Table I. Bond Distances (Å) and Bond Angles (deg)

Al(1)–O(3)	1.873 (6)	Mn(1)–C(2)	1.818 (10)
C(3)–O(3)	1.248 (9)	Mn(1)–C(1)	1.859 (12)
C(3)–C(4)	1.541 (11)	C(2)–O(2)	1.144 (10)
Mn(1)–C(3)	1.818 (10)	C(1)–O(1)	1.143 (11)
O(3)–Al(1)–O(3)	92.5 (4)	C(2)–Mn(1)–C(2)	165.4 (6)
Al(1)–O(3)–C(3)	139.1 (5)	O(2)–C(2)–Mn(1)	176.5 (9)
Mn(1)–C(3)–O(3)	127.7 (6)	C(1)–Mn(1)–C(1)	85.8 (7)
Mn(1)–C(3)–C(4)	120.1 (7)	O(4)–Al(1)–O(4)	176.2 (4)
C(3)–Mn(1)–C(3)	93.0 (5)	O(3)–Al(1)–O(5)	175.5 (2)

140°; deep brown at 265°; ir (C_6H_{12} in cm^{-1}) ν(CO) 2065 m, 1985 s, sh, 1978 vs, 1960 s, ν(C=O) 1525, s; ^{1}H NMR ($CDCl_3$ vs. TMS), τ 7.28 (singlet).[5] Anal. for $C_{24}H_{18}O_{18}Mn_3Al$: Calcd: C, 36.66; H, 2.31; Mn, 20.96; Al, 3.43. Found: C, 36.50; H, 2.41; Mn, 20.66; Al, 3.45.

Since the formulation of compound **3** as a "metallo-acac" complex would represent the first member of possibly a large series of similar complexes, we obtained, commercially, an x-ray structural determination which was performed as a technical service.[6]

Crystal data: $Al[Mn(CO)_4(COCH_3)_2]_3$; M = 786.20, monoclinic; a = 13.948 (5) Å, b = 12.182 (6) Å, c = 19.545 (6) Å; $\alpha = \gamma = 90°$; β = 90.51 (2)°; Z = 4; d_{calcd} = 1.572 g/cm^3; space group $P2/n$. Intensity data were collected on a Syntex P$\bar{1}$ computer-controlled diffractometer using MoKα radiation. In the refinement of the structure, 2099 reflections having $F_o^2 > 3\,\sigma(F_o^2)$ were used. Anisotropic refinement of all non-hydrogen atoms gave the final agreement factors R_1 = 0.049 and R_2 = 0.070. An ORTEP view of the molecular structure of **3** is shown in Figure 1 and pertinent bond distances and bond angles are given in Table I. There are two independent molecules per unit cell each having a crystallographic C_2 axis passing through one of the manganese atoms and the aluminum atom. See paragraph at the end of paper regarding supplementary material.

The molecular structure belongs to the symmetry point group D_3. The chemically interesting structural features of the molecule are: (i) the aluminum and manganese atoms have only slightly distorted octahedral local symmetry; (ii) the "metallo-acac" ligand is symmetrical and essentially planar as expected from the resonance structure of **1**; (iii) the values of the following bond distances (Al-O(3), 1.873 (6) Å; C(3)-O(3), 1.277 (6) Å; C(3)-C(4), 1.541 (11) Å) and the following bond angles (Al-O(3)-C(3), 139.1 (5)°; O(3)-C(3)-Mn(1), 127.7 (6)°; C(3)-Mn(1)-C(3), 93.0 (5)°; O(3)-Al-O(3), 92.5 (4)°) observed within this "metallo-acac" ligand indicate, through comparison with the corresponding values observed in $Al(acac)_3$,[7] that the 93° angle centered at the Mn atom is compensated by increasing the other intraligand angles so as to maintain an O-Al-O angle of near 90°; and (iv) each of the two carbonyl groups on the manganese atoms which are aligned perpendicular to the "metallo-acac" plane are directed toward an open face of the aluminum coordination octahedral such that the C(2)-Mn(1)-C(2) angle is 165.4 (6)° rather than the expected 180°. Apparently, the aluminum atom is bonded very weakly to these six oxygen atoms through a long range (4.56 Å) Lewis acid-base interaction.

