element, iron, was obtained by adding the covalent radius of E minus the covalent radius of Fe to the values of the appropriate (Figure 1) bond lengths to obtain *a*, *b*, *c*, or *d*. The results were tabulated (only the more significant distances and angles *a*, *b*, *e*, *θ*, and *ψ* appear in Table I) and entered on a VAX computer, programmed to plot *a*, *b*, *c*, *d*, *e*, and *θ* or *ψ* against *ψ* or *θ*. The most significant of these plots are reproduced here as Figures 2–4 and 6–8. For the structural types 1–3, the trends of the data were extracted (Table II) and the result was plotted as Figure 5. This treatment resembles that in our work on the C–H···M group and derives from the Bürgi–Dunitz method. Deliberate care was taken to avoid any bias in choosing the structures for study. Data points were not selectively eliminated to "improve" the appearance of Figures 2–8. Assignment to the different types was based on the criteria described in the text. Some assignments of bent semibridging instead of linear semibridging II were essentially arbitrary in the overlap region described in the text. No data appear twice under two different types, however.

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Solution Structure and Dynamics of $Co_2(CO)_6(L^\frown L)$ and $Co_4(CO)_8(L^\frown L)_2$ Molecules

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The solution structure and dynamics of the molecules $Co_4(CO)_8(L^\frown L)_2$, where $L^\frown L$ = bis(diphenylphosphino)methane, bis(dimethylphosphino)methane, and (dimethylphosphino)(diphenylphosphino)methane, have been determined by ^{13}C and ^{31}P NMR spectroscopy. The structure is derived from the C_{3v} structure of $Co_4(CO)_{12}$ with four CO's replaced by the two di(tertiary phosphines). All eight carbonyls exchange at the same rate, indicating a concerted mechanism for the exchange process. The corresponding dimers, $Co_2(CO)_6L^\frown L$, are also fluxional in solution, and for these molecules the slow-exchange limit could not be reached. The tetramers are synthesized directly, in high yield, by pyrolysis of the dimers.

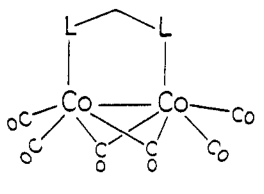
Introduction

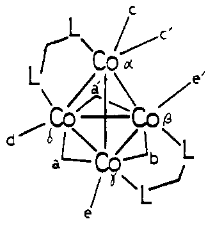
The ability of bis(diphenylphosphino)methane, DPM, to form bridged binuclear complexes has led to increased interest in this and related ligands.[1] The reaction of $Co_2(CO)_8$ with di(tertiary phosphines and arsines) is well-known to yield complexes of the formula $Co_2(CO)_6(L^\frown L)$.[2] A few of these have been characterized in the solid state and in solution.[3,4] A crystal structure has been reported for the arsine derivative, $Co_2(CO)_6(C_4F_4(AsMe_2)_2)$.[3] Recently there has been some interest in derivatives of $Co_2(CO)_6(DPM)$ (**1**), namely $Co_2(CO)_4(DPM)(\mu\text{-alkyne})$[5] and $Co_2(CO)_4(DPM)(\mu\text{-methylene})$,[6] because of their solution dynamics. Also, cobalt complexes having bridging hydrido, phosphido, and iodo ligands have been synthesized from $Co_2(CO)_6(DPM)$.[7]

Here we discuss the synthesis, structure, and solution dynamics of the series of compounds $Co_2(CO)_6(DPM)$ (**1**), $Co_2(CO)_6(DMPM)$ (**2**), $Co_2(CO)_6(DMM)$ (**3**), $Co_4(CO)_8(DPM)_2$ (**4**), $Co_4(CO)_8(DMPM)_2$ (**5**), and $Co_4(CO)_8(DMM)_2$ (**6**); DMM = bis(dimethylphosphino)methane, DMPM = (dimethylphosphino)(diphenylphosphino)methane.

