# Interconversion of Phosphido-Bridged Polynuclear Cobalt Carbonyl Complexes. Cleavage of the Phosphido Bridge during Hydroformylation Catalysis

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*Received September 9, 1982*

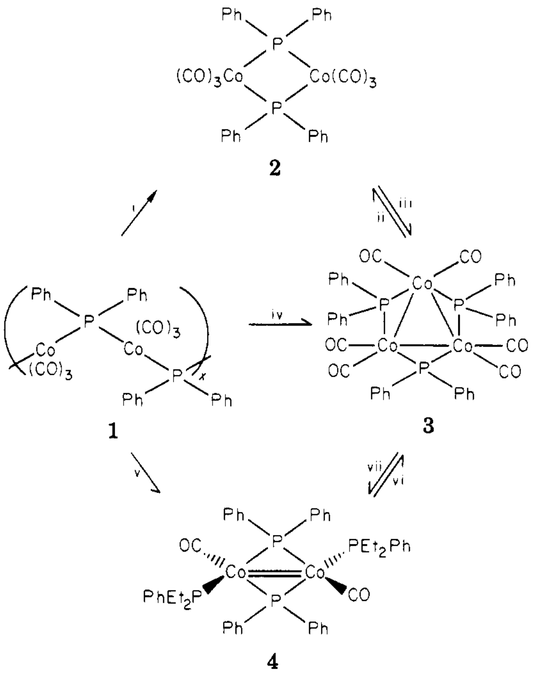
The interconversions of a series of phosphido-bridged cobalt carbonyl complexes have been examined. The oligomeric complex $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, **1**, originally prepared by Hayter[1] but incorrectly given the binuclear formulation $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, **2**, was found to lose CO upon heating to form trinuclear $Co_3(\mu\text{-}PPh_2)_3(CO)_6$, **3**, in near quantitative yield. Both **1** and **3** react with $PEt_2Ph$ upon heating to yield the new binuclear complex $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$, **4**, which has been spectroscopically characterized. Under milder conditions, trinuclear **3** reacts with $PEt_2Ph$ to produce mono- and disubstituted clusters $Co_3(\mu\text{-}PPh_2)_3(CO)_5(PEt_2Ph)$, **5**, and $Co_3(\mu\text{-}PPh_2)_3(CO)_4(PEt_2Ph)_2$, **6**. Binuclear **4** was observed to react with CO to displace $PEt_2Ph$ and reform trinuclear **3**. An authentic sample of binuclear $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, **2**, was prepared by heating either **1** or **3** under CO pressure (1000 psi). This compound has been spectroscopically characterized and was shown to be distinct from Hayter's oligomeric species **1**. Complex **1** functions as a catalyst/catalyst precursor for the hydroformylation of 1-hexene (1000 psi of $H_2/CO$ (1:1), 110 °C). However, it is irreversibly transformed into $Co_2(CO)_6(P(n\text{-}C_6H_{13})Ph_2)_2$ under hydroformylation conditions.

Binuclear and polynuclear transition-metal complexes are currently of high interest because of their potential to induce unique catalytic and stoichiometric transformations as a result of cooperative interaction between adjacent metals.[1] One of the problems with many of these compounds, however, is the relative ease with which they fragment under reaction conditions, thereby destroying the integrity of the initial complex.[1,2] One way to retard such fragmentation tendencies is to use bridging ligands to assist in holding the metals together.[3,4] In this regard we have been interested in the preparation of phosphido-bridged heteronuclear complexes[4] and sought to use $Co(CO)_4PPh_2$ as a reagent for the preparation of such compounds containing cobalt. While this species apparently results from the low-temperature reaction of $Na[Co(CO)_4]$ with $PPh_2Cl$[5] (eq 1) upon warmup to 25 °C, it loses CO to give other

$$Na[Co(CO)_4] + PPh_2Cl \xrightarrow[-60\ °C]{THF} Co(CO)_4PPh_2 + NaCl \tag{1}$$

products. In the course of investigating this reaction and its products, it rapidly became apparent that there are a series of phosphido-bridged cobalt carbonyl complexes which interconvert by rearrangement of the phosphido bridges under relatively mild conditions. We have studied these interconversions, Scheme I, and they are described in detail herein. Also discussed are other examples of reactions which irreversibly cleave the phosphido bridges, including such bridge elimination during the course of hydroformylation catalysis.[6]

Scheme I



(i) CO (1000 psi), 110 °C, 24 h; (ii) CO (1000 psi), 110 °C, 24 h; (iii) $h\nu$ (366 nm); (iv) 80 °C, 2–3 h, $N_2$ (1 atm); (v) $PEt_2Ph$, 110 °C, 48 h; (vii) $PEt_2Ph$, 110 °C, 3 h; (vi) CO (1 atm), 25 °C, 30 min; all reactions were conducted in toluene solution

A number of phosphido-bridged cobalt carbonyl complexes have been described previously in the literature.[7-10]

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[1] (a) Johnson, B. F. G., Ed. "Metal Clusters"; Wiley: New York, 1980. (b) Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982,** *29,* 1. (c) Muetterties, E. L. *Bull Soc. Chim. Belg.* **1976,** *85,* 451. (d) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abels, E., Eds.; Pergamon Press: London, 1982; Chapter 40.

[2] (a) Roberts, D. A.; Mercer, W. L.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982,** *104,* 910. (b) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980,** *19,* 2574.

[3] (a) Carty, A. J. *Adv. Chem. Ser.* **1982,** *No. 196,* 163. (b) *Pure Appl. Chem.* **1982,** *No. 54,* 113. (c) Finke, R. B.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981,** *103,* 1394 and references therein. (d) Huttner, G.; Schneider, J.; Muller, H. D.; Mohr, G.; von Seyerl, J.; Wolfhart, L. *Angew. Chem., Int. Ed. Engl.* **1979,** *18,* 76. (e) Werner, H.; Hofmann, W. *Ibid.* **1979,** *18,* 158. (f) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Ibid.* **1979,** *18,* 690.

[4] (a) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982,** *1,* 1008. (b) Breen, M. J.; Geoffroy, G. L. *Ibid.*, in press. (c) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Ibid.*, in press.

[5] (a) Müller, R.; Vahrenkamp, H. *Chem. Ber.* **1980,** *113,* 3359. (b) Burt, J. C.; Schmid, G. *J. Chem. Soc., Dalton Trans.* **1978,** 1385.

[6] Evidence is beginning to accumulate that these ligands are not as inert and as strongly binding as once thought. See ref 3a,b, for example.

