# Crystal Structures of Mercury(ii) Chloride and Bromide Addition Complexes of Carbonylchlorobis(triphenylphosphine)iridium(i)

By **Peter D. Brotherton, Colin L. Raston, Allan H. White,*** and **Stanley Bruce Wild,** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

The crystal structures of the oxidative-addition products of *trans*-[IrCl(CO)(PPh$_3$)$_2$] with HgCl$_2$ and HgBr$_2$ have been determined by X-ray diffraction. The structure of [IrCl$_2$(HgCl)(CO)(PPh$_3$)$_2$] was refined by least squares to R 0.059 (3 430 observed reflections). Crystals are monoclinic, space group $P2_1/n$, a = 15.805(2), b = 21.734(3), c = 10.537(1) Å, β = 92.13(2)°, Z = 4. The two chlorines bonded to the pseudo-octahedral iridium are mutually *cis* [Ir–Cl, 2.453(5), 2.401(4) Å], while the two PPh$_3$ ligands are *trans* [Ir–P, 2.387(4), 2.378(4) Å], with the HgCl group *trans* to the Ir–Cl bond [Ir–Hg, 2.570(1) Å]. The mercury atom lies close to a centre of symmetry and Ir–Hg–Cl is slightly perturbed from linearity by interaction of Hg with the chlorine of its inversion image [Hg–Cl, 2.366(5), Hg · · · Cl′, 3.148(5) Å; Ir–Hg–Cl, 172.2(1)°]. The structure of the isomorphous [IrBrCl(HgBr)(CO)-(PPh$_3$)$_2$] [a = 16.021(7), b = 21.788(6), c = 10.568(4) Å, β = 93.11(3)°] indicates that the oxidative-addition reaction is predominantly *trans* in this instance: the partial bromine occupancy of the equatorial chlorine site is *ca.* 0.15; R was 0.072 for 3 810 observed reflections.

TREATMENT of a benzene solution of *trans*-[Ir(CO)Cl-(PPh$_3$)$_2$] with either mercury(ii) chloride or bromide in ethanol produces [equation (1)] almost colourless solutions of the 1 : 1 adducts [IrCl$_2$(HgCl)(CO)(PPh$_3$)$_2$], (I), and [IrBrCl(HgBr)(CO)(PPh$_3$)$_2$], (II), respectively.[1]

$$trans\text{-}[IrCl(CO)(PPh_3)_2] + HgX_2 \rightleftharpoons$$
$$[IrClX(HgX)(CO)(PPh_3)_2] \quad (1)$$
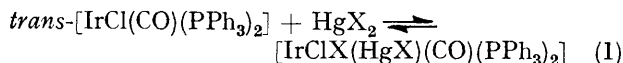
The adducts crystallize as colourless (I) or pale yellow (II) isomorphous prisms; crystals 0.10 × 0.15 × 0.25 mm (I) and 0.07 × 0.18 × 0.07 mm (II) were used for the crystallographic work. From the structure of (II) it appears that the oxidative-addition is predominantly *trans* in this instance.

EXPERIMENTAL

Experimental details are given for (I), with those for (II) in parentheses where different. Unit-cell calibration was carried out by a least-squares fit of the angular parameters

of 15 reflections with 2θ *ca.* 30° (20°) centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer; unique data sets in the range 2θ < 100° (50°) were gathered by conventional 2θ—θ scans yielding 3 446 (4 773) independent reflections, 3 430 (3 810) of these with $I > 2(3)\sigma(I)$ being considered 'observed' and used in the structure solution and refinement after correction for absorption.

Crystal Data.—C$_{37}$H$_{30}$Cl$_3$HgIrOP$_2$ (C$_{37}$H$_{30}$Br$_{2.15}$Cl$_{0.85}$-HgIrOP$_2$), M = 1 052 (1 149), Monoclinic, a = 15.805(2) [16.021(7)], b = 21.734(3) [21.788(6)], c = 10.537(1) [10.568(4)] Å, β = 92.13(2) [93.11(3)]°, D_m = 1.92(1) (2.07$_4$), Z = 4, D_c = 1.92 (2.073) g cm^{-3}, $F(000)$ = 1 992 (2 147). Cu-K_α radiation, Ni-filtered, λ = 1.541 8 Å [Mo-K_α radiation, monochromatic, λ = 0.710 79 Å]; μ(Cu-K_α) 180 cm^{-1} [μ(Mo-K_α) 100 cm^{-1}]. Space group $P2_1/n$ (C_{2h}^5, No. 14). Neutral-atom scattering factors Hg, Ir, Br, Cl, P corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[2,3]

