The Role of the Metal Atom in the Reversible Uptake of Molecular Oxygen. The Structures of the Molecular Oxygen Complexes Formed by Bis[bis(diphenylphosphino)ethane]iridium(I) Hexafluorophosphate and Its Rhodium Analog

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Abstract: The crystal and molecular structures of the molecular oxygen complexes of bis[bis(diphenylphosphino)ethane]iridium(I) hexafluorophosphate, $[Ir(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$, and bis[bis(diphenylphosphino)ethane]rhodium(I) hexafluorophosphate, $[Rh(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$, have been determined from three-dimensional X-ray data. The two complexes are nearly isostructural, and the inner coordination around each metal atom is trigonal bipyramidal, considering the oxygen molecule as a monodentate ligand. The oxygen molecule is attached to the metal atom in the π-bonding fashion, with the two oxygen atoms equidistant from the metal. In the iridium complex, where addition of the oxygen is irreversible, the strong metal-to-oxygen bond is accompanied by a weak O–O bond, the O–O distance being 1.625 (23) Å, which is considerably longer than that expected for two oxygen atoms linked by a σ bond (1.49 Å). In the rhodium complex, where addition of oxygen is reversible, the weaker metal-to-oxygen bond results in a stronger O–O bond, the O–O distance being 1.418 (11) Å. Crystal data: the iridium complex crystallizes in space group $P2_1/n$, (C_{2h}^5), of the monoclinic system, with four molecules in a unit cell of dimensions $a = 17.24$ (3), $b = 16.35$ (3), $c = 16.98$ (3) Å, and $\beta = 96.64$ (2)°. The structure has been refined by least-squares techniques to a conventional R factor of 6.7% on F, using 2177 reflections, collected by counter methods, for which $F^2 > 2\sigma(F^2)$. No crystallographic symmetry is imposed upon the discrete, monomeric ions. The Ir–P distances vary noticeably from 2.283 (7) to 2.452 (9) Å. The equivalent data for the analogous rhodium complex, prepared here for the first time, are $a = 17.18$ (2), $b = 16.49$ (2), $c = 16.96$ (2) Å, $\beta = 95.20$ (3)°, $Z = 4$, and space group $P2_1/n$. The least-squares refinement on F, using 2048 independent reflections, collected by counter methods, for which $F^2 > 3\sigma(F^2)$, converged to a conventional R factor of 5.2%. The Rh–P distances vary from 2.336 (4) to 2.362 (4) Å.

Oxidative-addition reactions of simple covalent molecules to $IrX(CO)[P(C_6H_5)_3]_2$ and $[Ir(diphos)_2]^+$ (diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) have been the subject of extensive research[1] recently. The addition of molecular oxygen to these parent molecules has been studied as a convenient laboratory system which is analogous to biological molecules such as hemoglobin. Thus the crystal and molecular structures of the molecular oxygen complexes of $IrX(CO)[P(C_6H_5)_3]_2$ (X = Cl and I) have been determined[2,3] in order to elucidate the mode of bonding of the oxygen molecule to the metal atom. It is apparent from these structures that the oxygen molecule is attached in the "π-bonding" manner, and that as the electronegativity of the halide substituent on the iridium atom decreases, so the strength of bonding of the oxygen molecule to the metal increases. This is reflected both in the reversibility of the addition of oxygen to the parent, and in the length of the O–O bond. For reversible addition (X = Cl), the O–O distance is 1.30 (3) Å, and for irreversible addition (X = I), the O–O bond length is 1.51 (3) Å. In a preliminary report[4] of the structure of $[Ir(O_2)(diphos)_2][PF_6]$, we have tried to rationalize the long O–O bond (1.66 Å then, but on further refinement, 1.625 (23) Å), which is longer than that expected for two oxygen atoms linked by a σ bond, in terms of a molecular orbital scheme which is an adaptation of the Chatt–Dewar π-bonding scheme proposed for Zeise's salt.

In this paper we present full details of the $[Ir(O_2)(diphos)_2][PF_6]$ structure, and also details of the preparation and structure of the rhodium analog. From our structural investigations of the oxygen complexes prepared from $IrX(CO)[P(C_6H_5)_3]_2$, we concluded that the strength of the metal–oxygen bond is related to the electron density available on the metal atom for back-bonding to the antibonding molecular orbitals on the oxygen molecule. In order to test this hypothesis, we decided to attempt the preparation of the rhodium analog of the iridium complex. In such a complex we anticipated that the electron density on the rhodium atom available for bonding to an oxygen molecule would be less than that on the iridium atom, and we expected a change in oxygen uptake properties in the direction achieved in going from iodo- to chlorocarbonylbis(triphenylphosphine)iridium. This should be reflected in a shortening of the O–O bond length. Support for this hypothesis was obtained from our failure to isolate the oxygen complex of iodocarbonylbis(triphenylphosphine)rhodium(I).

Throughout this paper we are using the term "reversible" addition to describe the formation of a molecular oxygen complex from which the oxygen molecule may be removed later, leaving the parent molecule unchanged. The removal of the oxygen molecule must be by means other than a chemical reaction, and oxygen gas must be recovered.

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Experimental Section

Preparations. $[Ir(O_2)(diphos)_2][PF_6]$ was prepared as described previously.[5,6] $[Rh(CO)_2Cl]_2$ was prepared by the method detailed in *Inorganic Syntheses*,[7] and was used without further purification to prepare $[Rh(diphos)_2]Cl$ by the method of Sacco and Ugo.[8] The yellow precipitate so obtained was washed with warm benzene and dried in air. $[Rh(diphos)_2]Cl$ (0.94 g, 0.001 mole) was dissolved in anhydrous methanol (75 ml) to give a yellow solution. Oxygen gas was bubbled into this solution at 20° for 30 min, and a twofold excess of ammonium hexafluorophosphate (0.36 g, 0.002 mole) dissolved in anhydrous methanol (20 ml) was added. The solution was cooled in ice while the flow of oxygen was continued. Brown, prismatic crystals were formed (yield 0.78 g, 73%). On dissolution of the crystals of the oxygen complex in methanol, or dichloromethane, and warming on a steam bath, oxygen gas was evolved. On evaporation to dryness, a sample of $[Rh(diphos)_2][PF_6]$ was obtained. (It was identified by analysis and the infrared spectrum.) Thus, the uptake of oxygen is reversible.

Anal.[9] Calcd for $[Rh(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$, $C_{52}H_{48}F_6O_2P_5Rh$: C, 58.01; H, 4.49; F, 10.59; P, 14.38. Found: C, 57.85; H, 4.44; F, 10.42; and P, 13.17.

From ir data no absorption due to the coordinated oxygen molecule could be detected, for the PF_6^- anion absorbs strongly in the region 840–900 cm^{-1}.

Collection and Reduction of the Intensity Data. Both compounds crystallize as pale brown prisms. Preliminary optical and X-ray examinations showed both belong to the monoclinic system.

The cell constants and their standard deviations for both of the compounds were determined at 22° from a least-squares refinement of the setting angles of a number of high-angle reflections carefully centered on a Picker four-circle automatic diffractometer.[10] The iridium complex crystallizes in a unit cell of dimensions $a = 17.24$ (3), $b = 16.35$ (3), $c = 16.98$ (3) Å, and $\beta = 96.64$ (2)° (19 reflections, Mo $K\alpha_1$ radiation, λ 0.7093 Å) and the rhodium complex in a unit cell of dimensions $a = 17.18$ (2), $b = 16.49$ (2), $c = 16.96$ (2) Å, and $\beta = 95.20$ (3)° (15 reflections, Mo $K\alpha_1$ radiation).

A study of Weissenberg and precession photographs of the iridium complex showed systematic absences of $h0l$ for $(h + l)$ odd, and $0k0$ for k odd, which are consistent only with space group C_{2h}^5-$P2_1/n$,[11] equipoints $\pm(x, y, z)$, $\pm(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$. The photographs of the rhodium complex show the same absences, closely similar cell dimensions, and comparable intensity gradations on all reciprocal lattice levels, and it is apparent that the two compounds are nearly isostructural. The calculated density of the iridium salt, assuming four formula units in the cell, is 1.64 g/cm^3, and a value of 1.64 (1) g/cm^3 was measured by flotation in a mixture of iodomethane and 1,1,2-trichloro-1,2,2-trifluoroethane. For four formula units of the rhodium complex per unit cell, the calculated density of 1.51 g/cm^3 agrees well with the value measured by flotation in a mixture of bromobenzene and dibromomethane of 1.49 (1) g/cm^3. Thus no crystallographic symmetry conditions need be imposed upon the ions.

