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Synthesis, characterization and the unpleasantly disordered crystal structure of $Ir(OMe)(CO)(PPh_3)_2(SO_4)$

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Abstract

The adducts of O_2 and SO_2 with *trans*-$MeOIr(CO)(PPh_3)_2$ are formed in equilibria and have been characterized. Reaction of the SO_2 adduct, $Ir(OMe)(SO_2)(CO)(PPh_3)_2$ with dioxygen leads to the sulfato complex, $Ir(OMe)(CO)(PPh_3)_2(SO_4)$, the structure of which has been determined. $Ir(OMe)(CO)(PPh_3)_2(SO_4)$ crystallizes in the monoclinic system with a 11.958(2), b 14.163(3), c 12.231(2) Å, β 118.365(12)°, V 1822.7(6) Å^3 and $Z = 2$. Diffraction data for $2\theta = 4.5$–$45.0°$ (Mo-K_α) were collected with a Syntex $P2_1$ diffractometer and the structure was solved (assuming space group $P2_1/m$ and an unpleasant 2-fold disordered model) and refined to $R = 4.8\%$ for all 2512 independent data ($R = 3.5\%$ for those 2042 data with $|F_0| > 6\sigma(|F_0|)$). The iridium(III) atom has a distorted octahedral coordination sphere with *trans* PPh_3 ligands and a *cis*-chelating bidentate O,O'-SO_4 group; the structure is completed by mutually *cis* OMe and CO ligands.

Introduction

We have examined a number of reactions of the sixteen electron iridium complexes, *trans*-$RIr(CO)L_2$ (R = alkyl or alkoxy, L = a phosphine) [1–12]. In many cases the presence of the R group gives rise to chemistry different to that of the halide analogues [7–12]. Thus we were quite interested in the lack of reactivity of $Ir(SO_2)(CO)(PPh_3)_2Cl$ toward O_2, since reaction of the dioxygen complex, $Ir(O_2)(CO)(PPh_3)_2Cl$, with SO_2 leads to formation of the sulfato complex, $Ir(SO_4)(CO)(PPh_3)_2Cl$ [13]. In this manuscript we report the reaction of *trans*-$MeOIr(CO)(PPh_3)_2$ with SO_2 and with O_2, the formation of the sulfato complex by reaction of O_2 with the SO_2 adduct and the crystal structure of the sulfato complex, $Ir(OMe)(CO)(PPh_3)_2(SO_4)$.

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Experimental

Iridium trichloride, $IrCl_3 \cdot xH_2O$, was loaned by Johnson Matthey Inc. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Beckman 4240; ^1H NMR and ^{31}P NMR spectra were recorded on a Varian EM390 or on a JEOL FX90Q.

Reaction of O_2 with trans-$MeOIr(CO)(PPh_3)_2$ at low temperature

0.20 g *trans*-$MeOIr(CO)(PPh_3)_2$ [8] in 30 ml toluene were placed in a Schlenk flask and brought out of the dry box. The flask was placed in a 0 °C bath and oxygen gas was bubbled through the solution. The reaction was monitored by IR and allowed to continue until the CO stretch of *trans*-$MeOIr(CO)(PPh_3)_2$ had disappeared. The IR in toluene of the pale yellow solution showed ν(CO) 1993vs, ν(OO) 850s,br cm^{-1}.

Attempts to isolate the solid by precipitation/filtration or solvent removal lead to the starting material which eventually decomposes under O_2 at room temperature.

Reaction of SO_2 with trans-$MeOIr(CO)(PPh_3)_2$

0.25 g *trans*-$MeOIr(CO)(PPh_3)_2$ in 40 ml toluene were placed in a Schlenk flask and brought out of the dry box. The solution was placed under an atmosphere of SO_2 and allowed to stir for 2 h. The yellow solution turned green and an IR of the solution showed a CO stretch at 2020 cm^{-1}. Presumably $Ir(SO_2)(OMe)(CO)(PPh_3)_2$ had been formed. Attempts to isolate the adduct by precipitation/filtration or solvent removal, lead to generation of starting material (loss of SO_2).

Reaction of O_2 with $Ir(SO_2)(OMe)(CO)(PPh_3)_2$. Preparation of $Ir(OMe)(CO)(SO_4)$-$(PPh_3)_2$

A solution of the SO_2 adduct under SO_2 was placed under an atmosphere of O_2. The solution was allowed to stir under O_2 for 14 h, after which the green solution had turned yellow. The solvent was removed to yield a yellow air-stable solid. IR in KBr showed ν(CO) 2040, $\nu(SO_4)$ 1290s, 1170vs, 890s, 878s cm^{-1}. ^1H NMR in benzene-d_6 showed 3.04(s), ~ 7 ppm (m); ^{31}P NMR in benzene d_6 showed + 0.471 ppm (s), (^1H decoupled). Microanal. Found: C, 50.95; H, 3.78. $C_{38}H_{33}IrO_6P_2S$ calc: C, 52.35; H, 3.81%. Crystals suitable for crystallographic analysis were grown by slow diffusion of pentane into a saturated solution of the solid in methanol.

