radicals formed by fission of C_3F_7–Fe bonds. Evidently the mode of decomposition is different from the shift of fluorine from fluoroalkyl groups to metals which occurs in the pyrolysis of fluoroalkylmetal carbonyls like $HCF_2CF_2Mn(CO)_5$, $CF_3Fe(CO)_4I$, or $(C_2F_5)_2Fe(CO)_4$.

The carbonyl stretching frequencies observed in the infrared spectra of the perfluoropropyliron–pyridine or –bipyridyl carbonyl complexes are about 60 cm.$^{-1}$ below those observed in perfluoropropyliron tetracarbonyl iodide and bis-(perfluoropropyl)-iron tetracarbonyl.[8] This drop in carbonyl stretching frequency can be understood in terms of a greater degree of π-bonding between iron and carbon atoms of the carbonyl groups in the pyridine or bipyridyl complexes. Such behavior is to be expected since in passing from the iron tetracarbonyl compounds to the iron dicarbonyl compounds carbonyl groups have been replaced by ligands believed to be less able to partake in π-bonding with iron. Consequently, the remaining carbonyl groups must accept more electron density from the iron atom to stabilize the complex, and in so doing the C–O bond acquires more double bond character and its absorption appears at a lower frequency.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON 6, WISCONSIN

The Molecular and Crystal Structure of $Os_3(CO)_{12}$

BY EUGENE R. COREY[1] AND LAWRENCE F. DAHL[2]

Received March 26, 1962

The crystal and molecular structure of $Os_3(CO)_{12}$ (previously formulated incorrectly as $Os_2(CO)_9$) has been determined by X-ray diffraction. Three-dimensional least-squares refinement of all atoms resulted in a final discrepancy factor, R_1, of 12.4%. The molecular unit of approximately D_{3h} symmetry consists of an equilateral triangular array of osmium atoms with four terminal carbonyls attached to each osmium; two of the carbonyls are approximately perpendicular to the plane of the osmium atoms while the other two are essentially in the plane. The three $Os(CO)_4$ fragments are linked to one another only by "bent" metal–metal bonds; the average Os–Os distance is 2.88 Å. The structure and bonding of $Os_3(CO)_{12}$ are discussed with respect to other metal carbonyl complexes, including $Fe_3(CO)_{12}$.

Introduction

Recent structural work[3] has shown that the dinuclear enneacarbonyls, $Ru_2(CO)_9$ and $Os_2(CO)_9$, were incorrectly formulated and are in fact trinuclear species with the formulas $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. In this paper we wish to present the results of a complete structural determination of $Os_3(CO)_{12}$. This work is part of a systematic investigation of the second and third row transition metal carbonyls.

Experimental

Single crystals of yellow $Os_3(CO)_{12}$ were prepared by the high pressure reaction of carbon monoxide and osmium tetroxide.[4] The unit cell lengths were determined from *hk*0 and 0*kl* precession photographs, while β was obtained from *h*0*l* Weissenberg photographs. Multiple film equi-inclination Weissenberg photographs were obtained for reciprocal levels *h*0*l* through *h*12*l* from a crystal of length 0.21 mm. (along the rotation axis *b*) and of average width 0.12 mm. Since the crystal was somewhat irregularly shaped, no absorption correction was made; the resulting systematic error was minimized by the use of separate scale factors for each reciprocal layer which were determined by least-squares. Zr-filtered Mo$K\alpha$ radiation (λ = 0.7107 Å.) was used to record 1873 independent diffraction maxima. The intensity of each reflection was estimated visually by comparison with a set of standard intensities. The raw intensities were corrected for Lorentz polarization effects. Timed-exposure *hk*0 and 0*kl* precession intensity data were used to scale the Weissenberg data and to calculate two-dimensional Patterson projections.

Results

Unit Cell and Space Group.—The parameters of the monoclinic unit cell are a = 8.10 ± 0.03 Å., b = 14.79 ± 0.04 Å., c = 14.64 ± 0.04 Å., β = 100° 27′ ± 20′. The angle and the axial ratios

---

[1] Petroleum Research Fellow.

[2] Author to whom correspondence should be addressed.

[3] E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.*, **83**, 2203 (1961).

[4] W. Hieber and H. Stallman, *Z. Elektrochem.*, **49**, 288 (1943).