The experimental and refinement procedures used in the data collection were the same for both compounds, and are similar to those described previously.[10,12]

A prismatic crystal of the iridium complex of dimensions 0.24 × 0.54 × 0.23 mm, with faces of the monoclinic forms {101} and {11$\bar{1}$}, was selected. The crystal chosen of the rhodium complex, which also had faces of monoclinic forms {101} and {11$\bar{1}$}, had approximate dimensions 0.25 × 0.26 × 0.25 mm. The dimensions of both crystals were carefully measured on a microscope fitted with a micrometer eyepiece in preparation for an absorption correction.

Both the rhodium and the iridium crystals were mounted on the diffractometer with the largest dimensions coincident with the spindle axis. For each this was the (010) direction. In order to minimize the possibility of multiple reflections, both crystals were deliberately misaligned by approximately 5° from the original setting. The mosaicities of the data crystals were checked by measuring ω scans through several strong reflections, using a narrow source and an open counter.[13] An average half-width of 0.1° for the iridium complex and 0.06° for the rhodium complex was satisfactory.

Mo $K\alpha$ radiation was used for the collection of each data set, with a θ–2θ scan technique, employing stationary-crystal, stationary-counter background counts of 10 sec at the beginning and end of each scan range. The iridium data were collected at a take-off angle of 1.3° and the rhodium data at a take-off angle of 1.4°. A symmetric scan range of 2° was used for the iridium complex, at a scan rate of 2°/min. The crystal to counter distance was 22.5 cm, with a counter aperture of 4 × 4 mm. Intensity data were collected from the hkl planes out to θ (Mo $K\alpha$) $\leq 20°$. Prior to data collection, all settings were checked for overlap, and those reflections where overlap was appreciable[14] (Δ(equatorial 2θ) = 2.5°, Δ(half-angular counter height) = 0.6°) were not collected. In all, 3110 reflections were measured. A unique data set of the hkl planes was collected for the rhodium complex, out to an angle θ (Mo $K\alpha$) of 17.5°. Beyond this value, there was a noticeable diminution in intensity on the films, and accordingly no higher angle reflections were collected. No check was made for overlap, since less than 3% of the iridium reflections were so affected, and the rhodium crystal showed a lower mosaicity and sharper 2θ scans. A total of 3044 reflections was measured. An asymmetric scan range was used for the collection of these data, 0.5° on the low 2θ side and 0.75° on the high 2θ side, at a scan rate of 1°/min. The crystal to counter distance was 30 cm, with a counter aperture 3.5 × 3.5 mm. For the collection of each data set the pulse height analyzer was set to accept a window of approximately 90% when centered on the Mo $K\alpha_1$ peak.

Coincidence losses for strong reflections were minimized by use of copper foil attenuators with attenuator factors of approximately 2.5. The diffracted beams of Mo $K\alpha$ radiation in both data collections were filtered through 3.0 mils of zirconium foil.

During the course of collection of each data set, the intensities of several standard reflections were measured periodically as a check on crystal and electronic stability. During the collection of the iridium data set the decrease in intensity ranged from 1 to 5%, averaging over the three standards chosen to 2.8%. A correction for decomposition was made on the basis of the decay of the standards with time. The four standards chosen for the rhodium data set showed a decrease of less than 1% of the original mean during data collection, and no correction for decomposition was made.

The data for both compounds were processed in the manner described previously.[10,12] After a correction for background, the standard deviation $\sigma(I)$ of the corrected intensity, I, was estimated using a value of p for both complexes of 0.05.

The intensities were then corrected for Lorentz-polarization effects. The calculated absorption coefficient, μ, for the iridium complex is 32.4 cm^{-1}.[11] A series of tests showed transmission factors varying from 0.57 to 0.32, so an absorption correction[15] was made. The value of the absorption coefficient for the rhodium compound is 6 cm^{-1}, and tests indicated that transmission factors did not vary by more than 1%. Thus no absorption correction was necessary for this compound.

The data for the iridium compound comprised a total of 3110 independent reflections, of which 626 were less than $\sigma(I)$. Of the total of 3044 independent reflections measured for the rhodium complex, 471 were less than $\sigma(I)$.

Solution and Refinement of the Structures

In the least-squares refinements, the function minimized is $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and w, the weighting function, is $4F_o^2/\sigma^2(F_o^2)$. The residuals R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The scattering factors used for P, F, O, and C were those tabulated

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by Ibers;[11] those for Ir and Rh were calculated by Cromer and Waber.[16] The hydrogen scattering factors were those calculated by Stewart, *et al.*[17] The effects of anomalous scattering were included in the structure factor calculations.[18] The values of $\Delta f'$ and $\Delta f''$ for Ir, Rh, and P were those given by Cromer.[19]

The iridium atom was located from an inspection of a three-dimensional Patterson function,[15] and the remaining nonhydrogen atoms were found from successive least-squares refinements and difference Fourier syntheses. In subsequent least-squares refinements, the iridium atom, the four phosphorus atoms coordinated to the metal, the aliphatic carbon atoms, and the two oxygen atoms were allowed to vibrate anisotropically. The phosphorus atom of the PF_6^- anion was given an isotropic thermal parameter, and the F_6 entity and the phenyl rings were constrained as groups with over-all group temperature factors.[2] The F_6 group was constrained to O_h symmetry, with a fluorine-atom-to-center-of-gravity-distance of 1.58 Å,[20] and the phenyl rings to D_{6h} symmetry, C–C distance 1.392 Å.

After four cycles of refinement, values of R_1 and R_2 of 0.079 and 0.092 were obtained for the 1784 reflections included in the refinement ($I > 3\sigma(I)$). The hydrogen atom contributions were calculated at this stage, treating the phenyl hydrogens as rigid groups and assuming a tetrahedral geometry around the aliphatic carbon atoms in the diphos rings. In these calculations a C–H bond distance of 0.9 Å and an isotropic thermal parameter of 5 Å^2 were used. A structure factor calculation including these contributions gave $R_1 = 0.080$ and $R_2 = 0.089$. A subsequent difference Fourier synthesis was calculated and showed clear evidence of disorder of the PF_6^- anion. From a model, a second octahedral array of fluorine atoms was apparent. This array was therefore included in the refinement. The over-all temperature factors of the F_6 groups (F_6–A and F_6–B) were constrained to be equal, and the atom multiplicity (the disorder parameter) α of the F_6–A group was refined in subsequent least-squares cycles. The disorder parameter for F_6–B is $(1 - \alpha)$, and the necessary constraints among various derivatives were taken into account in this calculation. After one cycle of least squares, in which the group orientation parameters, the disorder parameter, and the one temperature factor were refined, it was found possible to refine separate group temperature factors for the two F_6 arrays. The final refinement cycle, with all nongroup atoms, excepting the phosphorus atom of the PF_6, allowed to vibrate anisotropically, with individual isotropic thermal parameters for the carbon atoms in the groups, and with separate over-all temperature factors for the F_6 groups, led to convergence at $R_1 = 0.067$, $R_2 = 0.073$, and an error in an observation of unit weight of 1.93 electrons for the 2177 reflections for which $I > 2\sigma(I)$. The final value of the disorder parameter, α, is 0.60 (2).

An examination of the geometry of the cation at this stage revealed a surprisingly long O–O distance of 1.625 (23) Å. Accordingly, a total difference Fourier synthesis was calculated, but the highest electron density was only 0.85 e/Å^3, and this was in the neighborhood of the iridium atom, as were several other areas of high electron density. Therefore, in order to eliminate the unlikely possibility of a false minimum in the full-matrix, least-squares solution, which might have led to the long oxygen–oxygen bond, a set of structure factors was calculated, using all 3078 observed reflections for which $F^2 > 0$, and omitting the contributions from the oxygen atoms. A difference Fourier synthesis calculated from the structure factors so obtained showed two major areas of electron density, the interpolated centers of which were 1.58 Å apart. This O–O bond length is greater than that expected for a σ bond, and is not significantly different from the refined oxygen atom positions (1.625 (23) Å). A statistical analysis of the weighted R values of all reflections showed no unusual trends with $|F_o|$, indices, or $\lambda^{-1} \sin \theta$.

We therefore conclude that there is no false minimum in the least-squares refinement, that the parameters obtained are essentially independent of the weighting scheme used, and that the derived value of the O–O bond length, long though it is, is as accurate as can be determined from our available data.

