aqueous solution because of the strong self-interaction of water molecules. With the bases in a close proximity to each other, short-ranged, attractive forces (forces proportional to $(1/r)6$ or even to $(1/r)3$) begin to become dominant, which most likely involve π electrons polarizabilities and energies through electrostatic interaction.[6,34]

The recent paper by Helmkamp and Kondo[35] is of significance in providing further understanding about the nature of the molecular forces participating in the association. They reported that the apparent free energy for self-association (ΔF, cal/mole) of 9-methylpurine in aqueous solution at 25° is -380, while the ΔF for purine and 6-methylpurine are -440 and -1100, respectively.[2,3] The concentration dependence of the chemical shifts ($\Delta\delta$) of the protons of 6-methylpurine[4] correspondingly is much higher than those of 9-methylpurine and purine.[4,35] This difference between the C-6 methylation *vs.* N-methylation is unlikely to be due to the loss of contribution of hydrogen bonding to the association, by the removal of the N-H in the N-9 methylation. The reasons are that these molecules associate mainly through stacking, as shown by the upfield shift observed,[2,3,35] and that they do not associate in organic solvents. At present, there is also no obvious reason why this difference is caused by a steric effect. The best explanation we can propose is that the N-9 alkylation has blocked the tautomerization of the N-H between the N-9 and N-7 at the five-membered ring of the purine derivatives. The blockage of this tautomerization causes a reduction in the allowable patterns of electron distribution in the system and should, therefore, decrease the polarizability of the molecule. This decrease may lead to a lowering of the tendency of association in stacking. Comparison of the thermodynamic qualities of the association with the polarizability of these compounds will be of significant value. Helmkamp and Kondo[30] have also reported that the substitution of isopropyl or *t*-butyl at the N-9 position will have a much smaller effect on the extent of association of the alkylated compound than when substitution by these groups is at C-8, C-2, or C-6 positions. However, the concentration dependence of the chemical shifts ($\Delta\delta$) observed for the N-9 alkylated compounds is slightly higher than for those substituted at various carbon atoms. These data imply the possibility that the N-9-substituted compounds may have a different mode of association than that of the carbon-substituted compounds, besides having comparatively lower association constants.

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[34] S. Hanlon, *Biochem. Biophys. Res. Commun.*, 23, 861 (1966).

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Communications to the Editor

Organometallic Pnicogen Complexes.[1] III. Preparation and Structural Characterization of the Triarsenic–Cobalt Atom Cluster System $As_3Co(CO)_3$. The First Known X_3–Transition Metal Analog of Group Va Tetrahedral X_4 Molecules[2,3]

Sir:

A comprehensive investigation of the field of arsenic–metal carbonyl clusters has resulted in the isolation and characterization of a truly unusual molecule, $As_3Co(CO)_3$, which represents another member of the arsenic–metal cluster series derived by the successive replacement of As atoms in the tetrahedral As_4 molecule with electronically equivalent $Co(CO)_3$ groups.[3,4] The synthesis and X-ray investigation of this remarkable arsenic–metal carbonyl complex, which is distinguished from yellow As_4 (and white P_4) by high air stability and striking ease of formation,[5,6] was a consequence of our attempt to prepare a group Va analog of the antiaromatic chalcogen metal atom clusters $XCo_3(CO)_9$ (X = S, Se).[7–9]

The reaction of $Co_2(CO)_8$ and $[AsCH_3]_5$ in hexane at 200° under 100 atm of carbon monoxide yields a variety of products. Chromatography on silica gel with hexane elutes pure $As_3Co(CO)_3$, and sublimation in a sealed tube at 35° and 10 mm pressure produces clear yellow hexagonal plates. The mass spectrum of this diamagnetic complex[10] shows not only all As_3Co-

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[1] The terms "pnicogen" (Greek, πνιγμόζ—a choking, suffocation) and "pnictide" have been introduced as group names for the group Va family of elements (N, P, As, Sb, and Bi) analogous to the use of "chalcogen" and "chalcogenide" as group names for the group VIa elements. The fact that these terms have been gaining scientific favor in the past several years (as stated by E. F. Westrum, Jr., *Progr. Sci. Technol. Rare Earths*, 2, 76 (1966) is typified by their usage in the following references: F. J. Kohl, J. E. Prusaczyk, and K. D. Carlson, *J. Am. Chem. Soc.*, **89**, 5501 (1967); A. T. Howe and P. J. Fensham, *Quart. Rev.* (London), 21, 521 (1967).