The structures were solved by the heavy-atom method

1 R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.
2 D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
3 D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

TABLE 1

Atomic fractional cell parameters (x, y, z) and thermal parameters $(\times 10^3\ \text{Å}^2)$, with least-squares estimated standard deviations in parentheses

(I) x, y, z: for Hg, Ir $\times 10^5$, Cl, P $\times 10^4$, others $\times 10^3$

Atom	x	y	z		Atom	x	y	z
Ir	29 824(4)	36 978(3)	40 463(6)		C(3)	482(2)	196(1)	239(2)
Hg	39 629(5)	44 398(3)	53 028(7)		C(4)	564(2)	186(1)	294(3)
Cl(1)	2 087(3)	3 001(2)	2 752(4)		C(5)	577(1)	200(1)	419(3)
Cl(2)	4 735(3)	5 109(3)	6 687(4)		C(6)	516(1)	231(1)	499(2)
Cl(3)	2 018(3)	3 852(2)	5 725(4)					
C	381(1)	364(1)	293(1)		**Phenyl ring (4)**			
O	433(1)	361(1)	221(1)		C(1)	256(1)	456(1)	134(1)
P(1)	3 516(3)	2 814(2)	5 157(4)		C(2)	199(1)	436(1)	038(2)
P(2)	2 316(3)	4 547(2)	2 997(4)		C(3)	222(1)	432(1)	−090(2)
					C(4)	302(1)	446(1)	−120(2)
Phenyl ring (1)					C(5)	366(1)	465(1)	−028(2)
C(1)	392(1)	297(1)	678(1)		C(6)	341(1)	472(1)	100(2)
C(2)	468(1)	332(1)	695(2)					
C(3)	498(2)	346(1)	819(3)		**Phenyl ring (5)**			
C(4)	454(2)	322(1)	925(2)		C(1)	116(1)	459(1)	297(2)
C(5)	380(2)	291(1)	907(2)		C(2)	066(1)	409(1)	326(2)
C(6)	348(1)	275(1)	778(2)		C(3)	−025(1)	415(1)	319(2)
					C(4)	−061(1)	468(1)	291(3)
Phenyl ring (2)					C(5)	−011(1)	517(1)	266(5)
C(1)	280(1)	218(1)	539(2)		C(6)	076(1)	513(1)	262(1)
C(2)	311(1)	158(1)	539(2)					
C(3)	255(2)	110(1)	575(2)		**Phenyl ring (6)**			
C(4)	173(1)	120(1)	618(2)		C(1)	259(1)	532(1)	359(1)
C(5)	144(1)	182(1)	612(2)		C(2)	279(1)	580(1)	275(2)
C(6)	193(1)	231(1)	567(2)		C(3)	296(1)	638(1)	332(2)
					C(4)	289(2)	650(1)	456(3)
Phenyl ring (3)					C(5)	267(1)	603(1)	536(2)
C(1)	438(1)	243(1)	435(2)		C(6)	250(1)	543(1)	488(2)
C(2)	417(1)	227(1)	307(2)					

(II) x, y, z: Ir, Hg $\times 10^5$, Br, Cl, P $\times 10^4$; others $\times 10^3$

