University Research Committee.

Registry No. $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$, 59874-22-5; $Co_2(CO)_4[P(C_6H_5)_3]_2(\mu\text{-}As_2)$, 71341-70-3; $Co_2(CO)_6(\mu\text{-}As_2)$, 26202-29-9; $Co_2(CO)_8$, 10210-68-1; $AsCl_3$, 7784-34-1.

Supplementary Material Available: Listings of structure factor amplitudes for $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$ and $Co_2(CO)_4[P(C_6H_5)_3]_2(\mu\text{-}As_2)$ (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Presented in part at the national meeting of the American Crystallographic Association, Norman, OK, March 1978. (b) Based in part upon a dissertation submitted by C.F.C. to the Graduate School of the University of Wisconsin, Madison, in partial fulfillment of the requirements for the Ph.D. degree, December 1975.

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(5) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633–5.

(6) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1–11.

(7) Calculations were performed on a UNIVAC 1108 computer. Programs used included original or modified versions of: (a) Lawton, S. L.; Jacobson, R. A. "The Reduced Cell and Its Crystallographic Applications", Report IS-1141; Iowa State University: Ames, IA, 1965. (b) Furnas, T. C., Jr. "Single Crystal Orienter Instruction Manual"; General Electric Co.: Milwaukee, WI, 1957. (c) ANGSET, a local version of "Orientation and Angle Setting General Program", Program B-101; Argonne National Laboratory: Argonne, IL, 1965. (d) OLDANG, a local version of "Orientation and Angle Setting General Program", Program B-101; Argonne National Laboratory: Argonne, IL, 1965. (e) DREDGE, a Fortran program for diffractometer data reduction: Epstein, E. F. Ph.D. Thesis (Appendix), University of Wisconsin, Madison, 1969. (f) SORTMERGE, a Fortran program for the merging and decay correction of data: Calabrese, J. C. Ph.D. Thesis (Appendix I), University of Wisconsin, Madison, 1971. (g) DEAR, a local Fortran absorption correction program by J. F. Blount based on the method given by Busing and Levy: Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–2. (h) Blount, J. F. "A Three-Dimensional Crystallographic Fourier Summation Program", Ph.D. Thesis (Appendix), University of Wisconsin, Madison, 1965. (i) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS, A Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. (j) MIRAGE: Calabrese, J. C. Ph.D. Thesis (Appendix III), University of Wisconsin, Madison, 1971. (k) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, A Fortran Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964. (l) PLANES: Smith, D. L. Ph.D. Thesis (Appendix IV), University of Wisconsin Madison, 1962.

(8) (a) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, pp 157–162. (b) *Ibid*, pp 215–216.

(9) $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2 = [\sum w_i||F_o - F_c||^2/w_i|F_o|^2]^{1/2} \times 100$. Least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights $w_i = 1/\sigma(F_o)^2$.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A* **1968**, *24*, 321–5.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(12) Vizo-Orosz, A; Palyi, G.; Markő, L. *J. Organomet. Chem.* **1973**, *60*, 625–6.

(13) Bor, G. *J. Organomet. Chem.* **1975**, *94*, 181–8.

(14) Hieber, W.; Beck, W. *Z. Anorg. Allg. Chem.* **1960**, *305*, 265–70.

(15) Bennett, M. J.; Mason, R. *J. Chem. Soc. A* **1968**, 75–81.

(16) Powell, H. M., unpublished work cited in: Parker, D. J.; Stiddard, M. H. B. *J. Chem. Soc. A* **1965**, 695–9.

(17) Ibers, J. A. *J. Organomet. Chem.* **1968**, *14*, 423–8.

(18) Bryan, R. F.; Manning, A. R. *Chem. Commun.* **1968**, 1316.

(19) Teo, B. K. Ph.D. Thesis, University of Wisconsin, Madison, 1973.

(20) (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103–17. (b) Campana, C. F.; Dahl, L. F., unpublished results.

(21) Maxwell, L. R.; Hendricks, S. B.; Mosely, V. M. *J. Chem. Phys.* **1935**, *3*, 699–709.

(22) Burns, J. H.; Waser, J. *J. Am. Chem. Soc.* **1957**, *79*, 859–65.

(23) Hedberg, K.; Hughs, E. W.; Waser, J. *Acta Crystallogr.* **1961**, *14*, 369–74.

(24) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5631–3.

(25) (a) Foust, A. S.; Gall, R. S.; Dahl, L. F., to be submitted for publication. (b) Campana, C. F.; Dahl, L. F., to be submitted for publication.

(26) (a) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120. (b) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18–20. (c) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037–43.

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Structural Characterization of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$: A Tricyclic Complex Containing a Bridging P_2 Ligand[1]

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Received November 9, 1978

A three-dimensional single-crystal X-ray structural determination of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$, a mono(triphenylphosphine)-substituted derivative of $Co_2(CO)_6(\mu\text{-}P_2)$, has revealed the first known example of a transition-metal complex with a diphosphide ligand symmetrically bonded to two metal atoms. Crystals of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ 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)°; $\rho_{obsd} = 1.50$ g/cm^3 vs. $\rho_{calcd} = 1.53$ g/cm^3 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 $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ is compared with those of $Fe_2(CO)_6(\mu\text{-}S_2)$ and $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$.

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 $Co(CO)_4^-$ with PCl_3 in a THF solution, Markó and co-workers[7] isolated an air-sensitive, red oil. The chemical analysis of this compound indicated that its molecular formula was $Co_2(CO)_6P_2$. An infrared spectrum (*n*-hexane solution) of $Co_2(CO)_6P_2$ 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 $Co_2(CO)_6P_2$ with those of the previously characterized $Co_2(CO)_6(\mu\text{-}As_2)$[10] and $Co_2(CO)_6[\mu\text{-}(CR)_2]$[11] complexes, they postulated a C_{2v}-$2mm$ $Fe_2(CO)_6(\mu\text{-}S_2)$-type[12] geometry for $Co_2(CO)_6P_2$.

