being close-packed with between eight and twelve cations associated about it, then the entropy change is of the right order of magnitude.

The slightly negative entropy change in the case of molybdate and the large positive entropy change in the case of tungstate are more difficult to explain. One characteristic of the chemistries of Mo(VI) and W(VI) compounds which distinguishes them from Cr(VI) compounds is the increased tendency toward sixfold coordination. It is probably this propensity for sixfold coordination which leads to the extremely complex polyoxy anion structures observed in the aqueous chemistry of molybdenum and tungsten. Lindqvist[5] has demonstrated that solid $Na_2W_2O_7$ and $Na_2M_2O_7$ are isomorphous and do not contain discrete $M_2O_7^{2-}$ ions but are polymeric in nature, consisting of chains of MO_6 octahedra sharing corners, with additional MO_4 tetrahedra sharing corners with two adjacent octahedra. This suggests that in solution ditungstates and dimolybdates form polymeric anions of a similar configuration containing both four- and sixfold coordinated species. If solvation with the solvent occurs through cation interaction with oxygens primarily bonded to one metal species, then the effective number of sites for solvation is decreased from the number available in the orthooxy anion. This decrease in solvation would cause an increase in entropy offsetting the decrease caused by formation of the oxide ion. The enthalpy of reaction for these three systems increases in the order Cr < Mo < W, which is the order which would be expected from comparison of heats of formation of the ortho salts. Whatever the explanation for the large entropy differences observed, it is clear that the basic properties of the ortho salts must be described in terms of the solvent in which they are placed.

Further studies on these systems are indicated. At present, work is underway to determine the effect of altering the cation ratio of the solvent. This should give information regarding the solvation of the oxide ion. If extensive polymers are formed in the case of dimolybdates and ditungstates, one could expect a significant difference in solubility of the ditungstates and dimolybdates as compared to the dichromates. Such studies are being initiated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

Structure of $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$, the Oxygen Adduct of a Synthetic Irreversible Molecular Oxygen Carrier

BY J. A. McGINNETY, ROBERT J. DOEDENS, AND JAMES A. IBERS

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The system $IrX(CO)(P(C_6H_5)_3)_2$ in benzene solution adds molecular oxygen reversibly when X is Cl and irreversibly when X is I. The crystal and molecular structure of $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$ has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R factor on F of 5.9% for 1255 reflections above background. The material crystallizes in space group C_{2h}^5-$P2_1/n$ of the monoclinic system, with four molecules in a cell of dimensions $a = 10.69$, $b = 22.86$, $c = 15.00$ A, $\beta = 93.05°$. The observed density is 1.80 g/cm^3, the same as that calculated for the above cell. The crystal structure consists of the packing of the discrete monomeric units $IrIO_2(CO)(P(C_6H_5)_3)_2$ and CH_2Cl_2. The molecular structure of $IrIO_2(CO)(P(C_6H_5)_3)_2$ closely resembles that reported earlier for $IrClO_2(CO)(P(C_6H_5)_3)_2$; the iridium atom, the two oxygen atoms, the carbonyl group, and the iodine atom are situated in the equatorial plane of a trigonal bipyramid, with phosphorus atoms above and below this plane. The two oxygen atoms are equidistant from the iridium atom, with an average Ir–O distance of 2.06 A. The O–O distance is 1.509 ± 0.026 A in this irreversibly oxygenated iodo compound, whereas it is 1.30 ± 0.03 A in the reversibly oxygenated chloro compound. This very significant change in the O–O bond length is consistent with the π-bonding scheme that Griffith applied to the bonding of molecular oxygen to the heme group in oxyhemoglobin.

Introduction

Previously[1,2] we reported the crystal and molecular structure of the oxygen adduct of the synthetic reversible molecular oxygen carrier $IrCl(CO)P(C_6H_5)_3)_2$.[3] As part of a continuing study of the structures of oxygenated adducts of various synthetic oxygen carriers, we have investigated the properties of the system $IrX(CO)(P(C_6H_5)_3)_2$, where X = Br, I, SCN, or N_3. This series of compounds, with the exception of the thiocyanato compound, reacts in solution with gaseous oxygen to form oxygenated species. For the halogen compounds the rate of reaction has been found[4] to increase in the order Cl < Br < I. We have found[5]

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(1) J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964).

(2) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(3) L. Vaska, *Science*, **140**, 809 (1963).

(4) P. B. Chock and J Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966)

that whereas the addition is reversible for the chloro compound, it is irreversible in solution for the iodo compound. The question of whether this difference in reversibility in solution manifests itself in structural differences in the oxygen adducts in the solid state is one that has been answered by the determination of the crystal and molecular structure of the oxygen adduct of the iodo compound and comparison of it with the structure of the oxygen adduct of the chloro compound. A preliminary account of this work has been published,[5] and in this paper we present our results in full.

Preparation of the Sample

$IrCl(CO)(P(C_6H_5)_3)_2$.—$IrCl_3 \cdot 3H_2O$ (1.0 g) was dissolved in warm diethylene glycol monomethyl ether (30 ml). Triphenylphosphine (5.0 g) was dissolved in the same solvent (20 ml) by warming and was added, with stirring, to the iridium chloride solution; a yellow precipitate formed. The mixture was refluxed until a clear, deep yellow solution was obtained. (If necessary, more solvent was added after 0.5 hr.) The mixture was then refluxed a further 2 hr. Solvent was then distilled off until about one-third of the original volume remained. The mixture was cooled, and methanol (100 ml) added. The product was filtered off and recrystallized from benzene under nitrogen using a Soxhlet apparatus. The over-all yield is 70–80%.

$IrI(CO)(P(C_6H_5)_3)_2$.—$IrCl(CO)(P(C_6H_5)_3)_2$ (1.0 g) was dissolved in refluxing benzene (30 ml) under nitrogen. To this was added a solution of lithium iodide (14 g) in hot ethanol (25 ml). A two-layer mixture was formed. More ethanol was added until a fully miscible, clear, refluxing solution was formed. The mixture was refluxed for 15 min and then methanol (100 ml) was added. After cooling, the product (0.8 g) was filtered off.

Exactly analogous procedures are used to prepare the series $IrX(CO)(P(C_6H_5)_3)_2$, where X = Br, SCN, or N_3 (from the chloro compound).

$IrIO_2(CO)(P(C_6H_5)_3)_2$.—A benzene solution of $IrI(CO)(P(C_6H_5)_3)_2$ reacts quantitatively with oxygen from the air when left exposed for 1 hr. Evaporation yields a brown powder which analyzes correctly for the O_2 adduct. *Anal.* Calcd for $IrIO_2(CO)P(C_6H_5)_3)_2$: Ir, 21.3; C, 49.2; H, 3.3; P, 6.9; O, 5.3; I, 14.0. Found: Ir, 23.6; C, 49.1; H, 3.7; P, 6.6; O, 4.7; I, 14.5.

Suitable crystals of this material could not be obtained from benzene solution. Those good crystals which formed in benzene disintegrated when not in contact with the mother liquor. It is possible that the crystals contain benzene of crystallization and that, once removed from solution, this benzene sets up a sufficient vapor pressure to destroy the crystal.

The powder obtained from the benzene solution was dissolved in dichloromethane; slow evaporation of the solution yielded good, reasonably stable crystals of the 1:1 aggregate of $IrIO_2(CO)(P(C_6H_5)_3)_2$ and CH_2Cl_2. *Anal.* Calcd for $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$: I, 13.3; Cl, 7.4. Found: I, 13.0; Cl, 7.1. Additional verification of this formulation is provided by the X-ray molecular weight and, of course, by the structure determination itself.

The oxygenated compound was not prepared in dichloromethane solution from the parent compound because a dichloromethane adduct of low solubility is formed, and oxygenation of this proceeds very slowly.

Collection and Reduction of the X-Ray Data

Crystals, prepared as described above, are dark brown, thick needles. On the basis of optical examination and preliminary X-ray photography, the crystals were assigned to the monoclinic system. The lattice constants at 27°, obtained by least-squares refinement of the setting angles of 17 reflections which had been carefully centered on a Picker four-circle automatic X-ray diffractometer,[6] are: $a = 10.693 \pm 0.008$, $b = 22.864 \pm 0.015$, $c = 14.997 \pm 0.011$ A, $\beta = 93.05 \pm 0.02°$ (λ(Cu Kα_1) 1.54056 A). The systematic abscences that were observed on Weissenberg and precession photographs are $h0l$ for $h + l$ odd and $0k0$ for k odd. These absences are consistent with the space group C_{2h}^5-$P2_1/n$. On this basis no piezoelectric effect is expected, and none could be observed. For four formula units in the cell the calculated density is 1.80 g/cm^3; the observed density is also 1.80 g/cm^3. No crystallographic symmetry conditions need be imposed on the molecules.

The procedures used in data collection and processing parallel those described previously.[6,7] The data were collected from a nearly spherical crystal of average diameter 0.204 mm. (Actually a more accurate description of the crystal shape is an oblate spheroid of maximum diameter 0.208 mm and minimum diameter 0.187 mm.) The linear absorption coefficient of the compound for Cu Kα radiation is 162.6 cm^{-1}, whereas it is 52.3 cm^{-1} for Mo Kα. This difference is not especially large, and, for the reasons detailed earlier, Cu Kα radiation was chosen. The diffracted beams were filtered through 1.0-mil Ni foil.

