Crystal and Molecular Structure of Chlorobis-[2-(diphenoxyphosphinooxy)phenyl](triphenyl phosphite)iridium(III), Formed by Metallation of Two Tertiary Phosphite Ligands

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The structure of the title complex has been determined from three-dimensional *X*-ray diffractometer data. The compound crystallizes in the space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions: a = 10·96, b = 19·20, c = 12·12 Å, α = 95·9, β = 108·0, and γ = 90·7°. The structure was solved by Patterson and Fourier methods and refined by least-squares, using 5780 observed reflections, to R 0·052. The structure consists of independent monomeric units. The iridium atom is in a distorted octahedral environment with three phosphorus atoms, two *ortho*-carbon atoms of the triphenyl phosphite groups, and one chloride ion acting as ligands. Cleavage of two β-C–H bonds and subsequent formation of Ir–C bonds is confirmed. Metal–ligand bond lengths are: Ir–C 2·09 and 2·12, Ir–P(*trans* to C) 2·268 and 2·291, Ir–P(*trans* to Cl) 2·194, and Ir–Cl 2·416 Å. A shortening of the Ir–P bonds of *ca.* 0·08 Å compared with equivalent bonds in triphenylphosphine complexes is discussed, as are the angular deformations of the phenyl rings.

REACTIONS involving the cleavage of aryl carbon–hydrogen bonds in tertiary phosphite complexes have been described[1] but, together with the many other studies of intramolecular substitution, little is known of the role of steric and electronic effects in these reactions. The present investigation is the first of a series in which we attempt to define these factors in both mono- and poly-nuclear complexes.

EXPERIMENTAL

Crystal Data.—$C_{54}H_{43}ClIrO_9P_3$, $M = 1155{\cdot}9$, $a = 10{\cdot}964(7)$, $b = 12{\cdot}117(7)$, $c = 23{\cdot}74(2)$ Å, $\alpha = 126{\cdot}5(3)$, $\beta = 81{\cdot}5(5)$, $\gamma = 108{\cdot}0(5)°$, $U = 2550$ Å^3, $D_m = 1{\cdot}55$ (by flotation), $Z = 2$, $D_c = 1{\cdot}592$, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 31·1 cm^{-1}.

Measurement of Intensities.—Colourless, well formed crystals of $IrCl[P(OPh)_2(OC_6H_4)]_2[P(OPh)_3]$ were prepared as reported previously.[2] Preliminary unit-cell data were obtained from precession photography. Lattice constants were determined from a least-squares refinement of the setting angles of 12 reflections which had been automatically centred on a Hilger and Watts four-circle diffractometer (Mo-K_α radiation).

Data were collected for a crystal of dimensions 0·25 × 0·20 × 0·15 mm. Corrections were made for Lorentz and polarization effects and for absorption (by the method of Wells), but not for extinction effects.

Intensity measurements (zirconium-filtered molybdenum radiation) were based on an ω—2θ scan routine with background measurements (stationary crystal, stationary counter) being made at the extremities of each scan. Each background count was taken over 15 s and each peak count was accumulated over 100 steps of 0·01° with 1 s counts at each step. The diffracted rays were collected by a circular aperture of 3·5 mm diameter, 250 mm from the crystal. Attenuators of aluminium foil were inserted in the diffracted beam if the count rate exceeded 8000 Hz.

Measurements were made for all the independent reflections with $2{\cdot}0° \leqslant \theta \leqslant 25°$ and resulted in 5758 intensities with $I \geqslant 3\sigma(I)$. No systematic variations in the intensities of the two standard reflections, measured after every 100 reflections, were observed.

The *X*-ray data were re-indexed finally to be consistent with the Delaunay reduced cell of dimensions $a = 10{\cdot}964$, $b = 19{\cdot}20$, $c = 12{\cdot}117$ Å, $\alpha = 95{\cdot}9$, $\beta = 108{\cdot}0$, and $\gamma = 90{\cdot}7°$. All the atomic positions and other parameters presented are referred to this cell.