Since a comparison of the Weissenberg and precession film intensities of the two complexes showed that the rhodium complex was very nearly isostructural with the iridium complex, the final iridium structure parameters were used as the starting atomic parameters for the refinement of the rhodium structure. The course of the refinement followed that of the iridium structure and with an error in an observation of unit weight of 1.59 electrons converged to values of $R_1 = 0.052$, $R_2 = 0.063$ for the 2048 independent reflections for which $I > 3\sigma(I)$. A disordered model was again used to describe the PF_6^- anion, and a value of $\alpha = 0.70$ (1) was determined for the disorder parameter. A total difference Fourier showed no peaks higher than 0.43 (6) e/Å^3. The 13 highest peaks were all associated with the disordered PF_6^- group. In Table I a listing of the structure amplitudes for the iridium complex is given as $10|F_o|$ and $10|F_c|$ (in electrons); in Table II the corresponding values are listed for the rhodium complex.[21] Table III shows the final positional, thermal, and group parameters of both structures. The derived positional parameters of the group atoms are compared in Table IV, and the calculated hydrogen positional parameters of both structures are listed in Table V.

As for the iridium complex, the agreement between $|F_o|$ and $|F_c|$ was subjected to a statistical analysis, as functions of $\lambda^{-1} \sin \theta$, $|F_o|$, and various combinations of Miller indices. Again no unusual trends were apparent.

Description of the Structures

Both crystal structures result from the packing of the approximately spherical cations and anions. Fluorine atom–phenyl carbon atom distances are all greater

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(21) Calculated and observed structure factors for $[Ir(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$ and $[Rh(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$ are deposited as Document No. NAPS-00414 with ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be obtained by citing the document number and remitting $1.00 for microfilm or $3.00 for a 35-mm photocopy. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table III. Final Least-Squares Parameters

(a) $[Ir(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$

Atom	x	y	z	β_{11}[a] or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.30725 (6)[b]	0.23279 (5)	0.09726 (5)	0.00460 (7)	0.00525 (6)	0.00356 (6)	−0.00101 (4)	−0.00081 (3)	0.00040 (4)
P_1	0.3231 (4)	0.3116 (4)	−0.0107 (4)	0.0059 (4)	0.0054 (3)	0.0038 (3)	−0.0008 (3)	−0.0004 (3)	0.0006 (3)
P_2	0.1817 (4)	0.2101 (4)	0.0313 (4)	0.0050 (4)	0.0054 (4)	0.0044 (3)	−0.0007 (3)	−0.0018 (3)	−0.0004 (3)
P_3	0.4285 (4)	0.2554 (4)	0.1706 (3)	0.0049 (4)	0.0057 (4)	0.0036 (3)	−0.0009 (3)	−0.0004 (3)	−0.0009 (3)
P_4	0.3729 (4)	0.1114 (4)	0.0522 (4)	0.0053 (4)	0.0088 (4)	0.0040 (3)	−0.0029 (3)	−0.0008 (3)	0.0015 (3)
O_1	0.2596 (10)	0.2958 (11)	0.1774 (9)	0.0078 (12)	0.0098 (12)	0.0029 (8)	−0.0002 (8)	−0.0015 (7)	0.0015 (7)
O_2	0.2624 (9)	0.1980 (12)	0.1948 (8)	0.0058 (11)	0.0131 (13)	0.0030 (8)	−0.0024 (8)	0.0006 (6)	0.0007 (8)
C_1	0.2585 (15)	0.2696 (12)	−0.0936 (12)	0.0034 (15)	0.0051 (12)	0.0041 (11)	−0.0007 (10)	−0.0009 (9)	0.0008 (9)
C_2	0.1786 (17)	0.2592 (12)	−0.0656 (15)	0.0071 (18)	0.0040 (13)	0.0060 (15)	−0.0004 (10)	−0.0023 (11)	0.0010 (10)
C_3	0.5027 (15)	0.2043 (15)	0.1165 (14)	0.0060 (17)	0.0050 (15)	0.0057 (13)	−0.0001 (10)	0.0011 (10)	0.0003 (10)
C_4	0.4740 (14)	0.1188 (14)	0.1006 (12)	0.0059 (15)	0.0058 (14)	0.0043 (12)	0.0012 (10)	−0.0007 (9)	−0.0009 (10)
PF	−0.2543 (5)	0.2079 (4)	0.1612 (4)	7.25 (19)					

Group	x_c[c]	y_c	z_c	δ	ϵ	η	B_1[d]	B_2	B_3	B_4	B_5	B_6
P_1–Ph_1	0.4886 (7)	0.3343 (6)	0.9289 (6)	−0.336 (15)	−2.343 (10)	−0.579 (14)	5.0 (5)	6.4 (6)	6.8 (6)	7.8 (7)	8.6 (7)	6.7 (6)
P_1–Ph_2	0.2619 (6)	0.4959 (6)	−0.0089 (6)	−2.802 (9)	3.108 (10)	1.458 (10)	5.1 (5)	6.3 (6)	7.5 (7)	7.7 (7)	8.3 (7)	7.2 (6)
P_2–Ph_3	0.0409 (7)	0.2873 (6)	0.1124 (6)	−0.411 (11)	2.996 (10)	2.600 (10)	5.1 (5)	7.7 (6)	7.4 (7)	8.7 (7)	9.2 (8)	6.6 (6)
P_2–Ph_4	0.1299 (6)	0.0248 (6)	0.0106 (6)	−1.994 (26)	−1.939 (10)	−0.145 (26)	5.7 (5)	5.8 (5)	6.8 (6)	6.7 (6)	7.3 (6)	7.3 (6)
P_3–Ph_5	0.4422 (6)	0.1848 (5)	0.3463 (6)	0.920 (10)	−2.889 (11)	1.818 (8)	5.2 (5)	6.2 (6)	8.0 (7)	8.1 (7)	7.7 (7)	6.8 (6)
P_3–Ph_6	0.4934 (7)	0.4352 (6)	0.2102 (5)	1.250 (11)	−2.889 (9)	0.188 (9)	5.7 (6)	6.5 (6)	8.4 (7)	6.6 (6)	7.7 (6)	6.2 (6)
P_4–Ph_7	0.3838 (6)	0.0657 (5)	0.8705 (6)	−1.306 (8)	3.109 (11)	1.812 (8)	5.4 (5)	6.5 (6)	6.5 (6)	5.9 (6)	7.2 (6)	6.6 (6)
P_4–Ph_8	0.3322 (6)	0.9436 (7)	0.1331 (7)	−3.043 (20)	2.107 (12)	1.303 (20)	7.6 (7)	7.6 (7)	8.1 (7)	7.9 (7)	8.2 (7)	7.2 (6)
F_6–A	−0.2579 (6)	0.2088 (6)	0.1591 (5)	2.480 (12)	2.720 (8)	−0.470 (9)	8.9 (5)					
F_6–B	−0.2518 (11)	0.2098 (10)	0.1627 (10)	0.319 (20)	−2.641 (14)	0.791 (16)	10.8 (8)					

Multiplicity factor of group F_6–A $\alpha = 0.60$ (2)

(b) $[Rh(O_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.31032 (6)	0.22622 (7)	0.09092 (6)	0.00307 (6)	0.00366 (6)	0.00301 (6)	0.00001 (4)	0.00051 (4)	−0.00018 (5)
P_1	0.3283 (2)	0.3061 (2)	−0.0190 (2)	0.0037 (2)	0.0035 (2)	0.0035 (2)	0.0003 (1)	0.0007 (2)	0.0001 (2)
P_2	0.1858 (2)	0.2035 (2)	0.0236 (2)	0.0032 (2)	0.0048 (2)	0.0033 (2)	0.0000 (2)	0.0005 (1)	−0.0003 (2)
P_3	0.4300 (2)	0.2528 (2)	0.1656 (2)	0.0037 (2)	0.0040 (2)	0.0035 (2)	−0.0002 (2)	0.0004 (2)	−0.0003 (2)
P_4	0.3757 (2)	0.1094 (2)	0.0526 (2)	0.0033 (2)	0.0037 (2)	0.0030 (2)	−0.0001 (1)	0.0005 (1)	−0.0001 (2)
O_1	0.2548 (5)	0.2855 (6)	0.1742 (5)	0.0039 (4)	0.0052 (6)	0.0038 (5)	−0.0001 (4)	0.0008 (3)	−0.0014 (4)
O_2	0.2569 (5)	0.2010 (6)	0.1897 (5)	0.0039 (5)	0.0049 (5)	0.0039 (5)	−0.0002 (4)	0.0007 (4)	−0.0003 (4)
C_1	0.2668 (8)	0.2614 (7)	−0.1006 (7)	0.0040 (7)	0.0042 (7)	0.0024 (6)	−0.0003 (6)	0.0002 (6)	−0.0002 (6)
C_2	0.1851 (8)	0.2524 (8)	−0.0748 (8)	0.0038 (8)	0.0044 (8)	0.0048 (8)	−0.0002 (6)	0.0000 (6)	−0.0002 (6)
C_3	0.5066 (7)	0.2032 (8)	0.1155 (8)	0.0039 (7)	0.0029 (7)	0.0043 (7)	−0.0014 (6)	0.0001 (6)	−0.0006 (6)
C_4	0.4784 (7)	0.1180 (8)	0.0940 (7)	0.0034 (7)	0.0045 (8)	0.0027 (7)	0.0010 (7)	0.0001 (5)	−0.0001 (6)
PF	−0.2517 (2)	0.2152 (3)	0.1539 (2)	5.44 (10)					