Results and Discussion

Synthesis. It is well-known that the reaction of certain phosphine and phosphite ligands with dicobalt octacarbonyl leads to rapid disproportionation.[8a] Very bulky phosphine and arsine ligands react more slowly by a dissociative pathway to yield the neutral dimers $Co_2(CO)_6L_2$ directly.[8b] In the case of the di(tertiary phosphines) we find that the addition of $L^\frown L$ to $Co_2(CO)_8$ gives the salt $[Co(CO)_3(L^\frown L)]^+[Co(CO)_4]^-$ according to eq 1. This





1 L^L = DPM
2 L^L = DMPM
3 L^L = DMM

4 L^L = DPM
5 L^L = DMPM
6 L^L ■ DMM

$$Co_2(CO)_8 + R_2P\text{–}CH_2\text{–}PR'_2 \xrightarrow{-CO} [Co(CO)_3(R_2P\text{–}CH_2\text{–}PR'_2)]^+[Co(CO)_4]^- \quad (1)$$

reaction is rapid and is over in a matter of minutes, as indicated by infrared spectroscopy. The reaction to form the neutral dimers, eq 2, is much slower, again as monitored by infrared spectroscopy

$$[Co(CO)_3(R_2P\text{–}CH_2\text{–}PR'_2)]^+[Co(CO)_4]^- \xrightarrow{-CO} Co_2(CO)_6(R_2P\text{–}CH_2\text{–}PR'_2) \quad (2)$$

of the reaction mixture. With the bulky di(tertiary phosphine) DPM, the neutral dimer is seen quite rapidly so that it is not possible to rule out some substitution by a dissociative pathway[8b] for DPM. For the ligands DPM, DMPM, and DMM, the approximate half-lives for reaction with $Co_2(CO)_8$ to yield $Co_2(CO)_6(L^\frown L)$ are 5 h, 1 day, and 4 days, respectively. As a general rule, bulky substituents on the di(tertiary phosphine) favor small-ring formation,[9-11] and it is therefore expected that the intermediate chelate complex should be more stable when DPM is used than DMM. However, in the synthesis of $Co_2(CO)_6(L^\frown L)$ the ligands DMPM and especially DMM stabilize the intermediate salt. This is reasonable due to the increased basicity of these ligands. With bis(dimethylphosphino)methane it is possible to isolate $[Co(CO)_3(DMM)]^+[Co(CO)_4]^-$ as a purple crystalline solid. Although reasonably pure when first isolated, the salt slowly

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Table I. Carbonyl Stretching Frequencies (cm^{-1})[a]

$Co_2(CO)_6(DPM)$	2040 m	2000 s	1984 vs			1820 m	1795 m
$Co_2(CO)_6(DMPM)$	2040 m	2000 s	1982 vs	1960 s		1815 m	1777 m
$Co_2(CO)_6(DMM)$	2025 m	1998 s	1978 vs			1813 m	1775 m
$Co_4(CO)_8(DPM)_2$	2010 s	1980 vs	1960 s		1828 m	1785 s	1770 s
$Co_4(CO)_8(DMPM)_2$	2010 s	1985 vs	1955 s		1819 m	1790 s	1750 m
$Co_4(CO)_8(DMM)_2$	2002 s	1969 s	1950 s		1820 w	1773 s	1760 s

[a] All infrared spectra were recorded in CH_2Cl_2.

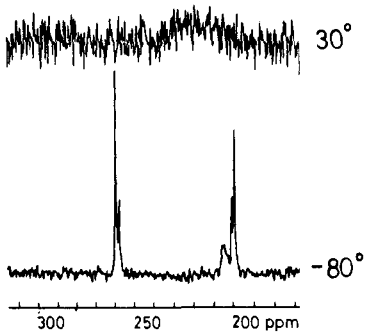

Figure 1. Carbon-13 NMR spectra for $Co_4(CO)_8(DPM)_2$ at 30 and -80 °C. The solvent is CD_2Cl_2; chemical shifts are from Me_4Si. At 30 °C all eight carbonyls are equivalent.

