Heteronuclear Cluster Systems. Part 13.† Synthesis of μ-Diphenyl-phosphido-bridged Carbonylmetal Complexes, and Crystal Structure of 1,2-μ-Carbonyl-1,1,2,2,3,3-hexacarbonyl-1,3;2,3-bis-μ-diphenylphosphido-*triangulo*-tricobalt

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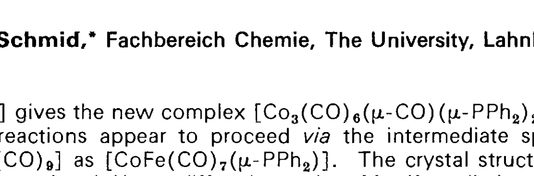
Reaction of PPh_2Cl with $Li[Co_3(CO)_{10}]$ or $[Co_2(CO)_8]$ gives the new complex $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ and the known complex $[\{Co(CO)_3(\mu\text{-}PPh_2)\}_2]$. Both reactions appear to proceed *via* the intermediate species $[Co(CO)_4(PPh_2)]$ which may be trapped using $[Fe_2(CO)_9]$ as $[CoFe(CO)_7(\mu\text{-}PPh_2)]$. The crystal structure of the title complex has been determined by three-dimensional *X*-ray diffraction using Mo-K_α radiation: a = 19.271(16), b = 11.870(3), c = 13.512(8) Å, β = 99.36°, Z = 4, space group $P2_1/a$, R = 0.069 7. The three cobalt atoms form an isosceles triangle, two sides of which are bridged by PPh_2 groups (one symmetrically, the other asymmetrically) and the third side also unequally by a carbonyl group.

THE preparation of the complex $[\{Co(CO)_3(PPh_2)\}_2]$, which is believed to contain doubly bridging diphenylphosphide groups, has been reported by several independent research groups [1-3]. One synthetic method is the reaction of P_2Ph_4 with $[Co_2(CO)_8]$. The parallel reaction of P_2Me_4 with $[Co_2(CO)_8]$, however, gives only a cluster complex formulated as $[Co_3(CO)_7(PMe_2)_2]$ whose structure has never been determined. Two suggestions were made, (A) and (B). In (A) the phosphorus groups bridge two cobalt atoms as in $[\{Co(CO)_3(\mu\text{-}PPh_2)\}_2]$; in (B) they are triply bridging, and the phosphorus atoms adopt a co-ordination number of five.



(A) (B)

Phosphorus bridging three cobalt atoms has previously been encountered for example in the cluster complexes

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† Part 12 is ref. 12.

[1] R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 823.
[2] W. Hieber and H. Duchatsch, *Z. Naturforsch.*, 1963, **B18**, 1132.
[3] W. Schweckendick, G.P., 1 072 244/1959.
[4] A. Vizi-Orosz, *J. Organometallic Chem.*, 1976, **111**, 61.

$[Co_3(CO)_9P]$ [4] and $[Co_3(CO)_9(PR)]$.[5] The structures of these complexes are believed to be based on a tetrahedral framework of Co_3P. An *X*-ray crystallographic investigation [6] of the structure of the analogous complex $[Co_3(CO)_9S]$ has indeed shown this tetrahedral arrangement to be present.

We now report the preparation of $[Co_3(CO)_6(\mu\text{-}CO)(PPh_2)_2]$ and the determination of its structure by *X*-ray diffraction. In addition, related studies on carbonylcobalt–chlorodiphenylphosphine systems are presented.