The mosaicity of the crystal was checked by a narrow-source, open-counter scan[8] through several strong reflections and the average half-width was 0.07°, a satisfyingly low value.

The crystal was initially aligned along the $\overline{3}0\overline{1}$ direction, but this orientation was changed before commencement of data collection by arbitrarily resetting the arcs of the goniometer head to zero. The effects of multiple scattering should therefore be minimal.[9] Data were collected by the θ–2θ scan technique at a takeoff angle of 1.8°. At this angle the peak intensity of a typical reflection was about 80% of its maximum value as a function of takeoff angle. A symmetric scan range of 2.2° in 2θ was used for all reflections. Stationary-

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[5] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, **155**, 709 (1967).

[6] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[7] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[8] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[9] W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The scan rate was 2°/min. A counter aperture 4.0 mm high by 6.0 mm wide was placed 21 cm from the crystal. The pulse-height analyzer was set to accept approximately a 95% window centered on the Cu $K\alpha_1$ peak.

Intensity data were collected for all four forms of this monoclinic crystal (hkl, $h\bar{k}l$, $\bar{h}k\bar{l}$, and $\bar{h}\bar{k}\bar{l}$) out to a 2θ value for Cu $K\alpha_1$ of 70°. At higher scattering angles there were very few reflections above background. A total of 5987 intensities were measured.

As a general check on electronic and crystal stability, the intensities of four standard reflections were measured periodically during the collection of the intensity data. Over the entire period of data collection, these standard reflections slowly decreased in intensity, the total decrease being from 17 to 35% of the original intensity. Further checks at the completion of the run indicated unambiguously that these intensity changes were the result of crystal, rather than electronic, instability. Unfortunately, the decrease in intensity differed from standard to standard, and hence no simple correction to bring all of the intensity data to a reliable, common scale is possible. All that could be done was to take the average decrease in the standards as a function of time as the appropriate correction factor. Since each of the four equivalent forms of a given reflection typically is collected at a different time during the experiment and since the weighting scheme depends upon agreement among these forms, the averaged data and their weights should represent in a reasonable way the scattering from the crystal at the midpoint of the experiment. Attempts to find the nature of this decomposition of the crystal were not successful. The decrease in intensity is not due to loss of either oxygen or methylene chloride, since the contributions of these moieties to the structure factors of the standard reflections are in no way related to the relative loss in intensity that was observed. Thus the following are the percentage loss in intensity and the percentage contributions to F_c of CH_2Cl_2 and O_2 for each of the standard reflections: 023, 21.5, −8.0, 7.3; $\bar{1}0\bar{3}$, 16.6, 14.2, 20.4; $\bar{4}\bar{1}0$, 35.0, −6.2, 0.8; 006, 28.2, 4.0, 1.9.

The intensity data were corrected for background, and then for Lorentz-polarization effects and for absorption. The absorption correction was based on a spherical model with $\mu R = 1.66$, where μ is the linear absorption coefficient and R is the radius of the sphere. The individual values of F_o^2 from given equivalent sets were then averaged to yield 1573 independent F_o^2 values. Standard deviations on F^2, $\sigma(F^2)$, were estimated both from the range of equivalent forms and from the individual standard deviations and the larger of the two estimates was chosen.[6] For these individual standard deviations a value of $p = 0.05$ [6] was used. Of the 1573 reflections, the range estimate was larger than the individual estimate for 865 reflections. The predicted value of the weighted R factor on F^2, $R_2(F^2)$, is 10.0%. Of the 1573 reflections, 318 had $F^2 < \sigma(F^2)$ and we describe these as being below background. Only the 1255 reflections with $F^2 \geqslant \sigma(F^2)$ were used in refinement.

Solution and Refinement of the Structure

Initial values of the atomic coordinates of the iridium atom were obtained from a three-dimensional Patterson function.[10] These parameters were refined by usual least-squares procedures, with minimization of the function $\Sigma w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The usual tabulation of atomic scattering factors for P, Cl, O, C, and H were used;[11] the values obtained by Cromer and Waber[12] were used for Ir and I. The effects of anomalous dispersion were included in F_c;[13] the values of f' and f'' for Ir, I, P, and Cl were those given by Cromer.[14] This refinement of the scale factor, positional parameters, and an isotropic thermal parameter for the Ir atom led to a conventional R factor, $R_1 = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$, of 49% and a weighted R factor, $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$, of 49%. The first difference Fourier map gave a clear indication of disorder in the position of the iodine atom. A similar disorder had been found in $IrClO_2(CO)(P(C_6H_5)_3)_2$.[1,2] In subsequent calculations the coordinates of both "half-iodine" atoms were included in the calculations. Succeeding least-squares and difference Fourier methods yielded, on the third difference Fourier map, the coordinates of all of the remaining nonhydrogen atoms, with the exception of those of the carbonyl group. Subsequent least-squares calculations were effected with the program NUGLS[6] in which the phenyl groups were refined as rigid groups (D_{6h} symmetry, C–C = 1.392 A). A difference Fourier map was computed at this point with no contributions from either half-iodine atom but with contributions from the rest of the atoms that had been located. This map showed two peaks of very nearly the same height (16.6 and 16.1 e/A^3) at the positions corresponding to the half-iodine atoms. This we take as justification for the subsequent procedure of assigning an occupancy factor of 0.5 to each of the iodine positions. This map also provided an indication of anisotropy in the Ir and P motions. In a subsequent calculation these atoms were allowed to vibrate anisotropically and the value of R_2 decreased from 11.9 to 9.4%. A difference Fourier map at this stage showed the presence of two "half-carbonyl" groups slightly separated from the two half-iodine atoms. Owing to the slight separation, the atomic coordinates of the half-carbonyl groups were fixed at the positions indicated by the difference Fourier map (Ir–C $\approx$ 1.85 A; C–O $\approx$ 1.05 A; $\measuredangle$Ir–C–O $\approx$ 174°) and these positions were not refined. A subsequent calculation, in which the isotropic thermal parameters

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(10) In addition to various local programs for the CDC 3400, the programs used in this work were local modifications of Zalkin's FORDAP Fourier program, the Busing-Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

(11) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962.

(12) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(13) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(14) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $IrIO_2(CO)P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

	x	y	z	β_{11}[a] or B, A^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.18567 (13)[b]	0.15625 (6)	0.25456 (9)	0.0184 (2)	0.00309 (4)	0.0075 (1)	0.00007 (8)	−0.0016 (1)	−0.00010 (6)
1''	−0.0683 (4)	0.1482 (2)	0.2673 (3)	0.0157 (7)	0.0034 (1)	0.0090 (4)	−0.0002 (2)	0.0021 (4)	0.0002 (2)
I'	0.2442 (5)	0.1450 (2)	0.0778 (3)	0.0162 (8)	0.0025 (1)	0.0071 (3)	0.0000 (2)	−0.0002 (4)	0.0002 (2)
P_1	0.1928 (8)	0.2605 (3)	0.2426 (5)	0.0134 (13)	0.0030 (3)	0.0058 (6)	−0.0001 (5)	−0.0025 (7)	−0.0000 (3)
P_2	0.2138 (7)	0.0532 (3)	0.2707 (5)	0.0122 (12)	0.0024 (2)	0.0065 (6)	−0.0003 (4)	−0.0003 (7)	−0.0004 (3)
Cl_1	−0.3522 (17)	0.1813 (8)	0.3755 (11)	22.9 (6)					
Cl_2	−0.2437 (14)	0.2895 (6)	0.3344 (10)	18.7 (5)					
O_1	0.2260 (23)	0.1656 (9)	0.3879 (14)	0.0284 (41)	0.0027 (6)	0.0085 (17)	−0.0015 (15)	−0.0027 (21)	0.0006 (9)
O_2	0.3454 (23)	0.1664 (10)	0.3387 (16)	0.0199 (36)	0.0045 (8)	0.0147 (23)	−0.0001 (15)	−0.0015 (23)	0.0008 (11)
C	−0.3178 (43)	0.2477 (21)	0.4089 (30)	15.4 (1.5)					
CO'C	0.020	0.147	0.22	3.0 (1.3)					
CO'O	−0.075	0.147	0.20	14.3 (2.5)					
CO''C	0.165	0.147	0.13	5.6 (1.7)					
CO''O	0.155	0.147	0.06	12.8 (2.3)					