Collection of the X-ray diffraction data for $Ir(OMe)(CO)(PPh_3)_2(SO_4)$

A pale yellow crystal of approximate orthogonal dimensions 0.27 × 0.30 × 0.40 mm^3 was inserted (in air) into a 0.3 mm-diameter thin-walled glass capillary, which was mounted on a eucentric goniometer and accurately centered on a Syntex $P2_1$, automated four-circle diffractometer. All subsequent set-up operations (i.e., determination of Laue group, accurate cell dimensions and crystal orientation matrix) were performed as described previously [14]. Details appear in Table 1. The final unit cell parameters were based upon a least-squares analysis of the setting angles (2θ, ω, χ) of the unresolved Mo-$K_{\bar{\alpha}}$ components of 25 reflections, well dispersed in reciprocal space, with 2θ = 20.9–26.4°.

Table 1

Experimental data for the X-ray diffraction study of $Ir(OMe)(CO)(PPh_3)_2(SO_4)$

A. Crystal parameters at 24 °C (297 K)

Crystal system: monoclinic
Space group: $P2_1/m(C_{2h}$; No. 11) [a]
a 11.958(2) Å
b 14.163(3) Å
c 12.231(2) Å
β 118.365(12)°

V 1822.7(6) $Å^3$
$Z = 2$
formula: $C_{38}H_{33}IrO_6P_2S$
Mol. wt 871.9
D_{calc} 1.59 g/cm^3

B. Measurement of intensity data

Diffractometer: Syntex $P2_1$
Radiation: Mo-$K_{\bar{\alpha}}$ (λ 0.710730 Å)
Monochromator: pyrolytic graphite ($2\theta_m = 12.2°$), equatorial mode; assumed 50% perfect/50% ideally mosaic for polarization correction.
Reflections measd: $+h$, $\pm k$, $\pm l$ for $2\theta = 4.5–45.0°$; 5228 data merged to 2512 unique data in point group C_{2h} ($R(I) = 1.69\%$, $R(wI) = 2.00\%$ for 2289 pairs of averaged data)
Scan type: coupled θ(crystal)–2θ(counter)
Scan range: $[2\theta(K_{\alpha_1}) - 0.9]–[2\theta(K_{\alpha_2}) + 0.9]°$
Scan speed: 4.0 °/min in 2θ
Background: stationary crystal and counter at each end of 2θ scan, each for 1/4 of total scan time
Standard reflections: 3 approximately mutually orthogonal reflections collected before every 97 data points; no decay observed.
Absorption coefficient: μ 40.7 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between 5 close-to-axial ψ scans

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[a] The final (disordered) structure has the full symmetry of space group $P2_1/m$. It is possible and probable that the crystal belongs to space group $P2_1$ with twinning along [010], see text.

The only systematic absences were $0k0$ for $k = 2n + 1$. In the monoclinic system, the possible space groups are the non-centrosymmetric $P2_1$ (C_2^2; No. 4) or the centrosymmetric $P2_1/m$ (C_{2h}^2; No. 11). Unit cell parameters are consistent with $Z = 2$ so that in the absence of disorder the crystallographic asymmetric unit is one formula unit in $P2_1$ or one-half of a formula unit (with crystallographic C_s or C_i symmetry imposed upon the molecule) in $P2_1/m$. The distinction between these is not trivial (vide infra).

Owing to the likelihood that the true space group was $P2_1$, we collected two forms of data ($+h$, $+k$, $\pm l$ and $+h$, $-k$, $\pm l$) in order to test the chirality of the crystal by possible differences caused by anomalous dispersion. All data were corrected empirically for the effects of absorption (by interpolation both in 2θ and ϕ between a set of normalized ψ-scans of 5 close-to-axial reflections). Following application of Lorentz and polarization factors, data were placed on an absolute scale by means of a Wilson plot. No datum was rejected; any reflection with $I(\text{net}) < 0$ was assigned the value $|F_0| = 0$.

Solution and refinement of the crystal structure of $Ir(OMe)(CO)(PPh_3)_2(SO_4)$

All calculations were performed by use of the SUNYAB-modified version of the Syntex XTL interactive crystallographic program package [15]. Scattering factors for neutral atoms were used in their analytical form [16] and were corrected for both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion [17]. The function minimized during the least-squares refinement process was $\Sigma w(|F_o| - |F_c|)^2$, where $1/w = [\sigma(|F_o|)]^2 + [0.015|F_o|]^2$.

Table 2

Intensity statistics for the diffraction data on $Ir(OMe)(CO)(PPh_3)_2(SO_4)$ [a]

Function	Observed	Theoretical	
		Acentric	Centric
$\langle \vert E \vert \rangle$	0.854	0.886*	0.798
$\langle \vert E \vert^2 \rangle$	1.000	1.000*	1.000*
$\langle \vert E \vert^2 - 1 \rangle$	0.807	0.736*	0.968
% $\vert E \vert > 1.0$	37.74	36.79*	31.73
% $\vert E \vert > 1.2$	25.76	23.69*	23.01
% $\vert E \vert > 1.4$	16.16	14.09	16.15*
% $\vert E \vert > 1.6$	9.12	7.73*	10.96
% $\vert E \vert > 1.8$	4.46	3.92*	7.19
% $\vert E \vert > 2.0$	2.23	1.89*	4.55
% $\vert E \vert > 2.5$	0.00	0.19*	1.24
% $\vert E \vert > 3.0$	0.00	0.01*	0.27

[a] Those indicators agreeing best with the observed data are indicated with an asterisk (*). The theoretical acentric statistics show a closer fit than do the centric statistics.

