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PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE TETRACOBALT $Co_4(CO)_{8-x}(P(C_6H_5)_3)_x(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ CLUSTERS ($x = 0, 2$). EFFECT OF TRIPHENYLPHOSPHINE SUBSTITUTION ON THE OCTAHEDRAL-LIKE Co_4P_2 CORE

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Summary

The syntheses, physicochemical properties, and X-ray crystallographic structure determinations of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, **1**, and $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, **2**, are described. **1** consists of four $Co(CO)_2$ groups arranged at the corners of a bonding cobalt rectangle whose shorter two sides are each spanned by a symmetrical bridging carbonyl ligand. This tetramer is capped above and below by quadruply bridging PC_6H_5 ligands to give an octahedral-like Co_4P_2 core such that the $Co_4(CO)_{10}P_2$ fragment (without phenyl rings) approximately conforms to D_{2h} symmetry. A substitution of two $P(C_6H_5)_3$ ligands in place of two carbonyls in **1** to give **2** gives rise to a *cis*-configuration (with respect to the tetracobalt plane) ideally possessing C_2 symmetry. In **2**, the observed distortion of the Co_4P_2 core (involving mainly a preferential elongation of two Co—P bonds by 0.10 Å and a lengthening of the two unbridged Co—Co bonds by 0.08 Å and the two more rigid CO-bridged Co—Co bonds by 0.03 Å) is attributed to increased intramolecular nonbonding interactions, while the resulting 0.11 Å asymmetrical coordination of each bridging carbonyl to its two cobalt atoms is ascribed to an electronic effect.

Introduction

Numerous organometallic sulfide-bridged clusters have been synthesized and structurally characterized, but systems containing electronically equivalent mo-

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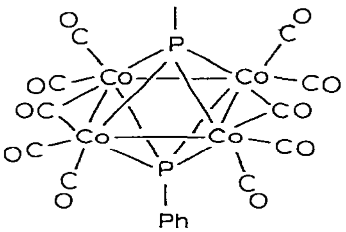
no(organo)phosphide ligands in place of sulfur ones have not been extensively studied. The fact that $Fe_3(CO)_9(\mu_3\text{-}PC_6H_5)_2$ [1,2] is structurally analogous to the $Fe_3(CO)_9(\mu_3\text{-}X)_2$ molecules (where X = S [2,3] and Se [4]) and $Co_3(CO)_9(\mu_3\text{-}PC(CH_3)_3)$ [5,6] resembles the $Co_3(CO)_9(\mu_3\text{-}X)$ molecules (where X = S [7—9] and Se [10]) led to the attempt by Ryan and Dahl [11] to prepare the corresponding PR complex of the unique $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}X)_2$ tetramers containing either sulfur [12,13] or tellurium [14,15] coordinated to a bonding rectangular array of metal atoms. Their synthesis and stereochemical characterization of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, **1**, which was then unprecedented in its possessing a square-pyramidal phosphorus atom attached to four transition metal atoms, resulted in subsequent preparations and structural studies by Ryan, O'Connor, and Dahl [6,16,17] of the C_6H_5As-bridged analog and the corresponding hydrido $[Co_4(CO)_8(\mu_2\text{-}CO)(\mu_2\text{-}H)(\mu_4\text{-}PC_6H_5)_2]^-$ monoanion. A by-product of their attempted oxidation of $[Co_4(CO)_8(\mu_2\text{-}CO)(\mu_2\text{-}H)(\mu_4\text{-}PC_6H_5)_2]^-$ was a different crystalline modification of the previously characterized $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ cluster [11].

Interest in **1** was stimulated from its use by Ryan and Pittman [18,19] as both a hydroformylation and hydrogenation catalyst with unusual responses to added phosphines [20]. This latter investigation [20], which revealed that the selectivity and reactivity of the hydroformylation reaction varied considerably with the addition of triphenylphosphine, provided the incentive for an investigation by O'Connor and Dahl [16] of the nature of products obtained from the reaction of **1** with triphenylphosphine. Both the mono- and bis-triphenylphosphine-substituted derivatives of **1** were isolated and spectroscopically characterized. An X-ray diffraction study of the bis-triphenylphosphine complex, **2**, was carried out in order to establish unambiguously the positions of the terminal carbonyls replaced by the two triphenylphosphine ligands as well as to assess the resulting geometrical changes on the basic architecture of the unsubstituted cluster system.

Herein are presented the syntheses and structural characterizations of **1** and **2** including a comparison of their structural features with those of the electronically equivalent sulfur-bridged analog. Details of the hydroformylation activity of clusters **1** and **2** are reported elsewhere [20].



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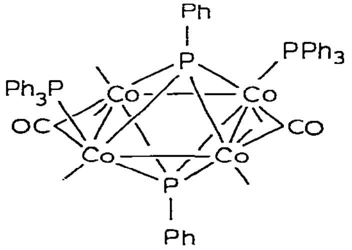

(2)

Experimental

Preparation and spectral characterization of 1 and 2

All reactions and manipulations were carried out under nitrogen in Schlenktype apparatus. All solvents were reagent grade and were used without further purification.

1 was prepared by the method of Ryan and O'Connor [6,11]. $Co_2(CO)_8$ (15.0 mmol) in toluene was reduced with an excess of Zn powder under CO atmosphere. The slow addition of a toluene solution of $C_6H_5PCl_2$ (7.4 mmol) to the above filtered solution produced gas evolution and changed the solution from light yellow to deep red. The solution was then refluxed for 12 h, cooled, and purified on a silica gel/hexane column by an elution with benzene to give a very soluble dark red crystalline product isolated in 30—35% yield (based on $C_6H_5PCl_2$).

A Fourier-transform infrared spectrum of **1** in CH_2Cl_2 exhibited three terminal carbonyl bands at 2040vs, 2032s, and 2016s cm^{-1} together with a band in the bridging carbonyl region at 1866w cm^{-1}. Evidence for the stoichiometry of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ was provided by its mass spectrum which exhibited the parent peak at *m/e* 732 and also peaks corresponding to successive loss of each of the ten carbonyls. The diamagnetism of this air-stable complex was established by magnetic measurements via the Faraday method. A ^1H NMR spectrum (JEOL MH-100) in acetone-d_6 showed a multiplet at τ 2.35 (vs. internal TMS) characteristic of the phenyl protons, while a ^{31}P NMR (Varian XL-100-15) in $CDCl_3$ revealed a broad resonance centered at -257.1 ppm (vs. 85% H_3PO_4 (aq), external). Dark red rhombic-shaped crystals were obtained by slow evaporation of a $CHCl_3$ solution under a stream of dry N_2. This method of crystal growth produced the triclinic form of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$. The monoclinic form of the complex was subsequently isolated as a by-product of the attempted oxidation of $[Ph_4As][Co_4(CO)_8(\mu_2\text{-}CO)(\mu_2\text{-}H)(\mu_4\text{-}PC_6H_5)_2]$, from which crystals were obtained by slow evaporation of a benzene/hexane mixture.

2 was synthesized by the method of O'Connor [16]. Triphenylphosphine (1.2 mmol) was added to **1** (0.41 mmol) in 125 ml of degassed toluene. The solution was refluxed for 5.5 h, after which the solvent was removed under vacuum and the residue adsorbed onto 6% neutral alumina. The sample was transferred onto a 6% neutral alumina column which was prepared and deoxygenated with hexane. Three bands were resolved on the column. The first band, eluted in hexane, was identified as unreacted starting material via infrared spectra. The second and third bands were eluted in a 2/1 mixture of hexane and toluene. The second band exhibited infrared carbonyl adsorptions at 2060s, 2016s, and 1840w cm^{-1}, while the third band had carbonyl absorptions at 2015s, 1985s, and 1820s cm^{-1}. These spectral data are consistent with band two being the monosubstituted triphenylphosphine product and band three being the disubstituted triphenylphosphine product. This tentative identification was verified for the band-two product by element analysis (Galbraith Microanalytical Laboratories, Knoxville, Tennessee) which gave the following results: Found: C, 48.7; H, 2.8; P, 9.3; 0, 15.0; Co, 24.2. $Co_4P_3C_{39}H_{25}O_9$ calcd.: C, 48.4; H, 2.6; F, 9.6; 0, 14.9; Co, 24.4%.

Crystals of the product (viz., **2**) from band three were obtained in the following way. A degassed hexane solution of **2** was placed in a schlenk tube which also contained a six-inch test tube approximately half full of degassed xylene. The schlenk tube was pumped and purged with nitrogen several times and then sealed. Slow diffusion of the more volatile hexane into the xylene produced suitable single crystals of **2** in about one week as the hexane solution became saturated.

Single-crystal data collection

In each case the crystal was mounted under an argon atmosphere inside a thin-walled Lindemann glass capillary. Approximate crystal dimensions were as follows: $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, 0.25 × 0.30 × 0.20 mm and $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ 0.10 × 0.34 × 0.65 mm. Intensities were collected on a NOVA-automated Syntex $P\bar{1}$ diffractometer equipped with a scintillation counter, a pulse height analyzer adjusted to admit 90% of the Mo-K_α($\lambda\alpha_1$ 0.70930 Å, $\lambda\alpha_2$ 0.71359 Å), and a crystal graphite monochromator set at a Bragg 2θ angle of 12.2°. Fifteen reflections were centered and used in a least-squares refinement to determine the lattice constants and orientation matrix.

The $\theta - 2\theta$ scan technique was used with a variable scan speed of from 4.00 to 24.00 degrees per minute in 2θ. Two standard reflections, measured after every 48 data reflections, showed no significant intensity changes during the entire data collection for either compound. Monoclinic data were sampled once within the range of $3.0° \leqslant 2\theta \leqslant 45.0°$ for two independent octants for each crystal. The data were reduced [21], corrected for background and polarization of the incident beam [22], and merged [23] to yield the independent data. The independent reflections were considered to be observed if the intensities were greater than $2\sigma(I)$ above background where $\sigma(I) = (S + B(t_s/t_b)^2 + EI^2)^{1/2}$ with S designating the scan count obtained in time t_s, E an empirical factor (0.0016) and I the integrated intensity equal to $S - B(t_s/t_b)$.