0276-7333/83/2302-0053$01.50/0

Of particular relevance to this study is the oligomeric compound $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, **1**, prepared by Hayter in 1964 by the reaction shown in eq 1 carried out at 25 °C or by reaction of $Co_2(CO)_8$ with $P_2Ph_4$.[8,9] The binuclear formulation **2** (Scheme I) was originally given to Hayter's product although anomalously high molecular weight values (6000–8000) were obtained for this compound.[8] These were attributed[8] to decomposition during the measurements, although other workers[11,12] have instead suggested an oligomeric structure such as that drawn in Scheme I for Hayter's product. Our observations reported herein are consistent with such a structure for **1**, and we have as well isolated and characterized an authentic sample of binuclear **2** and shown its spectral properties to be different from those of **1**. From the reaction of $Co_2(CO)_8$ with $P_2Ph_4$, Huntsman and Dahl[10] were also able to isolate a green compound of formula $Co_3(\mu\text{-}PPh_2)_3(CO)_6$ which was shown to have the triangular phosphido-bridged structure **3** (Scheme I) by a single-crystal X-ray diffraction study. A similar compound with bridging $\mu$-$PMe_2$ ligands has been described by Vahrenkamp and co-workers.[7b]

## Experimental Section

$Co_2(CO)_6(PMePh_2)_2$,[14] $Co_4(\mu\text{-}PPh_2)_2(CO)_{10}$,[7c,15] and $Na[Co(CO)_4]$[16] were prepared by literature procedures. $PPh_2H$, $PPh_2Cl$, $PHexPh_2$ (Hex = $n$-$C_6H_{13}$), $PEt_2Ph$, $P(OEt)Ph_2$, and $Co_2(CO)_8$ were purchased from Strem Chemical Co. The phosphines were used as received but $Co_2(CO)_8$ was resublimed (25 °C (0.1 mmHg)) before use. $Co_2(CO)_6(PHexPh_2)_2$ and $Co_2(CO)_6(P(OEt)Ph_2)_2$ were prepared by substituting $PHexPh_2$ and $P(OEt)Ph_2$ for $PMePh_2$ in the literature procedure for $Co_2(CO)_6(PMePh_2)_2$.[14,17] Solvents were dried by standard methods, and all reactions were conducted under a prepurified $N_2$ atmosphere. All transfers of air-sensitive materials were carried out in an $N_2$-filled glovebox.

IR spectra were recorded on a Perkin-Elmer 580 grating IR spectrophotometer by using 0.5-mm NaCl solution IR cells. These were sealed with Luer-Lock fittings and purged with $N_2$ to record spectra of air-sensitive solutions. Electron-impact (EI) mass spectra were obtained by using an AEI-MS9 mass spectrometer with a source voltage of 70 eV and probe temperatures in the 100–200 °C range. Field desorption (FD) mass spectra were obtained on a MAT 731 mass spectrometer by Dr. Thomas Criswell at the Eastman Kodak Research Laboratories, Rochester, N.Y. Gas chromatography mass spectra (GC/MS) were recorded on a Finigan 2200 spectrometer. NMR spectra were recorded on JEOL PS-100 FT, Bruker WH200, and Bruker WM360 NMR spectrometers. All reported $^1H$ chemical shifts are relative to $Me_4Si$. $^{31}P$ NMR chemical shifts are relative to external $H_3PO_4$ with downfield chemical shifts reported as positive. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N.Y.

**Preparation of $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, 1. Method 1.** $Na[Co(CO)_4]$ was prepared in situ by stirring $Co_2(CO)_8$ (2.00 g, 5.84 mmol) with NaOH (2.33 g, 58.4 mmol) in THF (75 mL) for 2.5 h until the color of $Co_2(CO)_8$ was discharged.[16] The suspension was filtered, and $PPh_2Cl$ (2.56 g, 11.68 mmol) was added via syringe, giving formation of a white precipitate (presumably NaCl) and an orange solution. Evolution of gas was noted during the addition time of 10 min. After being stirred for 5 h, the solution was filtered and THF removed in vacuo to give an orange solid. This material was extracted with 2–50-mL portions of toluene. Addition of 60 mL of hexane to the extract gave **1** as an orange solid (1.60 g, 4.87 mmol for $x = 1$, 42%): IR $\nu_{CO}$ (hexane) 2060 (vw), 2045 (m), 2007 (m), 1990 (vs), 1980 (w, sh), 1955 (w, sh), $\nu_{CO}$ ($CH_2Cl_2$) 2065 (vw), 2045 (m), 1995 (vs, br) $cm^{-1}$; $^{31}P\{^1H\}$ NMR (25 °C, benzene-$d_6$) $\delta$ 61.7 (s).

**Method 2.** $Co_2(CO)_8$ (2.00 g, 5.84 mmol) was dissolved in toluene (10 mL) in a 125-mL Erlenmeyer flask in an $N_2$-filled glovebox. To this solution was added dropwise by syringe 2.0 mL of $PPh_2H$ (10.6 mmol, $d = 1.07$ g $cm^{-3}$) resulting in vigorous gas evolution, presumably CO and $H_2$. After the solution had stirred for 8 h, hexane (70 mL) was added and **1** precipitated as an orange powder. This was removed by filtration, washed with 2–10-mL portions of hexane, and dried under $N_2$ for 12 h (**1**, 3.22 g, 9.81 mmol for $x = 1$, 78%). If this reaction is carried out in a closed reaction vessel under the pressure of the CO and $H_2$ released during the reaction, the product **1** is contaminated with significant amounts of **2**.

**Preparation of $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, 2.** Orange crystals of **2** slowly form when the supernatant solution from the preparation of $[Co(\mu\text{-}PPh_2)(CO)_3]_x$ (method 2, above) is allowed to stand for several days. These were removed to give **2** in 5.6% yield (0.23 g, 0.35 mmol). Alternatively, **2** quantitatively forms upon stirring **1** (0.328 g, 1 mmol) in toluene (30 mL) at 110 °C under 1000 psi of CO pressure for 24 h in a Parr Model 4561 T31S5 pressure reactor. Mixtures of **1** and **2** can be separated by chromatography on silica gel using $CH_2Cl_2$/hexane (70/30) in red light. Under these conditions **1** sticks to the top of the column, but **2** moves as an orange band: IR $\nu_{CO}$ (hexane) 2060 (m), 2040 (s), 2007 (vs), 1995 (vs) $cm^{-1}$; $^{31}P\{^1H\}$ NMR (25 °C, benzene-$d_6$) $\delta$ 114 (s); mp 148–150 °C; mass spectrum, $m/e$ (FD) = 656 ($M^+$) + fragment ions corresponding to loss of four CO's. Anal. Calcd for $C_{30}H_{20}Co_2O_6P_2$: C, 54.90; H, 3.13; Found: C, 54.85; H, 3.17.

