$(Bu_3P)Co(DH)_2Br$, 51194-40-2; $(Bu_3P)Co(DH)_2NO_3$, 51194-37-7; $(Bu_3P)Co(DH)_2Cl$, 24501-27-7; $(Bu_3P)Co(DH)_2NCS$, 51194-38-8; $(Bu_3P)Co(DH)_2C_5H_4N_5$, 61075-77-2; $(Bu_3P)Co(DH)_2C_5H_3N_4O$, 61024-89-3; $(Bu_3P)Co(DH)_2N_3$, 51194-39-9; $(Bu_3P)Co(DH)_2NO_2$, 51194-42-4; $(Bu_3P)Co(DH)CN$, 51194-44-6; $(Bu_3P)Co(DH)_2SO_2C_6H_4CH_3$, 55886-56-1; $(Bu_3P)Co(DH)_2P(O)(OCH_3)_2$, 61024-90-6; $(Bu_3P)Co(DH)_2CH_2Br$, 55886-62-9; $(Bu_3P)Co(DH)_2C_6H_4OCH_3$, 55886-64-1; $(Bu_3P)Co(DH)_2C_6H_5$, 55923-88-1; $(Bu_3P)Co(DH)_2C_6H_4Br$, 55886-65-2; $(Bu_3P)Co(DH)_2CH_3$, 51020-41-8; $[(Bu_3P)_2Co(DH)_2]As(C_6H_5)_4$, 61026-07-1; Bupy, 3978-81-2; $(CH_3O)_3P$, 121-45-9; Bu_3P, 998-40-3; ^{13}C, 14762-74-4.

Supplementary Material Available: Tables of ^{13}C NMR shifts and P–C coupling constants for series II and III, for additional compounds in series I, and for the X ligands, a more extensive tabulation similar to Table II but for ^1H NMR and ^{13}C NMR for all three series, and a summary of the least-squares correlations (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) K. D. Gailey, K. Igi, and B. E. Douglas, *Inorg. Chem.*, **14**, 2956 (1975); P. L. Gaus and A. L. Crumbliss, *ibid.*, **15**, 739 (1976).
(2) T. B. Brill and A. J. Kotlar, *Inorg. Chem.*, **13**, 470 (1974); J. M. Malin, C. F. Schmidt, and H. E. Toma, *ibid.*, **14**, 2924 (1975).
(3) K. W. Jennette, S. J. Lippard, and D. A. Ucko, *Biochim. Biophys. Acta*, **402**, 403 (1975).
(4) L. G. Marzilli, P. Politzer, W. C. Trogler, and R. C. Stewart, *Inorg. Chem.*, **14**, 2389 (1975).
(5) B. E. Mann, *Chem. Commun.*, 976 (1971); L. F. Farnell, E. W. Randall, and E. Rosenberg, *ibid.*, 1078 (1971); M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972); H. C. Clark and J. E. H. Ward, *ibid.*, **96**, 1741 (1974).
(6) W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, **13**, 1564 (1974).
(7) W. C. Trogler and L. G. Marzilli, *J. Am. Chem. Soc.*, **96**, 7589 (1974).
(8) W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, **14**, 2942 (1975).
(9) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
(10) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967.
(11) L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, **11**, 2050 (1972).
(12) L. G. Marzilli, R. C. Stewart, L. A. Epps, and J. B. Allen, *J. Am. Chem. Soc.*, **95**, 5796 (1973).
(13) J. B. Stothers, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1972, pp 159, 250.
(14) See supplementary material. More information and figures may be found in the Ph.D. dissertation of R. C. Stewart, Jr., The Johns Hopkins University, 1976.
(15) (a) W. McFarlane, *Proc. R. Soc. London, Ser. A*, **306**, 185 (1968); (b) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 4940 (1969); (c) see ref 13, pp 376, 378.
(16) Theoretical studies on six-membered aromatic nitrogen heterocycles are reviewed in Chapter 7 of ref 13.
(17) L. G. Marzilli, L. A. Epps, T. Sorrell, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **97**, 3351 (1975).
(18) A. Bigotto, E. Zangrando, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 96 (1976).
(19) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.
(20) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(21) See ref 13, p 199. Similar relationships between ^{13}C and ^1H NMR shifts were observed in Pt(II) complexes: M. A. M. Meester, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, **15**, 137 (1975).
(22) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(23) G. Singh, *J. Organomet. Chem.*, **99**, 251 (1975).
(24) G. Singh and G. S. Reddy, *J. Organomet. Chem.*, **42**, 267 (1972).
(25) K. R. Dixon, K. C. Moss, and M. Smith, *J. Chem. Soc., Dalton Trans.*, 990 (1974).
(26) W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 324 (1974).
(27) D. R. Coulson, *J. Am. Chem. Soc.*, **98**, 3111 (1976).