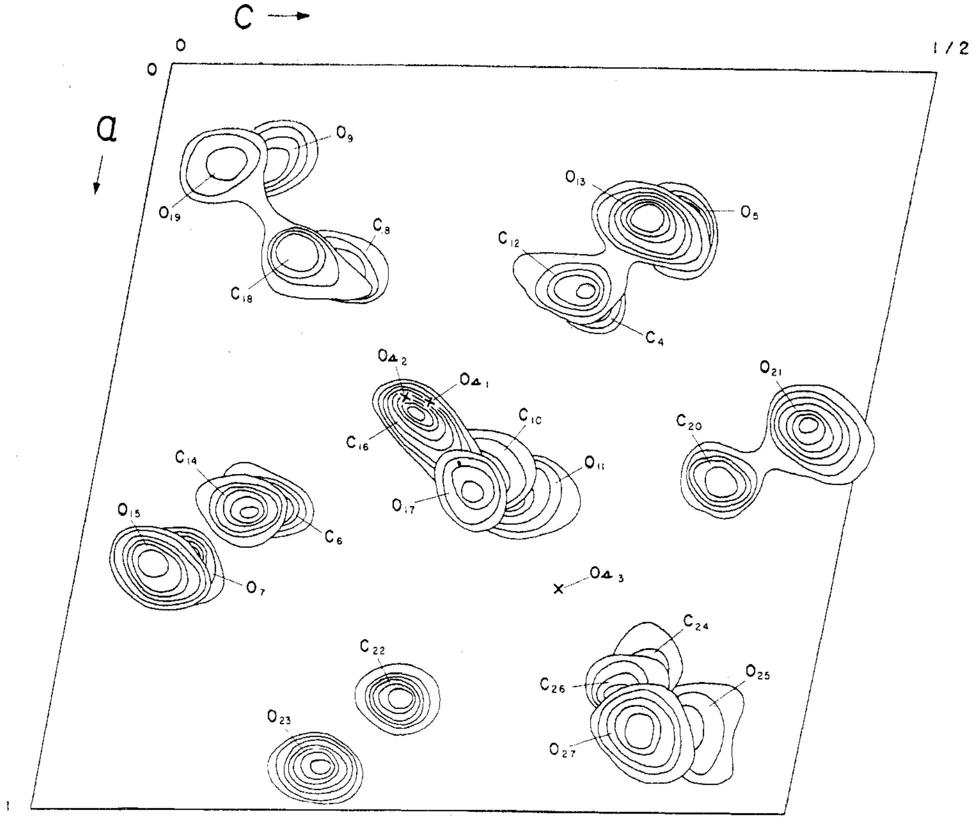

Fig. 1a.—A composite of contour sections of a three-dimensional partial-difference electron-density synthesis parallel to (010) showing the twelve carbonyl groups in one asymmetric molecular unit. The positions of the three osmium atoms, which are subtracted out, are indicated. Contours are at intervals of 1e/Å.^{3} with lowest contour at 2e/Å.^{3}.

of these unit cell parameters are given below, together with the X-ray data for the isomorphous $Ru_3(CO)_{12}$ and the optical data obtained by Steinmetz and reported by Manchot and Manchot[5] for the presumed ruthenium enneacarbonyl, $Ru_2(CO)_9$: "$Ru_2(CO)_9$" optical data by Steinmetz,[5] $a:b:c$ = 0.5496:1:0.9861, β = 100° 46′; $Ru_3(CO)_{12}$, X-ray data, $a:b:c$ = 0.546:1:0.984, β = 100° 47′; $Os_3(CO)_{12}$, X-ray data, $a:b:c$ = 0.548:1:0.990, β = 100° 27′.

The observed density[6] of 3.48 g./cc. for $Os_3(CO)_{12}$ agrees well with the calculated density of 3.49 g./cc. based on four trimeric species per unit cell. Systematic extinctions of $h0l$ reflections for $h + l$ odd and $0k0$ reflections for k odd indicate the probable space group $P2_1/n$, which was verified by the final structure.