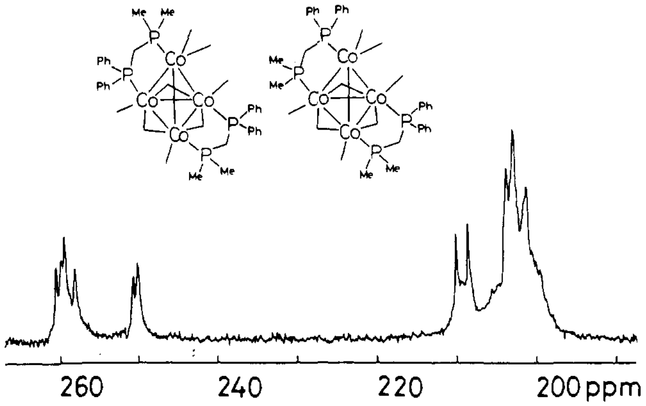

Figure 2. Low-temperature ^{13}C NMR spectrum of $Co_4(CO)_8(DMPM)_2$. The spectrum is consistent with the presence of two isomers as shown schematically.

converts to the corresponding neutral dimer even in the solid state.

The solution infrared spectra for the dimers **1–3** (Table I) are completely consistent with the structure shown schematically. This is the structure adopted by $Co_2(CO)_6(C_4F_4(AsMe)_2)_2)$ in the solid state.[3] Compound **2** shows extra infrared bands in the terminal region due to the unsymmetrical nature of the di(tertiary phosphine) DMPM.

Pyrolysis of $Co_2(CO)_6(DPM)$ and addition of DPM to $Co_4(CO)_{12}$[12] both give the tetramer $Co_4(CO)_8(DPM)_2$ as the major product, indicated by identical infrared, ^{31}P NMR, and ^{13}C NMR spectra. The weak band at 1890 cm^{-1} in the infrared spectrum of $Co_4(CO)_8(DPM)_2$ as obtained from $Co(CO)_{12}$ appears to be due to an impurity and not a semibridging carbonyl. When the compound is recrystallized, this band disappears. The pyrolysis of $Co_2(CO)_6(L\frown L)$ to give $Co_4(CO)_8(L\frown L)_2$ appears to be a clean and general synthetic route to the substituted tetranuclear clusters.

Solution Structure and Dynamics. Not surprisingly, the cobalt dimers **1–3** and the tetramers **4–6** undergo rapid bridge–terminal exchange in solution. For the dimers this exchange is fast at temperatures down to -60 °C, yielding a single resonance for all six carbonyl ligands.

Variable-temperature ^{13}C NMR spectra of the tetramers are more informative. Figure 1 shows the spectra of **4**, at -80 and 25 °C. At -80 °C **4** exhibits two bridging carbonyl resonances in a ratio of 2:1 and three terminal carbonyl resonances in a ratio of 2:1:2. This is completely consistent with the expected structure derived from C_{3v} $Co_4(CO)_{12}$ with three bridging carbonyls in the basal plane. For the rhodium tetramer $Rh_4(CO)_8(DPM)_2$ this structure has been confirmed by x-ray crystallography.[13] Other substituted derivatives of $Co_4(CO)_{12}$ also exhibit the same structure.[14]

The assignment of the spectrum at -80 °C is thus a,a′ 260.1 ppm, b 258.2 ppm, c,c′ 206.9 ppm, d 203.2 ppm, and e,e′ 201.7 ppm. The absolute assignment of c,c′ and e,e′ cannot be made with certainty with the available data. Switching the assignment does not change any of the arguments with regard to the dynamic behavior of **4**. At room temperature a single very broad resonance is observed, indicating that all eight carbonyls are exchanging.