Rings	x_c[c]	y_c	z_c	δ	ϵ	η
P_1 A	−0.0362 (12)	0.3256 (6)	0.1420 (8)	3.000 (19)	2.472 (14)	−0.680 (16)
P_1 B	0.4214 (13)	0.2985 (5)	0.1256 (8)	0.753 (15)	2.655 (13)	−0.752 (13)
P_1 C	0.2310 (12)	0.3245 (4)	0.4310 (8)	−1.282 (12)	2.880 (15)	1.990 (10)
P_2 L	0.4605 (12)	0.0154 (5)	0.1760 (8)	2.542 (16)	2.614 (12)	−2.530 (13)
P_2 M	−0.0104 (11)	−0.0272 (5)	0.1881 (8)	0.202 (21)	2.274 (11)	−2.563 (19)
P_2 N	0.2452 (11)	0.0062 (5)	0.4716 (8)	−2.143 (11)	2.891 (15)	1.303 (11)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}hl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] These group parameters have been defined in previous papers. See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

of the C and O atoms of the half-carbonyl groups and the anisotropic thermal parameters of the half-iodine were added to the variables, led to a value of R_2 = 6.9%. Inclusion of the fixed contributions to F_c of the phenyl hydrogen atoms (C–H = 1.08 A) reduced R_2 to 6.4%. In a final round of calculations the carbon atoms of the phenyl groups were assigned individually variable isotropic thermal parameters and the oxygen atoms were allowed to vibrate anisotropically. The final values of R_1 and R_2 for the 1255 reflections above background are 5.9 and 6.2%, respectively. The error in an observation of unit weight is 1.15; this is sufficiently close to the expected value to suggest that the absolute values of the weights are reasonable. The values of R_1 and R_2 based on F^2 are 7.7 and 11.8%, respectively. The latter value may be compared with that of 10.0% predicted from the agreement among the intensities of equivalent forms. The discrepancy may indicate some minor deficiencies in the model, for example, slight deviation from statistical disorder of the iodine atoms, failure to refine the half-carbonyl positions, or failure to allow all of the atoms (including the chlorine atoms of the methylene chloride) to vibrate anisotropically. Another possibility is that the crystal is deficient in methylene chloride. To check on this a least-squares calculation was carried out in which the occupancy factor of the three nonhydrogen atoms of the methylene chloride (as one variable) and the thermal parameters of these atoms were varied. The correlation coefficient between the occupancy factor and any of the thermal parameters was less than 0.6. The occupancy factor for methylene chloride converged to a value of 0.93 ± 0.02. We conclude that any possible deficiency in methylene chloride is very small.

A final difference Fourier map showed no peaks higher than 0.9 e/A^3, approximately 35% of the height of a phenyl carbon atom in this structure.

A final statistical analysis of the F_o and F_c values as a function of the indices, the scattering angle, and the magnitude of F_o showed no unusual trends and suggests that the relative weighting scheme is also a reasonable one.

In Table I we give the final values of the positional and thermal parameters, along with their standard deviations as derived from the inverse matrix. In Table II we give the fractional coordinates of the carbon atoms of the phenyl rings that can be derived from the data of Table I. In Table III we give the values in electrons of F_o and F_c (based on the parameters of Table I) for the 1255 reflections above background. The values of F_c for $F_o < \sigma(F_o)$ in no case exceeded 1.5 $\sigma(F_o)$. In Table IV we give the root-mean-square amplitudes of vibration for those atoms that were refined anisotropically. An indication of the directions of vibration is provided by Figures 1–3.

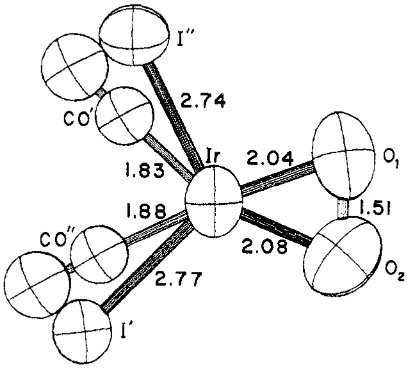

Figure 1.—A view of the disorder around iridium in the equatorial plane of the trigonal bipyramid.

Description of the Structure

The crystal structure consists of the packing of two monomeric molecular units, $IrIO_2(CO)(P(C_6H_5)_3)_2$ and CH_2Cl_2. In the iridium moiety, disorder occurs between iodine and the carbonyl group; in analogous examples such disordered groups are directly superimposed, but in this case the disorder was resolved.

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS

	x	y	z	B, A^2
		Group 1 (P_1 A)		
1	0.057 (2)	0.295 (1)	0.191 (1)	6.2 (4)
2	0.023 (2)	0.351 (1)	0.217 (1)	7.2 (4)
3	−0.070 (3)	0.382 (1)	0.168 (2)	8.5 (4)
4	−0.129 (2)	0.356 (1)	0.093 (1)	7.7 (4)
5	−0.095 (2)	0.300 (1)	0.067 (1)	8.5 (4)
6	−0.002 (3)	0.270 (1)	0.116 (1)	7.2 (4)
		Group 2 (P_1 B)		
1	0.323 (2)	0.282 (1)	0.178 (1)	6.6 (4)
2	0.441 (2)	0.256 (1)	0.192 (1)	6.6 (4)
3	0.539 (2)	0.273 (1)	0.140 (1)	7.4 (4)
4	0.519 (2)	0.315 (1)	0.073 (1)	6.6 (4)
5	0.402 (2)	0.341 (1)	0.059 (1)	7.4 (4)
6	0.304 (2)	0.324 (1)	0.112 (1)	6.6 (4)
		Group 3 (P_1 C)		
1	0.216 (2)	0.297 (1)	0.349 (1)	5.1 (4)
2	0.119 (1)	0.296 (1)	0.407 (2)	7.0 (4)
3	0.134 (2)	0.324 (1)	0.489 (1)	6.8 (4)
4	0.245 (2)	0.352 (1)	0.513 (1)	6.4 (4)
5	0.343 (1)	0.353 (1)	0.455 (2)	6.8 (4)
6	0.328 (2)	0.325 (1)	0.373 (1)	7.0 (4)
		Group 4 (P_2 L)		
1	0.351 (2)	0.029 (1)	0.218 (1)	5.4 (4)
2	0.461 (2)	0.060 (1)	0.240 (1)	6.9 (4)
3	0.570 (2)	0.046 (1)	0.198 (1)	6.7 (4)
4	0.570 (1)	0.002 (1)	0.134 (1)	6.5 (4)
5	0.460 (2)	−0.029 (1)	0.112 (1)	6.7 (4)
6	0.351 (2)	−0.015 (1)	0.154 (1)	6.9 (4)
		Group 5 (P_2 M)		
1	0.086 (3)	0.008 (1)	0.225 (1)	5.2 (4)
2	0.052 (2)	−0.043 (1)	0.268 (1)	6.6 (4)
3	−0.044 (3)	−0.078 (1)	0.232 (1)	6.8 (4)
4	−0.106 (3)	−0.062 (1)	0.152 (1)	7.0 (4)
5	−0.073 (2)	−0.011 (1)	0.108 (1)	6.8 (4)
6	0.023 (3)	0.024 (1)	0.144 (1)	6.6 (4)
		Group 6 (P_2 N)		
1	0.238 (2)	0.028 (1)	0.385 (1)	5.8 (4)
2	0.149 (2)	0.045 (1)	0.445 (2)	6.6 (4)
3	0.157 (2)	0.023 (1)	0.532 (1)	7.2 (4)
4	0.253 (2)	−0.015 (1)	0.559 (1)	6.6 (4)
5	0.341 (2)	−0.032 (1)	0.499 (2)	7.2 (4)
6	0.333 (2)	−0.011 (1)	0.412 (1)	6.6 (4)

The relative positions of all of the atoms in the equatorial plane of the iridium moiety are shown in Figure 1. In the asymmetric environment caused by the presence of methylene chloride, the two molecules which are disordered are best considered separately. Molecule 1 (containing I′ and CO′) has a fairly symmetrical arrangement of the carbonyl and iodine ligands relative to the oxygen group. Molecule 2 (containing I″ and CO″) has a much more unsymmetrical arrangement of ligands. There are several close contacts between methylene chloride and these ligands (see Table V), and we propose it is these steric requirements that are the primary cause of the resolving of the disordered groups. In addition to the steric repulsions, weak hydrogen bonds may be formed (*e.g.*, between H_1 and I′); it has been reported[15] that a hydrogen bond can be formed between an iodine ligand and a hydrogen atom on chloroform.

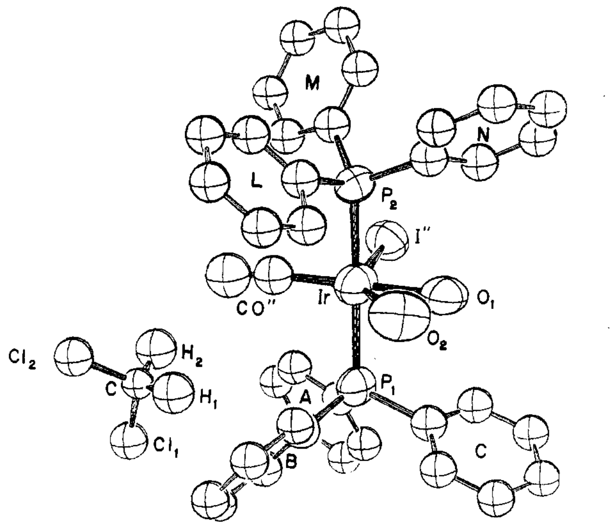

Figure 2.—A perspective drawing of the molecular structure of $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$. For pictorial purposes the carbonyl group and the dichloromethane molecule have artificially low thermal parameters. Only one set of the disordered carbonyl and iodine positions is shown.

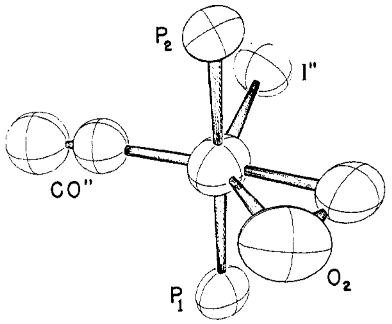

Figure 3.—A perspective drawing of the inner coordination sphere around iridium. Only one set of the disordered carbonyl and iodine positions is shown. With the exception of the carbonyl group, which has been assigned artificially low thermal parameters, the sizes of the various ellipsoids are dictated by the perspective view and by the amplitudes of vibration of the individual atoms.