Intensity statistics (see Table 2) were more in keeping with an acentric structure, so the structural solution was begun by assuming that the crystal belonged to the non-centrosymmetric space group $P2_1$. The phase-problem was solved by means of a Patterson synthesis which provided the x- and z-coordinates of the iridium atom; the y-coordinate was assigned the value 1/4. All remaining non-hydrogen atoms were located from a series of difference-Fourier syntheses. The carbonyl and methoxy ligands were found to be disordered; refinement of their occupancies indicated a 50%/50% disorder. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for the $IrP_2(SO_4)$ fragment, isotropic for all other atoms) with hydrogen atoms in calculated positions (d(C–H) 0.95 Å [18]) led to convergence with:

$$R_F \ (= 100\Sigma \| F_o | - | F_c \| / \Sigma | F_o |) = 7.0\%$$

$$R_{wF} \left(= 100\left[\Sigma w (| F_o | - | F_c |)^2 / \Sigma w | F_o |^2 \right]^{1/2} \right) = 6.6\%$$

$$GOF \left(= \left[\Sigma w (| F_o | - | F_c |)^2 / (NO - NV) \right]^{1/2} \right) = 2.375$$

The residuals are based upon all 4791 unique data corresponding to the point group C_s; NO = number of observations and NV = number of variables.

Since $P2_1$ is a polar space group, coordinates were inverted and the structure refined to convergence once again; the residuals were essentially unchanged, with $R_F = 7.0\%$, $R_{wF} = 6.6\%$ and $GOF = 2.374$. (This result is most unexpected, since $\Delta f'(\mathrm{Ir}) = -2.066$ e$^-$ and, especially, $\Delta f''(\mathrm{Ir}) = -7.990$ e$^-$ [17].)

The individual atomic parameters and interatomic distances (whose values had been carefully followed, with considerable dismay, during the refinement process) were now inspected closely. A number of anomalies were found, among the most notable of which were the following.

(a) Several atoms were associated with large thermal parameters (up to $B = 12.1$ Å^2 for C(65)).

(b) Many atoms were close to a pseudo-mirror plane at $y = 1/4$; others appeared to be interrelated by this mirror plane.

(c) Many equivalent bond distances showed widely varying values (e.g. C–C(phenyl) = 1.1–1.7 Å, P(1)–C(*ipso*) = 1.65–1.97 Å) whereas some were normal (e.g., P(2)–C(*ipso*) = 1.795–1.841 Å).

(d) These anomalies were common to both the original and the inverted coordinate sets, so are not a function of anomalous dispersion.

These types of anomalies are characteristic of a centric system which has erroneously been treated as acentric. We therefore transferred our attention to the centrosymmetric space group $P2_1/m$. Data with $\pm k$ were averaged ($R(I) = 1.69\%$ and $R_w(I) = 2.00\%$ for 2289 pairs of data) and the obvious centrosymmetric model (with the molecule bisected by a mirror plane at $y = 1/4$) was tried. This failed to refine satisfactorily. Certain atoms of the molecule did lie on the mirror plane at $y = 1/4$ (i.e., Ir, P(1), S, and O(4)) but certain others that should lie on the mirror plane in an ordered model did not (esp. P(2) and O(3)). The structure could not be solved as an ordered model with C_s symmetry in space group $P2_1/m$.

After a great deal of contemplation, we elected to try a third model. This was based upon that obtained from space group $P2_1$ with all atoms input independently into space group $P2_1/m$. A few atoms were input strictly at $y = 1/4$ (i.e., Ir, P(1), S, O(4)) owing their very close proximity to this now-special coordinate; two other atoms, C(11) and C(15), were not refined owing their proximity to $y = 1/4$ and the values obtained from refinement in space group $P2_1$ were retained. All atoms were assigned an occupancy of 1/2. Refinement converged smoothly to the much reduced residuals $R_F = 4.9\%$, $R_{wF} = 4.6\%$ and $GOF = 1.698$. A very minor correction was now made for the effects of secondary extinction. Here $g = 6.94 \times 10^{-9}$, where:

$$|F_{o,cor}| = |F_{o,uncor}|(1.0 + gI_o)$$

Final convergence was reached with $R_F = 4.8\%$, $R_{wF} = 4.6\%$ and $GOF = 1.688$ for all 2512 point-group (C_{2h}) independent data; the residuals for those 2042 data with $|F_0| > 6\sigma(|F_0|)$ were $R_F = 3.5\%$, $R_{wf} = 4.3\%$ and $GOF = 1.781$.

