

Table IV. Torsion Angles^a (deg) of the [2.2.2] Ligand When Alone and When Enclosing Various Ions

A-B-C-D ^b	pure [2.2.2]	Na- [2.2.2]	Ca- [2.2.2]	Sm- [2.2.2]
N(1)-C(1)-C(2)-O(1)	-69	-41	-57	-60
C(1)-C(2)-O(1)-C(3)	167	148	-178	-119
C(2)-O(1)-C(3)-C(4)	-180	-162	-97	156
O(1)-C(3)-C(4)-O(2)	-175	45	-59	14
C(3)-C(4)-O(2)-C(5)	175	-153	-96	157
C(4)-O(2)-C(5)-C(6)	94	163	-178	-180
O(2)-C(5)-C(6)-N(2)	-68	-58	-57	42
N(1)-C(7)-C(8)-O(3)	-76	c	-58	-48
C(7)-C(8)-O(3)-C(9)	90		-161	-130
C(8)-O(3)-C(9)-C(10)	174		-82	155
O(3)-C(9)-C(10)-O(4)	-178		-53	49
C(9)-C(10)-O(4)-C(11)	-172		-155	142
C(10)-O(4)-C(11)-C(12)	173		177	-148
O(4)-C(11)-C(12)-N(2)	-69		-34	-35
N(1)-C(13)-C(14)-O(5)	-67	c	-33	47
C(13)-C(14)-O(5)-C(15)	109		172	176
C(14)-O(5)-C(15)-C(16)	178		-149	144
O(5)-C(15)-C(16)-O(6)	179		-52	46
C(15)-C(16)-O(6)-C(17)	-176		-78	135
C(16)-O(6)-C(17)-C(18)	155		-164	-151
O(6)-C(17)-C(18)-N(2)	-68		-59	-47

^a Defined as the angle,¹⁴ measured counterclockwise, that the projection of bond A-B makes relative to the bond C-D when viewed along the direction B-C. Estimated standard deviations are about 1°. ^b A renumbering of atoms from other papers has been made in order to compare with the present work. Of necessity this is somewhat arbitrary because there is no way to distinguish between the N atoms or among the different strands of the ligands. ^c All three strands are identical because of threefold symmetry.

measured, but it is probably small in view of the strains induced by formation of these molecule ions.

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Registry No. $(\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2)\text{Sm}_2(\text{NO}_3)_6\cdot\text{H}_2\text{O}$, 71425-97-3.

Supplementary Material Available: A listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of the Mono- and Bis(triphenylphosphine)-Substituted Derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$. Effect of Phosphine Ligand Substitution on the Co_2As_2 Metal Cluster System¹

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The tricyclic dinuclear $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ complex and its mono- and bis(triphenylphosphine)-substituted derivatives have been prepared and characterized. Single-crystal X-ray diffraction analyses of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ have confirmed the postulated $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ -type geometry for the Co_2As_2 core and have revealed short As-As bond lengths of 2.273 (3) and 2.281 (3) Å, respectively, which is interpreted as an indication of significant As_2 multiple-bond character. A comparison of the molecular parameters for both of these derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ demonstrates that the tricyclic Co_2As_2 core remains largely unperturbed by the replacement of an axial carbonyl ligand with a triphenylphosphine ligand. Crystals of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ are triclinic, space group $P\bar{1}$, with $a = 11.391$ (8) Å, $b = 13.033$ (9) Å, $c = 9.120$ (7) Å, $\alpha = 108.17$ (1)°, $\beta = 103.84$ (1)°, and $\gamma = 74.22$ (1)°; $\rho_{\text{obsd}} = 1.82$ g/cm³ vs. $\rho_{\text{calcd}} = 1.80$ g/cm³ for $Z = 2$. Least-squares refinement gave $R_1(F) = 7.3\%$ and $R_2(F) = 7.4\%$ for 1911 independent reflections with $I > 2\sigma(I)$. Crystals of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ are monoclinic, space group C2, with $a = 12.685$ (5) Å, $b = 14.660$ (6) Å, $c = 10.107$ (4) Å, and $\beta = 97.73$ (1)°; $\rho_{\text{obsd}} = 1.59$ g/cm³ vs. $\rho_{\text{calcd}} = 1.61$ g/cm³ for $Z = 2$. Least-squares refinement gave $R_1(F) = 4.7\%$ and $R_2(F) = 5.3\%$ for 1093 independent observed reflections with $I > 2\sigma(I)$.

Introduction

$\text{Co}_2(\text{CO})_6\text{As}_2$ is a member of the homologous series $\text{As}_{4-n}[\text{Co}(\text{CO})_3]_n$ ($n = 0-4$) in which the arsenic atoms of the tetrahedral As_4 molecule are successively replaced by electronically equivalent $\text{Co}(\text{CO})_3$ moieties. The $\text{Co}_2(\text{CO})_6\text{As}_2$

complex was prepared from the reaction of $\text{Co}_2(\text{CO})_8$ with AsCl_3 .⁵ The molecular formula of this red, air-sensitive liquid (mp -10 °C) was determined from mass spectral analysis, and its diamagnetism was established by the NMR method. On the basis of the close similarity of the infrared spectrum of

$\text{Co}_2(\text{CO})_6\text{As}_2$ with that of the previously characterized $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ complex,⁶ a C_{2v} - $2mm$ $\text{Fe}_2(\text{CO})_6\text{S}_2$ -type geometry was proposed for $\text{Co}_2(\text{CO})_6\text{As}_2$. The molecular structure of this complex was established by the successful preparation and structural characterization of the monosubstituted triphenylphosphine derivative $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$.⁵ In addition to confirming the postulated $\text{Fe}_2(\text{CO})_6\text{S}_2$ -type geometry for the Co_2As_2 core, this structural determination revealed a short As-As bond length of 2.273 (3) Å, which was interpreted as evidence of significant As_2 multiple-bond character.

The subsequent preparation of the bis-substituted derivative $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ afforded an opportunity to assess the effects of the replacement of a second axial carbonyl ligand with a triphenylphosphine ligand. Infrared spectra for $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ and its mono- and bis(triphenylphosphine) derivatives indicate that the idealized C_{2v} $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ -type geometry is maintained in solution as well as in the solid state; however, there is a pronounced decrease in the carbonyl stretching frequencies with increased triphenylphosphine substitution. While the infrared spectra for these three complexes are not strictly comparable from symmetry considerations, the observed lowering of the carbonyl stretching frequencies provides evidence that the replacement of a π -acidic carbonyl ligand with a much better electron donating triphenylphosphine ligand brings about an electron redistribution which results in the net transfer of more electron density into the π^* orbitals of the remaining carbonyl ligands, thereby reducing their force constants and hence their stretching frequencies. Since some of the metal orbitals involved in bonding with the carbonyl ligands also interact strongly with the π -type orbitals of the bridging As_2 group, it was thought that an increase in metal back-bonding into the As_2 π^* orbitals resulting from triphenylphosphine substitution might have an appreciable bond-lengthening effect on the As_2 group. Single-crystal X-ray diffraction determinations have been carried out on both the $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ complexes in order to assess from a comparative analysis the effect of triphenylphosphine substitution on the geometry of the Co_2As_2 core and on the As-As bond length in particular.

Experimental Section

Preparation and Reactions. Unless otherwise stated, all manipulations were carried out under oxygen-free nitrogen in deaerated solvents. The preparations described below are typical in that a given reaction was carried out more than once, sometimes under slightly different reaction conditions.

