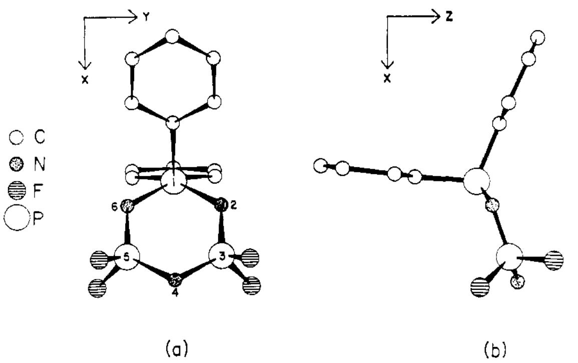

Figure 1. Views of one of the 1,1-$P_3N_3F_4(C_6H_5)_2$ molecules looking down (a) the *c* axis and (b) the *b* axis. In a there is a crystallographic mirror plane through atoms P(1) and N(4) and bisecting the two phenyl rings. In b the molecule is viewed along the normal to the mirror plane, and only half of the molecule is shown.

aluminum chloride and triethylamine yields a diphenylphosphonitrilic fluoride trimer, $P_3N_3F_4(C_6H_5)_2$ (I).[2] By analogy with the Friedel–Crafts reaction with the phosphonitrilic chloride trimer[3] and from phosphorus-31 and fluorine-19 nuclear magnetic resonance evidence, a geminally substituted structure was proposed for I.[2]

The crystal structure of the corresponding chloro derivative, $P_3N_3Cl_4(C_6H_5)_2$, has been determined and found to have a "slight" chair conformation.[4] In view of the often dramatic structural differences between fluorine-[5] and chlorine[6]-substituted phosphonitrilic halides, we have investigated the crystal structure of I.

The 1,1-diphenylphosphonitrilic fluoride trimer crystallizes as water-white needles belonging to the orthorhombic system, with $a = 14.74 \pm 0.01$, $b = 12.57 \pm 0.01$, and $c = 16.66 \pm 0.01$ A as determined on a precession camera (Mo Kα, λ 0.7107 A). There are eight molecules of 1,1-$P_3N_3F_4(C_6H_5)_2$ in the unit cell. The systematic absences indicate that the space group is either Pnma or Pn2_1a; the number of molecules per unit cell and various statistical tests suggest the former. A total of 1442 independent nonzero structure amplitudes was obtained by visual estimation of equiinclination Weissenberg photographs (Cu Kα, λ 1.5418 A) at 25°. The structure was solved by the symbolic addition procedure.[7] Full-matrix least-squares refinement incorporating anisotropic temperature factors has given an *R* factor of 0.10 on the 1442 observed nonzero reflections.

The resulting molecular structure is shown in Figure 1, and it confirms the previous assignment.[2] The crystal asymmetric unit contains two symmetry-independent molecules, each of which has a crystallographic mirror plane bisecting both the benzene rings and the phosphorus–nitrogen ring, with the result that the molecule is utilizing all its symmetry elements. There are three sets of phosphorus–nitrogen bond lengths which are slightly shorter than those found in the chloro derivative[4] but are distributed about the molecule in an analogous manner.

The conformation of the phosphorus–nitrogen ring, however, differs between the two compounds. The 1,1-diphenylphosphonitrilic chloride trimer exists as a "slight" chair, whereas the corresponding fluoride, to good approximation, has the phosphorus atom (P(1)), bearing the phenyl groups, 0.205 A above the plane of the other five atoms of the ring. The nitrogen atom (N(4)), opposite P(1), is slightly above (0.025 A) the central plane, although this displacement is only marginally significant.

Although this particular conformation has been observed in fused ring systems in the carbocyclic series (*e.g.*, in 4-bromoestrone)[8] and proposed in several other fused ring systems on the basis of models and infrared data,[9] this is the first example in an isolated six-membered ring system.

