Organometallic Pnicogen Complexes. VII. Synthesis, Structure, and Bonding of the Cubane-Like Metal Cluster [$Co_4(h^5\text{-}C_5H_5)_4P_4$]. The First Reported Organometallic Complex Containing a Naked Phosphorus Atom as a Ligand[1]

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received October 5, 1972*

Abstract: The successful preparation of the [$Co_4(h^5\text{-}C_5H_5)_4P_4$] tetramer and subsequent structural determination by single-crystal X-ray diffraction were carried out in order to provide an operational test of the effect of metal–metal interactions on the molecular parameters of a cubane-like M_4X_4 system upon change of the triply bridging X ligands from sulfur to phosphorus atoms. Greenish black, air-stable crystals of this organometallic complex containing a hitherto unreported "naked" phosphorus atom as a bridging ligand were obtained in very low yield by the reaction of $Co(h^5\text{-}C_5H_5)(CO)_2$ with white phosphorus. This molecular compound was characterized by mass spectrometry (which afforded its initial formulation as a tetramer) and by infrared and proton nmr measurements; the diamagnetic character of the molecule was established from the strong, sharp nmr signal of the cyclopentadienyl protons. In contradistinction to the type of tetragonal D_{2d} distortion present in the [$Co_4(h^5\text{-}C_5H_5)_4S_4$]$^+$ monocation (of different electronic structure), the observed type of tetragonal D_{2d} deformation of the [$Co_4(h^5\text{-}C_5H_5)_4P_4$] tetramer found from the X-ray investigation is analogous to that found in the isoelectronic [$Fe_4(h^5\text{-}C_5H_5)_4S_4$] tetramer but much more severe in degree. The six cobalt–cobalt distances in [$Co_4(h^5\text{-}C_5H_5)_4P_4$] divide into *two* shorter electron pair bonding values of 2.504 (2) Å (av) and *four* longer nonbonding values of 3.630 Å (av) (*vs.* 2.650 (av) and 3.363 Å (av) in the monoclinic phase and 2.631 (av) and 3.366 Å (av) in the orthorhombic phase of [$Fe_4(h^5\text{-}C_5H_5)_4S_4$]). The much larger variations of these two sets of metal–metal distances in [$Co_4(h^5\text{-}C_5H_5)_4P_4$] from the six chemically equivalent metal–metal distances of mean value of 3.295 Å for the assumed cubic T_d geometry of the cobalt–sulfur analog [$Co_4(h^5\text{-}C_5H_5)_4S_4$] (which does not possess any *net* metal–metal interactions) require a much greater distortion of the M_4X_4 geometry which is reflected in: (1) the resulting two sets of M–X–M bond angles of 68.8 (av) and 108.6° (av) in [$Co_4(h^5\text{-}C_5H_5)_4P_4$] being further from 95.3° (found in [$Co_4(h^5\text{-}C_5H_5)_4S_4$]) than the corresponding two sets of M–X–M bond angles found in monoclinic [$Fe_4(h^5\text{-}C_5H_5)_4S_4$] (73.9 and 98.0°) and in orthorhombic [$Fe_4(h^5\text{-}C_5H_5)_4S_4$] (73.3 and 98.0°); (2) extremely short P · · · P contacts of 2.57 Å for four of the six pairs of phosphorus atoms in [$Co_4(h^5\text{-}C_5H_5)_4P_4$] compared to the corresponding S · · · S contacts of 2.88 Å for the sulfur atoms in both monoclinic and orthorhombic [$Fe_4(h^5\text{-}C_5H_5)_4S_4$]. The observed tetragonal geometry of [$Co_4(h^5\text{-}C_5H_5)_4P_4$] is rationalized *via* the metal cluster MO model utilized for [$Co_4(h^5\text{-}C_5H_5)_4S_4$]^n ($n$ = 0, +1). The [$Co_4(h^5\text{-}C_5H_5)_4P_4$] compound crystallizes in the orthorhombic system with cell dimensions a = 11.309 (2), b = 18.250 (3), and c = 10.284 (2) Å and with centrosymmetric space group symmetry *Pmnb* such that each of the four tetramers per cell possesses crystallographic site symmetry C_s-m. Least-squares refinement of the structure with anisotropic thermal parameters utilized for all nonhydrogen atoms gave R_1 = 3.4% and R_2 = 4.5% at convergence for the 1228 independent diffraction maxima with $I > 2\sigma(I)$.

A significant amount of research in the field of organometallic chemistry has been directed toward the synthesis and characterization of complexes containing two or more transition metals.[2] Through interpretations of spectral and structural studies, these compounds have provided major contributions to the theory of chemical bonding in transition metal complexes.

In an attempt to systematize the stereochemical and bonding consequences resulting from the alteration of valence electrons in metal cluster systems, we have focused our attention upon the reactions of sulfur and sulfur-containing reagents with metal carbonyl and cyclopentadienyl deviatives along with characterization by structural and magnetic measurements of the resulting products. These investigations have provided direct crystallographic evidence that *atomic* sulfur can function in the following different modes of linkage to transition metals in organometallic complexes: (1) a doubly bridging, two-electron-donating ligand as discovered in [$Mo_2(h^5\text{-}C_5H_5)_2(O)_2(\mu\text{-}S)_2$][3] and in the [$Mo_3(h^5\text{-}C_5H_5)_3S_4$]$^+$ cation;[4] (2) a triply bridging, four-electron-donating, trigonal-pyramidal-like ligand as exemplified by $Co_3(CO)_9S$,[5] $M_3(h^5\text{-}C_5H_5)_3S_2$ (where M = Co,[6] Ni[7]), and [$Co_4(h^5\text{-}C_5H_5)_4S_4$]^n ($n$ = 0, +1);[8] (3) a quadruply bridging, four-electron-donating, square-pyramidal-like ligand as found in $Co_4(CO)_{10}S_2$;[9] and (4) a quadruply bridging, six-electron-donating, tetrahedral-like ligand as observed in [$Fe_2(CO)_6(\mu\text{-}SCH_3)$]$_2$S[10]

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and in $[Re_2Mo(h^5\text{-}C_5H_5)(CO)_8](S)[SMo(h^5\text{-}C_5H_5)(CO)_3]$.[11]

Although this extreme versatility of sulfur in atomic form as a ligand has given rise to a wide variety of unusual organometallic species such that it might be expected that this behavior of sulfur would be paralleled in the organometallic pnicogen complexes by the adjacent element phosphorus, notably absent from the compilations[2] of organometallic complexes of the group V pnicogens are any examples of phosphorus as an atomic ligand—*i.e.*, despite the large number of known complexes containing phosphine and phosphite ligands, no previous reports have been made of the coordination of a "naked" phosphorus atom to one or more transition metals in an organometallic complex.[12,13] In fact, only a relatively few transition metal complexes containing congeners of phosphorus (*i.e.*, the group V pnictides) as atomic ligands have been prepared (*vs.* those containing chalcogenides as atomic ligands); the crystallographically characterized ones include: (1) the nitrido complexes $Re(N)Cl_2[P(C_2H_5)_2(C_6H_5)]$,[14] $Re(N)Cl_2[P(C_6H_5)_3]_2$,[15] and $K_2[Os(N)Cl_5]$[16] which each possess a terminal nitrogen atom multiply bonded to one transition metal;[17] (2) the $[Ru_2Cl_8(H_2O)_2(\mu\text{-}N)]^{3-}$ anion[18] which contains a nitride ligand linearly bridging to two transition metals; (3) the $[Ir_3(N)(SO_4)(H_2O)_3]^{4-}$ anion[19] which possesses a trigonal-like nitrogen atom coordinated to three transition metals; (4) the $[Ni_4(h^5\text{-}C_5H_5)_4(As)_3]^+$ cation[20] for which each trigonal-pyramidal-like arsenic atom is bridged to three transition metals; (5) the $[Co_3(CO)_8As]_3$ molecule[21] for which each bare As ligand is tetrahedrally coordinated to four cobalt atoms; and (6) the cubane-like $[Co_4(CO)_{12}Sb_4]$ molecule[22] which has triply bridging antimony atoms.