An inspection of atomic thermal parameters and interatomic distances revealed that the previous anomalies were either no longer present or were markedly reduced. Thus, the maximum thermal parameter was now $B = 8.24$ Å^2 for C(65), C–C distances now were internally consistent (C(64)–C(65) = 1.284(35) Å, but all 35 others lie in the range 1.342(28)–1.436(15) Å, and P(1)–C(*ipso*) distances now have the reduced range of 1.749(13)–1.931(15) Å, vis à vis P(2)–C(*ipso*) = 1.767(21)–1.830(15) Å.

Final positional and thermal parameters are collected in Table 3.

Discussion

Adduct formation

Trans-MeOIr(CO)(PPh$_3$)$_2$ reacts with O_2 at low temperature (0 °C) to form the adduct, MeOIr(O$_2$)(CO)(PPh$_3$)$_2$. This adduct has infrared absorptions (ν(CO) 1993 and ν(OO) 850 cm^{-1} in solution) fully consistent with a dioxygen adduct [19]. All attempts to isolate this complex led to loss of O_2, reforming *trans*-

Table 3

Final positional parameters, isotropic and anisotropic thermal parameters for $Ir(OMe)(CO)(PPh_3)_2(SO_4)$

Atom	x	y	z	B (Å^2)
Ir	0.17718(4)	0.25000	0.19293(4)	
P(1)	0.19342(22)	0.25000	0.39628(22)	
P(2)	0.14556(31)	0.28129(22)	−0.01723(31)	
S	0.43251(22)	0.25000	0.28584(24)	
O(1)	0.33887(46)	0.16844(34)	0.25277(50)	
O(2)	0.33887(46)	0.33156(34)	0.25277(50)	
O(3)	0.51890(76)	0.28105(62)	0.41450(81)	
O(4)	0.49088(65)	0.25000	0.20624(71)	
C(2A)	0.1351(15)	0.0328(13)	0.1840(15)	5.22(36)
O(2A)	0.07316(83)	0.11737(67)	0.17540(84)	3.51(18)
C(2B)	0.0359(13)	0.3058(10)	0.1294(13)	3.31(27)
O(2B)	−0.0497(11)	0.14265(85)	0.0897(11)	5.80(26)
C(11)	0.04131	0.25935	0.39109	2.62
C(12)	0.0372(12)	0.3166(10)	0.4860(13)	3.63(28)
C(13)	−0.0806(13)	0.3321(11)	0.4844(14)	4.03(30)
C(14)	−0.1868(13)	0.29199(98)	0.3918(13)	4.09(32)
C(15)	−0.18876	0.23733	0.29958	3.16
C(16)	−0.0706(10)	0.22466(82)	0.2998(10)	2.84(27)
C(21)	0.2466(13)	0.1270(11)	0.4712(12)	2.74(26)
C(22)	0.1598(13)	0.0611(11)	0.4709(13)	3.80(29)
C(23)	0.2025(14)	−0.0274(12)	0.5261(14)	4.59(33)
C(24)	0.3298(15)	−0.0463(12)	0.5830(15)	4.90(34)
C(25)	0.4155(16)	0.0168(12)	0.5821(18)	3.43(31)
C(26)	0.3742(13)	0.1049(10)	0.5267(13)	3.21(26)
C(31)	0.2948(12)	0.33345(94)	0.5026(12)	2.24(23)
C(32)	0.2956(15)	0.4217(11)	0.4543(14)	3.98(31)
C(33)	0.3627(20)	0.4975(14)	0.5300(19)	5.35(45)
C(34)	0.4299(17)	0.4793(13)	0.6561(19)	5.54(40)
C(35)	0.4296(15)	0.3923(12)	0.7074(15)	4.87(34)
C(36)	0.3622(13)	0.3165(10)	0.6284(13)	3.74(28)
C(41)	0.2005(13)	0.1804(12)	−0.0666(13)	3.19(28)
C(42)	0.1896(16)	0.0897(13)	−0.0317(16)	4.33(39)
C(43)	0.2187(15)	0.0096(12)	−0.0760(15)	4.63(33)
C(44)	0.2694(19)	0.0151(14)	−0.1604(18)	4.77(36)
C(45)	0.2840(17)	0.1057(14)	−0.1935(17)	6.07(41)
C(46)	0.2521(16)	0.1873(12)	−0.1495(16)	5.36(37)
C(51)	−0.0247(12)	0.28479(81)	−0.1265(12)	3.09(28)
C(52)	−0.0817(12)	0.22417(94)	−0.2278(12)	3.76(32)
C(53)	−0.2118(12)	0.2328(16)	−0.3092(12)	4.79(38)
C(54)	−0.2781(16)	0.3025(13)	−0.2921(16)	5.24(36)
C(55)	−0.2254(18)	0.3644(14)	−0.1959(17)	6.06(41)
C(56)	−0.0984(16)	0.3553(13)	−0.1129(17)	5.55(38)
C(61)	0.2097(15)	0.3797(14)	−0.0571(16)	3.48(34)
C(62)	0.1397(16)	0.4306(13)	−0.1710(17)	5.65(39)
C(63)	0.1913(19)	0.5047(15)	−0.2037(18)	6.20(44)
C(64)	0.3160(22)	0.5338(18)	−0.1186(23)	7.46(53)
C(65)	0.3828(22)	0.4919(17)	−0.0143(22)	8.33(55)
C(66)	0.3322(18)	0.4164(14)	0.0199(18)	6.43(43)

