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Contribution from the Departments of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and University of Kentucky, Lexington, Kentucky 40506

Reactions of the Linked Cobalt Dimer $Co_2(CO)_6(Ph_2PCH_2PPh_2)$. Molecular Structure of $(\mu\text{-H})(\mu\text{-PPh}_2)Co_2(CO)_4(Ph_2PCH_2PPh_2)$

BRIAN E. HANSON,*[1a] PHILLIP E. FANWICK,*[1b] and JUDITH S. MANCINI[1a]

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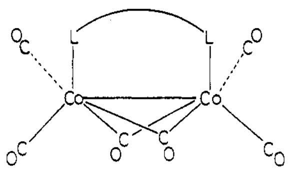
The dimer $Co_2(CO)_6(DPM)$ (**1**) (DPM = bis(diphenylphosphino)methane) reacts with hydrogen at moderate pressures (75 atm) to cleave the DPM ligand and yield $(\mu\text{-H})(\mu\text{-PPh}_2)Co_2(CO)_4(DPM)$ (**2**). This compound can also be synthesized directly from **1** and PPh_2H. Pyrolysis of **1** yields the tetranuclear cluster $Co_4(CO)_8(DPM)_2$. Oxidation of **1** yields the ionic compound $[Co_2(CO)_3(DPM)_2I]I$. Compound **2** crystallizes in the space group $P\bar{1}$, with $a = 10.627$ (1) Å, $b = 19.196$ (2) Å, $c = 10.251$ (1) Å, $\alpha = 95.430$ (8)°, $\beta = 91.491$ (10)°, $\gamma = 85.032$ (9)°, and $V = 2072.8$ Å^3. The structure was refined by using 4824 reflections having $F_o^2 > 10\sigma(F_o^2)$. The final residuals were $R = 0.056$ and $R_w = 0.096$. The cobalt atoms are bridged by a hydride ligand, a phosphido group, and a bis(tertiary phosphine); as a result the Co–Co bond is very long, 2.637 (1) Å. The hydride was found to bridge the two cobalt atoms, with Co–H distances of 1.41 (7) and 1.84 (7) Å. The influence of the μ-H and μ-PPh_2 groups is to bend two terminal carbonyls away from the cobalt–cobalt bond. The NMR spectrum shows the hydride as a doublet of triplets at −8.60 ppm.

Introduction

Substitution of carbon monoxide in cobalt carbonyl complexes by phosphine ligands has been studied extensively.[2] It is well-known that the reaction of monodentate phosphines and other nucleophiles with dicobalt octacarbonyl leads to disproportionation at room temperature yielding $[Co(CO)_3L_2][Co(CO)_4]$, which can be transformed into $[Co_2(CO)_6L_2]$ upon heating in benzene.[3] Much of the interest in the substitution reactions of cobalt carbonyls stems from modification of the hydroformylation catalyst $HCo(CO)_4$ with phosphine ligands.[4]

Bis(tertiary phosphines), which may bridge two cobalt atoms, readily replace two CO ligands to give $Co_2(CO)_6(L–L)$.



These compounds have been structurally characterized in the solid and in solution.[5,6] A crystal structure has been performed only on the As derivative, $Co_2(CO)_6(C_4F_4(AsMe_2)_2)$;[5] infrared studies have shown the phosphorus derivatives to have a similar structure. The basic structure is derived from $Co_2(CO)_8$,[7] in which a CO on each cobalt is replaced. Apart from the reactions of $Co_2(CO)_6(L–L)$ with alkynes,[6] little of the chemistry of the linked dimers has been investigated.

The reactions of $Co_2(DPM)(CO)_6$ (**1**) (DPM = bis(diphenylphosphino)methane) with molecular hydrogen have now been investigated with the goal of synthesizing phosphine-substituted hydridocobalt carbonyl complexes. Hydrogen-assisted cleavage of the DPM ligand is observed to give the phosphido-bridged compound $(\mu\text{-H})(\mu\text{-PPh}_2)Co_2(DPM)(CO)_4$ (**2**). Pyrolysis of **1** leads to the tetranuclear cluster $Co_4(DPM)_2(CO)_8$ (**3**). The molecular structure of **2** and some of the solution chemistry of **1** and **2** are reported.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen. Solvents were dried over molecular sieves and purged with nitrogen before use. Dicobalt octacarbonyl and triphenylphosphine were obtained from Pressure Chemical Co. and used without further purification. Bis(diphenylphosphino)methane was synthesized according to a literature preparation.[8] High-pressure reactions were performed in a Parr 300-mL minireactor. Elemental analyses were performed by the Analytical Services Department of VPI&SU.