When the unsymmetrical di(tertiary phosphine) DMPM is used to form **5**, two isomers are possible in solution. (In the solid state four isomers may be expected from consideration of the structure of $Rh_4(CO)_8(DPM)_2$;[13] however, in solution pairs of the structures should be identical.) Low-temperature ^{31}P and ^{13}C NMR studies confirm the existence of isomers in **5**. Figure 2 shows the ^{13}C NMR spectrum of $Co_4(CO)_8(DMPM)_2$ at -80 °C. The isomers are best resolved in the bridging region where six resonances, three for each isomer, are observed. In the schematic representation, a and a′ are no longer equivalent when $L\frown L$ is unsymmetrical. One possible assignment is indicated in Figure 2. Clearly, the isomers are not present in equal quantities. In the terminal region the resonances due to the isomers overlap to give a complicated pattern. The total integration of bridging to terminal carbonyls is 3:5, as expected. Significantly, there is no ^{31}P or ^{13}C NMR evidence for two isomers at room temperature. Thus the fluxional process interchanges the two isomers.

An indication of which isomer is more stable is given by ^{31}P NMR. The ^{31}P NMR data are listed in Table II. First we note that phosphorus bonded to the axial cobalt is distinguishable from phosphorus bonded to basal cobalts by ^{31}P NMR spectroscopy but that within the basal plane all three phosphorus atoms give the same chemical shift. This is demonstrated by the low-temperature ^{31}P NMR data for **6**.

The two isomers of **5** are shown schematically in Figure 2. In isomer A (Figure 2, left structure) the $-PMe_2$ groups are distinguishable by ^{31}P NMR spectroscopy. However, the basal $-PMe_2$ group in A overlaps with the $-PMe_2$ groups in isomer B. Likewise, the $-PPh_2$ groups in A overlap with the basal $-PPh_2$ group in B. Thus at low temperature four signals are observed in the ^{31}P NMR spectrum. These are the axial $-PMe_2$ group on A, the axial $-PPh_2$ group on B, the basal $-PPh_2$ groups on A and B, and the basal $-PMe_2$ groups on A and B. By comparison of the ^{31}P NMR spectrum of **5** with those of **4** and **6**, the $-PPh_2$ and $-PMe_2$ groups can be assigned definitively. Also it can be estimated from Figure 2 that the relative abundance of the two isomers is approximately 1:2. Thus the weakest signal in the low-temperature ^{31}P NMR spectrum of **5** will be the $-PR_2$ group bonded to the axial cobalt in the least abundant isomer. From the table this is clearly a $-PPh_2$ group. Thus isomer B in Figure 2 is less abundant than isomer A.

The variable-temperature ^{13}C NMR spectra for $Co_4(CO)_8(DMM)_2$ (**6**), are shown in Figure 3. At -80 °C **6** exhibits two bridging peaks at 258.7 and 249.9 ppm with a ratio of 1:2 and also two terminal carbonyl peaks at 199.4 and 197.7 ppm with a ratio of 3:2. The observation of only two terminal carbonyl

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Table II. ^{1}H, ^{13}C, and ^{31}P NMR Data (ppm)

^{1}H NMR[a]

	Ph	CH_2	CH_3
$Co_2(CO)_6(DPM)$	7.5 (m)	3.15 (t, 10.1 Hz)	
$Co_2(CO)_6(DMPM)$	7.37 (m)	2.25 (t, 9 Hz)	1.40 (d, 3.6 Hz)
$Co_2(CO)_6(DMM)$		1.77 (d, 13 Hz)	1.59 (t, 3.5 Hz)

^{31}P NMR[b]