Markó and co-workers[7] prepared $Co_2(CO)_5[P(C_6H_5)_3]P_2$, a monosubstituted triphenylphosphine derivative of $Co_2(CO)_6P_2$, by refluxing a benzene solution of $Co_2(CO)_6P_2$ with a twofold excess of $P(C_6H_5)_3$ for 3 h. An infrared spectrum (*n*-hexane solution) of this phosphine derivative exhibited carbonyl stretching frequencies at 2072.4 (s), 2027.1 (s),

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2020.5 (s), 2006.8 (w), and 1984.2 (m) cm^{-1}, which is in complete analogy with similar spectra for the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$[10] and $Co_2(CO)_5[P(C_6H_5)_3][\mu\text{-}(CR)_2]$[13] complexes.

Previous X-ray structural studies on the electronically and structurally related $Co_2(CO)_6(\mu\text{-}(CC_6H_5)_2)$[14] and $Co_2(CO)_{6-n}[P(C_6H_5)_3]_n(\mu\text{-}As_2)$ (where n = 1[10] or 2[15]) complexes revealed short bridging C–C and As–As bond lengths at approximately double-bond distances which have been interpreted as an indication of signficant X–X multiple-bond character (where X is the metal-bonded atom of the bridging P_2, As_2, or $(CR)_2$ ligand).[10] By analogy to similar systems, the P–P distance in $Co_2(CO)_6(\mu\text{-}P_2)$ was expected to be in the range of a P–P double bond. An X-ray diffraction analysis of the monosubstituted triphenylphosphine derivative $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ has therefore been carried out to establish the molecular structure and thereby to determine experimentally the bridging distance as well as to detect any systematic deformation of the Co_2P_2 core due to the replacement of one of the two axial carbonyl groups with a triphenylphosphine ligand.

The $Co_2(CO)_6(\mu\text{-}P_2)$ molecule may be regarded as the first metal–carbonyl derivative of the P_2 molecule. This P_2Co_2-type complex is also structurally related to the electronically equivalent P_4, $P_3Co(CO)_3$,[9] $PCo_3(CO)_9$,[9] and $Co_4(CO)_{12}$[16] molecules as a dimetal derivative of P_4 in which the phosphorus atoms have been replaced by two $Co(CO)_3$ moieties. The $P_{4-n}[Co(CO)_3]_n$ (n = 0–4) series is electronically equivalent to the analogous As_4 series consisting of the As_4, $As_3Co(CO)_3$,[17] $As_2Co_2(CO)_6$,[10] $AsCo_3(CO)_9$, and $Co_4(CO)_{12}$[16] molecules.

Experimental Section

Single-Crystal Data Collection. $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ was prepared as described by Markó and co-workers.[7] Crystals suitable for X-ray analysis were grown by the slow evaporation of a pentane solution of the compound at −10 °C. A dark red crystal of approximate dimensions 0.16 mm × 0.28 mm × 0.40 mm in the [100], [010], and [001] directions, respectively, was used for the collection of X-ray intensity data. The crystal was glued to the inner wall of an argon-filled glass capillary with epoxy cement and mounted such that the *c* axis was nearly parallel to the goniometer axis. The crystal was then optically and X-ray aligned on a Nova-automated Syntex $P\bar{1}$ diffractometer. The angular coordinates of 15 reflections, which were carefully centered with Mo Kα radiation (with $\lambda(K\alpha_1)$ 0.709 26 Å, $\lambda(K\alpha_2)$ 0.713 54 Å), were least-squares refined to yield lattice parameters of a = 10.467 (3) Å, b = 12.785 (3) Å, c = 10.186 (3) Å, α = 108.76 (2)°, β = 99.80 (2)°, and γ = 82.10 (2)° for a reduced triclinic unit cell of $P\bar{1}$ symmetry (C_i^1—No. 2).[18] The experimental density of 1.50 g/cm^3, measured by the flotation method, is in accord with a value of 1.53 g/cm^3 calculated for a unit cell volume of 1266.9 (5) Å^3 containing two $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ formula species. All atoms occupy the general twofold set of positions (2*i*): $\pm(x, y, z)$.[17] The total number of electrons in the unit cell, $F(000)$, is 584.

Intensity data were collected via the θ–2θ scan mode with a scintillation counter and pulse-height analyzer adjusted to admit 90% of the Mo Kα peak. The Bragg 2θ angle for the highly oriented graphite-crystal monochromator was 12.2°, while a takeoff angle of 4° was used for the incident beam. Variable scan speeds with a minimum of 0.5°/min and variable scan widths based on the overall intensity and width of the peak were employed. A (stationary crystal)–(stationary counter) background measurement for half of the total scan time was made on each side of a peak. Two standard reflections were measured every 50 reflections to monitor instrument stability as well as crystal alignment and decay. Corrections were made for an observed 5% linear decrease in the standard intensities during the data collection period.

All independent reflections corresponding to four octants, hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$, of the intensity-weighted reciprocal lattice were collected for 3° ≤ 2θ ≤ 45°. After the data were corrected for background and Lorentz–polarization effects, the structure factor amplitudes were calculated[19a] and averaged.[19b] Of the 3531 reflections that were sampled, 1532 were considered observed with $I > 2.5\sigma(I)$. Since transmission coefficients varied from 0.65 to 0.78, an absorption correction[19c] was applied to the data with a linear absorption coefficient, μ, of 15.83 cm^{-1} for Mo Kα radiation (0.710 69 Å).[20a]

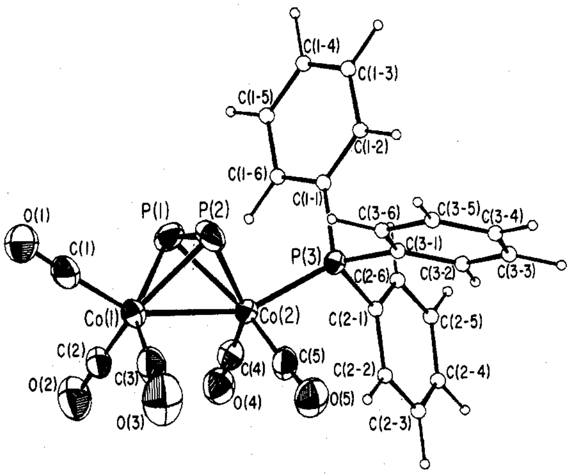


Figure 1. Configuration of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ molecule showing the atom-labeling scheme. Anisotropically refined atoms are represented by 30% thermal ellipsoids.

