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Further Examples of (Diphenylphosphido)-Bridged Dicobalt Complexes: $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2$ and $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2$

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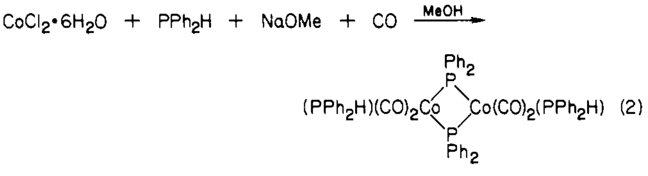
The new binuclear complex $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2$ (**1**) was obtained in 61% yield from the reaction of $CoCl_2{\cdot}6H_2O$ with PPh_2H, NaOMe, and CO. It has been spectroscopically characterized and its crystal structure determined. It crystallizes in the space group $P2_1/c$ with $a = 11.742$ (6) Å, $b = 21.037$ (6) Å, $c = 21.732$ (10) Å, $\beta = 91.16$ (4)°, $V = 5367$ (7) Å^3, and $Z = 4$. The structure refined for the 3789 reflections with $I > 2\sigma(I)$ to $R_1 = 0.084$ and $R_2 = 0.096$. The two Co atoms are nonbonded but bridged by two μ-PPh_2 ligands. Each Co is further coordinated by two CO's and a PPh_2H ligand. When complex **1** is heated, it loses two CO's and transforms quantitatively into $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H_2)$ (**2**). Spectral data for complex **2** imply it to be similar to the previously characterized $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$ with a Co–Co double bond.

Cobalt(II) salts in methanol solution are known to absorb CO in the presence of thiols and bases to yield polynuclear carbonyl complexes containing thiolate ligands (e.g. eq 1).[1] We now report

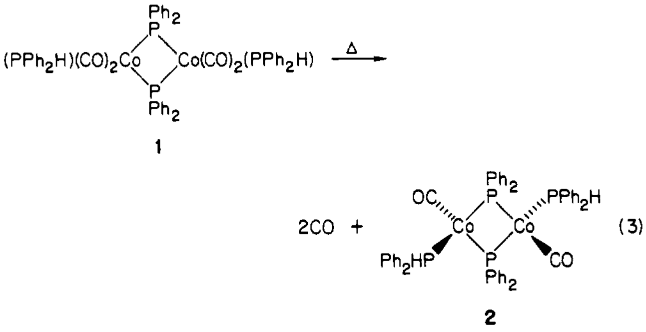
$$CoCl_2{\cdot}6H_2O + EtSH + NaOH + CO \xrightarrow{MeOH} Co_4(CO)_4(\mu\text{-}SEt)_8 + Co_3(CO)_3(\mu\text{-}CO)(\mu\text{-}SEt)_5 \quad (1)$$

that secondary phosphines react in a similar fashion to yield a binuclear μ-PPh_2 complex with terminal PPh_2H ligands (eq 2).



1 (61%)

Complex **1** has been spectroscopically characterized and its crystal structure determined. It can be viewed as a PPh_2H-substituted derivative of the recently characterized compound $Co_2(\mu\text{-}PPh_2)_2(CO)_6$[2,3] with a slightly bent Co_2P_2 core. Upon heating, complex **1** loses CO and transforms into $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2$ (**2**), for which spectroscopic data imply the structure shown in eq 3.



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Experimental Section

General Procedures and Instrumentation. Diphenylphosphine was prepared from PPh_3 by the method of ref 4. If not under CO, reactions were conducted under a prepurified Ar atmosphere. IR spectra were recorded on a Carl Zeiss IR 75 spectrophotometer. ^{31}P NMR spectra were obtained on a Bruker WP-200 FTNMR spectrometer using 85% H_3PO_4 as reference; downfield chemical shifts are reported as positive. Gas chromatography was performed on a Hewlett-Packard 5830A instrument.