$Co_2(CO)_6(DPM)$. A 250-mL round-bottom flask equipped with a side-arm gas adapter and fitted with a septum stopper was charged with 3 g of $Co_2(CO)_8$ (0.0088 mol) and 20 mL of methylene chloride. A separate flask was charged with 3.4 g of bis(diphenylphosphino)methane (dissolved in methylene chloride). The DPM solution was degassed and then transferred via syringe to the flask containing the $Co_2(CO)_8$ solution. The reaction is complete when evolution of carbon monoxide ceases. The product is obtained as an orange, crystalline, air-stable solid upon addition of hexane at −78 °C (yield 5.0 g (80%)).

IR (Nujol): ν_{CO} 2042 (m), 2000 (s), 1989 (s), 1975 (s), 1812 (m), 1799 (m) cm^{-1}. Anal. Calcd for $C_{31}H_{22}Co_2O_6P_2$: C, 55.6; H, 3.29. Found: C, 55.4; H, 3.20. ^{1}H NMR ($CDCl_3$): δ 7.5 (20, m); 3.15 (2, t) (J(PH) = 10.1 Hz).

$(\mu\text{-H})(\mu\text{PPh}_2)Co_2(CO)_4(DPM)$. A 300-mL autoclave was charged with 1 g of $Co_2(CO)_6(DPM)$ and 100 mL of benzene and then degassed by pressurizing with hydrogen and venting. The autoclave was pressurized with hydrogen (70 atm, 20 °C) and heated with stirring to 100 °C for 12 h. Hydrogen was vented from the cooled autoclave, and the green-black solution was transferred under nitrogen to a round-bottom flask with a side-arm gas adapter. After removal of solvent the residue was recrystallized from toluene–hexane. The product is obtained as an analytically pure, green crystalline solid (isolated yield 20%).

IR (Nujol): ν_{CO} 1989 (w), 1963 (s), 1932 (s), 1918 (m) cm^{-1}. Anal. Calcd for $C_{41}H_{33}Co_2O_4P_3$: C, 61.5; H, 4.16. Found: C, 62.56; H, 4.25. ^{1}H NMR ($CDCl_3$): δ 7.2–7.7 (30, m); 4.17 (2, t) (J(PH) = 11.0 Hz); −8.60 (1, doublet of triplets) (J(PH) = 64.9, 32.7 Hz).

Alternatively, this compound can be prepared in higher yield from the oxidative addition of diphenylphosphine to **1** in refluxing benzene.

$Co_4(CO)_8(DPM)_2$. A 300-mL autoclave was charged with 1 g of $Co_2(CO)_6(DPM)$ and 60 mL of benzene and then degassed with hydrogen. The autoclave was pressurized with hydrogen or nitrogen

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(7 atm, 20 °C) and heated with stirring to 100 °C for 12 h. The pressure was vented from the cooled reactor, and the green-black solution was transferred under nitrogen to a round-bottom flask. The benzene was removed under vacuum and the residue recrystallized from toluene–hexane. The product obtained is an analytically pure, black, crystalline solid (isolated yield 60%).

IR (Nujol): ν_{CO} 2008 (s), 1976 (s), 1948 (vs), 1829 (m), 1782 (m), 1756 (m) cm^{-1}. Anal. Calcd for $C_{58}H_{44}Co_4O_8P_4$: C, 56.70; H, 3.58; P, 10.10. Found: C, 57.28; H, 3.58; P, 10.38.

$Co_2(CO)_3(DPM)_2I_2$. A 100-mL round-bottom flask with a side-arm gas adapter was charged with 1 g of $Co_2(CO)_6(DPM)$ (0.0015 mol), 0.58 g of DPM (0.0015 mol), and enough THF to completely dissolve both solids. The solution was degassed with nitrogen. A separate flask was charged with 0.38 g of iodine (0.0015 mol) dissolved in THF, and degassed. The iodine solution was added to the $Co_2(CO)_6(DPM)$ solution. The temperature was maintained at 45 °C for 10 h. The product precipitates from solution as an air-stable, dark orange powder, which was filtered in air and then washed with hexane (isolated yield 1 g, 55%).

IR (Nujol): ν_{CO} 1988 (s), 1944 (s), 1816 (m) cm^{-1}. Anal. Calcd for $C_{53}H_{44}Co_2I_2O_3P_4$: C, 51.99; H, 3.62. Found: C, 51.96; H, 3.60.

Reaction of 2 with C_6H_5CCH. A solution of 0.3 g of (μ-H)(μ-PPh_2)Co_2(DPM)$(CO)_4$ (0.00039 mol) in 30 mL of benzene was brought to reflux under N_2. Phenylacetylene (0.050 mL, 0.00047 mol) was added by syringe, and reflux was continued for 5 h. The red solution was reduced in volume under vacuum and chromatographed on Florisil (eluent CH_2Cl_2–hexane). Removal of solvent yields a red crystalline solid (isolated yield 0.25 g).

IR (hexane solution): ν_{CO} 2030 (s), 2005 (s), 1983 (s), 1961 (w) cm^{-1}. Anal. Calcd for $C_{37}H_{28}Co_2O_4P_2$: C, 62.02; H, 3.94. Found: C, 62.48, H, 4.17. ^1H NMR ($CDCl_3$): δ 7.45 (25, m); 5.78 (1, t) (J(PH) = 8.1 Hz); 3.32 (2, ABX_2) (J(PH) = 0.6 Hz, J(HH) = 21 Hz).