**Preparation of $Co_3(\mu\text{-}PPh_2)_3(CO)_6$, 3.** $Co_2(CO)_8$ (2.00 g, 5.84 mmol) was dissolved in toluene (50 mL), and 2.0 mL of $PPh_2H$ (10.6 mmol, $d = 1.007$ g $cm^{-3}$) was added via syringe resulting in vigorous gas evolution. This solution was stirred at reflux for 2 h. Hexane (25 mL) was added after the solution was cooled to give **3** as a green microcrystalline solid (2.9 g, 3.22 mmol, 83%): IR $\nu_{CO}$ ($CH_2Cl_2$) 2027 (m), 1990 (vs, br), 1985 (m, sh), 1960 (w, sh) $cm^{-1}$; $^{31}P\{^1H\}$ NMR (25 °C, benzene-$d_6$) $\delta$ 244 (s);[10] mass spectrum, $m/e$ (EI) = 900 ($M^+$) + fragment ions corresponding to loss of six CO's.

**Preparation of $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$, 4. Method 1.** To **1** (0.328 g, 0.5 mmol) in tetrahydrofuran (THF, 35 mL) was added 0.3 mL of $PEt_2Ph$ (0.24 g, 1.44 mmol), and the reaction mixture was refluxed for 7 h. The solution was concentrated in vacuo to ca. 5 mL, and 20 mL of hexane was added. The solution was filtered and stored at 0 °C for 24 h during which time black crystals of **4** deposited. The supernatant was decanted, and the black solid was washed with 2–10-mL portions of hexane and then dried under $N_2$ to give **4** in 18% yield (0.08 g, 0.09 mmol): IR $\nu_{CO}$(THF) 1905 (vs, br) $cm^{-1}$; $^{31}P\{^1H\}$ NMR (25 °C, benzene-$d_6$) $\delta(\mu\text{-}PPh_2)$ 175.8 (s), $\delta(PEt_2Ph)$ 48.5 (s); mass spectrum, $m/e$ (EI) = 876 ($M^+$) + fragment ions corresponding to loss of two CO's. Anal. Calcd for $C_{46}H_{50}O_2P_4Co_2$: C, 63.02; H, 5.75. Found: C, 63.18; H, 5.88.

**Method 2.** $Co_2(CO)_8$ (2.00 g, 5.84 mmol) and $PPh_2H$ (2.00 mL) were dissolved in toluene (40 mL) in a 250-mL Carius tube. After the solution was stirred for 30 min at 25 °C 2.5 mL of $PEt_2Ph$

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(7) (a) Vizi-Orosz, A.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1973**, *60*, C25. (b) Marko, L.; Marko, B. *Inorg. Chim. Acta* **1975**, *14*, L39. (c) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (d) Burt, J. C.; Boese, R.; Schmid, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1387. (e) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626. (f) *J. Organomet. Chem.* **1978**, *155*, C41. (g) *Chem. Ber.* **1979**, *112*, 2347. (h) *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 731. (i) Dobbie, R. C.; Whittaker, D. *J. Chem. Soc., Dalton Trans.* **1973**, 2427. (j) Hutching, L. D.; Light, R. W.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 266. (k) Grobe, J.; Stierand, H. *Z. Anorg. Chem.* **1969**, *371*, 99.

(8) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823.

(9) An apparently similar compound was described in: Hieber, W.; Duchatsch, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1963**, *B18*, 1132. Schweckendiek, W. German Patent 1 072 244, Dec 31, 1959.

(10) Huntsman, J. R. Ph.D. Thesis, University of Wisconsin, Madison, Wisc., 1973.

(11) Ginsberg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

(12) Private communication from H. Vahrenkamp to L. F. Dahl, cited as ref 24 in ref 11.

(13) Cerriani, S.; Ratcliff, B.; Ugo, R. *Gazz. Chim. Ital.* **1974**, *104*, 1161.

(14) $[Co_4(\mu\text{-}PPh)_2(CO)_{10}]$: mass spectrum, $m/e$ 732 (parent ion) + ions corresponding to loss of 10 CO's; IR (toluene) 2042 (vs), 2032 (vs), 2019 (vs), 1995 (w), 1878 (m) $cm^{-1}$ (lit.[7c] 2040 (vs), 2032 (s), 2016 (s), 1876 (w) $cm^{-1}$).

(15) Edgell, W. F., Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932.

(16) (a) $[Co_2(CO)_6(PHexPh_2)_2]$: IR 1955 (s, br) $cm^{-1}$; $^{31}P\{^1H\}$ NMR $\delta$ 59.6 (s). (b) $[Co_2(CO)_6\{P(OEt)Ph_2\}_2]$: IR 1970 (m, sh), 1955 (s, br) $cm^{-1}$; $^{31}P\{^1H\}$ NMR $\delta$ 165.3; $^1H$ NMR $\delta$(Ph), 7.67, 7.5, $\delta(CH_2)$ 4.04 (m), $\delta(CH_3)$ 1.42 (t, $J_{^1H\text{-}^1H} = 6.5$ Hz).

(17) Klug, H. P.; Alexander, L. E. "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials"; Wiley: New York, 1974.

was added and the Carius tube evacuated. This mixture was heated to 140 °C for 8 h and then cooled to 25 °C. Hexane (25 mL) was added and the Carius tube sealed, heated to 100 °C for 30 min, cooled to 25 °C, and stirred for 6 h. The black crystalline product which formed was filtered, washed with 5–10-mL portions of hexane, and dried in vacuo (4, 3.63 g, 4.14 mmol, 71%).

**Preparation of $Co_3(\mu\text{-}PPh_2)_3(Co)_5(PEt_2Ph)$, 5.** To 3 (0.450 g, 0.50 mmol) dissolved in $CH_2Cl_2$ (20 mL) in a 75-mL Carius tube was added 0.25 mL of $PEt_2Ph$ (0.20 g, 1.20 mmol). The Carius tube was evacuated, sealed, and heated to 80 °C for 2 h. After the solution was cooled the green residue was dissolved in toluene (20 mL), filtered, and chromatographed under $N_2$ on a 2 × 30 cm column of silica gel (230–400 mesh) using 30% toluene/hexane as eluant. A green fraction of 5 elutes first followed by a small green fraction of 3. Evaporation of solvent from the first fraction yields 5 in 64% yield (0.33 g, 0.32 mmol): IR $\nu_{CO}$ ($CH_2Cl_2$) 1995 (m), 1965 (vs br), 1930 (m sh) $cm^{-1}$; $^{31}P\{^1H\}$ NMR (25 °C, benzene-$d_6$) $\delta(\mu\text{-}PPh_2)$ 274.5 (s, 1), $\delta(\mu\text{-}PPh_2)$ 198.8 (s, 2), $\delta(PEt_2Ph)$ 31.1 (s, 1); mass spectrum $m/e$ (FD) = 1038 ($M^+$). Anal. Calcd for $C_{51}H_{45}O_5P_4Co_3$: C, 59.00; H, 4.35. Found: C, 59.21; H, 4.53.