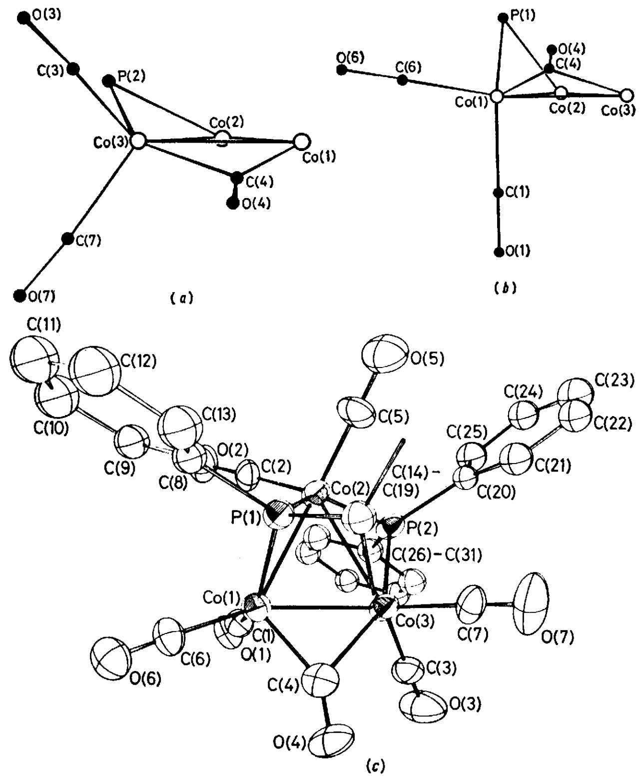
RESULTS AND DISCUSSION

The reaction of $[Co_2(CO)_8]$ with PPh_2Cl yields as major product the orange crystalline complex $[\{Co(CO)_3(\mu\text{-}PPh_2)\}_2]$ (1), thus providing an alternative route to this complex. The i.r. spectrum, which correlates well with that reported by Hayter,[1] and the elemental analysis support this formulation. The ^{31}P n.m.r. spectrum in benzene shows a singlet 61.7 p.p.m. downfield from H_3PO_4. This indicates a small increase in electron density on the phosphorus atom relative to PPh_2Cl (80.5 p.p.m.).[7]

The dark green-black crystalline cluster complex $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ (2) is also produced in the reaction of $[Co_2(CO)_8]$ with PPh_2Cl. The complex is moderately stable in air in the solid state. Its i.r. spectrum shows a very complex pattern in the carbonyl-stretching region indicating a general lack of symmetry in the molecule. The presence of at least one bridging carbonyl group is indicated by a band at 1 856 cm^{-1}.

An *X*-ray crystallographic analysis shows the structure of (2) to be based on an isosceles triangle of cobalt atoms each of which bears two terminal carbonyl ligands. Diphenylphosphide groups bridge the two longer sides of the triangle and a carbonyl group the third side. It is interesting to note that the environments of Co(1) and Co(3) are very different. As may be seen from Figures (*a*) and (*b*), Co(1) has an approximately octahedral arrangement of ligands, whereas Co(3) may be considered to have a pentagonal-pyramidal environment. This difference is also shown by comparison of the bridging ligands. The P(2) bridge is rather asymmetric, whereas P(1) symmetrically bridges Co(1) and Co(2). The bridging carbonyl ligand is also markedly asymmetric, being located nearer to Co(1). The analysis further reveals the presence of two peaks of electron density in the apparent gap in the base of the pyramid round Co(3). This electron density is evidently the cause of the very different environments of Co(1) and Co(3). The structure could not be refined further, so that it cannot be determined whether a hydrogen atom occupies this position.

Attempts to locate a metal hydride in the n.m.r. spectrum were inconclusive, despite phosphorus-decoupling and Fourier-transform techniques, due to the low solubility of (2). However, a very weak broad signal was detected at *ca.* 18—19 p.p.m. which may be attributed to such a proton. The analogous complex $[Co_3(CO)_7(PMe_2)_2]$ probably has the same structure as (2), although this has not been determined.[1] Also, although the previous molecule was shown to be diamagnetic, no conclusions were drawn as to whether it contained a cobalt–hydride bond, since no evidence for the hydride was



Environments of (*a*) Co(1) and (*b*) Co(3) in $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ (2). (*c*) Molecular structure of (2). One phenyl group of P(1) is omitted for clarity

found in the ^1H n.m.r. spectrum. As Hayter indicated,[1] such a signal may be overlooked due to coupling to phosphorus.