Solution and Refinement of the Structure.—The structure was solved by the usual Patterson and heavy-atom Fourier methods. Refinement was carried out using programme CRYSQ[3] in the block-diagonal mode minimising the function $\Sigma w(|F_o| - |F_c|)^2$. Unit weights were given to all observations. The iridium, chlorine, and phosphorus atoms were included with anisotropic thermal parameters and the carbon and oxygen atoms with isotropic thermal parameters. R converged to 0·052. An analysis of $\Delta = (|F_o| - |F_c|)$ against F_o and $\sin\theta/\lambda$ showed no systematic trends. A ΔF synthesis calculated using the refined parameters showed no excursions of magnitude greater than 1·7eÅ^{-3}.

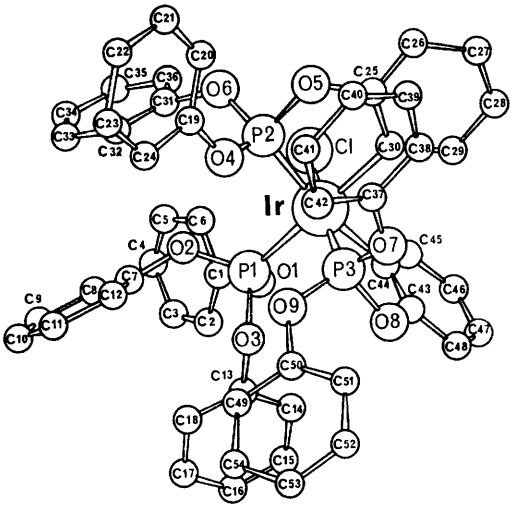

FIGURE 1

Atomic positional and thermal parameters are presented in Table 1. Important intramolecular dimensions are summarised in Table 2. Figure 1 is a perspective view giving the labelling of the atoms and Figure 2 is a view of the atoms co-ordinated to iridium with their thermal

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[1] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[2] E. W. Ainscough and S. D. Robinson, *Chem. Comm.*, 1970, 863.

[3] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *X*-Ray System, 1970, Atlas Computer Laboratory.

motions (50% probability). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20451 (6 pp., 1 microfiche).†

TABLE 1

Atomic co-ordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^2$)