**Hydroformylation Catalysis.** To the glass liner of a Parr Model 4561 T31S5 300-mL pressure reactor was added the complex to be studied, toluene (50 mL), and 1-hexene (50 mL). The complex concentration was ~4 × $10^{-3}$ M in Co in all reactions examined. The reactor was purged three times with carbon monoxide and hydrogen and then pressurized to 1000 psi with a 1:1 mixture of CO and $H_2$. The reactor was heated to 110 °C and stirred for 24 h. At operating temperature, an initial pressure of 1250 psi was obtained. The reaction mixture following catalysis was analyzed by gas chromatography using a Varian Model 1440 gas chromatograph with a flame ionization detector and a 6 ft × $^1/_8$ in. stainless-steel column of 10% Carbowax on Chromosorb W at a column temperature of 65 °C.

## Results

**Preparation and Further Characterization of $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, 1.** The reaction of $Na[Co(CO)_4]$ with $PPh_2Cl$, eq 1, was examined initially as a potential route to the desired $Co(CO)_4PPh_2$ synthetic reagent. At –60 °C in THF solution these reagents react to give a pale orange solution which most likely contains $Co(CO)_4PPh_2$.[5] However, upon warm-up to –20 °C, carbon monoxide begins to be evolved and the solution darkens. Gas evolution ceases after 1.5 h at this temperature with a total of 0.93 mol of CO evolved per mol of Co, indicating the transformation shown in eq 2. No further changes occur upon warm-up to 25 °C.

$$xCo(CO)_4PPh_2 \xrightarrow{-20\ °C} xCO + [Co(\mu\text{-}PPh_2)(CO)_3]_x \quad (2)$$

The orange-brown solid which precipitates from this solution upon addition of hexane shows IR bands ($CH_2Cl_2$) at 2065 (vw), 2045 (m), and 1995 (vs, br) $cm^{-1}$ (Figure 1a), indicative of terminal but not bridging CO's. Its $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at $\delta$ 61.7. This material appears similar to the compound isolated by Hayter[8] and originally given the binuclear formation $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, 2, although other workers[11,12] have instead suggested the oligomeric structure $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, 1.

Hayter's[8] high molecular weight values (6000–8000) are consistent with an oligomeric formulation as are also our observations of a markedly decreasing solubility of the compound as it is repeatedly dissolved and precipitated from solution, implying an increasing degree of oligomerization. Further support for its oligomeric character comes from its X-ray powder diffraction pattern. *No diffraction lines were observed* over the scan range 10° ≤ $2\theta$ ≤ 60°, implying an amorphous rather than a crystalline material.[17] The most convincing evidence that this material is not the binuclear complex 2 is our isolation and structural characterization[18] of 2 and our demonstration that the spectral properties of 2 are significantly different from those of 1 (see below).

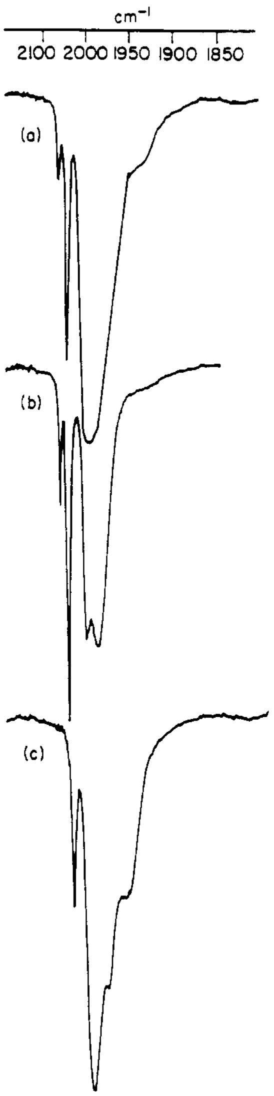

**Figure 1.** Infrared spectra of (a) $[Co(\mu\text{-}PPh_2)(CO)_3]_x$, 1, (b) $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, 2, and (c) $Co_3(\mu\text{-}PPh_2)_3(CO)_6$, 3, in $CH_2Cl_2$ solution.

The oligomeric complex 1 is most conveniently prepared by the direct reaction of $PPh_2H$ with $Co_2(CO)_8$ (eq 3).

$$Co_2(CO)_8 + 2PPh_2H \xrightarrow[toluene]{25\ °C} [Co(\mu\text{-}PPh_2)(CO)_3]_x + 2CO + H_2 \quad (3)$$
$$85\text{–}90\%$$

Simply stirring these reagents together in toluene solution at 25 °C under an $N_2$ atmosphere results in vigorous gas evolution, presumably $H_2$ and CO, and precipitation of 1. Temperature control of this reaction is critical since the trinuclear cluster $Co_3(\mu\text{-}PPh_2)_3(CO)_6$, 3, forms at elevated temperatures (see below).

**Preparation and Characterization of $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, 2.** An authentic sample of the *binuclear* complex $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, 2, was first obtained by allowing the supernatant solution from the preparation of 1 via eq 3 to stand for several days *in the dark.* During this time reddish orange crystals of 2 slowly form and can be isolated in ~6% yield by decantation of the mother liquor. This complex has been fully characterized spec-

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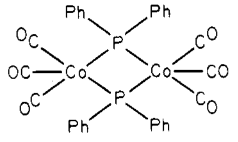
[18] Harley, A. D.; Whittle, R.; Geoffroy, G. L. *Organometallics*, submitted for publication.

troscopically and shown to have the binuclear structure **2** by a complete single-crystal X-ray diffraction study, details of which are described separately.[18] Its IR spectrum shows only terminal $\nu_{CO}$ bands (Figure 1b), and its $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at $\delta$ −114.2. The far upfield position of the $\mu$-PPh$_2$ resonance is consistent with this ligand bridging two metals not joined by a metal–metal bond. Numerous correlations have shown that the $\mu$-PR$_2$ ligands in compounds with metal–metal bonds generally display downfield ($\delta$ 50 → $\delta$ 300) $^{31}$P NMR resonances, whereas upfield ($\delta$ 50 → $\delta$ −200) resonances are observed for compounds in which the $\mu$-PR$_2$ ligand bridges two metals not joined by a metal–metal bond.[3a,19] A parent ion at *m/e* 656 and fragment ions corresponding to successive loss of four CO's are apparent in the field desorption mass spectrum of **2**. In contrast to **1**, the binuclear complex **2** is air stable in the solid state and in solution and can be readily purified by chromatography on silica gel under red darkroom lights. Binuclear complex **2** is *extremely* light sensitive, losing CO and rearranging to trinuclear **3** upon photolysis (eq 4). Both IR



**2**

$$\underset{\mathbf{2}}{3Co_2(\mu\text{-}PPh_2)_2(CO)_6} \xrightarrow[CH_2Cl_2]{h\nu} 2Co_2(\mu\text{-}PPh_2)_3(CO)_6 + 6CO \qquad (4)$$

and $^{31}$P NMR monitoring show the conversion of **2** into **3** to be complete following 30 min photolysis with Pyrex-filtered medium-pressure Hg arc lamp irradiation ($\lambda \geq 300$ nm). Even solid samples of **2** are light sensitive and slowly decompose to **3** upon standing under fluorescent room lights.