This paper reports the synthesis and structural characterization of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$, a novel organometallic complex which contains phosphorus atoms each triply bridging three transition metals. A particular goal of the investigation (which in fact initiated it) was the opportunity to make a detailed comparison of its cubane-like tetrameric structure with those of the isoelectronic neutral $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecule (which has been characterized in the solid state by X-ray diffraction both in an orthorhombic crystalline phase[23] and in a monoclinic crystalline phase[24]) and of the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ tetramers ($n = 0, +1$).[8] This comparison has not only provided important stereochemical information regarding the degree of alteration of the M_4X_4 skeleton upon replacement of the four iron atoms with cobalt atoms and sulfur atoms with phosphorus atoms (thereby transmuting $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ into $[Co_4(h^5\text{-}C_5H_5)_4P_4]$) but also has given further insight concerning the relationship of electronic structure to molecular configuration of cubane-like M_4X_4 cluster systems.

Experimental Section

Preparation and Characterization. $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ was prepared by the refluxing of a toluene solution of $Co(h^5\text{-}C_5H_5)(CO)_2$ with a stoichiometric amount of white phosphorus. Although the red solution turns dark green in a few hours, the reflux was continued for 12 hr after which no trace of P_4 was observed. After filtration, a number of attempts at purification by elution chromatography were made. Although several supporting media and a host of solvents were used, all attempts to chromatograph the complex proved fruitless. However, slow evaporation under nitrogen of the toluene solution produced lustrous green-black, air-stable crystals with a morphology similar to a slightly distorted tetragonal bipyramid. The formulation of the complex as $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ was based on mass spectral data, presented in Table I, which included the parent ion peak as the highest observed peak. The diamagnetic character of the compound was indicated by a strong cyclopentadienyl proton

Table I. Mass Spectral Data for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$[a]

Ion	*m/e*	Intensity[b]
$Co_4(C_5H_5)_4P_4^+$	620	30.7
$Co_4(C_5H_5)_4P_2^+$	558	1.1
$Co_4(C_5H_5)_3P_4^+$	555	0.4
$Co_4(C_5H_5)_3P_2^+$	493	3.4
$Co_4(C_5H_5)_2P_4^+$	490	0.3
$Co_3(C_5H_5)_3P_3^+$	465	0.4
$Co_3(C_5H_5)_3P_2^+$	434	0.3
$Co_3(C_5H_5)_2P_4^+$ or $Co_4(C_5H_5)_3^+$	431	5.4
$Co_4(C_5H_5)_2P_2^+$	428	0.7
$Co_4(C_5H_5)P_4^+$	425	1.2
$Co_3(C_5H_5)_2P_3^+$	400	0.3
$Co_2(C_5H_5)_2P_4^+$ or $Co_3(C_5H_5)_3^+$	372	0.4
$Co_3(C_5H_5)P_4^+$ or $Co_4(C_5H_5)_2^+$	366	0.3
$Co_4(C_5H_5)P_2^+$	363	1.0
$Co_4P_4^+$	360	0.4
$Co_3(C_5H_5)_2P^+$	338	0.4
$Co_3(C_5H_5)P_3^+$	335	0.3
$Co_2(C_5H_5)_2P_2^+$	310	3.0
$Co_3(C_5H_5)P_2^+$	304	0.7
$Co_4P_2^+$	298	0.5
$Co_2(C_5H_5)P_3^+$	276	0.4
$Co_3(C_5H_5)P^+$	273	0.4
Co_4P^+	267	0.5
$Co_2(C_5H_5)P_2^+$	245	0.5
$Co_2(C_5H_5)P^+$	214	0.8
$Co(C_5H_5)_2^+$	189	46.7
$Co_2P_2^+$	180	3.1
$Co(C_5H_5)P^+$	155	20.0
Co_2P^+	149	2.1
Co_2^+	118	12.0
CoP^+	90	100.0

[a] Mass spectra were recorded on an AEI MS-902 mass spectrometer at 70 eV with a probe temperature of 180°. Samples were introduced into the ion source by a direct inlet system. [b] Intensity values are presented as relative ion abundances with respect to the base peak at *m/e* 90.

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[12] An unusual rhodium complex containing phosphorus which deserves mention is $L_2Rh(P_4)Cl^6$ (where L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$, and $(C_6H_5)_3As$) which is formed by the reaction of L_3RhCl with P_4 at −78° in CH_2Cl_2 or Et_2O. Although the structures of these complexes have not yet been ascertained by X-ray crystallography, spectral measurements have been reasonably interpreted by Ginsberg and Lindsell[13] to indicate that the tetrahedral P_4 molecule is intact as a ligand.

[13] A. P. Ginsberg and W. E. Lindsell, *J. Amer. Chem. Soc.*, **93**, 2082 (1971).

[14] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[15] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[16] D. Bright and J. A. Ibers, *ibid.*, **8**, 709 (1969).

[17] No corresponding analogs are known for any second or higher row elements of the main groups IV, V, and VI.

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magnetic resonance signal at τ 5.52 (*vs.* TMS external) measured on a Varian T-60 spectrometer. The solid-state infrared spectrum[25] of the tetramer displayed absorption bands characteristic of the cyclopentadienyl ligands.

X-Ray Data Collection. Weissenberg and precession photographs of the tetrameric complex revealed Laue symmetry D_{2h}-$2/m$-$2/m2/m$ consistent with the orthorhombic crystal system. Systematic absences for $\{h0l\}$ of $h + l = 2n + 1$ and for $\{hk0\}$ of $k = 2n + 1$ are compatible with two possible space groups, *Pmnb* and *P*2$_1$*nb* (nonstandard settings of *Pnma* (D_{2h}^{16}, No. 62) and *Pna*2$_1$ (C_{2v}^{9}, No. 33), respectively). The former centrosymmetric space group was determined by the structure ultimately found. For the collection of intensity data, a single crystal with dimensions 0.16 × 0.20 × 0.75 mm along the [110], [$\bar{1}$10], [001] directions, respectively, was cemented with epoxy cement onto a thin glass fiber such that the *c* direction was approximately parallel to the spindle axis of the goniometer. The crystal was then mounted and aligned on a Nova-automated Syntex P$\bar{1}$ diffractometer.