[2] For previous papers in this series, see (I) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967); (II) L. F. Dahl, W. R. Costello, and R. B. King, *ibid.*, **90**, 5422 (1968).

[3] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn. April 1969.

[4] A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 5633 (1969).

[5] The yellow arsenic allotrope, As_4 (which is less stable than white P_4), is metastable under all conditions. When exposed to light even at $-180°$ it rapidly changes to gray arsenic (isomorphous with black phosphorus); it is rapidly oxidized by air at room temperature.[6]

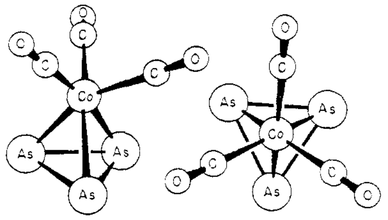
[6] *Cf.* P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Longmans, Green and Co., Ltd., London, 1962, p 736.

[7] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 6, 1229 (1967).

[8] C. E. Strouse and L. F. Dahl, *Discussions Faraday Soc.*, in press.

[9] C. E. Strouse and L. F. Dahl, submitted for publication.

[10] Faraday magnetic measurements at room temperature kindly performed by Mr. Michael Camp confirmed the expected diamagnetism.



$As_3Co(CO)_3$

Figure 1. Idealized C_{3v} molecular configuration of $As_3Co(CO)_3$. The crystallographically demanded molecular site symmetry is C_3.

$(CO)_n^+$ ions (n = 0–3) but also all possible $As_xCo_y^+$ ions (x = 0–3; y = 0, 1). Its infrared spectrum in hexane solution shows the two strong bands characteristic of a symmetrical cobalt tricarbonyl: the nondegenerate A_1 vibration at 2083 cm^{-1} and the degenerate one at 2039 cm^{-1}.

X-Ray photographs of $As_3Co(CO)_3$ show trigonal C_{3i}-$\bar{3}$ Laue symmetry with no systematic absences. Successful refinement of the structure in $P\bar{3}$ confirmed our initial choice of this centrosymmetric space group. The hexagonal lattice parameters are a = 6.345 (15) Å and c = 13.58 (3) Å; ρ_{calcd} = 2.84 g cm^{-3} for z = 2. Three-dimensional intensity data resulting in a total of 246 independent observed reflections (*i.e.*, with $F_o > 4\sigma(F_o)$) were collected with Mo Kα radiation on a four-angle automated General Electric diffractometer. The structure was solved by the usual Patterson–Fourier techniques and refined by full-matrix least squares with isotropic atomic temperature factors to an R_1 = 17.5%, with anisotropic As and Co thermal parameters to R_1 = 5.4%, and with all atoms anisotropic to R_1 = 5.0%.

The molecular structure (Figure 1) consists of a $Co(CO)_3$ group coordinated to a triangular As_3 basal fragment. Each of the two centrosymmetrically related molecules in the unit cell is crystallographically constrained to possess C_3-3 symmetry; however, the geometry of the $As_3Co(CO)_3$ molecule closely conforms to C_{3v}-3m symmetry with each of the three carbonyl groups *trans* to an As–Co bond. This staggered conformation of the three carbonyl groups relative to the three arsenic atoms is not unexpected from both orbital and stereochemical considerations.