Group	x_c	y_c	z_c	δ	ϵ	η	B_1	B_2	B_3	B_4	B_5	B_6
P_1–Ph_1	0.4984 (4)	0.3343 (3)	0.9218 (4)	−0.306 (9)	−2.299 (6)	−0.558 (8)	3.9 (3)	5.1 (4)	5.9 (4)	6.5 (4)	5.8 (4)	4.8 (3)
P_1–Ph_2	0.2612 (3)	0.4884 (4)	−0.0147 (4)	−2.778 (5)	3.097 (6)	1.485 (5)	3.8 (3)	5.1 (3)	5.4 (4)	5.5 (4)	5.9 (4)	4.8 (3)
P_2–Ph_3	0.0449 (4)	0.2876 (4)	0.1068 (3)	−0.416 (7)	2.945 (6)	2.608 (6)	4.7 (3)	6.2 (4)	6.9 (4)	6.7 (4)	7.8 (5)	6.3 (4)
P_2–Ph_4	0.1285 (3)	0.0192 (4)	0.0072 (4)	−1.95 (2)	−1.946 (6)	−0.08 (2)	4.1 (3)	5.0 (3)	5.5 (4)	6.3 (4)	6.8 (4)	5.2 (4)
P_3–Ph_5	0.4403 (4)	0.1821 (4)	0.3423 (4)	0.971 (6)	−2.906 (7)	1.823 (6)	5.0 (3)	5.3 (3)	7.7 (4)	7.3 (4)	7.2 (4)	5.7 (4)
P_3–Ph_6	0.4901 (4)	0.4329 (4)	0.2084 (3)	1.288 (6)	−2.894 (6)	0.229 (6)	4.4 (3)	5.3 (4)	6.6 (4)	6.4 (4)	6.3 (4)	5.6 (4)
P_4–Ph_7	0.3845 (4)	0.0625 (3)	0.8697 (4)	−1.246 (5)	3.099 (6)	1.812 (5)	3.6 (3)	4.2 (3)	5.4 (4)	5.2 (4)	5.8 (4)	4.0 (3)
P_4–Ph_8	0.3329 (3)	0.9438 (4)	0.1396 (4)	−3.03 (1)	2.138 (6)	1.30 (1)	3.5 (3)	4.6 (3)	5.2 (4)	5.4 (4)	5.1 (4)	4.6 (3)
F_6–A	−0.2537 (3)	0.2162 (3)	0.1532 (3)	2.496 (7)	2.654 (4)	−0.449 (5)	8.0 (3)					
F_6–B	−0.2493 (7)	0.2170 (8)	0.1566 (7)	1.29 (2)	2.47 (1)	−0.86 (1)	8.7 (7)					
				Multiplicity factor of group F_6–A		$\alpha = 0.695$ (15)						

[a] Form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in the following tables are the estimated standard deviations in the least significant digits. [c] For definition of group parameters, see R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). [d] B_n is the temperature factor of atom C_n in the phenyl ring in Å^2).

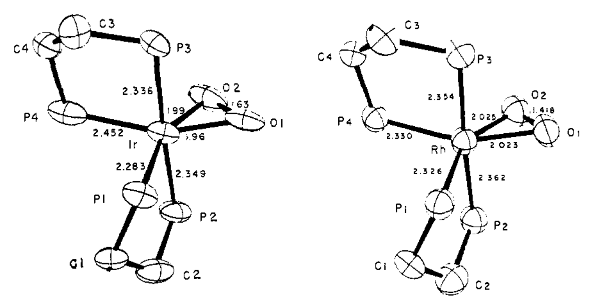

Figure 1. The inner coordination spheres of $[Ir(O_2)(diphos)_2][PF_6]$ and the rhodium analog.

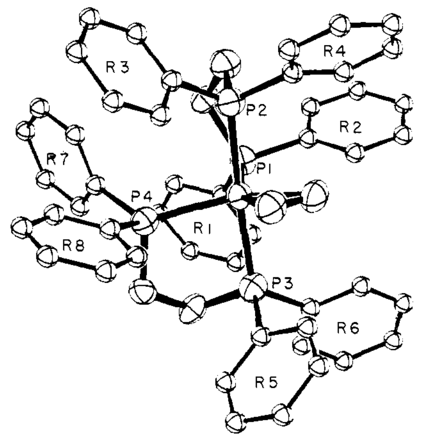

Figure 2 An over-all perspective view of the $[Rh(O_2)(diphos)_2]^+$ cation, with the ring numbering scheme used.

than 3.0 Å. Fluorine atom–hydrogen atom distances (other than phenyl hydrogen atoms) are greater than 2.38 Å in both structures, and the cations and anions are thus essentially discrete.

The two cations are nearly isostructural, the main differences between them being in the O–O bond length and slightly differing inner coordination spheres. Both cations have approximately trigonal-bipyramidal configurations. The inner coordination spheres of both cations are shown in Figure 1, and an over-all view of the rhodium cation, including the phenyl rings and the numbering system used, is given in Figure 2. The same atom numbering system was used for both complexes.

In Tables VI and VII, selected interatomic distances and angles, together with their standard deviations as estimated from the inverse matrices, are compared. In both compounds the spatial arrangement of the oxygen molecule and the metal atom is in the π-bonding arrangement observed for the oxygen complexes of $IrX(CO)[P(C_6H_5)_3]_2$ (X = Cl, I).[2,3] The data summarizing the geometry of the attachment of the oxygen molecule to the metal for the four known oxygen complexes in this series are given in Table VIII.

In the rhodium cation, where the addition of oxygen is reversible, the Rh–O distances of 2.026 (8) and 2.025 (9) Å correspond to a mean distance of 2.025 (7) Å, which is significantly longer than the mean distance 1.976 (14) Å, corresponding to the Ir–O distances of 1.961 (18) and 1.990 (16) Å. As addition of oxygen is to the rhodium parent is reversible, the weaker metal–oxygen bond is accompanied by a stronger O–O bond, manifested in a shorter O–O distance of 1.418 (11) Å. In the iridium complex, where addition of oxygen is