The angular coordinates (2θ, ω, ϕ, χ) of 15 peaks, which were centered with monochromatic Mo Kα radiation ($\lambda(K\alpha_1)$ 0.70926 Å, $\lambda(K\alpha_2)$ 0.71354 Å), were least-squares refined to yield lattice parameters $a = 11.309$ (2), $b = 18.250$ (3), and $c = 10.284$ (2) Å. The experimental density of 1.92 (2) g cm^{-3}, measured by the flotation method, is in accord with the value of 1.940 g cm^{-3} calculated for a unit cell of volume 2122.4 Å^3 containing four $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ formula species.

Intensity data were collected *via* the ω-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 crystal graphite monochromator was 12.2°, while the takeoff angle for the incident beam was 2.0°. Both variable scan speeds (minimum speed 2°/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 one-third of the total scan time was made on each side of the peak. Two reflections, which were periodically measured every 50 reflections, were used as standards for instrument stability as well as crystal alignment and decay. During the entire experiment, no significant changes (>3%) in the intensities of these standard reflections were observed. All independent reflections within the sphere $2\theta \leq 45.0°$ were sampled. For each reflection the intensity and its standard deviation were calculated with the formulas given elsewhere[8] with the only modification being a linear correction to compensate for the variable scan speeds. All data were first corrected for Lorentz-polarization effects including the polarization produced by the monochromator and then were reduced to $|F_o|$; 1228 observed reflections with $I > 2\sigma(I)$ were obtained for use in the structural determination. Since the transmission coefficients varied from 0.36 to 0.48 (based on a linear absorption coefficient of 34.90 cm^{-1} for Mo Kα radiation), an absorption correction was applied to the individual structure factors.[26] No corrections for extinction were made.

Solution and Refinement of the Structure. The structure of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ was determined by heavy-atom techniques. Due to overlap of vectors, an interpretation of a three-dimensional Patterson map[27] yielded the initial location of only one cobalt atom. Successive Fourier syntheses[27] finally revealed the coordinates of all nonhydrogen atoms in the unit cell. On the basis of centrosymmetric *Pmnb* symmetry[28] each tetrameric molecule was found to be arranged about a crystallographic mirror plane with two cobalt and two phosphorus atoms located on the mirror plane. The mirror plane bisects two of the cyclopentadienyl rings such that each ring has one carbon and one hydrogen atom sitting on the mirror plane. The crystallographically independent unit thus consists of three cobalt atoms, three phosphorus atoms, one complete cyclopentadienyl ring, and two cyclopentadienyl rings of which only three carbon and three hydrogen atoms are independent. Full-matrix isotropic least squares[29,30] of this model resulted in $R_1 = 8.5\%$ and $R_2 = 11.7\%$. Further refinement which utilized anisotropic thermal parameters for all nonhydrogen atoms reduced R_1 to 3.4% and R_2 to 4.5% at convergence. The final goodness-of-fit parameter was 1.61 which indicates a small underestimation in the standard deviation of an observation of unit weight. Throughout the latter stages of refinement, idealized coordinates for the cyclopentadienyl hydrogen atoms were included in the structure factor calculations with isotropic thermal parameters of 3.0 Å^2. Neither the positional nor the thermal parameters of these hydrogen atoms were allowed to vary during a least-squares cycle, but their positions were recalculated based on the shifts of the carbon atoms after each least-squares cycle with the program MIRAGE.[31] A final Fourier difference map revealed no residual electron density greater than 0.5 e/Å^3.

The scattering factor tables used for all nonhydrogen atoms were those of Hanson, *et al.*,[32] while those for the hydrogen atoms were by Stewart, *et al.*[33] Real and imaginary corrections for anomalous dispersion (*viz.*, $\Delta f' = 0.4$, $\Delta f'' = 1.1$ for Co; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for P)[34] were included in the structure factor calculations.

The positional and thermal parameters for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ obtained from the output of the last least-squares cycle are presented in Table II.[35] Interatomic distances and angles with estimated standard deviations, calculated from the variance-covariance matrix,[36] are provided in Table III. Some least-squares planes[37] of interest were calculated. All illustrations were drawn with the aid of ORTEP.[38]

Results and Discussion

General Description of the Crystal and Molecular Structure. $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ crystallizes as distinct tetrameric molecules with the cubane-like architecture of crystallographic site symmetry C_s-m depicted in Figures 1 and 2. Each cobalt of similar localized environment is bonded to one *pentahapto*cyclopentadienyl ring, three phosphorus atoms, and *one* cobalt atom such that it achieves a closed-shell electronic configuration. On the basis of cylindrical symmetry for each cyclopentadienyl ring, the molecule possesses a tetragonal D_{2d}-$\bar{4}2m$ configuration within experimental error (Figure 3). One of the two symmetry-related molecular mirror planes corresponds to the crystallographic mirror plane bisecting the molecule. The packing in the orthorhombic unit cell (Figure 4) appears to be dictated by long range van der Waals forces in that there are no intermolecular H···H distances less than the van der Waals contact distance of 2.4 Å; the closest nonhydrogen separation between molecules is a C(cyclopentadienyl)···C(cyclopentadienyl) contact of 3.5 Å.

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(25) Infrared spectra (KBr pellet) were measured on a Beckman IR-10 infrared spectrometer.

(26) J. F. Blount, "DEAR," based on a method given by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(27) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

(28) For the space group *Pmnb* the general eightfold set of positions (8d) are the following: $\pm(x, y, z;\ {}^1/_2 - x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z;\ x, {}^1/_2 + y, {}^1/_2 - z)$. The four-fold set of special positions (4c) on mirror planes are the following: $\pm({}^1/_4, y, z;\ {}^1/_4, {}^1/_2 + y, {}^1/_2 - z)$.

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

(30) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(31) J. C. Calabrese, "MIRAGE," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1971.

(32) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(33) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(34) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1968, p 215.

(35) Observed and calculated structure factors for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-2175. Remit check or money order for \$3.00 for photocopy and \$2.00 for microfiche.

(36) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(37) D. L. Smith, "PLANES," Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

(38) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

Table II. Final Positional and Thermal Parameters for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$[a]

A. Positional Parameters

Atom	x	y	z
Co(1)	$^1/_4$	0.57388 (5)	0.40645 (10)
Co(2)	$^1/_4$	0.58596 (5)	0.64870 (9)
Co(3)	0.36083 (7)	0.75282 (4)	0.49858 (6)
P(1)	$^1/_4$	0.69412 (11)	0.35538 (18)
P(2)	$^1/_4$	0.70984 (10)	0.65903 (18)
P(3)	0.38877 (13)	0.63143 (7)	0.51942 (13)
C(1-1)	$^1/_4$	0.4569 (5)	0.3902 (10)
C(1-2)	0.3473 (6)	0.4843 (4)	0.3327 (7)
C(1-3)	0.3135 (6)	0.5312 (3)	0.2332 (6)
C(2-1)	$^1/_4$	0.5703 (5)	0.8530 (8)
C(2-2)	0.3514 (5)	0.5364 (3)	0.7998 (6)
C(2-3)	0.3126 (5)	0.4828 (3)	0.7101 (6)
C(3-1)	0.4333 (15)	0.8350 (8)	0.3830 (11)
C(3-2)	0.3963 (9)	0.8656 (4)	0.4963 (19)
C(3-3)	0.4596 (10)	0.8360 (6)	0.5908 (8)
C(3-4)	0.5316 (7)	0.7872 (5)	0.5421 (12)
C(3-5)	0.5160 (11)	0.7862 (6)	0.4110 (13)
H(1-1)[b]	$^1/_4$	0.4216	0.4647
H(1-2)	0.4309	0.4729	0.3571
H(1-3)	0.3666	0.5594	0.1735
H(2-1)	$^1/_4$	0.6108	0.9186
H(2-2)	0.4355	0.5486	0.8208
H(2-3)	0.3647	0.4504	0.6564
H(3-1)	0.4025	0.8470	0.2943
H(3-2)	0.3341	0.9040	0.5080
H(3-3)	0.4533	0.8481	0.6854
H(3-4)	0.5886	0.7562	0.5921
H(3-5)	0.5581	0.7551	0.3458