Preparation of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2{\cdot}2MeCN$ (1). $CoCl_2{\cdot}6H_2O$ (2.38 g, 10 mmol) was dissolved under Ar in methanol (25 mL) in a 250-mL two-necked flask equipped with a magnetic stirrer. To this was added dropwise PPh_2H (3.74 g, 20 mmol) dissolved in methanol (25 mL). A deep purple solution resulted. After the mixture was stirred for 30 min, the Ar atmosphere was changed to CO, and 1.08 g (20 mmol) of NaOMe in 25 mL of methanol was added dropwise (3 h). During addition, CO absorption was observed and measured with a gas buret. Stirring was continued for 12 h, during which time about 400 mL of CO was absorbed, and a red precipitate formed. After CO absorption ceased, the methanol was removed in vacuo and the residue dissolved in 120 mL of acetonitrile. This solution was filtered to remove NaCl and the filtrate stored at room temperature for 24 h, during which time red crystals of **1** were deposited (3.2 g, 61%). The product may be recrystallized by dissolving it in a small amount of CH_2Cl_2 at room temperature, adding three volumes of acetonitrile, and letting the solution stand for a few hours, during which time large crystals of **1** form. Anal. Calcd for $C_{56}H_{48}Co_2N_2O_4P_4$: C, 63.75; H, 4.55; Co, 11.19; N, 2.65; P, 11.76. Found: C, 63.3; H, 4.6; Co, 11.3; N, 2.6; P, 12.1. IR ν(CO) (CH_2Cl_2): 2041.5 vw, 1986 m, 1964.5 m, 1925 s cm^{-1}. ^{31}P NMR: δ 43.7 (PPh_2H, d, $J(^{31}P\text{-}^1H) = 360$ Hz), −102.9 (μ-PPh_2, s).

Preparation of $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2$ (2). Complex **1** (1.5 g) was heated under Ar in boiling cyclohexane (40 mL) until all the red complex **1** had disappeared (~1 h) and was transformed into **2**. The black crystalline product (**2**) that precipitated was removed by filtration and dried in vacuo. Anal. Calcd for $C_{50}H_{42}Co_2P_4$: C, 65.50; H, 4.58; Co, 12.88; P, 13.53. Found: C, 62.7; H, 4.8; Co, 12.9; P, 13.5. IR ν(CO) (CH_2Cl_2): 1917.5 cm^{-1}. ^{31}P NMR: δ 182.7 (μ-PPh_2, s), 33.8 (PPh_2H, d, $J(^{31}P\text{-}^1H) = 332$ Hz).

Preparation of 3. $CoCl_2{\cdot}6H_2O$ (2.38 g, 10 mmol) was dissolved under Ar in methanol (25 mL), and PPh_2H (0.37 mL, 20 mmol) in methanol solution (25 mL) was added with stirring. A green precipitate formed that was filtered off after 3 h, washed with diethyl ether, and dried; yield 4.2 g (68%). The product (**3**) was recrystallized from acetone: mp 123–126 °C; absorption maxima in acetone 14 900 and 17 500 cm^{-1}. The product is a nonelectrolyte in acetone, and its magnetic moment is 3.16 μ_B (calculated as $CoCl_2(PPh_2H)_2$).

Preparation of 4. The product **3** from the above reaction (200 mg) was dissolved in methanol (10 mL) and stirred under CO for 2 h. During this time a strong band appeared in the IR spectrum at 1931 cm^{-1} accompanied by two much weaker bands at 1964 and 2018 cm^{-1} (beginning of the formation of **5**). The reaction mixture was evaporated to dryness and the resulting green powder recrystallized from acetone. The large, dark green to wine red crystals show only one ν(CO) band at 1931 cm^{-1} (in methanol): mp 103–105 °C; absorption maxima in acetone 14 630 and 16 900 cm^{-1}. The product is a nonelectrolyte in acetone, and its magnetic moment is 3.26 μ_B (calculated as $CoCl_2(CO)(PPh_2H)_2$).

Formation of 5. Substance **3** (200 mg) was dissolved in methanol (10 mL) and reacted with 100 bar of CO at room temperature for 12 h. The resulting solution is reddish brown and shows two strong ν(CO) bands at 1964 and 2018 cm^{-1}. When the solvent was evaporated in vacuo, a green oil was obtained that could not be crystallized. UV–vis absorption maxima in acetone are at 14 500 and 16 900 cm^{-1}. When the reaction was conducted in $(CH_3)_2CHOH$ solution under 100 bar of CO pressure

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† The Pennsylvania State University.