Determination of the Structure.—The coördinates of the osmium atoms were determined from two-dimensional Patterson projections calculated on an IBM 650 computer. The osmium positions were refined on an IBM 704 computer with the Busing and Levy full matrix least squares program.[7] A discrepancy factor, R_1, of 14.7% was obtained for the three-dimensional Weissenberg data. Carbon and oxygen atomic positions were established from a three-dimensional partial-difference Fourier synthesis[8] in which the contributions of the osmium atoms were subtracted from the structure factors. Figure 1a illustrates the superimposed contour sections parallel to (010) for the twelve carbonyl groups in one asymmetric unit. Even for an atom as heavy as osmium (atomic number 76), the carbonyls are clearly resolved, and the molecular configuration is apparent.

Figure 1b shows an [010] projection of the molecule drawn from the final positional coördi-

---

(5) W. Manchot and W. J. Manchot, *Z. anorg. allgem. Chem.*, **226**, 385 (1936).

(6) W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

(7) W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," ORXLS, 1959.

(8) W. G. Sly and D. P. Shoemaker, "Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer," MIFR1, 1961.

nates of the atoms. A few other peaks comparable in size to carbon and oxygen peaks appeared in the first difference synthesis but were readily discarded as false maxima on the basis of unreasonable bonding distances and angles. A final total difference synthesis, in which contributions of all refined atoms to the structure factors were removed, revealed a sharp decrease in the peak heights of these extra maxima.

The final least-squares refinement of the structure with individual isotropic thermal parameters and variable weights gave a discrepancy factor of 12.4%.[9] Variable weights were assigned to the observed structure factors according to the functions

$$\sqrt{w} = 20/F_0 \text{ if } I_0 > \sqrt{20}I_{\min};$$
$$\sqrt{w} = I_0^2/F_0I^2_{\min} \text{ if } I_0 \leq \sqrt{20}I_{\min}$$

Some of the reflections with high intensities were removed in an attempt to correct for extinction errors, but no improvement was detected in the results. Scattering factors from Berghuis, *et al.*,[10] were used for carbon and oxygen; the scattering factors of Thomas and Umeda[11] were used for osmium. Table I gives the final positional coordinates and thermal parameters with their standard deviations.

Discussion

Triosmium dodecacarbonyl consists of discrete molecules (Fig. 2) of approximate point group symmetry D_{3h}. The osmium atoms are located at the corners of an equilateral triangle. Four terminal carbonyl groups are bonded to each osmium atom—two carbonyls are approximately perpendicular to the plane of the osmium atoms, while the other two lie essentially in the plane. The osmium tetracarbonyl fragments are linked to one another only by metal–metal bonds; the average Os–Os distance is 2.88 Å. The electronic configuration about each osmium is consistent with the observed diamagnetism.[6] Beck and Lottes[6] have reported that the infrared spectrum of $Os_3(CO)_{12}$ is compatible with the X-ray results.

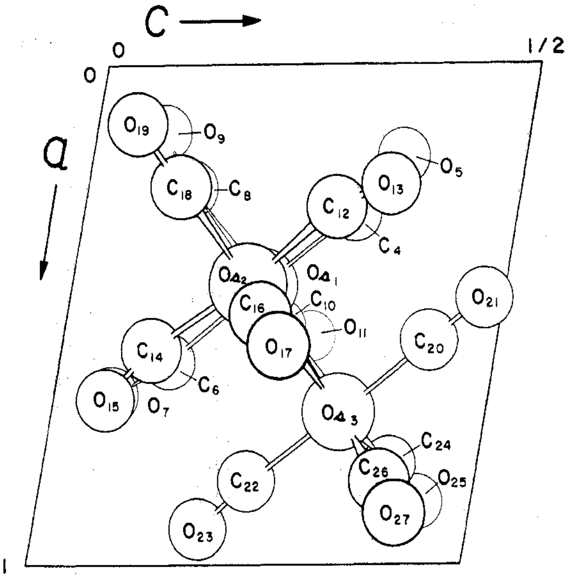

Fig. 1b.—[010] projection of the $Os_3(CO)_{12}$ molecule.

The standard deviations for the intramolecular distances and angles (listed in Tables II and III) are too large to allow meaningful comparisons of the two types of carbonyl groups present in $Os_3(CO)_{12}$. This uncertainty in metal–carbon and carbon–oxygen distances is expected in the presence of the heavy osmium atoms. The insensitivity of the X-ray data to the carbonyl groups also is reflected in their erratic individual temperature factor values and their correspondingly large standard deviations. The average Os–C and C–O bond lengths of 1.95 and 1.14 Å., respectively, are similar to the average Mo–CO and C–O bond lengths in $[C_5H_5Mo(CO)_3]_2$ (1.96 and 1.16 Å.)[12] and $C_7H_8Mo(CO)_3$ (1.97 and 1.15 Å.).[13] The covalent radii for Mo and Os are 1.29 and 1.25₅ Å., respectively.