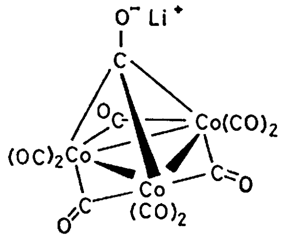
The reaction of PPh_2Cl with the salt $Li[Co_3(CO)_{10}]$ whose proposed [8] structure is shown in (C), was also studied. The same two products (1) and (2) were again found. In contrast, the reaction of the complex ion with $SiMe_3Cl$,[9] $NMe_3{\cdot}BH_2I$,[9] $[Ti(cp)_2Cl_2]$[10] (cp = $\eta\text{-}C_5H_5$), or MeCOBr [11] results in attack at the oxygen atom of the $\geqslant C\text{-}O^-$ group with retention of the Co_3C cluster framework and formation of the complexes $[Co_3(CO)_9(COR)]$ [R = $SiMe_3$, $BH_2(NMe_3)$, $Ti(cp)_2Cl$, or C(O)Me]. The

$$[Co_3(CO)_{10}]^- \xrightleftharpoons{\text{solvent}} [Co(CO)_4]^- + [Co_2(CO)_6L_n] \quad (1)$$

reaction reported here suggests that in toluene $[Co_3(CO)_{10}]^-$ dissociates in an equilibrium reaction (1) (L =

[5] L. Marko and B. Markó, *Inorg. Chim. Acta*, 1975, **14**, L39.
[6] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.
[7] K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307.
[8] S. A. Fieldhouse, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *Chem. Comm.*, 1970, 181.
[9] C. D. M. Mann, A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *J. Organometallic Chem.*, 1970, **24**, C61.
[10] G. Schmid, V. Bätzel, and B. Stutte, *J. Organometallic Chem.*, 1976, **113**, 67.
[11] V. Bätzel and G. Schmid, *Chem. Ber.*, 1976, **109**, 3339.

solvent) to the reactive $[Co(CO)_4]^-$ and solvent-stabilised $[Co_2(CO)_6]$.



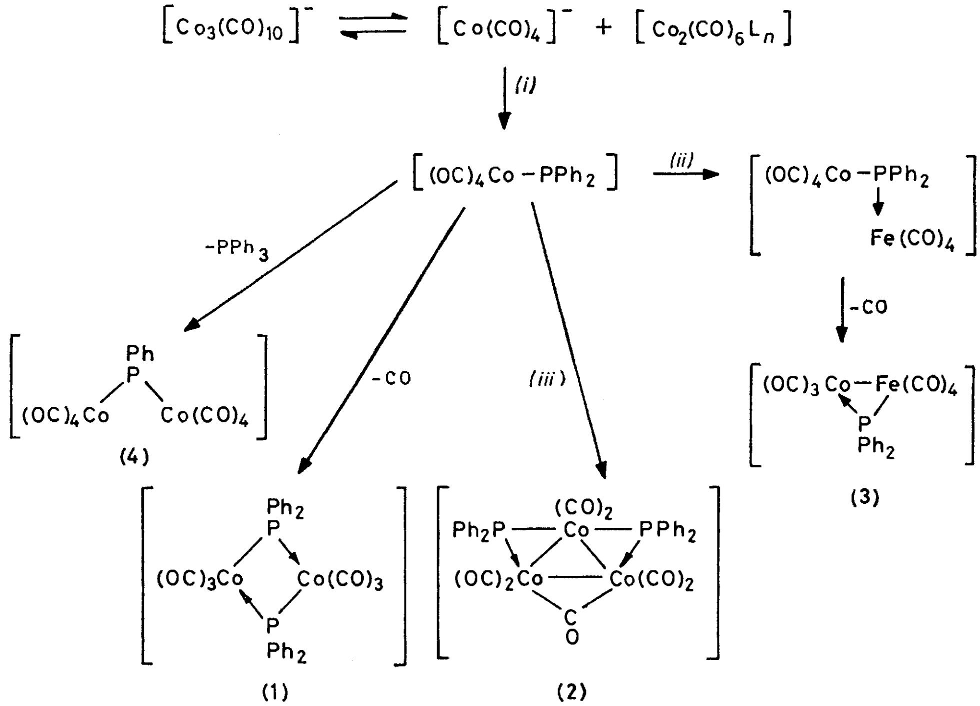
(C)

Assuming that $[Co(CO)_4]^-$ ions are the reactive species in toluene solutions of $Li[Co_3(CO)_{10}]$, then the initial product in the reaction with PPh_2Cl is probably $[Co(CO)_4(PPh_2)]$. The nucleophilic character of the phosphorus atom in this complex then causes room-temperture dimerisation accompanied by displacement of carbon monoxide. If PPh_2Cl is added to a solution of $Li[Co_3(CO)_{10}]$ at <-25 °C no appreciable gas evolution occurs, although reaction proceeds, and it appears that the species $[Co(CO)_4(PPh_2)]$ may be stable at low temperatures. In fact at -50 °C a small amount of red solid believed to be $[Co(CO)_4(PPh_2)]$ may be isolated, but rapid decomposition occurs at >-25 °C even in an inert atmosphere.