Preparation of $\text{Co}_2(\text{CO})_6(\mu\text{-As})$. Method A. One gram of $\text{Co}_2(\text{CO})_8$ (Strem Chemical Co.) was dissolved in 150 mL of freshly distilled tetrahydrofuran. One milliliter of anhydrous AsCl_3 (ROC/RIC Chemical Co.) was added dropwise over a period of 1 h with vigorous stirring, which was continued for 24 h. As the reaction proceeded, carbon monoxide gas was slowly evolved, the solution became dark red, and a small amount of cobalt chloride precipitated. The reaction mixture was evaporated to dryness at room temperature and the residue extracted with hexane. The product was purified by chromatography on a silica gel column, from which the $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ was eluted with hexane. Large platelike crystals of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ were grown from a saturated hexane solution at -20°C .

Method B. Ten grams of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 3.98 g of As_2O_3 , and 100 mL of methanol were placed in an autoclave under 200 atm of CO and 100 atm of H_2 at 150°C for 2 days. This method, which produced a good yield of the desired product with very little solid residue, appears to provide an suitable method for a large-scale production of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$.

Preparation of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$. A benzene solution of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ and a slight excess of $\text{P}(\text{C}_6\text{H}_5)_3$ were refluxed for 10 h. The resulting red solution was evaporated to dryness, the residue extracted with hexane, and the extract chromatographed on a silica gel column. Elution with pure hexane removed a small amount of unreacted $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ while elution with 3:1 hexane/benzene

removed a deep red band, from which crystals of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ were grown by slow evaporation at -10°C .

Preparation of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$. $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ was prepared by the prolonged (>15 h) refluxing of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ in benzene with a large excess of triphenylphosphine. The resulting solution contained a combination of unreacted $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$, the monosubstituted $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$, and the bis-substituted $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$. These compounds were separated from each other by column chromatography on a silica gel-hexane column. Unreacted $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ was first eluted with hexane, followed by the elution of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ with 3:1 and 1:1 hexane-benzene solutions, respectively. Dark red crystals of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ suitable for X-ray examination were obtained by slow evaporation from an octane-hexane solution at -10°C .

Infrared Spectra. A high-resolution infrared spectrum (*n*-hexane solution) of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ exhibits carbonyl stretching frequencies at 2093.5 (m), 2058.0 (vs), 2039.0 (s), 2034.0 (s), and 2021.0 (mw) cm^{-1} . A high-resolution infrared spectrum (*n*-hexane solution) of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ contains bands at 2066.7 (s), 2021.9 (s), 2016.3 (s), 1999.6 (w), and 1978.4 (w) cm^{-1} , while a low-resolution, solid-state (KBr pellet) infrared spectrum of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ exhibits carbonyl bands at 2010 (vs), 1970 (vs), and 1955 (s) cm^{-1} .

X-ray Data Collection. (a) $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$. Single crystals of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ were grown as noted above. The external features of these crystals indicated no specific symmetry, and the Laue symmetry of several crystals examined by oscillation, Weissenberg, and precession photographs was no higher than C_2 . Reduced triclinic cell parameters were derived^{7a} from the lattice parameters obtained by film methods, and the reduction process indicated no additional symmetry. A suitable single crystal was then centered in the X-ray beam of a General Electric four-circle automated diffractometer.^{7b}

Lattice parameters and instrument constants were acquired^{7c,d} from the setting angles of 27 carefully centered reflections, and intensity data (all eight octants) were collected for $2\theta < 40^\circ$ with Zr-filtered Mo K α radiation (λ 0.710 69 Å). Symmetric 2θ scans of 2.0° were used with 10-s background counts at the start and finish of each scan. Four standard reflections were observed after every 100 reflections and scale factors calculated from the observed intensities of these standards did not vary by more than 1.2% about their mean during the entire data collection. The 4491 observed diffraction maxima were corrected for Lorentz-polarization^{7e} effects and then were merged^{7f} to give 1911 independent reflections with $|F_o| > 4\sigma(F_o)$. No absorption correction was applied, since the crystal was lost after data collection before the appropriate measurements were made. Although the linear absorption coefficient for $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ is 45.5 cm^{-1} for Mo K α radiation, the equant habit of the crystal reduces the importance of such a correction.

The measured lattice constants (22°) and estimated standard deviations for the triclinic unit cell of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ are $a = 11.391$ (8) Å, $b = 13.033$ (9) Å, $c = 9.120$ (7) Å, $\alpha = 108.17$ (1) $^\circ$, $\beta = 103.84$ (1) $^\circ$, $\gamma = 74.22$ (1) $^\circ$; $V = 1174$ Å³. The calculated density for two molecules per unit cell is 1.80 g/cm^3 which agrees well with the experimental (floatation) value of 1.82 g/cm^3 .

(b) $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$. A large crystal of approximate dimensions 0.25 mm \times 0.70 mm \times 0.40 mm was glued to a glass fiber with epoxy cement. The crystal was aligned along the a axis of a triclinic unit cell with approximate lattice parameters of $a = 11.32$ Å, $b = 20.38$ Å, $c = 17.25$ Å, $\alpha = 106.5^\circ$, $\beta = 92.5^\circ$, and $\gamma = 77.5^\circ$. The systematic absences observed on preliminary Weissenberg and precession photographs for $\{hkl\}$ data were $h + k \neq 2n$, $h + l \neq 2n$, and $k + l \neq 2n$, corresponding to an F -centered triclinic lattice. The crystal was transferred to a General Electric XRD-6 Datex-controlled diffractometer equipped with a full-circle E&A goniometer. After a careful optical and X-ray alignment of the crystal was made, 16 reflections were manually centered^{7b} and used in a least-squares refinement^{7c} to determine the lattice constants and orientation parameters from which the angle settings of all data were generated.^{7d} Intensity data were collected by the θ - 2θ scan technique at a takeoff angle of 2° with constant speed scans of $2^\circ/\text{min}$ in 2θ . Symmetric scan widths of 3.0° in 2θ were used for $5^\circ \leq 2\theta \leq 10^\circ$, 2.0° for $10^\circ < 2\theta \leq 20^\circ$, and 1.5° for $20^\circ < 2\theta < 45^\circ$. (Stationary crystal)-(stationary counter) background measurements were done for 20 s

at both extremes of each scan range. Zirconium-filtered Mo $K\alpha$ radiation (λ 0.71069 Å) was used with a scintillation detector, followed by a pulse-height analyzer adjusted to accept about 90% of the Mo $K\alpha$ pulse distribution. Intensity data from ca. 2400 nonsystematically absent reflections were measured twice for an asymmetrical unit of hkl , $h\bar{k}l$, $hk\bar{l}$, and $\bar{h}\bar{k}l$ in the F -centered triclinic reciprocal lattice, during which time four standard reflections were measured every 100 reflections. The intensities of each of these standards decreased linearly by ca. 10% over the total data collection time.

Structure factors were calculated from intensity data by means of the data reduction program DREDGE⁷⁶ in which the intensities (I) were corrected for background and Lorentz-polarization effects. Reflections were considered observed for $I > 2\sigma(I)$. The data were corrected for the above-mentioned linear decay and then merged⁷⁷ to yield 2083 independent observed reflections for the triclinic unit cell. The data were corrected for absorption effects⁷⁸ on the basis of a calculated linear absorption coefficient, μ , of 28.26 cm^{-1} for Mo $K\alpha$ radiation⁷⁹ with extreme values of transmission coefficients ranging from 0.47 to 0.51.

