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Synthesis and Properties of Cobalt(I) Compounds. 5. Properties of Tris(triphenyl phosphite)cobalt(I) Halides

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Several reactions of $CoX[(PhO)_3P]_3$ (X = Cl, Br) are described. These include disproportionation, zinc reduction, reaction with water, and reaction with carbon monoxide. The preparation and properties of a new cobalt–cobalt bonded species are described.

The use of $CoX[(PhO)_3P]_3$ compounds as catalysts with in situ generation of the complexes was first indirectly disclosed in 1971 and has been further disclosed more recently.[1] Methods for the isolation of these complexes have only recently been found.[2] The chemistry of the triphenyl phosphite complexes has now been explored under a variety of conditions. The complexity of the reactions with zinc or water in acetonitrile explains the need for careful choice of reaction conditions for the preparation of $CoX[(PhO)_3P]_3$ by zinc reduction of CoX_2 in acetonitrile.[2]

Zinc Reduction and Disproportionation

These compounds are quite reactive in solution. In all of the cases examined, the solutions tend to decompose to give cobalt(II) complexes and black magnetic precipitates at temperatures as low as 45 °C. Addition of triphenyl phosphite stabilizes the solutions. At 15–20 °C solutions in benzene or acetone are stable for several hours without added $(PhO)_3P$, but even in these cases on long standing mixtures of black magnetic precipitate and blue liquids formed. The stabilization by free triphenyl phosphite is striking. With neat $(PhO)_3P$ as solvent the decomposition is not rapid even at 100 °C.

Nitrile solvents are a special case. Even cool acetonitrile solutions decompose but, instead of black magnetic precipitates, either $CoH[(PhO)_3P]_4$ or $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ is formed (along with the cobalt(II) complexes) depending on whether the acetonitrile contains traces of water or is thoroughly dry. Substantial amounts of $(PhO)_3P$ stabilize the acetonitrile solutions to these disproportionation reactions, but zinc reacts with wet or dry acetonitrile solutions with or without added $(PhO)_3P$ to give the same solid products. These reactions are summarized in Figure 1. The reaction with zinc is very solvent dependent. A benzene solution was essentially inert to zinc.

Disproportionation of $CoX[(PhO)_3P]_3$

The behavior in acetonitrile solution is not simple even in the absence of zinc. Acetonitrile solutions of the green $CoX[(PhO)_3P]_3$ compounds typically changed from pink to blue to amber or green in hours or minutes at room temperature and the solutions "stopped" changing color at either amber or green, and either green or white crystals formed. At higher temperatures (e.g., above 45 °C) blue solutions and a black magnetic solid formed. The reaction in nonpolar solvents or in warm acetonitrile appears to be a simple disproportionation to cobalt(II) complexes and metallic cobalt based on the attraction of the black precipitate to a small magnet and the visible spectrum of the blue solution produced.

Careful drying of the acetonitrile and a study of the electronic spectra as a function of time led to several interesting observations. The visible spectrum of a dry acetonitrile solution of $CoCl[(PhO)_3P]_3$ obtained immediately after its preparation no longer had the ~775-nm peak characteristic of benzene or tetrahydrofuran solutions. Repeated scans then showed a decline in absorption at 850 nm concurrent with the appearance of peaks typical of tetrahedral Co(II) complexes in the 550–750-nm region and the 470-nm peak of $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ simultaneously appeared on the tail out of the UV. In one case the decomposition of a solution of 55 mg of $CoCl[(PhO)_3P]_3$ in 7 ml of dry acetonitrile was followed for 3 days at room temperature. The dark green crystals which formed were collected (5.5 mg). They had the same visible spectrum as $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ formed by zinc reduction of $CoX[(PhO)_3P]_3$.

The rate of loss of the 850-nm intensity and appearance of the 470- and 690-nm peaks depended on the concentration. The changes were more rapid in dilute solutions. The nature of the anion is also important since the changes were faster for the chloride than for the bromide under the same conditions. The most dramatic effect on the rates of the changes in the electronic spectra was produced by added ligand. The nitrile solutions became essentially stable at room temperature even in wet acetonitrile if triphenyl phosphite was present at 10 vol % or more.

Measurements of electrical conductivity and magnetic moment were made on fresh solutions of $CoBr[(PhO)_3P]_3$ in dry acetonitrile. The magnetic moment determined by the Evans[4] technique at 220 MHz was 3.2 μ_B at 20 °C and was nearly constant in 0.5 h at 20 °C. Electrical conductivity measurements gave initially $\Lambda = 4.7$ which increased in 9 min to 6.8. Addition of 10 vol % $(PhO)_3P$ at this point caused an immediate drop of the conductivity to $\Lambda = 4.8$ which was then constant for 2 h. The conductivity of tetrabutylammonium bromide (vacuum-dried at 110 °C) at the same molar concentration in the same solvent was 130. This compares to values of $\Lambda = 123$ and 131 reported[5] for similar concentrations of tetramethylammonium bromide and tetraethylammonium bromide in acetonitrile. The magnetic data argue strongly against immediate conversion of the bulk of the complex to any five-coordinate species in acetonitrile. The conductivity data in acetonitrile argue strongly against immediate conversion of the bulk of the original complex to any ionic species but do suggest a reversible formation of a small amount of an ionic species with loss of coordinated $(PhO)_3P$.