Complex **2** is most conveniently prepared simply by heating toluene solutions of the oligomeric complex **1** or the trinuclear complex **3** under CO pressure (eq 5 and 6).

$$\underset{\mathbf{1}}{[Co(\mu\text{-}PPh_2)(CO)_3]_x} \xrightarrow[\substack{\text{toluene}\\ \text{CO, 1000 psi}}]{110\ ^\circ C,\ 24\ h} (x/2)Co_2(\mu\text{-}PPh_2)_2(CO)_6 \qquad (5)$$

$$\underset{\mathbf{3}}{2Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 6CO \xrightarrow[\substack{\text{toluene}\\ \text{1000 psi}}]{110\ ^\circ C,\ 24\ h} \underset{\mathbf{2}}{3Co_2(\mu\text{-}PPh_2)_2(CO)_6} \qquad (6)$$

From such reactions **1** and **3** can be quantitatively transformed into **2**. The CO pressure is necessary for the **1** → **2** conversion since otherwise **1** loses CO and rearranges to the trinuclear cluster **3** (see below).

**Preparation of Co$_3$($\mu$-PPh$_2$)$_3$(CO)$_6$, 3.** Huntsman and Dahl[10] isolated the trinuclear cluster **3** from the reaction of Co$_2$(CO)$_8$ with P$_2$Ph$_4$ and characterized it by an X-ray diffraction study. We find that this complex is most conveniently prepared in high yield simply by heating Co$_2$(CO)$_8$ with PPh$_2$H (eq 7). Note that this is the same reaction used to prepare the oligomeric complex **1** (eq 3) except for the different temperatures involved (25 °C for **1**; 110 °C for **3**). The oligomeric complex **1** may be an intermediate in the synthesis of **3** via eq 7 since we find that **1** loses CO and is quantitatively converted into **3** upon heating under N$_2$ (eq 8). The trinuclear complex **3** shows

$$3Co_2(CO)_8 + 6PPh_2H \xrightarrow[\substack{\text{toluene}\\ N_2}]{110\ ^\circ C,\ 2\ h} \underset{\mathbf{3}\ (83\%)}{2Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 12CO + 3H_2 \qquad (7)$$

$$\underset{\mathbf{1}}{[Co(\mu\text{-}PPh_2)(CO)_3]_x} \xrightarrow[N_2,\ \text{toluene}]{80\ ^\circ C,\ 2\text{–}3\ h} \underset{\mathbf{3}}{(x/3)Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 3CO \qquad (8)$$

only terminal $\nu_{CO}$ bands (Figure 1c) and a singlet at $\delta$ 244 in its $^{31}P\{^1H\}$ NMR spectrum.[10] A parent ion at *m/e* 900 and fragment ions corresponding to stepwise loss of the six CO's are apparent in its electron-impact mass spectrum. Trinuclear complex **3** is thermally stable up to ~110 °C under an N$_2$ atmosphere, although when heated under CO pressure it rearranges to give **2** in quantitative yield (see eq 6). Prolonged heating of **3** under N$_2$ at 150 °C induces an irreversible transformation into Co$_4$($\mu$-PPh)$_2$(CO)$_{10}$, a compound previously characterized by Dahl and Ryan.[7c]

**Preparation and Characterization of Co$_2$($\mu$-PPh$_2$)$_2$(CO)$_2$(PEt$_2$Ph)$_2$, 4.** Reaction of the oligomeric complex **1** with PEt$_2$Ph was found to result in the formation of the new binuclear complex Co$_2$($\mu$-PPh$_2$)$_2$(CO)$_2$(PEt$_2$Ph)$_2$, **4**, albeit in relatively low yield (eq 9).

$$\underset{\mathbf{1}}{[Co(\mu\text{-}PPh_2)(CO)_3]_x} + PEt_2Ph \xrightarrow[THF]{66\ ^\circ C} xCO + \underset{\mathbf{4}\ (18\%)}{(x/2)Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2} \qquad (9)$$

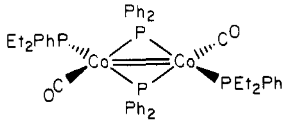
This complex is most conveniently prepared in 70% yield by the direct reaction of a 1:2:2 mixture of Co$_2$(CO)$_8$, PEt$_2$Ph, and PPh$_2$H (eq 10). Complex **4** also forms when

$$Co_2(CO)_8 + 2PEt_2Ph + 2PPh_2H \xrightarrow[\text{toluene}]{110\ ^\circ C,\ 4\ h} \underset{\mathbf{4}\ (70\%)}{Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2} + 6CO + H_2 \qquad (10)$$

trinuclear complex **3** is heated to 140 °C in a sealed Carius tube containing excess PEt$_2$Ph (eq 11).

$$\underset{\mathbf{3}}{2Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 6PEt_2Ph \xrightarrow[\substack{\text{toluene}\\ \text{Carius tube}}]{140\ ^\circ C} \underset{\mathbf{4}}{3Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2} + 6CO \qquad (11)$$

This new complex has been characterized spectroscopically and by a complete single-crystal X-ray diffraction study, details of which are given in the following paper.[20] The latter showed it to have the binuclear structure sketched. The coordination geometry about Co is pseudotetrahedral (neglecting the metal–metal bond) with each Co ligated by two $\mu$-PPh$_2$ ligands, one CO, and one PEt$_2$Ph. The Co$_2$($\mu$-P)$_2$ core is planar, and the very short Co–Co bond length of 2.343 (2) Å implies a formal metal–metal double bond.[20] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two



**4**

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[19] (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* *1981*, *204*, C27. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (d) Johannsen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3438.

[20] Harley, A. D.; Whittle, R.; Geoffroy, G. L. *Organometallics*, submitted for publication.

broad singlets at $\delta$ 173.4 ($\nu_{1/2}$ = 42 Hz) and $\delta$ 48.5 ($\nu_{1/2}$ = 65 Hz) that integrate in a 1:1 intensity ratio and are respectively assigned to the equivalent bridging $\mu$-PPh$_2$ ligands and to the equivalent terminal phosphines. The downfield position of the former is consistent with this ligand bridging a metal–metal bond.[19,20] Upon allowing the protons to couple to the phosphorus nuclei in the $^{31}$P NMR spectrum, only the $\delta$ 48.5 resonance shows significant broadening, as expected because of coupling to the $C_2H_5$ protons. Although the $^{31}$P{$^1$H} resonances of 4 are inherently broad, no discernible coupling was observed between the phosphorus nuclei, consistent with the pseudotetrahedral arrangement of these ligands about Co with relatively little s character in the metal–ligand bonding orbitals. The $^{31}$P{$^1$H} NMR resonances sharpen upon cooling to −80 °C and shift slightly in position to $\delta$ 176.5 ($\nu_{1/2}$ = 34 Hz) and 53.3 ($\nu_{1/2}$ = 22 Hz), respectively. The broadening is apparently due to quadrapolar coupling to the $^{59}$Co nuclei rather than to some fluxional process. A parent ion at *m/e* 876 and fragment ions corresponding to stepwise loss of the two CO's are apparent in the EI mass spectrum of **4**.