Figure 3 shows the [100] projection of the $Os_3(CO)_{12}$ unit cell and indicates the packing of the molecular crystal as determined by the symmetry requirements of $P2_1/n$. Minimum van der Waals distances (3.0 Å.) for O···O contacts are similar to those found for $Mn_2(CO)_{10}$ (3.0₅ Å.)[14] and $Fe_5(CO)_{15}C$ (2.9 Å.).[15]

The relationship of the molecular structure of $Os_3(CO)_{12}$ to that of $Fe_3(CO)_{12}$ is of interest. The

---

(9) Calculated and observed structure factors are deposited as Document 7184 with the American Documentation Institute, Auxiliary Publication Project, Photo Duplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

(10) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(11) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(12) F. C. Wilson and D. P. Shoemaker, *ibid.*, **27**, 809 (1957).

(13) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

(14) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957); L. F. Dahl and R. E. Rundle, to be published.

(15) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, to be published

TABLE I

ATOMIC PARAMETERS

	x	y	z	B	σ_x	σ_y	σ_z	σ_B
Os_1	0.4431	−0.0246	0.2233	1.25	0.0003	0.0002	0.0002	0.06
Os_2	.4412	0.1698	.2059	1.31	.0003	.0002	.0002	0.06
Os_3	.6962	0.0812	.3389	1.32	.0003	.0002	.0002	0.05
C_4	.300	−0.011	.319	0.4	.008	.004	.004	1.2
O_5	.202	−0.012	.366	3.2	.006	.003	.004	1.0
C_6	.596	−0.032	.129	2.0	.008	.004	.004	1.1
O_7	.658	−0.040	.068	4.6	.007	.004	.004	1.3
C_8	.251	−0.044	.135	2.9	.009	.005	.005	1.4
O_9	.137	−0.069	.076	5.3	.007	.004	.004	1.2
C_{10}	.526	−0.145	.253	1.4	.008	.004	.004	1.2
O_{11}	.545	−0.215	.291	5.4	.008	.004	.004	1.3
C_{12}	.287	0.180	.296	3.6	.008	.004	.004	1.2
O_{13}	.239	.188	.356	6.4	.007	.004	.004	1.2
C_{14}	.571	.153	.105	2.4	.008	.004	.004	1.1
O_{15}	.669	.163	.062	3.4	.006	.003	.003	0.9
C_{16}	.502	.285	.228	1.5	.009	.005	.005	1.4
O_{17}	.565	.353	.254	4.2	.007	.004	.004	1.2
C_{18}	.246	.180	.109	1.5	.008	.004	.004	1.1
O_{19}	.120	.197	.046	7.4	.008	.004	.004	1.3
C_{20}	.554	.088	.431	2.3	.007	.004	.004	1.2
O_{21}	.469	.104	.487	3.1	.006	.003	.003	1.0
C_{22}	.836	.070	.244	0.8	.008	.004	.004	1.2
O_{23}	.928	.064	.194	3.6	.006	.003	.003	1.0
C_{24}	.799	−0.026	.408	4.8	.013	.007	.006	2.0
O_{25}	.875	−0.081	.446	3.7	.006	.004	.003	1.1
C_{26}	.834	0.188	.398	4.4	.010	.006	.005	1.5
O_{27}	.897	0.246	.423	4.2	.006	.004	.003	1.1

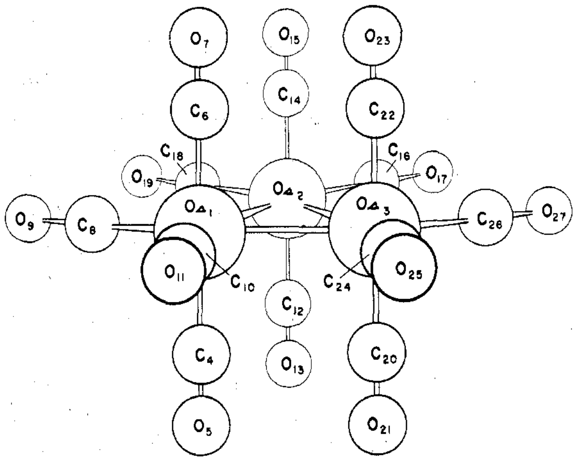

Fig. 2.—The molecular configuration of $Os_3(CO)_{12}$.