The complex $[CoFe(CO)_7(\mu\text{-}PPh_2)]$ (3) was prepared by treatment of $[Fe_2(CO)_9]$ with a toluene solution of $Li[Co_3(CO)_{10}]$ and PPh_2Cl at -78 °C. The yield obtained by adding $[Fe_2(CO)_9]$ to a reaction mixture of $Na[Co(CO)_4]$ and PPh_2Cl at -78 °C is considerably higher than from $Li[Co_3(CO)_{10}]$. This is further evidence that $[Co(CO)_4]^-$ anions are the reactive species in solutions of $Li[Co_3(CO)_{10}]$.

The i.r. spectrum of (3) exhibits absorptions for terminal carbonyl groups but none in the bridging-carbonyl region. The mass spectrum shows a parent ion at *m/e* **496**, and peaks corresponding to stepwise loss of seven carbonyl groups. A field-desorption mass spectrum also gave the molecular ion as *m/e* **496**, and so confirmed the presence of only seven and not the expected eight carbonyl groups. After total decarbonylation the $[CoFe(PPh_2)]^+$ ion appears to fragment further to $[CoFeP]^+$. Loss of the phosphorus atom completes the decomposition. Alternative fragmentation patterns for (3) are also in evidence and the ions $[Co(PPh_2)]^+$, $[Fe(CO)_4]^+$, and Fe^+ may be identified.

On the basis of the mass and i.r. spectra and microanalysis a structure for (3) is proposed in which the diphenylphosphide ligand acts formally as a three-electron donor, bridging the two metal atoms. The cobalt atom bears three carbonyl groups and the iron four. A metal–metal bond is necessary to satisfy the electronic requirements of the two metals.



SCHEME (*i*) PPh_2Cl; (*ii*) $[Fe_2(CO)_9]$; (*iii*) $[Co_2(CO)_6L_n]$ or $[Co_2(CO)_8]$

Varying yields of a third product may also be isolated from the reaction of PPh_2Cl with $Li[Co_3(CO)_{10}]$. The i.r. spectrum [12] and elemental analysis surprisingly indicate the molecular formula $[\{Co(CO)_4\}_2PPh]$ (4). The possibility that this product is formed from an impurity of $PPhCl_2$ in the PPh_2Cl is unlikely since reaction solutions from which (4) may be isolated at lower temperatures yield only (1) at room temperature. A mechanism for the reaction may be suggested (see Scheme) in which the

[12] J. C. Burt and G. Schmid, preceding paper.

proposed intermediate $[Co(CO)_4(PPh_2)]$ follows an alternative mode of decomposition eliminating PPh_3.

EXPERIMENTAL

Microanalyses were either by the central analytical division of the Department of Chemistry, Philipps-Universität, Marburg, or by the A. Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer and calibrated using polystyrene. The Fourier-transform ^{31}P n.m.r. spectrum was obtained on a Varian XL 100 spectrometer, using H_3PO_4 as external standard, the mass spectrum of (3) on a Varian CH7 machine.

All the operations were carried out under an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen by distilling over potassium (toluene), $Li[AlH_4]$ (diethyl ether or light petroleum), or sodium diphenylketyl (tetrahydrofuran). The samples of PPh_2Cl, $[Co_2(CO)_8]$, and $[Fe_2(CO)_9]$ were obtained commercially. The salts $Na[Co(CO)_4]$ [13] and $Li[(Co_3(CO)_{10}]$ [8] were prepared according to literature methods.

Reactions.—$[Co_2(CO)_8]$ *with* PPh_2Cl. A toluene solution (10 cm^3) of PPh_2Cl (0.6 cm^3, 710 mg, 3.23 mmol) was added dropwise to a stirred toluene solution (40 cm^3) of $[Co_2(CO)_8]$ (1.0 g, 2.92 mmol) at room temperature. Slow evolution of carbon monoxide immediately commenced. After stirring for 18 h the orange-red reaction mixture was filtered. Light petroleum (20 cm^3) was added to the filtrate, precipitating a solid which was recrystallised from toluene–light petroleum and identified as $[\{Co(CO)_3(\mu\text{-}PPh_2)\}_2]$ (1), 410 mg (21%), m.p. 148—150 °C (Found: C, 54.6; H, 3.20; Co, 18.05. Calc. for $C_{30}H_{20}Co_2O_6P_2$: C, 54.9; H, 3.05; Co, 18.0%); ν(CO) at 2 045w, 1 995vs, and 1 968 (sh) cm^{-1} in Nujol mull.