An absorption correction was applied [22] to the intensity data for $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$. The range of transmission coefficients, based on a linear absorption coefficient of 13.8 cm^{-1} for Mo-K_α radiation [24], ranged from 0.53 to 0.72. The crystal data for the two compounds are summarized in Table 1.

Structural determination and refinements

The automatic scattering factors of Cromer and Mann [25] for the nonhydrogen atoms and Stewart et al., [26], for the hydrogen atoms were used in all structure factor calculations on both compounds. Anomalous dispersion corrections [27] were applied to the scattering factors of Co and P in both structural determinations.

(a) *$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$*. The possible space group choices were limited to $P2_1$ and $P2_1/m$. Analysis began under noncentrosymmetric $P2_1$ symmetry. Analysis of the three-dimensional Patterson map [28] vectors (via PHASE [29]) yielded initial positions for four cobalt atoms. Fourier syntheses [28] based on the cobalt positions yielded coordinates for all remaining nonhydrogen atoms. Five isotropic full-matrix least-squares refinements [30] led to $R_1 = 10.0\%$ and $R_2 = 11.9\%$ *. The atoms for the two independent phenyl rings were fit [31] to

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* $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100$ and $R_2 = [\Sigma w_i||F_0| - |F_c||^2/w_i|F_0|^2]^{1/2} \times 100$. All least squares refinements were based on the minimization of $\Sigma w_i||F_0| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(|F_0|)^2$. The standard deviation of an observation of unit weight, σ_1, is defined by $[\Sigma w_i||F_0| - |F_c||^2/(n - p)]^{1/2}$ where σ_c is determined by counting statistics and where n denotes the number of observations and p the number of parameters varied during the least-squares refinement. For appropriately weighted data and normally distributed errors the expected value of σ_1 is unity.

TABLE 1

CRYSTAL DATA FOR TWO TETRAMERIC COBALT CARBONYL SYSTEMS

	$Co_4(CO)_{10}(PPh)_2$ (1)	$Co_4(CO)_8(PPh_3)_2(PPh)_2C_6H_6$ (2)
a (Å)	11.375(5)	10.561(5)
b (Å)	13.891(9)	25.228(13)
c (Å)	9.057(5)	21.101(8)
α (deg)	90.00(—)	90.00(—)
β (deg)	112.77(3)	93.25(4)
γ (deg)	90.00(—)	90.00(—)
Vol (Å^3)	1320	5613
Space group	$P2_1$	$P2_1/n$
Z	2	4
$F(000)$	720	2600
$\rho_{(calcd)}$(g/cm^3)	1.84	1.51
$\rho_{(obsd)}$(g/cm^3) [a]	1.84	1.52
R_1 [b]	6.0	8.6
R_2 [b]	6.2	10.4
e^-/Å^3 [c]	0.8	2.1

[a] Observed density measured by flotation. [b] $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100$ and $R_2 = [\Sigma w_i||F_0| - |F_c||^2/\Sigma w_i|F_0|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma w_i||F_0| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_0)^2$. [c] Maximum peak density from a final difference Fourier map.

idealized groups of D_{6h} symmetry with C—C distances of 1.39 Å and C—H distances of 1.08 Å. Idealized hydrogen positions were not varied during least-squares refinement but were recalculated after every other cycle.

Full-matrix least-squares refinement [30] with anisotropic thermal parameters for the cobalt and phosphorus atoms and isotropic ones for all other nonhydrogen atoms converged at $R_1 = 6.0\%$ and $R_2 = 6.2\%$. Calculation of the structure factors with corrections for anomalous dispersion gave an identical value of $R_1 = 6.0\%$ on interchange of the signs of all *hkl* indices from plus to minus.

A final full-matrix least-squares cycle [32] was then performed where positional parameters for all nonhydrogen atoms were varied. The final discrepancy factors for the 1342 independent reflections with $I \geqslant 2\sigma(I)$ were $R_1 = 6.0\%$ and $R_2 = 6.2\%$ with $\sigma_1 = 1.26$ and no $\Delta/\sigma \geqslant 0.15$. A final Fourier difference map, which showed the largest peak maxima to be less than 0.8 e^-/Å^3, revealed no unusual features.

The positional and thermal parameters from the output of the final full-matrix least-squares cycle are given in Table 2, while interatomic distances and angles [33] are given in Table 3. Selected least-squares planes [34] as well as observed and calculated structure factors are given in the supplementary material.

(b) $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2 \cdot C_6H_6$. Similar to the method used for **1**, the probable space group was found to be $P2_1/n$ and the first Fourier synthesis [28] phased on three cobalt atoms gave $R_1 = 58.9\%$. Successive Fourier syntheses provided initial coordinates for all remaining nonhydrogen atoms. Four cycles of isotropic least-squares refinement [30] led to $R_1 = 11.92\%$ and $R_2 = 15.19\%$. The carbon atoms for the phenyl rings were fitted [31] to an idealized ring of D_{6h} symmetry with C—C distances of 1.39 Å and C—H distances of 1.08 Å.

TABLE 2

ATOMIC PARAMETERS FOR $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$

Atom	x	y	z	B (Å^2)
Co(1)	−0.2908(2)	−0.0084 [d]	−0.0145(3)	[c]
Co(2)	−0.4110(2)	−0.1538(3)	0.0186(3)	[c]
Co(3)	−0.3209(2)	−0.2580(2)	−0.1644(3)	[c]
Co(4)	−0.1984(2)	−0.1141(3)	−0.1971(3)	[c]
P(1)	−0.2101(5)	−0.1566(4)	0.0331(6)	[c]
P(2)	−0.4000(5)	−0.1081(5)	−0.2159(6)	[c]
C(1,2)	−0.4092(21)	−0.0300(17)	0.0848(27)	4.8
O(1,2)	−0.4604(17)	0.0263(14)	0.1478(20)	6.7
C(3,4)	−0.2012(16)	−0.2478(14)	−0.2608(22)	3.1
O(3,4)	−0.1545(14)	−0.2919(12)	−0.3353(18)	5.0
C(1—1)	−0.1687(27)	0.0463(21)	0.1321(33)	7.1
O(1—1)	−0.0816(22)	0.0791(18)	0.2382(28)	9.2
C(1—2)	−0.3521(19)	0.0980(16)	−0.1315(24)	3.7
O(1—2)	−0.3832(15)	0.1686(13)	−0.1978(19)	6.3
C(2—1)	−0.3677(22)	−0.2143(18)	0.2067(30)	5.3
O(2—1)	−0.3465(16)	−0.2592(15)	0.3186(22)	7.2
C(2—2)	−0.5742(25)	−0.1716(21)	−0.0694(29)	6.0
O(2—2)	−0.6803(18)	−0.1979(14)	−0.1191(22)	7.2
C(3—1)	−0.2696(29)	−0.3556(23)	−0.0513(38)	7.4
O(3—1)	−0.2442(16)	−0.4232(14)	0.0430(20)	6.7
C(3—2)	−0.4511(21)	−0.3080(17)	−0.3268(26)	4.5
O(3—2)	−0.5351(16)	−0.3452(12)	−0.4305(20)	6.1
C(4—1)	−0.0321(22)	−0.0954(18)	−0.1172(26)	5.1
O(4—1)	0.0776(18)	−0.0934(14)	−0.0619(22)	7.7
C(4—2)	−0.2297(18)	−0.0551(16)	−0.3805(26)	3.7
O(4—2)	−0.2537(15)	−0.0131(13)	−0.5025(20)	5.8
C(1)	−0.0729(19)	−0.1943(16)	0.2092(25)	3.7
C(2)	−0.0575(20)	−0.1637(17)	0.3565(25)	4.2
C(3)	0.0477(23)	−0.2017(19)	0.4889(30)	5.7
C(4)	0.1275(21)	−0.2617(19)	0.4642(28)	5.5
C(5)	0.1167(22)	−0.2900(18)	0.3188(28)	5.1
C(6)	0.0160(21)	−0.2623(18)	0.1906(26)	4.6
C(7)	−0.5363(17)	−0.0736(14)	−0.3847(22)	2.8
C(8)	−0.5559(19)	−0.1068(17)	−0.5376(24)	4.3
C(9)	−0.6660(20)	−0.0838(16)	−0.6694(26)	4.3
C(10)	−0.7536(19)	−0.0243(15)	−0.6479(24)	4.0
C(11)	−0.7411(21)	0.0098(17)	−0.5003(26)	4.7
C(12)	−0.6293(16)	−0.0150(14)	−0.3649(20)	2.8
H(1)	−0.1197	−0.1186	0.3736	6.0
H(2)	0.0576	−0.1764	0.6020	6.0
H(3)	0.2068	−0.2867	0.5664	6.0
H(4)	0.1788	−0.3393	0.3025	6.0
H(5)	0.0016	−0.2815	0.0741	6.0
H(6)	−0.4883	−0.1503	−0.5512	6.0
H(7)	−0.6767	−0.1081	−0.7785	6.0
H(8)	−0.8355	−0.0068	−0.7448	6.0
H(9)	−0.8058	0.0523	−0.4838	6.0
H(10)	−0.6173	0.0102	−0.2564	6.0

[a] The estimated standard deviations of the least significant figures are given in parentheses. [b] In the final full-matrix least-squares cycle performed on a UNIVAC 1110 computer, only the positional parameters of the nonhydrogen atoms were varied; Idealized hydrogen positions (at 1.08 Å from their respective carbon atoms) were not varied during least-squares refinement but were recalculated after every other cycle so as to take into account the changes in coordinates of the carbon atoms. [c] Anisotropic temperature factors of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$ were used. The resulting thermal coefficients ($\times 10^4$) are given below:

TABLE 2 (continued).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	71	46	115	—1	33	—18
Co(2)	57	58	103	3	29	7
Co(3)	69	41	117	4	35	5
Co(4)	69	42	119	0	45	—6
P(1)	73	42	98	4	38	3
P(2)	53	42	94	8	21	—11

[d] The y parameter of one atom Co(1) was not varied during refinement in order to define the origin, as is required by the space group $P2_1$

Refinement was continued with anisotropic thermal parameters for all atoms except for phenyl ring carbons, which were refined isotropically, and for hydrogens which were assigned as fixed contributors with assigned isotropic temperature factors of 6.0 Å^2. A difference Fourier map revealed the positions of four carbon atoms of the benzene molecule of solvation. These four atoms were fitted to a rigid ring of D_{6h} symmetry, and idealized positions for the other two carbon and all six hydrogen atoms were calculated. This benezene molecule was refined in all further least squares cycles as a rigid group with variation of only the centroid of the phenyl ring and the group isotropic temperature factor.

