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THE STRUCTURE OF THE METALLATED IRIDIUM COMPLEX $[(C_8H_{12})Ir\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(OCH_2)_3CMe\}]$

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Summary

The crystal structure of $[(C_8H_{12})Ir\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(OCH_2)_3CMe\}]$ has been determined. a 18.32, b 18.98, c 9.35 Å, U 3251 Å³, $Pn2_1a$, Z = 4, R = 0.048, 2541 observed data.

The coordination about the iridium atom is distorted trigonal bipyramidal; the two phosphorus atoms are equatorial, the σ -bonded carbon is axial, and the bidentate cyclooctadiene is bonded axial–equatorial. The Ir–C(axial) bonds are longer than the Ir–C(equatorial) bonds: 2.22, 2.26; 2.17, 2.19 Å. The Ir–C(σ) bond length is 2.19 Å, not significantly different from the formally π -bonded C to Ir distances. The Ir–P lengths of 2.201 and 2.240 Å and the P–Ir–P angle of 108.7° are normal. The longer Ir–P bond is in the five-membered chelate ring. The inertness to substitution is discussed.

Introduction

The ability of a ligand to form a five-membered ring has been shown to promote internal cyclometallation reactions thus accounting for the numerous reactions of this type undergone by $P(OPh)_3$ [1]. In contrast, bulky phosphines can undergo internal cyclometallations by promoting ligand lability through interligand non-bonded repulsion [2]. Because the bulky ligand tri-*o*-tolylphosphite combines these two factors, we have studied the reactions of $[CODIrCl]_2$ (I; COD = 1,5-cyclooctadiene) with this ligand under a variety of conditions in the hopes of finding routes to multiply-metallated iridium complexes [3]. We have found that the neutral product analysing for “[CODIr{P(*o*-tolyl)₃}₂]” (II) was the only complex isolated from I and $P(O\text{-}o\text{-tolyl})_3$ in cold ethanol, in



Fig. 1. Schematic formulae. (a) Monometallated, with normal bidentate COD group. (b) Dimetallated, with the COD held by one sigma bond and one pi-donor bond.

contrast to the reactions of $P(OPh)_3$ which formed $[CODIr\{P(OPh)_3\}_3]^+$ with I under the same conditions. The corresponding neutral triphenylphosphite derivative " $[CODIr\{P(OPh)_3\}_2]$ " (III) was obtained by heating the cation in boiling ethanol [4]. Both II and III were white, precluding them from being square-planar iridium(I) species; and a structure containing a five-coordinate iridium(I) atom, internally metallated to one $P(OPh)_3$ ligand, (Fig. 1a) was proposed for these compounds [4]. Attempts to replace the cyclooctadiene ligand in II and III by a series of neutral ligands L ($L = PMePh_2$, PMe_2Ph , PMe_3 and $P(OCH_2)_3CMe$) gave only the mono-substituted products " $[CODIrL\{P(OPh)_3\}]$ " and " $[CODIrL\{P(O-o-tolyl)_3\}]$ " which was unusual considering how readily the diene in $[CODIrL_2]^+$ and $[CODIrL_3]^+$ can be replaced to give $[IrL_4]^+$ and $[IrL_5]^+$ cations [5]. As tri-*o*-tolylphosphite has recently been shown to form dimetallated species with I [3], this inability to replace the COD in II and III led us to consider that the structure in Fig. 1b was possible for these compounds. We have recently undertaken studies of the kinetic and preparative aspects of oxidative addition reactions of HPF_6 , haloacids and halogens with II and III and have characterised a range of iridium(III) products containing a chelated cyclooctadiene ligand. It was necessary to know the details of the molecular structure of $[CODIr\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(OCH_2)_3CMe\}]$ (IV) and the crystal structure has therefore been determined.

Experimental

i. Preparation

$[CODIr\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(O-o-tolyl)_3\}]$ (II). To a suspension of $[CODIrCl]_2$ (0.74 g) in ethanol (30 ml) was added $P(O-o-tolyl)_3$ (2.4 g). The mixture was stirred for 3 h and then filtered. Recrystallisation of the resultant precipitate from dichloromethane/ethanol gave the product as white prisms (1.1 g, 50%).