Although not as completely characterized as **4**, spectroscopic data imply that a complex analogous to **4** forms with P($n$-Bu)$_3$. When the oligomeric complex **1** is heated with excess P($n$-Bu)$_3$, a brownish orange solid is isolated which shows a parent ion at *m/e* 916 and fragment ions corresponding to loss of two CO's in its EI mass spectrum. This corresponds to the formula $Co_2(\mu\text{-}PPh_2)_2(CO)_2\{P(n\text{-}Bu)_3\}_2$, analogous to **4**. The IR spectrum of this material shows a strong $\nu_{CO}$ band at 1900 cm$^{-1}$ (cf. **4**, $\nu_{CO}$ = 1905 cm$^{-1}$) with a weak shoulder at 1912 cm$^{-1}$. Whether or not a PR$_3$ derivative of structure **4** can form is apparently dependent upon the size of the PR$_3$ ligand since when **1** is heated with excess PPh$_3$, only trinuclear **3** is produced.

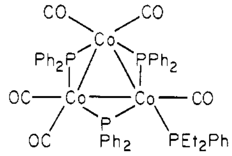
Although the binuclear complex **4** appears thermally stable when heated to 110 °C under N$_2$, it rapidly reacts with CO at 25 °C and 1 atm of pressure to displace PEt$_2$Ph and quantitatively yield the trinuclear cluster **3** (eq 12).

$$\underset{\mathbf{4}}{3Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2} + CO \xrightarrow[\text{toluene}\atop\text{1 atm}]{25\ ^\circ C} \underset{\mathbf{3}}{2Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 6PEt_2Ph \quad (12)$$

In contrast to the reactivity with CO, **4** is apparently inert toward H$_2$. No net reaction was observed when **4** was heated in the presence of H$_2$ (110 °C, 1000 psi, 24 h), and **4** was recovered unchanged.

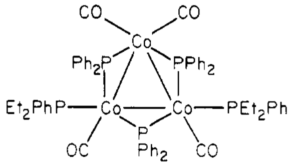
**Reaction of $Co_3(\mu\text{-}PPh_2)_3(CO)_6$, 3, with PEt$_2$Ph.** As noted above when **3** is heated with excess PEt$_2$Ph at 140 °C in a Carius tube, the binuclear complex **4** is produced. However, when less severe conditions are used, substituted derivatives of **3** form. When **3** is heated at 80 °C in the presence of a 2.4 molar excess of PEt$_2$Ph, the monosubstituted derivative $Co_3(\mu\text{-}PPh_2)_3(CO)_5(PEt_2Ph)$, **5**, is produced in 64% isolated yield (eq 13). This species has been characterized spectroscopically and by a satisfactory C, H analysis. Its field desorption mass spectrum shows a parent ion at the expected *m/e* 1038. Only terminal $\nu_{CO}$ bands are seen in its IR spectrum (see Experimental Section), and three broad resonances ($\nu_{1/2} \simeq$ 130 Hz) are observed in its 25 °C $^{31}$P{$^1$H} NMR spectrum at $\delta$ 274.5 (s), 198.8 (s), and 31.1 (s) in a 1:2:1 relative intensity ratio. The downfield resonances are attributed to one nonequivalent and two equivalent $\mu$-PPh$_2$ ligands, and the $\delta$ 31.1 singlet is assigned to the terminal PEt$_2$Ph ligand. The structure sketched is implied. Coupling between the terminal PEt$_2$Ph resonance and the two equivalent $\mu$-PPh$_2$ bridging ligands was not resolved, although all the resonances are extremely broad, presumably because of coupling to the quadrapolar $^{59}$Co nuclei.

$$\underset{\mathbf{3}}{Co_3(\mu\text{-}PPh_2)_3(CO)_6} + PEt_2Ph \xrightarrow[\text{CH}_2\text{Cl}_2\atop\text{Carius tube}]{80\ ^\circ C,\ 2\ h} \underset{\mathbf{5}\ (64\%)}{CO_3(\mu\text{-}PPh_2)_3(CO)_5(PEt_2Ph)} + CO \quad (13)$$



**5**

When the reaction of **3** with PEt$_2$Ph was monitored by $^{31}$P{$^1$H} NMR spectroscopy, in addition to the resonances due to **5**, less intense broad singlets were observed at $\delta$ 248.3, ($\nu_{1/2} \simeq$ 134 Hz), 177.6 ($\nu_{1/2} \simeq$ 134 Hz), and 51.8 ($\nu_{1/2} \simeq$ 64 Hz) which integrate in an approximate 2:1:2 ratio. The complex which gives these resonances has not been isolated, but the $^{31}$P{$^1$H} NMR pattern is consistent with formation of a small amount of the disubstituted cluster $Co_3(\mu\text{-}PPh_2)_3(CO)_4(PEt_2Ph)_2$, **6**. The downfield $^{31}$P{$^1$H} NMR resonances are assigned to two equivalent and one inequivalent $\mu$-PPh$_2$ ligand, and the $\delta$ 51.8 resonance is assigned to two equivalent PEt$_2$Ph ligands. A reasonable structure is that sketched.



**6**

When the reaction of $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$, **4**, with CO (eq 12) is monitored by $^{31}$P{$^1$H} NMR spectroscopy, resonances due to **5** and **6** grow in and then decrease in intensity as the resonance due to **3** appears. In an independent experiment it was observed that a solution containing **5** and **6** quantitatively reacts with CO to form **3** and release free PEt$_2$Ph (eq 14). Thus, both complexes **5** and **6** are likely intermediates in the **4** → **3** conversion (eq 12).

$$\underset{\mathbf{5}}{Co_3(\mu\text{-}PPh_2)_3(CO)_5(PEt_2Ph)} + \underset{\mathbf{6}}{Co_3(\mu\text{-}PPh_2)_3(CO)_4(PEt_2Ph)_2} + CO \xrightarrow[\text{CH}_2\text{Cl}_2\atop\text{1 atm}]{25\ ^\circ C,\ 15\ min} \underset{\mathbf{3}}{Co_3(\mu\text{-}PPh_2)_3(CO)_6} + PEt_2Ph \quad (14)$$

**Hydroformylation Catalysis.** Complex **1** has been found to function as a hydroformylation catalyst/catalyst precursor. A mixture of C$_7$ aldehydes is produced from 1-hexene and **2** under the hydroformylation conditions given in eq 15. Table I gives the relative rates of product formation and isomer yield of **1** compared to $Co_2(CO)_8$, $Co_2(CO)_6(PMePh_2)_2$, and $Co_2(CO)_6(PHexPh_2)_2$, (Hex = $n$-$C_6H_{13}$). $Co_2(CO)_8$ is a far more efficient catalyst than the other three complexes, in accord with published data,[21]

$$\text{1-hexene} + CO + H_2 \xrightarrow[\text{1250 psi, toluene}]{\text{catalyst, 110 °C}} C_7 \text{ aldehydes} \quad (15)$$

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[21] Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* **1968**, *13*, 469.