Full-matrix least-squares cycles [32] were performed with anisotropic thermal parameters utilized for all atoms except for the phenyl ring carbons, which were refined isotropically, and for the hydrogen atoms which were assigned fixed positions and isotropic temperature factors. A final full-matrix cycle computed with variation of the positional parameters for all nonhydrogen atoms and variation of the group parameters for the benzene solvent molecule yielded R_1 = 8.6% and R_2 = 10.4% for the 4628 independent data with no shift-over-error ratio Δ/σ, greater than 0.05. A final difference Fourier map, which showed the largest peak maxima to be 2.1 e^-/Å^3 near the solvent molecule, revealed no other anomalous features.

The positional and thermal parameters from the output of the final full-matrix least-squares cycle are given in Tables 4 and 5. Interatomic distances and angles [33] with estimated standard deviations are listed in Table 6. Selected least-squares plane [34] and interplanar angles are presented in the supplementary material together with the observed and calculated structure factors *.

Results and discussion

(a) Structural description of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, 1

The monoclinic crystal form of the tetracobalt carbonyl cluster imposes no

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* This supplementary material, as well as the tables of observed and calculated structure factor amplitudes for monoclinic $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, 1, and $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2$-$(PC_6H_5)_2 \cdot C_6H_6$, 2, have been deposited as NAPS Document No. 03562 (40 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513. Grand Central Station, New York, NY 10017. A copy may be secured by citing the document number, remitting $ 10.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 3

INTERATOMIC DISTANCES AND ANGLES FOR MONOCLINIC $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$

A. Intramolecular Distances (Å) [a]

Co(1)—Co(2)	2.521(4)	C(1,2)—O(1,2)	1.24(2)
Co(3)—Co(4)	2.519(4)	C(3,4)—O(3,4)	1.18(2)
	2.520(av)		1.21(av)
Co(1)—Co(4)	2.710(4)	C(1—1)—O(1—1)	1.17(3)
Co(2)—Co(3)	2.685(4)	C(1—2)—O(1—2)	1.13(2)
	2.698(av)	C(2—1)—O(2—1)	1.13(3)
		C(2—2)—O(2—2)	1.17(3)
Co(1) ... Co(3)	3.691(5)	C(3—1)—O(3—1)	1.23(3)
Co(2) ... Co(4)	3.691(5)	C(3—2)—O(3—2)	1.17(2)
		C(4—1)—O(4—1)	1.15(2)
P(1) ... P(2)	2.537(6)	C(4—2)—O(4—2)	1.18(2)
			1.17(av)
Co(1)—P(1)	2.227(6)		
Co(2)—P(1)	2.239(6)	P(1)—C(1)	1.82(2)
Co(3)—P(1)	2.243(6)	P(2)—C(7)	1.77(2)
Co(4)—P(1)	2.219(6)		1.80(av)
Co(1)—P(2)	2.244(6)		
Co(2)—P(2)	2.266(6)	C(1)—C(2)	1.35(3)
Co(3)—P(2)	2.244(6)	C(2)—C(3)	1.43(3)
Co(4)—P(2)	2.234(6)	C(3)—C(4)	1.31(3)
	2.240(av)	C(4)—C(5)	1.33(3)
		C(5)—C(6)	1.33(3)
Co(1)—C(1,2)	1.91(2)	C(6)—C(1)	1.44(3)
Co(2)—C(1,2)	1.82(2)	C(7)—C(8)	1.39(3)
Co(3)—C(3,4)	1.89(2)	C(8)—C(9)	1.39(3)
Co(4)—C(3,4)	1.94(2)	C(9)—C(10)	1.37(3)
	1.89(av)	C(10)—C(11)	1.37(3)
		C(11)—C(12)	1.43(3)
Co(1)—C(1—1)	1.69(3)	C(12)—C(7)	1.40(2)
Co(1)—C(1—2)	1.79(2)		
Co(2)—C(2—1)	1.79(3)		
Co(2)—C(2—2)	1.73(3)		
Co(3)—C(3—1)	1.66(3)		
Co(3)—C(3—2)	1.78(2)		
Co(4)—C(4—1)	1.76(2)		
Co(4)—C(4—2)	1.76(2)		
	1.75(av)		

B. Bond Angles (deg) [a]

Co(4)—Co(1)—Co(2)	89.7(1)	Co(4)—Co(1)—C(1—1)	109.2(9)
Co(1)—Co(2)—Co(3)	90.3(1)	Co(4)—Co(1)—C(1—2)	103.9(7)
Co(2)—Co(3)—Co(4)	90.3(1)	Co(3)—Co(2)—C(2—1)	107.7(8)
Co(3)—Co(4)—Co(1)	89.7(1)	Co(3)—Co(2)—C(2—2)	103.7(9)
	90.0(av)	Co(2)—Co(3)—C(3—1)	100.7(10)
		Co(2)—Co(3)—C(3—2)	109.1(7)
Co(2)—Co(1)—P(1)	55.9(2)	Co(1)—Co(4)—C(4—1)	106.1(8)
Co(2)—Co(1)—P(2)	56.4(2)	Co(1)—Co(4)—C(4—2)	109.8(7)
Co(1)—Co(2)—P(1)	55.4(2)		106.3(av)
Co(1)—Co(2)—P(2)	55.6(2)		
Co(4)—Co(3)—P(1)	55.2(2)	Co(2)—Co(1)—C(1,2)	45.9(7)
Co(4)—Co(3)—P(2)	55.6(2)	Co(1)—Co(2)—C(1,2)	49.0(7)
Co(3)—Co(4)—P(1)	56.1(2)	Co(4)—Co(3)—C(3,4)	49.8(6)
Co(3)—Co(4)—P(2)	56.0(2)	Co(3)—Co(4)—C(3,4)	47.9(5)
	55.8(av)		48.2(av)
Co(4)—Co(1)—P(1)	52.3(2)	Co(4)—Co(1)—C(1,2)	135.4(7)
Co(4)—Co(1)—P(2)	52.6(2)	Co(3)—Co(2)—C(1,2)	139.0(7)

TABLE 3 (continued)

B. Bond Angles (deg)[a]

Co(3)—Co(2)—P(1)	53.3(2)	Co(2)—Co(3)—C(3,4)	139.6(6)
Co(3)—Co(2)—P(2)	53.1(2)	Co(1)—Co(4)—C(3,4)	137.3(6)
Co(2)—Co(3)—P(1)	53.1(2)		137.8(av)
Co(2)—Co(3)—P(2)	53.8(2)		
Co(1)—Co(4)—P(1)	52.6(2)	P(1)—Co(1)—C(1—1)	96.4(10)
Co(1)—Co(4)—P(2)	52.9(2)	P(2)—Co(1)—C(1—2)	93.6(7)
	53.0(av)	P(1)—Co(2)—C(2—1)	92.1(8)
		P(2)—Co(2)—C(2—2)	92.7(8)
P(1)—Co(1)—P(2)	69.1(2)	P(1)—Co(3)—C(3—1)	93.8(11)
P(1)—Co(2)—P(2)	68.5(2)	P(2)—Co(3)—C(3—2)	93.0(8)
P(1)—Co(3)—P(2)	68.9(2)	P(1)—Co(4)—C(4—1)	95.6(7)
P(1)—Co(4)—P(2)	69.4(2)	P(2)—Co(4)—C(4—2)	94.8(6)
	69.0(av)		94.0(av)
Co(2)—Co(1)—C(1—1)	125.9(9)	P(1)—Co(1)—C(1—2)	155.8(7)
Co(2)—Co(1)—C(1—2)	128.7(6)	P(2)—Co(1)—C(1—1)	161.2(10)
Co(1)—Co(2)—C(2—1)	121.8(8)	P(1)—Co(2)—C(2—2)	155.9(8)
Co(1)—Co(2)—C(2—2)	126.5(9)	P(2)—Co(2)—C(2—1)	158.3(8)
Co(4)—Co(3)—C(3—1)	129.8(10)	P(1)—Co(3)—C(3—2)	159.7(7)
Co(4)—Co(3)—C(3—2)	122.3(7)	P(2)—Co(3)—C(3—1)	154.3(10)
Co(3)—Co(4)—C(4—1)	128.5(8)	P(1)—Co(4)—C(4—2)	161.1(7)
Co(3)—Co(4)—C(4—2)	124.1(7)	P(2)—Co(4)—C(4—1)	158.7(7)
	126.0(av)		158.1(av)
P(1)—Co(1)—C(1,2)	94.4(7)	Co(1)—C(1—1)—O(1—1)	176(3)
P(2)—Co(1)—C(1,2)	90.9(7)	Co(1)—C(1—2)—O(1—2)	175(2)
P(1)—Co(2)—C(1,2)	96.7(7)	Co(2)—C(2—1)—O(2—1)	174(2)
P(2)—Co(2)—C(1,2)	92.7(7)	Co(2)—C(2—2)—O(2—2)	170(3)
P(1)—Co(3)—C(3,4)	92.2(6)	Co(3)—C(3—1)—O(3—1)	170(3)
P(2)—Co(3)—C(3,4)	97.9(6)	Co(3)—C(3—2)—O(3—2)	177(2)
P(1)—Co(4)—C(3,4)	91.5(6)	Co(4)—C(4—1)—O(4—1)	173(2)
P(2)—Co(4)—C(3,4)	96.6(5)	Co(4)—C(4—2)—O(4—2)	178(2)
	94.1(av)		174(av)
Co(1)—P(1)—Co(2)	68.7(2)	Co(1)—C(1,2)—O(1,2)	131(2)
Co(3)—P(1)—Co(4)	68.7(2)	Co(2)—C(1,2)—O(1,2)	143(2)
Co(1)—P(2)—Co(2)	68.0(2)	Co(3)—C(3,4)—O(3,4)	142(2)
Co(3)—P(2)—Co(4)	68.4(2)	Co(4)—C(3,4)—O(3,4)	135(2)
	68.5(av)		138(av)
Co(1)—P(1)—Co(4)	75.1(2)	Co(1)—C(1,2)—Co(2)	85(1)
Co(2)—P(1)—Co(3)	73.6(2)	Co(3)—C(3,4)—Co(4)	82(1)
Co(1)—P(2)—Co(4)	74.5(2)		84(av)
Co(2)—P(2)—Co(3)	73.1(1)		
	74.1(av)	P(1)—C(1)—C(2)	121(2)
		P(1)—C(1)—C(6)	119(2)
Co(1)—P(1)—C(1)	125.7(7)	P(2)—C(7)—C(8)	121(2)
Co(2)—P(1)—C(1)	124.4(7)	P(2)—C(7)—C(12)	120(1)
Co(3)—P(1)—C(1)	122.9(7)		
Co(4)—P(1)—C(1)	123.8(7)		
Co(1)—P(2)—C(7)	124.0(7)		
Co(2)—P(2)—C(7)	122.5(6)		
Co(3)—P(2)—C(7)	125.3(7)		
Co(4)—P(2)—C(7)	127.3(6)		
	124.5(av)		
C(1—1)—Co(1)—C(1—2)	96(1)		
C(2—1)—Co(2)—C(2—2)	103(1)		
C(3—1)—Co(3)—C(3—2)	100(1)		
C(4—1)—Co(4)—C(4—2)	96(1)		
	99(av)		