structure of the latter compound has been the subject of much speculation, and many different molecular configurations have been proposed.[16–21]

TABLE II

MOLECULAR BOND LENGTHS

Bond	Length (Å.)	Std. dev. (Å.)
Os_1–Os_2	2.886	0.009
Os_1–Os_3	2.873	.010
Os_2–Os_3	2.884	.010
C_4–O_5	1.14	.07
C_6–O_7	1.11	.07
C_8–O_9	1.20	.08
C_{10}–O_{11}	1.19	.08
C_{12}–O_{13}	1.03	.07
C_{14}–O_{15}	1.11	.07
C_{16}–O_{17}	1.16	.08
C_{18}–O_{19}	1.27	.07
C_{20}–O_{21}	1.19	.07
C_{22}–O_{23}	1.13	.07
C_{24}–O_{25}	1.11	.10
C_{26}–O_{27}	1.03	.08
Os_1–C_4	1.99	.07
Os_1–C_6	2.01	.06
Os_1–C_8	1.86	.08
Os_1–C_{10}	1.92	.07
Os_2–C_{12}	1.98	.06
Os_2–C_{14}	1.97	.06
Os_2–C_{16}	1.79	.08
Os_2–C_{18}	1.93	.06
Os_3–C_{20}	1.93	.06
Os_3–C_{22}	1.95	.06
Os_3–C_{24}	1.98	.10
Os_3–C_{26}	2.04	.08

---

(16) W. Hieber and E. Becker, *Ber.*, **63**, 1405 (1930).

(17) R. Brill, *Z. Krist.*, **78**, 36 (1931).

(18) W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

(19) N. W. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* (London), **A144**, 521 (1934).

(20) R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

(21) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **27**, 323 1957).

TABLE III

MOLECULAR ANGLES

	Degrees	Std. dev.		Degrees	Std. dev.
Os_1–Os_2–Os_3	59.72	0.14	C_8–Os_1–C_{10}	103.0	3.1
Os_2–Os_3–Os_1	60.17	0.26	C_{16}–Os_2–C_{18}	102.5	3.1
Os_3–Os_1–Os_2	60.11	0.17	C_{24}–Os_3–C_{26}	104.8	3.6
Os_1–C_4–O_5	169.5	5.4	O_9–Os_1–O_{11}	99.7	1.6
Os_1–C_6–O_7	168.9	6.0	O_{17}–Os_2–O_{19}	105.0	1.5
Os_1–C_8–O_9	170.5	6.6	O_{25}–Os_3–O_{27}	104.5	1.3
Os_1–C_{10}–O_{11}	159.2	5.4			
Os_2–C_{12}–O_{13}	163.4	6.2	C_4–Os_1–C_6	176.5	3.4
Os_2–C_{14}–O_{15}	160.3	5.3	C_{12}–Os_2–C_{14}	172.9	3.6
Os_2–C_{16}–O_{17}	167.4	6.8	C_{20}–O_3–C_{22}	177.6	3.2
Os_2–C_{18}–O_{19}	173.6	5.4			
Os_3–C_{20}–O_{21}	170.6	5.2	O_5–Os_1–O_7	175.3	1.2
Os_3–C_{22}–O_{23}	174.3	5.6	O_{13}–Os_2–O_{15}	175.1	1.4
Os_3–C_{24}–O_{25}	171.5	8.5	O_{21}–Os_3–O_{23}	178.1	1.2
Os_3–C_{26}–O_{27}	174.2	7.3			
C_6–Os_1–C_{10}	82.7	2.5	O_7–Os_1–O_{11}	91.0	1.5
C_4–Os_1–C_{10}	99.2	2.5	O_5–Os_1–O_{11}	89.9	1.4
C_6–Os_1–C_8	93.1	2.7	O_7–Os_1–O_9	87.5	1.5
C_4–Os_1–C_8	89.2	2.8	O_5–Os_1–O_9	87.8	1.2
C_{14}–Os_2–C_{18}	86.4	2.4	O_{15}–Os_2–O_{19}	90.7	1.4
C_{12}–Os_2–C_{18}	87.3	2.4	O_{13}–Os_2–O_{19}	92.6	1.5
C_{14}–Os_2–C_{16}	95.1	2.7	O_{15}–Os_2–O_{17}	88.5	1.4
C_{12}–Os_2–C_{16}	89.4	2.7	O_{13}–Os_2–O_{17}	87.1	1.5
C_{22}–Os_3–C_{24}	92.9	3.3	O_{23}–Os_3–O_{25}	89.7	1.3
C_{20}–Os_3–C_{24}	86.2	3.1	O_{21}–Os_3–O_{25}	91.0	1.3
C_{22}–Os_3–C_{26}	91.6	2.7	O_{23}–Os_3–O_{27}	89.8	1.3
C_{20}–Os_3–C_{26}	90.8	2.7	O_{21}–Os_3–O_{27}	88.3	1.3