B. Anisotropic Thermal Parameters[c]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co(1)	47.5 (9)	15.4 (3)	71.6 (11)	0[d]	0	−6.2 (5)
Co(2)	46.2 (10)	14.8 (3)	69.0 (11)	0	0	6.1 (5)
Co(3)	58.6 (8)	15.2 (3)	64.6 (8)	−6.7 (3)	3.7 (5)	1.5 (3)
P(1)	63.0 (19)	17.8 (6)	54.6 (19)	0	0	−0.5 (9)
P(2)	55.7 (18)	16.1 (6)	50.3 (18)	0	0	1.4 (9)
P(3)	38.7 (12)	17.1 (5)	75.0 (16)	−1.3 (6)	−1.8 (10)	0.7 (6)
C(1-1)	168 (15)	22 (3)	125 (12)	0	0	−16 (5)
C(1-2)	87 (7)	32 (2)	143 (9)	17 (3)	−14 (6)	−35 (4)
C(1-3)	146 (7)	27 (2)	107 (7)	−24 (3)	57 (6)	−30 (3)
C(2-1)	130 (12)	23 (3)	73 (9)	0	0	8(4)
C(2-2)	73 (6)	28 (2)	100 (6)	−2 (3)	−24 (5)	18 (3)
C(2-3)	81 (5)	17 (2)	107 (6)	9 (3)	2 (5)	19 (3)
C(3-1)	294 (23)	75 (6)	166 (13)	−112 (10)	−101 (15)	85 (8)
C(3-2)	95 (9)	14 (2)	521 (32)	−4 (4)	−22 (15)	22 (7)
C(3-3)	164 (12)	46 (4)	159 (10)	−50 (6)	50 (10)	−43 (6)
C(3-4)	69 (7)	39 (3)	287 (17)	−29 (4)	−39 (9)	36 (6)
C(3-5)	192 (14)	52 (4)	220 (15)	−70 (6)	158 (13)	−58 (7)

[a] In this and subsequent tables the estimated standard deviations of the last significant figures are given in parentheses. [b] The positional parameters for the hydrogen atoms were recalculated after each least-squares cycle and fixed at 1.0 Å from their respective carbon atoms. Isotropic thermal parameters were fixed at 3.0 Å^2. [c] Anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were used. [d] For those atoms located on a crystallographic mirror plane and refined anisotropically (*viz.*, Co(1), Co(2), P(1), P(2), C(1-1), and C(2-1)), β_{12} and β_{13} are required by symmetry to be zero.

Stereochemical Influence of the Cobalt–Cobalt Bonds. Comparison of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ with $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$. In order to analyze the stereochemistry and bonding of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule, its average distances and bond angles are compared in Table IV with those of the three related cubane-like tetramers $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$[23,24] and $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ (n = 0, +1).[8] Several important geometric features emerge from examination of the corresponding molecular parameters of the M_4X_4 framework.

First, a drastic deformation of the Co_4P_4 core of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule to its observed tetragonal D_{2d} geometry has occurred from an idealized cubic T_d geometry possessed by the Co_4S_4 core of the cobalt–sulfur analog $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ which (with the availability of four additional valence electrons formally due to the replacement of four phosphorus atoms with four sulfur ones) does not possess any *net* metal–metal interactions. In striking contrast to the cobalt-cobalt nonbonding distances of 3.295 Å (av) in the $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule, the six cobalt-cobalt distances in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule are divided under assumed D_{2d} symmetry into *two* chemically equivalent *short* bonding distances of 2.501 (2) and 2.507 (2) Å and *four* chemically equivalent *long* nonbonding distances of 3.624 (1) Å (for two crystallographically identical distances) and 3.637 (1) Å (for the other two crystallographically identical distances). The two short bonding distances of average value 2.504 Å are well within the range of 2.4–2.8 Å found for electron pair cobalt–cobalt bonds in other organometallic complexes. The formation of these two short cobalt-cobalt bonds pro-

Table III. Interatomic Distances (Å) and Angles (deg) for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ Based on Idealized D_{2d} Geometry

	A. Interatomic Distances		
Co(1)-Co(2)	2.501 (2)	Co(1)···Co(3)	3.624 (1)
Co(3)-Co(3′)	2.507 (2)	Co(2)···Co(3)	3.637 (1)
	2.504 (av)		3.630 (av)
Co(1)-P(3)	2.217 (2)	P(1)···P(2)	3.136 (3)
Co(2)-P(3)	2.218 (2)	P(3)···P(3′)	3.139 (3)
Co(3)-P(1)	2.211 (2)		3.138 (av)
Co(3)-P(2)	2.216 (2)		
	2.216 (av)	Co(1)-P(1)	2.256 (2)
		Co(2)-P(2)	2.263 (2)
P(1)···P(3)	2.572 (2)	Co(3)-P(3)	2.248 (2)
P(2)···P(3)	2.564 (2)		2.256 (av)
	2.568 (av)		
Co(1)-C(1-1)	2.141 (9)	C(1-1)-C(1-2)	1.346 (9)
Co(1)-C(1-2)	2.111 (6)	C(1-1)-C(1-3)	1.388 (9)
Co(1)-C(1-3)	2.073 (6)	C(1-3)-(C(1-3′)	1.436 (14)
Co(2)-C(2-1)	2.120 (8)	C(2-1)-C(2-2)	1.412 (8)
Co(2)-C(2-2)	2.132 (5)	C(2-2)-C(2-3)	1.414 (8)
Co(2)-C(2-3)	2.108 5)	C(2-3)-C(2-3′)	1.416 (12)
Co(3)-C(3-1)	2.082 (8)	C(3-1)-C(3-2)	1.358 (15)
Co(3)-C(3-2)	2.097 (8)	C(3-2)-C(3-3)	1.322 (14)
Co(3)-C(3-3)	2.110 (7)	C(3-3)-C(3-4)	1.307 (12)
Co(3)-C(3-4)	2.079 (7)	C(3-4)-C(3-5)	1.359 (14)
Co(3)-C(3-5)	2.064 (7)	C(3-5)-C(3-1)	1.323 (15)
	2.102 (av)		1.371 (av)
	B. Bond Angles		
P(1)-Co(1)-P(3)	70.20 (5)	P(3)-Co(1)-P(3′)	90.11 (8)
P(2)-Co(2)-P(3)	69.78 (5)	P(3)-Co(2)-P(3′)	90.08 (8)
P(1)-Co(3)-P(3)	70.47 (6)	P(1)-Co(3)-P(2)	90.22 (7)
P(2)-Co(3)-P(3)	70.10 (6)		90.16 (av)
	70.14 (av)		
		Co(3)-P(1)-Co(3′)	69.08 (7)
Co(1)-P(1)-Co(3)	108.43 (7)	Co(3)-P(2)-Co(3′)	68.90 (7)
Co(2)-P(2)-Co(3)	108.58 (7)	Co(1)-P(3)-Co(2)	68.66 (5)
Co(1)-P(3)-Co(2)	108.51 (6)		68.82 (av)
Co(2)-P(3)-Co(3)	109.05 (7)		
	108.64 (av)		
C(1-2′)-C(1-1)-C(1-2)	109.7 (9)	C(3-5)-C(3-1)-C-(3-2)	107.9 (9)
C(1-1)-C(1-2)-C(1-3)	109.1 (7)	C(3-1)-C(3-2)-C(3-3)	107.2 (9)
C(1-2)-C(1-3)-C(1-3′)	106.0 (4)	C(3-2)-C(3-3)-C(3-4)	109.5 (9)
C(2-2′)-C(2-1)-C(2-2)	108.5 (7)	C(3-3)-C(3-4)-C(3-5)	107.9 (9)
C(2-1)-C(2-2)-C(2-3)	107.7 (5)	C(3-4)-C(3-5)-C(3-1)	107.4 (9)
C(2-2)-C(2-3)-C(2-3′)	108.1 (3)		