Atom	x	y	z	U		Atom	x	y	z	U
Ir	29 146(8)	36 984(7)	4 065(1)			**Ring (3)**				
Hg	39 018(9)	44 605(8)	5 264(1)			C(1)	435(2)	243(2)	436(3)	46(10)
Br(1)	1 898(3)	2 986(2)	2 772(4)			C(2)	405(2)	220(2)	313(3)	44(10)
Br(2)	4 667(3)	5 206(2)	6 700(4)			C(3)	468(3)	194(2)	239(4)	82(15)
Cl(3)	2 067(10)	3 869(8)	585(1)			C(4)	551(3)	186(2)	292(4)	84(15)
Br(3)	1 891(23)	3 845(19)	5 784(35)			C(5)	571(3)	205(2)	408(4)	97(16)
P(1)	3 490(6)	2 811(5)	5 156(8)			C(6)	512(2)	234(2)	483(3)	53(11)
P(2)	2 253(6)	4 554(4)	3 008(8)							
C	368(—)	362(—)	290(—)			**Ring (4)**				
O	418(1)	357(1)	215(2)			C(1)	252(2)	456(1)	136(3)	30(8)
						C(2)	199(2)	432(2)	041(3)	52(10)
Phenyl rings						C(3)	226(2)	427(2)	−080(3)	41(9)
Atom	x	y	z	U		C(4)	306(2)	443(2)	−111(3)	59(11)
Ring (1)						C(5)	362(2)	468(2)	−015(2)	36(9)
C(1)	401(2)	298(2)	676(3)	46(9)		C(6)	335(2)	472(2)	103(3)	41(9)
C(2)	471(2)	332(2)	687(3)	50(10)						
C(3)	505(3)	348(2)	809(4)	94(16)		**Ring (5)**				
C(4)	467(3)	327(2)	915(4)	93(16)		C(1)	111(2)	461(2)	292(3)	45(10)
C(5)	397(3)	289(2)	905(4)	83(15)		C(2)	058(3)	415(2)	335(4)	75(13)
C(6)	359(2)	279(2)	779(4)	64(12)		C(3)	−028(3)	423(2)	336(5)	108(18)
						C(4)	−064(3)	474(2)	280(4)	86(15)
Ring (2)						C(5)	−017(3)	513(2)	216(5)	92(16)
C(1)	276(2)	218(1)	542(3)	25(8)		C(6)	074(3)	508(2)	222(4)	76(14)
C(2)	307(2)	157(2)	542(3)	57(11)						
C(3)	260(2)	109(2)	578(3)	58(11)		**Ring (6)**				
C(4)	178(3)	121(2)	623(4)	75(13)		C(1)	253(2)	530(2)	362(3)	41(9)
C(5)	140(3)	179(2)	621(4)	87(15)		C(2)	277(2)	580(2)	294(4)	63(12)
C(6)	198(2)	230(2)	579(3)	57(11)		C(3)	291(3)	639(2)	304(4)	63(12)
						C(4)	279(2)	653(2)	469(5)	101(17)
						C(5)	252(3)	605(2)	546(5)	106(18)
						C(6)	241(2)	546(2)	487(3)	48(10)

and refined by 9 × 9 block-diagonal least squares, the parameters of (i) the $IrHgP_2Cl_3CO$ ($IrHgP_2ClBr_2CO$) cores and (ii) the individual phenyl rings being refined as single blocks in order to approximate to a full-matrix procedure; in (I) all atoms were refined anisotropically according to the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$, but in (II) only the Hg, Ir, Br, and P atoms could be refined significantly in this manner and the remainder were treated isotropically. Hydrogen atoms could not be located in difference maps for either structure and were neglected. In (I), refinement was straightforward and converged with parameter shifts $<0.2\sigma$, R being 0.059 and R' $[=(\Sigma w|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ 0.076, in a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$, a value of $n = 10$ being found appropriate.

Refinement of (II) was much less straightforward than expected in spite of the greater extent of the data set. With the data cut at $I > \sigma(I)$, R could not be reduced below 0.10, and more drastic (and less justifiable) cuts at $I > 2,3\ \sigma(I)$ did not reduce R to <0.08; although the intensity of the data set was rather less than that of (I), this did not seem a valid reason for the inability to reduce R to a satisfactory value. In addition, the thermal tensor for the chlorine atom was found to be non-positive definite. Inspection of a difference map showed a pronounced region of electron density at the periphery of the chlorine atom opposite the Ir–Cl bond and it was considered desirable to explore the possibility of partial occupancy of the site by a bromine atom. It was estimated from the difference map that the site

(1.54 Å) and was constrained at Ir–C, 1.80 Å, and the weak data has been cut rather drastically, indicating a possible deficiency in the description of the 'high-angle scatterers,' probably the bromines, which may deviate slightly in occupancy of their sites from the assigned values; the data of (II), however, were less reliable than those of (I). Computation was carried out on our CDC 6200 machine with a local variant of the 'X-Ray '72' system.[4] Structure amplitude tables, anisotropic thermal parameters of the heavy atoms, least-squares planes of the phenyl rings, and detailed phenyl ring geometries, are deposited as Supplementary Publication No. SUP 21763 (35 pp., 1 microfiche).*

The phenyl carbon atoms are labelled C(n 1—6) where n is the ring number [$n = 1$—6, where $n = 1$—3 are attached to

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses. Values for (II) follow those for (I); alternative atoms in (II) are given in square brackets