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Table I. Crystallographic Data for the Structure Determination of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2CH_3CN$ (**1**)

	Crystal Data		
mol formula	$C_{56}H_{48}Co_2O_4P_4N_2$	V, Å^3	5367 (7)
space group	$P2_1/c$	Z	4
a, Å	11.742 (6)	δ(calcd), g cm^{-3}	1.345
b, Å	21.037 (6)	δ(measd), g cm^{-3}	1.356
c, Å	21.732 (10)	temp, °C	21
β, deg	91.16 (4)	cryst dimens, mm	0.27 × 0.42 × 0.95
abs coeff (not cor), cm^{-1}	7.82		
	Intensity Data		
diffractometer	Enraf-Nonius CAD4	no. of total data	6994
radiation	Mo Kα (λ = 0.71073 Å)	no. of unique data	6620
monochromator	graphite cryst	no. of obsd data, $I < 2\sigma(I)$	3789
scan technique	θ–2θ	no. of std rflcns, h^{-1}	3
scan speed, deg/min	1.0–5.0	drift cor: empirical; anisotropic	0.968–1.000; 0.805–1.033
scan width, deg	1.35 + 0.347 tan θ	R_1	0.084
data collcd	$+h,+k,\pm l$	R_2	0.096
2θ limits	$3.2 < 2\theta < 44.12$	GOF	6.094

Table II. Atomic Positional Parameters for $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2$ (**1**)

	x	y	z		x	y	z
Co1	0.8054 (2)	0.2945 (1)	0.0361 (1)	C34	0.983 (2)	0.067 (1)	0.163 (1)
Co2	0.6770 (2)	0.2957 (1)	0.1794 (1)	C35	0.867 (2)	0.080 (1)	0.167 (1)
P1	0.9807 (4)	0.2912 (3)	0.0043 (2)	C36	0.825 (2)	0.143 (1)	0.163 (1)
P2	0.8467 (4)	0.2725 (2)	0.1374 (2)	C41	0.530 (1)	0.330 (1)	0.039 (1)
P3	0.6332 (4)	0.2783 (2)	0.0785 (2)	C42	0.478 (2)	0.310 (1)	−0.020 (1)
P4	0.5013 (4)	0.2944 (3)	0.2108 (2)	C43	0.406 (2)	0.355 (2)	−0.049 (1)
O1A	0.725 (1)	0.225 (1)	0.073 (1)	C44	0.379 (2)	0.413 (2)	−0.028 (2)
O1B	0.774 (1)	0.432 (1)	0.025 (1)	C45	0.430 (2)	0.434 (1)	0.032 (2)
O2A	0.753 (1)	0.227 (1)	0.288 (1)	C46	0.503 (2)	0.389 (1)	0.064 (1)
O2B	0.720 (1)	0.432 (1)	0.188 (1)	C51	0.569 (1)	0.200 (1)	0.064 (1)
C1A	0.759 (1)	0.251 (1)	0.027 (1)	C52	0.451 (1)	0.193 (1)	0.072 (1)
C1B	0.790 (1)	0.379 (1)	0.031 (1)	C53	0.403 (2)	0.132 (1)	0.065 (1)
C2A	0.721 (1)	0.253 (1)	0.246 (1)	C54	0.467 (2)	0.079 (1)	0.054 (1)
C2B	0.702 (2)	0.379 (1)	0.186 (1)	C55	0.583 (2)	0.087 (1)	0.047 (1)
C1	1.009 (1)	0.346 (1)	−0.060 (1)	C56	0.635 (2)	0.146 (2)	0.056 (1)
C2	1.064 (2)	0.403 (1)	−0.052 (1)	C61	0.477 (1)	0.345 (1)	0.279 (1)
C3	1.078 (2)	0.443 (1)	−0.102 (1)	C62	0.432 (2)	0.404 (1)	0.270 (1)
C4	1.035 (2)	0.429 (1)	−0.161 (1)	C63	0.421 (2)	0.445 (1)	0.324 (1)
C5	0.980 (2)	0.373 (1)	−0.170 (1)	C64	0.457 (2)	0.423 (1)	0.382 (1)
C6	0.967 (2)	0.328 (1)	−0.120 (1)	C65	0.500 (2)	0.361 (1)	0.389 (1)
C11	1.044 (2)	0.216 (1)	−0.019 (1)	C66	0.513 (1)	0.323 (1)	0.337 (1)
C12	1.154 (2)	0.218 (1)	−0.047 (1)	C71	0.431 (1)	0.220 (1)	0.232 (1)
C13	1.205 (2)	0.163 (2)	−0.062 (1)	C72	0.487 (2)	0.163 (1)	0.225 (1)
C14	1.153 (2)	0.104 (2)	−0.053 (1)	C73	0.430 (2)	0.107 (1)	0.241 (1)
C15	1.048 (2)	0.103 (1)	−0.029 (1)	C74	0.320 (2)	0.109 (1)	0.267 (1)
C16	0.993 (2)	0.158 (1)	−0.011 (1)	C75	0.267 (2)	0.165 (1)	0.270 (1)
C21	0.956 (1)	0.320 (1)	0.179 (1)	C76	0.318 (2)	0.226 (1)	0.256 (1)
C22	0.998 (2)	0.296 (1)	0.237 (1)	N1	0.781 (2)	0.475 (1)	0.439 (1)
C23	1.075 (2)	0.337 (1)	0.271 (1)	N2	0.705 (3)	0.027 (2)	0.293 (2)
C24	1.109 (2)	0.394 (1)	0.244 (1)	C1N	0.779 (2)	0.449 (1)	0.388 (2)
C25	1.070 (2)	0.416 (1)	0.187 (1)	C2N	0.685 (3)	0.060 (2)	0.337 (2)
C26	0.992 (2)	0.379 (1)	0.155 (1)	C1M	0.804 (3)	0.404 (2)	0.341 (2)
C31	0.898 (1)	0.192 (1)	0.150 (1)	C2M	0.665 (3)	0.107 (2)	0.378 (2)
C32	1.016 (2)	0.178 (1)	0.145 (1)	H1	1.09 (1)	0.33 (1)	0.05 (1)
C33	1.056 (2)	0.114 (1)	0.148 (1)	H2	0.43 (1)	0.32 (1)	0.17 (1)