Table I. Relative Rates and Isomer Yields upon Hydroformylation of 1-Hexene[a]

| catalyst precursor | relative rate | linear/ branched C- aldehyde ratio[b] |
|---|---|---|
| $Co_2(CO)_6(PMePh_2)_2$ | 1.0 | 3.50 |
| $Co_2(CO)_6(PHexPh_2)_2$ | 1.3 | 2.78 |
| $[Co(\mu\text{-}PPh_2)(CO)_3]_x$ | 2.0 | 3.33 |
| $Co_2(CO)_8$ | 130 | 2.05 |

[a] [1-hexene] = 4 M; catalyst concentration = 0.004 M in C; 1250 psi of 1:1 $CO/H_2$ at 110 °C; toluene solvent. [b] 1-Heptanal/a mixture of 2-methylhexanal and 3-ethylpentanal.

but its linear/branched product ratio is of course inferior to the phosphine-substituted derivatives. The high linear/branched ratio of 3.33 found by using **1** as catalyst precursor compared to the 2.05 value of $Co_2(CO)_8$ strongly argues against catalysis through decomposition of **1** to produce a small amount of highly active $Co_2(CO)_8$. If this did occur, the product ratio would reflect $Co_2(CO)_8$ catalysis, i.e., 2.05. Furthermore, IR spectra of reaction solutions following 12-h catalysis with **1** as a catalyst precursor show no evidence for $HCo(CO)_4$ or $Co_2(CO)_8$ formation. Likewise, there is no visible metal deposition.

However, $^{31}P\{^1H\}$ NMR spectra of reaction solutions following 12-h catalysis using **1** as catalyst precursor show only a single resonance at $\delta$ 59.6 which is not due to **1** but which may be assigned to $Co_2(CO)_6(PHexPh_2)_2$, by comparison to an authentic sample.[16a] Reactions run for shorter time periods show two $^{31}P$ NMR singlets at $\delta$ 61.7 and 59.6 due to **1** and $Co_2(CO)_6(PHexPh_2)_2$, respectively. Thus, **1** is transformed irreversibly into $Co_2(CO)_6(PHexPh_2)_2$ during the course of the catalysis reaction (eq 16). The experimental data do not allow an unambiguous distinction as to the extent of hydroformylation catalysis by **1** and $Co_2(CO)_6(PHexPh_2)_2$ in these solutions. However, the different product ratio obtained by using **1** as a catalyst precursor compared to the use of $Co_2(CO)_6(PHexPh_2)_2$ alone implies that **1** or some other derivative of **1** must have hydroformylation activity. It was also observed that binuclear $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ reacts with 1-hexene under hydroformylation conditions to also give $Co_2(CO)_6(PHexPh_2)_2$.

$$[Co(\mu\text{-}PPh_2)(CO)_3]_x + \text{1-hexene} + H_2 \rightarrow (x/2)Co_2(CO)_6(PHexPh_2)_2 \quad (16)$$

A similar bridge elimination reaction was observed when **1** was heated under a 1:1 $H_2/CO$ atmosphere (110 °C, 1000 psi) in toluene solution containing 10% ethanol. The product formed was $Co_2(CO)_6(P(OEt)Ph_2)_2$, as determined by comparison of its spectra data to that of an authentic sample[16b] (eq 17). No reaction of **1** with EtOH occurs at 25 °C under 1 atm of $H_2/CO$.

$$\underset{\mathbf{1}}{[Co(\mu\text{-}PPh_2)(CO)_3]_x} + 2EtOH \xrightarrow[1000\text{ psi, }CO/H_2]{110\ °C,\ 8\ h} (x/2)Co_2(CO)_6\{P(OEt)Ph_2\}_2 \quad (17)$$

## Discussion

We were led into the chemistry described herein during our attempts to use "$Co(CO)_4PPh_2$" as a reagent for the synthesis of phosphido-bridged mixed-metal compounds containing Co. While this species can apparently be generated at low temperature by the reaction of $[Co(CO)_4]^-$ with $PPh_2Cl$,[5] it is not stable above −20 °C. Upon warmup it loses CO and gives rise to a series of phosphido-bridged Co carbonyl complexes. A perusal of the literature demonstrates that the complexity of this chemical system is not generally appreciated, as it was not to us at the onset of this study. In particular, a number of reports have described studies of the compound prepared according to Hayter's recipe[8] and in which Hayter's binuclear $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ formulation was accepted as correct.[10,22] Our data and that of others,[11,12] including Hayter's own molecular weight measurements,[8] clearly show that the compound obtained from Hayter's synthetic procedure is not binuclear but rather must have an oligomeric structure such as that drawn in Scheme I.

One of the most significant achievements of the present study was our discovery of methods for obtaining authentic binuclear $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, **2**, and its complete characterization via the X-ray diffraction study described in a separate paper.[18] As described above, this species can be prepared in essentially quantitative yield by heating either oligomeric **1** or trinuclear **3** under CO pressure. It is a well-behaved compound which can be easily purified by chromatography on silica gel and is only moderately air sensitive, although it is extremely light sensitive.

As illustrated by the spectra presented in Figure 1, compounds **1**–**3** are not easily distinguished by infrared spectroscopy and this may have led to some of the confusion which has existed. They all show broad absorption in the 1970–2010-cm$^{-1}$ region and a sharp peak in the 2020–2060-cm$^{-1}$ region. Furthermore, both oligomeric complex **1** and binuclear complex **2** have similar melting points, melting with decomposition in the 148–151 °C range, and they both give orange solutions. However, trinuclear complex **3** gives green solutions and is thus easily distinguished from **1** and **2**. The best method for distinguishing **1** from **2** is via $^{31}P\{^1H\}$ NMR spectroscopy since the resonance for **1** ($\delta$ 61.7 (s)) is far downfield from that of **2** ($\delta$ −114 (s)).