From a valence-bond electron-bookkeeping viewpoint the structure of $As_3Co(CO)_3$ may be simply described in terms of localized electron-pair σ bonds involving for the cobalt atom six trigonally distorted octahedral-like orbitals and for each arsenic atom four tetrahedral-like orbitals with one occupied by an unshared electron pair. This formal substitution of an electronically equivalent $Co(CO)_3$ group in place of an As atom in As_4 results in a closed-shell electronic configuration for both the arsenic and cobalt atoms.[10]

The important molecular parameters are (1) an As–As bond length of 2.372 (5) Å; (2) an As–Co bond length of 2.439 (5) Å; (3) Co–C and C–O bond lengths of 1.813 (19) and 1.117 (15) Å, respectively; (4) As–Co–As, Co–As–As, and As–As–As bond angles of 58.2 (1), 60.9 (1), and 60.0° (–), respectively; (5) an As–Co–CO (*trans*) bond angle of 149.0 (5)° and an As–Co–CO (*cis*) average bond angle of 95.3 (4)°; (6) OC–Co–CO and Co–C–O angles of 103.6 (5) and 176.9 (15)°, respectively.

The most conspicuous structural feature is that the As–As bond length of 2.372 (5) Å in $As_3Co(CO)_3$ is significantly shorter than the As–As bond lengths in As_4 vapor (2.44 Å,)[11] $[AsCH_3]_5$ (2.428 (8) Å),[12] and $[AsC_6H_5]_6$ (2.456 (5) Å)[13] but is considerably longer than the double-bond-like As–As bond length of 2.273 (3) Å in the mono(triphenylphosphine) derivative of $As_2Co_2(CO)_6$.[3,4] This striking As–As bond shortening on formal replacement of an As atom with a $Co(CO)_3$ group lends considerable support to the proposition that the extreme instability of the As_4 molecule relative to that of $As_3Co(CO)_3$ and $As_2Co_2(CO)_6$ is largely a consequence of coulombic repulsions involving interorbital electron pairs on the same arsenic atom as well as those on different arsenic atoms. From localized electron-pair repulsion arguments the more electronegative $Co(CO)_3$ group effectively functions as an "electron sink" which by sufficient removal of electron charge from the triarsenic fragment (through electron delocalization from the filled lone-pair (and filled 3d) arsenic orbitals as well as from the cobalt-bonding arsenic orbitals) decreases electron-pair interactions among the arsenic atoms as reflected in the significantly shorter As–As distances. The delocalized nature of the bonding in $As_3Co(CO)_3$ is best considered from a molecular orbital representation. On the basis of C_{3v} symmetry the relevant orbitals for the triarsenic fragment are classified as follows: 3d and 4d ($3a_1 + 2a_2 + 5e$), 4s ($a_1 + e$), and 4p ($2a_1 + a_2 + 3e$). Similar classification for the valence cobalt orbitals gives 3d ($a_1 + 2e$), 4s (a_1), and 4p ($a_1 + e$). The pertinent carbonyl orbitals can be classified as σ-donor electron pair ($a_1 + e$), π ($a_1 + a_2 + 2e$), and π^* ($a_1 + a_2 + 2e$). It is readily apparent that molecular orbitals can be compounded from a_1 and e combinations but not from the a_2 representation since there are no a_2 cobalt orbitals. Hence, the startling stability of the $As_3Co(CO)_3$ molecule relative to the As_4 molecule must be rationalized in terms of a more extensive electron donation from not only the mainly cobalt-bonding arsenic ($a_1 + e$) orbitals but also the normally filled lone-pair (and 3d) triarsenic ($a_1 + e$) orbitals to the corresponding valence cobalt ($a_1 + e$) orbitals. Since under a delocalized MO formulation the e combinations for both these cobalt-bonding orbitals and the unshared electron-pair orbitals have antibonding properties with respect to the triarsenic framework, any net partial shift of these electrons to the cobalt atom would thereby account for a bond strengthening between arsenic atoms in accord with the smaller As–As distances observed in $As_3Co(CO)_3$ compared to those in yellow As_4. Of course, the accumulation of electron density on the cobalt atom due to charge transfer is in turn dissipated by the tricarbonyl π^* ($a_1 + e$) orbitals which act as the "electron sink" by accepting charge from the electron-filled cobalt 3d ($a_1 + e$) orbitals.