Contribution No. 2398 from the Central Research & Development Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Synthesis and Properties of Cobalt(I) Compounds. 4. Syntheses of Tris(triphenyl phosphite)cobalt(I) Halides

LAWRENCE W. GOSSER

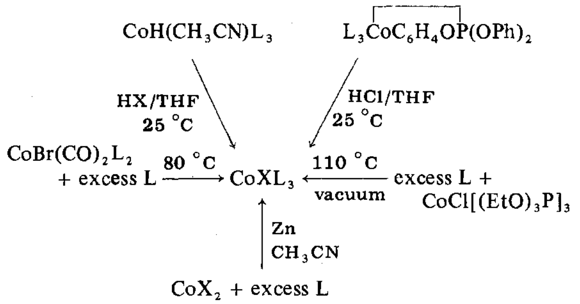
Received July 14, 1976 AIC60510B

Three methods of preparation of $CoX[(PhO)_3P]_3$ (X = Cl, Br) are given. Conversion to the known cobalt(I) compounds $\{Co[(EtO)_3P]_5\}^+Cl^-$ and $CoBr(CO)_2[P(OPh)_3]_2$ is demonstrated.

The preparation of the four-coordinate cobalt(I) halide complexes, $CoXL_3$, has been previously described in the cases where L is trimethylphosphine, triphenylphosphine, and triethyl phosphite.[1] The analogous triphenyl phosphite complexes, on the other hand, have not previously been isolated even though their use as catalysts with in situ formation has been disclosed.[2] The preparation and characterization of the complexes $CoX[(PhO)_3P]_3$ has now been completed. Reaction of these complexes with triethyl phosphite gave the known cobalt(I) complexes $\{Co[(EtO)_3P]_5\}^+X^-$.[1b] Reaction of $CoBr[P(OPh)_3]_3$ with excess carbon monoxide gave the known cobalt(I) halide complex, $CoBr(CO)_2[(PhO)_3P]_2$.

The methods developed for the preparation of $CoCl[(PhO)_3P]_3$ and $CoBr[(PhO)_3P]_3$ are summarized in Scheme I. The two top routes use HX to react with a cobalt hydride or cobalt aryl. The center two routes are ligand-exchange reactions and do not require reduction or oxidation. The bottom route is a reduction of cobalt halide by metallic zinc. All of the routes work fairly well but have individual difficulties. The bottom route in particular is simple in materials and concept, but can easily go wrong.

Scheme I. Syntheses of $CoX[(PhO)_3P]_3$($L = (PhO)_3P$; X = Cl, Br)



The magnetic moments of the $CoX[P(OPh)_3]_3$ complexes were found to be about 3.2–3.4 μ_B at room temperature. This is close to the values previously observed for the analogous complexes with tertiary phosphine[8] or triethyl phosphite[1b] ligands.