The remaining toluene–light petroleum solution was reduced in volume to 5 cm^3 and another 15 cm^3 of light petroleum were added. After standing overnight at 0 °C, green-black crystals of 1,2-*μ-carbonyl*-1,1,2,2,3,3-*hexacarbonyl*-1,3;2,3-*bis-μ-diphenylphosphido*-triangulo-*tricobalt* (2) formed, 60 mg (4%), m.p. 160—162 °C (Found: C, 50.25; H, 2.70. Calc. for $C_{31}H_{20}Co_3O_7P_2$: C, 50.05; H, 2.70%); ν(CO) at 2 060m, 2 034m, 1 995 (sh), 1 983vs, 1 977vs, 1 962s, 1 852s, and 1 815w cm^{-1} in Nujol mull.

$Li[Co_3(CO)_{10}]$ *with* PPh_2Cl. A toluene solution (10 cm^3) of PPh_2Cl (0.5 cm^3, 600 mg, 2.73 mmol) was added dropwise to a stirred toluene solution (40 cm^3) of $Li[Co_3(CO)_{10}]$ {prepared from $[Co_2(CO)_8]$; 1.0 g, 2.92 mmol}, at 0 °C. After stirring for 15 min at 0 °C, the evolution of carbon monoxide ceased. The red-brown reaction mixture was allowed to rewarm to room temperature and was filtered. Addition of light petroleum (25 cm^3) to the filtrate precipitated an orange solid which was recrystallised from toluene–light petroleum to give (1) (100 mg, 5%). The remaining solution was reduced in volume to 20 cm^3, cooled to 0 °C, and light petroleum (20 cm^3) added. Green-black crystalline (2) precipitated slowly overnight, 30 mg (2%) (Found: C, 49.8; H, 2.75%).

Preparation of μ-Diphenylphosphido-tricarbonylcobalt tetracarbonyliron (Co–Fe) (3).—(*a*) A toluene solution (10 cm^3) of PPh_2Cl (0.5 cm^3, 600 mg, 2.73 mmol) was added dropwise to a toluene suspension (40 cm^3) of $Li[Co_3(CO)_{10}]$ {prepared from $[Co_2(CO)_8]$; 1.0 g, 2.92 mmol} at −78 °C. Tetrahydrofuran (10 cm^3) and $[Fe_2(CO)_9]$ (500 mg, 1.37 mmol) were then added and stirring continued for 1 h. The mixture was allowed to warm slowly to room temperature, and was then filtered. Solvent was removed from the filtrate, and the residue pumped *in vacuo* for 30 min to remove $[Fe(CO)_5]$ formed during the reaction. A light petroleum extract (30 cm^3) of the residue was then chromatographed on silica gel. The first band eluted with light petroleum was evaporated to give a dark red solid. This was recrystallised from light petroleum to give (3), 20 mg (1%), m.p. 78—80 °C (Found: C, 45.2; H, 1.90%; *M* 496. Calc. for $C_{19}H_{10}CoFeO_7P$: C, 45.95; H, 2.00%; *M* 496); ν(CO) at 2 094m, 2 037vs, 2 007vs, 2 003s, 1 981w, and 1 972m cm^{-1} in light petroleum.

(*b*) A toluene solution (10 cm^3) of PPh_2Cl (0.2 cm^3, 200 mg, 0.91 mmol) was added dropwise to a suspension of $Na[Co(CO)_4]$ (200 mg, 1.03 mmol) in toluene (45 cm^3) and diethyl ether (5 cm^3) at −78 °C. After stirring for 1 h, $[Fe_2(CO)_9]$ (250 mg, 0.69 mmol) was added. Stirring was continued for 3 h at −78 °C and then 24 h at room temperature. The reaction mixture was filtered, solvent removed, and the residue pumped *in vacuo* for 30 min. This was then extracted with light petroleum (40 cm^3). After concentration and cooling to −30 °C for 2 d, a black solid was precipitated. Recrystallisation from light petroleum gave (3), 60 mg (12%) (Found: C, 46.15; H, 2.10%).