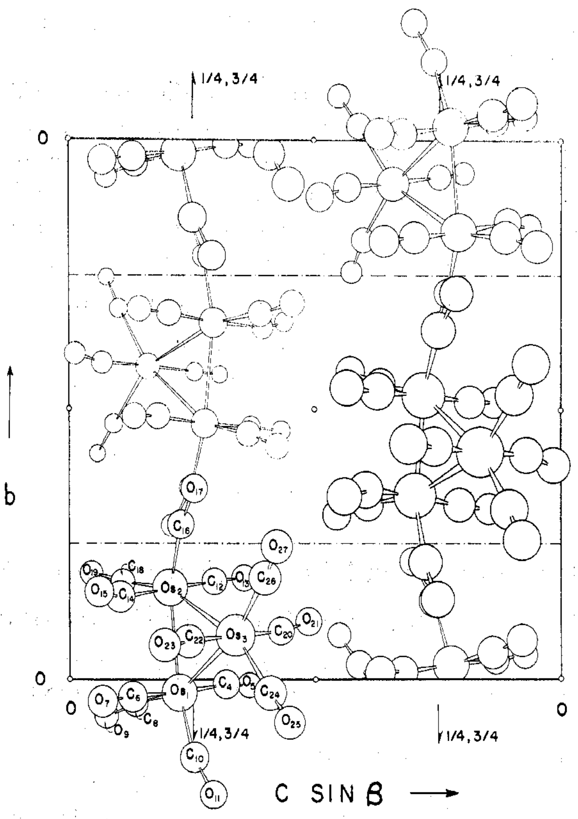

Fig. 3.—[100] projection of the unit cell.

An X-ray study[22] of $Fe_3(CO)_{12}$, however, has shown that the iron atoms are arranged at the corners of an equilateral triangle with an approximate Fe–Fe distance of 2.75 Å. Disordering of the molecules in the crystal (as also found for $Co_4(CO)_{12}$[23]) has prevented a detailed analysis of the carbonyl positions. In light of the structural information for $Os_3(CO)_{12}$ there now appears to be little doubt that the molecular configuration of $Fe_3(CO)_{12}$ is similar (if not identical) to that determined for $Os_3(CO)_{12}$, even though the two compounds are not isomorphous. The average Fe–Fe distance is approximately 0.1 Å. shorter than the average Os–Os distance, as would be expected for isostructural molecules. Furthermore, the three-dimensional Fourier syntheses with trial phases for $Fe_3(CO)_{12}$ strongly support such a configuration.[22] The 1875-cm.$^{-1}$ band observed in the single-crystal infrared spectrum[21] of $Fe_3(CO)_{12}$, which is suggestive of bridging carbonyls, apparently is caused by other crystalline interactions or is the result of Fermi resonance. Triangular arrangements also have been found for the metal atoms in $(C_5H_5)_3Ni_3(CO)_2$,[24,25] $Co_3(CO)_9CCH_3$,[26] one form of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)$,[27] and $Fe_3(CO)_{11}^{2-}$.[28]

To a first approximation the metal–metal bonding can be rationalized in terms of the overlap of octahedral-type osmium orbitals which, in contrast to the overlapping metal orbitals in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, do not point directly at one another. Such a metal–metal bond, which involves non-axially symmetric electron-pair charge distribution between two metals, has been formulated from semi-quantitative molecular orbital theory for $Co_2(CO)_6(C_6H_5C_2C_6H_5)$.[29] These so-called "bent" bonds are compatible with the molecular configurations now known for $Co_2(CO)_8$,[30] $Co_2(CO)_9C_2H_2$,[31] $(C_5H_5)_3Ni_3(CO)_2$,[24,25]

---

[22] L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

[23] P. Corradini, *ibid.*, **31**, 1676 (1959).