for 12 h, the formation of acetone (0.16 mmol, 82% of theoretical) was identified by GLC.

Transformation of 5 into 1 and 2. A solution of **5** was prepared from **3** (200 mg, 0.39 mmol) in methanol (10 mL) under CO as described above (24 h). The solvent was removed in vacuo and the residue dissolved in methanol (3 mL) containing Et_3N (0.2 mL). After the mixture was stirred under Ar for 24 h, a brown precipitate formed that was filtered off and dissolved in dichloromethane. The strong ν(CO) band at 1918 cm^{-1} in the IR spectrum of this precipitate showed that it consisted mainly of **2**, but low-intensity peaks (2042, 1986, 1965, and 1925 cm^{-1}) also suggested the presence of **1**. When this solution was placed under a CO atmosphere and stirred for 1 h, **2** was almost completely transformed into **1**, as shown by the intensity changes of the IR absorption bands.

Crystal Structure of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2MeCN$ (1). A crystal of **1** obtained as described above was oriented along its longest axis in a 0.5-mm capillary that was in turn mounted in a random orientation on an Enraf-Nonius CAD-4 automated diffractometer. It was optically centered, and 25 centering reflections were located and used to determine the orientation matrix. A summary of the important crystallographic data is presented in Table I. The drift corrections, derived from variations in the standards, are shown in the table and were used to allow for slight crystal motion or temperature changes during data collection. Symmetry-related data collected were removed by averaging (mean discrepancy 0.091). Details of the data collection and reduction as well as the computer programs used have been previously described.[5a] In this case the structure was solved by using the standard SDP programs,[5b] but the final refinement was accomplished on an IBM 3081 computer using the X-RAY 67 program package.[5c]

The Co and P atoms were located by Patterson heavy-atom techniques. Subsequent cycles of least-squares refinement and difference Fourier syntheses yielded the positions of the two phosphine hydrogen atoms. The remaining hydrogen atoms were not included in the structure refinement. Two acetonitrile molecules of crystallization were found per

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(5) (a) Horrocks, W. D., Jr.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* **1982**, *21*, 3265. (b) "Enraf Nonius Structure Determination Package"; Enraf-Nonius: Delft, The Netherlands, 1975. (c) Stuart, J. "X-RAY 67"; University of Maryland: College Park, MD, 1967.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2CH_3CN$ (1)