Transformation of the data to the conventional reduced primitive triclinic unit cell,^{7a} followed by a systematic examination of intensities, revealed that the true unit cell was a C -centered monoclinic cell having dimensions of $a = 12.685$ (5) Å, $b = 14.660$ (6) Å, $c = 10.107$ (4) Å, and $\beta = 97.71$ (1)° with a unit cell volume of 1863 Å³. The observed density measured by the flotation method, 1.59 g/cm^3 , is in agreement with a calculated density of 1.61 g/cm^3 for $Z = 2$. The total number of electrons per unit cell, $F(000)$, is 904.

Solution and Refinement of Structures. (a) $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$. An examination of the Patterson function calculated^{7h} from the merged data revealed trial coordinates for the $\text{Co}_2\text{As}_2\text{P}$ portion of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ which was consistent with the space group $P\bar{1}$. Two successive electron density maps calculated^{7h} on the basis of this model revealed the positions of all remaining nonhydrogen atoms (the 18 phenyl carbon, 5 carbonyl carbon, and 5 carbonyl oxygen atoms). Two cycles of isotropic full-matrix least-squares refinement⁷ⁱ reduced the conventional residuals to $R_1(F) = 14.2\%$ and $R_2(F) = 14.4\%$.⁹ Four more cycles of full-matrix least-squares refinement⁷ⁱ were performed with anisotropic thermal parameters for the $\text{Co}_2\text{As}_2\text{P}$ fragment and isotropic temperature factors for all carbon and oxygen atoms. In this refinement, each phenyl ring (with hydrogen atoms) was also constrained to its well-known geometry.⁷ⁱ This calculated model lowered the residuals to $R_1(F) = 7.3\%$ and $R_2(F) = 7.4\%$.

Table I lists the output positional and thermal parameters from the final cycle of least-squares refinement. Interatomic distances and bond angles with standard deviations, calculated with the Busing-Martin-Levy ORFFE program,^{7k} are listed in Table II. Selected least-squares planes^{7l} are given in Table III. The observed and calculated structure factor amplitudes are available as supplementary material.

(b) $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$. The heavy-atom method applied to a computed three-dimensional Patterson synthesis^{7h} revealed initial coordinates for the cobalt, arsenic, and phosphorus atoms. Subsequent Fourier syntheses^{7h} established the positions for all remaining nonhydrogen atoms. The structure was refined by a least-squares technique⁷ⁱ to values of $R_1(F) = 7.7\%$ and $R_2(F) = 8.9\%$,⁹ with positional and isotropic thermal parameters for all nonhydrogen atoms being varied. At this point, hydrogen atoms were fitted to phenyl rings in idealized positions.⁷ⁱ The refinement was continued with all nonphenyl atoms varied anisotropically and all phenyl carbon atoms varied isotropically. Hydrogen atoms were given fixed isotropic temperature factors of 5.0 Å², and their idealized coordinates were recalculated after each least-squares cycle.⁷ⁱ Anomalous dispersion corrections were made for As ($\Delta f' = -0.1$, $\Delta f'' = 2.2$), Co ($\Delta f' = 0.4$, $\Delta f'' = 1.1$), and P ($\Delta f' = 0.1$, $\Delta f'' = 0.2$),^{8b} and residuals for hkl and $\bar{h}\bar{k}l$ were compared to determine the correct enantiomer. A final full-matrix least-squares refinement⁷ⁱ cycle, in which all nonhydrogen parameters were varied, yielded discrepancy values of $R_1(F) = 4.7\%$ and $R_2(F) = 5.3\%$ with no Δ/σ values greater than 0.5 and with a goodness-of-fit value of 1.83 for 1093 independent observed monoclinic data. The minimum data-to-parameter ratio throughout the refinement was 8:1. A final Fourier difference map showed no unusual features, with the largest peak maximum being only 0.3 $e/\text{Å}^3$.^{7h} The atomic scattering factors for all nonhydrogen atoms are from Cromer and Mann,¹⁰ while those for hydrogen atoms are from Stewart et al.¹¹

The positional and thermal parameters from the output of the final full-matrix least-squares refinement are given in Table IV. Interatomic distances and bond angles with estimated standard deviations, calculated with the Busing-Martin-Levy ORFFE program,^{7k} are listed in Table V. Selected least-squares planes^{7l} are given in Table VI. The observed and calculated structure factor amplitudes are available as supplementary material.

Results and Discussion

The crystal structures of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ reveal significant distortions of the Co_2As_2 cores of these molecules from the C_{2v} - $2mm$ geometry which the parent $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ complex is presumed to possess. In both the mono- and bis-substituted derivatives, triphenylphosphine substitution has occurred at the axial positions trans to the electron-pair Co-Co bond.

The localized environment about each cobalt atom in these dimeric complexes may be described (with the neglect of cobalt-cobalt bonding) as a distorted tetragonal pyramid with two equatorial carbonyl ligands and two bridging arsenic atoms at the corners of the basal plane and either an axial carbonyl ligand or a triphenylphosphine ligand at the apex. The cobalt atoms are displaced by 0.31–0.36 Å out of the mean basal planes toward the apical ligands. The dinuclear cobalt molecules arise from the junction of the basal planes of two tetragonal pyramids along the As-As line at sharp dihedral angles of 58.4 and 57.8° in the mono and bis derivatives, respectively. The resulting six-coordination about each cobalt atom can be viewed conceptually as octahedral-like with a "bent" Co-Co bond occupying the sixth coordination site.

The mono-substituted $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ complex crystallizes with two discrete molecules in a $P\bar{1}$ unit cell. Although the Co_2As_2 core of this molecule nearly possesses C_{2v} - $2mm$ symmetry, the actual site symmetry of the entire molecule is C_1 -1. The crystal structure of this complex exhibits three significant distortions from C_{2v} - $2mm$ symmetry which are illustrated by the interatomic distances. The first distortion involves a twisting of the $\text{Co}(\text{CO})_3$ fragment about the Co-Co internuclear line which results in significantly different nonbonding contacts of C(2)···As(1) (3.03 Å) vs. C(3)···As(2) (3.23 Å) and of C(1)···As(1) (3.15 Å) vs. C(1)···As(2) (2.97 Å). The second distortion may be viewed as a symmetrical translation of the As_2 fragment away from Co(1) and toward Co(2) which results in the average bond length of 2.37 Å for both As-Co(2) bonds being significantly smaller than the average bond length of 2.41 Å for both As-Co(1) bonds. The third distortion may be viewed as an independent motion of C(2) and O(2) away from Co(2) which is illustrated by the approximate equivalence of the C(3)···Co(2), C(4)···Co(1), and C(5)···Co(1) nonbonding distances (3.22–3.26 Å) compared with the much longer C(2)···Co(2) distance (3.41 Å).