Structural Determination and Refinement. The heavy-atom method, applied to a three-dimensional Patterson synthesis,[19d] revealed initial positions for the cobalt and phosphorus atoms. Successive Fourier syntheses[19d] established the positions for all remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement[19e] with variation of only the positional parameters were followed by four more cycles with variable isotropic temperature factors to yield $R_1(F)$ = 15.6% and $R_2(F)$ = 17.9%.[21] The coordinates of the phenyl hydrogen atoms were fixed at idealized positions at 1.01 Å from their attached carbon atoms and recalculated after each cycle.[19f] Anomalous dispersion corrections were made for Co ($\Delta f'$ = 0.4, $\Delta f''$ = 1.1) and P ($\Delta f'$ = 0.1, $\Delta f''$ = 0.2).[20b] At this point all nonhydrogen atoms except the phenyl carbon atoms were assigned anisotropic thermal factors, and block-diagonal least-squares refinement[19e] was carried out until apparent convergence, followed by a final cycle of full-matrix least-squares refinement[19g] in which all nonhydrogen parameters were varied. The final discrepancy values were $R_1(F)$ = 6.7% and $R_2(F)$ = 7.4% with no Δ/σ values greater than 0.1 and with a final goodness-of-fit value of 1.65 for 1532 independent observed triclinic data. A final Fourier difference map[19d] showed no unusual features with the largest peak maximum being only 0.5 e/Å^3. The minimum data-to-parameter ratio throughout the refinement was 7:1. The atomic scattering factors for all nonhydrogen atoms are from Cromer and Mann,[22] while those for hydrogen atoms are from Stewart et al.[23]

The positional and thermal parameters from the output of the final full-matrix least-squares cycle are given in Table I. Interatomic distances and bond angles with estimated standard deviations, calculated with the Busing–Martin–Levy ORFFE[19h] program, are listed in Table II. Selected least-squares planes[19i] are given in Table III. The observed and calculated structure factor amplitudes are available as supplementary material.

Results and Discussion

The crystal structure of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ consists of the packing of discrete molecules with two centrosymmetrically related molecules per unit cell. The true geometry of each $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ molecule conforms to C_1-1. A perspective view of a single molecule showing the atom-labeling scheme is presented in Figure 1.

The skeleton of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ molecule is a completely bonded Co_2P_2 fragment which possesses an idealized C_{2v} geometry, as shown in Figure 2. The localized environment about each cobalt atom in this complex may be described (with the neglect of cobalt–cobalt bonding) as a distorted tetragonal pyramid with two equatorial carbonyl ligands and two bridging phosphorus atoms at the corners in the basal plane and with either an axial carbonyl ligand or a triphenylphosphine ligand at the apex. The cobalt atoms are perpendicularly displaced by 0.30 and 0.35 Å out of the mean

Table I. Atomic Parameters[a] for $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$

A. Atomic Positional Parameters

	x	y	z
Co(1)	0.1218 (2)	0.1093 (2)	−0.1985 (2)
Co(2)	0.2277 (2)	0.1890 (2)	0.0568 (2)
P(1)	0.1521 (7)	0.2914 (4)	−0.0869 (5)
P(2)	0.3148 (6)	0.1890 (5)	−0.1307 (5)
P(3)	0.3348 (4)	0.3132 (3)	0.2310 (3)
C(1)	0.0930 (20)	0.1120 (15)	−0.3718 (20)
O(1)	0.0805 (17)	0.1146 (13)	−0.4838 (14)
C(2)	−0.0359 (21)	0.1077 (16)	−0.1648 (20)
O(2)	−0.1412 (15)	0.1065 (17)	−0.1462 (19)
C(3)	0.1890 (19)	−0.0238 (16)	−0.2199 (17)
O(3)	0.2340 (15)	−0.1173 (12)	−0.2331 (15)
C(4)	0.0884 (20)	0.2013 (14)	0.1366 (17)
O(4)	−0.0016 (13)	0.2103 (12)	0.1921 (14)
C(5)	0.3169 (18)	0.0755 (16)	0.0762 (17)
O(5)	0.3828 (12)	−0.0067 (10)	0.0894 (13)
C(1-1)	0.4613 (12)	0.3749 (10)	0.1848 (12)
C(1-2)	0.4641 (13)	0.4894 (10)	0.2247 (13)
C(1-3)	0.5677 (14)	0.5285 (11)	0.1840 (15)
C(1-4)	0.6565 (14)	0.4589 (13)	0.1112 (14)
C(1-5)	0.6518 (15)	0.3467 (12)	0.0692 (15)
C(1-6)	0.5533 (14)	0.3033 (11)	0.1090 (14)
H(1-2)	0.3937	0.5449	0.2842
H(1-3)	0.5705	0.6212	0.2170
H(1-4)	0.7360	0.4932	0.0800
H(1-5)	0.7246	0.2889	0.0102
H(1-6)	0.5478	0.2127	0.0773
C(2-1)	0.4211 (13)	0.2540 (10)	0.3674 (13)
C(2-2)	0.3555 (14)	0.1885 (11)	0.4155 (15)
C(2-3)	0.4206 (15)	0.1456 (11)	0.5233 (15)
C(2-4)	0.5419 (16)	0.1667 (12)	0.5728 (16)
C(2-5)	0.6104 (15)	0.2304 (13)	0.5318 (16)
C(2-6)	0.5456 (14)	0.2739 (11)	0.4233 (14)
H(2-2)	0.2537	0.1716	0.3706
H(2-3)	0.3656	0.0935	0.5590
H(2-4)	0.5944	0.1317	0.6608
H(2-5)	0.7113	0.2480	0.5741
H(2-6)	0.5994	0.3262	0.3857
C(3-1)	0.2362 (13)	0.4307 (10)	0.3276 (13)
C(3-2)	0.2527 (14)	0.4714 (11)	0.4733 (14)
C(3-3)	0.1785 (15)	0.5603 (12)	0.5431 (15)
C(3-4)	0.0824 (16)	0.6123 (13)	0.4470 (17)
C(3-5)	0.0641 (17)	0.5745 (15)	0.3347 (20)
C(3-6)	0.1365 (17)	0.4814 (13)	0.2574 (17)
H(3-2)	0.3351	0.4275	0.5319
H(3-3)	0.1982	0.5903	0.6625
H(3-4)	0.0215	0.6846	0.5329
H(3-5)	−0.0184	0.6161	0.2726
H(3-6)	0.1185	0.4533	0.1420