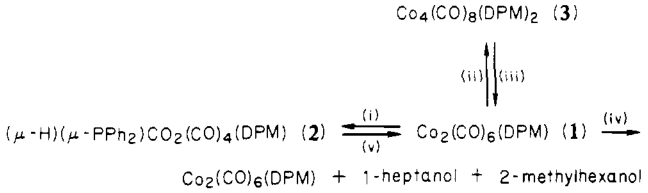
Hydroformylation of 1-Hexene. A 300-mL autoclave reactor was charged with 0.1 g of $Co_2(CO)_6(DPM)$ (0.00015 mol)8 20 mL of benzene and 20 mL of 1-hexene (0.156 mol) and then pressurized to 70 atm with H_2–Co(1:1). The temperature was brought to 120 °C and the reaction allowed to proceed for 8 h. The ratio of *n*-heptanal to 2-methylhexanal was determined by gas chromatography and ^1H NMR. Only traces of the respective alcohols were observed.

Crystal Preparation and Data Collection for (μ-H)(μ-PPh_2)Co_2(DPM)$(CO)_4$. Single crystals were obtained by recrystallization from toluene. A parallelepiped of dimensions 0.20 × 0.23 × 0.32 mm was mounted on the tip of a glass fiber with epoxy. Indexing and data collection were done by an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using Mo Kα radiation and a takeoff angle of 4.2°. The unit cell on the basis of a least-squares fit of 25 reflections with $19° > 2\theta > 28°$ was determined to be a = 10.627 (1) Å, b = 19.196 (2) Å, c = 10.251 (1) Å, α = 95.430 (8)°, β = 91.491 (10)°, γ = 85.032 (9)°, and V = 2072.8 Å^3. The 25 peaks used in the centering routine were very sharp and symmetrical. For a dimeric formulation $Z = 2$ and ρ_{calcd} = 1.28 g/cm^3. The experimental density, by flotation, was found to be 1.25 ± 0.05 g/cm^3.

Data were collected at 22 °C with use of the θ–2θ scan technique to a maximum 2θ of 50°. The vertical aperture was 4.0 mm while the horizontal aperture was calculated from the formula (1.50 + 1.00 tan θ) mm. The scan width was determined by (0.6 + 0.35 tan θ)° while the scan rate was either the maximum to scan the peak in 60 s or to produce an intensity 50 times greater than $\sigma(I)$. Of the 7291 reflections collected only the 4824 reflections with $F^2 > 10\sigma(F^2)$ were used during refinement. The value of the p factor used to calculate $\sigma(F_2)$ was 0.02.[9] Three standard reflections were monitored after every hour of beam exposure and displayed no systematic variation in intensity. Because the linear absorption coefficient was only 9.83 cm^{-1} and two 360° Ψ scans near X = 90° displayed less than a 10% variation of intensity, no absorption correction was applied.

Solution and Refinement. All calculations were perfomed on the IBM 370/165 computer located at the University of Kentucky Computing Center. The programs used included Ibers' NUCLS least-squares program (based on the Busing–Levy program ORFLS) Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program and Johnson's ORTEP thermal ellipsoid plotting program. Corrections for anomalous dispersion were included in the scattering factor tables for cobalt and phosphorus atoms. The least-squares refinement minimized the function $\sum w(F_o - F_c)^2$, where the weighting factor $w = 1/\sigma(F_o)^2$.

Scheme I[a]



[a] Key: (i) H_2, 70 atm, 100 °C; (ii) reflux in benzene; (iii) CO, 70 atm, 100 °C; (iv) H_2–CO (1:1), 70 atm, 120 °C, 0.15 mmol of $Co_2(CO)_6(DPM)$, 0.16 mol of 1-hexene in benzene; (v) CO, 70 atm, 100 °C, 15% yield.

Possible space groups for the triclinic cell are $P\bar{1}$ and $P1$. Because $Z = 2$ for this cell, refinement was commenced in $P\bar{1}$ and converged to the final structure. The initial cobalt and phosphorus positions were determined from a Patterson map, and the other atom positions were obtained from difference Fourier maps during refinement. At this point the residuals were $R_1 = 0.062$ and $R_2 = 0.102$. It was noted that there was very poor agreement between F_o and F_c for those reflections near 0k0. Refinement of an isotropic extinction parameter converged at a value of -0.3697×10^{-6} without changing the residuals. The hydridic hydrogen was located in a difference Fourier map and refined. The positions for all the hydrogens bonded to carbon atoms were calculated assuming a bonding distance of 0.95 Å. These positions and isotropic temperature factors of 6.0 Å^2 were held fixed during the final least-squares cycles. The final values of the residuals were $R_1 = 0.056$ and $R_2 = 0.096$. The residuals for the L shells displayed a regular increase from $R_1 = 0.027$ for $L = -12$ up to $R_1 = 0.108$ for $L = 1$ and back to $R_1 = 0.045$ for $L = 12$. A similar trend was observed for the H shells. The cause of this variation is unknown. A final difference map showed no significant electron density. This and the fact that the experimental density closely agrees with the calculated density indicates that all atoms are accounted for. The final coordinates for all atoms are given in Table I. Bond distances and angles for the non-phenyl atoms are listed in Table II. Tables of temperature factors, phenyl atomic distances and angles, selected planes, and calculated and observed structure factors are available as supplementary material Tables IV–VII, respectively.