Preparation of μ-Phenylphosphinediyl-bis(tetracarbonylcobalt) (4).—A toluene solution (10 cm^3) of PPh_2Cl (0.48 cm^3, 570 mg, 2.60 mmol) was added dropwise to a stirred toluene suspension (40 cm^3) of $Li[Co_3(CO)_{10}]$ {from $[Co_2(CO)_8]$; 1.0 g, 2.92 mmol} at −78 °C. Stirring was continued for 30 min. The resulting red solution was filtered at −60 °C, and the solvent volume reduced to 5 cm^3. Cooled light petroleum was added, followed by stirring at −30 °C. Some solid was precipitated and discarded, and the liquid layer decanted. More light petroleum (30 cm^3) was added and a second portion of solid was precipitated. This was recrystallised from toluene–light petroleum at room temperature to give orange (4), 60 mg (5%), m.p. 95 °C (decomp.) (Found: C, 37.7; H, 1.80; Co, 25.7; P, 7.05. Calc for $C_{14}H_5Co_2O_8P$: C, 37.35; H, 1.10; Co, 26.2; P, 6.90%).

Crystal Structure of Complex (2).—A single crystal of $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ with dimensions 0.20 × 0.18 × 0.3 mm was selected and orientated inside a thin-walled capillary. The crystal was then mounted on an automatic four-circle diffractometer (Philips PW 1100, graphite monochromator, ω—2 θ scan, Mo-K_α radiation) equipped with a peak searching program.

Crystal data. $C_{31}H_{20}Co_3O_7P_2$, M = 743.27, Monoclinic, a = 19.271(16), b = 11.870(3), c = 13.512(8) Å, β = 99.36°, U = 3 050 Å^3, Z = 4, D_c = 1.869 g cm^{-3}, $F(000)$ = 1 507.9, space group $P2_1/a$, μ(Mo-K_α) = 16.6 cm^{-1}.

The observed systematic absences of $h0l$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $h00$ for $h = 2n + 1$ uniquely indicated the space group to be $P2_1/a$, which was subsequently confirmed by the successful refinement of the resulting structure. A total of 3 725 independent reflections was collected within the range of $1 \leqslant \theta \leqslant 20°$ for $\pm h \pm k\ l$ and θ = 20—22° for $\pm hkl$. The time of measurement per reflection was 40 s with 2 × 5-s background. Of these reflections, 1 815 were set below an observation limit of $F_{min.} = \sigma(F) = 6.5$, and another eight reflections having small θ, being shaded by the primary beam stop, were also omitted from the least-squares refinement. No absorption correction was applied.

A Fourier synthesis based on the best E map provided the locations of the cobalt and phosphorus atoms. These were

[13] W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, 1958, **B13**, 192.

isotropically refined in a full-matrix calculation to R 0.33, within two cycles using the SHELX-76 program. A difference-Fourier map revealed all the non-hydrogen atoms. The phenyl carbon atoms were refined as rigid groups, each as a regular hexagon of carbon atoms having a fixed C–C bond length of 1.395 Å. Thus it was only necessary to further refine the locations and orientations of the four pivot atoms within their ring. Three cycles lowered the R factor to 0.1064 with isotropic thermal motion. Block-matrix four-cycle refinement of all the atoms including hydrogen in calculated positions (C–H 1.08 Å) reduced R to 0.0697. The thermal motion of all the hydrogen atoms was assumed to be equal and was refined to U_{ij} 0.120 8 Å^2.

TABLE 1

Bond lengths (Å) in the molecule $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$

Co(1)–Co(2)	2.571(3)	Co(3)–C(7)	1.824(17)
Co(2)–Co(3)	2.584(3)	C(1)–O(1)	1.128(21)
Co(3)–Co(1)	2.482(3)	C(2)–O(2)	1.186(19)
Co(1)–P(1)	2.163(4)	C(3)–O(3)	1.139(23)
Co(2)–P(1)	2.174(4)	C(4)–O(4)	1.148(19)
Co(2)–P(2)	2.170(4)	C(5)–O(5)	1.160(24)
Co(3)–P(2)	2.210(4)	C(6)–O(6)	1.115(20)
Co(1)–C(1)	1.792(17)	C(7)–O(7)	1.097(22)
Co(1)–C(6)	1.792(17)	P(1)–C(8)	1.838(4)
Co(1)–C(4)	1.823(15)	P(1)–C(14)	1.819(4)
Co(2)–C(2)	1.733(16)	P(2)–C(20)	1.850(4)
Co(2)–C(5)	1.729(19)	P(2)–C(26)	1.825(4)
Co(3)–C(3)	1.780(19)	(C–C) ring	1.395 (fixed)