	Bond Lengths		
Co1-P1	2.185 (5)	Co2-P2	2.261 (5)
Co1-P2	2.290 (5)	Co2-P3	2.272 (5)
Co1-P3	2.264 (5)	Co2-P4	2.186 (5)
Co1-C1A	1.73 (2)	Co2-C2A	1.77 (2)
Co1-C1B	1.78 (3)	Co2-C2B	1.77 (2)
P1-H1	1.79 (14)	P4-H2	1.45 (14)
Co···Co	3.486 (3)		
	Bond Angles		
P1-Co1-P2	96.7 (2)	P4-Co2-P3	95.9 (2)
P1-Co1-P3	168.1 (2)	P4-Co2-P2	165.5 (2)
P2-Co1-P3	75.7 (2)	P2-Co2-P3	76.1 (2)
P1-Co1-C1A	91.1 (6)	P4-Co2-C2A	89.0 (6)
P1-Co1-C1B	96.3 (6)	P4-Co2-C2B	98.4 (6)
P2-Co1-C1A	135.6 (7)	P2-Co2-C2A	88.7 (6)
P2-Co1-C1B	106.2 (6)	P2-Co2-C2B	95.4 (6)
P3-Co1-C1A	88.3 (6)	P3-Co2-C2A	95.9 (2)
P3-Co1-C1B	94.6 (6)	P3-Co2-C2B	139.8 (8)
C1A-Co1-C1B	116.4 (9)	C2A-Co2-C2B	113 (1)
Co1-P2-Co2	99.9 (2)	Co1-P3-Co2	100.4 (2)

molecule of **1**. In the final cycle of full-matrix least squares, all nonhydrogen atom positional and anisotropic parameters, the phosphine hydrogen positional parameters (fixed at $B = 5.0$ Å^2), and the positional and isotropic thermal parameters of the acetonitrile molecules were refined to give final residuals of $R_1 = 0.084$ and $R_2 = 0.096$ by using a unit-weighting scheme. The relatively large residuals are apparently due to the low parameter/data ratio of 6.4 used in the least-squares refinement. In the final cycle, the average shift/error was less than 0.070. A final electron density map was essentially featureless with the largest peak (0.6 e Å^{-3}) located near Co1. Final positional parameters are listed in Table II. Tables of thermal parameters and structure factors are given in the supplementary material.

Results and Discussion

Synthesis and Spectroscopic Characterization of 1 and 2. Complex **1** results in good yield from the combination of reagents given in eq 2. Preparative, infrared, and GLC data show that reaction 2 proceeds via reduction of Co(II) (by methanol or phosphine) accompanied by the stepwise coordination of CO and elimination of HCl under the influence of a base. The reaction is complex and appears to involve several competing pathways with eq 4–7 representing the overall process. $CoCl_2$ reacts with

$$\mathrm{CoCl_2} \xrightarrow[\text{MeOH or acetone}]{\mathrm{PPh_2H}} \underbrace{\mathrm{CoCl_2(PPh_2H)_2} + \mathrm{CoCl(PPh_2H)_3}}_{\mathbf{3}} \tag{4}$$

$$\mathbf{3} + \mathrm{CO} \xrightarrow{\mathrm{MeOH}} \underbrace{\mathrm{CoCl_2(CO)(PPh_2H)_2} + \mathrm{CoCl(CO)(PPh_2H)_3}}_{\mathbf{4}} \tag{5}$$

$$\mathbf{4} + \mathrm{CO} \xrightarrow{\mathrm{MeOH}} \underset{\mathbf{5}}{\mathrm{CoCl(CO)_2(PPh_2H)_2}} \tag{6}$$

$$\mathbf{5} \xrightarrow{\mathrm{NaOMe}} \underset{\mathbf{2}}{\mathrm{Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2}} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} \underset{\mathbf{1}}{\mathrm{Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2}} \tag{7}$$

diphenylphosphine in methanol or acetone as solvent to give a green precipitate (**3**) that can be recrystallized from acetone. Its elemental composition varies from preparation to preparation with Co:P:Cl ratios between 1:2.06:1.86 and 1:2.46:1.52, suggesting it to be a mixture of $CoCl_2(PPh_2H)_2$ and $CoCl(PPh_2H)_3$.[6] Its magnetic moment (3.16 μ_B) is also consistent with this formulation. Starting from $CoBr_2$, Issleib obtained under similar conditions three different cobalt–diphenylphosphine complexes.[7]