$MeOIr(CO)(PPh_3)_2$, or to decomposition. As is the case for *trans*-$Ir(CO)(PPh_3)_2Cl$, the O_2 adduct is formed in an equilibrium.

trans-$MeOIr(CO)(PPh_3)_2 + O_2 \rightleftharpoons MeOIr(O_2)(CO)(PPh_3)_2$

Table 3 (continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	1.81(2)	6.70(3)	2.06(2)	0.00	0.83(1)	0.00
P(1)	2.27(10)	3.96(14)	2.36(11)	0.00	1.21(9)	0.00
P(2)	2.72(14)	3.47(26)	2.29(13)	0.38(11)	1.13(12)	0.09(11)
S	2.00(11)	7.46(19)	2.86(12)	0.00	0.89(9)	0.00
O(1)	5.10(26)	3.23(25)	6.67(30)	1.19(21)	4.29(24)	0.82(22)
O(3)	2.79(37)	5.48(93)	3.23(40)	−0.98(35)	0.50(32)	−0.61(36)
O(4)	3.45(34)	8.26(53)	5.17(41)	0.00	3.00(33)	0.00

The relative stability of the dioxygen complexes $Ir(O_2)(CO)(PPh_3)_2X$ [4,20,21] are in the order $X = OMe < Cl < I < Me$. This order clearly depends on the donor ability of the X group. For $X = OMe$ and Cl (in which the O_2 is lost in the absence of an O_2 atmosphere) the O–O stretching frequency is ~ 850 cm^{-1} [19], while for $X = Me$ (in which the O_2 cannot readily be removed) the O–O stretching frequency is lower at 827 cm^{-1} [4].

An adduct is also obtained when *trans*-$MeOIr(CO)(PPh_3)_2$ is treated with SO_2. The SO_2 is not tightly bound and is readily lost during attempts to isolate the adduct. This is in contrast to the behavior of the SO_2 adduct of *trans*-$Ir(CO)(PPh_3)_2Cl$, which is stable [13]. With the alkoxide there is also the possibility of insertion of SO_2 into the Ir–OMe bond as has previously been demonstrated for a platinum alkoxide [22]. However, we see no evidence of such an insertion in the present case.

Reaction of the SO_2 adduct with O_2

Bubbling O_2 through a solution of the SO_2 adduct produces the sulfato complex, $Ir(OMe)(CO)(PPh_3)_2(SO_4)$ [13]. This complex is stable and has been fully characterized by infrared spectroscopy, NMR spectra (^1H and ^{31}P) and microanalysis. The infrared absorptions for the sulfate are consistent with a bidentate bonding mode [23,24]. Because this complex contains an unusual mix of hard ligands (OMe^-, SO_4^{2-} as a bidentate ligand) and soft ligands (CO and 2 PPh_3) we have determined its crystal structure.

The crystal structure and space group

As outlined in the experimental section, the best model (i.e., lowest values for R_F, R_{wF} and GOF) is obtained with a (totally) two-fold disordered structure in space group $P2_1/m$. To our minds there are two possible explanations.

(1) The true space group is $P2_1/m$ and the site can be occupied by molecules in either of two orientations.

(2) The true space group is $P2_1$ and the structure has an artificial disorder imposed upon it by twinning (in a 50%–50% manner) along [010].

It is difficult to distinguish between these two, but the intensity statistics lead us marginally to prefer the latter explanation. In either case we believe that our approach to the solution of this problem will be of significant interest to others.

The molecular structure

Numbering of atoms in the isolated ordered molecule is shown in Fig. 1. A stereoscopic view appears as Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5. Despite a severe disorder/twinning problem, the molecular geome-