In wet (about 0.2% or more water) or dry acetonitrile solutions similar color changes occurred, but the changes took place much more quickly in wet acetonitrile. However, in wet acetonitrile the solid product which formed was white rather than green. In one case the solid was isolated and shown to be $CoH[(PhO)_3P]_4$ by 220-MHz ^1H NMR. It thus appears that similar processes take place with or without zinc in both wet and dry acetonitrile. It seems reasonable to speculate that similar intermediates are involved with either zinc or a cobalt(I) complex acting as the reducing agent.

Reaction of $CoX[(PhO)_3P]_3$ with $(EtO)_3P$

The reaction of $CoCl[(PhO)_3P]_3$ with $(EtO)_3P$ in acetone or acetonitrile gave a yellow color quickly and a ~390-nm peak appeared in the visible spectrum. Subsequent experiments with $CoBr[(PhO)_3P]_3$ showed that the reaction rate was greatly influenced by solvent polarity. The reaction was very

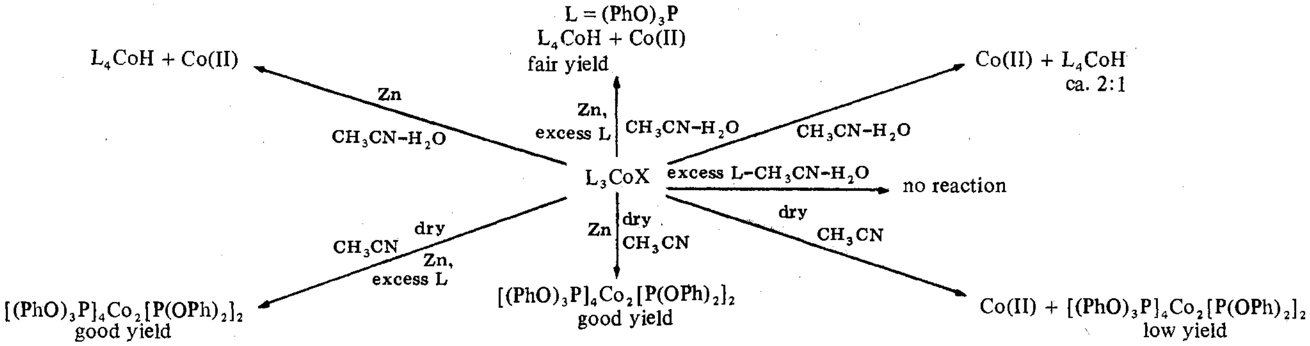

Figure 1. Reactions of [(PhO)$_3$P]$_3$CoX in nitrile solvents.

much faster in acetone than in tetrahydrofuran or benzene. In 50 vol % tetrahydrofuran in acetone semiquantitative experiments showed that the rate of appearance of the ~390-nm peak of $\{Co[(EtO)_3P]_5\}^+X^-$ was strongly dependent on the concentration of (EtO)$_3$P. Similar observations were made in the reaction of CoCl[(EtO)$_3$P]$_3$ with excess (EtO)$_3$P.[6] In one case the $\{Co[(EtO)_3P]_5\}^+X^-$ product of the reaction of (EtO)$_3$P with CoCl[(PhO)$_3$P]$_3$ was isolated and characterized.[2] Reaction with (EtO)$_3$P resembles more the reaction with zinc than that with carbon monoxide where the reaction is rapid even in nonpolar solvents.

Reactions with Carbon Monoxide

The availability of the cobalt(I) halides with trialkyl and triaryl phosphite ligands has made it possible to compare their reactions with carbon monoxide. In contrast to the reaction with zinc or (EtO)$_3$P, the CoX[(PhO)$_3$P]$_3$ compounds react rapidly with carbon monoxide in benzene solution. Two key points are that the carbonyl formation can be reversed under mild conditions and that the monocarbonyl CoBr(CO)-[(PhO)$_3$P]$_3$ has very limited stability. It is not favored in solution without large amounts of excess ligand or in the presence of excess CO. The addition of 1 equiv of CO to CoBr[(PhO)$_3$P]$_3$ gave a solution of Co(CO)$_2$Br[(PhO)$_3$P]$_2$, unreacted CoBr[(PhO)$_3$P]$_3$, and free (PhO)$_3$P. Similarly, Co(CO)Br[(PhO)$_3$P]$_3$ dissolved at room temperature to give a solution of the same composition unless the solvent contained a large concentration of (PhO)$_3$P.

This is in contrast to the behavior of the CoX[(EtO)$_3$P]$_3$ complexes with CO. With these complexes addition of less than 1 equiv of CO did give the monocarbonyl complex Co(CO)X[(EtO)$_3$P]$_3$. In fact, while the dicarbonyl complex can be formed by adding an excess of CO to CoX[(EtO)$_3$P]$_3$, a solution containing Co(CO)$_2$X[(EtO)$_3$P]$_2$ and 1 equiv of (EtO)$_3$P forms the monocarbonyl complex readily at room temperature.