$[CODIr\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(OCH_2)_3CMe\}]$ (IV). A mixture of II (0.25 g) and $P(OCH_2)_3CMe$ (0.11 g) was refluxed in benzene (20 ml) for 2 h. Removal of the solvent under reduced pressure gave an oil which produced white prisms (0.13 g, 65%) on recrystallisation from dichloromethane/ethanol.

ii. Determination of the crystal structure

Data were collected on the Philips four-circle diffractometer at the National Physical Research Laboratory, C.S.I.R. with graphite-monochromated $Mo-K_{\alpha}$ radiation (λ 0.7107 Å) for θ between 3 and 25° . The $\omega - 2\theta$ scan mode was used; scan width was 0.9° , the scan time was 30 s and the background was

TABLE 1
FRACTIONAL ATOMIC COORDINATES^a

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Ir	0.22030(2)	1.10000	1.05110(5)	
P(1)	0.2472(2)	1.1819(2)	0.8930(4)	2.81(7)
P(2)	0.3242(2)	1.0499(2)	1.1261(4)	3.00(7)
O(1.1)	0.2623(6)	1.2611(6)	0.9450(12)	4.8(2)
O(1.2)	0.3177(6)	1.1696(6)	0.7912(11)	4.5(2)
O(1.3)	0.1866(6)	1.1936(6)	0.7723(13)	5.3(3)
O(2.1)	0.3236(5)	1.0043(5)	1.2709(11)	4.2(2)
O(2.2)	0.4009(4)	1.0899(7)	1.1594(9)	4.1(2)
O(2.3)	0.3501(5)	0.9924(5)	1.0097(10)	4.0(2)
C(1)	0.1023(7)	1.0844(8)	1.0283(14)	4.3(3)
C(2)	0.1338(8)	1.0205(10)	1.1147(18)	4.8(3)
C(3)	0.1196(10)	1.0288(9)	1.2836(20)	6.0(4)
C(4)	0.1450(9)	1.0876(12)	1.3607(17)	6.0(4)
C(5)	0.2045(8)	1.1345(8)	1.2799(16)	4.4(3)
C(6)	0.1792(8)	1.1871(8)	1.1872(17)	4.5(3)
C(7)	0.1013(10)	1.2046(11)	1.1494(22)	6.4(5)
C(8)	0.0562(10)	1.1435(10)	1.0949(20)	6.0(4)
C(9)	0.2763(9)	1.3146(9)	0.8334(19)	5.2(4)
C(10)	0.3323(9)	1.2258(9)	0.6851(19)	5.4(4)
C(11)	0.1995(9)	1.2448(10)	0.6659(20)	5.5(4)
C(12)	0.2766(9)	1.2834(9)	0.6915(17)	4.6(3)
C(13)	0.2942(9)	1.3367(10)	0.5765(20)	5.6(4)
C(1.1)	0.3830(8)	0.9723(8)	1.3381(16)	4.0(3)
C(1.2)	0.4035(9)	1.0004(9)	1.4727(17)	4.7(3)
C(1.3)	0.4605(9)	0.9641(9)	1.5461(19)	5.2(4)
C(1.4)	0.4939(11)	0.9082(10)	1.4870(20)	5.8(4)
C(1.5)	0.4763(10)	0.8815(10)	1.3515(21)	6.2(5)
C(1.6)	0.4189(9)	0.9165(9)	1.2701(19)	5.3(4)
C(1.7)	0.3681(10)	1.0624(9)	1.5389(19)	5.6(4)
C(2.1)	0.4334(9)	1.1375(9)	1.0680(19)	5.7(4)
C(2.2)	0.4322(11)	1.2058(12)	1.0960(23)	7.6(6)
C(2.3)	0.4795(11)	1.2487(11)	0.9814(21)	6.3(5)
C(2.4)	0.5094(12)	1.2100(13)	0.8901(25)	8.3(6)
C(2.5)	0.5094(11)	1.1374(11)	0.8549(24)	7.4(5)
C(2.6)	0.4730(8)	1.1112(12)	0.9466(17)	5.8(4)
C(2.7)	0.3973(11)	1.2309(12)	1.2123(23)	7.7(5)
C(3.1)	0.3015(8)	0.9828(9)	0.9020(17)	4.6(3)
C(3.2)	0.3183(9)	0.9232(8)	0.8070(17)	4.5(3)
C(3.3)	0.2683(9)	0.9145(9)	0.6956(18)	5.0(4)
C(3.4)	0.2084(9)	0.9517(10)	0.6692(19)	5.5(4)
C(3.5)	0.1895(9)	1.0045(9)	0.7706(18)	4.9(4)
C(3.6)	0.2377(8)	1.0228(8)	0.8809(17)	4.1(3)
C(3.7)	0.3832(10)	0.8793(10)	0.8299(20)	5.7(4)