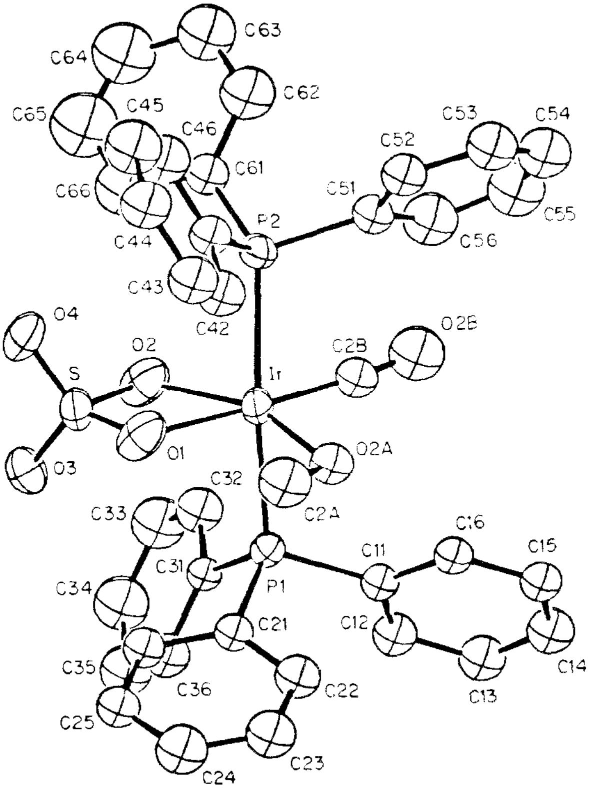


Fig. 1. Labelling of atoms in the deconvoluted molecular structure of disordered Ir(OMe)(CO)-$(PPh_3)_2(SO_4)$.

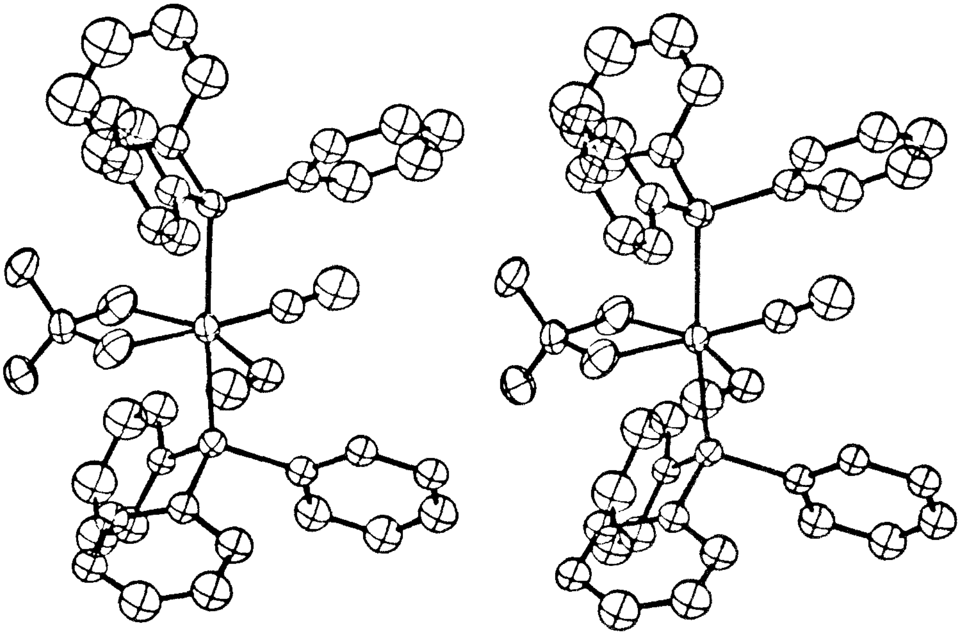


Fig. 2. Stereoscopic view of the molecular unit of Ir(OMe)(CO)$(PPh_3)_2(SO_4)$.

Table 4

Interatomic distances (Å) for Ir(OMe)(CO)$(PPh_3)_2(SO_4)$

A. Iridium – ligand bond lengths			
Ir–P(1)	2.401(3)	Ir–O(2A)	2.206(10)
Ir–P(2)	2.454(3)	Ir–C(2B)	1.684(16)
Ir–O(1)	2.065(6)	Ir · · · S	2.705(3)
Ir–O(2)	2.065(6)		
B. Phosphorus – carbon bond lengths			
P(1)–C(11)	1.795(13)	P(2)–C(41)	1.792(17)
P(1)–C(21)	1.931(15)	P(2)–C(51)	1.830(15)
P(1)–C(31)	1.749(13)	P(2)–C(61)	1.767(21)
C. Sulfur – oxygen bond lengths			
S–O(1)	1.524(6)	S–O(3)	1.481(9)
S–O(2)	1.524(6)	S–O(4)	1.443(9)
D. Carbon – oxygen bond lengths			
O(2A)–C(2A)	1.385(21)	C(2B)–O(2B)	1.159(20)
E. Carbon – carbon bond lengths			
C(11)–C(12)	1.436(15)	C(41)–C(42)	1.379(25)
C(12)–C(13)	1.417(24)	C(42)–C(43)	1.372(26)
C(13)–C(14)	1.360(22)	C(43)–C(44)	1.426(29)
C(14)–C(15)	1.359(15)	C(44)–C(45)	1.383(28)
C(15)–C(16)	1.423(13)	C(45)–C(46)	1.402(27)
C(16)–C(11)	1.363(12)	C(46)–C(41)	1.419(25)
C(21)–C(22)	1.395(23)	C(51)–C(52)	1.392(18)
C(22)–C(23)	1.379(23)	C(52)–C(53)	1.397(21)
C(23)–C(24)	1.367(27)	C(53)–C(54)	1.342(28)
C(24)–C(25)	1.363(27)	C(54)–C(55)	1.359(26)
C(25)–C(26)	1.394(22)	C(55)–C(56)	1.374(30)
C(26)–C(21)	1.379(23)	C(56)–C(51)	1.393(24)
C(31)–C(32)	1.384(21)	C(61)–C(62)	1.433(26)
C(32)–C(33)	1.396(26)	C(62)–C(63)	1.369(30)
C(33)–C(34)	1.382(29)	C(63)–C(64)	1.415(35)
C(34)–C(35)	1.384(26)	C(64)–C(65)	1.284(35)
C(35)–C(36)	1.414(23)	C(65)–C(66)	1.387(34)
C(36)–C(31)	1.377(19)	C(66)–C(61)	1.412(29)

try is unequivocally established although certain interatomic distances may be of marginal reliability.

