irradiation.[13] The deviations observed at the higher dosages for the nonhydrogenated, highly crystalline polymer can be attributed to there being more than one cross-linking reaction with a retardation developing in the production of gel as the concentration of vinyl groups becomes depleted.

We can conclude that the enhanced cross-linking efficiency that is observed in the usual crystalline polyethylene is a real effect and not a consequence of any experimental artifacts.[13] The close similarity in cross-linking efficiency between the crystalline and amorphous polymer in the absence of the vinyl end group indicates that this enhancement is a unique and specific chemical effect and would not be generally expected in other crystalline polymers.

(13) M. Dole and K. Katsuura, *J. Polymer Sci.*, **3B**, 467 (1965).

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Received April 26, 1967

The Crystal Structure of Twinned Tetrarhodium Dodecacarbonyl[1,2]

Sir:

Although the molecular structures of $Co_4(CO)_{12}$[3] and $Ir_4(CO)_{12}$[4] have recently been completely characterized in the solid state, little structural information has been reported for the presumed tetranuclear metal carbonyl of the congener element rhodium. A structure similar to that of $Co_4(CO)_{12}$ was suggested by Beck and Lottes[5] for the reddish orange $[Rh(CO)_3]_n$ (first prepared by Hieber and Lagally[6]) on the basis of its volatility, diamagnetism, and the resemblance of its *solution* infrared spectrum with that of $Co_4(CO)_{12}$. A three-dimensional X-ray investigation of the rhodium complex was undertaken in order to establish its tetrameric character and to ascertain the relationship of its structure to those of the stereochemically dissimilar $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$. Our interest in obtaining unambiguous molecular parameters for this complex in the *solid* state has been stimulated by recent work concerning the possible intramolecular rearrangement of $Co_4(CO)_{12}$ in solution.[7–9] All initial attempts to determine the crystalline structure of $Rh_4(CO)_{12}$ were unsuccessful owing to twinning and/or disorder of a different nature from that in the disordered crystalline structure of $Co_4(CO)_{12}$.[3a] Our continued effort to resolve this problem, however, has now provided the conclusive results reported here.

The rhodium tricarbonyl complex was synthesized by the high-pressure carbonylation of anhydrous $RhCl_3$ with freshly reduced copper as halogen acceptor.[6] A large number of optically acceptable crystals, obtained by recrystallization from several organic solvents, were examined by X-ray diffraction photographs before crystallographically suitable crystals were found; these crystals invariably showed D_{2h}-mmm Laue symmetry. The resultant orthorhombic unit cell has lattice dimensions $a = 9.24$ A, $b = 12.02$ A, $c = 17.74$ A; $\rho_{obsd} = 2.58$ g cm^{-3} *vs.* $\rho_{calcd} = 2.52$ g cm^{-3} based on four $Rh_4(CO)_{12}$ species per cell. Systematic absences of l odd for $\{h0l\}$ and k odd for $\{0k0\}$ indicate a c glide and a 2_1 axis in the b direction.

Three-dimensional film data were collected with Mo Kα radiation from two tiny crystals from which 962 independent intensity maxima corresponding to one octant of the reflection sphere were obtained. Attempts to interpret a three-dimensional sharpened Patterson function in terms of any orthorhombic space group involving either or both of the above symmetry elements were unsuccessful. Instead the only trial model which conformed to the above symmetry and Patterson vector requirements (and which later was confirmed by least-squares refinement) was based on an incoherent twinning mechanism involving a monoclinic single crystal of symmetry $P2_1/c$ and β angle of 90°. The presence of either a (100) or (001) twin mirror plane operating on the reciprocal lattice of this monoclinic unit cell would give rise to the same apparent unit cell for the twinned composite and thereby would result in the observed pseudo-orthorhombic diffraction symmetry with no streaking.[10,11]

The determination of the carbonyl positions in this twinned crystal was accomplished by successive Fourier syntheses for which application of derived mathematical relations[12] permitted a breakdown of the observed orthorhombic $|F(hkl)_o|^2$ data for the twinned composite into the $|F(hkl)_{o'}|$ and $|F(\bar{h}kl)_{o'}|$ coefficients for the monoclinic single crystal component. This Fourier analysis was compicated by the fact that the initial atomic coordinates obtained for the crystallographically

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[1] Research jointly sponsored by the National Institutes of Health and the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation, and by the National Science Foundation (GP 4919) at the University of Wisconsin.