In Figure 2 the over-all molecular structure is displayed, and in Figure 3 the inner coordination sphere around the iridium atom is shown. (For the sake of clarity, these two diagrams do not show the disordered array; instead molecule 2 is drawn.) The inner coordination sphere is trigonal bipyramidal when O_2 is considered as a monodentate ligand. A best weighted least-squares plane was defined through the two half-iodine atoms, the two oxygen atoms, and the iridium atom. The displacements in angstroms from this plane (with their standard deviations) are: Ir, 0.0014 (14); I′, 0.0022 (38); I″, 0.0017 (43); O_1, 0.043 (20); O_2, 0.036 (23). Thus there are no significant deviations from this plane. However, the P_1–Ir–P_2 angle of 170.9 (0.3)° differs significantly from the expected value of 180° for a perfect trigonal bipyramid. The two sets of atoms I′, Ir, I″ (*i.e.*, approximately the equatorial plane) and P_1, Ir, P_2 define two planes which are in-

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[15] M. F. Rettig and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 2966 (1966).

Table III

Observed and Calculated Structure Amplitudes (×10) (in electrons) for $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

K	L	FO	FC
**** H = 0 *****			
0	2	4796	4658
0	4	1961	1959
0	6	3735	3659
0	8	1989	2009
0	10	1253	1237
1	-10	747	752
1	-9	414	407
1	-6	475	384
1	-5	517	514
1	-4	1079	1077
1	-3	576	571
1	-2	181	19
1	1	163	98
1	7	483	539
1	11	368	315
2	-10	350	395
2	-8	407	591
2	-5	3051	3053
2	-4	194	219
2	-2	1173	1154
2	0	2219	2215
2	1	3733	3593
2	3	3061	3001
2	6	707	711
2	7	2344	2264
2	9	979	967
2	11	979	918
3	-10	419	447
3	-7	267	194
3	-6	316	274
3	-4	496	424
3	-1	323	283
3	3	2674	2445
3	5	502	439
3	9	761	725
4	-10	673	571
4	-6	1825	1904
4	-5	1350	1320
4	-4	2275	2270
4	-3	1749	1632
4	-2	1271	1266
4	-1	1174	1152
4	0	1180	1177
4	7	1520	1417
4	8	638	544
4	9	793	795
5	-10	844	820
5	-6	297	346
5	-4	2001	1898
5	-2	762	626
5	1	734	650
5	3	591	563
5	5	297	307
5	7	451	492
6	-9	313	276
6	-7	674	706
6	-5	689	698
6	-2	966	1027
6	-1	2377	2251
6	0	5712	5558
6	4	1052	1067
6	6	2007	2044
6	8	1070	1090
6	10	696	616
7	-6	332	310
7	-5	619	575
7	-4	552	559
7	-3	572	481
7	1	767	710
7	2	1133	1052
8	-7	1594	1638
8	-6	500	456
8	-4	222	149
8	0	443	336
8	1	4677	4577
8	3	2363	2294
8	5	2041	2054
8	9	939	886
9	2	862	865
9	3	606	580
9	4	297	254
9	5	323	157
9	7	370	322
10	-9	476	464
10	-6	2295	2260
10	-3	817	776
10	0	3915	3813
10	1	1214	1177
10	2	2400	2324
10	4	2496	2498
10	7	447	477
10	8	1107	1077
11	-8	303	157
11	-6	451	464
11	-3	410	345
11	-1	304	343
11	4	709	642
11	5	745	734
12	-7	986	942
12	-5	1473	1510
12	-4	815	819
12	-2	975	1006
12	0	1183	1198
12	1	1675	1704
12	3	750	807
12	6	950	956
13	-6	262	231
13	1	285	377
13	2	434	386
13	4	418	367
13	5	405	392
14	-6	755	754
14	-4	467	473
14	-3	788	813
14	-2	582	583
14	-1	1201	1092
14	0	1285	1227
14	5	728	686
15	-3	274	201
15	1	490	491
15	4	448	454
16	-2	927	835
16	0	1518	1350
**** H = 1 *****			
0	-11	765	661
0	-9	590	557
0	-7	1664	1652
0	-5	2197	2192
0	-3	2116	2262
0	-1	4368	4559
0	1	4095	4081
0	3	1718	1774
0	5	3357	3347
0	7	2769	2749
0	9	1089	1210
1	-11	587	517
1	-10	859	870
1	-9	744	700
1	-8	657	646
1	-7	550	572
1	-6	972	899
1	-5	1871	1812
1	-4	2103	2036
1	-3	1050	1048
1	-2	890	864
1	-1	1215	1112
1	0	1247	1202
1	1	2143	2086
1	2	1309	1133
1	3	2296	2209
1	4	383	345
1	5	934	899
1	6	1056	1006
1	7	1452	1445
1	8	227	239
1	9	231	164
2	-11	427	412
2	-10	429	407
2	-9	420	414
2	-8	226	175
2	-7	571	582
2	-6	1595	1570
2	-5	723	769
2	-4	386	543
2	-3	746	767
2	-2	2002	2181
2	-1	861	864
2	0	2973	3000
2	1	653	587
2	2	2335	2224
2	3	474	453
2	4	1945	1967
2	5	1013	1015
2	6	2949	2886
2	7	335	420
2	8	1086	1166
2	9	468	458
2	10	1185	1151
3	-10	818	825
3	-9	224	194
3	-8	271	327
3	-6	1451	1401
3	-5	443	448
3	-4	2546	2692
3	-3	536	516
3	-2	459	485
3	-1	448	491
3	0	1488	1456
3	1	178	112
3	2	2549	2321
3	3	772	791
3	5	729	719
3	6	562	843
3	8	969	945
4	-10	253	212
4	-7	371	327
4	-6	811	823
4	-5	1248	1217
4	-4	605	668
4	-2	1346	1450
4	-1	1364	1448
4	0	557	637
4	1	866	858
4	2	339	371
4	3	1152	996
4	4	889	903
4	5	1206	1224
4	6	1197	1168
4	7	910	953
4	8	457	557
4	9	600	635
4	10	690	667
5	-9	671	663
5	-7	246	213
5	-5	2128	2152
5	-4	448	465
5	-3	2629	2628
5	-2	413	430
5	-1	2306	2206
5	0	415	403
5	1	2630	2489
5	3	2421	2218
5	5	472	424
5	6	213	146
5	7	1240	1267
5	10	276	196
6	-7	968	946
6	-6	845	823
6	-5	886	885
6	-4	264	102
6	-3	431	607
6	-2	450	295
6	-1	2173	2224
6	0	1170	1103
6	1	2415	2316
6	2	646	610
6	5	1148	1182
6	6	672	640
6	7	1318	1314
6	8	257	212
6	9	731	718
6	10	279	321
7	-10	647	618
7	-9	392	401
7	-8	432	327
7	-7	369	383
7	-6	576	525
7	-5	540	562
7	-4	1469	1548
7	-3	657	715
7	-2	256	305
7	-1	698	697
7	0	1635	1669
7	2	2031	1944
7	3	311	306
7	4	1231	1162
7	6	1533	1534
7	7	625	684
8	-8	414	345
8	-7	218	244
8	-6	1562	1604
8	-4	697	916
8	-3	357	369
8	-2	1835	1888
8	-1	296	254
8	0	2502	2448
8	1	330	332
8	2	1802	1806
8	3	226	202
8	4	1505	1527
8	5	230	240
8	6	2257	2273
8	7	250	287
8	8	1153	1167
8	9	257	252
9	-9	429	495
9	-8	540	529
9	-7	251	248
9	-6	1036	1029
9	-5	972	1008
9	-4	807	831
9	-3	1011	1040
9	-2	895	877
9	-1	906	886
9	0	1318	1273
9	1	1849	1810
9	2	756	764
9	3	647	584
9	4	403	264
9	6	536	519
9	7	1222	1233
9	9	373	336
10	-8	358	459
10	-7	648	628
10	-6	490	455
10	-5	1280	1276
10	-4	643	584
10	-3	633	619
10	-2	997	954
10	-1	2194	2196
10	0	544	576
10	1	2325	2256
10	2	1002	1022
10	3	1177	1169
10	4	989	1063
10	5	2200	2259
10	6	476	403
10	7	1534	1637
10	8	375	421
11	-7	594	614
11	-6	271	278
11	-5	1419	1438
11	-4	920	934
11	-3	1111	1184
11	-1	444	468
11	0	450	472
11	1	828	805
11	2	624	620
11	3	971	940
11	4	287	393
11	5	341	421
11	7	649	673
12	-7	695	715
12	-6	670	692
12	-5	540	561
12	-4	192	69
12	-3	856	920
12	-2	239	206
12	-1	991	1007
12	0	1379	1489
12	1	1011	1024
12	2	775	730
12	3	657	701
12	4	469	416
12	5	667	725
12	6	1118	1166
12	7	591	576
13	-6	414	401
13	-5	336	277
13	-4	1034	1073
13	-3	247	220
13	-2	644	748
13	0	995	1057
13	1	394	375
13	2	891	915
13	4	242	288
13	6	442	468
14	-6	545	512
14	-5	370	387
14	-4	480	484
14	-3	239	226
14	-2	772	796
14	-1	299	418
14	0	591	746
14	2	537	602
14	4	443	390
14	5	451	470
14	6	648	563
15	-5	518	556
15	-3	511	490
15	-2	370	431
15	-1	483	505
15	1	1065	1173
15	2	212	193
15	3	553	575
15	5	302	232
16	-3	302	250
16	-2	244	235
16	-1	773	818
16	1	865	869
16	3	484	455
**** H = 2 *****			
0	-10	627	673