	PPh_2	PMe_2
$Co_2(CO)_6(DPM)$	60.39	
$Co_2(CO)_6(DMPM)$	60.18 (d, 210 Hz)	37.83 (d, 210 Hz)
$Co_2(CO)_6(DMM)$		39.42
$Co_4(CO)_8(DPM)_2$	24.29	
$Co_4(CO)_8(DMPM)_2$	20.66	7.59 (br, s)
	27.23 (~1)[c]	14.75 (~2)[c]
	20.0 (~6)[c]	7.50 (~5)[c]
$Co_4(CO)_8(DMM)_2$		11.80 (br, s)
		12.15 (~3)[c]
		11.10 (~1)[c]

^{13}C NMR[d]

	bridging carbonyls	terminal carbonyls
$Co_4(CO)_8(DPM)_2$[e]	260.1, 258.2	206.9, 203.2, 201.7
$Co_4(CO)_8(DMPM)_2$[a]	260.5, 259.8, 259.4, 258.1, 250.7, 250.0	210.0, 208.5, 203.8, 203.1, 201.3
$Co_4(CO)_8(DMM)_2$[e]	258.7, 249.9	199.4, 197.7

[a] Chemical shifts from Me_4Si. [b] Chemical shifts from 85% phosphoric acid, temperature recorded at 25 °C unless noted otherwise. [c] Number in parentheses refers to relative intensity; recorded at −60 °C. [d] Chemical shifts from Me_4Si. [e] Recorded at −80 °C.

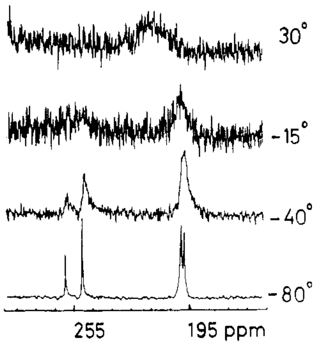

Figure 3. Variable-temperature ^{13}C NMR spectra for $Co_4(CO)_8(DMM)_2$ from −80 to +30 °C. Bridge–terminal exchange is frozen on the NMR time scale at −80 °C. All eight carbonyls broaden at the same rate as the temperature is raised.

resonances indicates an accidental degeneracy of chemical shifts. As the temperature is raised, the ^{13}C resonances of **6** all broaden at the same rate. Finally, at room temperature a single broad line is observed at 214 ppm. Thus all eight carbonyls appear to exchange simultaneously, as previously observed in **4** and **5** above.

It is apparent from the room-temperature spectra in Figures 1 and 3 that only a very broad carbonyl resonance is observed for compounds **4** and **6**. A similar result is obtained for compound **5**. The broad peaks are centered at the weighted-average position of the carbonyl resonances observed at low temperature. Thus we base the postulated exchange mechanism (vide infra) on the scrambling of all eight carbonyl ligands.

Proposed Mechanism for Carbonyl Exchange. It is well-known that $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and their phosphine derivatives have structures that may be described as distorted icosahedra.[15,16] The problem of ligand exchange in M_4L_{12} molecules has most recently been described in terms of a polytopal rearrangement of the icosahedral array of ligands.[15] The icosahedron is considered to open to form a cuboctahedron; formation of a new icosahedral arrangement of ligands then exchanges ligands. When one considers an isolated icosahedron, there are five degenerate ways of forming a cuboctahedron.[15] This degeneracy is lifted when a tetrahedron of cobalts is placed within the icosahedron, as discussed by Johnson and Benfield.[15] Further restrictions are placed on the arrangement when molecules **4**–**6** are considered.