Preparation from Cobalt Hydrides and HX

The triphenylphosphinecobalt hydride complexes $CoHN_2[Ph_3P]_3$ and $CoH_3[Ph_3P]_3$ are reported to produce the four-coordinate complex $CoCl[Ph_3P]_3$ readily by reaction with HCl under mild conditions.[4] Several attempts were made to produce $CoCl[(PhO)_3P]_3$ by the reaction of the well-known cobalt hydride $CoH[(PhO)_3P]_4$ with HCl. The hydride was surprisingly unreactive in HCl solutions under mild conditions. Experiments at temperatures from room temperature up to about 100 °C showed that $CoH[P(OPh)_3]_4$ could be destroyed by anhydrous HCl, and in some cases dark green solutions were obtained. In none of these cases, however, was $CoCl[(PhO)_3P]_3$ detected. The visible spectra suggested that the green colors were produced by a strong tail out of the UV region combined with a typical cobalt(II) pattern in the 550–700-nm region.

Recently, much more reactive cobalt complexes with triphenyl phosphite ligands became available.[5] Both $CoH(CH_3CN)[P(OPh)_3]_3$ and $[(PhO)_3P]_3\overline{CoC_6H_4OP}(OPh)_2$ reacted with anhydrous HCl or HBr, and the complexes $CoX[P(OPh)_3]_3$ were formed. In a set of preliminary experiments analysis of the gas phase by mass spectroscopy showed that the reaction between $CoH(CH_3CN)[(PhO)_3P]_3$ and HCl liberated hydrogen gas in an approximately stoichiometric quantity when either 1 equiv or excess HCl was introduced. This reaction appeared to be complete in a few minutes at room temperature. The reaction of HCl with $[(PhO)_3P]_3\overline{CoC_6H_4OP}(OPh)_2$ was not as rapid. These mixtures were typically left at room temperature for several hours before the product, $CoCl[(PhO)_3P]_3$, was isolated. Presumably triphenyl phosphite was the other product of this reaction, although this was not confirmed experimentally.

Preparation from $CoCl[(EtO)_3P]_3$

Heating a mixture of excess $(PhO)_3P$ and $CoCl[(EtO)_3P]_3$ to just under the decomposition point (ca. 110 °C) under vacuum gave smooth conversion of the brown triethyl phosphite complex to the green triphenyl phosphite complex. There was no black deposit or other indication of decomposition during this transformation.

The reverse reaction, conversion of $CoCl[(PhO)_3P]_3$ to $\{Co[(EtO)_3P]_5\}^+Cl^-$, takes place readily at room temperature. This 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 rate of the reaction with $(EtO)_3P$ was greatly influenced by solvent polarity. The reaction was faster in acetone than in THF or benzene. In 50 vol % THF in acetone semiquantitative experiments showed that the rate of appearance of the ~390-nm peak of $\{Co[(EtO)_3P]_5\}^+Br^-$ was strongly dependent on the concentration of $(EtO)_3P$. Similar observations were made in the reaction of $CoCl[(EtO)_3P]_3$ with excess $(EtO)_3P$.[1b] In one case the $\{Co[(EtO)_3P]_5\}^+Cl^-$ product of this reaction was isolated and characterized as described in the Experimental Section. There was no indication of reaction of $CoCl[(PhO)_3P]_3$ with excess $(PhO)_3P$ to produce five-coordinate complexes even in neat $(PhO)_3P$. This may be due to the large size of the $(PhO)_3P$ ligand. The size of the ligands has been shown to be important in nickel(0) chemistry.[6]

Reduction of $CoCl_2/(PhO)_3P$ Mixtures

The reduction of $CoCl_2/(PhO)_3P$ mixtures can give a variety of results depending on the details. Under some circumstances, especially with sodium borohydride and hydrated cobalt salts such as $Co(NO_3)_2{\cdot}6H_2O$, a good yield of the hydride $CoH[(PhO)_3P]_4$ can be obtained from ethanol solution[7a] or from acetonitrile solution.[2b] Similar conditions have been employed to prepare the $CoXL_3$ cobalt(I) compounds from CoX_2/L solutions in ethanol by reduction with sodium borohydride or metallic zinc in cases where the ligands are triarylphosphines or diarylalkylphosphines.[8] The catalytic behavior of $CoX_2/(PhO)_3P$/reducing agent mixtures suggested the formation of $CoX[(PhO)_3P]_3$ compounds but these were not isolated.[2]