[2] Presented in part by C. H. Wei at the National Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967.

[3] (a) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966); (b) P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959); P. Corradini and A. Sirigu, *Ric. Sci.*, **36**, 188 (1966).

[4] G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; G. R. Wilkes and L. F. Dahl, to be published.

[5] W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

[6] W. Hieber and H. Lagally, *Z. Anorg. Allgem. Chem.*, **251**, 96 (1943).

[7] F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

[8] H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

[9] E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc., Sect. A*, 148 (1967).

[10] Since completion of our structural analysis, we have learned from private correspondence (1967) that Dr. W. Murayama of the Central Laboratories of Ajinomoto Co., Inc. (Kawasaki, Japan), has also carried out an X-ray study of $Rh_4(CO)_{12}$. Although his attempts to unravel the carbonyl atomic positions from Fourier maps were unsuccessful, it is noteworthy that his interpretation of the orthorhombic crystal data was based on an identical monoclinic twinning model of symmetry $P2_1/c$.

[11] For either a (100) or (001) twinning plane the two enantiomorphous monoclinic reciprocal lattices (with $\beta^* = 90°$) superimpose so that the observed and calculated intensities, $|F(hkl)_o|^2$ and $|F(hkl)_c|^2$, for the pseudo-orthorhombic reciprocal lattice of the twinned composite are related to the corresponding quantities of the monoclinic reciprocal lattice, $|F(hkl)_{o'}|^2$ and $|F(\bar{h}kl)_{o'}|^2$ and $|F(hkl)_{c'}|^2$ and $|F(\bar{h}kl)_{c'}|^2$, by the following relationships

$$|F(hkl)_o|^2 = m|F(hkl)_{o'}|^2 + (1 - m)|F(\bar{h}kl)_{o'}|^2$$

$$|F(hkl)_c|^2 = m|F(hkl)_{c'}|^2 + (1 - m)|F(\bar{h}kl)_{c'}|^2$$

where m represents the fraction of one monoclinic component lattice. Since the symmetry of the twinned composite is orthorhombic within experimental error, m must be approximately 0.5. A value of $m = 0.504 \pm 0.009$ was obtained when m was refined as a variable parameter by least squares.

[12] In order to estimate magnitudes of the monoclinic structure factors, $F(\bar{h}kl)_{o'}$ and $F(\bar{h}kl)_{o'}$, the observed orthorhombic $|F(hkl)_o|^2$ was apportioned as follows.

$$|F(hkl)_{o'}| = \left[|F(hkl)_o|^2 \frac{|F(hkl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2}$$

$$|F(\bar{h}kl)_{o'}| = \left[|F(hkl)_o|^2 \frac{|F(\bar{h}kl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2}$$

independent tetrahedron of rhodium atoms were to a first approximation interrelated by a mirror plane coincident with the c_b glide plane in the centrosymmetic monoclinic unit cell. Because of this additional pseudomirror plane, the rhodium atoms made no contribution to the calculated structure factors for $\{hkl\}$ with l odd, and the generated space group $P2_1/m$ (obtained from a halving of the c-axis length through omission of the l odd reflections) was used for both the initial least-squares refinement[13,14] of the rhodium atoms and the subsequent Fourier synthesis phased on the rhodium atoms only. Hence, this first approximation to an electron-density map contained mirror-image peaks in addition to any peaks which possibly represented actual carbon and oxygen atoms. From stereochemical considerations supplemented by knowledge of the structure of $Co_4(CO)_{12}$, initial carbonyl position were obtained. Since the contribution of these light atoms to the calculated structure factors destroyed the quasi-mirror symmetry imposed by the rhodium atoms, all further Fourier maps and least-squares refinements[13,14] were based on the original monoclinic $P2_1/c$ space group with the inclusion of all diffraction data. These atom-seeking procedures were reiterated twice before all 24 light atoms were located. Final unweighted discrepancy values[15] based on isotropic full-matrix least-squares refinement[13,14] were $R_1(F)_T = 0.10$ and $R_1(F^2) = 0.17$.