^a Estimated standard deviations in the last significant figure are given in parentheses.

counted for 30 s for each peak. Three reflexions were used as standards and remeasured every hour: no decomposition was observed. Of the 3296 reflexions which were measured (including space group extinctions), 2541 were classed as observed, $I > 1.65\sigma(I)$. Only Lorentz and polarization corrections were applied (μ 44.9 cm⁻¹). A temperature-sharpened Patterson map showed the *x*, *z* coordinates of the iridium to be 0.22, 0.05. The *y* coordinate was set at the arbitrary value of 0.10. The positions of the two P atoms were readily deduced from the subsequent Fourier map, but their addition to the structure factor calculations did not remove the pseudo-mirror symmetry in the Fourier maps, and the remain-

ing C and O atoms were only found with some difficulty. The 43-atom structure was refined by block-diagonal least-squares to $R = 0.048$ for 2541 observed data; Ir anisotropic, all other atoms isotropic. Weighting was proportional to $1/\sigma(F)$; scattering factors were from the International Tables for Crystallography [6]. Calculations were done on a Burroughs 5700 computer with the local set of programs [7]. The final atomic coordinates are given in Table 1 (the thermal parameters and lists of observed and calculated structure factors are available from the authors.

Crystal data

a 18.320(10), b 18.980(10), c 9.350(5) Å, U 3251 Å³, orthorhombic $Pn2_1a$;
 ρ_{calc} 1.63, ρ_{obs} 1.62(2) g cm⁻³; $Z = 4$, $M = 799$, IrP₂O₆C_{3.4}H_{4.1}.

Discussion

The coordination about the iridium in IV is shown in Fig. 2, and is most simply described as distorted trigonal bipyramidal with the two P atoms and one C=C group equatorial and the σ -bonded *ortho* carbon and second C=C group axial. Tables 2 and 3 give the more important bond lengths and angles. The coordination geometry of IV is similar to (but certainly not identical with) those of the compounds [CODIr(Me)(PMe₂Ph)₂] [8,9], [CODIr(Me)(DIPHOS)] [8,10], [CODIr(Me)(DPPP)] [11], [Ir(C₂H₄)₂(PPh₃)(PPh₂C₆H₄)], [Ir(CO)₂(PPh₃)(PPh₂C₆H₄)], and [Ir(C₂H₄)₂(P-*i*-Pr₃)(P-*i*-Pr₂(C₃H₆))] [12]. The pertinent bond angles are listed in Table 4 and show quite clearly that the only major differences between IV and the σ -bonded methyl analogues are an increase in the P-Ir-P angle and a concomitant reduction in the pseudo-axial (C)-Ir-(C=C) angle in