[24] O. S. Mills, A. A. Hock, and G. Robinson, presented at XVIIth International Congress of Pure and Applied Chemistry, Munich, September, 1959.

[25] A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 640–648.

[26] P. W. Sutton and L. F. Dahl, to be published.

[27] R. P. Dodge and V. Schomaker, private communication, 1961.

[28] O. S. Mills, private communication, 1961.

[29] D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960).

[30] G. G. Sumner and H. P. Klug, Abstracts of Papers, National Meeting of the American Crystallographic Association, Boulder, Colorado, July–August, 1961.

[31] O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

$Co_3(CO)_9CCH_3$,[26] $Rh_2(CO)_4Cl_2$,[32] and $Fe_2(CO)_6(SC_2H_5)_2$.[33]

A more detailed description of the bonding will be deferred until completion of our current investigation of the isomorphous $Ru_3(CO)_{12}$ structure. This study with a less heavy metal (atomic number 44) will provide more accurate carbon and oxygen positional parameters and will make possible a comparison of molecular features of the two compounds.

Acknowledgments.—The authors wish to acknowledge the use of the computing facilities of NAL (University of Wisconsin) and MURA (Madison) and the generous financial support given this work by both the Petroleum Research Advisory Board (Fund No. 471A) and the Atomic Energy Commission (Contract No. AT-(11-1)-1121).

---

[32] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

[33] L. F. Dahl and C. H. Wei, to be published.

Contribution from Department of Chemistry,
Florida State University, Tallahassee, Florida

Photochemical Formation of Some Metal Hexacarbonyl–Acetonitrile Derivatives

By GERARD R. DOBSON, MOSTAFA F. AMR EL SAYED,
INGO W. STOLZ, AND RAYMOND K. SHELINE

Received February 21, 1962

The photoproduction of several new metal hexacarbonyl derivatives (M = Cr, Mo, W) in the solvent acetonitrile was followed spectrophotometrically by observation of the growth and decay of the carbonyl stretching bands in the 2200–1700 cm.$^{-1}$ region of the infrared. Isolation and analysis of the tungsten derivatives indicate that the reactions involve an equilibrium among the species $M(CO)_6$, $M(CO)_5(CH_3CN)$, $M(CO)_4(CH_3CN)_2$ and, in the cases of Mo and W, $M(CO)_3(CH_3CN)_3$. Arguments are given in support of the hypothesis that the radical $M(CO)_5$ is the initiating species in these reactions.

When the metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are dissolved in various organic solvents, and the resulting colorless solutions are exposed to ultraviolet radiation, they turn bright yellow almost immediately, and the color change is accompanied by the formation of new carbonyl stretching bands in the 2200–1700 cm.$^{-1}$ region of the infrared. If acetonitrile is the solvent used, the spectral changes are extensive and complex, suggesting extensive reaction between the solvent and the hexacarbonyl.

Spectra

The spectral changes of the metal hexacarbonyl–acetonitrile solutions were conveniently followed by exposing such solutions to ultraviolet radiation supplied by a General Electric AH-6 mercury arc lamp. Exposures were made directly in sealed sodium chloride infrared cells, and after irradiation the spectra were recorded immediately on a Perkin-Elmer Model 221 prism grating spectrophotometer. Some initial studies were made using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Table I lists the frequencies of the bands observed after such irradiations.

The complex nature of the reactions responsible for the spectral changes is borne out by the observation that the new bands are formed and decay back in a random manner, though, in general, as the irradiation proceeds, bands of lower frequency increase in intensity at the expense of

Table I

Approximate Frequencies, Observed Bands, 2200–1700 cm.$^{-1}$ Region, of Irradiated $M(CO)_6$–Acetonitrile Solutions

$Cr(CO)_6$ (in cm.$^{-1}$)	$Mo(CO)_6$ (in cm.$^{-1}$)	$W(CO)_6$ (in cm.$^{-1}$)
~2140	~2140	~2140
2075	2075	2075
2020	2030	2025
1980	1985	1980
1940	1945	1940
....	1910	1910
1895	1890	1897
1850	1840	1835
....	1790	1790