Table IV. Selected Distances and Bond Angles for Several Cubane-Like Tetramers[a]

Molecule	$[Fe(h^5\text{-}C_5H_5)S]_4$	$[Fe(h^5\text{-}C_5H_5)S]_4$	$[Co(h^5\text{-}C_5H_5)P]_4$	$[Co(h^5\text{-}C_5H_5)S]_4^+$	$[Co(h^5\text{-}C_5H_5)S]_4$
Ref	*b*	*c*	*d*	*e*	*e*
Site symmetry	C_2-2	C_s-*m*	C_s-*m*	S_4-$\bar{4}$	C_2-2
Idealized geometry	D_{2d}	D_{2d}	D_{2d}	D_{2d}	T_d
M···M	[2] 2.650 (6) [4] 3.363 (6)	[2] 2.631 (2) [4] 3.366 (2)	[2] 2.504 (2) [4] 3.630 (1)	[4] 3.172 (5) [2] 3.330 (5)	[6] 3.295 (1)
X···X	[4] 2.880 (7) [2] 3.334 (9)	[4] 2.884 (3) [2] 3.344 (6)	[4] 2.568 (2) [2] 3.138 (2)	[2] 2.929 (10) [4] 3.085 (8)	[6] 2.990 (1)
M-X	[8] 2.204 (4) [4] 2.250 (8)	[8] 2.206 (2) [4] 2.256 (3)	[8] 2.216 (1) [4] 2.256 (1)	[4] 2.215 (5) [8] 2.219 (5)	[12] 2.230 (1)
M-X-M	[4] 73.9 (2) [8] 98.0 (2)	[4] 73.3 [8] 98.0	[4] 68.82 (3) [8] 108.64 (3)	[8] 91.3 (2) [4] 97.2 (3)	[12] 95.31 (2)
X-M-X	[8] 80.6 (2) [4] 98.2 (2)	[8] 80.5 [4] 98.7	[8] 70.14 (2) [4] 90.16 (4)	[4] 82.6 (2) [8] 88.1 (2)	[12] 84.34 (3)

[a] [ ] means the number of bond distances and angles having the values listed in the right column. [b] Reference 24. [c] Reference 23. [d] This work. [e] Reference 8.

duces (in conjunction with analogous M-X bond lengths for the M_4X_4 core in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecules) a concomitant increase in the four cobalt–cobalt nonbonding distances (to 3.63 Å (av)) in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule compared to the average cobalt–cobalt nonbonding distance (of

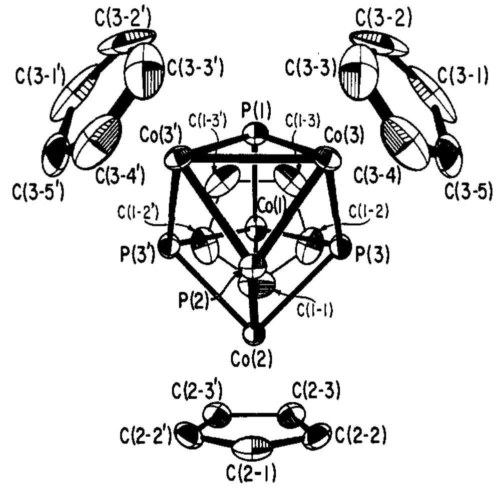

Figure 1. The $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ tetramer which possesses $D_{2d}\text{-}\bar{4}2m$ molecular symmetry and crystallographic site symmetry $C_s\text{-}m$. Thermal ellipsoids of 40% probability are shown for each nonhydrogen atom.

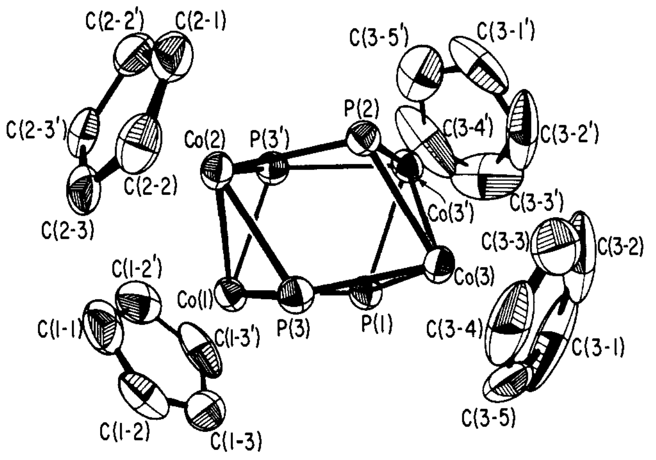

Figure 2. A view of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ which clearly reveals the $D_{2d}\text{-}\bar{4}2m$ molecular symmetry of the tetramer.

3.295 Å) in $[Co_4(h^5\text{-}C_5H_5)_4S_4]$. This pronounced deformation in the Co_4P_4 core of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ also gives rise to *two larger* P···P nonbonding distances of 3.138 Å (av) and *four smaller* P···P nonbonding distances of only 2.568 Å (av) for the distorted tetrahedron of phosphorus atoms *vs.* an intermediate average value of 2.990 Å found for the nonbonding distances in the pseudoregular tetrahedron of sulfur atoms present in the T_d-assumed Co_4S_4 architecture of the $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule. The extent of the distortion within the Co_4P_4 core from a cubic T_d geometry can also be readily appreciated by an examination of bond angles. Whereas the $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule possesses 12 similar Co–S–Co angles of 95.3° (av) and 12 similar S–Co–S angles of 84.3° (av), in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule the 12 Co–P–Co angles diverge to *four* chemically analogous (*i.e.*, with three crystallographically different) values of 68.8° (av) and *eight* chemically analogous (*i.e.*, with four crystallographically different) values of 108.6° (av), while the 12 P–Co–P angles likewise split into *four* chemically similar values of 90.2° (av) and *eight* chemically similar values of 70.1° (av).