With such marked contrast in the behavior of the triethyl phosphite and triphenyl phosphite complexes, it was interesting to see how the triphenylphosphine complexes behave under similar conditions. The relative stabilities of the two carbonyls in the triphenylphosphine system are intermediate between those of the phosphite complexes. The dicarbonyl complex Co(CO)$_2$Br[Ph$_3$P]$_2$ is readily formed from CoBr[Ph$_3$P]$_3$ and excess CO.[7] The monocarbonyl Co(CO)Br[Ph$_3$P]$_3$ is the predominant species formed when 1 equiv or less of carbon monoxide is added based on the predominance of a single ~1960-cm^{-1} carbonyl peak. On standing, however, the 1920- and 1980-cm^{-1} peaks of the known dicarbonyl complex Co(CO)$_2$Br[Ph$_3$P]$_2$[7] intensify. The rate of this intensification was greatly diminished in the presence of ca. 15–20% by weight of free triphenylphosphine in tetrahydrofuran. A solution of the dicarbonyl complex Co(CO)$_2$Br[Ph$_3$P]$_2$[7] with the same excess of free triphenylphosphine under similar conditions did not show conversion of the 1920–1980-cm^{-1} pair of bands to the 1960-cm^{-1} band so apparently both the initial formation of the species with the 1960-cm^{-1} band and its stabilization by free triphenylphosphine are kinetic effects.

Table I

Water	(PhO)$_3$P	Zn	Product	Yield
1%	None	200 mg	CoH[(PhO)$_3$P]$_4$	90 mg, 30%
1%	None	None	CoH[(PhO)$_3$P]$_4$	80 mg, 26%
	None	200 mg	[(PhO)$_3$P]$_4$Co$_2$-[P(OPh)$_2$]$_2$	100 mg, 48%
1%	1 g	300 mg	CoH[(PhO)$_3$P]$_4$	150 mg, 50%

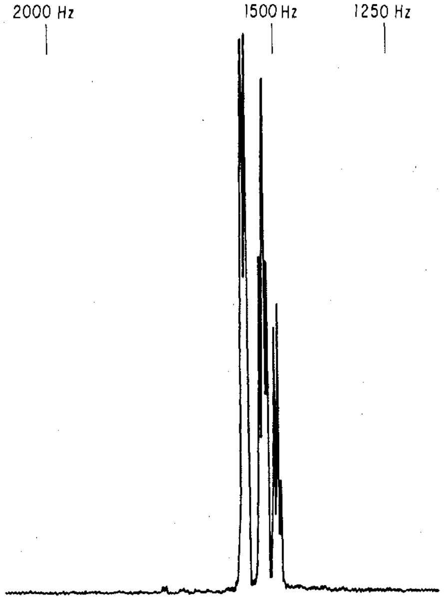

Figure 2. The 220-MHz ^{1}H NMR spectrum of HCo[P(OPh)$_3$]$_4$ in C$_6$D$_6$; values in Hz downfield from (CH$_3$)$_4$Si.

Experimental Section

The IR spectra were recorded with Perkin-Elmer Models 467 and 137. A Beckman Model 25 and a Cary 17 were used for the electronic spectra. The ^{1}H NMR spectra were obtained with a Varian 220-MHz instrument. The ^{31}P spectra were obtained with a Bruker 90-MHz instrument modified for Fourier transform operation. The melting points were obtained with an uncalibrated Mel Temp apparatus. The triphenyl phosphite and triethyl phosphite were commercial samples. The tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored over sodium in nitrogen. The reaction mixtures were proteced from contact with air. A nitrogen-filled glovebox was used for many of the operations.

Zinc Reduction and Disproportionation of CoBr[(PhO)$_3$P]$_3$. The influence of excess (PhO)$_3$P, water, and zinc dust on the fate of CoBr[(PhO)$_3$P] dissolved in acetonitrile is illustrated by some small-scale experiments which are summarized in Table I. In each case 250 mg (0.23 mmol) of CoBr[(PhO)$_3$P]$_3$ was dissolved in 5 ml of an acetonitrile solution containing water, zinc, or (PhO)$_3$P as indicated. The solids which then formed were collected and identified.

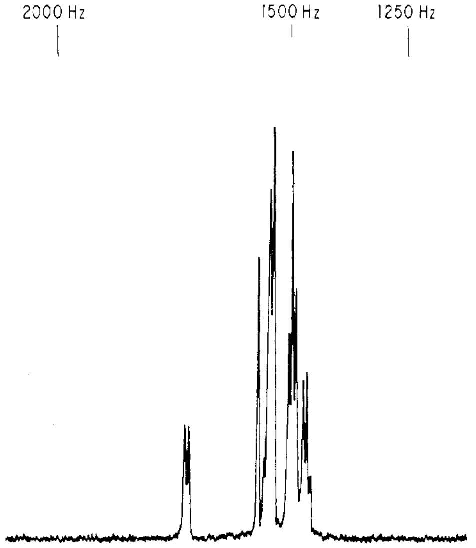

Figure 3. The 220-MHz ^1H NMR spectrum of $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ in C_6D_6; values in Hz downfield from $(CH_3)_4Si$.