0	-8	409	472
0	-6	1579	1567
0	-4	878	838
0	-2	1157	1017
0	0	2719	2946
0	2	1174	1261
0	4	487	655
0	6	1333	1434
0	8	954	999
0	10	783	691
1	-10	714	708
1	-9	754	714
1	-8	714	727
1	-7	342	307
1	-6	935	895
1	-5	804	773
1	-4	1977	1983
1	-3	954	902
1	-2	2060	2195
1	-1	1138	1212
1	0	1589	1834
1	1	617	645
1	2	265	166
1	5	730	753
1	6	1357	1340
1	7	605	634
1	8	1308	1307
1	10	263	275
2	-10	388	477
2	-8	490	507
2	-7	988	1014
2	-6	532	443
2	-5	1598	1584
2	-4	594	581
2	-3	351	394
2	-2	840	851
2	-1	2477	2499
2	0	1438	1501
2	1	1665	1627
2	2	1421	1417
2	3	301	113
2	4	353	294
2	5	1687	1722
2	6	259	311
2	7	1071	1141
2	8	597	620
2	9	449	419
2	10	320	258
3	-10	385	303
3	-9	710	664
3	-7	337	361
3	-5	1154	1173
3	-4	531	517
3	-3	599	641
3	-2	912	917
3	-1	802	900
3	0	338	299
3	1	3752	3630
3	2	736	740
3	3	257	112
3	4	360	330
3	5	647	681
3	6	454	362
3	7	1386	1377
3	8	207	172
3	9	510	481
3	10	312	275
4	-8	309	293
4	-7	629	676
4	-6	857	918
4	-5	867	858
4	-4	361	317
4	-3	945	968
4	-1	998	949
4	0	1257	1205
4	1	211	117
4	2	446	357
4	3	740	740
4	4	387	244
4	5	707	759
4	6	805	785
4	7	315	352
4	8	381	378
4	9	286	175
4	10	316	238
5	-10	617	476
5	-8	232	224
5	-7	441	387
5	-6	447	501
5	-4	1441	1432
5	-1	722	740
5	0	662	451
5	2	2197	2105
5	3	597	592
5	4	580	616
5	5	561	544
5	6	853	843
5	7	289	215
5	8	856	858
6	-8	316	321
6	-7	193	140
6	-6	1017	1035
6	-4	412	381
6	-3	322	244
6	-2	384	408
6	-1	770	780
6	0	2051	2009
6	1	301	259
6	5	752	743
6	7	224	135
6	8	601	603
7	-9	478	487
7	-8	445	473
7	-6	393	431
7	-5	608	670
7	-4	729	711
7	-3	1045	1043
7	-2	615	645
7	-1	790	764
7	0	1310	1363
7	1	1143	1120
7	2	285	337
7	5	774	34
7	7	1303	1401
7	8	205	161
7	9	599	580
8	-9	288	275
8	-7	141	789
8	-6	530	568
8	-5	1050	1059
8	-3	615	607
8	-2	309	282
8	-1	1640	1580
8	1	1989	1917
8	2	1118	1052
8	3	234	211
8	4	362	403
8	5	1386	1394
8	6	209	279
8	7	971	1052
8	8	508	487
8	9	476	439
9	-9	649	589
9	-8	222	230
9	-7	636	691
9	-6	347	322
9	-5	1168	1222
9	-4	908	905
9	-3	1140	1106
9	-2	237	177
9	-1	1149	1182
9	0	574	607
9	1	1255	1244
9	2	752	702
9	5	730	775
9	6	476	497
9	7	990	956
9	8	574	586
10	-8	328	322
10	-7	212	159
10	-6	1098	1080
10	-5	515	567
10	-4	564	630
10	-3	473	550
10	-2	390	395
10	-1	621	631
10	0	1579	1542
10	1	554	489
10	2	391	343
10	3	1272	1243
10	4	760	813
10	5	250	245
10	6	1343	1337
10	8	733	632
11	-8	673	638
11	-7	287	304
11	-6	793	766
11	-5	471	530
11	-4	1094	1131
11	-3	259	209
11	-2	645	686
11	-1	563	552
11	0	614	652
11	1	563	578
11	2	1416	1403
11	3	211	112
11	4	876	836
11	5	204	226
11	6	747	716
12	-7	401	382
12	-6	550	523
12	-5	411	407
12	-4	403	481
12	-2	708	724
12	-1	828	833
12	0	679	627
12	1	589	542
12	2	388	385
12	4	471	458
12	5	509	503
12	6	618	587
12	7	461	353
13	-5	741	685
13	-3	518	522
13	-2	360	386
13	-1	235	156
13	0	435	428
13	1	817	852
13	3	319	285
13	4	608	759
13	5	336	325
13	6	320	315
14	-5	275	286
14	-1	539	495
14	0	347	317
14	1	607	551
14	2	339	373
14	5	342	287
15	-4	367	365
15	-3	417	316
15	-1	675	643
15	0	396	374
15	2	631	542
16	-2	320	271
16	0	689	667
16	2	335	240
**** H = 3 *****			
0	-7	1153	1202
0	-5	415	391
0	-1	2620	2753
0	1	2054	1911
0	3	648	316
0	5	1966	1959
0	7	1707	1672
0	9	732	700
1	-10	936	984
1	-9	1236	1234
1	-8	730	705
1	-7	1123	1152
1	-6	1055	1054
1	-5	2604	2671
1	-4	1646	1650
1	-3	1922	2017
1	-2	768	838
1	-1	725	797
1	0	998	1062
1	1	2311	2326
1	2	1112	1066
1	3	1651	1759
1	4	488	528
1	5	1245	1227
1	6	904	663
1	7	1341	1358
1	8	352	339
1	9	384	485
2	-7	617	601
2	-6	1172	1130
2	-5	843	796
2	-4	1130	1147
2	-3	372	405
2	-2	1228	1355
2	-1	564	637
2	0	2327	2402
2	1	176	107
2	2	1006	1027
2	4	792	891
2	5	790	776
2	6	1610	1666
2	7	436	413
2	8	639	632
2	9	353	352
2	10	578	499
3	-10	998	1016
3	-9	360	392
3	-8	825	867
3	-7	220	237
3	-6	1130	1180
3	-5	602	562
3	-4	1734	1800
3	-3	386	353
3	-2	1977	2190
3	-1	482	557
3	0	1721	1841
3	1	351	318
3	2	1477	1446
3	4	1080	1050
3	6	1269	1340
3	7	317	263
3	8	1014	1044
3	9	337	378
4	-9	454	445
4	-7	281	316
4	-6	479	472
4	-5	723	655
4	-4	630	563
4	-3	653	688
4	-2	1237	1375
4	-1	2000	2009
4	0	1527	1513
4	1	1271	1290
4	2	247	122
4	3	267	324
4	5	1198	1173
4	6	693	744
4	7	736	757
4	9	295	246
5	-9	695	705
5	-8	319	287
5	-7	610	676
5	-5	1405	1356
5	-4	221	322
5	-3	593	593
5	-2	736	733
5	-1	220	459
5	0	357	341
5	1	1224	1221
5	3	820	753
5	4	563	504
5	5	466	490
5	6	303	292
5	7	1068	1111
5	9	313	341
6	-9	226	198
6	-7	658	691
6	-6	863	911
6	-5	252	206
6	-4	341	256
6	-1	1315	1373
6	0	587	696
6	1	879	887
6	2	225	[illegible]
6	3	179	74
6	4	336	390
6	5	1047	1047
6	6	731	731
6	7	881	900
6	9	380	[illegible]
7	-9	555	507
7	-8	648	659
7	-7	550	574
7	[illegible]	1223	1171
7	[illegible]	982	1027
7	[illegible]	[illegible]	[illegible]
7	[illegible]	1046	1044
7	-2	363	321
7	[illegible]	584	[illegible]
7	[illegible]	1213	1301
7	[illegible]	521	577
7	[illegible]	1517	1469
7	4	381	12
7	5	744	709
7	6	764	921
7	7	443	418
7	8	[illegible]	635
8	[illegible]	425	[illegible]
8	[illegible]	1014	1041
8	[illegible]	505	185
8	[illegible]	692	655
8	-3	246	277
8	-2	832	769
8	-1	376	367
8	0	1987	1931
8	2	1317	1322
8	4	890	930
8	6	1306	1347
8	8	783	742
9	-8	917	931
9	-7	542	514
9	-6	1193	1194
9	-5	1030	1003
9	-4	1102	1094
9	-3	780	772
9	-2	1145	1216
9	-1	527	583
9	0	1599	1667
9	1	1127	1066
9	2	1518	1408
9	3	585	588
9	4	1044	1043
9	5	220	63
9	6	1207	1180
9	7	754	745
9	8	665	640
10	-7	473	460
10	-5	888	863
10	-4	241	266
10	-3	807	755
10	-1	1576	1607
10	0	212	135
10	1	1237	1262
10	3	640	646
10	4	256	273
10	5	1033	1096
10	6	228	123
10	7	939	966
11	-7	841	902
11	-5	1568	1484
11	-4	456	486
11	-3	1529	1557
11	-1	1256	1384
11	0	499	508
11	1	1281	1309
11	2	216	182
11	3	1277	1301
11	4	332	305
11	5	810	860
11	7	881	830
12	-6	641	649
12	-4	483	397
12	-3	490	452
12	-2	541	526
12	-1	531	528
12	0	1112	1170
12	2	472	488
12	4	594	583
12	5	317	251
12	6	958	969
13	-6	759	719
13	-4	1155	1138
13	-3	359	344
13	-2	422	401
13	-1	323	332
13	0	915	931
13	2	1037	988
13	3	388	350
13	4	439	287
13	5	581	587
14	-1	508	563
14	0	412	322
14	1	388	422
14	6	254	167
15	-3	436	357
15	-2	471	497
15	-1	237	244
15	0	290	353
15	1	637	602
**** H = 4 *****			
0	-8	548	569
0	-4	1213	1179
0	-2	225	168
0	0	442	400
0	2	580	532
0	4	642	509
0	6	861	954
0	8	425	414
1	-9	704	700
1	-8	800	800
1	-7	916	1017
1	-6	1616	1612
1	-5	1563	1533
1	-4	[illegible]	2566
1	-3	1532	1516
1	-2	[illegible]	1617
1	-1	1179	1259
1	0	2445	[illegible]
1	1	2053	[illegible]
1	2	2739	[illegible]
1	3	866	918