Table IV. Derived Group Atom Positional Parameters

Atom	Iridium x	Iridium y	Iridium z	Rhodium x	Rhodium y	Rhodium z
R_1-C_1	0.4139 (8)	0.3263 (16)	0.9515 (9)	0.4229 (4)	0.3240 (9)	0.9438 (5)
R_1-C_2	0.4675 (10)	0.3789 (10)	0.9930 (7)	0.4748 (5)	0.3756 (6)	0.9872 (4)
R_1-C_3	0.5422 (11)	0.3869 (12)	0.9705 (10)	0.5503 (6)	0.3858 (7)	0.9652 (6)
R_1-C_4	0.5634 (8)	0.3423 (17)	0.9064 (10)	0.5739 (4)	0.3445 (10)	0.8998 (6)
R_1-C_5	0.5098 (10)	0.2896 (11)	0.8648 (8)	0.5220 (5)	0.2930 (6)	0.8564 (5)
R_1-C_6	0.4351 (11)	0.2816 (12)	0.8874 (9)	0.4465 (6)	0.2827 (7)	0.8783 (5)
R_2-C_1	0.2889 (9)	0.4157 (7)	−0.0084 (10)	0.2901 (5)	0.4095 (4)	−0.0157 (6)
R_2-C_2	0.2821 (9)	0.4609 (10)	−0.0785 (8)	0.2802 (5)	0.4542 (6)	−0.0856 (4)
R_2-C_3	0.2550 (10)	0.5411 (10)	−0.0789 (8)	0.2513 (5)	0.5330 (6)	−0.0846 (5)
R_2-C_4	0.2348 (9)	0.5761 (7)	−0.0093 (11)	0.2323 (5)	0.5672 (4)	−0.0137 (6)
R_2-C_5	0.2417 (10)	0.5309 (11)	0.0608 (8)	0.2423 (5)	0.5225 (6)	0.0562 (5)
R_2-C_6	0.2687 (10)	0.4507 (10)	0.0612 (8)	0.2712 (5)	0.4437 (6)	0.0552 (4)
R_3-C_1	0.1024 (9)	0.2523 (9)	0.0778 (9)	0.1057 (5)	0.2505 (6)	0.0714 (5)
R_3-C_2	0.0995 (9)	0.3368 (9)	0.0881 (9)	0.1033 (5)	0.3347 (6)	0.0777 (6)
R_3-C_3	0.0380 (12)	0.3717 (7)	0.1227 (10)	0.0425 (7)	0.3718 (4)	0.1131 (6)
R_3-C_4	−0.0205 (9)	0.3222 (11)	0.1470 (10)	−0.0159 (5)	0.3246 (7)	0.1421 (6)
R_3-C_5	−0.0176 (9)	0.2378 (11)	0.1367 (10)	−0.0134 (5)	0.2404 (7)	0.1358 (6)
R_3-C_6	0.0438 (11)	0.2028 (6)	0.1021 (10)	0.0474 (7)	0.2034 (4)	0.1004 (6)
R_4-C_1	0.1529 (29)	0.1064 (10)	0.0175 (8)	0.1528 (18)	0.0997 (7)	0.0118 (5)
R_4-C_2	0.1645 (15)	0.0547 (12)	0.0831 (7)	0.1647 (9)	0.0496 (8)	0.0779 (4)
R_4-C_3	0.1415 (18)	−0.0268 (8)	0.0761 (8)	0.1404 (11)	−0.0310 (5)	0.0733 (5)
R_4-C_4	0.1069 (29)	−0.0567 (11)	0.0036 (9)	0.1043 (18)	−0.0614 (7)	0.0026 (6)
R_4-C_5	0.0953 (15)	−0.0050 (12)	−0.0620 (7)	0.0924 (9)	−0.0112 (8)	−0.0636 (5)
R_4-C_6	0.1183 (18)	0.0765 (8)	−0.0550 (7)	0.1167 (10)	0.0693 (5)	−0.0589 (4)
R_5-C_1	0.4385 (10)	0.2139 (9)	0.2689 (7)	0.4366 (6)	0.2102 (6)	0.2647 (4)
R_5-C_2	0.3861 (8)	0.2426 (8)	0.3190 (10)	0.3818 (5)	0.2363 (6)	0.3149 (7)
R_5-C_3	0.3897 (9)	0.2136 (9)	0.3964 (9)	0.3856 (5)	0.2082 (6)	0.3925 (6)
R_5-C_4	0.4458 (11)	0.1558 (10)	0.4237 (7)	0.4441 (7)	0.1540 (6)	0.4200 (4)
R_5-C_5	0.4982 (9)	0.1270 (9)	0.3736 (11)	0.4988 (5)	0.1279 (6)	0.3697 (7)
R_5-C_6	0.4946 (8)	0.1561 (8)	0.2962 (9)	0.4951 (5)	0.1560 (6)	0.2921 (6)
R_6-C_1	0.4646 (10)	0.3572 (7)	0.1919 (9)	0.4637 (6)	0.3553 (4)	0.1879 (5)
R_6-C_2	0.4143 (7)	0.4188 (11)	0.2112 (9)	0.4112 (4)	0.4139 (6)	0.2096 (5)
R_6-C_3	0.4431 (10)	0.4968 (8)	0.2295 (9)	0.4377 (6)	0.4916 (5)	0.2301 (6)
R_6-C_4	0.5222 (11)	0.5133 (7)	0.2284 (9)	0.5166 (7)	0.5106 (5)	0.2289 (6)
R_6-C_5	0.5726 (7)	0.4517 (11)	0.2091 (10)	0.5691 (4)	0.4519 (7)	0.2073 (6)
R_6-C_6	0.5437 (9)	0.3737 (9)	0.1908 (9)	0.5426 (5)	0.3743 (5)	0.1868 (5)
R_7-C_1	0.3812 (11)	0.0860 (8)	0.9498 (6)	0.3814 (6)	0.0827 (5)	0.9491 (4)
R_7-C_2	0.3145 (8)	0.0566 (8)	0.9044 (10)	0.3162 (4)	0.0493 (5)	0.9063 (5)
R_7-C_3	0.3171 (8)	0.0363 (8)	0.8252 (10)	0.3192 (5)	0.0290 (5)	0.8270 (5)
R_7-C_4	0.3864 (11)	0.0454 (9)	0.7912 (6)	0.3875 (6)	0.0423 (5)	0.7904 (4)
R_7-C_5	0.4531 (8)	0.0749 (9)	0.8365 (10)	0.4528 (5)	0.0757 (5)	0.8332 (6)
R_7-C_6	0.4504 (8)	0.0952 (8)	0.9158 (10)	0.4498 (4)	0.0960 (5)	0.9125 (5)
R_8-C_1	0.3469 (22)	0.0160 (9)	0.0944 (11)	0.3472 (11)	1.0145 (5)	0.0984 (5)
R_8-C_2	0.3431 (10)	0.9423 (12)	0.0530 (7)	0.3442 (5)	0.9401 (6)	0.0593 (4)
R_8-C_3	0.3284 (17)	0.8698 (8)	0.0917 (11)	0.3299 (9)	0.8694 (4)	0.1005 (6)
R_8-C_4	0.3175 (22)	0.8712 (9)	0.1718 (11)	0.3186 (11)	0.8731 (5)	0.1807 (6)
R_8-C_5	0.3213 (10)	0.9449 (12)	0.2131 (7)	0.3215 (5)	0.9475 (6)	0.2198 (4)
R_8-C_6	0.3360 (17)	0.0174 (9)	0.1744 (11)	0.3358 (9)	1.0182 (4)	0.1786 (5)
PF_A-F_1	−0.3123 (11)	0.2759 (10)	0.1142 (9)	−0.3089 (6)	0.2837 (5)	0.1124 (5)
PF_A-F_2	−0.2036 (11)	0.1418 (9)	0.2039 (9)	−0.1985 (6)	0.1488 (5)	0.1940 (5)
PF_A-F_3	−0.2062 (10)	0.2784 (9)	0.2032 (9)	−0.2046 (5)	0.2839 (5)	0.2014 (5)
PF_A-F_4	−0.3097 (10)	0.1393 (9)	0.1149 (9)	−0.3028 (6)	0.1486 (5)	0.1051 (5)
PF_A-F_5	−0.2043 (9)	0.2097 (12)	0.0896 (8)	−0.1983 (5)	0.2235 (7)	0.0841 (4)
PF_A-F_6	−0.3116 (9)	0.2079 (12)	0.2285 (8)	−0.3092 (5)	0.2089 (7)	0.2223 (4)
PF_B-F_1	−0.1804 (14)	0.1998 (22)	0.2292 (14)	−0.1912 (12)	0.2651 (17)	0.1067 (11)
PF_B-F_2	−0.3233 (14)	0.2199 (22)	0.0963 (14)	−0.3075 (12)	0.1689 (16)	0.2065 (11)
PF_B-F_3	−0.2265 (20)	0.1294 (13)	0.1210 (16)	−0.1796 (10)	0.1962 (14)	0.2207 (11)
PF_B-F_4	−0.2772 (19)	0.2903 (13)	0.2044 (16)	−0.3191 (10)	0.2377 (14)	0.0926 (10)
PF_B-F_5	−0.1993 (19)	0.2623 (17)	0.1115 (16)	−0.2325 (17)	0.1367 (10)	0.1102 (11)
PF_B-F_6	−0.3043 (19)	0.1574 (18)	0.2140 (16)	−0.2661 (17)	0.2972 (10)	0.2031 (11)

irreversible, the stronger metal–oxygen bond is accompanied by a much weaker O–O bond, resulting in a longer O–O distance of 1.625 (23) Å. Ir–O bond lengths of 2.09 (3) and 2.04 (3) Å were observed in the reversible complex $Ir(O_2)Cl(CO)(P(C_6H_5)_3)_2$,[2] and values of 2.082 (22) and 2.035 (20) Å in the irreversible complex $Ir(O_2)I(CO)(P(C_6H_5)_3)_2$.[3]

The Rh–P distances vary from 2.326 (4) to 2.362 (4) Å. The mean value of 2.348 (8) Å is significantly longer than that of 2.306 (6) Å observed[22] in the parent square-planar complex. Similar values of 2.355 and 2.336 Å were observed in $Rh(CS)Cl[P(C_6H_5)_3]_2$,[23] of 2.371 (16) and 2.367 (16) Å in $Rh(SO_2)Cl(CO)[P(C_6H_5)_3]_2$,[24] and a mean value of 2.322 (5) Å for the three Rh–P bonds in $Rh(H)(CO)[P(C_6H_5)_3]_3$.[25]

