(77 kcal/mole[11]), then $D(P_2H_2-H) = 47$ kcal/mole. As the heat of formation of gaseous diphosphine is 5.0 ± 1.0 kcal/mole,[12] the heat of formation of P_2H_2 is 26 ± 5 kcal/mole. If one assumes that $D(P-H)$ equals the average P–H bond energy, one obtains D (HP=PH) = 74 kcal/mole. This result for the phosphorus–phosphorus double bond energy is between the value for the single bond energy, 48 kcal/mole,[11] and the value for the triple bond energy, 117 kcal/mole.[11]

The residual $PH_3{}^+$ ion intensity is due to the formation of PH_3 as evidenced by the appearance potential of $PH_3{}^+$ shifting down about 3 ev on activation of the reactor to 10.4 ± 0.3 ev, a value equal to the ionization potential of PH_3.[4] The appearance potential of the $PH_2{}^+$ ion with the reactor hot corresponded to that of $PH_2{}^+$ formed by dissociative ionization of PH_3.[4]

The contribution of PH_3 to the residual ion intensities was then subtracted out yielding the approximate mass spectrum of P_2H_2 which is given in Table I.

Table I. Relative Abundances of the Principal Ions from P_2H_2

Ion	Rel abundance at 50 ev
$P_2H_2{}^+$	24
P_2H^+	39
$P_2{}^+$	100
$PH_2{}^+$	0.5 (?)
PH^+	5
P^+	60

The nitrogen analog of this compound has been prepared[13] by the decomposition of hydrazoic acid in an electric discharge and identified by mass spectrometry. It may be noted that the difference between the ionization potentials of N_2H_4 (9.00 ev[14]) and N_2H_2 (9.85 ev[13]) is in the same direction and is of the same order of magnitude as that between P_2H_4 and P_2H_2 measured in this work.

(11) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths and Co. Ltd., London, 1958.
(12) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).
(13) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).
(14) V. H. Dibeler, J. L. Franklin, and R. M. Reese, *J. Am. Chem. Soc.*, **81**, 68 (1959).

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Molecular Structures of Triiron Dodecacarbonyl and Tetracobalt Dodecacarbonyl

Sir:

All further speculation concerning the probable structures of $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ in the *solid state* can be laid to rest; the structures of these two important transition metal carbonyls have been *ascertained* from three-dimensional X-ray investigations.

Although a disordered triangular iron structure originally was proposed by Dahl and Rundle[1] for Fe_3-

$(CO)_{12}$ as being the only model compatible with their X-ray work, initial interpretations of subsequent Mössbauer resonance and other spectral measurements[2-5] rejected the triangular iron model in favor of ones involving a linear array of iron atoms. From a structural analysis[6] of the $HFe_3(CO)_{11}{}^-$ anion,[7] however, Dahl and Blount[8] proposed a molecular configuration for Fe_3-$(CO)_{12}$ involving a triangular arrangement of iron atoms which they showed to be in agreement with the X-ray, reinterpreted Mössbauer, and solid-state infrared data of $Fe_3(CO)_{12}$. The same triangular model for Fe_3-$(CO)_{12}$ independently was suggested by Erickson and Fairhall[9] from their Mössbauer spectrum of $HFe_3(CO)_{11}{}^-$.

In a vigorous effort to unravel the actual structure of $Fe_3(CO)_{12}$, a new sample was prepared, and three-dimensional photographic data were recollected with Mo Kα radiation from a particularly good crystal which yielded 539 independent intensity maxima. From Patterson and Fourier methods the disordered crystal structure of $Fe_3(CO)_{12}$ was elucidated and refined by least squares to $R_1 = 12.5\%$.[10]

The idealized molecular configuration of C_{2v}-2mm symmetry (Figure 1) is in accord with the molecular model of $Fe_3(CO)_{12}$ derived from $HFe_3(CO)_{11}{}^-$[8] and can be considered as being formed by the insertion of a *cis*-$Fe(CO)_4$ group at one of the three bridging carbonyl positions of $Fe_2(CO)_9$. The twelve carbonyl groups are approximately disposed toward the vertices of an icosahedron. The two chemically equivalent Fe–Fe distances of 2.69 and 2.68 A and the third shorter distance of 2.55 A (individual esd, 0.01 A) for the isosceles iron