Results and Discussion

Some of the high-pressure chemistry of $Co_2(CO)_6(DPM)$ is outlined in Scheme I.

Pyrolysis of **1**, either in the autoclave or in refluxing benzene, gave the black crystalline compound $Co_4(CO)_8(DPM)_2$ (**3**) in good yield. The cluster was identified by the similarity of its infrared spectrum to the known rhodium analogue, $Rh_4(CO)_8(DPM)_2$, which has been structurally characterized by X-ray crystallography.[10]

Pyrolysis of **1** was also carried out under an atmosphere of H_2 in an attempt to synthesize new hydridocobalt carbonyl clusters. The isolated product, (μ-H)(μ-PPh_2)$Co_2(CO)_4$(DPM) (**2**), qualifies as a new hydridocobalt carbonyl dimer but is obviously not formed in a straightforward manner. Yields for this reaction are variable, ranging from 10 to 35% after recrystallization. No other new compounds have been isolated from this reaction; however, compound **3** is sometimes present in small quantities. The tetranuclear cluster **3** cannot be converted directly to **2** under similar reaction conditions. Therefore its presence in reaction i indicates that the dimer, **1**, may react via pathway iii at high H_2 pressures. Cleavage of coordinated DPM by H_2 has been previously observed in $Mn_2(CO)_8(DPM)$.[11] This pathway represents a new route to the diphenylphosphido group. Previously observed methods include metathesis of $KPPh_2$ with a transition-metal halide,

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Table I. Positional Parameters for the Atoms of (μ-H)(μ-PPh_2)Co_2(DPM)$(CO)_4$