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Table V. Calculated Hydrogen Atom Parameters

Atom[a,b]	Iridium x	Iridium y	Iridium z	Rhodium x	Rhodium y	Rhodium z
C_1H_1	0.277	0.218	−0.111	0.288	0.203	−0.119
C_1H_2	0.256	0.306	−0.140	0.265	0.298	−0.155
C_2H_1	0.145	0.231	−0.104	0.150	0.219	−0.117
C_2H_2	0.156	0.315	−0.062	0.162	0.312	−0.072
C_3H_1	0.555	0.206	0.147	0.562	0.202	0.154
C_3H_2	0.510	0.233	0.067	0.522	0.237	0.065
C_4H_1	0.479	0.088	0.150	0.482	0.081	0.146
C_4H_2	0.509	0.090	0.067	0.512	0.090	0.052
R_1H_2	0.456	0.407	1.034	0.459	0.402	1.029
R_1H_3	0.579	0.419	0.997	0.584	0.419	0.993
R_1H_4	0.613	0.346	0.891	0.623	0.351	0.886
R_1H_5	0.524	0.261	0.822	0.537	0.266	0.814
R_1H_6	0.401	0.249	0.859	0.413	0.249	0.850
R_2H_2	0.294	0.439	−0.124	0.292	0.432	−0.131
R_2H_3	0.250	0.571	−0.125	0.245	0.562	−0.130
R_2H_4	0.217	0.629	−0.010	0.214	0.618	−0.013
R_2H_5	0.229	0.554	0.105	0.230	0.544	0.101
R_2H_6	0.274	0.422	0.106	0.278	0.415	0.100
R_3H_2	0.138	0.368	0.073	0.141	0.365	0.060
R_3H_3	0.037	0.427	0.130	0.041	0.426	0.117
R_3H_4	−0.060	0.346	0.169	−0.056	0.349	0.164
R_3H_5	−0.056	0.207	0.151	−0.052	0.210	0.154
R_3H_6	0.045	0.149	0.095	0.049	0.149	0.096
R_4H_2	0.186	0.072	0.130	0.188	0.069	0.124
R_4H_3	0.149	−0.062	0.118	0.148	−0.064	0.116
R_4H_4	0.092	−0.111	−0.002	0.089	−0.114	−0.001
R_4H_5	0.073	−0.026	−0.109	0.070	−0.031	−0.109
R_4H_6	0.111	0.109	−0.097	0.110	0.102	−0.102
R_5H_2	0.351	0.281	0.303	0.344	0.271	0.297
R_5H_3	0.357	0.233	0.430	0.350	0.225	0.425
R_5H_4	0.448	0.136	0.474	0.446	0.136	0.470
R_5H_5	0.533	0.088	0.391	0.536	0.093	0.388
R_5H_6	0.528	0.137	0.264	0.530	0.139	0.260
R_6H_2	0.364	0.410	0.213	0.360	0.401	0.210
R_6H_3	0.413	0.538	0.242	0.404	0.529	0.244
R_6H_4	0.543	0.565	0.240	0.533	0.561	0.242
R_6H_5	0.625	0.462	0.208	0.620	0.464	0.207
R_6H_6	0.576	0.334	0.179	0.576	0.336	0.173
R_7H_2	0.270	0.050	0.926	0.272	0.041	0.930
R_7H_3	0.274	0.017	0.795	0.278	0.008	0.799
R_7H_4	0.388	0.032	0.740	0.390	0.030	0.739
R_7H_5	0.498	0.080	0.814	0.497	0.085	0.810
R_7H_6	0.494	0.114	0.945	0.492	0.118	0.940
R_8H_2	0.349	0.939	0.001	0.352	0.937	0.008
R_8H_3	0.325	0.821	0.065	0.328	0.821	0.076
R_8H_4	0.308	0.823	0.197	0.310	0.828	0.208
R_8H_5	0.316	0.945	0.265	0.314	0.951	0.272
R_8H_6	0.341	1.064	0.201	0.338	1.067	0.203

[a] All atoms were allotted values of $B = 5.0$ Å^2. [b] C_1 in the phenyl ring is attached to P; numbering is then sequential with H_2 attached to C_2.

The Ir–P distances vary considerably from 2.283 (7) to 2.452 (9) Å, a range which far exceeds Ir–P distances in comparable structures[2,3,26–29] (Table IX). It is interesting that the shortest and longest of the four Ir–P bonds lie in the equatorial plane of the trigonal bipyramid. A similar, but much less dramatic, trend is observed in the rhodium analog. The reasons for these distortions are not obvious to us, although a "*trans*" effect may be eliminated, since in both complexes the two oxygen atoms are equidistant from the metal. In these circumstances one is always tempted to invoke "packing forces" as the explanation, but there are no close contacts involving the phenyl rings and the phosphorus atoms.

The equations of the least-squares planes including the metal, the oxygen, and the equatorial phosphorus atoms for each of the complexes are given in Table X, together with the perpendicular distances of the atoms from the planes. In both structures the oxygen molecule lies at an angle to the plane formed by the metal and the two equatorial phosphorus atoms, 13 (1) and 14.0 (6)° for the iridium and the rhodium complexes, respectively. A study of the P(equatorial)–M–P(axial) angles (Table VII) shows significant deviations from 90°, and the deviations of the oxygen atoms from the least-squares planes are considered to be due more to distortions from the ideal trigonal-bipyramidal configuration of the phosphorus atoms (possibly caused by ring strain) than any deviation particularly attributable to the mode of bonding of the oxygen molecule.

The P–C–C–P moiety of each of the diphos rings is puckered in a manner similar to that observed for coordinated ethylenediamine rings. The dihedral angle

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Table VI. Selected Intramolecular Bond Distances (Å)

Bond	Iridium	Rhodium
M–P$_1$	2.283 (7)	2.326 (4)
M–P$_2$	2.349 (7)	2.362 (4)
M–P$_3$	2.336 (7)	2.354 (4)
M–P$_4$	2.452 (9)	2.350 (4)
M–O$_1$	1.961 (18)	2.026 (8)
M–O$_2$	1.990 (16)	2.025 (9)
P$_1$–P$_2$	3.10 (1)	3.116 (6)
P$_1$–P$_3$	3.51 (1)	3.553 (6)
P$_1$–P$_4$	3.52 (1)	3.532 (6)
P$_1$–O$_1$	3.50 (2)	3.632 (10)
P$_1$–O$_2$	4.19 (2)	4.221 (10)
P$_2$–P$_4$	3.65 (1)	3.605 (6)
P$_2$–O$_1$	3.02 (2)	3.035 (9)
P$_2$–O$_2$	2.96 (2)	2.967 (10)
P$_3$–P$_4$	3.17 (1)	3.131 (6)
P$_3$–O$_1$	3.00 (2)	3.072 (10)
P$_3$–O$_2$	3.09 (2)	3.154 (10)
P$_4$–O$_1$	4.29 (2)	4.216 (10)
P$_4$–O$_2$	3.54 (2)	3.565 (9)
P$_1$–C$_1$	1.83 (2)	1.820 (13)
P$_2$–C$_2$	1.83 (3)	1.853 (14)
P$_3$–C$_3$	1.86 (3)	1.825 (13)
P$_4$–C$_4$	1.84 (2)	1.845 (13)
C$_1$–C$_2$	1.52 (3)	1.515 (17)
C$_3$–C$_4$	1.50 (3)	1.520 (16)
O$_1$–O$_2$	1.625 (23)	1.418 (11)
P$_1$–R$_1$C$_1$	1.78 (2)	1.82 (2)
P$_1$–R$_2$C$_1$	1.80 (2)	1.83 (1)
P$_2$–R$_3$C$_1$	1.80 (2)	1.83 (2)
P$_2$–R$_4$C$_1$	1.78 (3)	1.81 (3)
P$_3$–R$_5$C$_1$	1.79 (2)	1.82 (2)
P$_3$–R$_6$C$_1$	1.80 (2)	1.82 (2)
P$_4$–R$_7$C$_1$	1.81 (2)	1.82 (1)
P$_4$–R$_8$C$_1$	1.79 (2)	1.83 (2)

Table VII. Selected Intramolecular Bond Angles (Degrees)