The factors which lead to a stable conformation in phosphorus–nitrogen ring systems are different from those that apply in carbocyclic and simple heterocyclic systems. In the parent phosphonitrilic halides, the nitrogen lone pair is taken to be donated to energetically favorable phosphorus d orbitals.[10] This is referred to as the π' system. The replacement of a fluorine atom by a phenyl group causes an expansion in the phosphorus d-orbital size, and consequently there is less efficient overlap with the nitrogen σ orbitals. The π' system is, therefore, weakened at the phenyl-substituted phosphorus atoms, thereby giving it greater flexibility to move out of the plane of the ring. The fluorine atoms on the remaining two phosphorus atoms tend to pull nitrogen lone-pair and σ-bonding electrons closer to their respective centers than chlorine atoms do. This is reflected in the slightly shorter bond lengths between N(2)–P(3) and N(4)–P(3) in the fluorine-substituted case than in the chlorine-substituted case.[11] Therefore, the remaining five ring atoms remain virtually planar. The deviation of N(4) from the plane is of the order of magnitude of the corresponding deviations in trimeric phosphonitrilic chloride, $P_3N_3Cl_6$.[12]

Acknowledgment. We have benefited from discussions with Mrs. S. M. Johnson concerning the symbolic addition procedure, while Miss Leslie Brooks assisted in the data estimation.

---

[2] C. W. Allen, Doctoral Dissertation, University of Illinois, 1967.

[3] H. Bode and H. Bach, *Chem. Ber.*, **75**, 215 (1942).

[4] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **19**, 693 (1965).

[5] H. McD. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 4777 (1961).

[6] R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, **15**, 539 (1962).

[7] See, *e.g.*, J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966). The procedure was carried out with the aid of a series of programs developed by E. B. Fleischer, A. Stone, and R. Dewar at the University of Chicago.

[8] D. A. Norton, G. Kartha, and C. T. Lu, *ibid.*, **16**, 89 (1963); H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, **23**, 439 (1967).

[9] E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, 167 (1958).

[10] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

[11] In 1,1-$P_3N_3Cl_4(C_6H_5)_2$,[4] N(2)–P(3) is equal to 1.55 ± 0.005 and N(4)–P(3) is equal to 1.578 ± 0.005 A, whereas in the 1,1-$P_3N_3F_4$-$(C_6H_5)_2$, N(2)–P(3) is equal to 1.54 ± 0.01 and N(4)–P(3) is equal to 1.56 ± 0.01 A.

[12] A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

Christopher W. Allen, Iain C. Paul, Therald Moeller
W. A. Noyes Chemical Laboratory
University of Illinois, Urbana, Illinois 61801

Received August 10, 1967

The Crystal and Molecular Structure of $Zn[Co(CO)_4]_2$

Sir:

Although transition metal derivatives of group II metals have been known for over 30 years,[1] it is only

[1] M. P. Shubert, *J. Am. Chem. Soc.*, **55**, 4563 (1933).

relatively recently that their structures have been studied in detail. Analysis of the infrared,[2,3] and Raman[4] spectra of $Hg[Co(CO)_4]_2$ and $Cd[Co(CO)_4]_2$ in solution led several workers to exclude the presence of bridging carbonyl groups and to suggest a linear structure, $(CO)_4Co-M-Co(CO)_4$, with a trigonal arrangement of CO groups about cobalt. The nearly linear Fe–Hg–Co cluster and the trigonal environment around the cobalt atom found[5] in the X-ray crystallographic structure determination of π-$C_5H_5(CO)_2Fe-Hg-Co(CO)_4$ lends support to these interpretations. The only known compounds of zinc that might be expected to involve the direct bonding of zinc to transition metal atoms are $Zn[Co(CO)_4]_2$[6] and $Zn[Co(CO)_3PPh_3]_2$.[7] In a recent communication[8] it was suggested, on the basis of infrared and Raman spectral data, that $Zn[Co(CO)_4]_2$ has a structure similar to that proposed for the mercury and cadmium analogs. The preliminary results of a three-dimensional, single-crystal, X-ray diffraction analysis of $Zn[Co(CO)_4]_2$ which confirm this suggestion are reported herein.

The analysis shows that the crystal consists of discrete molecules which conform closely to D_{3d}-3m symmetry (Figure 1). The two cobalt atoms are linearly attached to the zinc atom with no bridging carbonyl groups supporting the Zn–Co bonds; consequently, the zinc atom is restricted to a coordination number of two. The Co–Zn–Co angle is 177.8° (0.1)[9] and the two Zn–Co bond lengths average to 2.305 A (0.002, 0.002).[9] The geometry around the cobalt atom is trigonal bipyramidal with one CO group and one Zn atom occupying the axial positions. The three equatorial CO groups are slightly bent toward the central Zn atom; the six Zn–Co–C angles average 81.1° (0.5, 0.7, 1.3), 9° short of 90°. The two groups of three equatorial CO groups are staggered in relation to one another. The eight Co–C bond lengths average 1.76 A (0.02, 0.02, 0.03), somewhat shorter than the average of the six nonbridging Co–C bond lengths, 1.80 A, observed in the $Co_2(CO)_8$ molecule.[10] The axial Co–C bond length is apparently 0.03 A longer than the three equatorial Co–C bond lengths involving the same Co atom, but the objective significance of this difference is marginal at the present stage of structure refinement. The bond lengths of eight C–O bonds average 1.154 A (0.02, 0.01, 0.02) and are in general agreement with those observed in other carbonyl compounds.