atom	x^a	y	z
Co(1)	0.53896 (8)	0.25417 (5)	0.37238 (9)
Co(2)	0.37092 (8)	0.25358 (5)	0.17845 (9)
P(1)	0.6565 (2)	0.32512 (9)	0.2882 (2)
P(2)	0.4549 (2)	0.33171 (9)	0.0754 (2)
P(3)	0.3836 (2)	0.18930 (10)	0.3405 (2)
O(11)	0.7180 (6)	0.1493 (3)	0.4687 (6)
O(12)	0.4247 (7)	0.3588 (4)	0.5673 (6)
O(21)	0.2997 (6)	0.1509 (3)	0.9685 (6)
O(22)	0.1615 (6)	0.3484 (3)	0.2862 (7)
C(B1)	0.5556 (7)	0.3832 (3)	0.1882 (7)
C(11)	0.6492 (8)	0.1901 (4)	0.4255 (9)
C(12)	0.4692 (8)	0.3183 (5)	0.4910 (8)
C(21)	0.3314 (7)	0.1912 (4)	0.0510 (8)
C(22)	0.2443 (7)	0.3109 (4)	0.2444 (7)
C(111)	0.7826 (6)	−0.2873 (4)	0.1809 (7)
C(112)	0.8102 (8)	0.2148 (4)	0.1613 (8)
C(113)	0.909 (1)	0.1876 (5)	0.082 (1)
C(114)	0.9789 (9)	0.2297 (7)	0.0219 (10)
C(115)	0.9538 (9)	0.2994 (8)	0.038 (1)
C(116)	0.8559 (8)	0.3298 (5)	0.1189 (10)
C(121)	0.7397 (7)	0.3869 (4)	0.3994 (6)
C(122)	0.6912 (8)	0.4542 (4)	0.4405 (8)
C(123)	0.754 (1)	0.4960 (5)	0.5302 (9)
C(124)	0.8702 (10)	0.4718 (5)	0.5814 (9)
C(125)	0.9194 (8)	0.4058 (6)	0.5410 (9)
C(126)	0.8565 (7)	0.3626 (4)	0.4507 (8)
C(211)	0.3399 (7)	0.3956 (4)	0.0055 (7)
C(212)	0.2890 (8)	0.4554 (4)	0.0749 (8)
C(213)	0.1916 (8)	0.4965 (4)	0.0217 (9)
C(214)	0.1494 (9)	0.4800 (5)	−0.101 (1)
C(215)	0.1983 (9)	0.4220 (6)	−0.1714 (10)
C(216)	0.2916 (8)	0.3803 (5)	−0.1190 (8)
C(221)	0.5592 (7)	0.3072 (4)	0.9381 (7)
C(222)	0.6030 (9)	0.3586 (5)	−0.1317 (9)
C(223)	0.6841 (9)	0.3411 (6)	−0.2335 (8)
C(224)	0.7230 (9)	0.2745 (6)	−0.2666 (9)
C(225)	0.6855 (9)	0.2200 (6)	−0.2014 (10)
C(226)	0.6000 (8)	0.2378 (5)	−0.0981 (8)
C(311)	0.4234 (7)	0.0954 (4)	0.3055 (7)
C(312)	0.5065 (9)	0.0715 (4)	0.2080 (9)
C(313)	0.543 (1)	−0.0002 (5)	0.178 (1)
C(313)	0.497 (1)	−0.0461 (5)	0.250 (1)
C(315)	0.415 (1)	−0.0247 (6)	0.348 (1)
C(316)	0.376 (1)	0.0460 (5)	0.377 (1)
C(321)	0.2554 (7)	0.1944 (4)	0.4570 (8)
C(322)	0.2775 (9)	0.2062 (6)	0.5890 (9)
C(323)	0.185 (1)	0.2036 (10)	0.676 (1)
C(324)	0.069 (1)	0.1925 (10)	0.632 (2)
C(325)	0.0383 (10)	0.1798 (9)	0.499 (2)
C(326)	0.1346 (8)	0.1829 (6)	0.410 (1)
H(1)	0.535 (7)	0.228 (4)	0.229 (7)
H(B11)	0.609	0.409	0.138
H(B12)	0.505	0.416	0.244
H(112)	0.759	0.184	0.204
H(113)	0.929	0.136	0.074
H(114)	1.046	0.209	−0.033
H(115)	1.002	0.331	−0.007
H(116)	0.838	0.381	0.133
H(122)	0.611	0.472	0.405
H(123)	0.717	0.542	0.561
H(124)	0.915	0.501	0.644
H(125)	1.0	0.390	0.575
H(126)	0.891	0.316	0.424
H(212)	0.322	0.469	0.162
H(213)	0.153	0.537	0.074
H(214)	0.082	0.510	−0.139
H(215)	0.168	0.408	0.740
H(216)	0.328	0.339	0.829
H(222)	0.574	0.408	0.893
H(223)	0.714	0.377	0.719
H(224)	0.780	0.262	0.659
H(225)	0.713	0.171	0.776
H(226)	0.569	0.200	0.948
H(312)	0.542	0.106	0.158
H(313)	0.601	−1.016	0.104
H(314)	0.478	0.096	0.766
H(315)	0.610	0.060	0.601
H(316)	0.315	0.061	0.448
H(322)	0.362	0.215	0.622
H(323)	0.200	0.209	0.769
H(324)	−0.005	0.196	0.691
H(325)	−0.045	0.169	0.466
H(326)	0.115	0.179	0.317

[a] Estimated standard deviations in the last figures are given in parentheses in this and all subsequent tables.

metathesis of PPh_2Cl with a transition-metal anion, and decomposition of coordinated triphenylphosphine.[12,13]

In the pyrolysis of **1** no decomposition of the DPM ligand is observed in the absence of added H_2. For this reason we postulate that a cobalt hydride species formed in situ initiates attack on coordinated DPM. In a separate experiment it was shown that $HPPh_2$ readily oxidatively adds to **1** to yield **2** (vide supra) and is thus a potential intermediate in the high-pressure reaction.

The apparent activation of H_2 in the synthesis of **2** is not surprising on the basis of the wealth of catalytic activity of cobalt carbonyl hydrides. In this regard the dimer **1** hydroformylates 1-hexene under the conditions in pathway iv. The apparent reaction rate and distribution of straight-chain to branched products (1-heptanol–2-methylhexanol, 2.7:1) is similar to that obtained for $HCo(CO)_3(PPh_2Et)$.[14] Compound **1** can be isolated from the hydroformylation solution at the end of a batch run in greater than 80% yield. The actual catalyst precursor could be any one of the following hydridocobalt carbonyl complexes $HCo(CO)_3(DPM)Co(CO)_3H$, $HCo(CO)_3(DPM)$, or $HCo(CO)_4$. Under hydroformylation conditions no decomposition of DPM is observed.