Angle	Iridium	Rhodium
P$_1$–M–P$_2$	84.0 (2)	83.3 (1)
P$_1$–M–P$_3$	98.9 (2)	98.8 (1)
P$_1$–M–P$_4$	96.0 (3)	98.1 (1)
P$_2$–M–P$_3$	176.3 (2)	175.9 (1)
P$_2$–M–P$_4$	99.0 (2)	99.8 (1)
P$_3$–M–P$_4$	82.9 (2)	83.4 (1)
P$_1$–M–O$_1$	111.1 (5)	113.0 (3)
P$_2$–M–O$_1$	88.7 (5)	87.2 (3)
P$_3$–M–O$_1$	88.2 (5)	88.8 (3)
P$_4$–M–O$_1$	152.5 (5)	148.8 (3)
P$_1$–M–O$_2$	157.5 (6)	151.9 (3)
P$_2$–M–O$_2$	85.7 (5)	84.7 (3)
P$_3$–M–O$_2$	90.7 (5)	91.8 (3)
P$_4$–M–O$_2$	105.4 (6)	108.9 (3)
O$_1$–M–O$_2$	48.6 (7)	41.0 (3)
M–O$_1$–O$_2$	66.6 (8)	69.5 (5)
M–O$_2$–O$_1$	64.8 (8)	69.6 (5)
M–P$_1$–C$_1$	106.7 (8)	105.6 (4)
P$_1$–C$_1$–C$_2$	107 (2)	108.0 (9)
C$_1$–C$_2$–P$_2$	113 (2)	111.9 (9)
C$_2$–P$_2$–M	106.8 (9)	107.3 (4)
M–P$_3$–C$_3$	106.9 (8)	107.4 (4)
P$_3$–C$_3$–C$_4$	106 (2)	107.3 (9)
C$_3$–C$_4$–P$_4$	115 (2)	115.8 (9)
C$_4$–P$_4$–M	104.8 (7)	107.2 (4)
M–P$_1$–R$_1$C$_1$	124.0 (7)	123.9 (5)
M–P$_1$–R$_2$C$_1$	116.5 (6)	115.4 (5)
C$_1$–P$_1$–R$_1$C$_1$	104.9 (10)	106.1 (6)
C$_1$–P$_1$–R$_2$C$_1$	101.6 (9)	102.5 (6)
R$_1$C$_1$–P$_1$–R$_2$C$_1$	100.7 (8)	101.1 (6)
M–P$_2$–R$_3$C$_1$	115.9 (6)	113.7 (6)
M–P$_2$–R$_4$C$_1$	116.3 (9)	117.7 (7)
C$_2$–P$_2$–R$_3$C$_1$	106.4 (10)	105.7 (6)
C$_2$–P$_2$–R$_4$C$_1$	108.9 (12)	109.6 (9)
R$_3$C$_1$–P$_2$–R$_4$C$_1$	102.0 (10)	102.1 (7)
M–P$_3$–R$_5$C$_1$	114.8 (5)	113.9 (4)
M–P$_3$–R$_6$C$_1$	121.4 (6)	122.2 (6)
C$_3$–P$_3$–R$_5$C$_1$	107.0 (9)	105.6 (5)
C$_3$–P$_3$-R$_6$C$_1$	105.9 (9)	106.5 (5)
R$_5$C$_1$–P$_3$–R$_6$C$_1$	99.8 (7)	100.0 (4)
M–P$_4$–R$_7$C$_1$	125.1 (6)	122.3 (3)
M–P$_4$–R$_8$C$_1$	115.7 (8)	115.5 (5)
C$_4$–P$_4$–R$_7$C$_1$	105.5 (9)	104.6 (5)
C$_4$–P$_4$-R$_8$C$_1$	98.5 (11)	100.8 (6)
R$_7$C$_1$–P$_4$–R$_8$C$_1$	103.6 (10)	104.0 (5)

Table VIII. Comparative Details of Some Molecular Oxygen Complexes

Compound	O–O, Å	M–O, Å	Chemical properties
$Ir(O_2)Cl(CO)[P(C_6H_5)_3]_2$	1.30 (3)	2.09 (3) 2.04 (3)	Reversible
$Ir(O_2)I(CO)[P(C_6H_5)_3]_2$	1.509 (26)	2.035 (20) 2.082 (22)	Irreversible
[Rh(O$_2$)diphos$_2$][PF$_6$]	1.418 (11)	2.026 (8) 2.025 (9)	Reversible
[Ir(O$_2$)diphos$_2$][PF$_6$]	1.625 (23)	1.961 (18) 1.990 (16)	Irreversible

between the planes formed by Ir, P$_1$, and C$_1$ and Ir, P$_2$, and C$_2$ is 29 (1)°; that between the planes formed by Ir, P$_3$, and C$_3$ and Ir, P$_4$, and C$_4$ is 27 (1)°. The analogous values for the rhodium complex are 29.9 (5) and 28.4 (5)°. The mean of the P_n–C_n (n = 1, 2, 3, and 4) distances in the rhodium complex is 1.836 (8) Å; the equivalent value for the iridium compound is 1.838 (8) Å. The mean of the phosphorus–α-carbon atom distances in the rhodium compound is 1.822 (3) Å, in in the iridium compound, 1.793 (4) Å. A mean value of 1.82 (1) Å was observed for these bonds in the rhodium parent. For the second type of P–C bond, there is significantly more multiple bond character in the oxygenated iridium compound.

The group parameters are essentially the same, within experimental error, for both compounds. The absence of electron density in a total difference Fourier synthesis of each analysis in the regions of the phenyl rings is again evidence that the refinement of the phenyl rings as groups is a justifiable and desirable procedure.[25]

It is perhaps surprising that the values observed for the disorder parameter α agree well (α_{Ir} = 0.60 (2) and α_{Rh} = 0.70 (2)). This method of treating the PF_6^- anion disorder appears to represent a reasonable description of the arrangement of the anions in the lattice, although it certainly is not a unique description. It is encouraging that the values observed for the group temperature factors of F$_6$–A and F$_6$–B in both analyses are in fairly close agreement.

The root-mean-square components of thermal displacement along the principal axes are given in Table XI. The directions of these principal axes of vibration may be inferred from the figures. The bond distances were corrected for thermal motion, using both a riding model and assuming the atoms to move independently, but the corrected values did not affect the trends discussed above.

Discussion

For some time now, there has been considerable discussion concerning the nature of the bonding of unsaturated molecules to transition metals.

Table IX. Ir-P Bond Distances

Complex	Bond distances, Å		Ref
$Ir(O_2)Cl(CO)(P(C_6H_5)_3)_2$	2.38 (1)	2.36 (1)	2
$Ir(O_2)I(CO)(P(C_6H_5)_3)_2$	2.386 (8)	2.391 (8)	3
$Ir(Cl)(SO_2)(CO)(P(C_6H_5)_3)_2$	2.359 (9)	2.328 (8)	26
$[Ir(Cl)(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$	2.408 (3)	2.407 (3)	27
$[Ir(I)(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$	2.367 (10)	2.353 (11)	28
$[Ir(diphos)_2(CO)]Cl$	2.37 (2)	2.37 (2)	29
$[Ir(O_2)(diphos)_2][PF_6]$	2.283 (7) 2.336 (7)	2.349 (7) 2.452 (9)	This work

Table X. Equatorial Least-Squares Planes

	Iridium	Rhodium
	$14.215x + 5.321y + 6.198z = 6.208$	$13.989x + 5.641y + 6.668z = 6.219$
Atom	Distance, Å	Distance, Å
M	0.001 (1)	0.004 (1)
P_1	−0.023 (6)	−0.026 (4)
P_4	0.010 (6)	0.004 (4)
O_1	0.16 (2)	0.118 (8)
O_2	−0.22 (1)	−0.227 (9)

Table XI. Root-Mean-Square Components of Thermal Displacement (in Å) along Principal Axes

	Iridium			Rhodium		
M	0.202 (2)	0.246 (2)	0.307 (2)	0.200 (2)	0.218 (2)	0.227 (2)
P_1	0.22 (1)	0.26 (1)	0.32 (1)	0.214 (6)	0.218 (6)	0.244 (6)
P_2	0.19 (1)	0.28 (1)	0.33 (1)	0.211 (6)	0.225 (6)	0.258 (6)
P_3	0.20 (1)	0.28 (1)	0.30 (1)	0.220 (6)	0.230 (6)	0.243 (6)
P_4	0.22 (1)	0.24 (1)	0.40 (1)	0.204 (6)	0.220 (6)	0.230 (6)
O_1	0.18 (3)	0.35 (2)	0.38 (2)	0.20 (2)	0.24 (1)	0.29 (1)
O_2	0.20 (3)	0.28 (3)	0.44 (2)	0.23 (2)	0.24 (1)	0.26 (1)
C_1	0.19 (4)	0.24 (4)	0.30 (3)	0.19 (2)	0.24 (2)	0.25 (2)
C_2	0.22 (4)	0.24 (3)	0.39 (4)	0.23 (2)	0.25 (2)	0.27 (2)
C_3	0.26 (4)	0.28 (4)	0.30 (4)	0.16 (3)	0.25 (2)	0.27 (2)
C_4	0.23 (3)	0.26 (3)	0.34 (3)	0.20 (2)	0.20 (2)	0.27 (2)

Chatt[30] and Dewar[31] proposed a π-bonding scheme to explain the coordination of the ethylene molecule to platinum in Zeise's salt. A σ bond is formed by donation from a filled π-bonding orbital on the ligand to an unfilled metal d or hybrid orbital. Back-donation then occurs, to offset the resultant dipole, from a filled metal orbital to a π^*-antibonding orbital on the ligand molecule.