In contrast to the disordered crystalline structure of $Co_4(CO)_{12}$ for which coherent scattering interference must occur, our crystalline samples of $Rh_4(CO)_{12}$ conform to an incoherent twinning model. However, the derived molecular structure of $Rh_4(CO)_{12}$ possesses a configuration strikingly similar to that of $Co_4(CO)_{12}$. Its idealized structure (Figure 1) of C_{3v}-3m symmetry consists of four tetrahedrally arranged rhodium atoms in which an apical $Rh(CO)_3$ group is symmetrically coordinated by only Rh–Rh bonds to a basal $Rh_3(CO)_9$ fragment containing three identical $Rh(CO)_2$ groups located at the vertices of an equilateral triangle and linked in pairs to one another by both a bridging carbonyl group and a Rh–Rh bond. The twelve CO groups are disposed at corners of an icosahedron which encompasses the tetrahedron of rhodium atoms. Of particular interest is the dissimilarity of this molecular structure with that of $Ir_4(CO)_{12}$ for which the idealized tetrahedral molecule of T_d-$\bar{4}3m$ symmetry is stabilized by Ir–Ir bonds only (without bridging carbonyls).[4] This difference in structural type is the first proven case for corresponding metal carbonyls of the second- and third-row transition metal members of a group.

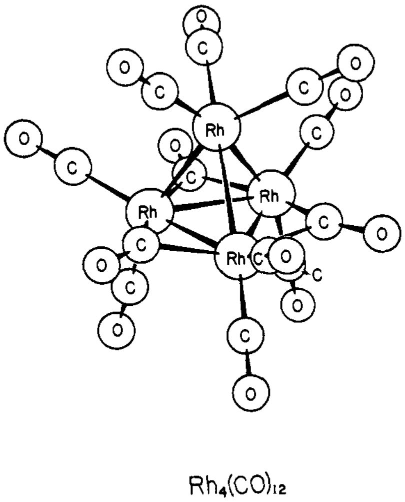

Figure 1. Molecular configuration of $Rh_4(CO)_{12}$.

The six Rh–Rh bonding distances in $Rh_4(CO)_{12}$ range from 2.70 to 2.80 A (individual esd, 0.01 A) with no apparent difference in length between the three carbonyl-bridged basal–basal Rh–Rh bonds and the three apical–basal Rh–Rh bonds. The weighted average Rh–Rh value of 2.73 A is 0.24 A longer then the average Co–Co bond length of 2.49 A (individual esd, 0.02 A) in $Co_4(CO)_{12}$ and 0.05 A longer than the average Ir–Ir bond length of 2.68 A (individual esd, 0.02 A) in $Ir_4(CO)_{12}$. It falls within the range of average Rh–Rh bond lengths observed in $[C_5H_5RhCO]_3$ (2.62 A),[16] $(C_5H_5)_2Rh_2(CO)_3$ (2.68 A),[16] rhodium metal (2.69 A),[17] and $Rh_6(CO)_{16}$ (2.78 A).[18] The average values for the other molecular parameters of $Rh_4(CO)_{12}$ are not unlike those in these other rhodium carbonyl complexes.

Acknowledgments. The use of CDC 1604 computers both at the University of Wisconsin Computing Center (made possible by financial support from NSF and WARF) and at the ORNL Computing Center is gratefully acknowledged. The authors are indebted to Drs. J. R. Einstein, W. R. Busing, and H. A. Levy of ORNL for helpful discussions.

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[13] The function minimized was $\Sigma w[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2$, where s is the adjusted scale factor.

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

[15] (a) For a twinned composite

$$R_1(F)_T = \frac{\Sigma\{||F(hkl)_{o'}| - s|F(hkl)_{c'}|| + ||F(\bar{h}kl)_{o'}| - s|F(\bar{h}kl)_{c'}||\}}{\Sigma\{|F(hkl)_{o'}| + |F(\bar{h}kl)_{o'}|\}}$$

(b) $$R_1(F^2) = \frac{\Sigma||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|}{\Sigma|F(hkl)_o|^2}$$

(c) For X-ray photographic data the usual unweighted $R_1(F)$ value for an untwinned crystal is normally about one-half the unweighted $R_1(F^2)$ [*cf.* G. M. Brown, *Acta Cryst.*, 20, 921 (1966)]. The observed discrepancy factors are within an acceptable range for a successful structural determination and thereby signify that our incoherent twinning model must be essentially correct.

[16] O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966).

[17] *Cf.* L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p S9.

[18] E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

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A Novel Isomerization in the Diels–Alder Reaction of α-Pyrone and Bis(trimethylsilyl)acetylene

Sir:

Derivatives of α-pyrone have been used to prepare aromatic compounds *via* Diels–Alder reactions with acetylenedicarboxylic acid esters,[1] and we have used the

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