This work represents the first description of linear, unsupported metal–zinc–metal bonding; formally, at least, the coordination around the zinc atom resembles that found in the covalent dialkyls of zinc.[11] In view of this and the similarities in the chemical properties of the two types of compounds (*e.g.*, their extreme sensitivity to oxygen), it may be inferred that the Zn–Co and Zn–C bonds are not radically different in character.

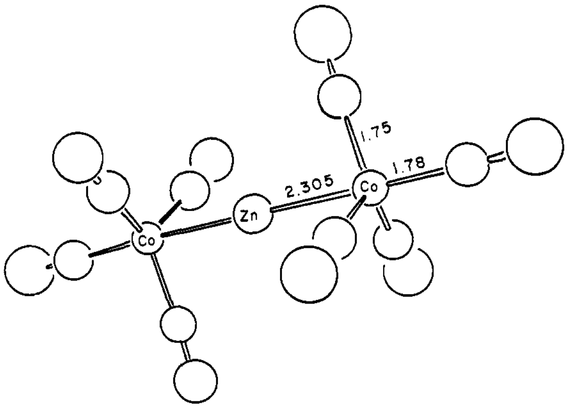

Figure 1. A perspective view of the $Zn[Co(CO)_4]_2$ molecule. The bond lengths shown are averages taken in accordance with the idealized symmetry of D_{3d}.

The crystal used in this study was prepared by the high-pressure reaction of zinc metal with dicobalt octacarbonyl, as originally described by Hieber and Teller[6] and modified by Schrauzer, Bastian, and Fosselius.[12] It was sealed in a thin-walled capillary tube filled with argon. X-Ray investigation, using Weissenberg and precession techniques, revealed that the crystal is monoclinic and belongs to the space group $P2_1/c$. The cell dimensions as determined by least-squares treatment of the 2θ angles of some 22 reflections measured on a Picker four-circle diffractometer are a = 6.646 (0.003), b = 15.777 (0.006), c = 12.685 A (0.005), cos β = −0.1932 (0.0003), and β = 101° 8.5′. With four molecules in this unit cell, the density is calculated to be 2.073 g/cc. It was observed that a crystal specimen floated in hexane–bromoform solution of 2.1-g/cc density, sank in a solution of 1.9-g/cc density. Three-dimensional intensity data were collected on a four-circle Picker diffractometer using Zr-filtered Mo Kα radiation and a scanning technique. The 2994 independent reflections lying within the range $2\theta < 55°$ were used in the subsequent analysis. Solution of the structure by means of the heavy-atom method was followed by four cycles of isotropic, full-matrix, least-squares refinement, yielding a conventional R of 0.148. Inasmuch as the absorption coefficient of the crystal for Mo Kα radiation is 4.5 mm^{-1} and the specimen used for recording intensities was needle shaped (0.44 × 0.125 × 0.10 mm), correction of the amplitude data for absorption is prerequisite to further refinement of structure. Incorporation of these corrections with subsequent anisotropic refinement of structure should yield a significantly more accurate description of the $Zn[Co(CO)_4]_2$ molecule than that which is presented at this time.

Acknowledgment. This investigation was supported in part by National Science Foundation Grant GP-6710X, by Public Health Research Grant 5-ROI-GM09370, and by the Advanced Research Projects Agency.

B. Lee, J. M. Burlitch, J. L. Hoard
Department of Chemistry, Cornell University
Ithaca, New York 14850

Received October 4, 1967

---

(2) K. Noack, *Helv. Chim. Acta*, **47**, 1555 (1964).

(3) G. Bor and L. Marko, *Spectrochim. Acta*, **16**, 1105 (1960).

(4) H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

(5) R. F. Bryan and H. P. Weber, *Acta Cryst.*, **21**, A138, (1966).

(6) W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942).

(7) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1259 (1957).

(8) J. M. Burlitch, *J. Organometal. Chem.* (Amsterdam), **9**, P9 (1967).

(9) The first number in parentheses is the estimated standard deviation. The second and third numbers, when given, are respectively the mean and maximum deviations from the average value.

(10) G. G. Summer, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, **17**, 732 (1964).

(11) K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.*, **38**, 1516 (1960).

(12) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).