For the oxygen molecule (O–O bond length 1.21 Å), an early scheme was proposed in which electron transfer occurred to the ligand, which then assumed the character of the superoxide ion, O_2^-, O–O bond length 1.28 Å, or the peroxide ion, O_2^{2-}, O–O bond length 1.49 Å, depending upon whether one or two electrons were transferred. This type of bonding scheme seems particularly applicable to the ammine complexes of Co(III), but the diamagnetism of the compound $IrCl(CO)(O_2)[P(C_6H_5)_3]_2$, in which the O–O bond length of 1.30 Å approximates that of the superoxide ion, suggests that there is no formal transfer of an electron to the oxygen molecule. And, of course, the geometry of bonding of the ammine complexes, where the metal–oxygen bond is a σ bond, compared with the π-bonded attachment of the oxygen molecule in these d^8 systems, suggests that here an entirely different approach is needed.

We will discuss the possible addition of oxygen to these d^8 systems on the basis of the π-bonding scheme of Chatt and Dewar. For the oxygen molecule to form a π bond with the metal complex, hereafter referred to as the substrate, several conditions must be fulfilled. Firstly, there must be available on the substrate an empty orbital of the correct energy and symmetry to overlap with the oxygen π-bonding orbitals to form a σ bond. Similarly, an essentially nonbonding, filled d orbital (or hybrid orbital) must exist on the substrate through which electron density can be back-donated to the oxygen ligand into the π-antibonding orbitals. The degree of back-bonding which occurs will depend upon the relative energies and the amount of overlap between the orbitals.

Of the four complexes in the present series, those with the diphos ligands will be considered first. We believe that, especially for the iridium complex, there is extensive back-donation to the ligand. This is manifested both in the long O–O bond (1.625 Å) and in the strong, short metal–O bonds (mean, 1.976 Å). That there is considerable electron movement throughout the molecule to the oxygen ligand is evident from the short $P–C_1$ distances in the phenyl rings (mean, 1.793 Å). Thus we conclude that here the orbital energies are exceptionally favorable for overlap, and that extensive back-donation occurs which effectively reduces the bond order of the oxygen molecule to less than 1.0. In the rhodium complex, the overlap between the ligand and the substrate orbitals is presumably less, owing to the higher energies of the rhodium d orbitals compared with those of iridium. As a result, back-donation still occurs, but to a degree insufficient to distort the $P–C_1$ distances in the phenyl rings (mean, 1.822 Å), the same distance observed in the rhodium parent complex $[Rh(diphos)_2][ClO_4]$.[22] That some electron density has been transferred to the oxygen molecule is evident from the increase in the O–O bond length to 1.418 Å. Owing to the lower degree of orbital overlap, the Rh–O distances (mean, 2.025 Å) are significantly longer than the Ir–O distances (mean, 1.976 Å), in spite of the decrease in ionic radius expected for the change from Ir to Rh. The changes in the geometry of the M–O–O entity and in uptake properties can only be ascribed to the variation in the energies of the d orbitals, since in both compounds the ligand field around the metal is the same.

The two complexes formed by the system $Ir(O_2)X(CO)[P(C_6H_5)_3]_2$ (X = Cl or I) might therefore be

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(30) J. Chatt, *J. Chem. Soc.*, 2939 (1953).

(31) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C71 (1951).

expected to show changes in uptake properties and molecular geometry analogous to those observed in the diphos complexes. Here the energy of the substrate orbitals is varied by the change in the halide substituent, X. With the more electronegative chlorine atom the overlap between the orbitals is such that back-donation to the oxygen molecule only occurs to the extent that the O–O bond is lengthened to 1.30 Å. With the less electronegative substituent, iodine, more back-donation occurs to give an O–O bond length of 1.51 Å. From the chemical properties of the systems we might expect the M–O distances to be shorter for X = I than for X = Cl. However, within the standard deviations assigned to the M–O distances in these compounds, no significant difference is detected (Table VIII).

In a recent discussion[32] of the bonding of molecular oxygen to transition metals, the coordinated molecule was likened to the excited states of oxygen gas.[33] Indeed, there is considerable resemblance between the excited oxygen species observed spectrally and the coordinated molecule with the filled antibonding molecular orbitals. However, we feel that the range of O–O bond distances found in this series is too great to allow a facile allocation of a different excited state to the oxygen molecule in each of the four complexes.

The electronic factors affecting reversible oxygen uptake in these systems now appear to be well understood. Increased electron density at the metal, either by substitution of better donating ligands (P > I > Cl) or by change of metal (Ir > Rh > Co), will assure increasing uptake properties. It is impossible to predict precisely whether or not a substrate will have molecular orbitals of energy and symmetry suitable for overlap with the oxygen molecular orbitals to form a π bond between the oxygen and the substrate. However, the present range of complexes could be extended. Thus, if a molecular oxygen complex of cobalt were desired, then the system to try would be one in which the energies of the substrate orbitals, which are of course higher than those of the comparable rhodium orbitals, are decreased by using a stronger base as a ligand (*e.g.*, bis(dimethyl-) or bis(diethylphosphino)ethane). It is possible, however, that the higher energies of the cobalt orbitals would favor the formation of a σ bond. Similarly, in the $MX(CO)(P(C_6H_5)_3)_2$ systems, we would expect the X = Br compound to show an O–O bond length intermediate between the Cl and the I complexes, with similar intermediate uptake properties. If Rh were to be substituted for Ir, then the scheme discussed above leads us to predict that the uptake properties of the complex where X = Cl would be much poorer than those where X = I, and owing to the increase in the energies of the substrate orbitals upon the substitution of Rh for Ir, the uptake properties of the rhodium systems would be poorer than the iridium systems. And, indeed, this trend is observed. We were unable to prepare solid samples of the oxygen complex of $RhI(CO)[P(C_6H_5)_3]_2$, though an interaction may occur in solution.[34] We have observed no interaction between O_2 and $RhCl(CO)[P(C_6H_5)_3]_2$.

One lesson may be drawn from these structural studies. Similarity in unit cell dimensions is too often taken to imply similar correspondence in structural parameters. However, in the present instance the two structures with closely similar cell dimensions have widely differing structural parameters (the O–O bond lengths) and different chemical properties (the reversibility of oxygen addition).

Acknowledgment. We are grateful to the National Institutes of Health for their support of this work.

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[32] R. Mason, *Nature*, 217, 543 (1968).

[33] The similarity of a simple molecule bound to a metal to the molecule in an excited state appears to have been pointed out first by L. E. Orgel, "An Introduction to Transition Metal Chemistry: Ligand Field Theory," Methuen and Co., Ltd., London, 1960, p 137.

[34] L. Vaska, private communication.

The Crystal Structure of Bis(isoquinoline-1-carboxaldehyde thiosemicarbazanato)nickel(II) Monohydrate

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Abstract: The crystal structure of bis(isoquinoline-1-carboxaldehyde thiosemicarbazanato)nickel(II) monohydrate was determined. The ligand is a potent tumor inhibitor that was believed to function because of its metal-chelating ability. The formation of the nickel complex involving the tridentate ligand is compatible with the chelation hypothesis. The compound crystallizes in the monoclinic space group C2/c with $a = 17.884$, $b = 17.567$, $c = 15.901$ Å, $\beta = 101.57°$, and eight molecules per cell. The final R for 2464 observed reflections is 0.060. The distorted octahedral molecules are held together by a hydrogen-bond system involving N—H···N, N—H···O, and O—H···S hydrogen bonds. The presence of the rare O—H···S hydrogen bond is an unusual feature of the structure.

A large number of α-(N) heterocyclic thiosemicarbazones with definite carcinostatic activity were reported by French and Blanz.[1] Their hypothesis was that a thiosemicarbazone which could function as a tridentate chelate capable of forming octahedral com-

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