The bis-substituted $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ complex crystallizes in the monoclinic space group $C2$ with two molecules per unit cell with each molecule located on a crystallographic twofold axis (Figure 1). Although the configuration of the entire $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ molecule (with the phenyl rings included) is of C_2 - 2 symmetry, the Co_2As_2 core is of approximate C_{2v} - $2mm$ geometry. The crystal structure of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ indicates that the solid-state geometry of the molecule deviates substantially from the idealized C_{2v} - $2mm$ geometry. The nature of these distortions from the ideal geometry is clearly illustrated in Figure 2 which shows that the $\text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ fragment has been twisted about the Co-Co internuclear line resulting in the significantly different nonbonding contacts of C(1)···As(1) (2.89 Å) vs. C(2)···As(1') (3.28 Å) and of P(1)···As(1) (3.70 Å) vs. P(1)···As(1') (3.41 Å). The appreciable degree of distortion on the molecule from ideal C_{2v} geometry is also revealed by a comparison of perpendicular distances of equivalent atoms (under assumed C_{2v} symmetry) from the two

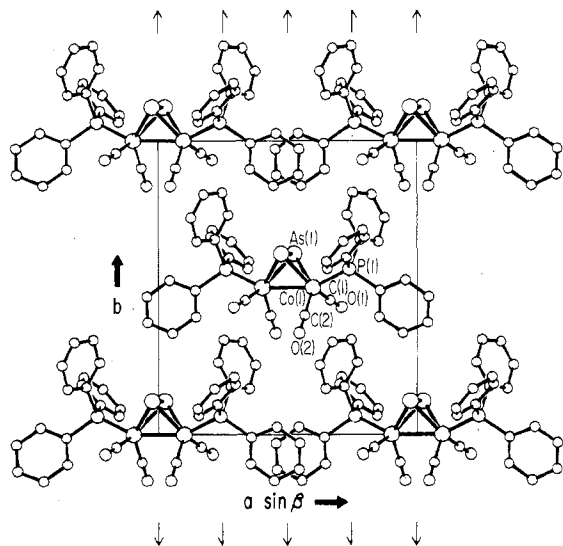


Figure 1. [001] projection showing two $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ molecules in a unit cell of C_2 symmetry.

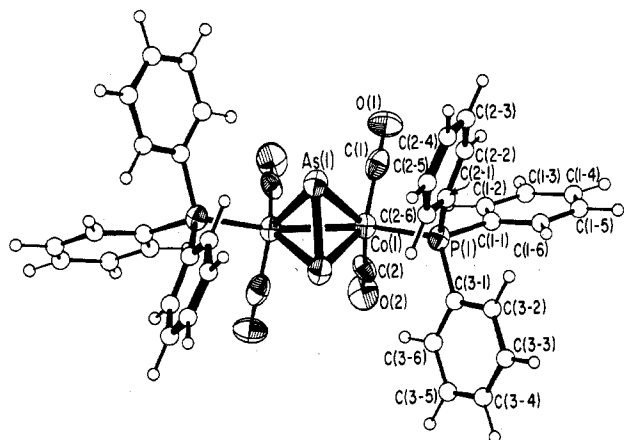


Figure 2. View of the $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ molecule illustrating the crystallographically imposed C_2 molecular symmetry.

molecular mirror planes²⁰ (Table III, planes B and C) which are approximately perpendicular to each other (dihedral angle 90.8°). As a result of the above twisting distortion, the phosphorus atoms lie 0.36 \AA out of the plane defined by the two cobalt atoms and the midpoint of the arsenic-arsenic bond. In addition to the above distortion, a much smaller type of distortion involves a slight twisting of the As-As fragment with respect to the Co-Co fragment about the crystallographic twofold axis, resulting in slightly different cobalt-arsenic distances for Co(1)-As(1) ($2.406(2) \text{ \AA}$) and Co(1)-As(1') ($2.389(2) \text{ \AA}$). These distortions from the idealized C_{2v} geometry expected for the parent $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ complex are thought to result from the steric effects of the large triphenylphosphine ligands.

A high-resolution infrared spectrum of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ exhibits carbonyl stretching frequencies at 2093.5 (m), 2058.0 (vs), 2039.0 (s), 2034.0 (s), and 2021.4 (mw) cm^{-1} , while a similar spectrum for $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ ¹² exhibits carbonyl stretching frequencies at 2083.5 (s), 2043.5 (vs), 2007.0 (s), and 1991.0 (mw) cm^{-1} .¹²⁻¹³ The close similarity in the infrared spectra of these two compounds allows the gross $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ geometry to be assigned with confidence as the solid-state C_{2v} $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ -type structure, which has been shown on the basis of dipole moment and infrared spectral analysis¹⁴ to remain unchanged for solutions of $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$. A high-resolution infrared spectrum (*n*-hexane so-

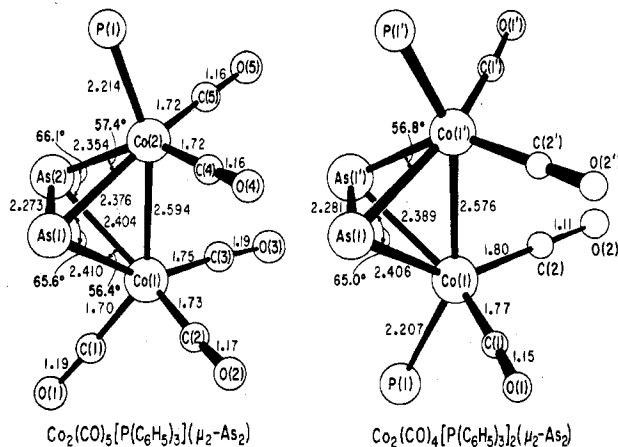


Figure 3. Comparison of the geometries of the $\text{Co}_2(\text{CO})_{6-n}(\text{P})(\mu\text{-As}_2)$ fragments of the $\text{Co}_2(\text{CO})_{6-n}[\text{P}(\text{C}_6\text{H}_5)_3]_n(\mu\text{-As}_2)$ molecules ($n = 1, 2$).

lution) for $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ exhibits bands at 2066.7 (s), 2021.9 (s), 2016.3 (s), 1999.6 (w), and 1978.4 (m) cm^{-1} , while a low-resolution, solid-state (KBr pellet) infrared spectrum for $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ exhibits carbonyl stretching frequencies at 2010 (vs), 1970 (vs), and 1955 (s) cm^{-1} . Although these spectra for $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ and its mono- and bis(triphenylphosphine) derivatives are not strictly comparable, an apparent decreasing trend in the carbonyl stretching frequencies with triphenylphosphine substitution is consistent with an increase in the degree of back-bonding into the remaining carbonyl π^* orbitals as π -acceptor carbonyl ligands are replaced by strong σ -donor ligands, such as triphenylphosphine.

In both the mono- and bis(triphenylphosphine) derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$, the triphenylphosphine substitution has occurred at the axial positions (i.e., trans to the Co-Co bond). Phosphine substitution at the axial positions in these $\text{M}_2(\text{CO})_6(\mu\text{-X}_2)$ molecules is favored by both electronic and steric influences as a consequence of reduced competition with better π -accepting carbonyl ligands (electronic effect) and reduced steric hindrance involving the bulky $\text{P}(\text{C}_6\text{H}_5)_3$ group (steric effect). The previously characterized $\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2$,^{15,16} $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$,^{17,18} and $\text{Fe}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3][(\mu\text{-NC}_6\text{H}_{11})_2\text{C}=\text{NC}_6\text{H}_{11}]$ ¹⁹ complexes are analogous examples of complexes in which phosphine substitution takes place at positions trans to the metal-metal bond. In all of these complexes, the metal-metal distances are essentially identical with those of the corresponding unsubstituted parent molecules.

The close resemblance of the molecular configurations of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ is clearly illustrated in Figure 3, and a comparison of their molecular parameters is summarized in Table VII. The remarkable similarity of all comparable bond lengths and angles in these two complexes provides convincing evidence that the molecular geometry of the parent $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ molecule is not significantly perturbed by the replacement of axial carbonyl ligands by triphenylphosphine ligands. A similar example of the insensitivity of molecular geometry to triphenylphosphine substitution was provided by the recent structural determination of the $\text{Fe}_2(\text{CO})_6[(\mu\text{-NC}_6\text{H}_{11})_2\text{C}=\text{NC}_6\text{H}_{11}]$ ¹⁹ and its mono(triphenylphosphine) derivative,¹⁹ which revealed that within experimental error, the bond distances and angles in the derivative do not depart significantly from those in the parent molecule. These structural studies provide an experimental demonstration of the utility of triphenylphosphine substitution as a tool in the structural characterization of transition-metal-carbonyl complexes.