Although complex **3** has a large molecular weight and high thermal stability it dissolves readily in methylene chloride and chloroform and it is moderately soluble in toluene. The number and relative intensities of the ν(CO) vibrations are consistent with a *cis*-$R_2M(CO)_4$ species.[8] The values of the chemical shift of the methyl resonance (τ 7.28) and the C=O stretching frequency (1525 cm^{-1}) reported here are lower than the corresponding values observed for $Al(acac)_3$, τ 8.00[9,10] and 1589[11] cm^{-1}, and are closer to those values observed in $Al(3\text{-bromo-acac})_3$, τ 7.69[10] and 1560[12] cm^{-1}. This similarity is consistent with the expectation of the strong σ-electron withdrawing nature of an $Mn(CO)_4$ group. The influence of the metal group on the ligand π-electron system must await more detailed studies such as introducing a paramagnetic ion in place of the aluminum ion.

Extensive research effort is being applied to extend the preparation of "metallo-acac" complexes using various acyl, carboalkoxy, and carbamyl complexes and diverse organolithium reagents. Substitution of the central coordinating ion and the possible catalytic activity of these complexes are being investigated, also.

Acknowledgments. We thank the Research Corporation and the University Research Council of Vanderbilt University for support of this research.

Supplementary Material Available. A listing of data, structure factor amplitudes, refinement procedures, least-squares planes, interatomic bond distances and angles, and positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6903.

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Synthesis, Structure, and Bonding of a Mono(organo)phosphido-Bridged Tetracobalt Carbonyl Cluster, $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$. A New Mode of Transition Metal Coordination for a PR Ligand[1]

Sir:

We wish to report the isolation and stereochemical characterization of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ which is unprecedented in its possessing a pentacoordinate phosphorus atom bonded to four transition metal atoms. The structural results are also of interest in relation with other chalcogenido- and phosphido-bridged metal clusters in providing bond-length evidence for the existence of *attractive* interligand P···P interactions which appear to be considerably stronger than the corresponding interligand S···S interactions. This work was a direct result of our involvement in

Table I. Selected Mean Distances and Bond Angles for the Three $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}X)_2$ Complexes Containing an Octahedral-Like Co_4E_2 Core[a-c]

	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$[d]		$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2$[e]		$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}Te)_2$[f]	
Co_4E_2 Core		Co_4P_2		Co_4S_2		Co_4Te_2
Co–Co (CO-Bridged)	[2]	2.519 (2)	[1]	2.48 (1)	[1]	2.58 (2)
Co–Co (Unbridged)	[2]	2.697 (2)	[1]	2.60 (1)	[1]	2.88 (2)
Co–E	[8]	2.244 (E = P)	[4]	2.26 (1) (E = S)	[4]	2.54 (1) (E = Te)
Co–E–Co (CO-Bridged)	[4]	68.4 (1) (E = P)	[2]	66.6 (3) (E = S)	[2]	61.0 (3) (E = Te)
Co–E–Co (Unbridged)	[4]	74.0 (E = P)	[2]	70.2 (3) (E = S)	[2]	68.9 (3) (E = Te)
E···E	[2]	2.544 (3) (E = P)	[1]	2.74 (2) (E = S)	[1]	3.30 (1) (E = Te)

[a] Based upon an assumed D_{2h} geometry for the $Co_4(CO)_{10}P_2$ fragment (without the phenyl rings) and for the sulfur and tellurium molecules. The three molecules each possess crystallographic site symmetry C_i-$\bar{1}$ with the chalcogenido-bridged molecules each having *one* one-half molecule and the phenylphosphido-bridged molecule having *two* one-half molecules in the crystallographically independent unit. [b] Each esd given in parentheses represents that of a single observation rather than an estimated standard deviation of the mean. [c] Brackets [] designate the number of equivalent distances or angles having values listed in right column. [d] This work. [e] Reference 6b. [f] Reference 7b.

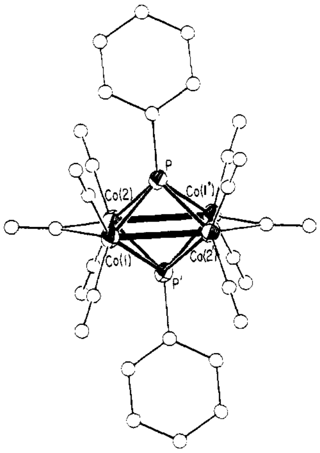

Figure 1. The $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ molecule with crystallographic site symmetry C_i-$\bar{1}$ is drawn with 20% probability thermal ellipsoids for the Co and P atoms. The $Co_4(CO)_{10}P_2$ fragment (without the phenyl rings) ideally conforms to a D_{2h}-*mmm* geometry.

determining changes in the chemical and physical properties of various metal sulfide clusters upon formal substitution of electronically equivalent mono(organo)phosphide ligands in place of sulfur ones. The fact that the recently prepared $Fe_3(CO)_9(\mu_3\text{-}PC_6H_5)_2$ trimer,[2] containing two PR ligands trigonally coordinated to three metal atoms, was shown[3] to be structurally analogous to the $Fe_3(CO)_9(\mu_3\text{-}X)_2$ molecules (X = S[4], Se[5]) led to our attempt to prepare the corresponding PR complex of the unique $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}X)_2$ tetramers containing either sulfur[6] or tellurium[7] coordinated to a bonding rectangular array of metal atoms.