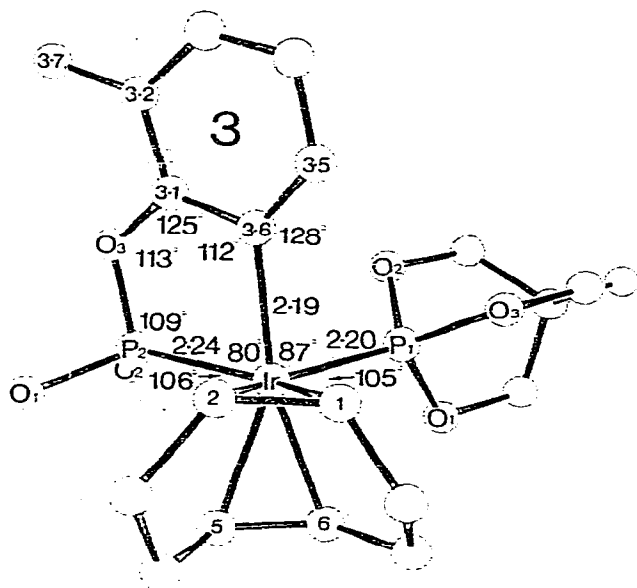


Fig. 2. A projection of the molecule showing the coordination about the iridium atom. The numbering system has been simplified e.g. O1 on P2 is O(2.1), O3 on P1 is O(1.3) in Table 2. Phenyl rings 1 and 2 on P(2) are omitted.

TABLE 2

BOND LENGTHS^a AND INTRAMOLECULAR NON-BONDED SEPARATIONS (Å)

Ir—C(1)	2.19(1)	Ir—P(1)	2.201(5)
Ir—C(2)	2.17	Ir—P(2)	2.240(5)
Ir—C(5)	2.26	C(1)—C(2)	1.45(2)
Ir—C(6)	2.22	C(5)—C(6)	1.40
Ir—C(3.6)	2.19	C(2)—C(3)	1.61(3)
P(1)—O(1.1)	1.60	C(3)—C(4)	1.54
P(1)—O(1.2)	1.62	C(4)—C(5)	1.60
P(1)—O(1.3)	1.60	C(6)—C(7)	1.51
P(2)—O(2.1)	1.61	C(7)—C(8)	1.51
P(2)—O(2.2)	1.63	C(8)—C(1)	1.54
P(2)—O(2.3)	1.61	C(9)—C(12)	1.45
O(1.1)—C(9)	1.48(2)	C(10)—C(12)	1.50
O(1.2)—C(10)	1.48	C(11)—C(12)	1.61
O(1.3)—C(11)	1.43	C(12)—C(13)	1.51
O(2.1)—C(1.1)	1.40	C(1.2)—C(1.7)	1.48(4)
O(2.2)—C(2.1)	1.38	C(2.2)—C(2.7)	1.35
O(2.3)—C(3.1)	1.36	C(3.2)—C(3.7)	1.47
C(1)···P(1)	3.47	C(1)···C(6)	2.83
C(2)···P(2)	3.51	C(2)···C(5)	2.84
C(5)···P(2)	3.07	C(1)···O(1.3)	3.52
C(6)···P(1)	3.02	C(5)···O(2.1)	3.30
P(1)···P(2)	3.61	C(6)···O(1.1)	3.07
Ir···C(2.7)	4.35	C(2)···O(2.1)	3.80

^a Estimated standard deviations are given in parentheses.

IV. On the other hand, the diethylene compounds described by Perego et al. [12] have the σ -bonded carbon atoms *trans* to one P atom, while the two ethylene groups and the second P atom (closest to the Ir—C bond) lie in the equatorial plane of the trigonal bipyramid. The difference in the arrangements of the