In Figure 4 structure A is a representation of the ligand icosahedron in **4** or **6** where positions 2 and 11 and positions 8 and 9 are occupied by the di(tertiary phosphines). There is only one way to place the Co_4 tetrahedron within this framework to yield the observed structure. Thus the face defined by 4, 5, and 9 has all terminal ligands bonded to the axial cobalt (α). The basal plane cobalts (β, γ, and δ) are directed at edges 1,2, 10,11, and 7,8. Finally, positions 3, 6, and 12 define bridging carbonyls. This numbering scheme is identical with that used by Johnson and Benfield.[15] It should be further noted that A is chiral and its mirror image is also possible (A′). Also, all eight carbonyls are unique in A; however, rapid racemization generates a time-averaged mirror plane. This accounts for the observed low-temperature spectra for **4**–**6**. Structure A may open to give a cuboctahedral structure, B. There is only one possible pathway for this that satisfies the following criteria: (1) each cobalt is bonded to just one phosphorus atom in B, (2) all cobalts in B have three terminally bonded ligands, and (3) $\mathrm{L}\frown\mathrm{L}$ does not span the diagonal of a square face. These conditions are satisfied only if edges 4,8, 1,5, 2,3, 7,12, 6,11, and 9,10 in A are opened. Structure B in Figure 4 thus represents an all-terminal, $Ir_4(CO)_{12}$[13] type structure. The cobalts are directed toward faces 4,5,9, 3,7,8, 1,2,6, and 10,11,12.

Closing opposite vertices on the square faces in B to go to structure C is not possible, as this places the phosphines in unrealistic positions. Thus A and B and their mirror images are the only structures that may interconvert. In transforming A to B a slight reorientation of the cobalts is necessary. Although structure B has 2-fold symmetry, this is not sufficient to make all eight carbonyls equivalent.

The pathway represented by the interconversion of A and B results in the exchange of the three bridging carbonyl positions, 3, 6, and 12, with three terminal carbonyl positions, 10, 4, and 7. Carbonyl positions 1 and 5 are exchanged but represent terminal sites. This is a direct result of the fact that the 2-fold axis in B relates the following positions: 3, 10; 6, 4; 12, 7; 1, 5; 2, 9; 8, 11.

The key to complete carbonyl exchange is the racemization of A. If A is in equilibrium with its mirror image A′ and also in equilibrium with B, then B is in equilibrium with its mirror image B′. This is shown schematically in Figure 4. If all of these processes are fast on the NMR time scale, then B is in rapid equilibrium with B′. This generates a time-averaged D_{2d} structure in which all eight carbonyls are equivalent.

A realistic model for racemization is simply rotation of a triangular face in structure A. The only face that may be rotated that does not either place phosphine in a bridging position or place two phosphines on a cobalt is face 4,5,9. This is the face of all terminal ligands on the axial cobalt, α. Structure A′ in Figure 4 is numbered to represent the result of rotation of face 4,5,9 and oriented to emphasize its mirror relationship with A. The pathway represented by A′ $\rightleftarrows$ B′ now allows the terminal carbonyls 1 and 5 to occupy bridging positions.

In summary, carbonyl exchange involves rapid racemization and icosahedral–cuboctahedral rearrangements. The racemization involves a partial rotation of the three ligands bonded to the axial cobalt. The polytopal rearrangement corresponds closely to simple bridge–terminal exchange as originally proposed by Cotton.[17]

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen. Solvents were either distilled or dried over molecular sieves and purged with N_2 before use. Dicobalt octacarbonyl (Strem Chemicals) was purified by sublimation and used immediately. The ligands DPM,[18] DMPM,[19] and DMM[19] were synthesized by literature methods. The