Both $CoH[P(OPh)_3]_4$ and $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ are nearly insoluble in acetonitrile and simply precipitate or crystallize from the reaction mixtures. In addition to the compounds being different colors, their ^1H (see Figures 2 and 3) NMR spectra are quite different even in just the aromatic region and the ^{31}P NMR spectra are quite different as well. The structure of the green solid was determined by x-ray diffraction.[3]

Preparation of $[(PhO)_3P]_4Co_2[P(OPh)_2]$ by Zinc Reduction of $CoX[(PhO)_3P]_3$. To avoid the reaction of $CoX[(PhO)_3P]_3$ with water in acetonitrile, nominally anhydrous Eastman acetonitrile was dried over ca. one-third of a bottle of 4A molecular sieves for several days and a new bottle of zinc dust was opened under nitrogen in the glovebox. A mixture of 5 g (4.7 mmol) of $CoBr[(PhO)_3P]_3$, 4 g (61 mmol) of zinc dust, and 100 ml of acetonitrile was stirred at room temperature. Within about 1 h the original green solid appeared to have dissolved and greenish solid was beginning to form in a red-amber liquid. After 3 days at room temperature the solid was collected, washed with acetonitrile, and then washed with hexane and dried. The green solid was then dissolved in THF and the residual zinc was filtered out. The THF was evaporated from the green filtrate under reduced pressure. The residue was triturated with hexane and the solid was collected, washed, and dried, yielding 3.6 g (85% yield). Evaporation of the acetonitrile from the initial filtrate and trituration of the residue with hexane gave 1.9 g of dry red solid. Analysis of this red solid showed 13.2% Zn, 6.8% Co, and 37% Br. The zinc clearly acted as a reducing agent to produce acetonitrile-soluble zinc salts. This red residue was a mixture, but it was not further characterized. In a subsequent experiment with nearly the same conditions, 3.5 g of red acetonitrile-soluble product was obtained from 10 g of $CoBr[(PhO)_3P]_3$. Crystallization of the green reaction product from methylene chloride–hexane gave 6.3 g (75% yield) of dark green crystalline solid.

About 2.7 g of the green acetonitrile-insoluble solid was recrystallized from ca. 10 ml of hot benzene to give 2 g of large dark green shiny crystals (mp ~120–160 °C dec; evacuated capillary).

Anal. Calcd for $[(C_6H_5O)_3P]_4Co_2[P(OC_6H_5)_2]_2$: C, 64.29; H, 4.5; Co, 6.57; mol wt 1793. Calcd for $[(C_6H_5O)_3P]_4Co_2[P(OC_6H_5)_2]_2{\cdot}C_6H_6$ ($C_{96}H_{80}O_{16}P_6Co_2{\cdot}C_6H_6$): C, 65.44; H, 4.63; Co, 6.30; mol wt 1871. Found: C, 65.68, 66.09; H, 4.73, 4.78; Co, 6.0; N and Br, <0.3; mol wt 1998 (cryoscopic in benzene).

The ^1H NMR spectra in $DCCl_3$ and THF-d_9 showed benzene present.

The 36.43-MHz ^{31}P NMR spectrum in C_6D_6 showed just two peaks: one at 327 and one at 128 ppm downfield from external 85% H_3PO_4. (The signal from $[Co(CO)_3(PhO)_3P]_2$ was at 167 ppm downfield from 85% H_3PO_4.) The material was diamagnetic as judged by the sharp ^1H NMR spectrum and the coincidence of internal and external tetramethylsilane. The visible spectrum was characterized by a broad band at ca. 710 nm, ϵ 1130, and a sharper, much stronger peak at ca. 470 nm, ϵ 9140, in benzene. The ^1H NMR and visible spectra are shown in Figures 3 and 4.

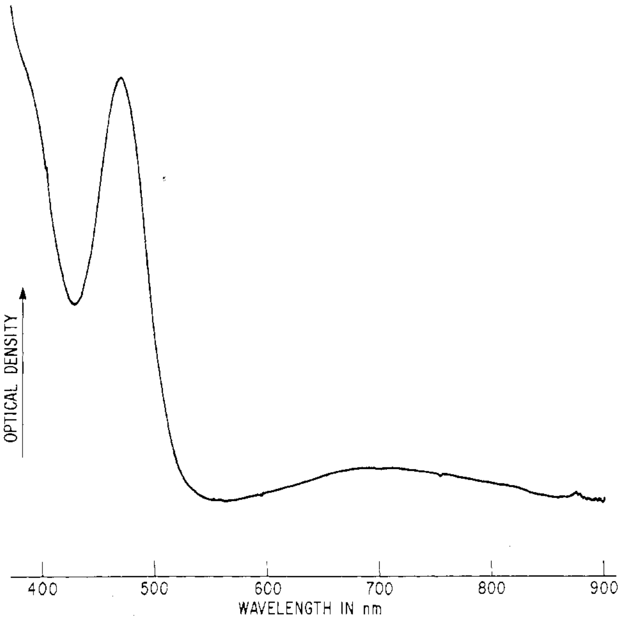

Figure 4. Visible spectrum of $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$ in benzene.