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[a] The distances and bond angles of the $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}P)_2$ fragment were averaged in accord with an idealized D_{2h} geometry.

TABLE 4

ATOMIC PARAMETERS FOR THE CLUSTER CORE OF $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{—}PC_6H_5)_2 \cdot C_6H_6$ [a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.0417(1)	0.2452(1)	0.0836(1)	46	15	15	2	4	1
Co(2)	—0.1501(1)	0.3036(1)	0.0588(1)	49	13	11	1	1	1
Co(3)	—0.3041(1)	0.2241(1)	0.0992(1)	44	14	11	0	—1	0
Co(4)	—0.1145(1)	0.1632(1)	0.1155(1)	46	12	11	1	1	0
P(1)	—0.1416(2)	0.2182(1)	0.0345(1)	61	13	10	—1	4	—1
P(2)	—0.1202(2)	0.2511(1)	0.1480(1)	45	12	11	—1	0	—1
P(2′)	—0.2098(2)	0.3841(1)	0.0923(1)	55	13	15	0	3	1
P(4′)	—0.0400(2)	0.1179(1)	0.2020(1)	53	13	14	0	5	1
C(1—1)	0.1365(9)	0.2167(6)	0.0251(7)	85	21	26	3	14	4
O(1—1)	0.1955(8)	0.1957(6)	—0.0109(6)	154	47	44	21	52	—8
C(1—2)	0.1634(8)	0.2604(6)	0.1454(6)	51	17	21	—8	8	—5
O(1—2)	0.2418(7)	0.2693(5)	0.1817(5)	89	30	28	—14	—11	—3
C(2—1)	—0.2244(9)	0.3157(6)	—0.0170(7)	101	18	14	—1	1	0
O(2—1)	—0.2808(7)	0.3225(5)	—0.0653(5)	152	24	19	17	—18	1
C(3—1)	—0.4223(9)	0.2219(7)	0.0371(7)	62	36	16	—8	—16	—6
O(3—1)	—0.5030(8)	0.2251(6)	0.0012(6)	122	65	22	—3	—26	8
C(3—2)	—0.4013(8)	0.2432(6)	0.1622(6)	51	17	17	—1	—1	3
O(3—2)	—0.4687(7)	0.2544(5)	0.1993(5)	73	31	27	1	22	—3
C(4—1)	—0.0684(9)	0.1122(6)	0.6324(6)	105	14	13	—2	—2	2
O(4—1)	—0.0388(8)	0.0806(5)	0.0289(5)	226	21	25	33	—4	—9
C(1,2)	0.0248(9)	0.3179(6)	0.0478(7)	53	20	19	8	0	2
O(1,2)	0.0964(7)	0.3490(5)	0.0301(5)	72	24	46	—11	21	13
C(3,4)	—0.2875(9)	0.1488(6)	0.1216(6)	73	20	16	1	2	2
O(3,4)	—0.3596(7)	0.1137(4)	0.1320(5)	71	17	52	—8	2	7

[a] The estimated standard deviations of the least significant figures are given in parenthesis. Anisotropic temperature factors of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$. The listed temperature factors are $\times 10^4$.

symmetry constraints on its molecular geometry which is viewed in Fig. 1. Its molecular configuration consists of a $Co_4(CO)_8(\mu_2\text{-}CO)_2$ fragment containing four $Co(CO)_2$ groups arranged at the corners of a bonding cobalt rectangle whose shorter two sides are each spanned by a symmetrical bridging carbonyl ligand. The tetramer is capped above and below by quadruply bridging PC_6H_5 ligands to give an octahedral-like Co_4P_2 core such that the $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ molecule conforms closely to an orthorhombic D_{2h}-*mmm* geometry. The observed slight distortions from an idealized D_{2h} geometry are a bending of the plane of the four cobalt atoms and a twisting deformation, by ca. 3.2°, of the phenyl rings with respect to the plane containing P(1), P(2), the midpoint of Co(1)—Co(2), and the midpoint of Co(3)—Co(4). The two phenyl rings in the independent molecule are within 6.1° of being parallel to each other.

The two CO-bridged electron-pair Co—Co bonds of 2.520 Å (av) are 0.18 Å shorter than the two unbridged electron-pair Co—Co bonds of 2.698 Å (av) in harmony with the observation that the constraining influence of bridging carbonyls generally gives rise to shorter electron-pair metal—metal bonds. The bond lengths and angles for the Co_4P_2 core agree within experimental error with those preliminarily reported for the Co_4P_2 core of the molecules crystallized in the triclinic form [11]. The eight independent Co—CO(terminal) bonds possess a mean value of 1.75 Å which is 0.14 Å shorter than the average value of 1.89 Å for the four independent Co—CO(bridging) bonds.

TABLE 5

ATOMIC PARAMETERS FOR CARBON AND HYDROGENS OF THE PHOSPHINE LIGANDS IN $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2 \cdot C_6H_6$ [a,b]

	x	*y*	*z*	*B* (Å^2)
C(1)	−0.1576(9)	0.1968(5)	−0.0469(6)	3.12
C(2)	−0.2433(9)	0.1575(6)	−0.0657(6)	3.42
C(3)	−0.2581(10)	0.1432(7)	−0.1295(8)	4.88
C(4)	−0.1914(10)	0.1677(7)	−0.1723(8)	5.58
C(5)	−0.1062(10)	0.2058(7)	−0.1580(9)	5.71
C(6)	−0.0879(10)	0.2222(6)	−0.0927(7)	4.41
C(7)	−0.1083(8)	0.2738(5)	0.2285(6)	2.51
C(8)	−0.0109(9)	0.2554(6)	0.2714(6)	3.28
C(9)	−0.0084(9)	0.2715(6)	0.3343(7)	4.07
C(10)	−0.1054(10)	0.3039(7)	0.3559(8)	5.27
C(11)	−0.1966(10)	0.3222(7)	0.3153(8)	5.03
C(12)	−0.1994(9)	0.3070(6)	0.2502(7)	3.32
CA(1)	−0.1139(8)	0.4232(5)	0.1518(6)	2.93
CA(2)	−0.1410(9)	0.4773(7)	0.1608(7)	4.34
CA(3)	−0.0689(10)	0.5065(7)	0.2033(8)	4.69
CA(4)	0.0298(10)	0.4834(7)	0.2376(8)	5.08
CA(5)	0.0597(10)	0.4305(7)	0.2284(8)	5.27
CA(6)	−0.0137(9)	0.4010(6)	0.1850(7)	3.59
CB(1)	−0.2185(9)	0.4307(6)	0.0259(6)	3.24
CB(2)	−0.3286(10)	0.4577(7)	0.0044(8)	5.46
CB(3)	−0.3259(12)	0.4893(8)	−0.0493(9)	6.18
CB(4)	−0.2235(12)	0.4966(7)	−0.0822(9)	6.16
CB(5)	−0.1155(13)	0.4723(9)	−0.0612(10)	7.93
CB(6)	−0.1087(12)	0.4377(8)	−0.0062(9)	6.44
CC(1)	−0.3745(8)	0.3858(5)	0.1181(5)	3.05
CC(2)	−0.4111(9)	0.4098(6)	0.1726(7)	3.90
CC(3)	−0.5354(10)	0.4096(6)	0.1879(7)	4.68
CC(4)	−0.6245(10)	0.3870(7)	0.1503(8)	4.69
CC(5)	−0.5926(10)	0.3628(7)	0.0973(8)	4.99
CC(6)	−0.4651(9)	0.3608(6)	0.0802(7)	3.75
CD(1)	−0.1171(8)	0.1205(5)	0.2781(6)	2.88
CD(2)	−0.2114(9)	0.1576(6)	0.2849(7)	3.67
CD(3)	−0.2730(10)	0.1605(7)	0.3427(8)	4.89
CD(4)	−0.2372(10)	0.1256(7)	0.3895(8)	5.74
CD(5)	−0.1449(10)	0.0902(7)	0.3848(9)	5.78
CD(6)	−0.0832(9)	0.0856(6)	0.3259(7)	4.19
CE(1)	−0.0499(9)	0.0480(6)	0.1838(6)	3.23
CE(2)	−0.1677(10)	0.0218(6)	0.1858(7)	4.40
CE(3)	−0.1868(11)	−0.0301(7)	0.1645(8)	5.23
CE(4)	−0.0846(12)	−0.0577(8)	0.1406(9)	6.34
CE(5)	0.0291(12)	−0.0336(8)	0.1414(9)	5.97
CE(6)	0.0474(10)	0.1816(7)	0.1615(7)	4.83
CF(1)	0.1318(8)	0.1279(5)	0.2219(6)	2.77
CF(2)	0.1847(9)	0.1338(6)	0.2832(7)	4.21
CF(3)	0.3174(11)	0.1383(7)	0.2928(8)	5.40
CF(4)	0.3919(10)	0.1385(6)	0.2431(8)	4.92
CF(5)	0.3380(10)	0.1352(6)	0.1815(8)	4.85
CF(6)	0.2092(9)	0.1310(6)	0.1712(7)	3.67
H(2)	−0.3012	0.1422	−0.0316	6.00
H(3)	−0.3199	0.1074	−0.1375	6.00
H(4)	−0.1976	0.1413	−0.2170	6.00
H(5)	−0.0367	0.2100	−0.1906	6.00
H(6)	−0.0180	0.2449	−0.0846	6.00
H(8)	0.0567	0.2324	0.2558	6.00
H(9)	0.0603	0.2582	0.3654	6.00
H(10)	−0.1923	0.3150	0.4020	6.00
H(11)	−0.2687	0.3461	0.3291	6.00