TABLE 3

BOND ANGLES IN DEGREES^a

P(1)—Ir—P(2)	108.7(5)	O(1.1)—P(1)—O(1.2)	100(2)
P(1)—Ir—C(3.6)	87(1)	O(1.2)—P(1)—O(1.3)	99
P(2)—Ir—C(3.6)	80	O(1.3)—P(1)—O(1.1)	102
P(1)—Ir—C(1)	105	O(2.1)—P(2)—O(2.2)	96
P(2)—Ir—C(2)	106	O(2.2)—P(2)—O(2.3)	101
P(1)—Ir—C(6)	86	O(2.3)—P(2)—O(2.1)	102
P(2)—Ir—C(5)	86	C(1)—C(2)—C(3)	124
Ir—P(1)—O(1.1)	120	C(2)—C(3)—C(4)	109
Ir—P(1)—O(1.2)	118	C(3)—C(4)—C(5)	116
Ir—P(1)—P(1.3)	115	C(4)—C(5)—C(6)	118
Ir—P(2)—O(2.1)	119	C(5)—C(6)—C(7)	128
Ir—P(2)—O(2.2)	127	C(6)—C(7)—C(8)	115
Ir—P(2)—O(2.3)	109	C(7)—C(8)—C(1)	113
P(1)—O(1.1)—C(9)	117(2)	C(8)—C(1)—C(2)	122
P(1)—O(1.2)—C(10)	116	O(2.3)—C(3.1)—C(3.2)	114
P(1)—O(1.3)—C(11)	118	O(2.3)—C(3.1)—C(3.6)	125
P(2)—O(2.1)—C(1.1)	127	C(3.1)—C(3.6)—Ir	112(1)
P(2)—O(2.2)—C(2.1)	124	C(3.5)—C(3.6)—Ir	128
P(2)—O(2.3)—C(3.1)	113		

^a Estimated standard deviations are given in parentheses.

TABLE 4

COMPARISON OF IMPORTANT BOND ANGLES AND LENGTHS IN THE GEOMETRICALLY RELATED COMPOUNDS^a

	CODIrMe- (DIPHOS) (Ref. 10)	CODIrMe- (DPPP) (Ref. 11)	CODIrMe- (PMe ₂ Ph) ₂ (Ref. 9)	IV (This work)
<i>Bond angles</i>				
P—Ir—P	84.9	93.4	101.5	108.7
C—Ir—P	85.2	87.3, 84.7	87.0, 84.5	87, 80
C—Ir—(C=C) _{ax}	169.4	166.3	163.7	155, 165
C—Ir—(C=C) _{eq}	85.3	83.8	82.8	84, 89
(C=C)—Ir—(C=C)	84.0	83.2	86.4	80, 80, 90, 93
<i>Bond lengths</i>				
Ir—C(σ)	2.133	2.153	2.202	2.19
Ir—P	2.308	2.309, 2.337	2.316, 2.329	2.201, 2.240
Ir—(C=C) _{ax}	2.106	2.127	2.117	2.22, 2.26
Ir—(C=C) _{eq}	2.011	2.033	2.078	2.17, 2.19

^a The data in columns 1—3 are from Table VII in ref. 11; the angles involving the C=C groups are calculated for the middle of the double bond. In column 4 the angles are to the individual C atoms.

bonded C=C moieties in these two groups of compounds appears to be a geometric and not electronic effect. Figure 3 shows an idealised bipyramidal compound, MX₅, in which the M—X lengths are 2.20 Å. The non-bonded axial—equatorial and equatorial—equatorial X···X separations are 3.11 and 3.81 Å, respectively. It is thus evident that a bidentate ligand cannot bond equatorial—equatorial if its bite is not close to 3.8 Å. Because the maximum separation between the two C=C groups in the COD molecule is only about 2.7 Å, the COD group will be constrained to have one C=C in an equatorial site while the second is in an axial site. If both C=C groups are to be bonded in equatorial positions, they would have to be further apart, about 3.8 Å. We conclude, therefore, that in any five-coordinate complex with trigonal bipyramidal geometry, a COD ligand will be bonded axial—equatorial. The deductions drawn here reflect a point of view that differs from those of Churchill and Bezman [11] who favoured an interpretation based on factors such as electronegativity and π -acceptor capability. Structure IIa in ref. 11 should be compared with Fig. 1 in ref. 12. Where there is no constraint from the diene system, one P atom and the σ -bonded C atom are axial. However, in every case [9–12] the σ -bonded C atom is bonded axially.

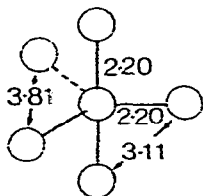


Fig. 3. An ideal trigonal bipyramidal molecule MX₅, showing the two different non-bonded X···X separations.

There is a further implication: the difference in bonding energy between equatorial and axial bonds must be very small for both σ - and π -donor ligands (i.e. phosphines and alkenes).