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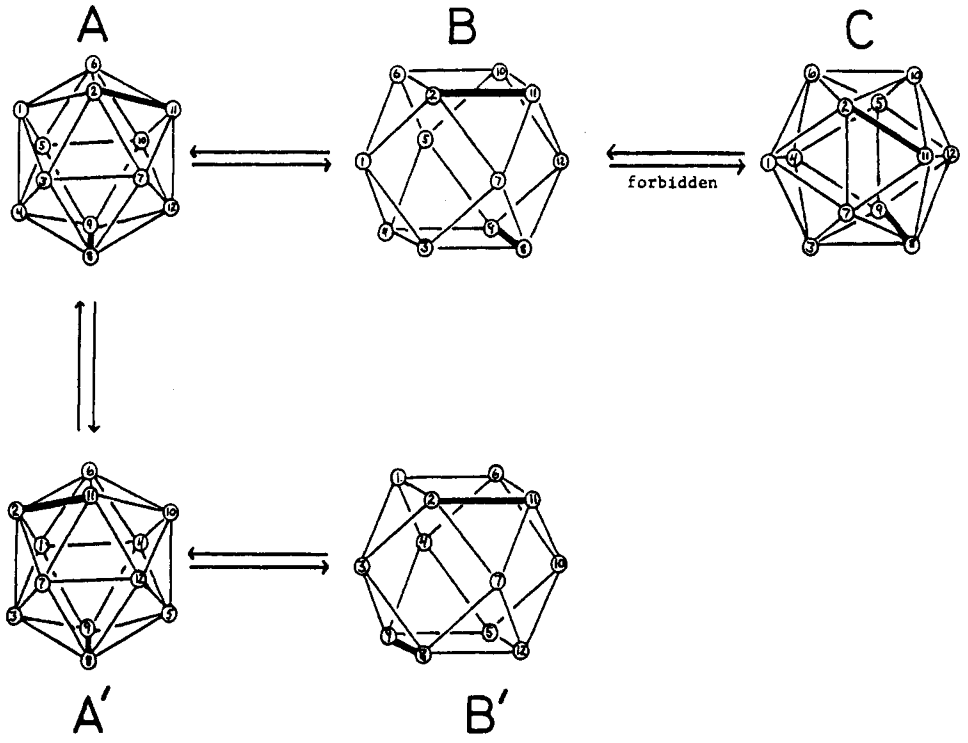

Figure 4. Schematic representation of the fluxional pathways in **4**–**6**. The numbering scheme is consistent with that of Johnson and Benfield.[15] Icosahedron A opens to cuboctahedron B by cleaving edges as described in the text. A goes to its mirror image A′ by rotating the face 4,5,9. The representation A′ is drawn to emphasize the mirror relationship with A. In A′ the α cobalt is directed to the face 4,5,9 while the basal cobalts, β,γ,δ, are directed at the edges 1,2, 7,8, and 10,11. The bridging carbonyls are 3, 6, and 12. Structure B′ is the mirror image of B. In B and B′ the cobalts are directed at the faces 4,5,9, 3,7,8, 10,11,12, and 1,2,6. Only one orientation of B′ is shown in which 2,11 is superposable. Rotation by 180° superposes 8,9.

reactions forming cobalt phosphine dimers were followed by solution infrared spectroscopy until the reaction was complete (as seen by the disappearance of the band at 1890 cm^{-1} due to $Co(CO)_4^-$).

Proton NMR spectra were recorded on a Varian EM390 spectrometer. Carbon-13 and phosphorus-31 NMR spectra were recorded on either a JEOL FX200, an IBM WP200, or an IBM WP270 NMR spectrometer. Variable-temperature ^{13}C NMR spectra were recorded on the IBM WP200 NMR spectrometer on samples enriched in ^{13}CO. All ^{13}C-enriched compounds were synthesized from $Co_2(CO)_8$ enriched to 15% in ^{13}CO.

All NMR solvents were degassed prior to use. Chemical shifts in ppm are reported from Me_4Si (^1H and ^{13}C NMR spectra) or 85% aqueous H_3PO_4 (^{31}P NMR spectra).

Infrared spectra were recorded on a Perkin-Elmer infrared spectrometer.

$Co_2(CO)_6(DPM)$ (1). A solution of $Co_2(CO)_8$ (3 g, 8.8×10^{-3} mol) was prepared in 20 mL of CH_2Cl_2. In a separate flask 3.4 g (8.8×10^{-3} mol) of DPM was dissolved in 20 mL of CH_2Cl_2, and then this solution was transferred dropwise via syringe to the solution of $Co_2(CO)_8$. After evolution of CO had ceased, the reaction mixture was allowed to stir for 30 h. The solution was filtered under N_2 and the product obtained as an orange-red, crystalline, air-stable solid upon addition of hexane at −78 °C. Yield: 5 g (80%). Anal. Calcd for $C_{31}H_{22}Co_2O_6P_2$: C, 55.6; H, 3.29. Found: C, 55.4; H, 3.20.