(1) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).
(2) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17a**, 494 (1962).
(3) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).
(4) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).
(5) G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1313 (1963).
(6) J. F. Blount, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; J. F. Blount and L. F. Dahl, to be published.
(7) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).
(8) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).
(9) N. E. Erickson and A. W. Fairhall, *ibid.*, **4**, 1320 (1965).
(10) In spite of the crystal disorders in both $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$, the molecular configurations were unambiguously apparent from the electron-density maps, which showed complete resolution of all carbon and oxygen peaks. The crystal-disordered model successfully utilized in the least-squares refinements of the two compounds assumes a random distribution of each molecule in one of two orientations such that on the average one-half of an atom occupies each atomic position. Since the Fourier maps of $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ showed a *near*-superposition of the corresponding half-atom carbon and oxygen peaks for the two orientations, the least-squares analyses were based on a half-atom weighting for only the disordered metal atoms and a whole-atom weighting for each of the light atoms in which each of the refined carbon and oxygen positions in both structures represents the *mean* of two half-atom positions. In $Co_4(CO)_{12}$ the twofold crystallographic axis which relates the two orientations of half-molecules to each other is coincident with one of the 15 molecular twofold axes of an *idealized* icosahedron. This twofold axis, which is also coincident with a three-fold *localized* axis of the tetrahedron of cobalt atoms, passes through a *basal* cobalt atom and transforms the other three cobalts (*i.e.*, the apical and other two basal cobalt atoms) of a given molecule into a hexagon of six half-cobalt atoms. In $Fe_3(CO)_{12}$ a crystallographic center of symmetry located to a first approximation at the centroid of a given triangle of iron atoms relates the two half-molecules to each other and thereby produces a hexagon of six half-iron atoms and *six* crystallographically independent carbonyl groups (with the assumption given above that each light atom in the *idealized* centrosymmetric icosahedron is the *mean* of two half-atoms). The resulting consequence for *each compound* is that either choice of the two possible orientations of the metal framework together with the twelve "whole" carbonyl groups (of which only *six* are crystallographically independent in our calculations) unambiguously yields the same molecular configuration. Details of the structural analyses and order–disorder phenomena for both compounds will be given elsewhere.
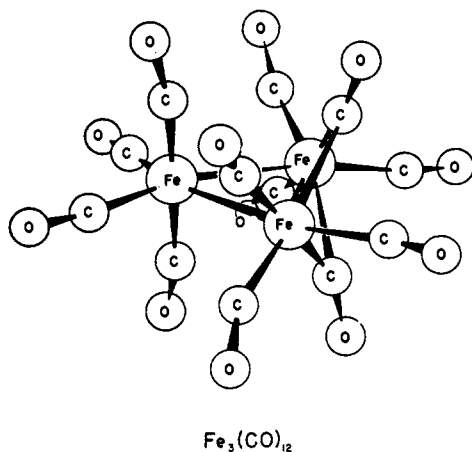
Fe₃(CO)₁₂

Figure 1. Molecular configuration of Fe₃(CO)₁₂.
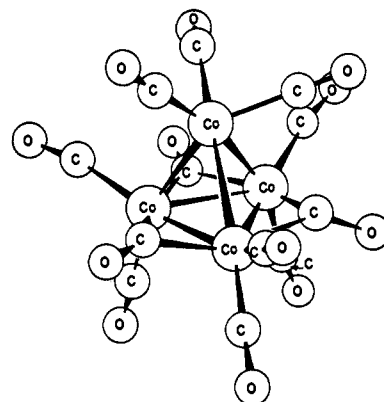
Co₄(CO)₁₂

Figure 2. Molecular configuration of Co₄(CO)₁₂.

triangle are in excellent agreement with the corresponding Fe–Fe distances in HFe₃(CO)₁₁⁻ (viz., 2.685, 2.696, and 2.577 Å with individual esd's of 0.003 Å).