TABLE 5 (continued)

	x	y	z	B (Å^2)
H(12)	−0.2723	0.3203	0.2196	6.00
HA(2)	−0.2215	0.4932	0.1371	6.00
HA(3)	−0.0934	0.5453	0.2111	6.00
HA(4)	0.0863	0.5062	0.2679	6.00
HA(5)	0.1379	0.4148	0.2508	6.00
HA(6)	0.0098	0.3627	0.1768	6.00
HB(2)	−0.4087	0.4537	0.0276	6.00
HB(3)	−0.4107	0.5092	−0.0648	6.00
HB(4)	−0.2217	0.5194	−0.1216	6.00
HB(5)	−0.0307	0.4742	−0.0860	6.00
HB(6)	−0.0288	0.4188	0.0064	6.00
HC(2)	−0.3391	0.4284	0.2014	6.00
HC(3)	−0.5563	0.4293	0.2293	6.00
HC(4)	−0.7161	0.3868	0.1617	6.00
HC(5)	−0.6587	0.3434	0.0662	6.00
HC(6)	−0.4415	0.3426	0.0383	6.00
HD(2)	−0.2391	0.1826	0.2486	6.00
HD(3)	−0.3451	0.1874	0.3461	6.00
HD(4)	−0.2868	0.1279	0.4315	6.00
HD(5)	−0.1224	0.0636	0.4195	6.00
HD(6)	−0.0164	0.0587	0.3221	6.00
HE(2)	−0.2437	0.0441	0.2048	6.00
HE(3)	−0.2783	−0.0445	0.1662	6.00
HE(4)	−0.1069	−0.0933	0.1242	6.00
HE(5)	0.0990	−0.0536	0.1208	6.00
HE(6)	0.1336	0.0350	0.1594	6.00
HF(2)	0.1274	0.1331	0.3213	6.00
HF(3)	0.3526	0.1421	0.3401	6.00
HF(4)	0.4874	0.1437	0.2523	6.00
HF(5)	0.3969	0.1363	0.1457	6.00
HF(6)	0.1716	0.1274	0.1269	6.00

Rigid body parameters [c]

	x	y	z	ϕ	θ	ρ	Group B (Å)^2
C_6H_6	0.3546(10)	0.0352(8)	0.0314(9)	−44.1(7)	−143.9(6)	125.1(6)	18.16

[a] The estimated standard deviations of the least significant figure are given in parentheses. [b] In the final full matrix least-squares cycle the positional and isotropic thermal parameters of the hydrogen atoms are assigned as fixed contributors obtained using idealized coordinates. The isotropic temperature factor was arbitrarily assigned as 6.0 Å^2 for all hydrogen atoms. [c] The benzene solvent molecule group refinement was based on the following model. The benzene ring was presumed to have D_{6h} symmetry with C—C bond lengths of 1.39 Å. The hydrogen atoms were located with a C—H bond length of 1.08 Å and at 120° angles to the adjacent carbon atoms. The orthonormal set (x', y', z') has x' along C(1)—C(4), y' along the perpendicular bisector of C(2)—C(3), and z' along x' cross y'.

Fig. 2 shows the two formula species per cell related by $P2_1$ symmetry. There are no close interactions between molecules as is illustrated by the fact that the shortest nonhydrogen separations exceed 3.0 Å.

(b) Structural description of $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2 \cdot C_6H_6$, **2**

Cluster **2** contains one independent molecule of crystallographic site symmetry C_i-$\bar{1}$. Fig. 3 shows its molecular configuration together with the benzene

TABLE 6

INTERATOMIC DISTANCES AND ANGLES FOR $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2 \cdot C_6H_6$

A. Intramolecular distances (Å) [a]

Co(1)—Co(2)	2.552(2)	Co(1)—C(1—2)	1.82(1)
Co(3)—Co(4)	2.551(1)	Co(3)—C(3—2)	1.79(1)
	2.552(av)		1.81(av)
Co(1)—Co(4)	2.785(2)	Co(1)—C(1,2)	2.02(1)
Co(2)—Co(3)	2.777(2)	Co(3)—C(3,4)	2.00(1)
	2.781(av)		2.01(av)
		Co(2)—C(1,2)	1.91(1)
Co(1) ... Co(3)	3.725(2)	Co(4)—C(3,4)	1.88(1)
Co(2) ... Co(4)	3.818(2)		1.90(1)
P(1) ... P(2)	2.540(5)	C(1—1)—O(1—1)	1.14(1)
		C(3—1)—O(3—1)	1.11(1)
Co(1)—P(1)	2.254(4)		1.13(av)
Co(3)—P(1)	2.258(3)		
	2.256(av)	C(1—2)—O(1—2)	1.12(1)
		C(3—2)—O(3—2)	1.12(1)
Co(2)—P(1)	2.261(4)		1.12(av)
Co(4)—P(1)	2.225(4)		
	2.243(av)	C(2—1)—O(2—1)	1.16(1)
		C(4—1)—O(4—1)	1.15(1)
Co(1)—P(2)	2.249(3)		1.16(av)
Co(3)—P(2)	2.255(3)		
	2.252(av)	C(1,2)—O(1,2)	1.18(1)
		C(3,4)—O(3,4)	1.21(1)
Co(2)—P(2)	2.323(4)		1.20(av)
Co(4)—P(2)	2.366(4)		
	2.345(av)	P(1)—C(1)	1.80(1)
Co(2)—P(2′)	2.288(4)	P(2)—C(7)	1.79(1)
Co(4)—P(4′)	2.268(4)		
	2.278(av)	P(2′)—CA(1)	1.86(1)
		P(2′)—CB(1)	1.84(1)
P(2) ... P(2′)	3.722(5)	P(2′)—CC(1)	1.85(1)
P(2) ... P(4′)	3.696(5)		
		P(4′)—CD(1)	1.84(1)
Co(1)—C(1—1)	1.79(1)	P(4′)—CE(1)	1.84(1)
Co(3)—C(3—1)	1.76(1)	P(4′)—CF(1)	1.86(1)
	1.78(av)		
		C(1)—C(2)	1.40(1)
Co(2)—C(2—1)	1.77(1)	C(2)—C(3)	1.39(2)
Co(4)—C(4—1)	1.79(1)	C(3)—C(4)	1.33(2)
	1.78(av)	C(4)—C(5)	1.35(2)
		C(5)—C(6)	1.44(2)
		C(6)—C(1)	1.40(2)

B. Intramolecular bond angles (deg) [a]

Co(4)—Co(1)—Co(2)	91.24(8)	Co(3)—Co(2)—P(1)	52.0(1)
Co(2)—Co(3)—Co(4)	91.44(7)	Co(1)—Co(4)—P(1)	52.0(1)
	91.34(av)		52.0(av)
Co(1)—Co(2)—Co(3)	88.58(8)	Co(2)—Co(1)—P(2)	57.5(1)
Co(3)—Co(4)—Co(1)	88.44(8)	Co(4)—Co(3)—P(2)	57.8(1)
	88.51(av)		57.6(av)
		Co(1)—Co(2)—P(2)	54.7(1)
Co(2)—Co(1)—P(1)	55.7(1)	Co(3)—Co(4)—P(2)	54.4(1)
Co(4)—Co(3)—P(1)	54.7(1)		54.6(av)
	55.2(av)		

TABLE 6 (continued)