B. Anisotropic Temperature Factors ($\times 10^4$)[b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	197 (4)	122 (2)	145 (3)	−64 (2)	−13 (3)	23 (2)
Co(2)	163 (3)	103 (2)	117 (3)	−43 (2)	7 (2)	35 (2)
P(1)	442 (13)	129 (5)	171 (7)	−115 (7)	−119 (8)	67 (5)
P(2)	302 (10)	273 (8)	134 (6)	−193 (8)	−23 (6)	67 (6)
P(3)	156 (6)	96 (3)	100 (4)	−31 (4)	1 (4)	34 (3)
C(1)	315 (35)	165 (20)	177 (29)	−105 (21)	−51 (28)	39 (21)
O(1)	467 (21)	292 (21)	179 (20)	−191 (20)	−98 (22)	84 (18)
C(2)	202 (35)	175 (22)	239 (32)	−38 (24)	62 (30)	−12 (20)
O(2)	197 (25)	380 (28)	408 (35)	−30 (22)	82 (26)	−8 (23)
C(3)	245 (34)	130 (19)	176 (25)	−59 (22)	67 (23)	−8 (20)
O(3)	358 (29)	178 (16)	293 (25)	11 (19)	56 (21)	14 (19)
C(4)	224 (33)	127 (17)	154 (25)	−4 (19)	54 (23)	12 (16)
O(4)	227 (24)	255 (19)	280 (25)	−61 (17)	99 (19)	22 (17)
C(5)	202 (30)	130 (19)	178 (25)	−21 (19)	75 (23)	26 (19)
O(5)	247 (22)	157 (15)	258 (21)	10 (14)	68 (17)	42 (16)

C. Isotropic Temperature Factors

atom	B, Å^2	atom	B, Å^2	atom	B, Å^2	atom	B, Å^2	atom	B, Å^2	atom	B, Å^2
C(1-1)	4.5 (3)	C(2-1)	5.0 (3)	C(3-1)	5.3 (3)	C(1-5)	7.2 (4)	C(2-5)	7.6 (4)	C(3-5)	9.7 (5)
C(1-2)	5.3 (3)	C(2-2)	6.6 (4)	C(3-2)	6.1 (3)	C(1-6)	5.9 (3)	C(2-6)	6.1 (3)	C(3-6)	8.2 (4)
C(1-3)	6.3 (3)	C(2-3)	6.9 (4)	C(3-3)	6.8 (4)	H(all)[c]	5.0				
C(1-4)	6.5 (3)	C(2-4)	7.3 (4)	C(3-4)	8.2 (4)						

[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 isotropic thermal parameter of each hydrogen atom was assigned a fixed value of 5.0 Å^2.

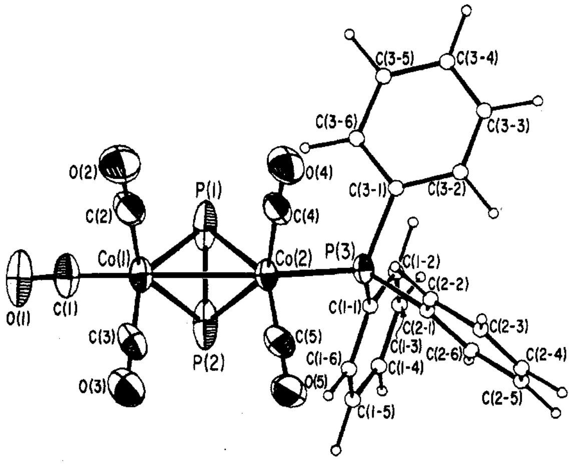


Figure 2. View of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ molecule illustrating the idealized C_s-m geometry of the $Co_2P(\mu\text{-}P_2)$ fragment (30% thermal ellipsoids).

basal planes toward the apical ligands (Table III, parts A and B). The dimeric molecule arises from the junction of the basal planes of these two pyramids along the P–P line at a sharp dihedral angle of 60.8° with the short Co–Co bonding distance causing a highly nonplanar Co_2P_2-bridged system of approximate C_{2v} symmetry. 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 Co_2P_2 fragment in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ is actually distorted slightly from C_{2v}-$2mm$ symmetry by a translation of the P_2 fragment away from Co(1) and toward the triphenylphosphine-substituted Co(2) which results in a smalll but nevertheless significant difference between the average bond lengths of 2.278 (5) Å for the two Co(1)–P distances and 2.249 (5) Å for the two Co(2)–P distances. This particular distortion of the Co_2P_2 core from an idealized C_{2v} to C_s-m geometry is presumed to be an effect of replacement of one of the axial carbonyl ligands of $Co_2(CO)_6(\mu\text{-}P_2)$ with a triphenylphosphine ligand. The well-known electron-donating ability of this phosphine ligand to Co(2) would presumably give rise to a relative increase in the amount of electron density back-bonded from Co(2) to the P_2 fragment which in turn would be expected to strengthen the Co(2)–P bonding interactions relative to the corresponding Co(1)–P

Table II. Distances and Angles[a] for $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2)$