Conversion of the tetranuclear cluster **3** back to the dimer **1** can be effected in nearly quantitative yield under moderate pressures of CO (reaction iii in Scheme I). This reaction stops with formation of **1**. No evidence for removal of the DPM ligand was obtained. The reaction of the phosphido-bridged compound **2** with CO gives **1** plus an uncharacterized cobalt(II) compound.[15]

Alkynes react readily with **2** in refluxing benzene, replacing $HPPh_2$ to yield the known compounds (alkyne)$Co_2(CO)_4$(DPM).[6] Many compounds of this general type with other bridging bidentate ligands have been synthesized.[16]

Oxidation of **1** by iodine in THF gives $Co_2(DPM)_2(CO)_3I_2$ (**6**) in low yield. The yield of **6** is increased dramatically if excess DPM is added to the reaction mixture. In the solid state **6** shows three CO stretches (two terminal and one bridging) in the infrared spectrum while in CH_2Cl_2 solution only two stretches are observed. In methanol and acetonitrile **6** behaves

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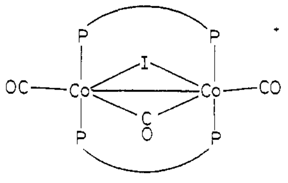
Table II. Selected Bond Distances and Angles for $(\mu\text{-}H)(\mu\text{-}PPh_2)Co_2(DPM)(CO)_4$

Distances, Å			
Co(1)–Co(2)	2.637 (1)		
Co(1)–P(1)	2.175 (2)	Co(2)–P(2)	2.178 (2)
Co(1)–P(3)	2.153 (2)	Co(2)–P(3)	2.156 (2)
Co(1)–C(11)	1.740 (8)	Co(2)–C(21)	1.755 (8)
Co(1)–C(12)	1.775 (9)	Co(2)–C(22)	1.768 (8)
Co(1)–H(1)	1.37 (8)	Co(2)–H(1)	1.84 (7)
C(11)–O(11)	1.126 (9)	C(21)–O(21)	1.154 (9)
C(12)–O(12)	1.131 (9)	C(22)–CO(22)	1.152 (9)
P(1)–C(B1)	1.842 (7)	P(2)–C(B1)	1.833 (7)
P(1)–C(111)	1.813 (7)	P(2)–C(211)	1.837 (7)
P(1)–C(121)	1.833 (7)	P(2)–C(221)	1.816 (7)
P(3)–C(311)	1.820 (7)	P(3)–C(321)	1.825 (7)
Angles, Deg			
Co(2)–Co(1)–P(1)	94.62 (6)	Co(1)–Co(2)–P(2)	95.35 (6)
–P(3)	52.32 (6)	–P(3)	52.21 (6)
–C(11)	132.7 (3)	–C(21)	134.3 (3)
–C(12)	102.9 (3)	–C(22)	103.0 (3)
–H(1)	43 (3)	–H(1)	34 (2)
P(1)–Co(1)–P(3)	146.20 (8)	P(2)–Co(2)–P(3)	147.46 (8)
–C(11)	102.8 (2)	–C(21)	102.9 (3)
–C(12)	95.4 (3)	–C(22)	95.8 (3)
–H(1)	78 (3)	–H(1)	85 (2)
P(3)–Co(1)–C(11)	97.2 (2)	P(3)–Co(2)–C(21)	100.0 (3)
–C(12)	98.7 (3)	–C(22)	94.5 (3)
–H(1)	72 (3)	–H(1)	67 (2)
C(11)–Co(1)–C(12)	118.3 (4)	C(21)–Co(2)–C(22)	116.0 (4)
–H(1)	98 (3)	–H(1)	106 (2)
C(12)–Co(1)–H(1)	143 (3)	Co(22)–Co(2)–H(1)	135 (2)
Co(1)–C(11)–O(11)	173.3 (8)	Co(2)–C(21)–O(21)	176.9 (8)
–C(12)–O(12)	179.5 (8)	–C(22)–O(22)	179.4 (7)
Co(1)–P(1)–C(B1)	108.8 (2)	Co(2)–P(2)–C(B1)	110.0 (2)
–C(111)	118.1 (2)	–C(211)	114.4 (2)
–C(121)	118.5 (2)	–C(221)	121.9 (3)
C(B1)–P(1)–C(111)	105.1 (3)	C(B1)–P(2)–C(211)	106.0 (3)
–C(121)	103.1 (3)	–C(221)	101.6 (3)
C(111)–P(1)–C(121)	101.5 (3)	C(211)–P(2)–C(221)	101.2 (3)
Co(1)–P(3)–Co(2)	75.48 (7)	C(311)–P(3)–C(321)	103.7 (4)
Co(1)–P(3)–C(311)	116.8 (3)	Co(2)–P(3)–C(311)	118.0 (3)
–C(321)	121.5 (3)	–C(321)	120.7 (3)

as a 1:1 electrolyte. This behavior is similar to that of the rhodium compounds $[Rh_2(DPM)_2(CO)_3Cl]Cl$[17] and $[Rh_2(DPM)_2(CO)_3Cl][BPh_4]$.[18] The crystal structure for the latter compound has been determined. The cationic dimer contains a bridging CO and a bridging chloride. A similar framework is likely for 6 as shown diagrammatically:



Unlike the case for the rhodium complexes the bridging CO in 6 is not labile. Compound 6 is stable with respect to CO loss under vacuum either as a solid or in solution at 80 °C.