A number of trial reductions of $CoCl_2/(PhO)_3P$ with zinc in nitrile solvents produced red-amber liquids and tan-gray solids which were shown by ^{1}H NMR to be impure $CoH[(PhO)_3P]_4$. However, with increasingly careful control of the reaction conditions it was possible to prepare $CoX[P(OPh)_3]_3$ by zinc reduction of solutions prepared from CoX_2 and $(PhO)_3P$.

Reaction with Carbon Monoxide

A benzene solution of $CoBr[(PhO)_3P]_3$ readily absorbed carbon monoxide even below 1 atm at room temperature yielding a yellow crystalline solid which was shown (see Experimental Section) to be the same carbonyl complex, $CoBr(CO)_2[(PhO)_3P]_2$, as prepared by Hieber and Duchatsch.[3] It was also shown that $CoBr[(PhO)_3P]_3$ could be regenerated from $CoBr(CO)_2[(PhO)_3P]_2$ in the presence of excess $(PhO)_3P$.[7b]

Experimental Section

The IR spectra were recorded with a Perkin-Elmer Model 467 spectrometer. A Beckman Model 25 spectrometer and a Cary Model 17 spectrometer were used for the electronic spectra. The ^{1}H NMR spectra were obtained with a Varian A-60 instrument. The ^{31}p NMR spectra were obtained with a Brucker 90-MHz instrument modified for Fourier transform operation. The melting points were obtained with an uncalibrated Mel Temp apparatus. Commercial anhydrous cobalt salts were used. The triphenyl phosphite was a commercial sample. The tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored over sodium in nitrogen. Commercial anhydrous acetonitrile was used. The reaction mixtures were protected from contact with air. A nitrogen-filled glovebox was used for many of the operations.

The magnetic moments were determined by the Evans method[9] using a solution of 9.4 ml of benzene, 0.20 ml of triphenyl phosphite, and 0.30 ml of tetramethylsilane as the solvent.

Preparation of $CoCl[(PhO)_3P]_3$ from $CoH(CH_3CN)[(PhO)_3P]_3$ and HCl. A solution of 10 g (9.7 mmol) of $CoH(CH_3CN)[P(OPh)_3]_3$[5b] in 100 ml of THF was stirred at room temperature while 35.5 ml of an anhydrous 0.335 N solution of HCl in THF was added at ca. 5 ml/min. When the HCl addition was complete, the solution was stirred for an additional 5 min at room temperature. The pressure in the flask was then reduced and the volatiles were evaporated without warming the flask. The green solid residue was dissolved in benzene at room temperature. The solution was filtered and the volatiles were removed under vacuum. The residue was redissolved in benzene and the solution was filtered. The green solid product was precipitated by the addition of pentane. This was collected and dried; yield 8.5 g. A repeat of this procedure gave 8.3 g of green solid. The combined product (ca. 17 g) was dissolved in 40 ml of benzene, and the solution was filtered. Hexane (ca. 70 ml total) was added in increments over several hours giving 11 g (14 mmol, 70% yield) of large dark green crystals which were dried under vacuum at room temperature; mp ca. 111 °C dec (evacuated capillary). Anal. Calcd for $C_{54}H_{45}O_9P_3CoCl$: C, 63.26; H, 4.42; Co, 5.75; Cl, 3.46. Found: C, 63.12; H, 4.49; Co, 5.60; Cl, 4.03. Visible spectrum (in benzene): 758 nm, ϵ 254; 710 nm (sh), ϵ 200; 413 nm, ϵ 106. The magnetic moment was 3.4 μ_B at 20 °C.