B. Intramolecular bond angles (deg) [a]

Co(1)—Co(2)—P(1)	55.5(1)	Co(4)—Co(1)—P(2)	54.8(1)
Co(3)—Co(4)—P(1)	55.9(1)	Co(2)—Co(3)—P(2)	53.8(1)
	55.7(av)		54.3(av)
Co(4)—Co(1)—P(1)	51.1(1)	Co(3)—Co(2)—P(2)	51.6(1)
Co(2)—Co(3)—P(1)	52.1(1)	Co(1)—Co(4)—P(2)	51.0(1)
	51.6(av)		51.3(av)
P(1)—Co(1)—P(2)	68.7(1)	Co(4)—Co(1)—C(1,2)	138.7(4)
P(1)—Co(3)—P(2)	68.5(1)	Co(2)—Co(3)—C(3,4)	137.8(4)
	68.6(av)		138.3(av)
P(1)—Co(2)—P(2)	67.3(1)	Co(3)—Co(2)—C(1,2)	139.9(4)
P(1)—Co(4)—P(2)	67.1(1)	Co(1)—Co(4)—C(3,4)	139.3(5)
	67.2(av)		139.6(av)
Co(1)—Co(2)—P(2′)	134.3(1)	P(1)—Co(1)—C(1—1)	93.1(5)
Co(3)—Co(4)—P(4′)	131.1(1)	P(1)—Co(3)—C(3—1)	94.5(5)
	132.7(av)		93.8(av)
Co(3)—Co(2)—P(2′)	113.3(1)	P(1)—Co(2)—C(2—1)	89.2(5)
Co(1)—Co(4)—P(4′)	113.6(1)	P(1)—Co(4)—C(4—1)	91.1(4)
	113.5(av)		90.2(av)
Co(2)—Co(1)—C(1—1)	124.6(5)	P(1)—Co(1)—C(1—2)	161.6(4)
Co(4)—Co(3)—C(3—1)	126.7(6)	P(1)—Co(3)—C(3—2)	162.4(4)
	125.7(av)		162.0(av)
Co(2)—Co(1)—C(1—2)	122.7(4)	P(2)—Co(1)—C(1—1)	156.7(5)
Co(4)—Co(3)—C(3—2)	123.1(4)	P(2)—Co(3)—C(3—1)	155.0(6)
	122.9(av)		155.9(av)
Co(1)—Co(2)—C(2—1)	126.5(5)	P(2)—Co(2)—C(2—1)	150.2(5)
Co(3)—Co(4)—C(4—1)	127.1(4)	P(2)—Co(4)—C(4—1)	152.5(4)
	126.8(av)		151.4(av)
Co(4)—Co(1)—C(1—1)	102.6(5)	P(2)—Co(1)—C(1—2)	94.8(4)
Co(2)—Co(3)—C(3—1)	101.5(6)	P(2)—Co(3)—C(3—2)	95.2(4)
	102.1(av)		95.0(av)
Co(4)—Co(1)—C(1—2)	113.1(4)	P(1)—Co(2)—P(2′)	164.9(1)
Co(2)—Co(3)—C(3—2)	113.3(5)	P(1)—Co(4)—P(4′)	165.6(1)
	113.2(av)		165.3(av)
Co(3)—Co(2)—C(2—1)	99.8(5)	P(2)—Co(2)—P(3′)	107.6(1)
Co(1)—Co(4)—C(4—1)	102.7(5)	P(2)—Co(4)—P(4′)	105.7(1)
	101.3(av)		106.7(av)
Co(2)—Co(1)—C(1,2)	47.7(4)	P(1)—Co(1)—C(1,2)	93.4(4)
Co(4)—Co(3)—C(3,4)	46.8(4)	P(1)—Co(3)—C(3,4)	91.0(4)
	47.3(av)		92.2(av)
Co(1)—Co(2)—C(1,2)	51.4(4)	P(1)—Co(2)—C(1,2)	96.2(4)
Co(3)—Co(4)—C(3,4)	51.0(5)	P(1)—Co(4)—C(3,4)	95.4(5)
	51.2(av)		95.8(av)
P(2)—Co(1)—C(1,2)	96.3(4)	Co(1)—C(1—1)—O(1—1)	177(1)
P(2)—Co(3)—C(3,4)	97.4(4)	Co(1)—C(1—2)—O(1—2)	176(1)
	96.9(av)	Co(2)—C(2—1)—O(2—1)	175(1)
		Co(3)—C(3—1)—O(3—1)	176(1)
P(2)—Co(2)—C(1,2)	97.0(4)	Co(3)—C(3—2)—O(3—2)	172(1)
P(2)—Co(4)—C(3,4)	97.3(5)	Co(4)—C(4—1)—O(4—1)	179(1)
	97.2(av)		
		Co(1)—C(1,2)—O(1,2)	135(1)
Co(1)—P(1)—Co(2)	68.8(1)	Co(3)—C(3,4)—O(3,4)	136(1)
Co(3)—P(1)—Co(4)	67.3(1)		136(av)
	69.1(av)		

TABLE 6 (continued)

B. Intramolecular bond angles (deg)[a]

Co(1)—P(1)—Co(4)	76.9(1)
Co(2)—P(1)—Co(3)	75.8(1)
	76.4(av)
Co(1)—P(2)—Co(2)	67.8(1)
Co(3)—P(2)—Co(4)	67.0(1)
	67.4(av)
Co(1)—P(2)—Co(4)	74.1(1)
Co(2)—P(2)—Co(3)	74.6(1)
	74.4(av)
Co(1)—P(1)—C(1)	124.3(4)
Co(3)—P(1)—C(1)	124.3(4)
	124.3(av)
Co(2)—P(1)—C(1)	120.6(5)
Co(4)—P(1)—C(1)	122.7(5)
	121.7(av)
Co(1)—P(2)—C(7)	125.4(4)
Co(3)—P(2)—C(7)	123.0(4)
	124.2(av)
Co(2)—P(2)—C(7)	125.2(4)
Co(4)—P(2)—C(7)	125.8(4)
	125.5(av)
C(1—1)—Co(1)—C(1—2)	100.5(7)
C(3—1)—Co(3)—C(3—2)	98.6(7)
	99.6(av)
C(2—1)—Co(2)—P(2')	90.3(5)
C(4—1)—Co(4)—P(4')	91.4(5)
	90.0(av)
P(2')—CA(1)—CA(2)	120(1)
P(2')—CA(1)—CA(6)	120(1)
P(2')—CB(1)—CB(2)	124(1)
P(2')—CB(1)—CB(6)	117(1)
P(2')—CC(1)—CC(3)	124(1)
P(2')—CC(1)—CC(6)	117(1)
P(4')—CD(1)—CD(2)	118(1)
P(4')—CD(1)—CD(6)	120(1)
P(4')—CE(1)—CE(2)	120(1)
P(4')—CE(1)—CE(6)	125(1)
P(4')—CF(1)—CF(2)	124(1)
P(4')—CF(1)—CF(6)	116(1)
Co(2)—C(1,2)—O(1,2)	144(1)
Co(4)—C(3,4)—O(3,4)	141(1)
	143(av)
Co(1)—C(1,2)—Co(2)	80.9(6)
Co(3)—C(3,4)—Co(4)	82.2(6)
	81.6(av)
Co(2)—P(2')—CA(1)	123.2(5)
Co(4)—P(2')—CB(1)	110.9(5)
Co(2)—P(2')—CC(1)	113.0(5)
CA(1)—P(2')—CB(1)	99.4(6)
CA(1)—P(2')—CC(1)	105.9(6)
CB(1)—P(2')—CC(1)	101.6(6)
Co(4)—P(4')—CD(1)	122.1(5)
Co(4)—P(4')—CE(1)	108.7(5)
Co(4)—P(4')—CF(1)	113.6(5)
CD(1)—P(4')—CE(1)	101.3(6)
CD(1)—P(4')—CF(1)	105.7(6)
CE(1)—P(4')—CF(1)	103.1(6)
P(1)—C(1)—C(2)	120(1)
P(1)—C(1)—C(6)	119(1)
P(2)—C(7)—C(8)	120(1)
P(2)—C(7)—C(12)	120(1)

[a] The distances and bond angles of the $Co_4(CO)_6(P)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}P)_2$ fragment were averaged in accord with an idealized C_2-2 geometry.

molecule of solvation. The four cobalt atoms constitute the corners of a rectangle. Again, the shorter sides are each spanned by a bridging carbonyl group. Of the six terminal carbonyls, two are attached to each of the diagonally-related cobalt atoms, Co(1) and Co(3), while one is bonded to each of the other two

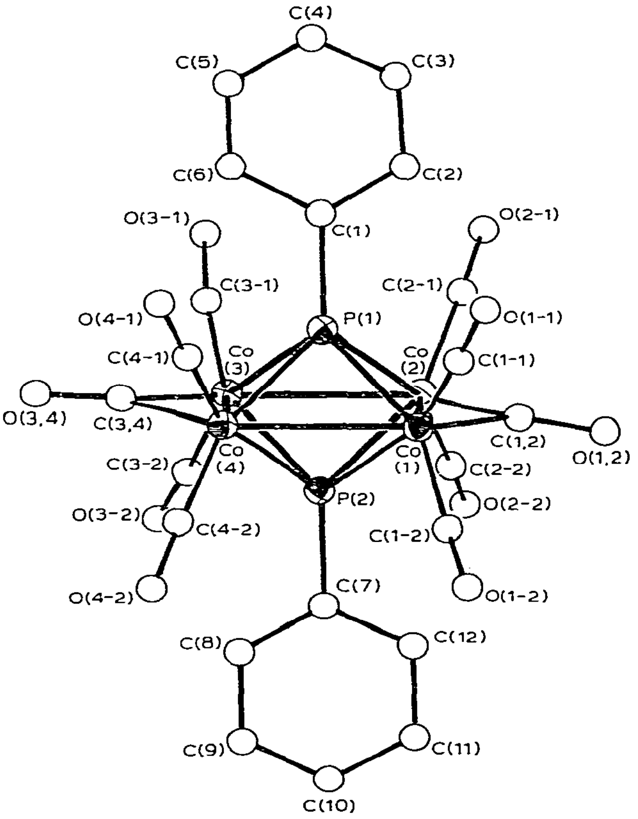

Fig. 1. Architecture of monoclinic $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$. The entire molecule of idealized D_{2h}-*mmm* geometry comprises the crystallographically independent unit.

cobalts, Co(2) and Co(3). Each of these latter two cobalt atoms is also coordinated to a triphenylphosphine ligand such that these two ligands are arranged in a *cis* configuration with respect to the tetracobalt plane (i.e., on the same side of the plane as the quadruply bridging phosphorus atom, P(2)). The entire molecule then has an idealized C_2-2 geometry with the twofold rotation axis passing through the two quadruply bridging PC_6H_5 ligands and the midpoint of the tetracobalt rectangular plane.

The two carbonyl-bridged Co—Co bonds of 2.552 Å (av) are 0.23 Å shorter than the nonbridged Co—Co bonds of 2.781 Å (av). The six independent Co—CO(terminal) distances range from 1.76(1) to 1.82(1) Å. The longer Co—CO(bridging) distances, which reflect in a twofold equivalent fashion a distinct asymmetrical coordination for each of the two bridging carbonyls (vide infra), vary from 1.88(1) to 2.02(1) with a mean of 1.95 Å. This bond-length trend is in accord with that found in other cobalt carbonyl clusters containing both terminal and bridging carbonyl ligands. The C—O distances for the terminal carbonyls have a range from 1.11(1) to 1.16(1) Å with a mean of 1.13 Å, while the C—O distances for the two doubly bridging carbonyl ligands are 1.18(1) Å and 1.21(1) Å.