The possible isomers of an octahedral iridium(III) complex of formula Ir(OMe)(CO)$(PPh_3)_2(SO_4)$ and containing a bidentate sulfate ligand are shown in Fig. 3; there are four distinct diastereoisomers, two of which are of C_s symmetry (**1** and **2**) and two of which have only C_1 symmetry and give rise to enantiomeric pairs (viz., **3a** and **3b**; **4a** and **4b**). The molecule under investigation corresponds to structure **1** (C_s idealized symmetry) in which the bulky PPh_3 ligands are in mutually *trans* positions.

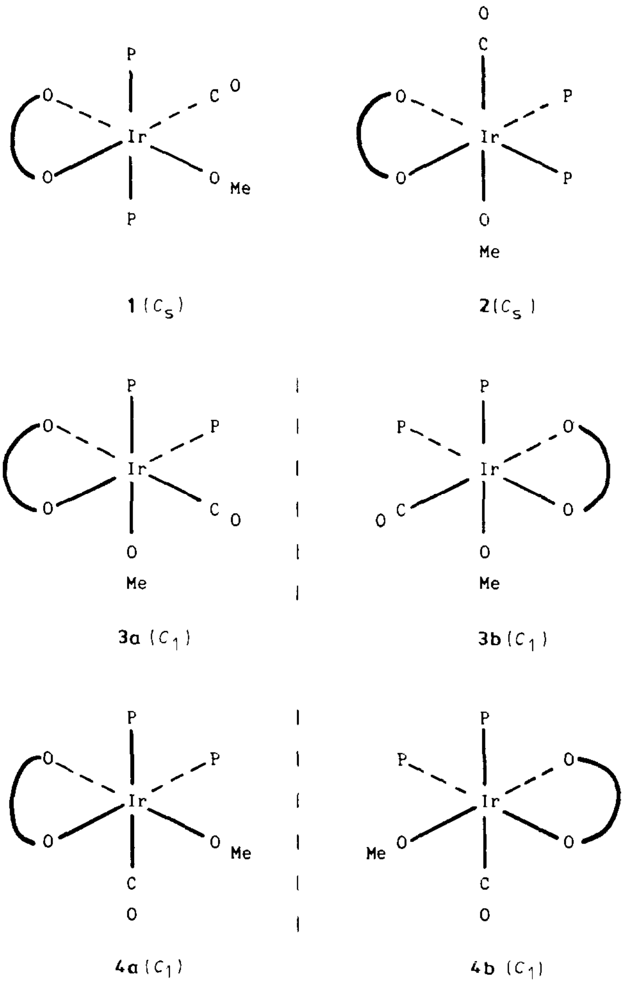
The two independent Ir–PPh_3 distances are Ir–P(1) 2.401(3) and Ir–P(2) 2.454(3) Å; the angle P(1)–Ir–P(2) is significantly distorted from linearity, with a value of 168.92(10)°. It is, perhaps, this distortion that prevents the molecule from acquiring

Table 5

Interatomic angles (°) for Ir(OMe)(CO)(PPh$_3$)$_2$(SO$_4$)

