 1988m, 1927vs | 118 |
| $[Co(CO)_3(P)_2]ClO_4$ | $PEt_3$ | 1989vs | 95 |
| | $PPr_3$ | 1987vs | 89 |
| | $PBu_3$ | 1991vs | 87 |

[a] In Nujol mull, if not otherwise stated. [b] In nitromethane, $10^{-3}$ *M* solution. [c] In tetrahydrofuran. [d] Not isolated in the solid state.

perature studied, a limiting spectrum had not yet been reached and the methyl signal was still broad and structureless.

The tris-carbonyl derivatives exhibit a single CO stretching mode, which suggests a trigonal bipyramidal structure with *trans*-phosphines.

The reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with carbon monoxide in the presence of the phosphines was also studied in a gas-buret apparatus, by measuring the CO uptake at constant pressure. Experiments were carried out at constant cobalt(II) perchlorate concentration (0.25 mmol in 10 ml of isopropyl alcohol), with a molar ratio phosphine:cobalt of 5:1. The apparent rate of CO absorption was very high with relatively small ligands ($HPEt_2$, HPMePh, etc.), and decreased with increasing size of the phosphine. The influence of the nature of the phosphine on the rate of formation of some $[Co(CO)_2(PR_3)_3]^+$ complexes is shown in Fig. 1.

It should be noted that the number of mols of carbon monoxide absorbed per mol of $Co(ClO_4)_2$ shows that in all cases the cobalt(II) originally present is

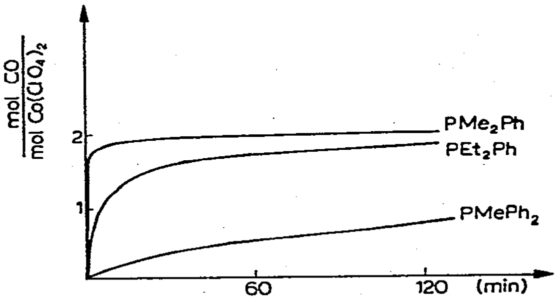

Fig. 1. Influence of the nature of the phosphine on the rate of formation of some $[Co(CO)_2(PR_3)_3]^+$ complexes. Solvent: isopropyl alcohol. $[Co(ClO_4)_2]$ = constant. Ratio $PR_3:Co(ClO_4)_2$ = 5.

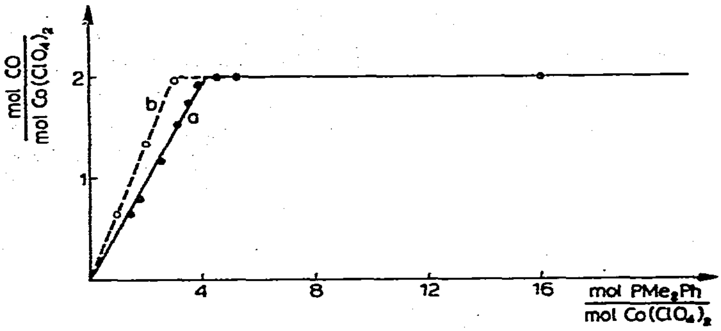

Fig. 2. Influence of the $PMe_2Ph$ concentration on the ratio of mol of CO taken up to mol of $Co(ClO_4)_2$ originally present. $[Co(ClO_4)_2]$ = constant. (a) In isopropyl alcohol. (b) In isopropyl alcohol containing potassium t-butylate.

quantitatively transformed into $[Co(CO)_n(P)_{5-n}]^+$ complexes. This fact rules out the possibility that disproportionation of cobalt(II) substrate is involved in the reaction.

The quantitative aspect of the carbonylation reaction of cobalt(II) perchlorate in isopropyl alcohol has been studied in detail in the case of dimethylphenylphosphine, which gives the least experimental difficulty. Experiments were carried out at constant $Co(ClO_4)_2$ concentration with increasing amounts of phosphine. As can be seen from Fig. 2, with increasing concentration of phosphine there is an initial increase of the ratio of mol of carbon monoxide taken up to the mol of cobalt(II) perchlorate. When the ratio $PMe_2Ph:Co(ClO_4)_2$ becomes $> 4$, $2.0 \pm 0.1$ mol of CO per mol of $Co(ClO_4)_2$ are absorbed, with quantitative formation of $[Co(CO)_2(PMe_2Ph)_3]ClO_4$. Addition of water to the isopropyl alcohol (5% in volume) does not appreciably change the rate of the reaction and the amount of carbon monoxide absorbed.