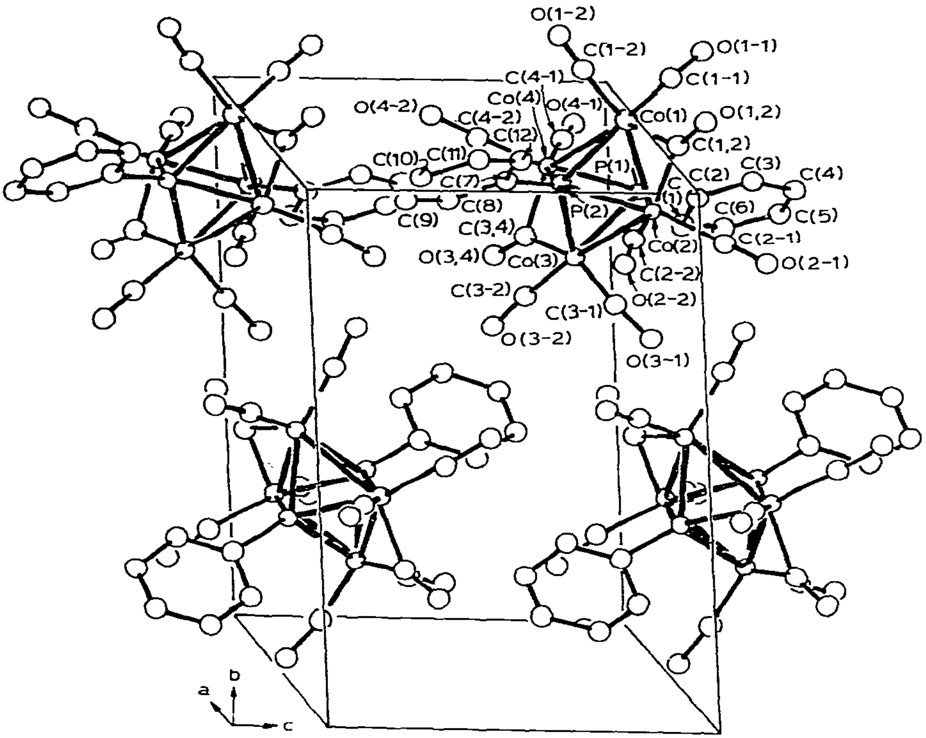

Fig. 2. View of the monoclinic unit cell of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ showing the two formula units per cell related by $P2_1$ symmetry.

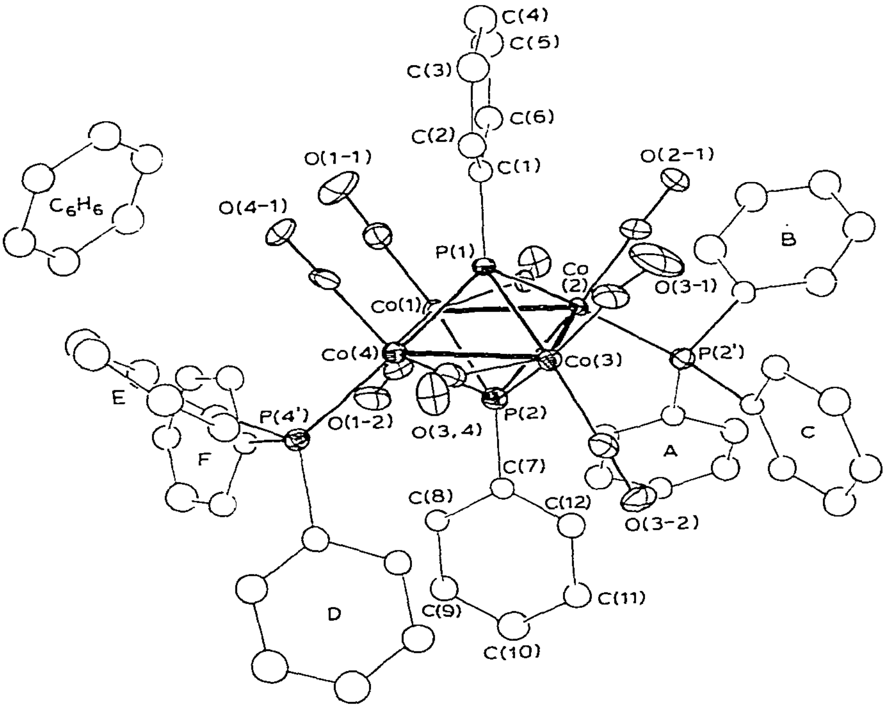

Fig. 3. View of molecular configuration of $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$. The entire molecule of idealized C_2-2 geometry comprises the crystallographic independent unit. The orientation of the benzene solvent molecule is also shown in this view. The hydrogen atoms as well as atom labels for the phenyl ring carbons of the triphenylphosphine ligands have been omitted for clarity.

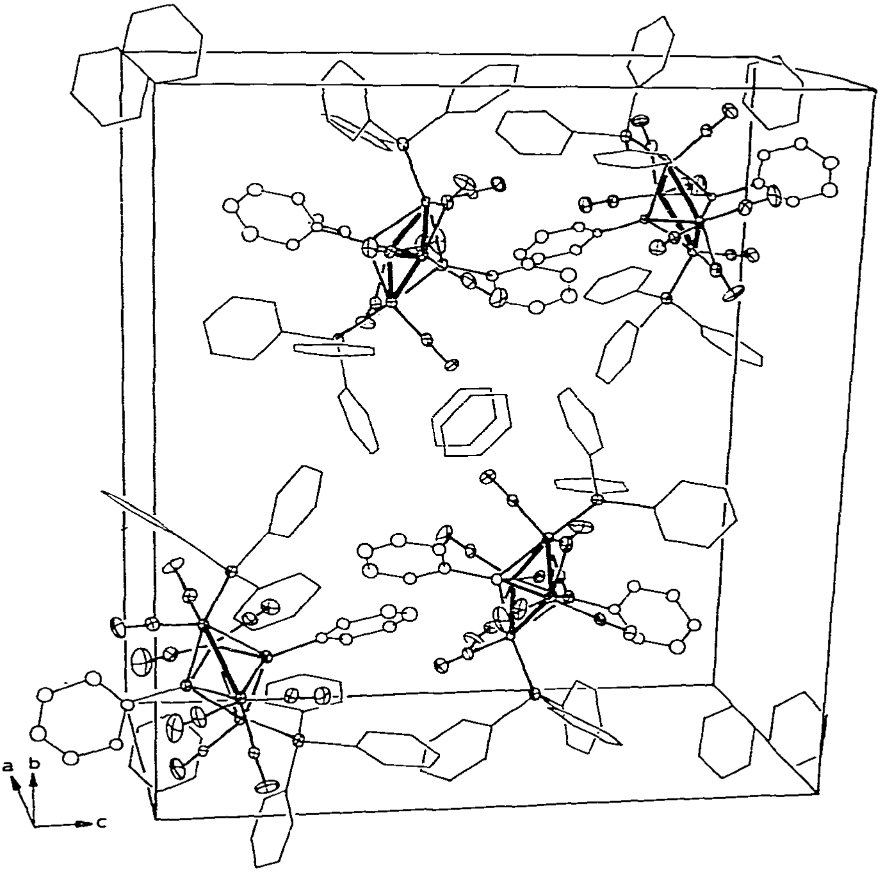

Fig. 4. Perspective view of the monoclinic unit cell of $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2 \cdot C_6H_6$ showing the four formula units per cell related by $P2_1/n$ symmetry.

The Co—P bond lengths observed in this structure are particularly interesting. The two equivalent Co(1)—P(1) and Co(3)—P(1) bonds have virtually identical values of 2.254(4) and 2.258(3) Å, while the Co(2)—P(1) and Co(4)—P(1) bonds, which are likewise equivalent under C_2 symmetry, have values of 2.261(4) and 2.225(4) Å, respectively. The corresponding Co(1)—P(2) and Co(3)—P(2) bonds have similar values of 2.249(4) and 2.255(4) Å, respectively, while the twofold equivalent Co(2)—P(2) and Co(4)—P(2) bonds have longer values of 2.323(4) and 2.366(4) Å, respectively. The observed variations in the Co—P(2) distances may be rationalized from steric considerations. The two cobalt atoms, Co(2) and Co(4), bonded to the $P(C_6H_5)_3$ ligands have longer Co—P(2) bond lengths due to the steric interactions of the phenyl substituents. The cobalt distances to P(1) may also be rationalized in terms of steric considerations in that the triphenylphosphine substituents have induced a slight puckering of the tetracobalt plane, as evidenced from least-squares plane calculations. The Co—P(1) distances thereby reflect the extent to which the tetracobalt plane has been distorted.

The orientation of the phenyl ring bonded to P(1) is comparable to the orientation observed in the parent cluster **1**, where the ring is in the plane defined by the two quadruply bridging phosphorus atoms, the midpoint of Co(1) and Co(2), and the midpoint of Co(3) and Co(4), such that the plane of the phenyl ring bisects the carbonyl-bridged Co—Co bonds. The phenyl ring on P(2), however, is rotated by 90° such that the plane of the phenyl ring bisects the Co(1)—Co(4) and Co(2)—Co(3) bonds. This is attributed to steric overcrowding involving the triphenylphosphine substituents, where the nonbonding interactions are minimized by the apical phenyl ring adopting this latter orientation.

Fig. 4 shows the unit cell containing four molecules related by $P2_1/n$ symmetry. The shortest nonhydrogen intermolecular contacts are greater than 3.2 Å which do not reflect any unusual crystal packing forces.

(c) *Analysis of the structural features for* $Co_4(CO)_{8-x}(PPh_3)_x(\mu_2\text{-}CO)_2(\mu_4\text{-}E)_2$ *molecules (where* $E = PC_6H_5$ *or S and* $x = 0$ *and 2).*

A summary of important molecular parameters for three tetracobalt carbonyl clusters is given in Table 7.

(i) *Analysis of the structural features for* $Co_4(CO)_{8-x}(P(C_6H_5)_3)_x(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ *(where* $x = 0$ *or 2).* Table 7 reveals the following important stereochemical trends resulting from triphenylphosphine substitution of **1** to give **2**: (a) In **2**, the two unbridged Co—Co bonds are longer by 0.08 Å (av) and the two CO-bridged Co—Co bonds are longer by 0.03 Å (av) than the corresponding Co—Co bonds in **1**. These bond-length increases upon phosphine substitution may be described as a steric consequence of the bulky $P(C_6H_5)_3$ ligands with the weaker unbridged Co—Co bonds being the most affected.