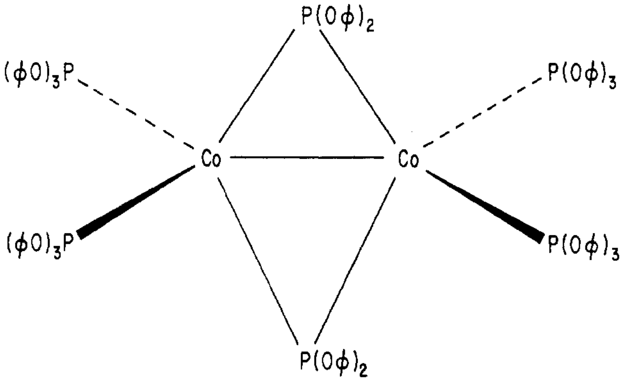

Figure 5.

The ESCA spectrum gave the following values (corrected to C_{1s}, 285.0 eV): $Co_{2p_{3/2}}$, 779.8 eV; P_{2p}, 132.9 ev. This compares well with the values obtained for $\{Co(CO)_3[(PhO)_3P]\}_2$ ($Co_{2p_{3/2}}$, 780.3 ev; P_{2p}, 133.2 eV) and suggests a high electron density on cobalt compared to Co(II) compounds.[8]

Other experiments showed that similar yields of materials with the same properties were obtained by zinc reduction of $CoBr[(PhO)_3P]_3$ in acetonitrile with as much as ~4 vol % free $(PhO)_3P$ present initially.

A small portion of the green acetonitrile-insoluble material was recrystallized from CH_2Cl_2–cyclohexane by allowing the CH_2Cl_2 to evaporate at room temperature. This gave nice single crystals. The x-ray diffraction study of these crystals[3] showed the compound to be $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$. See Figure 5 for a representation of the structure.

Preparation of $Co(CO)_2Br[Ph_3P]_2$. This was prepared by reacting $CoBr[Ph_3P]_3$ with excess carbon monoxide.[7]

Preparation of $Co(CO)_2Br[(PhO)_3P]_2$. This was prepared by reacting $CoBr[(PhO)_3P]_3$ with excess carbon monoxide.[2]

Preparation of $Co(CO)Br[(PhO)_3P]_3$. A solution was prepared from 50 ml of CH_2Cl_2, 1.5 g (4.8 mmol) of $(PhO)_3P$, and 1.5 g (1.8 mmol) of $Co(CO)_2Br[(PhO)_3P]_2$, and 150 ml of hexane was added. The mixture was left to concentrate by evaporation at room temperature. Filtration after 3 days gave about 1.75 g (89% yield) of red-brown crystals with a trace of yellow crystals. This mixture was redissolved in a solution of 1.5 g of $(PhO)_3P$ in 40 ml of CH_2Cl_2. The resulting solution was filtered, diluted with 40 ml of hexane, and left to evaporate at room temperature. Large brown crystals resulted with a few green crystals. The brown crystals were segregated manually, suspended in ether, and collected. The solid was washed with hexane and briefly vacuum-dried at room temperature, yielding 1.1 g (mp ~95 °C dec?; evacuated capillary).

Table II

Solvent	Initial $[[(PhO)_3P]_2Co(CO)_2Br]$, mg/ml	% converted to $[(PhO)_3P]_3CoBr$
20 vol % $(PhO)_3P$ in C_6H_6	6	11
20 vol % $(PhO)_3P$ in CH_2Cl_2	60	11
20 vol % $(PhO)_3P$ in CH_2Cl_2	6	11
Neat $(PhO)_3P$	70	6
Benzene	6	45

Anal. Calcd for $[(C_6H_5O)_3P]_3Co(CO)Br$: C, 60.18; H, 4.13; Co, 5.37. Found: C, 58.95; H, 4.16; Co, 5.61.

The IR spectrum (Nujol) showed a single carbonyl band at ca. 1960 cm^{-1}. In benzene solution it appeared to be substantially paramagnetic by the Evans method.[4] However, in $(PhO)_3P$ solution it appeared to be nearly diamagnetic. Examination of the visible spectra of these solutions revealed the probable cause of the variable paramagnetism values. All of the visible spectra of $CoBr(CO)[(PhO)_3P]_3$ solutions showed the broad ~775-nm peak of $CoBr[(PhO)_3P]_3$. The amounts of conversion of $CoBr(CO)[(PhO)_3P]_3$ into $CoBr[(PhO)_3P]_3$, $Co(CO)_2Br[(PhO)_3P]_2$, and $(PhO)_3P$ were indicated by the visible spectra and are shown in Table II. This implies that at 6 mg/ml in benzene the reaction $CoBr(CO)[(PhO)_3P]_3 \rightarrow CoBr[(PhO)_3P]_3 + Co(CO)_2Br[(PhO)_3P]_2 + (PhO)_3P$ had gone nearly to completion. This agrees with the observation that with 125 mg of $CoBr[(PhO)_3P]_3$ (0.12 mmol) in 4.3 ml of CH_2Cl_2 in IR spectrum of the solution indicated substantial formation of $CoBr(CO)_2[(PhO)_3P]_2$ after the addition of only 1 ml (0.04 mmol) of CO. On the other hand, in a solution of 1 ml (3.8 mmol) of $(PhO)_3P$, 3.5 ml of CH_2Cl_2, and 125 mg (0.12 mmol) of $CoBr[(PhO)_3P]_3$, the IR spectra indicated a fairly sharp onset of $Co(CO)_2Br[(PhO)_3P]_2$ formation only when the CO added exceeded 3 ml. With that amount of $(PhO)_3P$ present the first equivalent of CO went almost exclusively to form $CoBr(CO)[(PhO)_3P]_3$.