A. Bonding Distances (Å)

Co(1)–Co(2)	2.574 (3)	Co(2)–P(3)	2.212 (4)
P(1)–P(2)	2.019 (9)		
Co(1)–P(1)	2.270 (5)	P(3)–C(1–1)	1.828 (12)
Co(1)–P(2)	2.286 (5)	P(3)–C(2–1)	1.803 (13)
Co(2)–P(1)	2.243 (5)	P(3)–C(3–1)	1.837 (13)
Co(2)–P(2)	2.255 (5)	av	1.823
av	2.264		
Co(1)–C(1)	1.75 (2)	C(1)–O(1)	1.14 (2)
Co(1)–C(2)	1.75 (2)	C(2)–O(2)	1.15 (2)
Co(2)–C(3)	1.71 (2)	C(3)–O(3)	1.19 (2)
Co(2)–C(4)	1.76 (2)	C(4)–O(4)	1.15 (2)
Co(1)–C(5)	1.66 (2)	C(5)–O(5)	1.20 (2)
av	1.73	av	1.17
C(1–1)–C(1–2)	1.39 (2)	C(1–2)–H(1–2)	1.07
C(1–2)–C(1–3)	1.43 (2)	C(1–3)–H(1–3)	1.07
C(1–3)–C(1–4)	1.34 (2)	C(1–4)–H(1–4)	1.13
C(1–4)–C(1–5)	1.36 (2)	C(1–5)–H(1–5)	1.12
C(1–5)–C(1–6)	1.41 (2)	C(1–6)–H(1–6)	1.10
C(1–6)–C(1–1)	1.38 (2)	C(2–2)–H(2–2)	1.11
C(2–1)–C(2–2)	1.40 (2)	C(2–3)–H(2–3)	1.11
C(2–2)–C(2–3)	1.41 (2)	C(2–4)–H(2–4)	1.15
C(2–3)–C(2–4)	1.31 (2)	C(2–5)–H(2–5)	1.09
C(2–4)–C(2–5)	1.35 (2)	C(2–6)–H(2–6)	1.12
C(2–5)–C(2–6)	1.42 (2)		
C(2–6)–C(2–1)	1.35 (2)	C(3–2)–H(3–2)	1.14
C(3–1)–C(3–2)	1.39 (2)	C(3–3)–H(3–3)	1.13
C(3–2)–C(3–3)	1.35 (2)	C(3–4)–H(3–4)	1.10
C(3–3)–C(3–4)	1.33 (2)	C(3–5)–H(3–5)	1.16
C(3–4)–C(3–5)	1.36 (2)	C(3–6)–H(3–6)	1.12
C(3–5)–C(3–6)	1.40 (2)		
C(3–6)–C(3–1)	1.37 (2)		

B. Bond Angles (deg)

Co(1)–P(1)–Co(2)	69.6 (2)	P(1)–Co(1)–P(2)	52.6 (2)
Co(1)–P(2)–Co(2)	69.1 (2)	P(1)–Co(2)–P(2)	53.4 (2)
Co(1)–P(1)–P(2)	64.1 (2)	P(1)–Co(1)–Co(2)	54.7 (1)
Co(1)–P(2)–P(1)	63.2 (2)	P(1)–Co(2)–Co(1)	55.7 (1)
Co(2)–P(1)–P(2)	63.6 (2)	P(2)–Co(1)–Co(2)	54.9 (1)
Co(2)–P(2)–P(1)	63.0 (2)	P(2)–Co(2)–Co(1)	56.0 (1)
av	63.6	av	55.3
Co(1)–P(1)–P(2)	64.1 (2)	P(1)–Co(1)–Co(2)	54.7 (1)
Co(1)–P(2)–P(1)	63.2 (2)	P(2)–Co(1)–Co(2)	54.9 (1)
Co(2)–P(1)–P(2)	63.6 (2)	P(1)–Co(2)–Co(1)	55.7 (1)
Co(2)–P(2)–P(1)	63.0 (2)	P(2)–Co(2)–Co(1)	56.0 (1)
av	63.5	av	55.3
Co(1)–C(1)–O(1)	177 (2)	Co(2)–C(4)–O(4)	178 (2)
Co(1)–C(2)–O(2)	178 (2)	Co(2)–C(5)–O(5)	179 (2)
Co(1)–C(3)–O(3)	179 (2)		

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

Table III. Distances (Å) of Atoms from Selected Least-Squares Planes[a] in the $Co_2(CO)_5P(\mu$-$P_2)$ Fragment and Angles (deg) between the Normals of These Planes

A. Distances from the Plane Formed by P(1), P(2), C(2), and C(3)

$$-0.001X + 0.334Y - 0.943Z - 2.106 = 0$$

P(1)	−0.00	C(3)	0.00	O(3)	−0.27
P(2)	0.00	Co(1)	0.35	P(3)	−3.10
C(2)	0.00	O(2)	−0.19		

B. Distances from the Plane Formed by P(1), P(2), C(4), and C(5)

$$-0.510X - 0.505Y - 0.696Z + 2.540 = 0$$

P(1)	−0.03	C(5)	−0.02	O(5)	0.18
P(2)	0.03	Co(2)	−0.30	C(1)	2.80
C(4)	0.02	O(4)	0.20	O(1)	3.32

C. Distances from the Plane Formed by Co(1), Co(2), and the Midpoint of P(1)–P(2)

$$0.788X - 0.580Y - 0.207Z - 0.662 = 0$$

P(1)	−1.01	O(2)	−2.23	O(4)	−2.23
P(2)	1.01	C(3)	1.38	C(5)	1.38
C(1)	0.02	O(3)	2.33	O(5)	2.40
O(1)	0.07	C(4)	−1.35	P(3)	−0.13
C(2)	−1.34				

D. Distances from the Plane Formed by P(1), P(2), and the Midpoint of Co(1)–Co(2)

$$-0.302X - 0.072Y - 0.951Z + 0.176 = 0$$

Co(1)	1.29	O(2)	1.69	O(4)	−1.72
Co(2)	−1.29	C(3)	1.45	C(5)	−1.58
C(1)	2.82	O(3)	1.55	O(5)	−1.77
O(1)	3.79	C(4)	−1.53	P(3)	−3.26
C(2)	1.51				