TABLE 2

Angles (°) in the molecule $[Co_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$

Co(1)–Co(2)–Co(3)	57.5(1)		
Co(2)–Co(3)–Co(1)	61.0(1)	(C–C–C) phenyl ring	120 (fixed)
Co(3)–Co(1)–Co(2)	61.5(1)		
Co(2)–Co(1)–C(1)	92.0(5)	Co(2)–Co(3)–C(3)	144.8(6)
Co(2)–Co(1)–C(4)	115.1(4)	Co(2)–Co(3)–C(4)	104.7(4)
Co(2)–Co(1)–C(6)	136.5(5)	Co(2)–Co(3)–C(7)	110.6(5)
Co(2)–Co(1)–P(1)	53.8(1)	Co(2)–Co(3)–P(2)	53.1(1)
Co(3)–Co(1)–C(1)	88.4(6)	Co(1)–Co(3)–C(3)	118.0(6)
Co(3)–Co(1)–C(4)	56.4(5)	Co(1)–Co(3)–C(4)	45.9(5)
Co(3)–Co(1)–C(6)	157.8(5)	Co(1)–Co(3)–C(7)	125.2(5)
Co(3)–Co(1)–P(1)	88.3(1)	Co(1)–Co(3)–P(2)	106.4(1)
P(1)–Co(1)–C(1)	142.0(5)	P(2)–Co(3)–C(3)	100.0(5)
P(1)–Co(1)–C(4)	106.7(6)	P(2)–Co(3)–C(4)	151.2(5)
P(1)–Co(1)–C(6)	95.1(6)	P(2)–Co(3)–C(7)	106.2(5)
C(1)–Co(1)–C(6)	101.9(7)	C(3)–Co(3)–C(7)	97.9(8)
C(1)–Co(1)–C(4)	102.8(7)	C(3)–Co(3)–C(4)	90.5(6)
C(6)–Co(1)–C(4)	101.8(7)	C(7)–Co(3)–C(4)	98.7(7)
Co(1)–Co(2)–C(5)	146.1(6)	P(1)–Co(2)–C(5)	93.1(6)
Co(1)–Co(2)–C(2)	93.0(6)	P(2)–Co(2)–C(5)	97.2(6)
Co(3)–Co(2)–C(5)	121.5(6)	C(2)–Co(2)–C(5)	106.0(8)
Co(3)–Co(2)–C(2)	129.1(6)	Co(1)–C(4)–Co(3)	77.8(4)
P(1)–Co(2)–P(2)	138.2(2)	Co(1)–C(4)–O(4)	149.3(1.4)
P(1)–Co(2)–C(2)	110.5(5)	Co(3)–C(4)–O(4)	132.4(1.3)
P(2)–Co(2)–C(2)	105.4(5)		
Co(1)–P(1)–Co(2)	72.7(1)	Co(3)–P(2)–Co(2)	72.3(1)
Co(1)–P(1)–C(8)	118.3(2)	Co(3)–P(2)–C(20)	123.4(2)
Co(1)–P(1)–C(14)	121.6(2)	Co(3)–P(2)–C(26)	114.0(2)
Co(2)–P(1)–C(8)	120.9(2)	Co(2)–P(2)–C(20)	118.5(2)
Co(2)–P(1)–C(14)	119.5(2)	Co(2)–P(2)–C(26)	125.6(2)
C(14)–P(1)–C(8)	103.0(2)	C(26)–P(2)–C(20)	102.5(2)

All the attempts to locate an additional hydrogen atom (at a distance of *ca.* 1.63 Å from a cobalt atom) failed. However, a difference-Fourier map calculated using 951 reflections within a small θ range of 14.5° ($F_{min.}$ 6.3, R 0.062) showed two strong peaks with respective electron densities of 0.5 and 0.4 e Å^{-3} and several much lower peaks. The higher peak was located within a reasonable distance from Co(3) (1.7 Å), but too near to P(2) (1.6 Å), whilst the lower peak was 1.8 Å from Co(3) and only 1.64 Å from C(4). Thus neither peak could be identified as hydrogen. All the other peaks with electron density $\leqslant$0.25 e Å^{-3} were within 1.1 Å of cobalt or phosphorus atoms.