	x	y	z	U
Ir	1033·0(4)	2316·1(2)	2293·8(4)	*
Cl	−746(3)	2526(1)	617(2)	*
P(1)	1274(3)	1305(1)	1249(2)	*
P(2)	2214(3)	3126(1)	1742(2)	*
P(3)	2499(3)	2196(1)	3957(2)	*
O(1)	1439(7)	3797(4)	1317(6)	480(18)
O(2)	2724(8)	2835(4)	713(7)	538(20)
O(3)	3465(7)	3464(4)	2769(6)	504(19)
O(4)	2674(7)	1016(4)	1594(6)	495(18)
O(5)	391(8)	717(4)	1507(7)	545(20)
O(6)	741(7)	1142(4)	−137(6)	458(17)
O(7)	2402(8)	1581(4)	4712(7)	541(20)
O(8)	2427(7)	2838(4)	4881(7)	515(19)
O(9)	3958(8)	2213(4)	3975(7)	523(19)
C(1)	1279(11)	4100(6)	280(10)	484(27)
C(2)	1767(14)	4780(8)	401(12)	727(38)
C(3)	1524(15)	5104(8)	−639(14)	843(45)
C(4)	838(16)	4755(8)	−1699(14)	834(44)
C(5)	408(14)	4078(8)	−1770(13)	727(39)
C(6)	599(13)	3728(7)	−761(11)	648(34)
C(7)	3913(11)	2971(6)	548(10)	494(28)
C(8)	3955(14)	3427(7)	−238(12)	698(37)
C(9)	5150(16)	3526(9)	−435(14)	878(47)
C(10)	6232(14)	3166(8)	137(13)	763(40)
C(11)	6132(14)	2704(7)	892(12)	709(38)
C(12)	4958(13)	2602(7)	1127(11)	652(35)
C(13)	3887(11)	4189(6)	3011(10)	532(29)
C(14)	3240(13)	4620(7)	3546(12)	691(37)
C(15)	3712(17)	5336(9)	3805(15)	918(49)
C(16)	4762(18)	5526(10)	3513(16)	982(53)
C(17)	5432(17)	5083(9)	2981(15)	951(51)
C(18)	4966(15)	4343(8)	2697(13)	766(41)
C(19)	3122(11)	364(6)	1285(10)	482(27)
C(20)	2298(13)	−212(7)	821(11)	600(32)
C(21)	2812(13)	−851(7)	571(12)	674(36)
C(22)	4125(15)	−885(8)	781(13)	755(40)
C(23)	4956(16)	−278(9)	1265(14)	858(46)
C(24)	4436(14)	349(8)	1501(13)	711(38)
C(25)	−398(10)	944(6)	2165(10)	462(26)
C(26)	−1238(12)	438(7)	2287(11)	580(31)
C(27)	−2045(12)	651(7)	2974(11)	597(32)
C(28)	−1949(13)	1318(7)	3501(11)	616(33)
C(29)	−1071(11)	1816(6)	3360(11)	549(30)
C(30)	−284(10)	1635(5)	2670(9)	397(24)
C(31)	1149(11)	1456(6)	−978(10)	471(31)
C(32)	2374(12)	1463(6)	−1006(11)	570(31)
C(33)	2644(14)	1757(8)	−1911(12)	711(38)
C(34)	1694(15)	2005(8)	−2786(13)	791(42)
C(35)	462(15)	1992(8)	−2740(14)	812(43)
C(36)	112(13)	1707(7)	−1835(12)	652(35)
C(37)	2491(11)	860(6)	4411(10)	511(28)
C(38)	1441(13)	456(7)	4469(11)	667(36)
C(39)	1470(15)	−270(8)	4207(13)	794(43)
C(40)	2494(16)	−561(8)	3944(14)	828(44)
C(41)	3538(15)	−140(8)	3924(13)	779(42)
C(42)	3536(13)	597(7)	4168(11)	597(32)
C(43)	1352(12)	3241(6)	4519(10)	516(28)
C(44)	577(10)	3122(5)	3378(9)	402(24)
C(45)	−516(12)	3537(6)	3052(11)	568(31)
C(46)	−784(13)	4008(7)	3896(11)	639(34)
C(47)	20(13)	4089(7)	5048(11)	641(34)
C(48)	1136(13)	3705(7)	5380(11)	613(33)
C(49)	6050(13)	2693(7)	4702(11)	629(44)
C(50)	5048(11)	2393(6)	4966(10)	550(30)
C(51)	5089(14)	2245(8)	6056(13)	717(38)
C(52)	6225(16)	2426(8)	6984(14)	828(44)
C(53)	7237(15)	2741(8)	6734(14)	805(43)
C(54)	7217(16)	2859(8)	5634(14)	819(44)

* Anisotropic thermal parameters $U_{ij} \times 10^4$ refer to the expression: $T = \exp - 2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^*)$ for the following atoms

TABLE 1 (*Continued*)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	350(2)	332(2)	339(2)	−1(1)	82(1)	37(1)
Cl	379(15)	497(16)	475(16)	12(12)	78(12)	82(12)
P(1)	359(15)	368(14)	374(15)	−6(11)	115(12)	18(11)
P(2)	377(16)	354(14)	390(15)	−9(12)	96(12)	40(11)
P(3)	412(16)	419(16)	350(15)	23(12)	77(12)	66(12)

TABLE 2

Values of selected bond lengths and angles

(*a*) Distances (Å)

Ir–Cl	2·416(7)	Ir–P(3)	2·192(3)
Ir–P(1)	2·291(3)	Ir–C(30)	2·119(12)
Ir–P(2)	2·268(3)	Ir–C(44)	2·091(11)

	Min.	Max.	Range	No.	Mean
P–O	1·573	1·615	0·042	9	1·592
O–C	1·392	1·433	0·041	9	1·408
C–C	1·340	1·471	0·131	54	1·391

(*b*) Angles (°)