Preparation of $CoCl[(PhO)_3P]_3$ from $[(PhO)_3P]_3\overline{CoC_6H_4OP}(OPh)_2$ and HCl. A solution was prepared from 0.65 g (0.5 mmol) of $[(PhO)_3P]_3\overline{CoC_6H_4OP}(OPh)_2$[5a] and 5.0 ml of THF, and 2.5 ml of anhydrous HCl/THF (0.32 N) was added. Since green color developed only slowly, the solution was left at room temperature for 4 h. The volatiles were then evaporated from the dark green solution at room temperature under reduced pressure. The residue was triturated with hexane and the hexane was evaporated under vacuum. The residue was then dissolved in ca. 5 ml of benzene and the solution was filtered. The benzene was evaporated under vacuum and the residue was triturated with hexane. The solid was collected, giving 0.35 g (0.45 mmol, 90% yield); mp ca. 111 °C dec (evacuated capillary). The magnetic moment was 3.3 μ_B at 43 °C. Visible spectrum: 758 nm, ϵ 230; 710 nm (sh), ϵ 181; 413 nm, ϵ 85.

Preparation of $CoCl[(PhO)_3P]_3$ from $CoCl[(C_2H_5O)_3P]_3$. A mixture of 3 ml of triphenyl phosphite and 1.2 g (2.0 mmol) of $CoCl[(EtO)_3P]_3$[1b] was placed in a small flask with a magnetic stirring bar.

The flask was attached to a vacuum system and the pressure was reduced to ca. 0.1 mmHg. The mixture was stirred while the temperature was slowly increased by warming in an oil bath. After 70 min with the oil bath at ca. 110 °C the flask had lost 0.85 g of volatile material which was collected in the cold trap. There was no sign of decomposition to black magnetic solid in the pot. The clear green oily residue was left at room temperature under ca. 40 ml of hexane. The dark green crystals which formed were collected, washed, and dried, giving 1.5 g (1.5 mmol, 73% yield). Examination of the IR and ^{1}H NMR spectra of the volatiles recovered from the cold trap suggested that they were primarily triethyl phosphite. The green solid was crystallized three times from benzene/hexane to give 0.30 g (0.3 mmol, 15% yield) of dark green shiny crystals, mp ca. 111 °C dec (evacuated capillary). The magnetic moment was $\mu_{\mathrm{eff}} = 3.3\ \mu_{\mathrm{B}}$ at 43 °C. Visible spectrum: 758 nm, ϵ 238; 710 nm (sh), ϵ 189; 413 nm, ϵ 101. The Et–O and Ph–O groups have quite different IR spectra, especially in the 2700–3500-cm^{-1} region. The IR spectra of hexachlorobutadiene mulls showed that there could not be more than a few percent of C_2H_5O in the final solid product.

Preparation of $CoBr[(PhO)_3P]_3$ from $CoH(CH_3CN)[P(OPh)_3]_3$ and HBr. A solution of 5.0 g (4.8 mmol) of $CoH(CH_3CN)[P(OPh)_3]_3$[5b] in 50 ml of THF was stirred at room temperature and 17 ml of a freshly prepared 0.31 N solution of anhydrous HBr in ether was added. After an additional 3.5 min the pressure was reduced and the volatiles were evaporated. The residue was triturated with hexane and the hexane was removed under vacuum. The residue was then recrystallized three times from ca. 20 ml of benzene by adding ca. 100 ml of hexane to give 2.4 g (2.2 mmol, 47% yield) of dark green crystals, mp ca. 124 °C dec (evacuated capillary). Anal. Calcd for $C_{54}H_{45}O_9P_3CoBr$: C, 60.63; H, 4.24; Co, 5.51; Br, 7.47. Found: C, 60.39; H, 4.33; Co, 5.72; Br, 7.74. Visible spectrum (benzene): 773 nm, ϵ 257; 425 nm, ϵ 78. The magnetic moment was $\mu_{\mathrm{eff}} = 3.2\ \mu_{\mathrm{B}}$ at 37 °C.