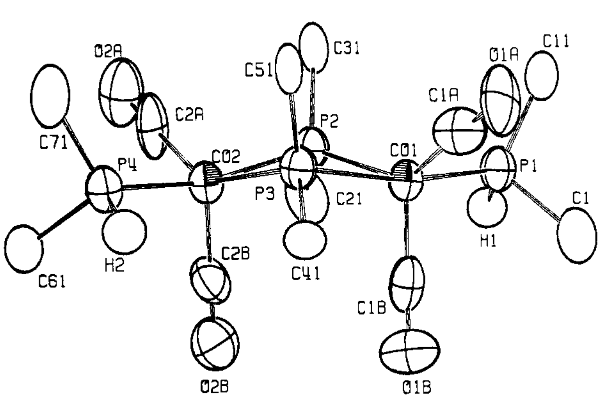

Figure 1. ORTEP drawing of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level, and only the phenyl carbons attached to phosphorus are drawn for clarity.

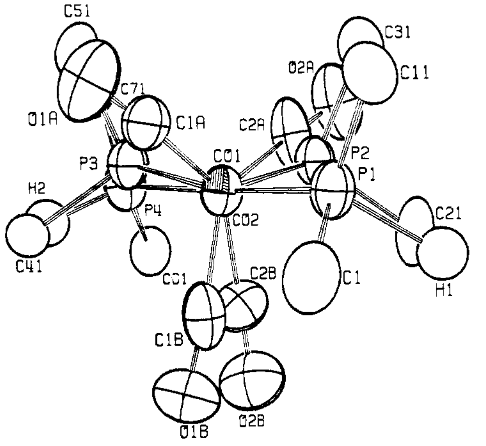

Figure 2. ORTEP view of **1** down the Co–Co axis.

Mixture **3** reacts in methanol solution with CO at atmospheric pressure, and a broad and strong ν(CO) band appears at 1931 cm^{-1}. The product formed can be isolated as a green powder that can be recrystallized from acetone. Again elemental analysis indicates a mixture of products with the Co:P:Cl atomic ratios varying around $CoCl_2(CO)(PPh_2H)_2$ and $CoCl(CO)(PPh_2H)_3$, and its magnetic moment (3.26 μ_B) is in accordance with this. The formation of $CoX_2(CO)(PR_3)_2$ adducts from $CoX_2(PR_3)_2$ complexes is well documented,[8,9] and the reaction of CO with $CoX(PR_3)_3$ complexes has been found to give the dicarbonyls $CoX(CO)_2(PR_3)_2$[6] (X = halide). The latter complexes are probably the final products with CO in our case, but apparently the coordination of the second CO by substitution of a diphenylphosphine ligand is a slow process (see below).

If the reaction of **3** with CO is carried out under pressure and for longer times, **5** is formed, as shown by the appearance of two ν(CO) bands at 1964 and 2018 cm^{-1}. This process is accompanied by the reduction of all cobalt to Co(I). Similar reduction of $CoX_2(CO)(PR_3)_2$ to $CoX(CO)_2(PR_3)_2$ complexes has been observed earlier.[9,10] The reductant is probably methanol, which may be transformed into formaldehyde. It is difficult to prove the formation of formaldehyde, but its role is supported by the observation that if the reaction between **3** and CO is carried out in isopropyl alcohol as solvent,[11] acetone is formed along with **5** (GLC evidence). Finally, the last step is the elimination of HCl from **5** under the influence of a base (NaOMe in the original preparation; Et_3N in the model experiment) to give an equilibrium mixture of complexes **1** and **2** from which, under CO and in MeCN as solvent, complex **1** crystallizes as red crystals with the

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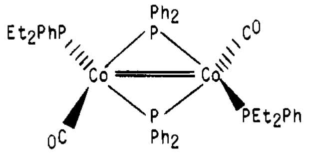
composition $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2MeCN$.

