SHORT STRUCTURAL PAPERS

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Tricarbonylbis(dimethylphenylphosphine)iridium(I) Perchlorate

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Abstract. $[Ir(CO)_3(PMe_2Ph)_2]ClO_4$, $IrP_2ClO_7C_{19}H_{22}$, monoclinic, $P2_1/c$, $a=10·45$ (1), $b=15·38$ (2), $c=14·71$ (2) Å, $\beta=99·6$ (2)°, $Z=4$, $D_x=1·86$, $D_m=1·84$ g cm^{-3}, $V=2331$ Å^3. The coordination of iridium is trigonal bipyramidal with the phosphine ligands in the axial positions. The orientation of the phenyl rings gives the cation approximate C_2 symmetry.

Introduction. Cell dimensions were determined from zero-level precession photographs (λ, Mo $K\alpha=0·7107$ Å). Systematic absences are $h0l$ for l odd and $0k0$ for k odd. Intensities were recorded on Weissenberg photographs of reciprocal-lattice layers $0kl$–$6kl$, and visual estimation gave 1020 independent F_o. No absorption corrections were applied. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations using the KDF9 program of Smith & Cruickshank. Scattering factors for iridium were taken from Cromer & Waber (1965) with inclusion of the real part, $\Delta f'$ of anomalous scattering; scattering factors for other atoms were from *International Tables for X-ray Crystallography* (1968). Atomic coordinates and seven layer scale factors were refined, together with anisotropic temperature factors for iridium and isotropic temperature factors for the other atoms. The weighting scheme used in the final cycles was $w=1/(5+F_o+0·02F_o^2)$ and the final R value was 10·4%. The atomic coordinates and thermal parameters are given in Table 1.*

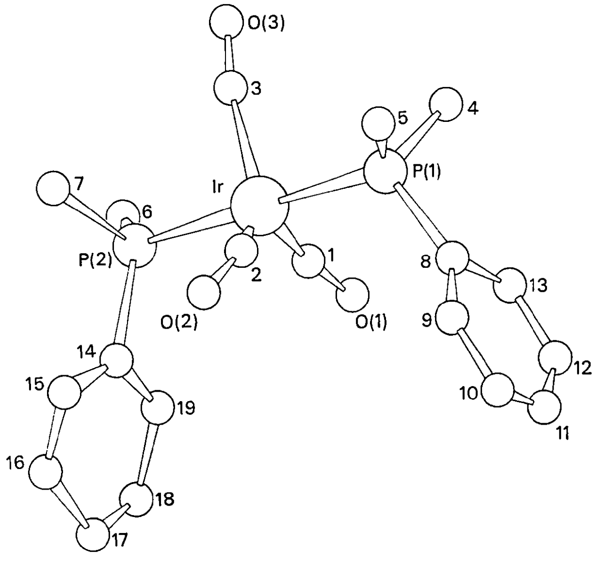

Fig. 1. Atom numbering in the complex cation.