(a) Iridium environment

Ir–C	1.80(2), 1.80	Hg–Ir–P(1)	93.3(1), 94.2(2)
Ir–Hg	2.570(1), 2.578(2)	Hg–Ir–P(2)	90.0(1), 88.4(2)
Ir–P(1)	2.387(4), 2.41(1)	Hg–Ir–Cl[Br(1)]	177.1(1), 176.6(1)
Ir–P(2)	2.378(4), 2.39(1)	Hg–Ir–Cl(3)	84.5(1), 82.7(4)
Ir–Cl[Br(1)]	2.453(5), 2.586(5)	P(1)–Ir–P(2)	174.4(2), 176.2(3)
Ir–Cl(3)	2.401(4), 2.41(2) *	P(1)–Ir–Cl[Br(1)]	87.8(2), 82.7(4)
C–Ir–Hg	86.4(5), 88.4	P(1)–Ir–Cl(3)	88.5(1), 88.1(5)
C–Ir–P(1)	90.9(5), 89.7	P(2)–Ir–Cl[Br(1)]	89.1(1), 88.3(2)
C–Ir–P(2)	93.9(5), 93.3	P(2)–Ir–Cl(3)	87.2(1), 89.5(5)
C–Ir–Cl[Br(1)]	90.9(5), 90.9	Cl[Br(1)]–Ir–Cl(3)	97.3(2), 98.1(4)
C–Ir–Cl(3)	171.7(5), 170.6	C–O	1.14(2), 1.115
		Ir–C–O	179(1), 180

(b) Mercury environment

Hg–Ir	2.570(1), 2.578(2)	Ir–Hg–Cl[Br(2)]	172.1(2), 170.0(1)
Hg–Cl[Br(2)]	2.366(4), 2.499(5)	Ir–Hg–Cl[Br(2$^{\rm I}$)]	104.4(1), 105.4(1)
Hg–Cl[Br(2$^{\rm I}$)]	3.148(5), 3.257(5)	Cl[Br(2)]–Hg–Cl[Br(2$^{\rm I}$)]	83.3(2), 84.4(1)
		Hg–Cl[Br(2)]–Hg$^{\rm I}$	97.6(2), 95.6(1)

Atoms with superscript I are at: $1 - x, 1 - y, 1 - z$

(c) Phosphorus atoms

P(1)–C(11)	1.83(2), 1.88(3)	P(2)–C(41)	1.80(2), 1.83(3)
P(1)–C(21)	1.81(2), 1.83(2)	P(2)–C(51)	1.83(2), 1.84(3)
P(1)–C(31)	1.84(2), 1.85(3)	P(2)–C(61)	1.83(2), 1.81(3)
Ir–P(1)–C(11)	114.5(6), 114(1)	Ir–P(2)–C(41)	110.7(5), 109(1)
Ir–P(1)–C(21)	117.9(6), 116(1)	Ir–P(2)–C(51)	118.0(5), 119(1)
Ir–P(1)–C(31)	113.1(5), 114(1)	Ir–P(2)–C(61)	116.9(5), 116(1)
C(11)–P(1)–C(21)	101.7(8), 105(1)	C(41)–P–C(51)	103.4(8), 104(1)
C(11)–P(1)–C(31)	106.2(8), 101(2)	C(41)–P–C(61)	105.4(8), 106(2)
C(21)–P(1)–C(31)	101.8(8), 103(2)	C(51)–P–C(61)	10.09(7), 101(2)

(d) Mean dimensions of benzene rings

C–C	1.41, 1.40
C–C–C	119.9, 119.9
P–C–C	119, 120

* For (II) Ir–Br(3) 2.54(4).

would be *ca.* 85% chlorine, 15% bromine occupancy; holding the populations constant, the other parameters of the two components were refined and it was found that Ir–Cl [which had previously been somewhat long (2.44 Å)] contracted to a value very similar to that observed for (I) while Ir–Br refined to a value not significantly different from that observed for the other Ir–Br bond *trans* to the mercury, R being reduced significantly in the process. A difference map calculated at this point showed no further significant features about the halogen atoms. It is possible, however, that the model remains somewhat deficient: R at refinement termination is still rather high (0.072) [R' at 0.078, is comparable with the value for (I), however, n being 3], the carbonyl atom adopts an unreasonably short Ir–C distance

* For details see Notice to Authors, No. 7 in *J.C.S. Dalton*, Index issue, 1975.

P(1)] and C(nl) is attached to the phosphorus. Cl(1) and Cl(3) are attached to iridium, Cl(2) to the mercury. In (II), Cl(1) and Cl(2) are replaced by Br(1) and Br(2); Cl(3) is *trans* to the carbonyl in both but in (II) is partly occupied by Br(3). Final atom parameters are listed in Table 1, interatomic distances and angles in Table 2.