The coordination sphere of the iridium has an approximate mirror plane perpendicular to the C(1)—C(2) and C(5)—C(6) bonds (see Fig. 2). This regularity was also found in the PMe_2Ph , DIPHOS and DPPP compounds [8–11] in spite of the large differences in the P—Ir—P angle. The similarities of the P—Ir—C angles (86, 86; 106, 105°) to the COD group imply that the Van der Waals repulsions between the two phosphite ligands and the COD group are also similar and probably have been reduced to a minimum. It is likely, therefore, that any differences or distortions in the geometry about the phosphorus atoms are not caused by non-bonded repulsions from the COD group.

The Ir—P and Ir—C bond lengths have some unusual characteristics, and are compared with those found in the related PMe_2Ph , DPPP and DIPHOS compounds in Table 4. The Ir—P lengths for these phosphite ligands are considerably shorter than the values found for the phosphine ligands [9–11]. This effect is commonly observed, and is well illustrated in the pair of compounds [$\text{LCr}(\text{CO})_5$], $\text{L} = \text{PPh}_3$, $\text{P}(\text{OPh})_3$ [13], where the Cr—phosphine bond is 2.422 Å, and the Cr—phosphite bond 2.309 Å. The Ir—C distances (2.17 to 2.26 Å) are similar to the Ir—P bond lengths. This differs from the case of the COD Ir phosphine compounds where the Ir—C bonds were consistently shorter than the Ir—P bonds by about 0.15 Å [9–11]. More interestingly, there is no significant difference between the Ir—C distance for the σ -bonded C atom and those of the π -bonded C=C groups. The same effect was found in the compounds [$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$] $_2(\text{CH}_2)_n$, $n = 3, 4$ [14] where the Fe—C bonds were between 2.08 and 2.13 Å.

Although the e.s.d.'s of the C—C bond lengths in the COD ring are large, the pattern of bond lengths, angles and torsion angles is internally consistent (Tables 2, 3, 5). The COD ring is twisted from the ideal tub conformation, but retains the approximate symmetry 2. The pattern of torsion angles is almost identical with both that found in the DPPP derivative [11] and those for the two COD rings in the compound [$(\text{COD})_2\text{Ir}(\text{SnCl}_3)$] [15] whose coordination geometry is also trigonal bipyramidal (see Table 5). The C—C bond of the

TABLE 5
TORSION ANGLES IN COD RINGS OF SIMILAR CONFORMATION

	IV (This work)	$(\text{COD})_2\text{Ir-}$ SnCl_3 (Ref. 15 ^a)	CODIrMe- (DPPP) (Ref. 11 ^b)
C(1)—C(2)—C(3)—C(4)	—59	—55, —52	47.9
C(2)—C(3)—C(4)—C(5)	—23	—24, —25	29.5
C(3)—C(4)—C(5)—C(6)	89	87, 92	91.3
C(4)—C(5)—C(6)—C(7)	—2	1, —2	3.9 (ax)
C(5)—C(6)—C(7)—C(8)	—54	—47, —46	56.1
C(6)—C(7)—C(8)—C(1)	—24	—31, —30	25.1
C(7)—C(8)—C(1)—C(2)	86	95, 95	90.0
C(8)—C(1)—C(2)—C(3)	4	2, —2	2.5 (eq).

^a Angles calculated from the positional coordinates in Table 1. ^b Taken from Table V.

axially bonded olefinic residue is 1.40 Å while the bond in the equatorially bonded residue is longer, 1.45 Å; and the shorter C—C linkage is associated with the longer Ir—C(ax) bonds. This is exactly the same result as was observed in the DPPP compound [11]. In $[(\text{COD})_2\text{Ir}(\text{SnCl}_3)]$ not only are both COD ligands held axial—equatorial, but the Ir—C(ax) bond lengths are consistently longer than the Ir—C(eq) bond lengths; mean values of 2.25 vs. 2.16 Å [15]. In the related DIPHOS and PMe_2Ph compounds [9,10] the Ir—C(ax) distances were also longer than the Ir—C(eq) distances; however, in both cases the conformation of the COD ring differed from that found in the DPPP compound. It seems therefore, that the COD ring is relatively flexible and that its conformation is determined by packing effects and not by the electronic properties of the other groups bonded to the Ir atom. On the other hand, the Ir—C lengths are noticeably affected by whether the C atoms are bonded to an axial or equatorial site. They are, however, relatively insensitive to the electronic characteristics of the other groups bonded to the iridium.