Structure of $(\mu\text{-}H)(\mu\text{-}PPh_2)Co_2(CO)_4(DPM)$ (2). A drawing of the entire molecule is provided in Figure 1. Figure 2 is a drawing of the molecule without the phenyl rings, providing a clearer view of the bonding about the metal atoms.

The cobalt–cobalt bond in 2 is bridged by three different groups, a diphenylphosphido bridge, bis(diphenylphosphino)methane, and a bridging hydride. Because of the numerous bridging ligands the cobalt–cobalt bond is quite long at 2.637 Å. This is substantially longer than the distance of 2.497 Å found in cobalt metal[19] or 2.522 and 2.525 Å in $Co_2(CO)_8$.[7] In a previously reported structure involving only a bridging phosphido group, $(\mu\text{-}P(CH_3)_2)(\eta^5\text{-}C_5H_5)Co_2(CO)_4$ (7), the cobalt–cobalt distance had increased to 2.593 Å.[20] The presence of the bridging hydride is probably responsible for the further increase noted here.[21] In view of the formula of 2 the presence of a cobalt–cobalt bond of bond order 1 is certain.

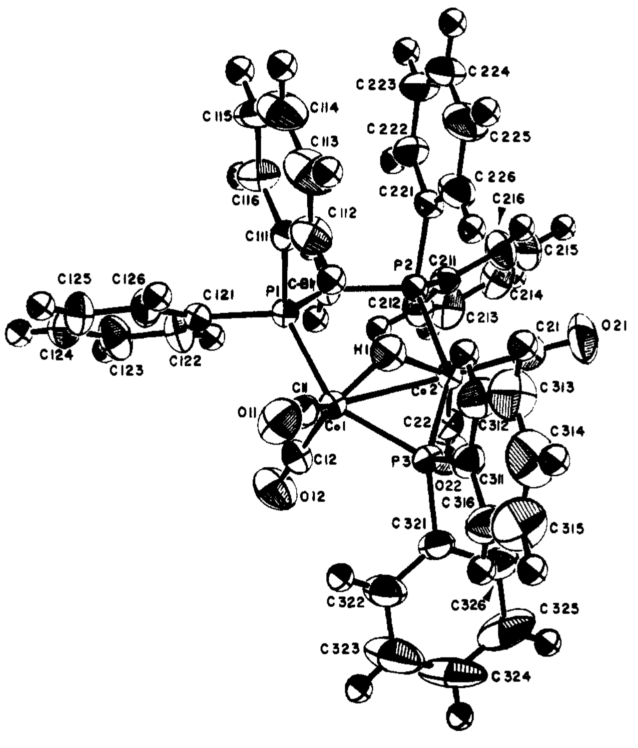


Figure 1. ORTEP drawing of 2 showing the atomic numbering scheme. Ellipsoids are drawn to enclose 50% of the electron density.

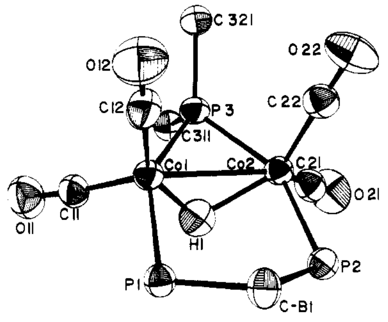


Figure 2. ORTEP drawing of 2 with phenyl groups omitted showing the eclipsed nature of the coordination geometry.

The coordination geometry about the two cobalts is quite interesting. The plane containing the cobalts and P(1) and P(2) intersects with the Co(1), Co(2), P(3) plane at an angle of only 5.6°; thus P(3) is nearly trans to P(1) and P(2). Two of the carbonyls, CO(12) and CO(22), are nearly perpendicular to the Co–Co bond, each making an angle of about 103° with it. These two carbonyls are also nearly perpendicular to the cobalt–phosphorus planes. The remaining two carbonyls CO(11) and CO(21) deviate from this pattern. These carbonyls make an angle of about 135° with the Co–Co bond.

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(20) Keller, E.; Vahrenkamp, H. *Z. Naturforsch., B* **1978**, *33B*, 537.

(21) Churchill et al. have observed that a single hydride bridge lengthens metal–metal bonds in osmium carbonyl clusters and that double bridges involving one hydride, $(\mu\text{-}H)(\mu\text{-}X)$ may lengthen or shorten the metal–metal bond.[22]

(22) See, for example: Churchill, M. R.; Lashewyez, R. A. *Inorg. Chem.* **1979**, *18*, 1926 and references therein.