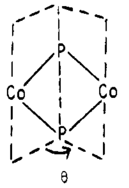
The molecular structure of **1** has been determined by X-ray crystallography and is shown in Figure 1. The spectroscopic data are consistent with this structure. In particular, its $^{31}P\{^1H\}$ NMR spectrum shows an upfield resonance at δ −102.9 s due to the μ-PPh_2 ligands and a PPh_2H resonance at δ 43.7 d. The latter shows a 360-Hz ^{31}P–^1H coupling in the ^1H-coupled ^{31}P NMR spectrum. The upfield position of the μ-PPh_2 resonance is consistent with the absence of a metal–metal bond in **1**.[2,12]

Upon being heated, complex **1** loses CO and forms $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2$ (**2**) in quantitative yield. This reaction is more conveniently carried out in refluxing cyclohexane since **2** is insoluble in this solvent and precipitates as it forms. Spectroscopic data imply that **2** is isostructural with $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$ (**6**)[13] and $Co_2(\mu\text{-}P\text{-}t\text{-}Bu_2)_2(L)_2(PMe_3)_2$ (L = CO, N_2),[14] whose structures have recently been established by X-ray diffraction studies. The latter showed short (2.343 (2) Å for **6**) Co–Co separations, consistent with the presence of metal–metal double bonds as required by the 18-electron rule, and a distorted tetrahedral geometry at each metal. The IR spectra of **2** and **6** are similar, with each showing a single ν(CO) stretch (**2**, 1917.5 vs cm^{-1}; **6**, 1905 vs cm^{-1}). The $^{31}P\{^1H\}$ NMR spectra are also similar, showing downfield resonances due to the μ-PPh_2 ligands (**2**, δ 182.7 s; **6**, δ 175.8 s). In **2**, the PPh_2H ligand appears as a doublet in the proton-coupled spectrum at δ 33.8 with J(P–H) = 332 Hz.



6

Crystal and Molecular Structure of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2CH_3CN$ (1). An ORTEP drawing showing the atom-numbering scheme is given in Figure 1. The Co atoms are bridged by the two μ-PPh_2 ligands, and each Co is further coordinated by two CO's and a PPh_2H ligand. Figure 2 shows a different view of the molecule down the Co–Co axis, which illustrates the slightly bent character of the $Co_2(\mu\text{-}P)_2$ core and the near-eclipsed arrangement of the terminal ligands. The dihedral angle (θ) between the P2–Co1–P3 and P2–Co2–P3 planes is 153.3°.



The two PPh_2H ligands lie on opposite sides of the molecule, an arrangement that minimizes steric interaction between these bulky ligands. The PPh_2H hydrogen atoms were located and refined; their positions are indicated in Figures 1 and 2.

The overall geometry of complex **1** is very similar to that of the bent form of $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ (**7**), from which it formally derives by substitution of two CO's by the PPh_2H ligands. In the bent form of complex **7**, the corresponding P1–Co1–P2/P1–Co2–P2 dihedral angle is 155.0° and the terminal ligands are also nearly eclipsed. Both complex **1** and the bent form of **7** can be viewed as comprised of two edge-shared CoL_5 square pyramids, as clearly illustrated in Figure 1.

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Registry No. **1**, 98541-18-5; **2**, 98541-19-6; **5**, 98541-22-1; $CoCl_2(PPh_2H)_2$, 98541-20-9; $CoCl_2(CO)(PPh_2H)_2$, 98541-21-0.

Supplementary Material Available: Tables of thermal parameters and structure factors (18 pages). Ordering information is given on any current masthead page.

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Improved Synthesis of 2,2,2-$(CO)_3$-2-MnB_5H_{10} via Heterogeneous Catalysis. Synthesis and Characterization of the New Rhenahexaborane 2,2,2-$(CO)_3$-2-ReB_5H_{10}

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An improved synthesis of the *nido*-manganahexaborane 2,2,2-$(CO)_3$-2-MnB_5H_{10} has been developed that utilizes H_2 pressures of ca. 100 atm and certain heterogeneous catalysts. Yields up to 41% have been obtained by using 5% Ru/C as catalyst. The new rhenahexaborane 2,2,2-$(CO)_3$-2-ReB_5H_{10} has been obtained in a similar manner and has been characterized spectroscopically. Possible mechanisms of formation of these metallaboranes in the catalyzed and uncatalyzed reactions are discussed.

Introduction

Metallaborane chemistry has rapidly become one of the most interesting and diverse areas of boron hydride research.[1] Our studies in this area have centered primarily on manganese–borane clusters (manganaboranes) and have yielded a variety of structural types.[2-7] Structural analogues of several of these clusters containing different metals are known, while others are thus far unique.

Many examples of metallahexaborane (MB_5) clusters are known, several of which exhibit the pentagonal-pyramidal

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