The O—P—O angles on P(1) and P(2) are similar, but there are significant differences between the Ir—P—O angles on the two P atoms. These are caused by the pentacyclic chelate ring: e.g. the angle Ir—P(2)—O(2.3) is only 109° compared with angles 115 – 120° about P(1) and Ir—P(2)—O(2.2) of 127° . The geometry of the tritolyolphosphite ligand can also be compared with the results found for the two triphenylphosphite ligands in $[\text{COD}(\text{Rh}_2\text{Cl}_2)\{\text{P}(\text{OPh})_3\}_2]$ [16]. Here the angles were: Rh—P—O 112 to 121 , and P—O—C 124 to 126° . The strain in the chelate ring is also seen in the angles between the Ir atom and the metallated carbon atom C(3.6): Ir—C(3.6)—C(3.1) 112° , Ir—C(3.6)—C(3.5) 128° , and in the C(3.6)—Ir—P angles: 80° within the ring, 87° to P(1). (Table 6 describes the planes associated with the chelate ring).

The difference of 0.04 Å between the Ir—P bond lengths seems to be significant: the difference between the mean P—O bond lengths (1.61 Å for P(1), 1.62 Å for P(2)) is far smaller. It is tempting to ascribe the lengthening of the Ir—P(2) bond to the strains in the chelate ring. However, this difference in Ir—P distances should be compared with the results observed in $[\text{IrCl}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OC}_6\text{H}_5)_2\}_2\{\text{P}$

TABLE 6

LEAST-SQUARES PLANES ASSOCIATED WITH THE CHELATE RING

Plane 1: Defined by atoms: Ir, P(2), O(2.3), C(3.1), C(3.6)

Plane 2: Defined by atoms: Ir, P(2), O(2.3), C(3.1), C(3.6), C(3.2), C(3.3), C(3.4), C(3.5), C(3.7)

Equations to the planes are of the form $Ax + By + Cz = D$ where A, B and C are direction cosines parallel to a, b and c, and D is the perpendicular distance from the origin

	A	B	C	D (Å)
Plane 1	0.512	0.684	-0.519	11.23
Plane 2	0.518	0.649	-0.558	10.19

Deviations from the plane (Å)

	Ir	P(2)	O(2.3)	C(3.1)	C(3.6)	C(3.2)	C(3.3)	C(3.4)	C(3.5)	C(3.7)
Plane 1	0.01	-0.03	0.04	-0.02	0.00	-0.18	-0.22	-0.17	-0.15	-0.25
Plane 2	-0.04	-0.06	0.08	0.07	0.06	-0.01	-0.01	0.01	-0.04	-0.06

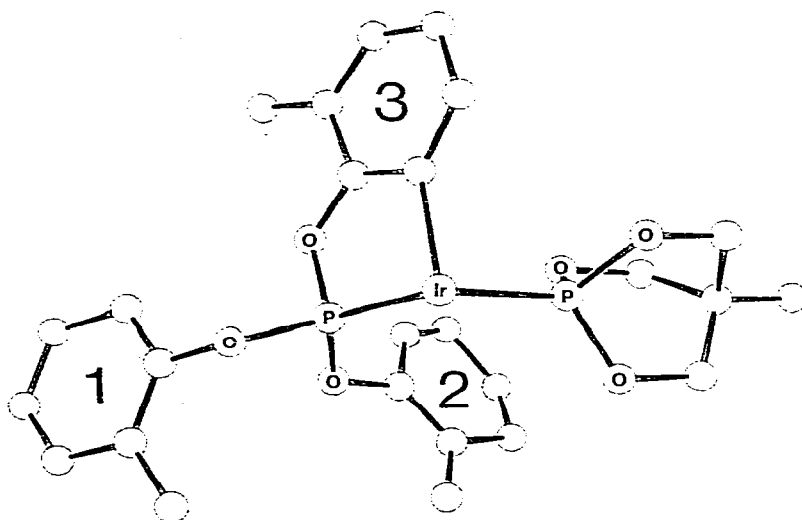


Fig. 4. A projection of the molecule showing the two phosphite ligands; the COD ring has been omitted. The methyl group on phenyl 2 shields the back of the iridium atom *trans* to the COD ligand.