Second, it is of prime significance that the particular kind of tetragonal D_{2d} deformation of the Co_4P_4 core in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule parallels that found for the Fe_4S_4 core of the isoelectronic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecule[23,24] in contradistinction to the kind of tetragonal D_{2d} distortion observed for the Co_4S_4 core of the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation (of different electronic structure).[8]

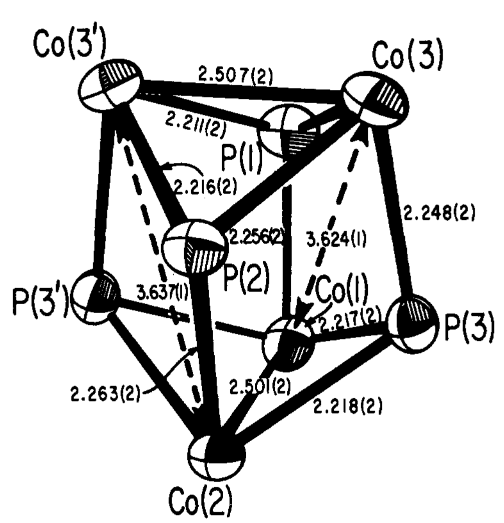

Figure 3. The Co_4P_4 core of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ with crystallographic independent interatomic distances.

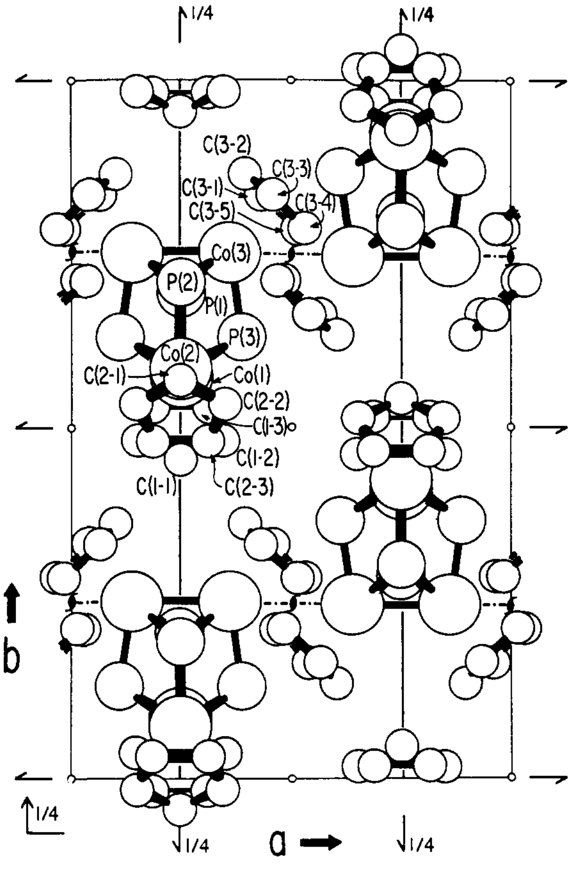

Figure 4. An [001] projection of the orthorhombic unit cell of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$.

Comparison of the corresponding distances and bond angles found in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecules in Table IV reveals that the D_{2d} tetragonal distortion of the M_4X_4 cluster system is much more *severe* in the cobalt–phosphorus tetramer as evidenced by: (1) the two metal-metal electron pair distances being 0.13-0.15 Å smaller, *viz.*, 2.504 Å (av) in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ *vs.* 2.650 (6) Å (av) and 2.631 (2) Å (av) in the monoclinic and orthorhombic phases of $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$; (2) the four chemically equivalent short X···X distances being much shorter, *viz.*, 2.568 (2) Å (av) in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ *vs.* 2.880 (7) (av) and 2.884 (3) Å (av) in monoclinic and orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$; and (3) more acute M-X-M bond angles for the two M_2X_2 fragments containing the metal-metal bonds, *viz.*, 68.82 (3)° in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ *vs.* 73.9 (2) and 73.3° in monoclinic and orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$.

This large tetragonal perturbation of the M_4X_4 core, primarily reflected from the M-M and X-X distances and in the M-X-M bond angles, is much less apparent but still statistically noticeable from an examination of the M-X distances. The 12 Co-P bond lengths (of which seven are crystallographically independent) are divided under assumed D_{2d} symmetry in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule into two distinct sets. One set for the two symmetry-related Co_2P_2 fragments containing the Co-Co bonds consists of *eight shorter* Co-P bonds (*i.e.*, four independent ones) of range from 2.211 (2) to 2.218 (2) Å with a mean length of 2.216 Å. The other set of *four longer* Co-P bonds (*i.e.*, three independent ones), which link the two Co_2P_2 fragments to each other, range from 2.248 (2) to 2.263 (2) Å with an average length of 2.256 Å. It is significant that an analogous difference in M-X bonds occurs in the $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecule for which the *eight shorter* Fe-S bonds average 2.204 Å in the monoclinic phase and 2.206 Å in the orthorhombic phase compared to the *four longer* Fe-S bonds of 2.250 Å (av) in the monoclinic phase and 2.256 Å (av) in the orthorhombic phase. In contrast, the 12 Co-S bonds in the T_d-assumed $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule range from 2.226 (2) to 2.234 (2) Å with a mean length of 2.230 Å.

The close similarity in the Fe-S, Co-P, and Co-S bond lengths of these M_4X_4 cubane-like complexes together with the above-discussed small differences in the M-X bond lengths encountered for the tetragonally deformed $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecules provide firm evidence that one of the most stringent steric requirements of a metal cluster geometry is the metal-ligand distance.[39-42] The metal-metal interactions, although apparently much weaker than the M-X bonds, nevertheless represent the dominant perturbation (or driving force) in any significant distortions of the M_4X_4 core such that (if the unpredictable effects of crystal packing forces are not considered to be a main factor) the resulting geometry of the M_4X_4 cluster is governed not only by the minimization of all nonbonded repulsions between the atoms but also by interorbital electron pair interactions which for a more electronegative bridging ligand X favor a wider bridging angle.[43-46] With respect to the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecules, the occurrence of a much greater tetragonal deformation of the Co_4P_4 architecture (relative to that of the isoelectronic Fe_4S_4 architecture) may be attributed to the intrinsic nature of the cobalt atoms (with a greater internuclear charge) to equilibrate in a structurally analogous and electronically equivalent complex at a shorter metal-metal bonding distance—*viz.*, 2.50 *vs.* 2.64 Å for the average Fe-Fe bonding distance in the $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecule. The less electronegative bridging phosphorus atom forms more acute Co-P-Co bond angles of 69° for the two Co_2P_2 fragments containing the cobalt-cobalt bonds in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ compared to the acute Fe-S-Fe bond angles of 73-74° for the corresponding two Fe_2S_2 fragments in $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$.