Preparation of $CoCl[(PhO)_3P]_3$ by Zinc Reduction of $CoCl_2$ in CH_3CN. A solution of 7.8 g (60 mmol) of commercial anhydrous cobalt dichloride was dissolved in 300 ml of commercial anhydrous acetonitrile. The solution was cooled to 15 °C and 3.0 ml of water was added followed by 90 ml (342 mmol) of triphenyl phosphite. After thorough mixing 1.80 g (28 mmol) of zinc dust (Fisher, Tech) was added followed by immediate vigorous shaking of the reaction vessel to keep the zinc suspended. After 5 min of vigorous agitation, the mixture was left at room temperature (20 °C) for 1 h and then filtered. After ca. 24 h at about 15 °C the supernatant green liquid was decanted from the large dark green crystals which had formed in the filtrate. These were washed with pentane and dried, giving 6.1 g (6 mmol, 10% yield) (4.7 g in another case). A repeat of this procedure with twice these amounts gave 19.3 g (19 mmol, 16% yield) of large green crystals. Thirty grams of material prepared in this way was dissolved in 200 ml of benzene/10 ml of $(PhO)_3P$ at room temperature. Slow dilution of the filtered solution with 700 ml of hexane gave large green crystals which were similarly recrystallized from 120 ml of benzene/6 ml of triphenyl phosphite/500 ml of hexane. The large green crystals weighed 24.1 g. Anal. Calcd for $C_{54}H_{45}O_9P_3CoCl$: C, 63.26; H, 4.42; Cl, 3.46. Found: C, 62.82; H, 4.49; Cl, 3.54. Visible spectrum: 410 nm, ϵ 84; 715 nm (sh); 755 nm, ϵ 210.

Preparation of $CoBr[(PhO)_3P]_3$ by Zinc Reduction of $CoBr_2$ in Acetonitrile. A solution of 8.8 g (40 mmol) of commercial anhydrous $CoBr_2$ in 200 ml of commercial anhydrous acetonitrile was cooled to 20 °C and 60 ml (228 mmol) of triphenyl phosphite was added. Zinc dust (1.25 g, 19 mmol) was then added and the mixture was immediately shaken vigorously for 5 min. The mixture was then left 15 min at room temperature before the green liquid was decanted. The green liquid was then left 3 days at 20 °C, and 26 g (24 mmol, 60% yield) of large green crystals was collected. Anal. Calcd for $C_{54}H_{45}O_9P_3CoBr$: C, 60.63; H, 4.24; Br, 7.47. Found: C, 60.80; H, 4.30; Br, 7.20. Visible spectrum: ϵ 90 at 425 nm; 715 (sh) nm; ϵ 280 at 773 nm.

Preparation of $CoBr(CO)_2[(PhO)_3P]_2$ from $CoBr[(PhO)_3P]_3$. A flask was charged with 5.35 g (5.0 mmol) of $CoBr[(PhO)_3P]_3$ and 100 ml of xylene. It was evacuated with an aspirator and filled with carbon monoxide to 0 psig (1 atm). When the magnetic stirrer was started, the pressure began to drop. As the pressure dropped, CO was added from a calibrated stainless steel reservoir. A total of 212 psi drop from a 19.9-ml volume of CO was required to maintain the flask at 1 atm. This corresponds to ca. 2 mol of CO/mol of cobalt. The reaction mixture was cooled to −35 °C for 2 h before filtration. The yellow solid was washed with pentane and dried at room temperature and 10 μ pressure for 3 h (4.0 g, 4.9 mmol, 98% yield). The ^{1}H NMR showed that the material contained ca. one xylene per six $(PhO)_3P$ units and that it was diamagnetic. Anal. Calcd for $[(C_6H_5O)_3P]_2CoBr(CO)_2 \cdot {}^1/_3C_8H_{10}$: Co, 6.93; C, 57.40; H, 3.95; Br, 9.39. Calcd for $[(C_6H_5O)_3P]_2CoBr(CO)_2$: Co, 7.23; C, 55.96; H, 3.71; Br, 9.8. Found: Co, 7.28; C, 57.36; H, 4.17; Br, 9.98.