(b) In **2**, the particular *cis*-coordination of $P(C_6H_5)_3$ ligands to Co(2) and Co(4) on the tetracobalt side near P(2) gives rise to 0.10 Å longer Co(2)—P(2) and Co(4)—P(2) bond lengths of 2.34 Å (av) relative to the Co(1)—P(2) and Co(3)—P(2) bond lengths of 2.24 Å (av); the latter mean is identical to the mean found in **1** for the presumed eight equivalent Co—P bond lengths. These particular bond-length variations are also readily attributed to intramolecular nonbonding repulsions involving the $P(C_6H_5)_3$ ligands.

(c) In contrast to the presumed symmetrical coordination of each of the two bridging carbonyls in **1** (i.e., both in the monoclinic structure presented here and in the previously reported triclinic structure [11]), each of the two bridging carbonyls in **2** is asymmetrically coordinated in an analogous fashion with Co—CO(bridging) bond lengths of 1.91(1) vs. 2.02(1) Å and 1.88(1) Å vs, 2.00(1) Å. The fact that the bridging carbon atoms are 0.11—0.12 Å closer to the triphenylphosphine-attached Co(2) and Co(4) atoms may be rationalized on the basis of an electronic effect. The replacement of a CO ligand with a better electron-donating $P(C_6H_5)_3$ ligand is expected to produce a greater electron density on Co(2) and Co(4), relative to that on Co(1) and Co(3), such that significantly larger π^*(CO) backbonding can occur to render stable a geometry with shorter Co(2)—CO(bridging) and Co(4)—CO(bridging) bonds.

(ii) *Comparison of structural parameters between phenylphosphido- and sulfur-bridged metal carbonyl clusters.* An examination of the molecular parameters (Table 7) for the Co_4E_2 core of the phosphido-bridged and sulfur-bridged tetracobalt decacarbonyl clusters reveals four important points when electronically equivalent PC_6H_5 ligands are formally substituted in place of sulfur atoms:

TABLE 7

SELECTED DISTANCES (Å) AND BOND ANGLES (deg) FOR THREE TETRACOBALT COMPLEXES CONTAINING AN OCTAHEDRAL-LIKE Co_4E_2 CORE [a]

	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ (1)	$Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ (2)			$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2$ [d]
Co_4E_2 Core	Co_4P_2		Co_4P_2		Co_4S_2
Co—Co (CO-Bridged)	2.526 [2] [b]		2.552 [2]		2.480(9) [1]
Co—Co (Unbridged)	2.698 [2]		2.781 [2]		2.598(10) [1]
E- - -E	2.537(6) [1]	Co(PPh$_3$) [b]	2.540(4) [1]	Co(CO) [b]	2.74(2) [1]
Co—E	2.240 [8]	2.243 [2] 2.345 [2]		2.256 [2] 2.252 [2]	2.258 [4]
Co—C (terminal)	1.75 [8]	1.78 [2]		1.78 [2] 1.81 [2]	1.69 [4]
Co—C (bridging)	1.89 [4]	1.90 [2]		2.01 [2]	1.89 [2]
Co—E—Co (CO-Bridged)	68.5 [4]	67.4 [2]		69.1 [2]	66.6 [2]
Co—E—Co (Unbridged)	74.1 [4]	74.4 [2]		76.4 [2]	70.2 [2]

[a] Average values given are based upon an assumed D_{2h} geometry in **1** ($x = 0$) and an assumed C_2 geometry in **2** ($x = 2$) for the $Co_4(CO)_{8-x}(P)_x(\mu_2\text{-}CO)_2(\mu_4\text{-}P)_2$ fragments (without phenyl rings) and an assumed D_{2h} geometry for the sulfur molecule. The $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ and $Co_4(CO)_6(P(C_6H_5)_3)_2(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ molecules have no imposed crystallographic site symmetry while the sulfur-bridged molecule possesses crystallographic site symmetry $C_i\text{-}\bar{1}$ with one-half of the molecule in the independent unit. [b] Square brackets [] designate the number of equivalent distance or bond angles having values listed in the left column. [c] The entries in the columns labelled Co(PPh$_3$) and Co(CO) refer to bond lengths involving the cobalt atoms bonded to triphenylphosphine ligands (i.e. Co(2) and Co(4)) and cobalt atoms bonded only to carbonyl ligands (i.e. Co(1) and Co(3)), respectively. The bond angles under the heading Co(PPh$_3$) refer to angles involving the bridging phosphorus atom on the same side of the cobalt plane as the triphenylphosphine ligands (i.e. P(2)) while angles with P(1) are under Co(CO). [d] Ref. 12.

(a) an enlargement by 0.10 Å in the unbridged Co—Co distance and by 0.04 Å in the CO-bridged Co—Co distance; (b) a large decrease in the E···E distance by 0.20 Å; (c) essentially no change in the Co—E bond lengths, and (d) an increase in the Co—E—Co bond angles by ca. 1.8° for the carbonyl-bridged and 4.0° for the unbridged sides. These four trends were also seen when phenylphosphido-bridged ligands formally replace sulfur atoms in iron carbonyl clusters. The $Fe_3(CO)_9$-$(\mu_3\text{-}X)_2$ molecules (where X = PC_6H_5 and S) [2,3] exhibit an analogous increase of ca. 0.1 Å in the metal—metal bond distance, a 0.3 Å decrease in the E···E distance, a very slight increase of 0.02 Å in the metal—E bond length, and an expansion of ca. 4.0° in the metal—E—metal bond angle when PC_6H_5 replaces sulfur.

In **1**, the relatively short P···P distance of 2.54 Å, which is unchanged in **2**, is only 0.3 Å greater than an accepted P—P single-bond distance [35]. Consequently, it was initially suggested by Ryan and Dahl [11] that the shorter P···P than S···S distances arise from distinct attractive bonding forces which (despite being small relative to metal—ligand interactions) do nevertheless cause considerable perturbations of the geometry. Such attractive P···P interactions have subsequently been indicated from parameter-free molecular orbital calculations via the the Fenske—Hall model carried out by Dahl and co-workers [36,37] on other phosphorus-bridged clusters containing similarly short P···P distances. A recent structural study [6,17] of Marko's [5] phosphido-bridged cobalt carbonyl cluster with only one bridging ligand, $Co_3(CO)_9(\mu_3\text{-}PC(CH_3)_3)$, presented an opportunity to examine the proposal that attractive interligand P···P interactions dictate the observed deformations in the tetracobalt and triiron carbonyl clusters. The study of this system revealed that a formal replacement of a sulfur atom by a phosphorus atom resulted in a similar increase of 0.08 Å in metal—metal bond lengths, a 0.01 Å decrease in Co—E distance, and a 3.4° increase in the Co—E—Co bond angles. Since there is no possibility of P···P interaction for this tricobalt cluster, this allows a modification of the hypothesis [11] that close P···P interactions may constitute the driving force in determining overall molecular geometries.

The results presented here indicate that the metal—E bond lengths and metal—E—metal bond angles strongly influence the metal—metal and E···E distances. For a given molecular framework there appears to be an "optimum" metal—E bond distance (at least for E = S and PC_6H_5) and metal—E—metal bond angle, which depend on E. Therefore, we conclude that a dominant factor contributing to the observed geometrical differences between electronically equivalent and structurally analogous RP- and S-bridged metal cluster complexes is connected with the occurrence of a wider metal—P—metal bond angle (viz., ca. 3—4°) than a metal—S—metal bond angle. A theoretical rationalization for this bond angle change is based upon the results of the Fenske—Hall MO model applied [37] to the electronically equivalent and structurally resembling cubane-like $M_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}X)_4$ clusters (M = Fe, X = S; M = Co, X = P). An examination reveals that the unshared electron pair on a P atom has a relatively large *p* AO character whereas the unshared electron pair on a S atom primarily possesses *s* AO character. It then follows that more *s* AO character for a P atom is involved in the bonding with the three metal atoms which thereby produces a wide M—P—M bond angle. A similar consideration of the *s*—*p* orbital character of the valence E orbitals for other corresponding RP- and S-bridged clusters also leads to wider Co—P—Co bond angles than Co—S—Co bond angles. Thus, it is presumed that for both the $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2$ and $Co_3(CO)_9(\mu_3\text{-}S)$ molecules the lone pair of the sulfur ligand is primarily contained in the 3*s* AO such that mainly the 3*p* AO's are involved in bonding with metal cluster orbitals. A formal replacement of each sulfur ligand by a RP one would then be expected to result in the contribution of considerable 3*p* phosphorus orbital character to the P—R bond, which in turn would lead to much greater 3*s* phosphorus orbital participation in the Co—P bonding thereby producing wider Co—P—Co bond angles. It is noteworthy that a small shortening of the Co—P bonds relative to the corresponding Co—S bonds would be expected with the greater 3*s* phosphorus orbital bond character. The observed similarity in the corresponding Co—P and Co—S bond lengths relative to the assumed covalent radius of phosphorus being 0.06 Å greater than that of sulfur is not inconsistent with these arguments. This same conclusion for the existence of wider Co—P—Co bond angles in the above clusters can also be reached by application of the valence-shell electron-pair repulsion concept. This model presumes that the unshared electron pair, on either a triply bridging or quadruply bridging sulfur ligand, would exert a larger repulsion and thereby would give rise to smaller metal—E—metal bond angles in a given metal cluster system than that produced by the corresponding bonding electron pair on either a triply or quadruply bridging PR ligand.

On the basis of the theoretical and experimental evidence indicating the existence of residual P···P interactions in other metal complexes, our current hypothesis also includes the belief that attractive interligand interactions in **1** and **2** may thereby not be a dominant factor in causing the observed geometries with the identically short P···P distances but instead may be mainly a concomitant effect. Further structural and molecular orbital investigations are needed to amplify these stereochemical-bonding implications.

Other custers which contain quadruply bridging phenylphosphido-bridged ligands are now known, and the corresponding metal—P—metal angles of 74.7° (av) for the $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ molecule [38] and 74.1° (av) for the $[Co_4(CO)_8(\mu_2\text{-}CO)(\mu_2\text{-}H)\text{-}(\mu_4\text{-}PC_6H_5)_2]^-$ anion [6] agree well with the value 74.0° (av) for $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$.

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