The successful synthesis of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ was accomplished by a reduction of $Co_2(CO)_8$ (15.0 mmol) in toluene with an excess of Zn powder under carbon monoxide atmosphere followed by a slow addition of $C_6H_5PCl_2$ (7.4 mmol) in toluene to the filtered solution. An immediate reaction occurred with gas evolution and a color change of the solution from light yellow to deep red. The solution was then refluxed for 12 hr, cooled, and purified on a silica gel column to give a very soluble dark red complex isolated in 30-35% yield. A Fourier-transform infrared spectrum exhibited three terminal carbonyl bands at 2040 (vs), 2032 (s), and 2016 (s) cm^{-1} together with a band in the bridging carbonyl region at 1866 (w) cm^{-1}. Evidence for the stoichiometry of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ was provided by its mass spectrum which exhibited the parent ion peak at *m/e* 732. The diamagnetism of this air-stable complex was established by magnetic measurements via the Faraday method.[8] A ^1H NMR spectrum in acetone-d_6 showed a multiplet at τ 2.35 (vs. internal TMS) characteristic of the phenyl protons.

An x-ray structural determination[9,10] revealed two independent half-molecules (of crystallographic site symmetry C_i – $\bar{1}$) with analogous molecular parameters which are deemed on the basis of sufficiently large intermolecular contacts not be markedly influenced by crystal packing forces. The molecular configuration (Figure 1) consists of a $Co_4(CO)_8(\mu_2\text{-}CO)_2$ fragment containing four $Co(CO)_2$ groups arranged at the corners of a bonding cobalt rectangle whose shorter two sides are each spanned by a symmetrical bridging carbonyl. The cobalt rectangle is capped above and below by quadruply bridging PC_6H_5 ligands to give an octahedral-like Co_4P_2 core such that the $Co_4(CO)_{10}P_2$ part of the resulting $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ molecule conforms closely to an orthorhombic D_{2h}-*mmm* geometry. The mean parameters of the octahedral Co_4P_2 core are compared in Table I with those for the analogous cores in the corresponding calcogenide complexes.

The close similarity in coordination of the phenylphosphido- and chalcogenido-bridged ligands to the common $Co_4(CO)_8(\mu_2\text{-}CO)_2$ fragment confirms the hypothesis[11] that each square pyramidal chalcogenide atom in this type of complex effectively functions as a four-electron-donating ligand to the set of four metal atoms with the remaining two valence electrons residing in a separate localized chalcogenide orbital as an unshared electron pair.

Prominent structural features for $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ (whose structure was much more precisely determined than those obtained from photographic data for the sulfur and tellurium analogues) include the following: (1) the CO-bridged electron-pair Co-Co bond of 2.519 (2) Å is 0.18 Å shorter than the unbridged electron-pair Co-Co bond of 2.697 (2) Å in harmony with the observation that bridging carbonyls generally give rise to shorter electron-pair metal-metal bonds. The much greater bond-length variation in the unbridged Co-Co bonds relative to the CO-bridged Co-Co bonds upon a change of the two quadruply bridging ligands from S to PR to Te (Table I) presumably reflects the constraining influence of the bridging carbonyls. (2) The Co-P distances range from only 2.237 (3) to 2.255 (3) Å; the closeness between the average Co-P and Co-S distances vs a 0.30 Å longer average Co-Te distance may be related primarily to the variation in covalent radii of P (1.10 Å), S (1.04 Å), and Te (1.37 Å). (3) The terminal carbonyl Co-C and C-O bonds vary from 1.777 (8) to 1.824 (9) Å and from 1.101 (10) to 1.144 (9)

Å, respectively, whereas the bridging carbonyl Co–C and C–O bonds vary from 1.928 (8) to 1.959 (9) Å and from 1.157 (9) to 1.164 (9) Å, respectively. These trends are in accord with those found in other metal carbonyl clusters. (4) The P–C(phenyl) bond length of 1.81 Å is that expected for a single-bond distance. No assessment from bond-length correlations of the differences in Co–P bonding between the five-coordinate phosphorus atoms in $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ and four-coordinate phosphorus atoms in other cobalt clusters is made at this time, partly due to a present lack of structural data for RP-bridged cobalt trimers.