Table I. Atomic Parameters^a for $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$

A. Atomic Positional Parameters							
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
As(1)	0.3565 (1)	0.0476 (1)	0.8913 (2)	H(1-5)	0.3958	0.0985	0.5884
As(2)	0.2377 (2)	0.0469 (2)	0.0587 (2)	H(1-6)	0.2780	0.1811	0.3708
Co(1)	0.1397 (2)	0.0499 (2)	0.7951 (2)	C(2-1)	0.2425	0.4334	0.2943
Co(2)	0.2216 (2)	0.2144 (2)	0.0007 (2)	C(2-2)	0.1781	0.5089	0.2076
P	0.3401 (3)	0.3072 (3)	0.1985 (4)	C(2-3)	0.0938	0.6023	0.2728
C(1)	0.1471 (17)	0.9115 (17)	0.7442 (22)	C(2-4)	0.0739	0.6203	0.4248
O(1)	0.1514 (14)	0.8150 (13)	0.7171 (18)	C(2-5)	0.1383	0.5448	0.5115
C(2)	0.1465 (14)	0.0724 (13)	0.6208 (19)	C(2-6)	0.2226	0.4514	0.4463
O(2)	0.1475 (11)	0.0924 (10)	0.5050 (15)	H(2-2)	0.1937	0.4948	0.0889
C(3)	-0.0144 (16)	0.1049 (13)	0.8199 (19)	H(2-3)	0.0435	0.6612	0.2051
O(3)	0.1191 (12)	0.8608 (10)	0.1747 (14)	H(2-4)	0.0080	0.6933	0.4758
C(4)	0.2256 (12)	0.2784 (11)	0.8632 (16)	H(2-5)	0.1227	0.5589	0.6302
O(4)	0.2310 (10)	0.3243 (9)	0.7751 (12)	H(2-6)	0.2729	0.3925	0.5140
C(5)	0.0863 (16)	0.2746 (13)	0.0759 (19)	C(3-1)	0.4568	0.3569	0.1491
O(5)	-0.0057 (12)	0.3190 (10)	0.1232 (15)	C(3-2)	0.4785	0.4626	0.2248
C(1-1)	0.4295	0.2450	0.3563	C(3-3)	0.5769	0.4945	0.1974
C(1-2)	0.5518	0.2549	0.4168	C(3-4)	0.6537	0.4207	0.0944
C(1-3)	0.6179	0.2086	0.5389	C(3-5)	0.6321	0.3150	0.0187
C(1-4)	0.5619	0.1523	0.6007	C(3-6)	0.5337	0.2831	0.0461
C(1-5)	0.4396	0.1425	0.5402	H(3-2)	0.4185	0.5202	0.3053
C(1-6)	0.3735	0.1888	0.4180	H(3-3)	0.5938	0.5771	0.2566
H(1-2)	0.5956	0.2988	0.3686	H(3-4)	0.7307	0.4457	0.0730
H(1-3)	0.7135	0.2163	0.5862	H(3-5)	0.6921	0.2574	-0.0617
H(1-4)	0.6136	0.1161	0.6962	H(3-6)	0.5168	0.2005	-0.0130

B. Rigid Body Parameters ^b						
	<i>x</i> ₀	<i>y</i> ₀	<i>z</i> ₀	ϕ , rad	θ , rad	ρ , rad
C ₆ H ₅ (1)	0.4296 (8)	0.2451 (7)	0.3563 (9)	1.922 (5)	3.146 (5)	2.296 (5)
C ₆ H ₅ (2)	0.2426 (7)	0.4334 (7)	0.2944 (11)	-2.494 (7)	2.731 (6)	-1.973 (6)
C ₆ H ₅ (3)	0.4569 (7)	0.3569 (7)	0.1492 (10)	-2.936 (6)	2.458 (5)	-2.924 (7)

C. Anisotropic Temperature Factors ($\times 10^4$) ^c						
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	60 (2)	78 (2)	217 (3)	-11 (1)	-22 (2)	14 (2)
As(2)	167 (2)	97 (2)	178 (3)	-66 (2)	-33 (2)	58 (2)
P	56 (4)	66 (3)	103 (6)	-19 (3)	7 (4)	25 (4)
Co(1)	62 (2)	75 (2)	152 (4)	-30 (1)	-12 (2)	16 (2)
Co(2)	52 (2)	66 (2)	112 (3)	-24 (1)	6 (2)	20 (2)

D. Isotropic Temperature Factors						
atom	<i>B</i> , Å ²	atom	<i>B</i> , Å ²	atom	<i>B</i> , Å ²	
C(1)	7.6 (5)	C(1-1)	3.8 (3)	C(2-5)	7.6 (5)	
O(1)	10.9 (4)	C(1-2)	4.7 (3)	C(2-6)	5.7 (4)	
C(2)	5.6 (4)	C(1-3)	6.0 (4)	C(3-1)	3.4 (3)	
O(2)	7.7 (3)	C(1-4)	5.7 (4)	C(3-2)	4.5 (3)	
C(3)	5.8 (4)	C(1-5)	5.5 (4)	C(3-3)	5.7 (4)	
O(3)	7.8 (3)	C(1-6)	4.2 (3)	C(3-4)	5.8 (4)	
C(4)	4.3 (3)	C(2-1)	4.2 (3)	C(3-5)	5.7 (4)	
O(4)	6.1 (2)	C(2-2)	4.9 (3)	C(3-6)	4.4 (3)	
C(5)	6.0 (4)	C(2-3)	6.2 (4)	H(all)	5.0 (..) ^d	
O(5)	8.4 (3)	C(2-4)	7.0 (4)			

^a The standard deviation of the last significant figure is given in parentheses after the number. ^b Rigid body parameters are defined in ref 7i. ^c The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^d The phenyl hydrogen isotropic thermal parameters were assigned a fixed value of 5.0 Å².

The only significant difference (at the 99% probability level) between structures of the two Co_2As_2 -type complexes is the Co-Co distance. Whether this slight difference (0.018 Å) in the two Co-Co distances is a result of electron redistribution or is merely due to steric effects is difficult to assess. However, the analogous Co-Co bond lengths in these two Co_2As_2 complexes point to the possibility of any trans-directional influence being small.

The insensitivity of the molecular parameters of the M_2X_2 fragments of the $\text{M}_2(\text{CO})_6(\mu\text{-X}_2)$ complexes to triphenylphosphine substitution at the axial positions may be rationalized on electronic grounds. Molecular orbital calculations on $\text{M}_2(\text{CO})_6\text{X}_2$ systems²⁰ have shown that the molecular orbitals primarily responsible for metal-metal bonding contain very little (<3%) axial carbonyl character. It is therefore not

surprising to observe essentially the same metal-metal distance before and after substitution. Also, the molecular orbitals which are responsible for either the M-X or X-X interactions are essentially orthogonal to the axial terminal ligands, indicating again that substitution at the axial positions (trans to the bent metal-metal bond) should not affect the M_2X_2 fragment to any appreciable extent. The significant decrease in the carbonyl stretching frequencies after each triphenylphosphine substitution must be due to a net increase in the electron density at the metal atoms via substitution of a carbonyl ligand with a better σ donor but worse π acceptor, which raises the energy of the metal d orbitals, resulting in more π back-bonding to the other carbonyl ligands.