The $As_3Co(CO)_3$ molecule represents a heretofore missing junction between the tetrahedral X_4 molecules and known cluster species notionally derived by the insertion of $M(CO)_3$ groups in place of X atoms. Examples of this homologous series of $X_n[M(CO)_3]_{4-n}$

[11] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, 3, 699 (1935).

[12] J. H. Burns and J. Waser, *J. Am. Chem. Soc.*, 79, 859 (1957).

[13] K. Hedberg, E. W. Hughes, and J. Waser, *Acta Cryst.*, 14, 369 (1961).

complexes (where n = 0–4) containing a bonded tetrahedral-like X_nM_{4-n} cluster fragment are as follows: (1) X_4 molecules of T_d symmetry, *e.g.*, white P_4 and yellow As_4; (2) $X_3M(CO)_3$ molecules of C_{3v} symmetry, none known before $As_3Co(CO)_3$;[14] (3) $X_2M_2(CO)_6$ molecules of C_{2v} symmetry, *e.g.*, $S_2Fe_2(CO)_6$[15] and $As_2Co_2(CO)_6$;[3,4] (4) $XM_3(CO)_9$ molecules of localized C_{3v} symmetry, *e.g.*, $SCo_3(CO)_9$,[7] $SeCo_3(CO)_9$,[9] and $RCCo_3(CO)_9$ (where R represents CH_3,[16] $C(O)CCo_3(CO)_9$,[17] $OBH_2N(C_2H_5)_3$,[18] $C_2HCo_2(CO)_6$,[19] and $C_3Co_3(CO)_9$[19]); (5) $M_4(CO)_{12}$ molecules of T_d symmetry, *e.g.*, $Ir_4(CO)_{12}$.[20–23]

Further characterization of $As_3Co(CO)_3$ by chemical and physical means (including redox reactions) is in progress to assess the chemical versatility of this complex.

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(14) Preliminary experiments indicate the existence of the presumably analogous $Sb_3Co(CO)_3$ complex.

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(16) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).

(17) G. Allegra, E. M. Peronaci, and R. Ercoli, *Chem. Commun.*, 549 (1966).

(18) F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2265 (1968).

(19) B. R. Penfold, R. J. Dellaca, and W. T. Robinson, Abstracts of Papers, National Meeting of the American Crystallographic Association, Seattle, Wash., March 1969.

(20) G. R. Wilkes and L. F. Dahl, submitted for publication.

(21) The molecular geometry of both $Co_4(CO)_{12}$[22] and $Rh_4(CO)_{12}$[23] differs from that of $Ir_4(CO)_{12}$ in possessing three bridging carbonyl groups such as to give C_{3v} symmetry.

(22) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(23) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *ibid.*, **89**, 4792 (1967).

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Organometallic Pnicogen Complexes. IV. Synthesis, Structure, and Bonding of New Organometallic Arsenic–Metal Atom Clusters Containing a Metal-Bridged Multiply Bonded As_2 Ligand: $Co_2(CO)_6As_2$ and $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$[1,2]

Sir:

Despite intensive research activity concerning (transition metal)–N_2 complexes,[3] there have been no previously known examples of (transition metal)–X_2 complexes for the other group Va family elements (X = P, As, Sb, Bi) even though vapor pressure and spectroscopic studies[4] demonstrate the existence at high temperatures of diatomic X_2 molecules for these congener elements in the gaseous state. This paper reports the preparation and structural characterization of two dicobalt–As_2 complexes, $Co_2(CO)_6As_2$ and a derivative $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$, which display *tetrahedral* M_2X_2 geometry rather than the *linear* M–X–X–M geometry recently established from Raman spectral studies[5] for the diruthenium–N_2 fragment in the bridging nitrogen $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ cation.[5,6] The molecular compound $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ has been found from an X-ray crystallographic analysis to contain the shortest known As–As bond length reported to date; the exceptionally short As–As distance has been interpreted from MO considerations in terms of a high degree of As–As multiple-bond character being present in the tetrahedral Co_2As_2 system.