Material from a similar, smaller scale preparation turned green and melted at ca. 105 °C (evacuated capillary). The filtrate yielded an oil (about 30% of starting material weight) which was shown by ^{31}P and ^{1}H NMR to be predominantly triphenyl phosphite. The ^{31}P NMR spectrum of the dicarbonyl complex consisted of a single peak 147 ppm downfield from external 85% H_3PO_4. This remained a single peak from room temperature down to −100 °C. The addition of triphenyl phosphite at room temperature resulted only in the appearance of the sharp 127-ppm peak of free triphenyl phosphite. Addition of excess CO to a solution of $CoBr[(PhO)_3P]_3$ produced a solution with the same ^{31}P NMR spectrum as given by a mixture of the yellow solid and $(PhO)_3P$. This confirmed that the addition of CO was accompanied by the loss of triphenyl phosphite from the complex. The IR (Nujol) showed two carbonyl bands 2030 and 1950 cm^{-1} in ca. 1:2 intensity ratio.

Preparation of $\{Co[(EtO)_3P]_5\}^+Cl^-$ from $CoCl[(PhO)_3P]_3$. A solution of 250 mg (6.24 mmol) of $CoCl[(PhO)_3P]_3$ and 0.50 ml of triethyl phosphite in 2.5 ml of acetone was left at room temperature for 6 h. The volatiles were removed under vacuum and the residue was triturated with hexane. The yellow solid was collected, dried, and weighed, giving 150 mg (100 % yield). The ^{1}H NMR spectrum and the IR (hexachlorobutadiene mull) were the same as those of authentic $\{Co[(EtO)_3P]_5\}^+Cl^-$. The visible spectrum was also the same as that of $\{Co[(EtO)_3P]_5\}^+Cl^-$, i.e., a single peak ϵ ca. 10^3 at 388 nm.[1b]

Registry No. $CoCl[(PhO)_3P]_3$, 61202-74-2; $CoBr[(PhO)_3P]_3$, 61026-10-6; $CoBr(CO)_2[(PhO)_3P]_2$, 14653-41-9; $\{Co[(EtO)_3P]_5\}^+Cl^-$, 53701-72-7; $CoH(CH_3CN)[P(OPh)_3]_3$, 58527-60-9; $[(PhO)_3P]_3\underline{CoC_6H_4OP}(OPh)_2$, 54870-21-2; $CoCl[(EtO)_3P]_3$, 15488-43-4.

References and Notes

(1) (a) H. F. Klein and H. H. Karsch, *Inorg. Chem.*, **14**, 473 (1975); (b) L. W. Gosser and G. W. Parshall, *ibid.*, **13**, 1947 (1974), and references therein.

(2) W. C. Drinkard, Jr., U.S. Patent 3 655 723 (1972); W. C. Drinkard, Jr., and B. W. Taylor, U.S. Patents 3 775 461 (1973) and 3 579 560 (1971).

(3) W. Hieber and H. Duchatsch, *Chem. Ber.*, **98**, 2530 (1965).

(4) R. C. White and J. G. Thatcher, U.S. Patent 3 692 864 (1972); A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968).

(5) L. W. Gosser, *Inorg. Chem.*, **14**, 1453 (1975); **15**, 1348 (1976); U.S. Patent, 3 927 056 (1975).

(6) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970); C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974).

(7) (a) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 96 (1970); (b) L. W. Gosser, *Inorg. Chem.*, following paper in this issue.

(8) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969); L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1213 (1972).

(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).