DISCUSSION

There is an extensive literature [5] describing oxidative addition reactions of *trans*-[IrCl(CO)(PPh$_3$)$_2$]. Kinetic data for the reactions have usually been interpreted in

4 'The X-Ray' Program System, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

5 J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

terms of two limiting mechanisms: (a), a concerted process involving a relatively non-polar transition-state,
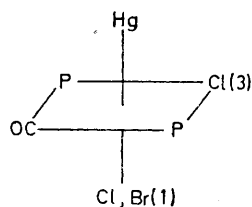

FIGURE 1 The iridium co-ordination in (I) and (II)

resulting in cis-addition; (b) an S_N2 attack by the iridium at an electrophilic centre in the substrate molecule involving a polar transition-state and usually yielding a trans-product. Process (a) is envisaged for H_2 or O_2 addition while (b) appears to occur in the reactions of alkyl and benzyl halides with the basic iridium(I) complexes. In view of the well known Lewis acidity of mercury(II) halides towards low-oxidation-state transition-metal complexes [6] it was considered of interest to establish the stereochemistry of (I) and (II) since their structures may provide an insight into the nature of the oxidative-addition mechanism.

origin does not appear to be well understood. The present values are not extreme and are unremarkable.

TABLE 3

Equations of two least-squares planes in the form $pX + qY + rZ = s$, where x,y,z are orthogonal right-handed Å axes defined with X parallel to a, and Z in the ac plane. Atom deviations (Å) are given in square brackets

Plane through Ir, Hg(1), Cl(2) and inversion images

	10^4p	10^4q	10^4r	s	σ	χ^2
(I)	$-5\ 992$	$7\ 571$	$-2\ 605$	2.238	0.01	63.6
	[Ir 0.01, Hg(1) -0.02, Cl(2) 0.01]					
(II)	$-5\ 416$	$7\ 531$	$-3\ 734$	2 051	0.02	35.4
	[Ir 0.01, Hg(1) -0.03, Cl(2) 0.01]					

The mercury–iridium bond appears to be the first such distance established crystallographically. The mercury geometry is approximately linear, with Ir–Hg–Cl angle $172(1)°$; the deviation from linearity appears to be a result of the orientation of the group close to the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ so that the rather close approach of the chlorine inversion image at 3.148(5) Å perturbs
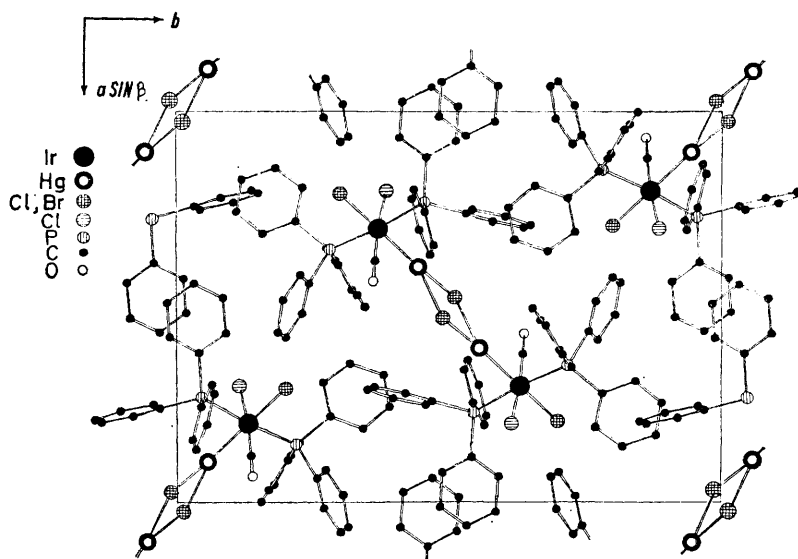

FIGURE 2   Unit-cell contents projected down c

Although six isomers are possible for (I), and eight for (II), the crystal structures (Figure 1) reveal the products to be those expected from an S_N2 type process (b) in which the nucleophilic iridium complex retains its trans-stereochemistry. The structure of (II) also suggests that ca. 15% exchange of halogen atoms has occurred during preparation and isolation. Large variations are reported for the many accurately determined iridium–carbonyl, –phosphorus, and –chlorine distances and their

the environment. If considered as a dimer, the [IrCl$_2$-(HgCl)(CO)$_2$] atoms of (I) comprise quite a good plane (Table 3), with the phosphine ligands projecting on either side; the same is true of (II).

Figure 2 shows a projection of the unit-cell contents.

6 K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, J. Chem. Soc., (A) 1968, 2851.