E. Angles between Normals to the Plane

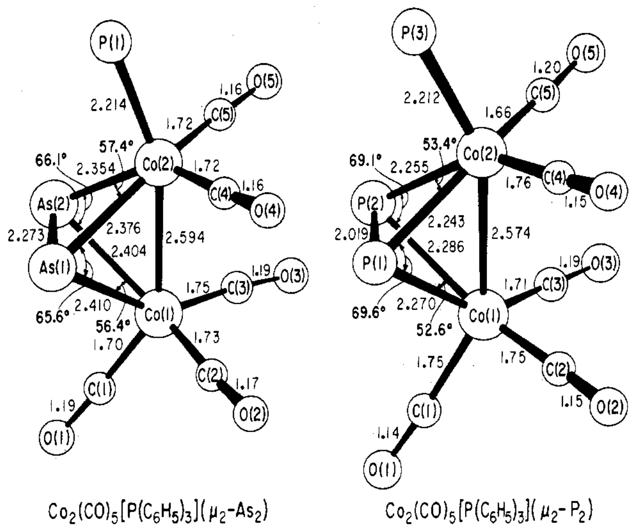
A and B	60.8	B and C	88.0
A and C	90.0	B and D	31.6
A and D	29.3	C and D	90.0

[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 $\sin \sigma = (1 - \cos^2 \beta - \cos^2 \mu)^{1/2}$.

interactions in accord with the observed bond-length differences. A completely analogous distortion of the Co_2As_2 core from an idealized C_{2v}-$2mm$ geometry toward a C_s-m geometry with corresponding differences in Co–As bond lengths has been observed for $Co_2(CO)_5[P(C_6H_3)_3](\mu$-$As_2)$.[15]

A high-resolution infrared spectrum of the parent $Co_2(CO)_6(\mu$-$P_2)$ molecule in hexane solution exhibits carbonyl stretching frequencies at 2100.6 (m), 2066.3 (vs), 2045.5 (s), 2041.5 (s), and 2028.5 (mw) cm^{-1}, while a similar spectrum[7] for its mono(triphenylphosphine) derivative, $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2)$, exhibits carbonyl stretching frequencies at 2072.4 (s), 2027.1 (s), 2020.5 (s), 2006.8 (w), and 1984.2 (m) cm^{-1}. A low-resolution solid-state (KBr pellet) infrared spectrum of $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2)$ exhibits carbonyl stretching frequencies which are nearly identical with those of the solution spectrum given above. The close similarity in the spectra of these two compounds and their resemblance to the spectrum of the previously characterized $Fe_2(CO)_6(\mu$-$S_2)$ molecule[12] provide convincing evidence that the isoelectronic $Co_2(CO)_6(\mu$-$P_2)$ molecule possesses the C_{2v} $Fe_2(CO)_6(\mu$-$S_2)$-type structure. The important bond lengths and angles for the Co_2P_2 core of the unsubstituted $Co_2(CO)_6(\mu$-$P_2)$ molecule are expected to be similar to those determined for its mono(triphenylphosphine) derivative in that the dimensions of the corresponding Co_2As_2 core of the $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$As_2)$ molecule were found from an X-ray diffraction examination to be little changed upon substitution of a second triphenylphosphine ligand for the remaining axial carbonyl ligand to give the $Co_2(CO)_4[P(C_6H_5)_3]_2(\mu$-$As_2)$ molecule.[15b] Although the infrared spectra for $Co_2(CO)_6(\mu$-$P_2)$ and $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2)$ are not strictly comparable from symmetry considerations, the apparent trend in carbonyl stretching frequencies with triphenylphosphine substitution provides evidence that the replacement of a π-acidic carbonyl ligand with a σ-donating triphenylphosphine ligand brings about an electron redistribution which results in the net transfer of more electron density to the π* orbitals of the remaining carbonyl ligands thereby reducing their force constants and stretching frequencies. This trend in carbonyl stretching frequencies correlates well with the previously mentioned distortion of the Co_2P_2 fragment.

The close resemblance of the molecular configurations of $Co_2(CO)_5[P(C_6H_5)_3(\mu$-$As_2)$ and $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2)$ is clearly illustrated in Figure 3, and a comparison of their molecular parameters is summarized in Table IV. The most notable feature of the comparison of these two structures is the remarkable similarity in all comparable bond lengths and bond angles. The P_2 fragment in the cobalt–phosphorus compound is translated slightly toward the triphenyl-



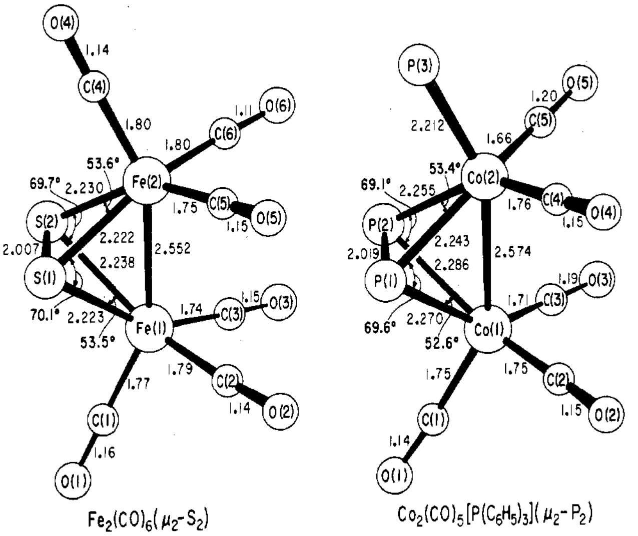
$Co_2(CO)_5[P(C_6H_5)_3](\mu_2\text{-}As_2)$ $Co_2(CO)_5[P(C_6H_5)_3](\mu_2\text{-}P_2)$

Figure 3. Geometries of the $Co_2(CO)_5P(\mu\text{-}X_2)$ fragments of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}X_2)$ molecules (X = As, P).