Gas chromatography of the reaction mixtures shows that the reduction of Co(II) is accompanied by formation of acetone. In several runs performed at molar ratio $PMe_2Ph:Co(ClO_4)_2 > 4$, the acetone formed during the reaction has been found to be about 0.5 mol per mol of Co ($0.46 \pm 0.03$). On the basis of these observations, the following stoichiometry can be reasonably proposed for the reaction in isopropyl alcohol:

$$2\,Co^{2+} + 8\,P + 4\,CO + (CH_3)_2CHOH \rightarrow 2\,[Co(CO)_2(P)_3]^+ + (CH_3)_2CO + 2\,[HP]^+$$

$$(P = PMe_2Ph) \qquad (1)$$

The formation of the phosphonium salt appears to be confirmed by the IR spectrum of the crude product obtained by evaporation of the reaction mixture, which shows a weak band at 2460 $cm^{-1}$, which can been attributed to the P—H stretching frequency [4]. A similar band is also present in the IR spectrum of the product of the equimolar amounts of perchloric acid and dimethylphenylphosphine.

In agreement with eqn. 1, when the carbonylation reaction is carried out in the presence of strong bases, such as potassium t-butylate, the quantitative conversion of cobalt(II) into $[Co(CO)_2(PMe_2Ph)_3]^+$ is achieved at a molar ratio $PMe_2Ph:Co(ClO_4)_2 > 3$ (Fig. 2, curve b).

No detailed mechanistic studies of this reaction have been made, but it seems likely that the reduction of cobalt(II) to cobalt(I) implies the initial formation of the cobalt(II) cation $[Co(PMe_2Ph)_4]^{2+}$, which gives the cobalt(I) derivative $[Co(CO)(PMe_2Ph)_4]^+$, probably via a $[Co(CO)(PMe_2Ph)_4]^{2+}$ intermediate. This first step is followed by a substitution reaction with formation of the biscarbonyl $[Co(CO)_2(PMe_2Ph)_3]^+$.

The following observations support the proposed scheme. (i) In an inert atmosphere, $Co(ClO_4)_2 \cdot 6H_2O$ reacts with $PMe_2Ph$ in isopropyl alcohol to give the tetrahedral $[Co(PMe_2Ph)_4](ClO_4)_2$ complex ($\mu_{eff}$ = 4.50 BM). This green compound takes up carbon monoxide in the solid state at low temperature (—78°C) to give a yellow carbonyl adduct. This latter is rather unstable, however, and is converted at room temperature, into a brown intractable oil. (ii) When the carbonylation reaction in isopropyl alcohol is carried out in the presence of a large excess of $PMe_2Ph$, (40:1 and more), two distinct absorption steps are clearly observed (Fig. 3). About one mol of CO per mol of cobalt is taken up in the first step, which is followed by a much slower absorption of another mol of CO. The IR spectra of the solution initially show a band at 1920 $cm^{-1}$, which can be attributed to the $[Co(CO)(PMe_2Ph)_4]^+$ complex. On standing, two bands at 2000 and 1940 $cm^{-1}$, typical of $[Co(CO)_2(PMe_2Ph)_3]^+$ gain in intensity, while the band at 1920 $cm^{-1}$ disappears. The strong retardation due to the excess of phosphine is expected, since $[Co(CO)(PMe_2Ph)_4]^+$ possesses an 18-electron shell. Therefore, it seems likely that substituion of $PMe_2Ph$ by CO in $[Co(CO)(PMe_2Ph)_4]^+$ to give $[Co(CO)_2(PMe_2Ph)_3]^+$ will proceed through a dissociative rather than an associative mechanism.

Carbonyl cobalt(I) complexes were also obtained in excellent yields by treating $Co(ClO_4)_2 \cdot 6H_2O$ and phosphines with carbon monoxide in primary alcohols. We have not investigated the reaction in sufficient detail to be certain of the overall stoichiometry, but in these cases, also, the alcohols are probably involved in the reduction process. Moreover, reductive carbonylation of $Co(ClO_4)_2 \cdot 6H_2O$ in the presence of phosphine also occurs in solvents such as tetrahydrofuran an isoamyl alcohol, in which, however, formation of phosphine oxide is observed.