Prime stereochemical features of both the $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ molecules

Table II. Distances and Angles^a for Co₂(CO)₈[P(C₆H₅)₃](μ-As₂)

A. Bonding Distances (Å)			
As(1)-As(2)	2.273 (3)	As(1)-Co(2)	2.376 (3)
Co(1)-Co(2)	2.594 (3)	As(2)-Co(1)	2.404 (3)
As(1)-Co(1)	2.410 (3)	As(2)-Co(2)	2.354 (3)
Co(1)-C(1)			
Co(1)-C(2)	1.70 (2)	C(1)-O(1)	1.19 (2)
Co(1)-C(3)	1.73 (2)	C(2)-O(2)	1.17 (2)
Co(2)-C(4)	1.75 (2)	C(3)-O(3)	1.19 (2)
Co(2)-C(5)	1.72 (2)	C(4)-O(4)	1.16 (2)
Co(2)-P	2.214 (4)	C(5)-O(5)	1.16 (1)
		P-C ₆ H ₅ (1)	1.828
		P-C ₆ H ₅ (2)	1.811
		P-C ₆ H ₅ (3)	1.824
B. Bond Angles (deg)			
Co(1)-As(1)-Co(2)	65.6 (1)	As(1)-Co(1)-As(2)	56.4 (1)
Co(1)-As(2)-Co(2)	66.1 (1)	As(1)-Co(2)-As(2)	57.4 (1)
Co-As-Co	65.8 ^b	As-Co-As	56.9 ^b
Co(1)-As(1)-As(2)	60.8 (1)	As(1)-Co(1)-Co(2)	57.8 (1)
Co(1)-As(2)-As(1)	61.8 (1)	As(2)-Co(1)-Co(2)	57.9 (1)
Co(2)-As(1)-As(2)	61.6 (1)	As(1)-Co(2)-Co(1)	56.6 (1)
Co(2)-As(2)-As(1)	62.0 (1)	As(2)-Co(2)-Co(1)	56.0 (1)
Co-As-As	61.5 ^b	As-Co-Co	57.1 ^b

^a The standard deviation of the last significant figure is given in parentheses following the number. ^b Average values.

Table III. Distances (Å) of Atoms from Selected Least-Squares Planes^a in the Co₂(CO)₈P(μ-As₂) Fragment and Angles (deg) between the Normals of These Planes

A. Distances from the Plane Formed by As(1), As(2), C(2), and C(3)					
$-0.166X - 0.929Y - 0.332Z + 1.129 = 0$					
As(1)	-0.095	C(3)	-0.074	O(3)	-0.30
As(2)	0.090	Co(1)	0.32	C(1)	2.01
C(2)	0.079	O(2)	-0.13	O(1)	3.19
B. Distances from the Plane Formed by As(1), As(2), C(4), and C(5)					
$-0.616X - 0.179Y - 0.767Z + 2.173 = 0$					
As(1)	-0.017	C(5)	-0.014	O(5)	0.21
As(2)	0.017	Co(2)	-0.33	P	-2.52
C(4)	0.014	O(4)	0.20		
C. Distances from the Plane Formed by Co(1), Co(2), and the Midpoint of As(1)-As(2)					
$-0.755X + 0.187Y - 0.628Z - 2.979 = 0$					
As(1)	1.136	C(2)	1.47	C(4)	1.38
As(2)	-1.136	C(3)	-1.23	C(5)	-1.42
C(1)	-0.25	O(2)	2.44	O(4)	2.31
O(1)	-0.50	O(3)	-2.00	O(5)	-2.34
P	0.012				
D. Distances from the Plane Formed by As(1), As(2), and the Midpoint of Co(1)-Co(2)					
$-0.405X - 0.629Y - 0.664Z + 1.727 = 0$					
Co(1)	1.296	O(1)	3.69	O(2)	1.82
Co(2)	-1.296			O(4)	-1.62
C(1)	2.27	C(2)	1.63	C(3)	1.41
P	-3.36	C(4)	-1.46	C(5)	-1.48
				O(3)	1.56
				O(5)	-1.63
E. Angles between Normals to Planes					
A and B	58.4	B and C	90.9		
A and C	95.2	B and D	29.4		
A and D	29.3	C and D	90.4		

^a The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the fractional triclinic unit cell coordinate system (x, y, z) as follows: $X = xa + yb \cos \gamma + zc \cos \beta$, $Y = yb \sin \gamma + zc \cos \mu$, $Z = zc \cos \sigma$. In the transformations $\cos \mu = (\cos \alpha - \cos \beta \cos \gamma) / \sin \gamma$ and $\sin \sigma = (1 - \cos^2 \beta - \cos^2 \mu)^{1/2}$.

are the exceptionally short As-As bond lengths of 2.281 (3) and 2.273 (3) Å, respectively, which are the shortest known As-As bond lengths reported to date. These distances are

Table IV. Atomic Parameters^a for Co₂(CO)₈[P(C₆H₅)₃](μ-As₂)