Table 1. *Atomic parameters and e.s.d.'s*

	x	y	z	U_{iso}
Ir(1)	0·0095 (2)	0·1032 (1)	0·1951 (1)	*
P(1)	0·2193 (17)	0·1114 (9)	0·1588 (10)	0·084 (5)
P(2)	−0·1918 (16)	0·0933 (8)	0·2372 (9)	0·073 (4)
Cl(1)	0·5126 (15)	0·3039 (9)	0·4553 (9)	0·087 (4)
O(1)	0·037 (4)	−0·090 (2)	0·206 (3)	0·12 (1)
O(2)	0·090 (4)	0·223 (2)	0·360 (3)	0·11 (1)
O(3)	−0·094 (7)	0·179 (4)	0·012 (5)	0·23 (3)
O(4)	0·590 (6)	0·285 (4)	0·392 (4)	0·24 (3)
O(5)	0·391 (6)	0·289 (4)	0·418 (4)	0·21 (2)
O(6)	0·512 (6)	0·244 (3)	0·517 (4)	0·18 (2)
O(7)	0·525 (5)	0·383 (3)	0·471 (4)	0·17 (2)
C(1)	0·017 (5)	−0·014 (3)	0·202 (3)	0·08 (2)
C(2)	0·086 (5)	0·181 (3)	0·288 (3)	0·09 (2)
C(3)	−0·070 (7)	0·151 (4)	0·077 (4)	0·12 (2)
C(4)	0·222 (6)	0·055 (4)	0·049 (4)	0·09 (2)
C(5)	0·286 (7)	0·224 (4)	0·158 (5)	0·14 (3)
C(6)	−0·302 (5)	0·022 (3)	0·168 (3)	0·09 (2)
C(7)	−0·272 (6)	0·193 (4)	0·220 (4)	0·12 (2)
C(8)	0·330 (6)	0·051 (3)	0·232 (4)	0·09 (2)
C(9)	0·402 (5)	0·084 (3)	0·321 (3)	0·07 (2)
C(10)	0·486 (5)	0·040 (3)	0·386 (3)	0·07 (2)
C(11)	0·495 (5)	−0·044 (3)	0·365 (3)	0·09 (2)
C(12)	0·443 (6)	−0·084 (3)	0·286 (4)	0·09 (2)
C(13)	0·363 (5)	−0·036 (3)	0·223 (3)	0·08 (2)
C(14)	−0·183 (5)	0·060 (3)	0·359 (3)	0·06 (1)
C(15)	−0·182 (5)	0·132 (3)	0·432 (3)	0·07 (2)
C(16)	−0·203 (6)	0·090 (3)	0·507 (4)	0·09 (2)
C(17)	−0·171 (6)	−0·002 (4)	0·536 (4)	0·11 (2)
C(18)	−0·171 (6)	−0·054 (4)	0·468 (4)	0·09 (2)
C(19)	−0·168 (6)	−0·027 (3)	0·371 (4)	0·09 (2)

* U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
0·060 (2)	0·074 (1)	0·048 (1)	0·015 (2)	0·055 (2)	0·002 (3)

Discussion. This compound is one of a series of five-coordinate cationic complexes of iridium(I) prepared by Deeming & Shaw (1970). Previously determined structures of five-coordinate iridium compounds are square

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* The observed and calculated structure factors have been deposited with the National Lending Library, England as Supplementary Publication No. SUP 30126. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

pyramidal, such as $[IrCl(CO)(NO)(PPh_3)_2]^+BF_4$ (Hodgson & Ibers, 1968) or trigonal bipyramidal such as $IrCl(CO)_2(PPh_3)_2$ (Payne & Ibers, 1969), whilst some have intermediate arrangements of ligands. This analysis shows that the $[Ir(CO)_3(PMe_2Ph)_2]^+$ ion has the trigonal bipyramidal arrangement with the phosphine ligands in the axial positions. Selected bond lengths and angles of the cation are given in Table 2, and Fig. 1 shows the structure of the complex cation with the atom numbering indicated. The two phosphine ligands are oriented so that each has its substituents staggered with respect to the equatorial carbonyl groups so that the two phosphines are almost mutually eclipsed. The cation has approximate twofold symmetry with the twofold axis ideally passing through Ir, C(3) and O(3). The mean C–C bond length is 1·40 (2) Å and the Cl–O bonds average 1·30 (3) Å. The latter bond length is undoubtedly shortened from its true value as a result of librational motion of the ion; the chlorine atom has $U_{iso}=0{\cdot}087$ Å² whilst O(4) to O(7) have U_{iso} of 0·17–0·24 Å².

Table 2. *Bond lengths and angles with their e.s.d.'s*

Dimensions related by the approximate twofold axis of the cation are given on the same line.