(OC₆H₅)₃] [17]. In this case the bond to the P atom of the non-chelated phosphite was similar in length to the bond to the P in the chelated phosphite; both of these P atoms were *trans* to σ -bonded C atoms. The bond to the third phosphorus, *trans* to the Cl atom, was significantly different in length. The pattern of Ir—P bond lengths in this dimetallated octahedral compound is what would be expected from the “structural *trans* effect” [18], but this argument does not fit IV which is trigonal bipyramidal with the two phosphorus atoms making similar angles with the C=C groups. Recent work [19] has shown that the phosphorus atom in a five-membered chelate ring shows a large down-field ³¹P chemical shift relative to phosphorus in the same ligand when it is monodentate and not metallated. This suggests that the bonding characteristics of a phosphorus atom in a five-membered chelate ring will also differ in an analogous way and that the difference of 0.04 Å found in IV is real and caused by the same phenomenon that is responsible for the large ³¹P shifts.

Figure 4 shows the arrangement of the two phosphite ligands on the iridium atom. The phenyl rings 1 and 2 are oriented so that the methyl groups are pointed inwards rather than away from the iridium atom. The tri-*o*-tolylphosphite ligand is clearly more bulky than the “cage” phosphite: Tolman [20] gives values of 141 and 101° for their respective cone angles. Yet the effective sizes of these two ligands are close to identical as far as the COD ligand is concerned viz. the pairs of angles C(1)—Ir—P(1), C(2)—Ir—P(2) and C(6)—Ir—P(1), C(5)—Ir—P(2) are equal (see Table 3) as are the non-bonded P...C and O...C separations (see Tab. 2). If the two ligands are assumed to be in contact, then the P(1)—Ir—P(2) angle represents the sum of the two half cone angles. The effective cone angle of the bonded tri-*o*-tolylphosphite ligand in this complex is therefore $2 \times (108.7 - 101/2) \approx 116^\circ$, which is considerably less than the accepted value for the uncoordinated ligand. This effect is also seen in [COD-(Rh₂Cl₂){P(OPh)₃}₂] [16] where the P—Rh—P angle is 91°, i.e. the effective cone angle of the P(OPh)₃ ligand is only 91° when bonded to the Rh atom. This

reduction in cone angle is accomplished by the meshing of the groups attached to the phosphorus atoms and the opening of the M—P—R angles as the P—M—P angle decreases [21,22].

The molecular geometry of the "cage" phosphite, $P(OCH_2)_3CCH_3$, is normal, and is essentially the same as found for the ligands in the pentakis cation $[Co\{P(OCH_2)_3CMe\}_5]^+$ where M—P—O and P—O—C lie between 114 and 119° and O—P—O between 99 and 103° [23].

Although the iridium atom is protected by the methyl group on phenyl ring 2, and the COD ligand is shielded by the methyl group on phenyl ring 1 (see Fig. 4), this does not appear to be the cause of the inertness of IV to substitution by phosphines because the triphenylphosphite analogue, with no methyl groups, is also inert to substitution. This type of explanation was given for the lack of reactivity of the square planar compound $trans-[IrCl(CO)(P\text{-}o\text{-}tolyl)_2]$ towards H_2 and O_2 addition [24], but in this case the Ir...CH₃ separation was considerably shorter. However, IV does react readily with CO to give $[(CO)_2Ir\{P(OC_6H_3Me)(OC_6H_4Me)_2\}\{P(OCH_2)_3CMe\}]$. This substitution process presumably occurs via a dissociative pathway; it is still unclear, therefore, why the diene could not be substituted by the other neutral donor ligands.

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