Scattering factors and anomalous dispersions for structure-factor calculations were taken respectively from refs. 14 and 15. Bond lengths and angles are given in Tables 1 and 2, final positional parameters in Table 3. Structure factors and thermal parameters are available as Supplementary Publication No. SUP 22314 (48 pp.).*

TABLE 3

Final positional parameters

Atom	x	y	z
Co(1)	0.097 4(1)	0.664 4(2)	0.304 0(2)
Co(2)	0.104 0(1)	0.491 6(2)	0.191 2(1)
Co(3)	0.176 5(1)	0.506 8(2)	0.369 2(1)
P(1)	0.143 1(2)	0.659 8(3)	0.168 0(3)
P(2)	0.129 6(2)	0.352 5(3)	0.294 9(3)
C(1)	0.030 2(8)	0.600 8(13)	0.362 7(11)
C(2)	0.013 5(8)	0.486 2(12)	0.155 3(12)
C(3)	0.180 5(9)	0.467 4(13)	0.497 1(14)
C(4)	0.170 3(9)	0.678 8(14)	0.407 7(12)
C(5)	0.139 5(10)	0.435 2(13)	0.092 6(14)
C(6)	0.066 9(8)	0.806 9(14)	0.287 5(12)
C(7)	0.270 4(9)	0.499 7(13)	0.364 0(13)
C(8)	0.102 7(5)	0.746 3(8)	0.061 3(7)
C(9)	0.029 9(5)	0.741 8(8)	0.031 8(7)
C(10)	−0.002 2(5)	0.806 2(8)	−0.049 3(7)
C(11)	0.038 5(5)	0.875 0(8)	−0.100 9(7)
C(12)	0.111 2(5)	0.879 5(8)	−0.071 5(7)
C(13)	0.143 4(5)	0.815 1(8)	0.009 6(7)
C(14)	0.236 7(4)	0.681 2(9)	0.169 9(7)
C(15)	0.275 0(4)	0.746 3(9)	0.245 7(7)
C(16)	0.346 5(4)	0.765 7(9)	0.246 5(7)
C(17)	0.379 7(4)	0.720 0(9)	0.171 3(7)
C(18)	0.341 4(4)	0.654 8(9)	0.095 5(7)
C(19)	0.269 9(4)	0.635 4(9)	0.094 7(7)
C(20)	0.182 4(5)	0.234 4(7)	0.257 3(7)
C(21)	0.247 6(5)	0.257 4(7)	0.229 8(7)
C(22)	0.285 9(5)	0.171 1(7)	0.193 9(7)
C(23)	0.259 0(5)	0.061 8(7)	0.185 7(7)
C(24)	0.193 8(5)	0.038 8(7)	0.213 2(7)
C(25)	0.155 4(5)	0.125 1(7)	0.249 1(7)
C(26)	0.068 2(5)	0.280 9(8)	0.363 1(7)
C(27)	−0.004 1(5)	0.288 7(8)	0.330 2(7)
C(28)	−0.050 7(5)	0.232 2(8)	0.381 7(7)
C(29)	−0.025 1(5)	0.167 7(8)	0.466 0(7)
C(30)	0.047 2(5)	0.159 9(8)	0.499 0(7)
C(31)	0.093 9(5)	0.216 5(8)	0.447 5(7)
O(1)	−0.013 2(6)	0.563 8(10)	0.399 4(10)
O(2)	−0.048 3(6)	0.487 0(11)	0.129 0(10)
O(3)	0.184 1(10)	0.440 1(13)	0.578 5(11)
O(4)	0.199 9(7)	0.731 7(10)	0.472 3(8)
O(5)	0.163 2(8)	0.399 0(12)	0.025 7(10)
O(6)	0.047 3(7)	0.895 4(10)	0.280 8(10)
O(7)	0.327 2(7)	0.492 9(12)	0.363 8(13)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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