Ir—P(1)	2·34 (2) Å	Ir—P(2)	2·29 (2) Å
Ir—C(1)	1·81 (5)	Ir—C(2)	1·89 (5)
Ir—C(3)	1·94 (6)		
P(1)–C(4)	1·84 (5)	P(2)–C(7)	1·74 (6)
P(1)–C(5)	1·86 (7)	P(2)–C(6)	1·78 (5)
P(1)–C(8)	1·72 (6)	P(2)–C(14)	1·85 (4)
C(1)–O(1)	1·19 (6)	C(2)–O(2)	1·24 (6)
C(3)–O(3)	1·04 (9)		
P(1)–Ir—P(2)	177·4 (5)°		
P(1)–Ir—C(1)	92 (2)	P(2)–Ir—C(2)	98 (2)°
P(1)–Ir—C(2)	80 (2)	P(2)–Ir—C(1)	87 (2)
P(1)–Ir—C(3)	93 (2)	P(2)–Ir—C(3)	89 (2)
C(1)–Ir—C(2)	126 (2)		
C(1)–Ir—C(3)	116 (2)	C(2)–Ir—C(3)	118 (2)
Ir—P(1)–C(4)	109 (2)	Ir—P(2)–C(7)	110 (2)
Ir—P(1)–C(5)	115 (2)	Ir—P(2)–C(6)	115 (2)
Ir—P(1)–C(8)	113 (2)	Ir—P(2)–C(14)	112 (2)
Ir—C(1)–O(1)	172 (4)	Ir—C(2)–O(2)	154 (4)
Ir—C(3)–O(3)	169 (7)		

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Tetra-arsenic Tetraselenide

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Abstract. As_4Se_4 is monoclinic, $P2_1/n$, $a=9{\cdot}55$ (1), $b=13{\cdot}80$ (1), $c=6{\cdot}74$ (2) Å, $\beta=106{\cdot}4$ (2)°, $Z=4$, $D_x=4{\cdot}82$ g cm^{-3}. Crystals were prepared by fusion of a 1:1 As:Se mixture followed by sublimation in vacuum. The structure is isostructural with α-As_4S_4, and consists of discrete As_4Se_4 molecules which possess almost exact $\bar{4}2m$ (D_{2d}) symmetry. Mean bond lengths (corrected for libration) and angles are: As–As 2·564, As–Se 2·388 Å; Se–As–As 101·2, Se–As–Se 94·1 and As–Se–As 98·1°.

Introduction. The mass spectra and X-ray powder photographs of the sublimation products of fused arsenic–selenium mixtures provide evidence for the existence of molecular arsenic selenides analogous to the established As_4S_3 and As_4S_4. The abundant positive ions in the mass spectra are: As_4S_3 ($As_4S_3^+$ 100, $As_3S_2^+$ 59, As_3S^+ 71, AsS^+ 88); As_4Se_3 ($As_4Se_3^+$ 100, As_3Se^+ 94, $AsSe^+$ 51); As_4S_4 ($As_4S_4^+$ 100, $As_3S_3^+$ 68, AsS^+ 90); and As_4Se_4 ($As_4Se_4^+$ 46, $As_4Se_3^+$ 100).

Experimental. A crystal of As_4Se_4 elongated along [001] with approximate dimensions 0·02 × 0·008 × 0·06 mm was sealed into a Lindemann glass capillary tube. Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers *hk*0 to *hk*7) with Mo $K\alpha$ radiation. The data were collected in an approximately 'constant count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. 1484 reflexions were measured, of which 223 were rejected because of background imbalance or because the net count was less than 3σ based on counting statistics; averaging of equivalent reflexions led to 684 unique reflexions. Systematic absences were observed for $h0l$ ($h+l$ odd) and $0k0$ (k odd). Absorption, Lorentz and polarization corrections were applied. Consistent unit-cell dimensions were obtained from diffractometer measurements ($\lambda=0{\cdot}71069$ Å), and by least-squares analysis of $\sin^2\theta$ values from powder photographs taken with a Guinier