The most distinguishing structural difference which has an important bearing upon the ability of the Co_4P_4 core to achieve a much greater tetragonal deformation is the extremely short contacts of 2.57 Å existing between four of the six pairs of the phosphorus atoms in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ compared to the corresponding S···S contacts of 2.88 Å for the sulfur atoms in $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$. This difference of 0.3 Å between the P···P and S···S separations is remarkable, especially in view of the fact that the "normal" van der Waals distance of 3.8 Å between two phosphorus atoms is *greater* than the "normal" van der Waals distance of 3.7 Å between two sulfur atoms.[47] It is highly significant that intraligand P···P distances of 2.6-2.7 Å have also been found in other phosphide structures[48] (*vide infra*), whereas the shortest known intraligand S···S distances (to our knowledge) are 2.8-2.9 Å.[23,24,49-52] These P-P distances, which are unusually short for nominally "nonbonded" ligand atoms, indicate the possible presence of attractive bonding forces between the phosphorus atoms which may involve contributions from the phosphorus 3d orbitals.[53,54] It is noteworthy that

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(39) It is of interest that the average Co–P and Ni–P bond length of 2.16 Å in $Co_2(h^5\text{-}C_5H_5)_2[\mu\text{-}P(C_6H_5)_2]_2$[40] and 2.15 Å in $Ni_2(h^5\text{-}C_5H_5)_2[\mu\text{-}P(C_6H_5)_2]_2$[40] are similar to each other but significantly shorter than the average Fe–S bond lengths of 2.26 Å in $Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2$[41] and 2.27 Å in $Fe_2(NO)_4(\mu\text{-}SC_2H_5)_2$.[42] These bond length comparisons were interpreted in terms of substantially greater π bonding for a bridging $P(C_6H_5)_2$ ligand than a bridging SC_2H_5 ligand.[40]

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(43) The large dependence of metal–metal bonding distances upon the particular ligand-bridged geometry and the influential role of the size and effective electronegativity of the bridging ligands (with the less electronegative atomic ligands giving rise to sharper M–X–M bond angles) has been clearly demonstrated for other chalcogen and pnicogen complexes of iron and cobalt.[44-46]

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(51) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, No. INOR 130; submitted for publication.

(52) Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, submitted for publication.

(53) It is noteworthy that Gray and coworkers[54] proposed that the interligand S···S distances of 3.04–3.17 Å range found in transition metal dithiolate structures (especially ones containing a trigonal-prismatic array of sulfur atoms) indicate some residual S–S bonding. Amma and coworkers[50] also concluded from their stereochemical analysis of the molecular structure of bis(dithiobiureto)nickel(II) that the short interchelate S···S distance of 2.89 Å in this complex is likewise a consequence of some residul S–S bonding.

(54) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3354 (1967); E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2956 (1966); R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).

the vapor from white phosphorus has been shown from an electron diffraction study to be composed of tetrahedral P_4 molecules with P–P distances of 2.21 (2) Å.[47] This value is within the 2.2 ± 0.05 Å range of covalent single bond P–P distances found both in other allotropic forms of phosphorus and in a variety of phosphorus compounds containing P–P linkages (except for α-P_4S_7 which has a P–P bond of 2.35 (1) Å).[47] In a classification of phosphide structures on the basis of observed P–P distances, Corbridge[48] noted the existence of structures with P···P distances of range 2.6–2.7 Å (*e.g.*, UP_2 and the MnP-type phosphides including CoP which has a P···P distance of 2.70 Å) and concluded that such a distance is too great for a normal type of covalent single bond but that "it is presumably influenced by the nature of the remaining linkages formed by the P atom." It is evident that such a situation prevails in the case of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule.

It is our prejudice that the extremely short P···P contacts are primarily nonbonding. On the basis of the reasonable assumption that the lone pair on each triply bridging X atom of the M_4X_4 core is localized in a tetrahedral-like orientation which is directed outwards from the centroid of the XM_3 part of the M_4X_4 core, then the nonbonding intramolecular repulsions among the bridging X ligands appear to be minimized along the X···X directions. Furthermore, of the two sets of M–X bond lengths clearly resolved in only the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ molecules, the set of larger M–X bond lengths is associated with the four M_2X_2 fragments (without the M–M bonds) containing the short X···X separations. It is our opinion that these larger M–X distances in the cobalt-phosphorus and iron-sulfur tetramers are a manifestation of an attempt to alleviate the steric pressures originating from the extremely short X···X distances. In the light of the resulting stereochemistry, it is somewhat surprising to us that $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ exists.[55,56]

The 11 independent cobalt-cyclopentadienyl carbon bond lengths in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ range from 2.064 (7) to 2.141 (9) Å with a weighted average of 2.102 Å. The distances between the cobalt atoms and centroids of the respective cyclopentadienyl rings are identical within the experimental error at 1.743, 1.746, and 1.751 Å. These values are also virtually identical with those found in $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ (1.742 and 1.747 Å),[8] in monoclinic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ (1.74 and 1.75 Å),[24] and in orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ (1.756, 1.757, and 1.757 Å).[23] The cyclopentadienyl carbon–carbon bond lengths in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ vary from 1.307 (12) to 1.436 (14) Å with a weighted average of 1.371 Å. The smaller C–C bond lengths expectedly are found for those cyclopentadienyl carbon atoms which in Figures 1 and 2 exhibit elongated thermal ellipsoids approximately within the mean plane of the cyclopentadienyl ring characteristic of high librational ring motion and/or crystal disorder involving at least two orientations for a given ring. Least-squares planes calculations reveal each cyclopentadienyl ring in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ to be essentially planar with no carbon atoms in a given ring deviating from the mean plane by more than 0.01 Å.

Bonding Description. The observed tetragonal D_{2d} distortion of the Co_4P_4 core of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule, attributed to the metal–metal interactions, may be rationalized qualitatively in this particular case by application of simple valence bond considerations (*i.e.*, in contrast to the electronic description of the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation[8] which is not possible from simple valence bond theory). In a simple bookkeeping of valence electrons, each cobalt atom in $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ needs nine electrons to achieve a closed-shell electronic configuration; with the donation of five electrons from the *pentahapto*cyclopentadienyl radical and one electron from each of the three phosphorus atoms, each cobalt is one electron short of the so-called EAN configuration. This situation is alleviated by the formation of two cobalt–cobalt electron pair bonds in accord with both the indicated diamagnetic character of the compound and resulting molecular geometry.[57]

The metal cluster MO model utilized to discuss qualitatively the bonding in $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ (n = 0, +1)[8] can also provide additional insight into the metal–metal interactions pertaining to the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule. This model, initially applied to other cubane-like M_4X_4 systems—*viz.*, $Co_4(CO)_{12}Sb_4$,[22] $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$,[22] and $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ (n = 0, +1)[58]—was then extended by Teo and Trinh-Toan in our laboratories to portray the topological nature of the metal cluster orbitals for the differently distorted iron tetrahedrons in the $[Fe_4(h^5\text{-}C_5H_5)_4S_4]^n$ (n = 0, +1, +2) complexes[52] and later generalized[59] to cover all probable electronic configurations found in dimeric, trimeric, and tetrameric metal cluster systems. This metal cluster model considers metal–ligand interactions involving both terminal and bridging ligands to be localized and hence to a first approximation factorizes them from the delocalized metal–metal interactions. Despite its simplicity and apparent drastic assumptions,[60] this model, which produces a conceptually digestable picture of the nature of metal–metal inter-