A two-dimensional X-ray diffraction study of Co₄(CO)₁₂ by Corradini[11] showed that the four cobalt atoms are located at the corners of a regular tetrahedron. From both two-dimensional Fourier maps and stereochemical considerations, Corradini[11] deduced an icosahedral molecular arrangement for the twelve carbonyl groups. However, the lack of resolution in the individual carbonyl groups on the Fourier projections coupled with a crystalline disorder did not make his geometrical assignment of the carbonyl groups unambiguous. Since Corradini[11] did not specify any statistical details, the reliability of his limited structural analysis could not be assessed. Furthermore, other possible alternative molecular models involving different arrangements of carbonyl groups subsequently were proposed for Co₄(CO)₁₂[12,13]

The reinvestigation of the structure of Co₄(CO)₁₂ was prompted by our three-dimensional X-ray studies of Rh₄(CO)₁₂[14] and Ir₄(CO)₁₂[15] which showed Ir₄(CO)₁₂ to be different from Rh₄(CO)₁₂ and Co₄(CO)₁₂. The tetrameric configuration of Ir₄(CO)₁₂ was found to possess approximately T_d cubic symmetry and to be stabilized by only iridium–iridium bonds.[15] Although the lattice parameter data of Rh₄(CO)₁₂ are similar to those of Co₄(CO)₁₂, attempts to determine the complete structure of Rh₄(CO)₁₂ were not successful due to a crystal disorder presumably of a different nature from that of Co₄(CO)₁₂ as indicated by the different observed space group symmetries for the two compounds.[14] However, Beck and Lottes[16] have shown that Rh₄(CO)₁₂ and Co₄(CO)₁₂ must have the same over-all molecular structure from the resemblance of their infrared spectra.

Orthorhombic crystals of Co₄(CO)₁₂ were prepared, and the crystal data were found to be in agreement with those of Corradini.[11] Three-dimensional photographic intensity data consisting of 529 independent reflections were taken with Mo Kα radiation. After considerable difficulty the entire structure was solved and refined to R₁ and R₂ values of 12.6%.[10]

(11) P. Corradini, J. Chem. Phys., 31, 1676 (1959).
(12) U. Krüerke and W. Hübel, Chem. Ber., 94, 2829 (1961).
(13) D. L. Smith, J. Chem. Phys., 42, 1460 (1965).
(14) C. H. Wei, G. R. Wilkes, and L. F. Dahl, unpublished research.
(15) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; G. R. Wilkes and L. F. Dahl, to be published.
(16) W. Beck and K. Lottes, Chem. Ber., 94, 2578 (1961).

The idealized molecular configuration of C₃ᵥ symmetry (Figure 2) consists of an apical Co(CO)₃ group coordinated by Co–Co bonds to a Co₃(CO)₉ fragment containing three identical Co(CO)₂ groups situated at the corners of an equilateral triangle with the cobalt atoms linked to one another by both symmetrical bridging carbonyl groups and Co–Co bonds. The twelve carbonyl groups are arranged in an icosahedral array about the tetrahedron of cobalt atoms. This molecular configuration is in agreement with that proposed by Corradini.[11] The six independent Co–Co bond lengths are equivalent within experimental error and have an average value of 2.49 Å (individual esd, 0.02 Å).

A salient feature is that the approximate molecular configuration of Fe₃(CO)₁₂ can be formally derived from that of Co₄(CO)₁₂ by the abstraction of a basal metal atom from the tetrahedron of cobalt atoms. The relative disposition of the other three metal atoms with respect to the icosahedron of carbonyl groups remains essentially invariant except that this more regular polyhedron in Co₄(CO)₁₂ collapses to some extent in Fe₃(CO)₁₂ in order that the twelve carbonyl ligands be coordinated to only three iron atoms.

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Direct Fluorination of Steroidal Olefins to cis-Vicinal Difluorides

Sir:

It has been shown that elemental fluorine will add smoothly to olefins.[1] The substrate was diluted with an

(1) R. F. Merritt and F. A. Johnson, J. Org. Chem., in press.