$Co_2(CO)_6(DMPM)$ (2). A solution of $Co_2(CO)_8$ (2.5 g, 7.3×10^{-3} mol) was prepared in CH_2Cl_2. In a separate flask a 15-mL solution of DMPM (1.95 g, 7.5×10^{-3} mol) in CH_2Cl_2 was prepared and added dropwise via syringe to the $Co_2(CO)_8$ solution. After addition the reaction mixture was allowed to stir for 4 days, at which time the reaction was complete. The solution was filtered under N_2 and the product obtained as an orange-brown, crystalline, slightly air-sensitive solid upon addition of hexane at −78 °C. Yield: 2 g (51%). Anal. Calcd for $C_{21}H_{18}Co_2O_6P_2$: C, 46.18; H, 3.32; P, 11.34; O, 17.56. Found: C, 45.98; H, 3.36; P, 11.47; O, 17.58.

$Co_2(CO)_6(DMM)$ (3). A CH_2Cl_2 solution of DMM (5 mL, 0.33 g, 2.4×10^{-3} mol) was added dropwise to a 10-mL solution of $Co_2(CO)_8$. When the addition was complete, the mixture was allowed to stir for 8 days. This was filtered, and addition of hexane at −78 °C gave the product as an orange, needlelike, crystalline, air-stable solid. Yield: 0.73 g (72%). Anal. Calcd for $C_{11}H_{14}Co_2O_6P_2$: C, 31.4; H, 3.32; P, 15.2; O, 22.8. Found: C, 30.98; H, 3.46; P, 14.4; O, 27.7.

Cobalt Tetramers. Approximately 0.5 g of one of the cobalt dimers (**1**, **2**, or **3**) was dissolved in 30 mL of toluene. The solution was then heated to 110 °C for 12 h. The black solution was then filtered and concentrated. When the solution was cooled below 0 °C overnight, the product was obtained as the pure black crystalline solid.

$Co_4(CO)_8(DPM)_2$ (4). Yield: 0.38 g (86%). Anal. Calcd for $C_{58}H_{44}Co_4O_8P_4$: C, 56.70; H, 3.58; P, 10.10. Found: C, 57.78; H, 3.58; P, 10.38.

$Co_4(CO)_8(DMPM)_2$ (5). Yield: 0.32 g (72%). Anal. Calcd for $C_{38}H_{36}Co_4O_8P_4$: C, 46.57; H, 3.67; P, 12.64; O, 13.0. Found: C, 45.93; H, 3.65; P, 12.55; O, 13.11.

$Co_4(CO)_8(DMM)_2$ (6). Yield: 0.36 g (84%). Anal. Calcd for $C_{18}H_{28}Co_4O_8P_4$: C, 29.5; H, 3.82; P, 16.9; O, 17.4. Found: C, 28.70; H, 3.80; P, 16.28; O, 17.15.

Compound **4** may be synthesized alternatively from $Co_4(CO)_{12}$ and DPM.[12] The black crystals obtained gave the same IR spectrum as $Co_4(CO)_8(DPM)_2$ (**4**) synthesized as above except for an additional weak band at 1890 cm^{-1} in both CH_2Cl_2 solution and Nujol mull. Subsequent recrystallization from toluene removed this band, which is tentatively assigned to $Co(CO)_4^-$.

Registry No. 1, 52615-19-7; **2**, 100190-65-6; **3**, 100190-66-7; **4**, 81533-57-5; **5A**, 100205-44-5; **5B**, 100205-42-3; **6**, 100205-43-4.

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