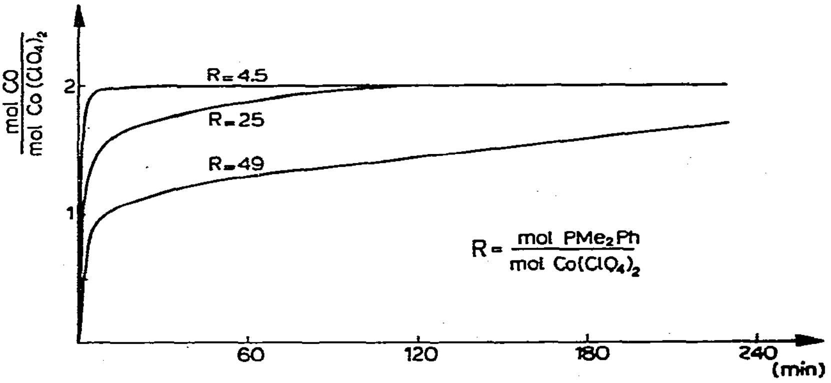

Fig. 3. Influence of $PMe_2Ph$ concentration on the rate of carbonylation of $Co(ClO_4)_2 \cdot 6H_2O$ in isopropyl alcohol. $[Co(ClO_4)_2]$ = constant.

It is noteworthy that carbonylation of cobalt(II) complexes of the type $[CoX_2(P)_n]$ ($n = 2, 3$; X = halogen, NCS, CN; P = tertiary phosphine) proceeds via a disproportionation reaction [5,6] according to the equation

$$2\ CoX_2(P)_n + 2\ CO \rightarrow CoX(CO)_2(P)_3 + Co(III)$$

In a similar manner, $[Co(CN)_5]^{3-}$ reacts with CO to give cobalt(I) and cobalt(III) derivatives [7]:

$$2\ [Co(CN)_5]^{3-} + 2\ CO \rightarrow [Co(CN)_3(CO)_2]^{2-} + [Co(CN)_6]^{3-} + CN^-$$

The different behavior of $[Co(P)_4]^{2+}$ complexes in the reaction with CO is probably related to the absence in these cobalt(II) substrates of anionic ligands which can stabilize the higher oxidation states (+3) of cobalt.

## Experimental

### *Apparatus*

Infrared spectra were obtained with a Perkin—Elmer 457 spectrophotometer. NMR spectra were taken on a Brucker HFX-90 spectrometer. Carbon monoxide uptakes were measured with a standard apparatus [5]: a known volume of isopropyl alcohol (10 ml) containing a weighed amount of phosphorus ligand was saturated with carbon monoxide at 25°C and then a known weight of $Co(ClO_4)_2 \cdot 6H_2O$ was added with stirring. The uptake of carbon monoxide was measured at constant pressure, with allowance for the vapor pressure of the solvent. Electrical conductivities were measured at 25°C using an LKB conductivity bridge.

### *Materials*

The tertiary phosphines were prepared by standard methods; diethyl- and dicyclohexyl-phosphines were made by Issleib's method [8]. The secondary phosphines $HP(C_6H_5)R$ (R = $CH_3$, $C_2H_5$, $C_6H_{11}$) were obtained by hydrolysis of the corresponding $LiP(C_6H_5)R$. Cobalt perchlorate hexahydrate, Reagent Grade (Fluka), was recrystallised before use.

### *Preparation of the complexes*

The general synthetic procedure involves the treatment of $Co(ClO_4)_2 \cdot 6H_2O$ in isopropyl alcohol (or in isopropyl alcohol—tetrahydrofuran mixture) with the appropriate phosphorus ligand in molar ratio 5:1 under an atmosphere of carbon monoxide at room temperature. Reaction times are reported in Table 1. The products, except those with the phosphines $HPEt_2$, HPEtPh and HPMePh, are slightly soluble in isopropyl alcohol and can be precipitated from isopropyl alcohol—tetrahydrofuran mixtures by evaporating tetrahydrofuran. The complex $[Co(CO)_2(PEt_3)_3]ClO_4$ can be isolated in the solid state only by carrying out the reaction in the presence of a large excess of $PEt_3$, otherwise the major product is $[Co(CO)_3(PEt_3)_2]ClO_4$. All the complexes were recrystallised from dichloromethane—2-propanol and stored under nitrogen. Analytical data and physical properties are reported in Tables 1 and 2.

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