We were also surprised to find that these phosphido-bridged cobalt carbonyl complexes can be induced to interconvert under relatively mild conditions. The various transformations observed are summarized in Scheme I. The oligomeric complex **1** can be readily converted into binuclear **2** and trinuclear **3** by heating in the absence or presence of CO, respectively, and reaction of **1** with $PEt_2Ph$ yields the binuclear complex **4**. However, we have not found any reaction conditions in which **1** can be reformed from either **2**, **3**, or **4**. These results suggest that **2** is the more thermodynamically stable form of $[Co(\mu\text{-}PPh_2)(CO)_3]_x$ but that **1** is the kinetically preferred product in the initial synthesis. In contrast, complexes **2** and **3** undergo essentially quantitative interconversion (eq 18).

$$\underset{\mathbf{3}}{2Co_3(\mu\text{-}PPh_2)_3(CO)_6} + 6CO \underset{h\nu,\ N_2}{\overset{\Delta,\ 1000\text{ psi}}{\rightleftharpoons}} \underset{\mathbf{2}}{3Co_2(\mu\text{-}PPh_2)_3(CO)_6} \quad (18)$$

Although binuclear complex **2** is thermally stable at least up to 110 °C, 366-nm photolysis induces loss of CO and formation of **3**. Even room light will slowly induce this conversion to occur, and the compound must be protected from light if it is to be preserved. When **3** is heated to 110 °C under CO pressure, **2** is quantitatively produced. Indeed, in the presence of CO complex **2** is the most stable of all the complexes examined.

Both the oligomeric complex **1** and the trinuclear complex **3** react with $PEt_2Ph$ to form **4** although much more stringent conditions are required with **3**. Under less vig-

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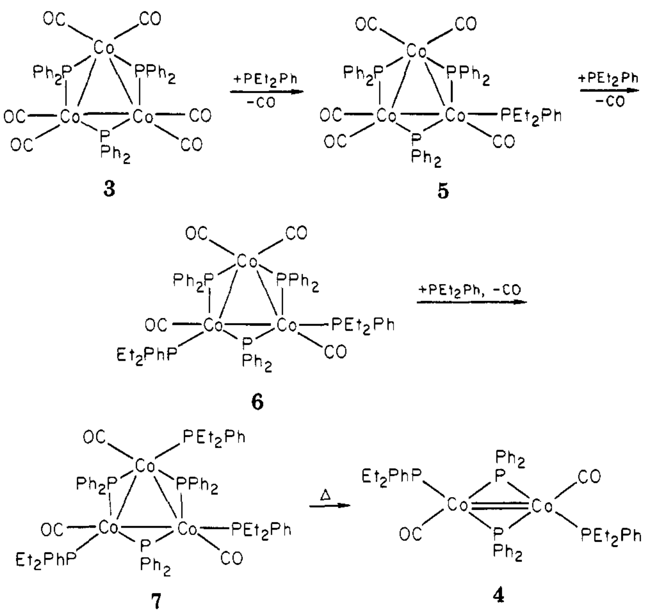
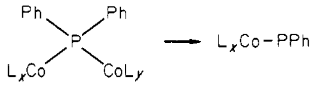
[22] (a) Bamford, C. H.; Maltman, W. R. *Trans. Faraday Soc.* **1966**, *62*, 2823. (b) Abel, E. W.; Hutson, G. V. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2339. (c) See also ref 7d.

Scheme II



orous conditions trinuclear complex **3** reacts with $PEt_2Ph$ to form first a monosubstituted derivative, **5**, and tentative evidence was obtained for the formation of a disubstituted product, **6**. It would seem likely that these are intermediates in the **3** → **4** conversion, Scheme II, with severe steric crowding in the substituted clusters forcing fragmentation to produce binuclear **4**. A trisubstituted cluster such as **7** should be quite crowded since it has nine phenyl rings and six ethyl groups packed around a relatively small $Co_3$ core. Likewise, the disubstituted cluster **6** posssesses eight phenyl and four ethyl substituents. Note that **7** and **4** have the same empirical formula $[Co(\mu\text{-}PPh_2)(CO)(PEt_2Ph)]_x$. Surprisingly, binuclear complex **4** was found to easily and quantitatively reform trinuclear complex **3** simply upon exposure to 1 atm of CO at 25 °C, Scheme I, but we have no evidence to bear on the mechanism of this transformation. However **4** is coordinatively unsaturated and would be expected to add nucleophiles such as CO, and the **4** → **3** transformation may proceed through such CO adducts.

The most significant conclusion to be drawn from the interconversions of these phosphido-bridged cobalt carbonyl derivatives discussed herein is that the bridging phosphido ligands are *not* sufficient to retard fragmentation and rearrangement reactions of these complexes. While there are reported examples of *chemical* transformations of phosphido ligands,[3a,b] to our knowledge there has been no other clear demonstration of the interconvertability of phosphido-bridged complexes in which the complex nuclearity changes as it does with this chemical system. There are, however, indications in the literature that such reactions may also occur for other metal derivatives,[23-25] as exemplified by the rearrangements which must occur during the syntheses of $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$[24] and $Rh_3(\mu\text{-}PPh_2)_3(CO)_5$[23d] from the reactions of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ with $LiPPh_2$ and $PPh_2H/Et_2NH$, respectively. We have no direct experimental evidence to bear on the *mechanism* of these rearrangement reactions, but it is clear that some Co–phosphido bonds must be broken in the course of the observed transformations, implying the formation of intermediates with pendant $PPh_2$ ligands (eq 19).



(19)

The irreversible transformation of the $\mu$-$PPh_2$ ligands of **4** and **2** into $PHexPh_2$ under 1-hexene hydroformylation catalysis conditions illustrates the care that must be exercised when interpreting the results of catalytic experiments employing phosphido-bridged complexes. These results further illustrate the fact that phosphido-bridged complexes may find only limited usefulness in catalysis because of such irreversible transformations which destroy the polynuclear character of the complex.[26]

**Acknowledgment.** This research was supported by the National Science Foundation (Grant CHE-8201160) and in part by grants from the Standard Oil Co. (Ohio) and Air Products and Chemicals, Inc. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978-1983), The John Simon Guggenheim Foundation for a fellowship (1982), and Drs. Thomas Criswell and Henry Gysling at the Eastman Kodak research laboratories for assistance in obtaining field desorption mass spectra.

**Registry No.** **1**, 83562-08-7; **2**, 15553-97-6; **3**, 83562-09-8; **4**, 83462-95-7; **5**, 83562-10-1; **6**, 83572-96-7; $Na[Co(CO)_4]$, 14878-28-5; $PPh_2Cl$, 1079-66-9; $Co_2(CO)_8$, 10210-68-1; $PPh_2H$, 829-85-6; 1-hexene, 592-41-6.

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(23) (a) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Chem. Commun.* **1981**, 587. (b) Haines, R. J.; Steen, N. D. C. T.; Laing, M.; Sommerville, P. *J. Organomet. Chem.* **1980**, *198*, C72. (c) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Chem. Commun.* **1981**, 407. (d) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Organomet. Chem.* **1981**, *209*, C34.

(24) Kreter, P. E.; Meek, D. W.; Christoph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27.

(25) Jamerson, J. C.; Pruett, R. L.; Billig, E.; Fiato, F. A. *J. Organomet. Chem.* **1980**, *193*, C43.

(26) A similar conclusion has been drawn by Carty and co-workers: Maclaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.