Cl–Ir–P(1)	87·4	P(1)–Ir–C(44)	88·4
Cl–Ir–P(2)	87·1	P(2)–Ir–P(3)	99·4
Cl–Ir–P(3)	172·2	P(2)–Ir–C(30)	79·6
Cl–Ir–C(30)	85·4	P(2)–Ir–C(44)	168·6
Cl–Ir–C(44)	93·2	P(3)–Ir–C(30)	91·5
P(1)–Ir–P(2)	103·1	P(3)–Ir–C(44)	79·6
P(1)–Ir–P(3)	95·3	C(30)–Ir–C(48)	89·0
P(1)–Ir–C(30)	172·2		
Ir–P(1)–O(1)	113·3	Ir–P(2)–O(6)	125·5
Ir–P(1)–O(2)	113·9	Ir–P(3)–O(7)	122·0
Ir–P(1)–O(3)	114·8	Ir–P(3)–O(8)	108·2
Ir–P(2)–O(4)	115·9	Ir–P(3)–O(9)	117·2
Ir–P(2)–O(5)	106·5		
O(1)–P(1)–O(2)	105·5	O(5)–P(2)–O(6)	95·6
O(1)–P(1)–O(3)	102·9	O(7)–P(3)–O(8)	97·8
O(2)–P(1)–O(3)	105·4	O(7)–P(3)–O(9)	104·1
O(4)–P(2)–O(5)	105·4	O(8)–P(3)–O(9)	104·7
O(4)–P(2)–O(6)	104·5		
P(1)–O(1)–C(1)	128·5	P(2)–O(6)–C(31)	127·9
P(1)–O(2)–C(7)	129·2	P(3)–O(7)–C(37)	126·8
P(1)–O(3)–C(13)	126·4	P(3)–O(8)–C(43)	114·8
P(2)–O(4)–C(19)	131·1	P(3)–O(9)–C(50)	126·3
P(2)–O(5)–C(25)	116·5		
O(1)–C(1)–C(2)	116·2	O(5)–C(25)–C(30)	120·0
O(1)–C(1)–C(6)	119·1	O(6)–C(31)–C(32)	123·7
O(2)–C(7)–C(8)	117·8	O(6)–C(31)–C(36)	112·0
O(2)–C(7)–C(12)	118·3	O(7)–C(37)–C(38)	112·8
O(3)–C(13)–C(14)	117·0	O(7)–C(37)–C(42)	122·1
O(3)–C(13)–C(18)	114·4	O(8)–C(43)–C(44)	118·4
O(4)–C(19)–C(20)	121·5	O(8)–C(43)–C(48)	115·5
O(4)–C(19)–C(24)	115·0	O(9)–C(50)–C(49)	113·2
O(5)–C(25)–C(26)	115·5	O(9)–C(50)–C(54)	124·6

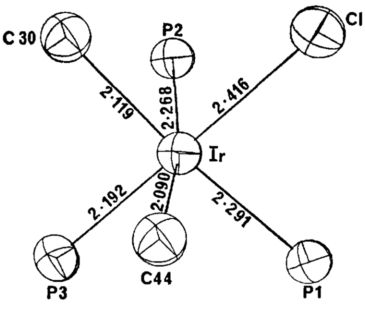

FIGURE 2

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

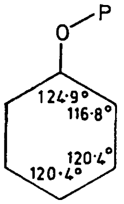
The atomic scattering factors used were those for Ir^{3+}, P, Cl^-, O, N, and C.[4] The effects of anomalous dispersion from the iridium only, were included in the calculations by use of the values of $\Delta f'$ and $\Delta f''$ given in ref. 5.

DISCUSSION

Description of the Molecular Structure.—Intramolecular aromatic substitution involving oxidative addition of a transition-metal ion to a β-carbon–hydrogen bond of a co-ordinated tertiary-phosphine or -phosphite is now well recognised, but the present complex is the first for which detailed stereochemical data have become available. The most significant feature of the analysis is the confirmation of the formation of two metal–carbon σ bonds of lengths 2·120 and 2·092 Å. The parallel formation of two five-membered chelate rings involves little steric strain: the metal–carbon bond lengths are identical, within experimental error, with those of the Ir–C(Me) bonds in di-μ-chloro-dichloro(dimethyl)tetracarbonyldi-iridium(III);[6] the chelate rings are essentially planar, the root-mean-square deviations of the atoms from each relevant plane being 0·05 Å; concessions to chelate formation are reflected in the mean P–O–C bond angles which are 116° for those involving the carbon atoms co-ordinated to the metal and 128° for the remainder and in the O–P–O angles which show significant distortions from C_{3v} symmetry in the case of P(2) and P(3), but average 104·6° for those around P(1) with none of the three dimensions differing significantly from the mean.