Table IV. Comparison of Molecular Bond Lengths (Å) and Bond Angles (deg) of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}X_2)$, Where X = As or P

	X = As	X = P
Co-Co	2.594 (3)	2.574 (3)
Co-X	2.407 (3)[a]	2.264 (5)[a]
X-X	2.273 (3)	2.019 (9)
Co-C	1.72 (2)[a]	1.73 (2)[a]
C-O	1.17 (2)[a]	1.17 (2)[a]
Co-P	2.214 (4)	2.212 (4)
P-C	1.82 (1)[a]	1.83 (1)
Co-X-Co	65.8 (1)[a]	69.4 (2)[a]
X-Co-X	56.9 (1)[a]	63.5 (2)[a]

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



$Fe_2(CO)_6(\mu_2\text{-}S_2)$ $Co_2(CO)_5[P(C_6H_5)_3](\mu_2\text{-}P_2)$

Figure 4. Geometries of the $Fe_2(CO)_6(\mu\text{-}S_2)$ molecule and the $Co_2(CO)_5P(\mu\text{-}P_2)$ fragment of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ molecule.

Table V. Comparison of Molecular Bond Lengths (Å) and Bond Angles (deg) of $M_2(CO)_{6-n}[P(C_6H_5)_3]_n(\mu\text{-}X_2)$ for M = Fe, X = S, n = 0 and M = Co, X = P, n = 1

	M = Fe, X = S	M = Co, X = P
M-M	2.552 (2)	2.574 (3)
M-X	2.228 (2)[a]	2.264 (5)[a]
X-X	2.007 (5)	2.019 (9)
M-C	1.78 (1)[a]	1.73 (2)[a]
C-O	1.14 (1)[a]	1.17 (2)[a]
M-X-M	69.9 (1)[a]	69.4 (2)[a]
X-M-X	53.5 (1)[a]	63.5 (2)[a]

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

phosphine-substituted cobalt atom in an analogous manner to that observed for the cobalt–arsenic compound. The major differences which exist between $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ and $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$ can be ascribed to the smaller covalent radius of a phosphorus atom vs. that of an arsenic atom. The average Co(1)–P and Co(2)–P bond lengths in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ are 0.13 and 0.12 Å shorter than the analogous Co–As bond lengths in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}As_2)$, while the P–P distance is 0.25 Å shorter than the corresponding As–As distance. These changes in the Co–X and X–X distances as an arsenic atom is replaced with a phosphorus atom correlate well with the difference in the covalent radii for arsenic (1.22 Å) and phosphorus (1.10 Å).[24] The Co–Co distance of 2.574 (3) Å in the cobalt–phosphorus complex is not appreciably shorter than the Co–Co distance of 2.594 (3) Å for the cobalt–arsenic complex.

The observed cobalt–cobalt single-bond length of 2.574 (3) Å in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ is not appreciably different from the mean Co–Co distances reported for $Co_2(\eta^5\text{-}C_5H_5)_2[\mu\text{-}P(C_6H_5)_2]_2$ (2.56 Å),[25] $Co_3(CO)_6[\mu\text{-}P(C_6H_5)_2]_3$ (2.58 Å),[26] $[Co_3(CO)_7P]_3$ (2.59 Å),[27] and $Co_3(CO)_9(\mu_3\text{-}PC_4H_9)$ (2.58 Å).[28] The mean cobalt–(bridging phosphorus) distance of 2.264 (5) Å in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ is somewhat longer than the mean Co–P bond lengths found in $Co_2(\eta^5\text{-}C_5H_5)_2[\mu\text{-}P(C_6H_5)_2]_2$ (2.16 Å), $Co_3(CO)_6[\mu\text{-}P(C_6H_5)_2]_3$ (2.17 Å), $[Co_3(CO)_7P]_3$ (2.17 Å), and $Co_3(CO)_9(\mu_3\text{-}PC_4H_9)$ (2.13 Å), yet shorter than the average Co–P distances in CoP (2.30 Å)[29] and CoP_2 (2.33 Å).[30] Although the homologously related $PCo_3(CO)_9$ and $P_3Co(CO)_3$ molecules[9] have not yet been structurally characterized, by analogy to the known $As_{4-n}Co_n$ systems the Co–P distances for $PCo_3(CO)_9$ are predicted to be shorter than 2.26 Å, while those for $P_3Co(CO)_3$ are predicted to be longer than 2.26 Å. Likewise, the P–P bond lengths are predicted to be intermediate between the corresponding distances in $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ (2.02 Å) and P_4 (2.21 Å).[31]

A prime stereochemical feature of the $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ structure is the short P–P distance of 2.019 Å, which is 0.20 Å shorter than the average P–P single bond distance of 2.21 (2) Å reported for a number of organophosphorus compounds[32] but 0.12 Å longer than the triple-bond distance of 1.893 Å observed in gaseous P_2.[33,34] The estimated P–P bond order for $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$, obtained from a (bond length)–(valence bond order) curve derived from the Pauling covalent radii for phosphorus atoms,[24] is 1.9.

The similar geometries of the $Fe_2(CO)_6(\mu\text{-}S_2)$ and $Co_2(CO)_5[P(C_6H_5)_3]\mu\text{-}P_2)$ molecules are shown in Figure 4, and their molecular parameters are compared in Table V. An examination of the X–X bond lengths reveals an important stereochemical difference between these two molecules. The (bond length)–(bond order) curves for sulfur and phosphorus suggest that the observed S–S bond length of 2.007 (5) Å for $Fe_2(CO)_6(\mu\text{-}S_2)$ corresponds to an estimated total S–S valence bond order of about 1.4 (or a π bond order of about 0.4), whereas the P–P bond length of 2.019 (9) Å for $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ corresponds to a P–P bond order of ca. 1.9 (or a π bond order of 0.9). The bond-length evidence, which points to a considerably greater bond order in the P–P bond of $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ compared to that in the S–S bond of $Fe_2(CO)_6(\mu\text{-}S_2)$, is in harmony with the expected relative difference in the electron distribution arising from the metal complexation of the free P_2 and S_2 ligands.