1	4	1697	1676
1	5	997	[illegible]
1	6	1724	1679
1	7	1116	1197
1	8	[illegible]	[illegible]
1	9	434	[illegible]
2	-9	750	784
2	-8	[illegible]	195
2	-7	490	497
2	-5	183	72
2	-3	[illegible]	[illegible]
2	-2	182	221
2	-1	274	160
2	0	379	341
2	1	542	415
2	2	192	150
2	3	560	540
2	4	285	315
2	5	965	933
2	6	306	297
2	7	592	626
2	9	343	259
3	-9	920	881
3	-8	321	375
3	-7	867	820
3	-5	1693	1735
3	-4	431	451
3	-3	1404	1433
3	-2	356	351
3	-1	2257	2315
3	0	647	577
3	1	3550	3485
3	2	439	437
3	3	2332	2332
3	4	255	287
3	5	1436	1608
3	6	297	214
3	7	1730	1813
3	9	881	834
4	-9	388	413
4	-8	741	820
4	-5	437	614
4	-3	270	218
4	-2	288	201
4	-1	251	216
4	0	226	154
4	1	938	879
4	2	574	620
4	3	824	759
4	5	399	317
4	6	637	616
4	8	330	243
5	-8	400	398
5	-7	345	369
5	-6	729	636
5	-4	1391	1329
5	-2	1102	1114
5	-1	282	289
5	0	1805	1806
5	2	2264	2259
5	4	923	1003
5	6	1577	1596
5	8	1159	1193
6	-8	625	685
6	-6	297	297
6	-4	971	998
6	-3	760	687
6	-2	629	549
6	-1	486	460
6	0	231	291
6	1	192	180
6	2	270	266
6	3	468	373
6	4	411	310
6	6	514	528
7	-8	559	584
7	-7	726	679
7	-6	633	683
7	-5	1649	1707
7	-4	972	951
7	-3	1398	1458
7	-2	633	611
7	-1	1072	1024
7	0	768	737
7	1	1974	1929
7	2	689	649
7	3	1125	1213
7	4	983	993
7	5	1026	1104
7	6	688	627
7	7	1433	1467
7	8	398	352
8	-7	281	336
8	-5	339	379
8	-4	363	286
8	-3	1076	1140
8	-2	303	241
8	0	274	209
8	1	788	749
8	2	646	631
8	3	327	418
8	4	268	168
8	5	419	475
8	7	390	379
9	-7	912	893
9	-6	711	677
9	-5	1375	1401
9	-4	1166	1237
9	-3	1330	1352
9	-2	976	950
9	-1	1666	1633
9	0	1656	1615
9	1	2005	1934
9	2	1383	1402
9	3	1174	1245
9	4	987	1045
9	5	1392	[illegible]
9	6	1058	[illegible]
9	7	1239	[illegible]
10	-4	759	721
10	[illegible]	469	453
10	[illegible]	[illegible]	335
10	6	[illegible]	704
11	-6	[illegible]	996
11	[illegible]	551	[illegible]
11	-4	1355	[illegible]
11	-3	548	[illegible]
11	[illegible]	[illegible]	[illegible]
11	0	1712	1706
11	1	876	902
11	2	2010	2041
11	4	1324	1285
11	5	248	107
11	6	[illegible]	1375
12	-3	397	397
12	-1	301	241
12	2	301	238
12	5	536	613
13	-3	1093	1043
13	-2	251	145
13	-1	1045	971
13	1	1318	1309
13	3	1032	958
13	4	459	401
14	-3	364	406
14	0	258	272
**** H = 5 *****			
0	-9	796	674
0	-5	623	598
0	-3	1506	1399
0	-1	958	992
0	1	886	1020
0	3	765	837
0	5	405	361
0	7	348	204
1	-9	505	436
1	-7	229	107
1	-6	376	357
1	-5	627	658
1	-4	735	792
1	-3	983	988
1	-2	546	570
1	-1	952	888
1	0	944	836
1	1	1835	1728
1	2	787	860
1	3	1335	1456
1	5	1287	1208
1	6	769	702
1	7	1511	1454
1	8	607	608
2	-8	615	614
2	-6	421	387
2	-5	242	181
2	-4	1090	1086
2	-3	558	561
2	-2	924	971
2	-1	441	395
2	0	288	352
2	1	437	486
2	2	1385	1339
2	3	606	573
2	4	957	967
2	5	353	348
2	7	434	496
3	-6	589	576
3	-5	319	329
3	-4	382	333
3	-2	384	418
3	0	1417	1330
3	1	318	377
3	2	909	974
3	4	846	929
3	6	1391	1327
3	8	1103	1025
4	-8	361	351
4	-5	378	312
4	-4	755	803
4	-3	1107	1234
4	-2	896	986
4	-1	430	500
4	1	572	591
4	2	1046	1073
4	3	1076	1085
4	4	854	850
4	5	418	416
4	6	409	323
5	-5	611	716
5	-4	211	158
5	-3	315	325
5	-2	255	253
5	0	332	287
5	1	830	925
5	3	814	856
5	4	198	86
5	5	826	728
5	7	1030	1024
6	-7	371	338
6	-5	434	367
6	-4	374	397
6	-3	920	893
6	-2	668	741
6	-1	704	789
6	0	451	432
6	1	763	803
6	2	563	550
6	3	778	770
6	4	242	342
6	5	497	501
7	-7	321	219
7	-5	218	187
7	-4	324	294
7	-3	505	474
7	-2	297	320
7	-1	449	500
7	0	691	493
7	1	728	736
7	2	931	981
7	3	554	516
7	4	569	468
7	5	423	403
7	6	[illegible]	[illegible]
8	-6	[illegible]	569
8	-4	1076	1000
8	[illegible]	1024	1125
8	[illegible]	761	790
8	[illegible]	[illegible]	451
8	2	[illegible]	1079
8	3	464	565
8	4	724	746
9	-6	678	[illegible]
9	-5	637	[illegible]
9	-4	797	757
9	-3	286	264
9	-2	822	826
9	-1	428	438
9	0	[illegible]	[illegible]
9	1	1086	1107
9	2	1343	1034
9	3	354	396
9	4	908	872
9	5	398	456
10	-6	235	40
10	-5	484	333
10	-3	884	907
10	-2	227	184
10	-1	207	174
10	1	546	464
10	3	936	934
10	5	380	310
11	-5	763	718
11	-3	760	643
11	-1	819	768
11	0	223	47
11	1	1246	1201
11	2	441	416
11	3	1038	1012
12	-4	403	402
12	-2	527	536
12	-1	350	346
12	1	514	500
12	2	457	448
12	3	465	357
13	-2	250	200
13	-1	297	257
13	0	459	321
**** H = 6 *****			
0	-4	727	732
0	-2	290	453
0	2	977	842
0	4	493	577
0	6	403	338
1	-7	211	110
1	-6	468	451
1	-4	797	861
1	-3	396	478
1	-2	511	471
1	-1	263	248
1	0	955	965
1	1	879	891
1	2	902	929
1	3	411	330
1	4	430	268
1	5	326	162
1	6	871	840
2	-7	256	158
2	-5	244	71
2	-4	279	218
2	-3	736	803
2	-2	356	447
2	-1	348	396
2	0	493	456
2	1	395	357
2	2	685	648
2	3	810	881
2	6	443	521
3	-5	563	565
3	-3	198	109
3	0	248	131
3	1	481	492
3	3	580	466
3	5	418	259
4	-5	241	138
4	-4	348	305
4	-3	441	418
4	-2	434	499
4	-1	455	548
4	1	288	198
4	2	572	639
4	3	705	664
4	5	316	306
5	-7	210	152
5	-4	529	[illegible]
5	-2	315	337
5	0	455	351
5	1	313	270
5	2	693	662
5	3	358	269
5	6	379	382
6	-4	388	350
6	-2	376	465
6	0	329	272
6	2	766	680
6	3	346	438
6	4	481	473
7	-5	437	426
7	-3	404	447
7	-2	365	401
7	-1	294	243
7	0	391	401
7	1	[illegible]	[illegible]
7	2	372	300
7	4	228	178
8	-5	370	214
8	[illegible]	[illegible]	[illegible]
8	-1	786	172
8	0	251	[illegible]
8	1	440	[illegible]
8	3	[illegible]	790
8	4	218	[illegible]
9	-4	[illegible]	[illegible]
9	-3	522	[illegible]
9	-1	574	[illegible]
9	0	[illegible]	[illegible]
9	1	706	[illegible]
9	2	421	[illegible]
9	4	591	[illegible]
10	-3	200	[illegible]
10	-2	565	[illegible]
10	-1	465	[illegible]
10	0	293	241
10	1	347	[illegible]
10	2	559	[illegible]
11	0	[illegible]	532
**** H = 7 *****			
0	-5	688	[illegible]
0	-3	1393	[illegible]
0	-1	1302	[illegible]
0	1	1101	[illegible]
0	3	900	[illegible]
1	-5	517	548
1	-4	474	[illegible]
1	-3	531	[illegible]
1	-2	680	[illegible]
1	-1	601	[illegible]
1	0	716	[illegible]
1	1	967	860
1	2	629	610
1	3	547	[illegible]
1	4	337	[illegible]
2	-5	276	[illegible]
2	-4	1035	[illegible]
2	-3	603	[illegible]
2	-2	883	[illegible]
2	-1	536	[illegible]
2	0	531	[illegible]
2	1	404	345
2	2	785	[illegible]
2	3	491	570
2	4	659	[illegible]
3	-4	364	[illegible]
3	0	626	[illegible]
3	1	311	302
3	2	614	[illegible]
3	4	252	[illegible]
4	-5	387	328
4	-4	476	[illegible]
4	-3	639	640
4	-2	400	393
4	-1	304	[illegible]
4	0	420	[illegible]
4	1	324	[illegible]
4	2	547	[illegible]
4	3	610	[illegible]
4	4	593	[illegible]
5	-4	219	25
5	-1	314	213
5	1	706	646
6	-4	358	356
6	-3	704	675
6	-2	353	361
6	-1	609	574
6	0	259	230
6	1	554	491
6	2	481	498
6	3	562	504
7	-2	317	212
7	0	672	[illegible]
7	1	300	315
7	2	566	[illegible]
8	0	546	464