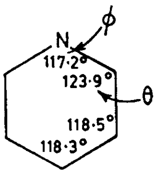
The mean iridium–phosphorus bond length (2·280 Å) for the bonds *trans* to the σ-bonded carbon atoms is 0·085 Å greater than that of the Ir–P(3) bond *trans* to the chloride ligand; this result is quantitatively in keeping with expectation from the experimental results and the theory of the *trans*-influence of ligands in planar and octahedral complexes.[7] The metal–phosphorus bond lengths are systematically shorter than those observed in analogous tertiary-phosphine complexes. For example, in *mer*-$IrCl_3(PMe_2Ph)_3$[8] the iridium–phosphorus bond *trans* to the chloride ion has a length of 2·277(6) Å, whereas the Ir–Cl bond *trans* to the phosphine ligand has a length of 2·429(6) Å which is identical, within experimental error, with that observed here. Two explanations, which are more complementary than exclusive, can be mentioned. (i) The phosphorus lone-pair orbital contributing to the metal–phosphorus σ-bond, has a very different *s–p* hybridisation in a tertiary-phosphine and -phosphite. Since the effective radius of a phosphorus '*s*' orbital is *ca.* 0·3 Å smaller than that of the '*p*' orbital,[9] our results would require that the phosphite-phosphorus lone pair orbital has significantly more '*s*' character than is the case for the corresponding phosphine. The mean O–P–O bond angle in the present complex is 104·6°, while the mean C–P–C bond angle in tertiary triphenylphosphine complexes of transition metals is *ca.* 103°; on this criterion, which may be misleading, it appears that the phosphorus uses substantially equivalent orbitals in the P–O and P–C σ-bonds.

(ii) A tertiary aryl phosphite ligand is a better π-acid than an arylphosphine even in complexes where the formal oxidation state of the metal is as high as +3. Here the qualitative argument is that it is the effective electronegativity of the oxygen atoms which makes the phosphorus virtual orbitals more energetically suitable for π bonding with the metal and, as a corollary, that the oxygen ' non-bonding ' orbitals are, at best, involved in some bonding interactions with the carbon atoms of the phenyl rings. The best evidence for this view comes from the average bond angles in the phenyl rings which are summarised in (I) (see also Table 2) (the phenyl groups of a co-ordinated triphenylphosphine ligand have six-fold symmetry within the experimental error of most structural determinations).



(I)

These data are analogous, while having a different sense, to those found in *N*-heterocycles such as pyridine (II), where Coulson and Looyenga[10] have shown an additivity relation for the bond angles so that successive replacements of CH by N may be treated as small, incremental perturbations. As in pyridine, it is only the bond angles, θ, in addition to ϕ, which show significant distortion from trigonal symmetry and which together argue that the *O*-substituted carbon atom is less electronegative than a normal sp^2 carbon atom and that there is considerable charge-transfer to the oxygen and *ortho*-carbon ring atoms.



(II)

One circumstantial evidence pointing towards the greater Lewis acidity, with respect to Ir^I, of triphenyl phosphite compared with triphenylphosphine, is the easy formation of the present complex containing two

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[7] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

[8] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

[9] C. A. Coulson and F. A. Gianturco, *J. Chem. Soc.* (*A*), 1968, 1618.

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metal–carbon σ-bonds. Bennett and Milner[11] have established parallel reactions with triphenylphosphine complexes but to give, as yet, products with only one cleaved C–H bond. A reasonable charge distribution on the metal (electroneutrality) will be achieved in both cases if qualitatively, metal–phosphite π-bonding is more effective than metal–phosphine back-donation of charge.

It must be conceded that the proposition of metal–ligand π-bonding in complexes of iridium(III) does not have immediate appeal; but changes in the σ-electron framework only do not presently seem able to provide a complete rationale for the metal–ligand bond lengths.

Crystal Structure.—There are no unusually short non-bonded atomic contacts. The general packing, as indeed the total molecular structure, reflects the substantial steric requirements of the tertiary phosphite ligands.

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[2/643 *Received*, 20*th March*, 1972]

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