Conversion of $Co(CO)_2Br[(PhO)_3P]_2$ + $(PhO)_3P$ to $CoBr((PhO)_3P]_3$. The coordination of CO can be completely reversed by sweeping dissociated CO from a benzene–$(PhO)_3P$ solution of $Co(CO)_2Br[(PhO)_3P]_2$ with a stream of nitrogen. In one experiment 169 mg (0.21 mmol) of $Co(CO)_2Br[(PhO)_3P]_2$ was dissolved in a solution of 16 ml of benzene and 2 ml (7.6 mmol) of $(PhO)_3P$. The solution was maintained at 80 °C for 1 h with a slow stream of nitrogen bubbling through. The residual green solution was diluted with benzene. The visible spectrum was qualitatively that of $CoBr[(PhO)_3P]_3$. The remaining solution was diluted with pentane and the resulting green solid was collected and dried. The IR (Nujol) spectrum showed no carbonyl bands. The visible spectrum in benzene was that of $CoBr[(PhO)_3P]_3$ (ϵ_{775} 280, ϵ_{425} 111). The remaining green solid was dissolved in benzene and exposed to CO. Addition of pentane caused the precipitation of a yellow solid with the IR spectrum of $Co(CO)_2Br[(PhO)_3P]_2$. The yellow solid crystallized nicely from CH_2Cl_2–pentane but the elemental analysis and ^{1}H NMR both show that about 1 mol of CH_2Cl_2 was retained in the crystal.

Preparation of Carbonyl Complexes from $CoCl[(EtO)_3P]_3$. In contrast to the $CoBr[(PhO)_3P]_3$–CO system described above, in the $CoCl[(EtO)_3P]_3$–CO system both the carbonyls $Co(CO)_2Cl[(EtO)_3P]_2$ and $Co(CO)Cl[(EtO)_3P]_3$ can be prepared by adding different amounts of CO to solutions of $CoCl[(EtO)_3P]_3$ without excess $(EtO)_3P$. For example, in one set of experiments with different amounts of CO added to serum vials each containing 22.4 mg (0.04 mmol) of $CoCl[(EtO)_3P]_3$ in 1 ml of CH_2Cl_2, the monocarbonyl appeared to be formed cleanly with 1 equiv of CO added, and the dicarbonyl with excess CO. (See Table III.)

Similar indications were provided by ^{31}P NMR spectra. After 5 ml of CO (1 equiv) was added to a solution of 115 mg of $CoCl[(EtO)_3P]_3$ in 2 ml of C_6D_6, the ^{31}P NMR showed almost entirely a single peak at 148 ppm downfield from external 85% H_3PO_4 with a trace at 139 ppm (free $(EtO)_3P$). Similarly, with 15 ml of CO (3 equiv), the ^{31}P NMR showed strong peaks at 146 and 139 ppm.

Conversion of $Co(CO)_2Cl[(EtO)_3Pl_2$ + $(EtO)_3P$ to $Co(CO)Cl[(EtO)_3P]_3$. A solution of 115 mg of $CoCl[(EtO)_3P]_3$ in 2 ml of benzene was treated with 15 ml of CO to produce a solution of the yellow dicarbonyl and free $(EtO)_3P$. It was then left in a dish to concentrate to an oil by evaporation at room temperature and in ca. 2.5 h the IR spectrum (neat) indicated almost complete conversion to $CoCl(CO)[(EtO)_3P]_3$. A benzene solution of pure $Co(CO)_2Cl[(EtO)_3P]_2$ treated in the same way gave essentially unchanged $Co(CO)_2Cl[(EtO)_3P]_2$.

Table III

Amt of CO added,[a] mmol	Carbonyl IR bands, cm^{-1}	Amt of CO added,[a] mmol	Carbonyl IR bands, cm^{-1}
0.02	1910	0.08	1910 and 1935 s, 1990
0.04	1910	0.12	1935, 1990

[a] $[(EtO)_3P]_3CoCl$ constant, 0.04 mmol.

Conversion of $Co(CO)Cl[(EtO)_3P]_3$ to $CoCl[(EtO)_3P]_3$. One equivalent (5 ml) of CO was added to a solution of 115 mg of $CoCl[(EtO)_3P]_3$ in 2 ml of C_6D_6. A solution of 100 μl of $(EtO)_3P$ in 5 ml of toluene was added. The solution was warmed to 60 °C and a slow stream of nitrogen was bubbled through for 1 h. The solution was diluted to 10.0 ml with hexane. The visible spectrum showed the ~780-nm peak of $CoCl[(EtO)_3P]_3$ with an intensity corresponding to ca. 70% conversion to $CoCl[(EtO)_3P]_3$. There was no 390-nm $\{Co[(EtO)_3P]_5\}^+Cl^-$ peak. About 7 ml of the solution was concentrated to a grease under vacuum and 1 ml of hexane was added. The IR (hexane) spectrum showed the 1910-cm^{-1} carbonyl peak still present but at only ca. one-fourth of the intensity expected for that concentration of $CoCl(CO)[(EtO)_3P]_3$.