Table IV

Root-Mean-Square Amplitudes of Vibration (A)

Atom	1	2	3
Ir	0.275 (2)	0.286 (2)	0.343 (2)
I′	0.256 (7)	0.282 (6)	0.311 (7)
I″	0.284 (7)	0.303 (7)	0.331 (7)
P_1	0.220 (14)	0.280 (12)	0.312 (12)
P_2	0.240 (14)	0.268 (13)	0.284 (12)
O_1	0.259 (32)	0.297 (31)	0.425 (30)
O_2	0.330 (31)	0.341 (33)	0.422 (33)

clined at 91.2 (1)°. The two phosphorus atoms and the iridium atom lie in a plane nearly at right angles to the equatorial plane, and the phosphorus atoms are bent away from the two half-iodine atoms toward the oxygen atoms.

Principal intramolecular distances are given in Table V. The Ir–P distances do not differ significantly from each other and the average Ir–P distance of 2.39 A is very close to the distance 2.37 A found in $IrCl(O_2)(CO)(P(C_6H_5)_3)_2$. The Ir–I distances differ by four standard deviations; however, the true error in the positional parameters of the half-iodine atoms may be larger than the values quoted because of the proximity of the half-carbonyl groups, the positions of which were not refined. The average Ir–I distance of 2.75 A is about the value expected. The Ir–O distances are very similar and the average Ir–O distance of 2.06 A is the same as that found in $IrCl(O_2)(CO)(P(C_6H_5)_3)_2$. The O_1–O_2 distance of 1.509 (26) A is significantly longer than the value of 1.30 (3) A observed in $IrCl(O_2)(CO)(P(C_6H_5)_3)_2$. The O–O distance in the iodo compound is that of a typical peroxide; the O–O distance in the chloro compound is that of a typical superoxide. Hence, these two compounds might best be named chlorosuperoxocarbonylbis(triphenylphosphine)iridium(II) and iodoperoxocarbonylbis(triphenylphosphine)iridium(III).

The iridium, half-iodine, phosphorus, and oxygen atoms were allowed to vibrate anisotropically. For these atoms the root-mean-square amplitudes of vibration along the principal axes of vibration are given in Table IV. While there can be some discussion as to the reality of motion derived in this way, it can be seen that these results are not completely random. None of the vibrations is extremely eccentric. For the iridium atom, the largest principal axis of vibration is in the equatorial plane, parallel to the O_1–O_2 direction. The vibrations of the two phosphorus atoms are ap-

TABLE V

SELECTED INTRA- AND INTERMOLECULAR DISTANCES

$\mathrm{Ir{-}P_1}$	2.391 (8)	$\mathrm{Cl_1{-}I'}$	5.070 (19)
$\mathrm{Ir{-}P_2}$	2.386 (8)	$\mathrm{Cl_2{-}I'}$	3.954 (15)
Ir–I′	2.767 (5)	$\mathrm{Cl_1{-}I''}$	3.598 (18)
Ir–I″	2.738 (5)	$\mathrm{Cl_2{-}I''}$	3.895 (15)
$\mathrm{Ir{-}O_1}$	2.035 (20)	$\mathrm{O_1{-}I'}$	4.688 (22)
$\mathrm{Ir{-}O_2}$	2.082 (22)	$\mathrm{O_2{-}I'}$	4.032 (24)
$\mathrm{O_1{-}O_2}$	1.509 (26)	$\mathrm{O_1{-}I''}$	3.568 (22)
Ir–CO′C	1.83	$\mathrm{O_2{-}I''}$	4.515 (24)
Ir–CO″C	1.88	$\mathrm{O_1{-}P_1}$	3.082 (21)
CO′C–CO′O	1.04	$\mathrm{O_1{-}P_2}$	3.112 (21)
CO″C–CO″O	1.05	$\mathrm{O_2{-}P_1}$	3.018 (24)
$\mathrm{P_1{-}I'}$	3.676 (9)	$\mathrm{O_2{-}P_2}$	3.093 (24)
$\mathrm{P_1{-}I''}$	3.825 (9)	I′–CO′C	3.29
$\mathrm{P_2{-}I'}$	3.603 (9)	I′–CO″C	1.18
$\mathrm{P_2{-}I''}$	3.714 (9)	I″–CO′C	1.21
I′–CO′O	3.96	I″–CO″C	3.32
I′–CO″O	0.98	$\mathrm{C{-}Cl_1}$	1.63 (4)
I″–CO′O	1.01	$\mathrm{C{-}Cl_2}$	1.70 (4)
I″–CO″O	4.02	$\mathrm{Cl_1{-}H_1}$	2.22
$\mathrm{P_1{-}P_2}$	4.76 (11)	$\mathrm{Cl_1{-}H_2}$	2.22
$\mathrm{P_1{-}CO'C}$	3.19	$\mathrm{Cl_2{-}H_1}$	2.34
$\mathrm{P_1{-}CO'O}$	3.89	$\mathrm{Cl_2{-}H_2}$	2.32
$\mathrm{P_1{-}CO''C}$	3.10	$\mathrm{H_1{-}I'}$	2.96
$\mathrm{P_1{-}CO''O}$	3.78	$\mathrm{H_1{-}I''}$	4.44
$\mathrm{P_2{-}CO'C}$	3.05	$\mathrm{H_2{-}I'}$	3.42
$\mathrm{P_2{-}CO'O}$	3.86	$\mathrm{H_2{-}I''}$	5.23
$\mathrm{P_2{-}CO''C}$	3.03	$\mathrm{H_1{-}CO'C}$	5.08
$\mathrm{P_2{-}CO''O}$	3.84	$\mathrm{H_1{-}CO''C}$	3.51
$\mathrm{O_1{-}CO'C}$	3.28	$\mathrm{H_1{-}CO'O}$	5.19
$\mathrm{O_1{-}CO''C}$	3.91	$\mathrm{H_1{-}CO''O}$	2.93
$\mathrm{O_2{-}CO'C}$	3.85	$\mathrm{H_2{-}CO'C}$	4.96
$\mathrm{O_2{-}CO''C}$	3.61	$\mathrm{H_2{-}CO''C}$	3.72
$\mathrm{P_1{-}P_1A_1}$[a]	1.79	$\mathrm{H_2{-}CO'O}$	4.99
$\mathrm{P_1{-}P_1B_1}$	1.81	$\mathrm{H_2{-}CO''O}$	2.88
$\mathrm{P_1{-}P_1C_1}$	1.81		
$\mathrm{P_2{-}P_2L_1}$	1.79		
$\mathrm{P_2{-}P_2M_1}$	1.82		
$\mathrm{P_2{-}P_2N_1}$	1.81		

[a] By $\mathrm{P_1A_1}$, we denote the α-carbon atom on ring A, that is, the carbon atom attached to $\mathrm{P_1}$.