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(55) For a cubane-like M_4X_4 system of D_{2d} tetragonal geometry with *two* short and *four* long M–M distances and with relatively rigid M–X bonds (*i.e.*, exemplified by the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_6H_5)_4S_4]$ molecules), a significant *decrease* in the M–M distance for each of the two M_2X_2 fragments containing the electron pair M–M bonds concomitantly should *increase* the four nonbonding M···M distances in the four other M_2X_2 fragments resulting in four *shorter* X···X distances in these four M_2X_2 fragments. Conversely, an *enlargement* of these four short X···X distances in turn should *increase* the two bonding M–M distances and *decrease* the four nonbonding M···M distances. Since electron pair Co–Co bonds in other organometallic cobalt complexes have been determined to range from 2.4 to 2.8 Å, a considerably larger Co–Co bonding distance (*e.g.*, 2.65 Å instead of the observed 2.50 Å) would have been anticipated in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule in order to relieve the presumably large steric pressures of the unusually short P···P separations by an increase in their distances. The actual geometry of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule thereby defies stereochemical expectancy.

(56) One may readily rationalize that the paucity to date of transition metal complexes with atomic phosphorus ligands (*vs.* the large number of known metal–sulfur clusters with naked sulfur atoms as ligands) primarily arises from the lack of phosphorus reagents with the ability to cleave their substituents either before or after metal complexation.

(57) An equivalent description is that each cobalt possesses a formal oxidation state of IV and achieves a noble gas magic number by donation of six electrons from the cyclopentadienyl anion, two electrons from each of the three phosphide anions, and one electron from another Co(IV) by virtue of an electron pair Co(IV)–Co(IV) bond.

(58) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3389 (1972).

(59) B. K. Teo and L. F. Dahl, manuscript in preparation.

(60) On the basis that the four extremely short P···P contacts in the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ molecule imply residual P–P bonding, rigorous molecular orbital calculations of these metal cluster systems (including the terminal ligands) may discern that the M_4X_4 core should properly be considered *in toto* as an eight-centered electron-delocalized system rather than simply viewed under our currently utilized qualitative metal cluster model as a system which regards complete electron delocalization only among the metal atoms.

actions, not only has rationalized the stereochemistry of a large number of metal clusters but also has led to successful predictions of probable geometries for metal cluster systems including the specific kind of tetragonal D_{2d} distortion found for the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation. The model is put to use here in connection with a correlation of the particular electron configuration of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ tetramer with its determined structure.

The inherent boundary conditions of this delocalized MO model and the details of the symmetry arguments utilized for the cubane-like M_4X_4 systems are presented elsewhere.[8,22,53] Under assumed cubic T_d symmetry three valence orbitals per metal atom available for direct metal–metal interactions are compounded into 12 tetrametal symmetry combinations (*viz.*, six bonding ones of $a_1 + e + t_1$ representation and six antibonding ones of $t_1 + t_2$ representation). The change in triply bridging ligands from sulfur to phosphorus, by which neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ (with its completely nonbonding tetrahedron of metal atoms being compatible with *full* occupancy of all 12 bonding and antibonding tetrametal symmetry orbital combinations) is transmuted into $[Co_4(h^5\text{-}C_5H_5)_4P_4]$, may be formally regarded to correspond to the removal of four electrons from the highest filled energy level(s) of the neutral cobalt–sulfur tetramer. Invariant to which of the triply degenerate tetrametal antibonding levels t_1 or t_2 lies highest in energy, under cubic T_d geometry the two remaining electrons in a triply degenerate level would give rise to either a $^3T_1$ or $^3T_2$ ground state. A resulting distortion of the Co_4P_4 framework to a tetragonal D_{2d} geometry is possible *via* a Jahn–Teller active vibration in order to break the orbital degeneracy of the ground state. Under D_{2d} symmetry the t_1 level splits to give an a_2 level and an e level, while the t_2 level splits into a b_2 level and an e level. An examination of the orbital character of the symmetry-adapted wave functions indicates that the observed tetragonal formation of *two* short and *four* long Co–Co distances would be expected to occur only if the four electrons are completely depopulated from a doubly degenerate orbital e which is primarily antibonding with respect to the Co(1)–Co(2) and Co(3)–Co(3′) bonds (*i.e.*, Co(4) is labeled as Co(3′) due to the crystallographic mirror-plane symmetry). These latter considerations of orbital character appear to eliminate the possibility that the four electrons have been abstracted from both the nondegenerate a_2 and b_2 orbitals. Each of these orbitals is primarily antibonding with respect to the Co(1)–Co(3), Co(1)–Co(3′), Co(2)–Co(3), and Co(2)–Co(3′) bonds such that their vacancy should instead lead to *four* short and *two* long Co–Co bonds. Hence, the observed molecular deformation precludes this possible arrangement of energy levels. The same kind of geometrical deformation present in both the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ tetramers strongly implies that the corresponding energy levels in these two isoelectronic species are similarly occupied.[61]

Acknowledgments. We are most pleased to acknowledge the financial support of the National Science Foundation (No. GP-19175X). One of us (G. L. S.) is indebted to Abbott Laboratories (North Chicago, Ill.) for a research fellowship (Sept. 1971–Aug. 1972). The use of the UNIVAC 1108 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. The authors wish to thank Dr. Trinh-Toan and Mr. Boon Keng Teo at the University of Wisconsin (Madison) for helpful consultations.

(61) Subsequent to our structural analysis of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$, we have noted that its crystalline orthorhombic phase is nearly isomorphous with the orthorhombic crystalline phase of $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ which was characterized from an X-ray diffraction study by Schunn, Fritchie, and Prewitt.[23] They found the orthorhombic unit cell of $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ to have the dimensions $a = 17.444$, $b = 10.488$, and $c = 11.348$ Å and space group symmetry *Pnam* [nonstandard setting of *Pnma* (D_{2h}^{16}, No. 62)] with each of the four molecules in the cell bisected by a crystallographic mirror plane of *Pnam*. By an appropriate transformation of axes, the close crystallographic similarities of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and the orthorhombic phase of $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ can be elucidated. For orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$, *Pnam* (with unprimed axes) is equivalent to the *Pmnb* space group of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ (with primed axes) by $a' = c = 11.348$, $b' = a = 17.444$, and $c' = b = 10.488$ Å. These primed lattice constants, which transform orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ into the space group *Pmnb*, parallel those given in this manuscript for $[Co_4(h^5\text{-}C_5H_5)_4P_4]$. Furthermore, a comparison of the corresponding positional parameters for the two complexes shows a close resemblance of the orientations of the $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ and $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ in their respective orthorhombic unit cells; this similarity is also apparent from a comparison of the packing diagram of $[Co_4(h^5\text{-}C_5H_5)_4P_4]$ in Figure 3 in this paper with that of orthorhombic $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$ in Figure 4 of the Schunn–Fritchie–Prewitt paper.[23]