Preparation of $Co(CO)_2Cl[(EtO)_3P]_2$. A solution of 1.1 g (1.9 mmol) of $CoCl[(EtO)_3P]_3$ in 5 ml of hexane was sparged with CO and then the pressure was increased to ca. 20 psig CO. After several days at −35 °C the large yellow crystals were collected, washed with cold hexane, and dried, giving 0.80 g (1.7 mmol, 87% yield); mp ~68 °C dec? (evacuated capillary). IR (Nujol) carbonyl bands were seen at 1935 and 1990 cm^{-1} with the 1935-cm^{-1} peak the stronger.

Anal. Calcd for $C_{14}H_{30}O_8P_2CoCl$: C, 34.83; H, 6.26. Found: C, 34.58; H, 6.28.

Preparation of $CoBr[(EtO)_3P]_3$. Nominally anhydrous cobalt(II) bromide (13.13 g, 60 mmol) was added to a solution of 10 ml (556 mmol) of water in 600 ml of anhydrous ethanol. The mixture was warmed to 60 °C and 28 ml (180 mmol) of triethyl phosphite was added followed by a solution of 16 ml (115 mmol) of triethylamine in 100 ml of ethanol. An immediate precipitate formed. On standing overnight the green supernatant liquid became yellow. The mixture was filtered and the yellow filtrate evaporated to dryness at room temperature. Extraction of the yellow residue with ether left the insoluble triethylamine hydrochloride. Evaporation of the yellow extract gave a yellow crystalline solid which was filtered and rinsed with pentane. Recrystallization gave 6.6 g (6.8 mmol, 11% yield) of yellow needles of diamagnetic pentakis(triethyl phosphite)cobalt(I) bromide.

Anal. Calcd for $C_{30}H_{75}BrCoO_{15}P_5$: C, 37.16; H, 7.80. Found: C, 37.06; H, 7.80.

The yellow solid was heated under high vacuum at 85–90 °C. The solid became black. The residue was extracted with pentane in a nitrogen atmosphere. Crystallization from pentane gave 3.07 g (4.8 mmol, 71% yield) of brown bromotris(triethyl phosphite)cobalt(I), mp 68–70 °C.

Anal. Calcd for $C_{18}H_{45}BrCoO_9P_3$: C, 33.92; H, 7.12; Br, 12.54; P, 14.58. Found (av): C, 34.04; H, 7.12; Br, 12.53; P, 14.25.

Preparation of $Co(CO)Cl[(EtO)_3P]_3$. A solution of 575 mg (0.97 mmol) of $CoCl[(EtO)_3P]_3$ in 2 ml of hexane was placed in a serum ampule and 25 ml (1 mmol) of CO was added by syringe. The resulting red-brown solution was then cooled to −35 °C. The red crystals were collected, washed with hexane, and dried, giving 450 mg (0.73 mmol, 75% yield); mp 38 °C (evacuated capillary). There were two strong carbonyl bands in the IR spectrum (Nujol) at 1903 and 1918 cm^{-1}, of about equal intensity.

Anal. Calcd for $C_{19}H_{45}O_{10}P_3CoCl$: C, 36.75; H, 7.31. Found: C, 36.58; H, 7.06.

Addition of Carbon Monoxide to $CoBr[(EtO)_3P]_3$. 1. Stepwise Addition. A solution was prepared from 130 mg (0.20 mmol) of $CoBr[(EtO)_3P]_3$ and 5 ml of CH_2Cl_2. Portions (1.0 ml) of this solution were placed in serum ampules and CO was added by syringe as indicated below. The carbonyl regions of the IR spectra showed clearly the stepwise formation of the monocarbonyl followed by the dicarbonyl. (See Table IV.)

Table IV

Amt of CO, ml	Carbonyl bands, cm^{-1}	Amt of CO, ml	Carbonyl bands, cm^{-1}
0.5	1910	2.0	1990, 1930
1.0	1910	3.0	1990, 1930

2. Preparation of $Co(CO)Br[(EtO)_3P]_3$. A solution of 2.2 g (3.5 mmol) of $CBr[(EtO)_3P]_3$ in 4 ml of hexane was placed in a serum bottle and CO was added from a 20-ml reservoir (total pressure drop 75 psi). The resulting solution was then cooled to −35 °C for several days. The dark red crystals were collected, washed with hexane, and vacuum-dried, giving 0.9 g (1.4 mmol, 39% yield); mp 35 °C (evacuated capillary). There was a single carbonyl at 1925 cm^{-1} (Nujol) and a benzene solution was essentially diamagnetic as judged by the Evans technique.[4]

Anal. Calcd for $C_{19}H_{45}O_{10}P_3CoBr$: C, 34.30; H, 6.82. Found: C, 34.11; H, 6.66.

3. Preparation of $Co(CO)_2Br[(EtO)_3P]_2$. A solution of 1.84 g (2.9 mmol) of $CoBr[(EtO)_3P]_3$ in 10 ml of hexane was placed in a pressure bottle and CO was added until the pressure remained at 30 psig. The mixture was cooled to −35 °C under CO pressure for several days. The yellow crystals were collected, washed with hexane, and vacuum-dried, giving 1.30 g (2.5 mmol, 85% yield); mp 70 °C (evacuated capillary). A benzene solution was essentially diamagnetic by the Evans method.[4] There were two IR carbonyl bands (Nujol): a strong one at 1932 and a much weaker one at 1990 cm^{-1}.