A. Atomic Positional Parameters						
	x	y	z			
Co	0.0981 (1)	0.0000	0.0535 (1)			
As	0.0251 (1)	0.1139 (1)	-0.1042 (1)			
P	0.2391 (2)	0.0621 (2)	0.1712 (3)			
C(1)	0.1647 (12)	-0.0429 (10)	-0.0764 (15)			
O(1)	0.2088 (9)	-0.0665 (9)	-0.1633 (11)			
C(2)	0.0665 (10)	-0.0944 (10)	0.1545 (14)			
O(2)	0.0463 (8)	-0.1550 (8)	0.2125 (11)			
C(1-1)	0.3585 (9)	-0.0096 (9)	0.1951 (11)			
C(1-2)	0.3553 (11)	-0.0992 (10)	0.1541 (14)			
C(1-3)	0.4461 (12)	-0.1550 (12)	0.1707 (15)			
C(1-4)	0.5430 (13)	-0.1185 (12)	0.2317 (16)			
C(1-5)	0.5465 (14)	-0.0298 (13)	0.2713 (18)			
C(1-6)	0.4569 (12)	0.0248 (11)	0.2585 (15)			
H(1-2)	0.2788	-0.1287	0.1059			
H(1-3)	0.4411	-0.2260	0.1361			
H(1-4)	0.6134	-0.1620	0.2438			
H(1-5)	0.6233	-0.0006	0.3213			
H(1-6)	0.4610	0.0967	0.2911			
C(2-1)	0.2812 (10)	0.1624 (9)	0.0859 (12)			
C(2-2)	0.3523 (12)	0.1556 (12)	-0.0056 (15)			
C(2-3)	0.3754 (13)	0.2361 (13)	-0.0790 (17)			
C(2-4)	0.3256 (13)	0.3146 (12)	-0.0581 (16)			
C(2-5)	0.2539 (13)	0.3218 (12)	0.0263 (15)			
C(2-6)	0.2304 (11)	0.2455 (10)	0.1009 (13)			
H(2-2)	0.3934	0.0916	-0.0199			
H(2-3)	0.4341	0.2283	-0.1501			
H(2-4)	0.3439	0.3760	-0.1184			
H(2-5)	0.2128	0.3869	0.0435			
H(2-6)	0.1721	0.2502	0.1737			
C(3-1)	0.2276 (9)	0.1009 (9)	0.3403 (11)			
C(3-2)	0.2974 (11)	0.1710 (11)	0.4050 (14)			
C(3-3)	0.2915 (12)	0.1946 (11)	0.5379 (15)			
C(3-4)	0.2174 (13)	0.1549 (12)	0.6028 (15)			
C(3-5)	0.1502 (11)	0.0874 (10)	0.5470 (14)			
C(3-6)	0.1544 (11)	0.0640 (10)	0.4136 (13)			
H(3-2)	0.3556	0.2020	0.3477			
H(3-3)	0.3458	0.2474	0.5831			
H(3-4)	0.2133	0.1741	0.7099			
H(3-5)	0.0906	0.0554	0.6012			
H(3-6)	0.1003	0.0100	0.3657			
B. Anisotropic Temperature Factors (×10 ⁴) ^b						
	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Co	40 (1)	24 (1)	75 (2)	-1 (1)	1 (1)	0 (1)
As	56 (1)	35 (1)	97 (2)	-7 (1)	-2 (1)	16 (1)
P	46 (2)	25 (2)	78 (4)	-6 (2)	2 (2)	2 (2)
C(1)	65 (11)	44 (8)	104 (18)	-9 (8)	-11 (12)	-5 (10)
O(1)	102 (10)	89 (8)	117 (13)	12 (8)	46 (10)	-28 (9)
C(2)	45 (9)	34 (8)	113 (17)	-3 (7)	17 (10)	12 (10)
O(2)	80 (9)	49 (6)	194 (17)	0 (6)	11 (10)	40 (9)
C. Isotropic Temperature Factors						
atom	B, Å ²	atom	B, Å ²	atom	B, Å ²	
C(1-1)	3.1 (2)	C(2-1)	3.3 (3)	C(3-1)	3.2 (2)	
C(1-2)	4.1 (3)	C(2-2)	5.2 (4)	C(3-2)	4.4 (3)	
C(1-3)	5.1 (3)	C(2-3)	5.7 (4)	C(3-3)	5.1 (3)	
C(1-4)	5.5 (4)	C(2-4)	5.6 (4)	C(3-4)	5.1 (3)	
C(1-5)	6.5 (4)	C(2-5)	5.2 (4)	C(3-5)	4.6 (3)	
C(1-6)	5.3 (4)	C(2-6)	3.8 (3)	C(3-6)	3.9 (3)	
				H(all) ^c	5.0	

^a The standard deviation of the last significant figure is given in parentheses after the number. ^b The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^c The hydrogen thermal factors were assigned a fixed value of 5.0 Å².

0.16–0.19 Å shorter than the average As-As single-bond lengths found in gaseous As₄ (2.44 Å),²¹ [AsCH₃]₃ (2.428 (8) Å),²² and [AsC₆H₅]₃ (2.456 (5) Å),²³ and 0.10 Å shorter than the As-As distance found in Co(CO)₃As₃ (2.372 (5) Å).²⁴ The significant As-As bond-shortening trend on substitution of Co(CO)₃ groups in place of arsenic atoms in As₄ may be

Table V. Distances and Angles^a for $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$

A. Bonding Distances (Å)			
Co(1)-Co(1')	2.576 (3)	Co(1)-P(1)	2.207 (3)
As(1)-As(1')	2.281 (3)	P(1)-C(1-1)	1.833 (12)
Co(1)-As(1)	2.406 (2)	P(1)-C(2-1)	1.821 (14)
Co(1)-As(1')	2.389 (2)	P(1)-C(3-1)	1.826 (12)
Co(1)-C(1)	1.77 (2)	C(1)-O(1)	1.15 (2)
Co(1)-C(2)	1.80 (1)	C(2)-O(2)	1.11 (1)
C(1-1)-C(1-2)	1.38 (2)	C(1-2)-H(1-2)	1.11 (1)
C(1-2)-C(1-3)	1.40 (2)	C(1-3)-H(3-1)	1.10 (2)
C(1-3)-C(1-4)	1.40 (2)	C(1-4)-H(1-4)	1.09 (2)
C(1-4)-C(1-5)	1.36 (2)	C(1-5)-H(1-5)	1.12 (2)
C(1-5)-C(1-6)	1.38 (2)	C(1-6)-H(1-6)	1.10 (2)
C(1-6)-C(1-1)	1.42 (2)	C(2-2)-H(2-2)	1.09 (2)
C(2-1)-C(2-2)	1.38 (2)	C(2-3)-H(2-3)	1.11 (2)
C(2-2)-C(2-3)	1.45 (2)	C(2-4)-H(2-4)	1.13 (2)
C(2-3)-C(2-4)	1.34 (2)	C(2-5)-H(2-5)	1.11 (2)
C(2-4)-C(2-5)	1.33 (2)	C(2-6)-H(2-6)	1.11 (1)
C(2-5)-C(2-6)	1.40 (2)	C(3-2)-H(3-2)	1.10 (1)
C(2-6)-C(2-1)	1.40 (2)	C(3-3)-H(3-3)	1.09 (2)
C(3-1)-C(3-2)	1.45 (2)	C(3-4)-H(3-4)	1.13 (2)
C(3-2)-C(3-3)	1.40 (2)	C(3-5)-H(3-5)	1.10 (1)
C(3-3)-C(3-4)	1.35 (2)	C(3-6)-H(3-6)	1.12 (1)
C(3-4)-C(3-5)	1.38 (2)		
C(3-5)-C(3-6)	1.40 (2)		
C(3-6)-C(3-1)	1.37 (2)		

B. Bond Angles (deg)			
Co(1)-As(1)-Co(1')	64.98 (7)	As(1)-Co(1)-As(1')	56.81 (7)
Co(1)-As(1)-As(1')	61.20 (6)	As(1)-Co(1)-Co(1')	57.18 (5)
Co(1)-As(1)-As(1')	61.98 (6)	As(1)-Co(1)-Co(1')	57.84 (5)
Co(1)-C(1)-O(1)	177 (2)		
Co(2)-C(2)-O(2)	177 (2)		

^a The standard deviation of the last significant figure is given in parentheses after the number.

Table VI. Distances (Å) of Atoms from Selected Least-Squares Planes^a in the $\text{Co}_2(\text{CO})_4\text{P}_2(\mu\text{-As}_2)$ Fragment and Angles (deg) between the Normals of These Planes

A. Distances from the Plane Formed by As(1), As(1'), C(1), and C(2)					
$-0.732X - 0.453Y - 0.509Z + 0.767 = 0$					
As(1)	0.21	C(2)	0.14	O(2)	0.49
As(1')	-0.18	Co(1)	-0.36	P(1)	-2.56
C(1)	-0.16	O(1)	-0.06		

B. Distances from the Plane Formed by Co(1), Co(1'), and the Midpoint of As(1)-As(1')					
$-0.416X + 0.000Y - 0.909Z + 0.000 = 0$					
As(1)	1.14	O(1)	2.68	O(2)	-1.81
C(1)	1.61	C(2)	-1.14	P(1)	-0.39

C. Distances from the Plane Formed by As(1), As(1'), and the Midpoint of Co(1)-Co(1')					
$-0.915X + 0.000Y - 0.403Z + 0.000 = 0$					
Co(1)	-1.29	O(1)	-1.97	O(2)	-1.13
C(1)	-1.70	C(2)	-1.20	P(1)	-3.25