A. Angles about the iridium atom			
P(1)–Ir–P(2)	168.92(10)	P(2)–Ir–C(2B)	88.86(52)
P(1)–Ir–O(1)	91.81(16)	O(1)–Ir–O(2)	68.03(22)
P(1)–Ir–O(2)	91.81(16)	O(1)–Ir–O(2A)	154.21(30)
P(1)–Ir–O(2A)	82.25(26)	O(1)–Ir–C(2B)	117.79(53)
P(1)–Ir–C(2B)	92.72(51)	O(2)–Ir–O(2A)	87.02(30)
P(2)–Ir–O(1)	97.16(17)	O(2)–Ir–C(2B)	172.48(53)
P(2)–Ir–O(2)	85.56(17)	O(2A)–Ir–C(2B)	87.65(57)
P(2)–Ir–O(2A)	86.86(27)		
B. Iridium – phosphorus – carbon angles			
Ir–P(1)–C(11)	112.43(10)	Ir–P(2)–C(41)	108.07(53)
Ir–P(1)–C(21)	109.76(46)	Ir–P(2)–C(51)	109.50(46)
Ir–P(1)–C(31)	117.16(47)	Ir–P(2)–C(61)	124.08(65)
C. Iridium – oxygen – sulfur angles			
Ir–O(1)–S	96.68(28)	Ir–O(2)–S	96.68(28)
D. Iridium – oxygen – carbon and iridium – carbon – oxygen angles			
Ir–O(2A)–C(2A)	118.2(10)	Ir–C(2B)–O(2B)	168.9(14)
E. Oxygen – sulfur – oxygen angles			
O(1)–S–O(2)	98.60(32)	O(2)–S–O(3)	96.35(43)
O(1)–S–O(3)	124.13(44)	O(2)–S–O(4)	110.56(37)
O(1)–S–O(4)	110.56(37)	O(3)–S–O(4)	113.60(47)
F. Carbon – phosphorus – carbon angles			
C(11)–P(1)–C(21)	100.55(46)	C(41)–P(2)–C(51)	103.56(69)
C(11)–P(1)–C(31)	108.02(47)	C(41)–P(2)–C(61)	104.99(83)
C(21)–P(1)–C(31)	107.53(65)	C(51)–P(2)–C(61)	104.81(78)
G. Carbon – carbon – carbon angles			
C(12)–C(11)–C(16)	117.89(78)	C(42)–C(41)–C(46)	115.0(16)
C(11)–C(12)–C(13)	119.5(12)	C(41)–C(42)–C(43)	124.7(17)
C(12)–C(13)–C(14)	118.3(14)	C(42)–C(43)–C(44)	121.1(17)
C(13)–C(14)–C(15)	124.8(13)	C(43)–C(44)–C(45)	114.8(18)
C(14)–C(15)–C(16)	116.4(18)	C(44)–C(45)–C(46)	123.9(19)
C(15)–C(16)–C(11)	122.95(87)	C(45)–C(46)–C(41)	120.5(17)
C(22)–C(21)–C(26)	119.9(14)	C(52)–C(51)–C(56)	118.6(14)
C(21)–C(22)–C(23)	119.8(15)	C(51)–C(52)–C(53)	119.3(14)
C(22)–C(23)–C(24)	118.9(16)	C(52)–C(53)–C(54)	119.6(16)
C(23)–C(24)–C(25)	121.8(17)	C(53)–C(54)–C(55)	122.9(18)
C(24)–C(25)–C(26)	119.7(17)	C(54)–C(55)–C(56)	118.4(19)
C(25)–C(26)–C(21)	119.7(15)	C(55)–C(56)–C(51)	121.2(17)
C(32)–C(31)–C(36)	121.1(14)	C(62)–C(61)–C(66)	113.9(17)
C(31)–C(32)–C(33)	121.9(16)	C(61)–C(62)–C(63)	122.2(19)
C(32)–C(33)–C(34)	116.4(19)	C(62)–C(63)–C(64)	118.2(21)
C(33)–C(34)–C(35)	123.1(19)	C(63)–C(64)–C(65)	122.5(25)
C(34)–C(35)–C(36)	119.4(19)	C(64)–C(65)–C(66)	120.1(24)
C(35)–C(36)–C(31)	118.1(14)	C(65)–C(66)–C(61)	123.1(20)

crystallographic $C_s(m)$ symmetry since Ir and P(1) lie at $y = 1/4$ but P(2) and the mirror-related P(2)(x, $1/2 - y$, z) are separated by 0.886(4) Å, i.e., each lies 0.443 Å from the crystallographic mirror plane.



1 (C_s) 2 (C_s) 3a (C_1) 3b (C_1) 4a (C_1) 4b (C_1)

Fig. 3. Possible isomers of Ir(OMe)(CO)(PPh_3)$_2$(*O*,*O'*-SO_4). [Here P = PPh_3 and $\widehat{O\ O}$ = SO_4.]

The sulfato ligand is in a bidentate mode [25*] with Ir–O(1) = Ir–O(2) = 2.065(6) Å and Ir · · · S 2.705(3) Å. This ligand is distorted from true T_d symmetry to C_{2v} symmetry by its coordination to iridium; thus, S–O(1) = S–O(2) = 1.524(6) Å as compared to S=O(3) 1.481(9) and S=O(4) 1.443(9) Å (average S=O 1.462 Å, i.e., some 0.062 Å shorter than the average formal S–O value of 1.524 Å). The O(1)–Ir–O(2) "bite" angle is 68.03(22)°.

The Ir–OMe distance of Ir–O(2A) 2.206(10) Å and the Ir–CO distance of Ir–C(2B) 1.684(16) are of limited accuracy because of the disorder between the two (cf. Ir–OMe 2.057(8) and Ir–CO 1.897(14) Å in the closely-related ordered trigonal bipyramidal species Ir(OMe)(CO)(PPh_3)$_2$(TCNE) [3]). The Ir–O(2A)–C(2A) angle is 118.2(10)° (with O(2A)–C(2A) 1.385(21) Å), while the Ir–C(2B)–O(2B) angle is 168.9(14)° (with a C≡O linkage of C(2B)–O(2B) 1.159(20) Å).

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* Reference number with asterisk indicates a note in the list of references.

Despite a severe disorder/twinning problem all other distances and angles in the structures are close to their expected values.

Supplementary Material Available

A table of amplitudes is available upon request from one of us (M.R.C.).

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