The ground-state ($^1\Sigma_g{}^+$) electronic configuration of the free P_2 molecule is $(\pi_u)^4(\sigma_g)^2$, giving rise to a total P–P bond order of *three* (and a π bond order of *two*). As indicated from the bond-length evidence, the coordination of the P_2 molecule as a bridging ligand to two cobalt atoms decrease the total P–P bond order to ca. 1.9. Since the P_2 σ-type orbitals are not expected to overlap appreciably with the metal orbitals, this decrease in total P_2 bond order should be reflected in a decrease in the P–P π bond order to 0.9 upon coordination. Such a decrease in the overall π bond order may be viewed conceptually as arising from two competing types of interactions: (1) a donation of electron density from the filled π orbitals of P_2 to the metal orbitals and (2) a back-bonding interaction involving the transfer of electron density from the filled metal orbitals into the empty π^* orbitals of P_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 whereby an electron may be transferred from the filled P_2 π orbitals to the empty P_2 π^* orbitals resulting in a decrease in P_2 bond order without a net transfer of charge to the metal atoms. Such a one-electron-transfer process would yield an electron distribution which resembles the $^1\Sigma_u{}^+$ excited state of P_2.

By comparison, the ground-state ($^3\Sigma_g{}^-$) electronic configuration of the free S_2 molecule is $(\pi_u)^4(\sigma_g)^2(\pi_g)^2$, corresponding to a total S–S bond order of *two* (and a net π bond order of *one*). In this case, the net transfer of one electron from the filled S_2 π orbitals to the half-filled S_2 π^* orbitals, via the same synergic (forward donation)–back-bonding mechanism described above, would reduce the net S_2 π bond order to *zero* and the total S_2 bond order to one. As also in the case of the dicobalt–diphosphorus molecule, a continuum of intermediate bond orders is possible depending upon the relative magnitudes of the $\pi(S_2) \rightarrow 3d(Fe)$ and $3d(Fe) \rightarrow \pi^*(S_2)$ interactions. An imbalance in the two processes would result in a net charge on the sulfur atoms.

Acknowledgment. We are grateful for the financial support rendered by the National Science Foundation (Grant No. CHE 77-24309) for this investigation. The use of the UNIVAC 1110 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

Registry No. $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$, 59874-25-8.

Supplementary Material Available: A listing of structure factor amplitudes for $Co_2(CO)_5[P(C_6H_5)_3](\mu\text{-}P_2)$ (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Presented in part at the national meeting of the American Crystallographic Association, Norman, OK, March 1978. (b) Based in part upon a dissertation submitted by C.F.C. to the Graduate School of the University of Wisconsin, Madison, in partial fulfillment of the requirement for the Ph.D. degree, December 1975.

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(5) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823–8.

(6) Gall, R. S.; Foust, A. S.; Pollick, P. J.; Wojcicki, A.; Dahl, L. F. "Abstracts"; American Crystallographic Association: Berkeley, CA, March 1974.

(7) Vizi-Orosz, A.; Palyi, G.; Markó, L. *J. Organomet. Chem.* **1973**, *60*, 625–6.

(8) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904–6.

(9) Vizi-Orosz, A. *J. Organomet. Chem.* **1976**, *111*, 614.

(10) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633–5.

(11) Bor, G. *Chem. Ber.* **1963**, *96*, 2644–6.

(12) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1–11.

(13) Varadi, A.; Vizi-Orosz, A.; Vastag, S.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225–33.

(14) (a) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18–20. (b) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037–43.

(15) (a) Foust, A. S. Ph.D. Thesis, University of Wisconsin, Madison, 1970. (b) Foust, A. S.; Campana, C. F.; Sinclair, J. D.; Dahl, L. F. *Inorg. Chem.*, preceding paper in this issue.

(16) (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821–2. (b) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384–97.

(17) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5631–3.

(18) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. I, p 75.

(19) Calculations were performed on a UNIVAC 1110 computer. Programs used included original or modified versions of: (a) FOBS, a Fortran diffractometer data reduction program: Calabrese, J. C., University of Wisconsin, Madison, 1972. (b) SORTMERGE: Calabresé, J. C. Ph.D. Thesis (Appendix I), University of Wisconsin, Madison, 1971. (c) DEAR, a Fortran absorption correction program by J. F. Blount based on the method given by Busing and Levy: Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–2. (d) MAP, a Fortran Fourier summation and molecular assemblage program: Calabrese, J. C., University of Wisconsin, Madison, 1972. (e) Calabrese, J. C. "A Crystallographic Variable Matrix Least-Squares Refinement Program", University of Wisconsin, Madison, 1972. (f) MIRAGE: Calabrese, J. C. Ph.D. Thesis (Appendix III), University of Wisconsin, Madison, 1971. (g) Busing, W. R.; Martin, K. O; Levy, H. A. "ORFLS, A Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. (h) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, A Fortran Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964. (i) PLANES: Smith, D. L. Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, 1962.

(20) (a) "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1968; Vol. III, pp 157–62. (b) *Ibid.*, pp 215–6.

(21) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.

(22) Cromer, D. T.; Mann, J. F. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–5.

(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(24) Pauling, L. "The Chemical Bond"; Cornell University Press: Ithaca, NY, 1967; p 136.

(25) Coleman, J. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 542–52.

(26) Huntsman, J. R.; Dahl, L. F., to be submitted for publication.

(27) Gall, R. S. Ph.D. Thesis, University of Wisconsin, Madison, 1973.

(28) Ryan, R. C.; O'Connor, J. P.; Markó, B.; Markó, L.; Dahl, L. F., to be submitted for publication.

(29) Rundqvist, S.; Nawapong, P. C. *Acta Chem. Scand.* **1965**, *19*, 1006–8.

(30) Rundvqvist, S. *Ark. Kemi* **1963**, *20*, 67–9.

(31) Maxwell, L. R.; Hendricks, S. R.; Mosley, V. M. *J. Chem. Phys.* **1935**, *3*, 699–709.

(32) Corbridge, D. E. C. *Top. Phosphorus Chem.* **1966**, *3*, 57.

(33) Herzberg, G. "Molecular Spectra and Molecular Structures. Infrared Spectra of Diatomic Molecules"; Van Nostrand: New York, NY, 1950.

(34) Douglas, A. E.; Rao, K. S. *Can. J. Phys.* **1958**, *36*, 565–70.