Anal. Calcd for $C_{14}H_{30}O_8P_2CoBr$: C, 31.89; H, 5.74. Found: C, 31.98; H, 5.65.

Registry No. $CoH[(PhO)_3P]_4$, 24651-64-7; $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$, 61024-91-7; $CoBr[(PhO)_3P]_3$, 61026-10-6; $[Co(CO)_3(PhO)_3P]_2$, 21118-36-5; $Co(CO)Br[(PhO)_3P]_3$, 61026-11-7; $Co(CO)_2Br[(PhO)_3P]_2$, 14653-41-9; $Co(CO)_2Cl[(EtO)_3P]_2$, 61026-12-8; $Co(CO)Cl[(EtO)_3P]_3$, 61026-13-9; $CoCl[(EtO)_3P]_3$, 15488-43-4; $Co(CO)Br[(EtO)_3P]_3$, 61025-73-8; $Co(CO)_2Br[(EtO)_3P]_2$, 61025-83-0; CO, 630-08-0; ^{31}P, 7723-14-0.

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Preparation, Structure, and Interconversion Kinetics of Mono- and Binuclear Aquo(nitrilotriacetato)cobaltate(III) Complexes

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Our attempts to synthesize the previously reported complex ion $K[Co(NTA)(OH)(H_2O)]\cdot nH_2O$ in the pure solid form failed, the procedure used inevitably leading to samples of the di-μ-hydroxo species, $K_2[Co_2(NTA)_2(OH)_2]$. The acid-catalyzed hydrolysis of this compound proceeds in two identifiable steps, each described by a rate equation of the form $k_{obsd} = k_2K_2[H^+]^2/(1 + K_2[H^+])$. The mechanistic implications of the rate data are discussed in relation to the considerable number of previous studies of μ-hydroxo-dicobalt(III) complex ions. It is concluded that a common multistep mechanism prevails, although the rate-determining characteristics of the mechanism vary considerably among the complexes considered.

Introduction

The first preparative study of the title complexes was carried out by Mori, Shibata, Kyuno, and Okubo,[1] who reported the existence of three different but related species. Two of these were stated to be mononuclear α and β geometric isomers of composition $K[Co(NTA)(OH)(OH_2)]$ (where NTA ≡ $[N(CH_2COO)_3]^{3-}$ ≡ nitrilotriacetate ion) and were postulated to differ only in the location of the aquo proton (see Figure 1). The third species proposed was the binuclear di-μ-hydroxo complex $K_2[Co_2(NTA)_2(OH)_2]$, also shown in Figure 1. The aquo–hydroxo isomerism is possible in the solid state but is probably questionable since facile proton transfer would be expected to render the suggested α and β forms indistinguishable. The structural proposals have also been questioned on the basis of NMR data[2] and conventional chemical evidence.[3] It now appears that Mori et al.'s α-$K[Co(NTA)(OH)(OH_2)]$ species is in fact binuclear[2] and is probably of the form already mentioned,[3] that their β-$K[Co(NTA)(OH)(OH_2)]$ does have the formula assigned but may be impure,[3] and that what they identified as a binuclear complex is in fact the species[3] $K[Co(HNTA)_2]\cdot 2H_2O$ (HNTA represents the monoprotonated triply coordinating form of NTA). While the last referenced work was in progress, we had become engaged in a similar type of preparative investigation since we wished to use the compound $Co(NTA)(OH_2)_2$ in an extension of our carbon dioxide uptake studies.[4] We found it rather easy to prepare aqueous solutions of the diaquo compound by decarboxylation of the carbonato congener $Co(NTA)CO_3^{2-}$, as reported in our kinetic study of the latter process.[5] However, our attempts to prepare pure solid samples of complexes of the formula $K[Co(NTA)(OH)(H_2O)]\cdot nH_2O$ by the published procedures[1-3] failed, our purified product inevitably turning out to be $K_2[Co(NTA)_2(OH)_2]$. Our kinetic studies of the acid-catalyzed hydrolysis of this di-μ-hydroxo species confirm some of the findings of Thacker and Higginson[3] which have been sufficiently extended to enable further clarification of the chemistry of this interesting system, as well as of related μ-hydroxo-cobalt(III) species.

Experimental Section

Materials. Nitrilotriacetic acid was obtained from Eastman Kodak Co. and used without further purification. All other chemicals were of reagent grade. Concentrated nitric acid was diluted to double the volume and then bubbled with nitrogen for about 2 h to remove dissolved oxides of nitrogen. The concentration of the acid was determined by titration with standard base and it was stored in the dark in a Pyrex container. The preparation of $K[Co(NTA)(OH)(OH_2)]$ was attempted according to the procedure of Mori et al.[1] and also by a slightly modified method in which the order of mixing of the reagents was reversed. A blue finely divided solid was obtained in both cases and was recrystallized from water at 55–60 °C. These products have identical spectra in aqueous solution (see Figure 2). After three more recrystallizations from water, deep purple platelets were obtained. These were washed five times with absolute ethanol