An examination of Table I shows that the major alteration in the Co_4E_2 core upon a replacement of the two sulfur atoms by PC_6H_5 ligands is the large decrease in the E···E distance from 2.74 (2) Å[12,13] for E = S to 2.544 (3) Å for E = P. Because of the close agreement between the covalent radii of S and P (and likewise between their van der Waal radii)[14] and because these structurally analogous molecules do not appear to exhibit unusual steric effects due to interligand overcrowding, a plausible explanation in our opinion for the 0.20 Å shortening of the E···E distance (to a value only 0.3 Å greater than an accepted single-bond P–P distance)[15] lies in the two P atoms being pulled toward each other due to attractive bonding interactions which may involve contributions from the phosphorus 3d orbitals. Since the Co–E bond lengths are essentially identical in these Co_4P_2 and Co_4S_2 cores, the observed deformation in the Co_4P_2 core to give the smaller E···E distance necessitates the concomitant increases in the corresponding Co–Co bond distances and corresponding Co–E–Co bond angles. Similar short P···P separations, which are 0.3 Å shorter than the corresponding S···S separations, exist in other types of organometallic clusters—viz., $Fe_3(CO)_9(\mu_3\text{-}PC_6H_5)_2$ (P···P, 2.592 (3) Å)[3] vs. $Fe_3(CO)_9(\mu_3\text{-}S)_2$ (S···S, 2.885 (2) Å)[4b] and $Co_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}P)_4$ (P···P, 2.57 Å)[16] vs. $Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4$ (S···S, 2.88 Å).[17] Although the possibility of residual P···P bonding was considered in the latter cubane-like molecule, it was concluded that the "extremely short P···P contacts are primarily nonbonding" due to the overall geometrical constraint imposed on the phosphorus atoms by the other atoms.[16] On the basis of the results presented here, we now propose that the short P···P distances in these organometallic clusters instead arise from distinct bonding forces which (despite being small relative to metal-ligand interactions) do nevertheless cause a considerable perturbation on the geometry; the much smaller P···P distances also imply considerably stronger P···P than S···S interactions for each of the above types of organometallic clusters.

The work presented here will be reported in full upon completion of complementary research which will include physical-chemical studies of related species as well as the application of the nonparameterized Fenske-Hall MO method[18] in order to provide an assessment of our bonding conclusions.

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Supplementary Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6904.

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(8) We are indebted to Mr. James Kleppinger at the University of Wisconsin (Madison) for making the magnetic susceptibility measurements.

(9) $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$: triclinic; $P\bar{1}$; a = 11.390 (6), b = 14.257 (10), c = 9.124 (6) Å; α = 97.99 (6), β = 113.27 (4), γ = 96.13 (5)°; V = 1326.4 Å^3; d_{calcd} = 1.83 g cm^{-3} for $Z = 2$. Least-squares refinement of the coordinates of all atoms with variable anisotropic thermal parameters for the nonhydrogen atoms and fixed isotropic ones for the hydrogen atoms gave $R_1(F)$ = 4.3% and $R_2(F)$ = 6.5% for 2661 independent diffractometry data ($I \geq 2\sigma(I)$).

(10) For computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal.

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Biosynthesis of the Indole Alkaloids. A Cell-Free System from *Catharanthus roseus*

Sir:

From the inception of experimental analysis of hypotheses for the biogenesis of the plant alkaloids it has been recognized[1] that problems of permeability,[2] compartmentation of metabolic pools,[3] and translocation phenomena[4] have imposed severe limitations on incorporation levels of labeled substrates in feeding studies with the intact higher plant. These factors seem to be particularly dominant in those species which produce complex indole alkaloids, where the reported specific incorporations of labeled "intermediates" are mainly in the range 10^{-1}–10^{-3}%.[5,6] Notwithstanding considerable progress in the delineation of the broad outlines[5,7] of alkaloid biosynthesis in *Catharanthus*, *Vinca*, and *Aspidosperma* spp., there would appear to be general agreement[1,4,5] that only with the advent of enzymological techniques for alkaloid synthesis could those criteria recently summarized by Cornforth[8] be met for the many postulated biointermediates on the tryptophan-secoiridoid pathway leading to the major alkaloid families.