TABLE VI

SELECTED INTERATOMIC ANGLES

I′–Ir–I″	109.6 (2)	$\mathrm{P_1{-}Ir{-}I'}$	90.6 (2)
$\mathrm{P_1{-}Ir{-}P_2}$	170.9 (3)	$\mathrm{P_1{-}Ir{-}I''}$	96.2 (2)
$\mathrm{O_1{-}Ir{-}O_2}$	43.0 (7)	$\mathrm{P_2{-}Ir{-}I'}$	88.4 (2)
CO′C–Ir–CO″C	69.2	$\mathrm{P_2{-}Ir{-}I''}$	92.7 (2)
$\mathrm{O_1{-}Ir{-}I''}$	95.6 (7)	Ir–CO′C–CO′O	173.4
$\mathrm{O_1{-}Ir{-}I'}$	154.7 (7)	Ir–CO″C–CO″O	173.5
$\mathrm{O_2{-}Ir{-}I'}$	111.8 (8)	$\mathrm{Cl_1{-}C{-}Cl_2}$	115.2 (29)
$\mathrm{O_2{-}Ir{-}I''}$	138.6 (8)	$\mathrm{P_1A_1{-}P_1{-}P_1B_1}$	106.2
I′–Ir–CO′C	89.0	$\mathrm{P_1B_1{-}P_1{-}P_1C_1}$	105.9
I′–Ir–CO″C	19.8	$\mathrm{P_1A_1{-}P_1{-}P_1C_1}$	104.3
I″–Ir–CO′C	20.6	$\mathrm{P_2L_1{-}P_2{-}P_2M_1}$	105.9
I″–Ir–CO″C	89.8	$\mathrm{P_2M_1{-}P_2{-}P_2N_1}$	104.0
$\mathrm{O_1{-}Ir{-}P_1}$	87.9 (6)	$\mathrm{P_2L_1{-}P_2{-}P_2N_1}$	103.9
$\mathrm{O_2{-}Ir{-}P_1}$	84.6 (7)		
$\mathrm{O_1{-}Ir{-}P_2}$	89.1 (6)		
$\mathrm{O_2{-}Ir{-}P_2}$	87.3 (7)		

proximately similar in direction and magnitude to those of the iridium atom. The motions of the half-iodine atoms will not be as meaningful as those of the other atoms because of the inadequacy of the description of the half-carbonyl groups. The oxygen atoms have their maximum vibration approximately in the equatorial plane in a direction most clearly shown in Figure 1. This motion of the oxygen atoms may be at least partially due to the superposition of the two separate disordered molecules; in the asymmetric molecule 2, the oxygen atoms could be displaced away from the iodine atom.

If one assumes that the "riding" model for correction of the effects of thermal motion on bond distances[16] is appropriate, then one finds that none of the bond distances within the inner coordination sphere, including the O–O distance, is lengthened appreciably.

The geometry of the triphenylphosphine groups does not differ significantly from that found in a number of previously studied structures.

The C–Cl bond lengths of 1.63 (4) and 1.70 (4) A in the dichloromethane molecule are somewhat shorter than the distance of 1.77 A found in a previous microwave study[17] of the gaseous molecule. In view of the very large thermal motions of the dichloromethane molecule in this structure, such shortening is not unexpected. The Cl–C–Cl bond angle of 115.2 (2.9)° does not differ significantly from the microwave value of 111.8°.

Discussion

The mode of attachment of oxygen in molecular oxygen carriers has long been a subject of discussion. A comparison can now be made between the structures of two closely related compounds, $\mathrm{IrCl(O_2)(CO)(P(C_6H_5)_3)_2}$ and $\mathrm{IrI(O_2)(CO)(P(C_6H_5)_3)_2}$, and this is of interest because the chloro compound is reversibly oxygenated whereas the iodo compound is irreversibly oxygenated. The results obtained here may perhaps be related to the natural molecular oxygen carriers, the most important of which is hemoglobin.

To us the most reasonable explanation of the bonding in these compounds is analogous to that proposed for oxygenated heme.[18] The processes now discussed are theoretical and have no semblance to the chemical intermediates of the oxygenation reaction. Prior to bonding, the O_2 group forms its prepared, or "valence," state; in this state the valence description is the same as in ethylene; *i.e.*, the oxygen atoms are sp^2 hybridized and the molecule has two lone electron pairs on each oxygen atom with one σ bond and one π bond, both occupied by one pair of electrons. In this state the O_2 molecule is diamagnetic. The O_2 molecule acts as a ligand by donating one pair of electrons from the π bond to iridium (and thus the O–O axis must be at right angles to the direction of coordination). Prior to oxygenation, the central atom, Ir(I), a d^8 system, was dsp^2 hybridized. The prepared state of iridium can be considered to be dsp^3 hybridized with one directional vacant orbital which, in oxygenation, receives the pair of electrons from the O_2 group. In conjunction with the formation of this bond, there is back-donation from one of the filled iridium d orbitals to the π^* orbital of the O_2 group. As electrons begin to be donated to iridium from oxygen, a dipole is set up which tends to

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stop further donation; the back-donation reduces this dipole and thus the over-all bond strength depends very largely upon the degree of back-donation that is possible. The extent of back-donation depends upon the availability of electrons at iridium and the chloro complex would be expected to form a weaker bond with oxygen than the iodo complex. In the formation of the bond to iridium, electrons are removed from an O–O bonding orbital and the back-donation is to a molecular orbital very similar to the lowest antibonding orbital in the "prepared" valence state of oxygen. Thus the more strongly the O_2 group is bound to iridium, the longer is the expected O–O distance. In this way, we rationalize the observed effects.

Infrared absorptions due to the O_2 group attached to a metal have been reported for a wide range of compounds. In general, the only band observed is in the region 840–900 cm^{-1}; such bands have been assigned to the O–O stretch. The positions of this absorption for some compounds of the general formula $IrX(O_2)(CO)(P(C_6H_5)_3)_2$ are 858 cm^{-1} (X = Cl), 862 cm^{-1} (X = Br, I), and 855 cm^{-1} ($X = N_3$). The facile assignment of this absorption as an O–O stretch does not explain why a difference of 0.2 A in O–O bond length between the oxygenated chloro and iodo compounds only results in a change of 4 cm^{-1} in the position of the absorption. Normally the position of an absorption should vary greatly with the bond length, *i.e.*, bond strength. For the system $Ir–O_2$ (C_{2v} symmetry), three infrared-active modes are expected: two symmetric and one antisymmetric. In this system, the absorption due to the antisymmetric mode is expected to occur at a wavelength lower than has been investigated. Of the two symmetric modes, we believe that the observed band corresponds to that mode analogous to the ν_1 mode in H_2O. The displacement coordinates of the oxygen atoms in this mode can be resolved into components along and perpendicular to the O–O bond. Because of the greater strength of the bond in the chloro compound, the displacement along the O–O bond should be less there than in the iodo compound. Because the O_2 group is more tightly bonded to iridium in the iodo compound the displacement normal to the O–O bond should be less there than in the chloro compound. Thus it seems probable that these changes in the displacements counterbalance one another and lead to essentially the same over-all displacement and hence the same observed frequency. The usual relations between bond strength and stretching frequencies strictly apply only to diatomic gaseous molecules, and the present case is an example where extension of these relations to polyatomic molecules is not successful.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Stereochemistry of Organophosphorus Complexes of Transition Metals

BY J. M. JENKINS AND J. G. VERKADE

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Syntheses for 20 new complexes of the type $[M(CO)_4L_2]$ and $[M'X_2L_2]$ where M = Cr, Mo, or W; M' = Pd or Pt; X = Cl or I; and L = $P(CH_3)_3$, $P(CH_2Cl)_3$, $P(CH_2O)_3CCH_3$, $P(N(CH_3)_2)_3$, $P(OCH_2)_3CC_2H_5$, and $P(OCH_2)_3C(CH_2)_4CH_3$ are described. An improved method is presented for the preparation of the dichloro Pt and Pd(II) complexes from the corresponding dichlorobis(benzonitrile)metal(II) compound in cases where the ligand or derived complex is easily solvolyzed. Both near- and far-infrared measurements are interpreted in terms of the *cis* and *trans* geometry of all of the complexes. Metal–phosphorus stretching frequencies from 220 to 214 cm^{-1} were assigned in three of the carbonyl complexes. The required number of metal–chlorine modes could be identified in all of the Pt and Pd(II) complexes: 329–362 cm^{-1} in the *trans* compounds and 289–334 cm^{-1} in the *cis*. Metal–iodine modes in the Pt and Pd(II) systems could be assigned with reasonable certainty in only two of the *trans* (151, 158 cm^{-1}) and one of the *cis* (157, 150 cm^{-1}) compounds because their intensities were generally low.

A number of examples of $P^{31}–P^{31}$ spin–spin coupling in various complexes containing two phosphorus nuclei have been reported.[1–5] In order to gain some insight into the nature of this interaction and its relation to the phosphorus–metal bond, a new experimental approach has been developed involving the study of $P^{31}–P^{31}$ spin–spin coupling constants in disubstituted complexes as a function of ligand strength and coordination geometry.[6] To enlarge the scope of our study, the preparation of new disubstituted complexes containing various phosphorus ligands was undertaken.

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