D. Angles between Normals to Planes			
A and B	80.9	B and C	90.8
A and C	28.9		

^a The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z), which is related to a monoclinic fractional unit cell coordinate system (x, y, z) by the transformation $X = xa + zc \cos \beta$, $Y = yb$, $Z = zc \sin \beta$.

rationalized from the premise that the more electronegative $\text{Co}(\text{CO})_3$ system effectively function as an "electron sink" which decreases the antibonding orbital character between the arsenic atoms by a partial charge transfer from the arsenic atoms to the $\text{Co}(\text{CO})_3$ system. A delocalized molecular orbital model incorporating this viewpoint has been utilized⁵ to explain the exceptional stability of the $\text{Co}(\text{CO})_3\text{As}_3$ molecule relative

Table VII. Comparison of Molecular Bond Lengths (Å) and Bond Angles (deg) $\text{Co}_2(\text{CO})_{6-n}[\text{P}(\text{C}_6\text{H}_5)_3]_n(\mu\text{-As}_2)$, Where $n = 1$ or 2

	$n = 1$	$n = 2$
Co-Co	2.594 (3)	2.576 (3)
Co-As	2.386 (3) ^a	2.398 (2) ^a
As-As	2.273 (3)	2.281 (3)
Co-C	1.72 (2) ^a	1.78 (2) ^a
C-O	1.17 (2) ^a	1.13 (2) ^a
Co-P	2.214 (4)	2.207 (4)
P-C	1.82 (1) ^a	1.83 (1) ^a
Co-As-Co	65.8 (1) ^a	65.0 (1) ^a
As-Co-As	56.9 (1) ^a	56.8 (1) ^a

^a The average value of the esd denotes the arithmetic mean of the individual esd's of the equivalent bond distances or angles.

to the As_4 molecule. The mean Co-As distances of 2.386 (3) and 2.398 (2) Å for the mono- and bis(triphenylphosphine) derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$, respectively, are intermediate between the average Co-As bond lengths reported for $\text{Co}(\text{CO})_3\text{As}_3$ (2.439 (5) Å)²⁴ and $[\text{Co}_3(\text{CO})_8\text{As}]_3$ (2.286 (5) Å).^{25,26} This decreasing trend in Co-As distances as successive arsenic atoms of the As_4 molecule are replaced by $\text{Co}(\text{CO})_3$ moieties is consistent with the above model, which predicts that as the number of arsenic atoms in the $\text{As}_{4-n}\text{Co}_n$ core decreases, all of the bonds involving the remaining arsenic atoms would be shortened as a result of the transfer of electron density to the $\text{Co}(\text{CO})_3$ moieties.

The short As-As distance in both $\text{Co}_2(\text{CO})_{6-n}[\text{P}(\text{C}_6\text{H}_5)_3]_n(\mu\text{-As}_2)$ complexes is interpreted as an indication of a high degree of As-As multiple-bond character. $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ and its triphenylphosphine derivatives are structurally and electronically related to the acetylene-bridged $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$ ²⁶ molecule in which the bridging acetylene C-C bond length of 1.37 Å^{26c} is near the normal C-C double-bond-length value of 1.33 Å. Although no (bond length)-(valence-bond order) curve exists for the As-As systems, it is presumed that the As-As distances in $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ and its triphenylphosphine derivatives correspond approximately to a double-bond length. This bond-length evidence indicates that there is an appreciable forward-bonding-back-bonding interaction which concomitantly results in a decrease of the total As-As bond order from *three* (as a neutral As_2 species) to approximately *two* upon coordination to the cobalt atoms. This decrease in the total As_2 bond order upon complexation arises as a result of a decrease in π bond order from *two* to roughly *one*. Such an overall decrease in π bond order may arise from two competing types of interactions: (1) the donation of electron density from the filled π orbitals of As_2 to the metal orbitals or (2) back-bonding involving the transfer of electron density from the metal orbitals into empty π^* orbitals of As_2 . Although both of these processes tend to decrease the π bond order, they transfer electron density in opposite directions. A synergic combination of these two processes provides a mechanism through which an electron may be transferred from the filled As_2 π orbitals to the empty As_2 π^* orbitals, resulting in a decrease in As_2 π bond order without any net transfer of charge to the metal atoms. The net result is an electron distribution which resembles the $^1\Sigma_u^+$ excited state of As_2 .

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Supplementary Material Available: Listings of structure factor amplitudes for $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ (21 pages). Ordering information is given on any current masthead page.

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Structural Characterization of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-P}_2)$: A Tricyclic Complex Containing a Bridging P_2 Ligand¹

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A three-dimensional single-crystal X-ray structural determination of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-P}_2)$, a mono(triphenylphosphine)-substituted derivative of $\text{Co}_2(\text{CO})_6(\mu\text{-P}_2)$, has revealed the first known example of a transition-metal complex with a diphosphide ligand symmetrically bonded to two metal atoms. Crystals of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-P}_2)$ are triclinic with space group $P\bar{1}$ and lattice constants $a = 10.467$ (3) Å, $b = 12.785$ (3) Å, $c = 10.186$ (3) Å, $\alpha = 108.76$ (2)°, $\beta = 99.80$ (2)°, and $\gamma = 82.10$ (2)°; $\rho_{\text{obsd}} = 1.50$ g/cm³ vs. $\rho_{\text{calcd}} = 1.53$ g/cm³ for $Z = 2$. Least-squares refinement gave $R_1(F) = 6.7\%$ and $R_2(F) = 7.4\%$ for 1532 independent reflections with $I > 2.5\sigma(I)$. The Co_2P_2 core of the molecule possesses an idealized C_{2v} geometry with a Co-Co bond distance of 2.574 (3) Å, a P-P bond length of 2.019 (9) Å, and an average Co-P bond length of 2.264 (5) Å. The molecular configuration of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-P}_2)$ is compared with those of $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ and $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$.

Introduction

A variety of organometallic complexes have been synthesized from the reactions of octacarbonyl dicobalt or the tetracarbonylcobaltate anion with phosphorus and various phosphorus-containing compounds.⁵⁻⁹ From the reaction of $\text{Co}(\text{CO})_4^-$ with PCl_3 in a THF solution, Markó and co-workers⁷ isolated an air-sensitive, red oil. The chemical analysis of this compound indicated that its molecular formula was $\text{Co}_2(\text{CO})_6\text{P}_2$. An infrared spectrum (*n*-hexane solution) of $\text{Co}_2(\text{CO})_6\text{P}_2$ exhibited carbonyl stretching frequencies at 2100.6 (m), 2066.3 (vs), 2045.5 (s), 2041.5 (s), and 2028.5

(mw) cm⁻¹. On the basis of the close similarity of the infrared spectra of $\text{Co}_2(\text{CO})_6\text{P}_2$ with those of the previously characterized $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ ¹⁰ and $\text{Co}_2(\text{CO})_6[\mu\text{-}(\text{CR})_2]$ ¹¹ complexes, they postulated a C_{2v} - $2mm$ $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ -type¹² geometry for $\text{Co}_2(\text{CO})_6\text{P}_2$.

Markó and co-workers⁷ prepared $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]\text{P}_2$, a monosubstituted triphenylphosphine derivative of $\text{Co}_2(\text{CO})_6\text{P}_2$, by refluxing a benzene solution of $\text{Co}_2(\text{CO})_6\text{P}_2$ with a twofold excess of $\text{P}(\text{C}_6\text{H}_5)_3$ for 3 h. An infrared spectrum (*n*-hexane solution) of this phosphine derivative exhibited carbonyl stretching frequencies at 2072.4 (s), 2027.1 (s),