Table III. Comparison of Bond Angles (Deg) in (μ-P(CH$_3$)$_2$)(η^5-C$_5$H$_5$)Co$_2$(CO)$_4$, **2**, Co$_2$(ffars)(CO)$_6$, and (C$_2$Ph$_2$)Co$_2$(DPM)(CO)$_4$

	$7^{a,b}$		2				Co$_2$(ffars)(CO)$_6$^{c}				(C$_2$Ph$_2$)Co$_2$(DPM)(CO)$_4$^{d}			
			Co(1)		Co(2)		Co(1)		Co(2)		Co(1)		Co(2)	
Co–Co	-P	52.6	-P(3)	52.3	-P(3)	52.2	-C(bridge)	50.0	-C(bridge)	50.4	-C(A1)	50.0	-C(A1)	51.6
	-C(21)	107.6	-C(12)	102.9	-C(22)	103.0	-C(6)	107.2	-C(5)	107.7	-C(COB)	102.2	-C(COC)	97.8
	-C(22)	128.7	-C(11)	132.7	-C(21)	134.3	-C(7)	130.0	-C(8)	129.9	-C(COA)	148.8	-C(COD)	149.8
	-C(23)	87.7	-P(1)	94.6	-P(2)	95.3	-As(1)	110.2	-As(2)	109.3	-P(1)	93.2	-P(2)	98.8
P(3)–Co	-C(21)	99.7	-C(12)	98.7	-C(22)	94.5								
	-C(22)	94.4	-C(11)	97.1	-C(21)	100.0								
	-C(23)	138	-P(1)	146.2	-P(2)	147.5								

[a] Data from ref 17. [b] Angles are around Co(2). [c] Data from ref 5a. [d] Data from ref 15a.

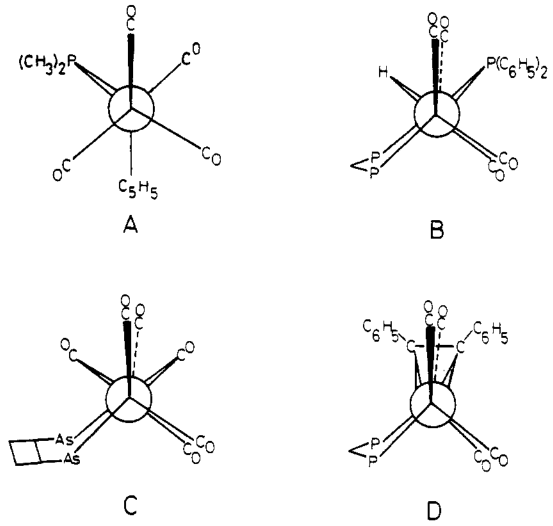

Figure 3. Schematic representations of (A) (μ-P(CH$_3$)$_2$)(η^5-C$_5$H$_5$)Co$_2$(CO)$_4$, (B) **2**, (C) Co$_2$(ffars)(CO)$_6$, and (D) (C$_2$Ph$_2$)Co$_2$(DPM)(CO)$_4$. The view is down the metal–metal bond. The carbonyl directed toward the top of the page is bent away from the bridging group(s).

In addition the plane containing Co(1), Co(2), C(11), and C(21) intersects the similar plane of the other carbonyl carbons at an angle of 150°, being tilted toward the phosphido group.

The location of the briding hydride was found in a difference Fourier map and refined. Its final position lies nearest carbonyls CO(11) and CO(21). The hydride thus appears to effect the opening of the Co–Co–C bond angles and the tilting of the plane toward the phosphido group. However, examination of several dimeric cobalt structures reveals similar structural features even in the case of (μ-P(CH$_3$)$_2$)(η^5-C$_5$H$_5$)Co$_2$(CO)$_4$ (**7**).[20] In this molecule the cobalts are quite different, one being bonded to a cyclopentadienyl ring and one terminal carbonyl while the other is bound to three terminal carbonyls. The only bridge is the dimethylphosphido group. A comparison of relevant bond angles between the cobalt bound to the three terminal carbonyls and those found in **2**, Co$_2$(ffars)(CO)$_6$, and (μ-H)(C$_2$Ph$_2$)Co$_2$(DPM)(CO)$_4$ is given in Table III. The geometries are quite similar as emphasized in Figure 3, which shows schematic representations of these four molecules as viewed down the cobalt–cobalt bond. In each case one carbonyl is bent away from the cobalt–cobalt bond. The bending can be readily attributed to the presence of at least one single-atom bridge. When the bridging ligand is an alkyne, the angle Co–Co–C opens up to 149° from ca. 130° in the other compounds.[16a] In **2** the hydride occupies the second bridging position. This site is empty in **7**, since no additional bridging ligand is required to satisfy the 18-electron rule.

The overall symmetry of the molecule deserves to be mentioned. The molecule is located at a general position in the unit cell and therefore is not required to possess any symmetry. However, as will be noted in Figure 1, the molecule is in a nearly eclipsed configuration with respect to the Co–Co bond and even the equivalent phenyl ring planes are in similar orientations. This results in the molecule nearly possessing a mirror plane that bisects the Co–Co bond and contains C(B1) and P(3). This is the highest symmetry the molecule could have.

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Supplementary Material Available: Listings of thermal parameters (Table IV), bond distances and angles for the phenyl rings (Table V), least-squares planes (Table VI), and observed and calculated structure factors (Table VII) (37 pages). Ordering information is given on any current masthead page.