$Co_2(CO)_6As_2$ is a red liquid (mp $\sim -10°$) produced by the reaction of $Co_2(CO)_8$ with excess $AsCl_3$ in THF and purified by chromatography on silica gel. Its mass spectrum shows the presence of all the possible $As_2Co_2(CO)_n^+$ ions (n = 0–6) with the most prominent species being the parent ion and the bare $As_2Co_2^+$ cluster. The molecular architecture of $Co_2(CO)_6As_2$ was established from an X-ray crystallographic analysis of the monosubstituted triphenylphosphine derivative, $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ (*vide infra*), which showed that the unsubstituted $Co_2(CO)_6As_2$ molecule must be structurally analogous to the electronically equivalent $Fe_2(CO)_6X_2$ molecules (X = S, Se).[7] The molecular configuration of $Fe_2(CO)_6S_2$ (Figure 1)[8] ideally possesses C_{2v}-2mm symmetry in the solid state; dipole moment and infrared spectral analysis[9] show its over-all molecular geometry to remain unchanged on dissolution. The close similarity of the infrared solution spectrum[10] of $Co_2(CO)_6As_2$ with that of $Fe_2(CO)_6S_2$ allows the gross $Co_2(CO)_6As_2$ geometry to be assigned with certainty as the C_{2v} $Fe(CO)_6S_2$-type structure.

In order to obtain a solid derivative $Co_2(CO)_6As_2$ suitable for X-ray examination, $Co_2(CO)_6As_2$ was refluxed in benzene with excess triphenylphosphine which afforded red $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$. This latter compound crystallizes in the triclinic system with two molecules in a unit cell of symmetry $P\bar{1}$ and of dimensions a = 11.391 ± 0.008 Å, b = 13.033 ± 0.009 Å, c = 9.120 ± 0.007 Å, α = 108.17 ± 0.02°, β = 103.84 ± 0.01°, γ = 74.22 ± 0.02°; $\rho_{calcd} = 2.02$ g cm^{-3} *vs.* $\rho_{obsd} = 1.97$ ± 0.06 g cm^{-3} (flotation method). Three-dimensional intensity data were collected with Mo Kα radiation on a General Electric four-angle automated diffractometer.

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(1) Previous paper in this series: A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 5631 (1969).

(2) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(3) *Cf.* A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, **1**, 360 (1968).

(4) K. D. Carlson, F. J. Kohl, and O. M. Uy in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, No. 72, J. L. Margrave, Ed., American Chemical Society, Washington, D. C., 1968, pp 245–260, and references cited therein.

(5) J. Chatt, A. B. Nikolsky, R. L. Richards, and J. R. Sanders, *Chem. Commun.*, 145 (1969).

(6) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967); D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

(7) From a valence-bond standpoint each of the metal atoms in these iron–sulfur and cobalt–arsenic cluster complexes possesses a closed-shell electronic configuration. The expected diamagnetic character of $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ was established from the Faraday method at room temperature; we are indebted to Mr. Michael Camp of the University of Wisconsin for performing this magnetic measurement for us.

(8) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(9) W. Hieber and W. Beck, *Z. Anorg. Allgem. Chem.*, **305**, 265 (1960), and references cited therein.

(10) In hexane solution $Co_2(CO)_6As_2$ exhibits three distinct terminal carbonyl absorption bands at 2100 (s), 2065 (ss), and 2040 (ss) cm^{-1}; for $Fe_2(CO)_6S_2$ the corresponding lower three carbonyl frequencies reported by Hieber and Beck[9] are 2081 (s), 2042 (ss), and 2005 (s) cm^{-1} in CCl_4 solution and 2081 (s), 2038 (ss), and 1996 (ss) in KBr pellet. These data are indicative of greater metal–carbonyl back-bonding in the iron complex due to larger π^*(CO) orbital participation in the electron-filled MO's.