992. *Metal–Metal Bonds. Part IV.*[1] *Formation of Iridium–Mercury Bonds by Oxidation with Mercury Halides*

By R. S. Nyholm and K. Vrieze

Compounds of the type $(Ph_3P)_2(CO)Cl_2Ir{-}HgCl$ are prepared in 30% yield by the treatment of $(Ph_3P)_2COCl_2IrH$ with mercury chlorides (as in the preceding paper), but quantitative yields are obtained by reaction of the square-planar complex $(Ph_3P)_2(CO)ClIr$ with mercuric chloride. By use of this general reaction a series of complexes of the type $(Ph_3P)_2(CO)ClYIr{-}HgY$ (where Y = Cl, Br, I, OAc, CN, and SCN) and $(Ph_3P)_2(CO)Br_2Ir{-}HgBr$ are formed by the reaction of the corresponding iridium(I) complex with mercuric or mercurous halides.

The compound $(Ph_3P)_2(CO)Cl_2Ir{-}HgCl$ reacts with triphenylphosphine (but not triphenylarsine) to give $(Ph_3P)_2(CO)IrCl$ and a mixture of 1 : 1 and 1 : 2 adducts of $HgCl_2$ and Ph_3P. In all cases the iridium–mercury bond is cleaved by halogens and by gaseous hydrogen chloride; in the case of $(Ph_3P)_2(CO)Cl_2Ir{-}HgCl$ the Ir–Hg bond is broken by molecular hydrogen at room temperature without the presence of a catalyst. The products are $(Ph_3P)_2(CO)Cl_2IrH$, mercurous chloride, mercury, and hydrogen chloride. The behaviour of several other square d^8 complexes with mercuric chloride has also been studied.

In view of the preparation of the rhodium–mercury bonded compounds (see preceding Paper) we have studied the reaction of mercuric chloride with $(Ph_3P)_2(CO)Cl_2IrH$ and $(Ph_3P)_2(CO)ClIrH_2$ in ethanol solution. These two hydrides had been prepared[2] by the oxidation of the univalent iridium compound $(Ph_3P)_2(CO)IrCl$ with hydrogen chloride and hydrogen, respectively. Both hydrides afforded the white complex $(Ph_3P)_2(CO)Cl_2IrHgCl$ in about 30% yield. It was not possible to replace both hydrogen atoms in the dihydride by HgCl groups to obtain a derivative containing two HgCl ligands.

The diamagnetic univalent iridium complex $(Ph_3P)_2(CO)IrCl$ has many unusual properties; it can also be oxidised by carbon tetrachloride and by methyl iodide to yield octahedral tervalent iridium compounds.[3] This led us to study the behaviour of this square complex with mercuric, mercurous, and other post-transition metal halides, to determine whether iridium-to-post-transition metal-to-metal bonds could be formed.

The treatment of the lemon yellow $(Ph_3P)_2(CO)IrCl$ in ethanol-benzene with mercuric chloride gave instantly at room temperature a colourless solution from which the white complex $(Ph_3P)_2(CO)Cl_2IrHgCl$ could be isolated. The reaction was studied by spectrophotometric titration at 4500 Å; exactly 1 mole of mercuric chloride is used for the oxidation of 1 mole of the iridium complex (see Figure 1). The monomeric complexes $(Ph_3P)_2(CO)Cl_2YIrHgY$ (Y = Cl, Br, I, OAc, CN, SCN) and $(Ph_3P)_2(CO)Br_2IrHgBr$ were formed quantitatively by addition of HgY_2 to solutions of $(Ph_3P)_2(CO)IrX$ in suitable solvents. Mercuric fluoride is, however, completely reduced to metallic mercury.

Attempts to attach two HgY groups to one iridium atom by use of Hg_2Y_2 (Y = Cl, Br, I, OAc) as the oxidant were not successful. In each case the compounds containing one Hg–Ir bond were formed, with the precipitation of mercury:

$$(Ph_3P)_2(CO)IrCl + Hg_2Y_2 \longrightarrow (Ph_3P)_2(CO)ClYIrHgY + Hg$$

The iridium–mercury complexes are stable to air, moisture, and ultraviolet irradiation. They are soluble in nitrobenzene, benzene, and chloroform, very slightly soluble in ethanol

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[1] Part III, R. S. Nyholm and K. Vrieze, preceding Paper; preliminary communication, *Chem. and Ind.*, 1964, 318.

[2] J. W. Diluzio and L. Vaska, *J. Amer. Chem. Soc.*, 1961, **83**, 2784; 1962, **84**, 679.

[3] F. A. Cotton and G. Wilkinson, "Inorganic Chemistry," Interscience, New York, 1961, p. 644.

and acetone, and insoluble in water. All are monomeric in benzene or chloroform, and behave as non-electrolytes in nitrobenzene.

The molar susceptibility of all the compounds, after being corrected for the diamagnetism of the ligands, is about +60 c.g.s. units. Temperature-dependence measurements from 80°K to room temperature showed this weak paramagnetism to be independent of temperature. The complexes thus have either a small temperature-independent paramagnetism, or, in view of the uncertainty in the values of the diamagnetic corrections, the metal atoms are diamagnetic.

TABLE 1

Properties of complexes of the type $(Ph_3P)_2(CO)ClYIr{-}HgY$, and of some related compounds

			Mol. wt. ($\sim 16 \times 10^{-3}$M-soln.)		ν(CO)
Compound	Colour	M. p.	Found	Calc.	(cm.$^{-1}$)
$(Ph_3P)_2(CO)ClIr$	Lemon yellow	323—325°	—	780	1944
$(Ph_3P)_2(CO)Cl_2Ir{-}Cl$	White	—	—	851	2080
$(Ph_3P)_2(CO)Cl_2Ir{-}H$	White	315—320	—	816	2045 ($CHCl_3$)
$(Ph_3P)_2(CO)Cl_2Ir{-}HgCl$	White	270	1039 (C_6H_6)	1051	2030 ,,
$(Ph_3P)_2(CO)ClBrIr{-}HgBr$	Pale yellow	275	1080 ,,	1140	2030 ,,
$(Ph_3P)_2(CO)ClIIr{-}HgI$	Yellow	248	1195 ,,	1234	2037 ,,
$(Ph_3P)_2(CO)Cl(OAc)Ir{-}HgOAc$ * ...	White	213	1098 ($CHCl_3$)	1077	2030 ,,
$(Ph_3P)_2(CO)Cl(CN)Ir{-}HgCN$ †	White	248	1041 ,,	1032	2070 ,,
$(Ph_3P)_2(CO)Cl(CNS)Ir{-}HgCNS$ ‡...	White	190	1090 ,,	1096	2066 ,,
$(Ph_3P)_2(CO)Br_2Ir{-}HgBr$	Pale yellow	260—265	— §	1185	2040 ,,

All derivatives are virtually non-electrolytes ($\Lambda_M \leqslant 1$ ohm^{-1} cm.^{2} mole^{-1} at 10^{-3}M in $PhNO_2$)

* CO_2^- bands at 1618, 1600, and 1575 cm.$^{-1}$ (asym.), and 1368 and 1316 cm.$^{-1}$ (sym.), in Nujol. † C–N bands at 2128 and 2150 cm.$^{-1}$, in $CHCl_3$. ‡ C–N bands at 2096 and 2130 cm.$^{-1}$, in $CHCl_3$. § Not sufficiently soluble.

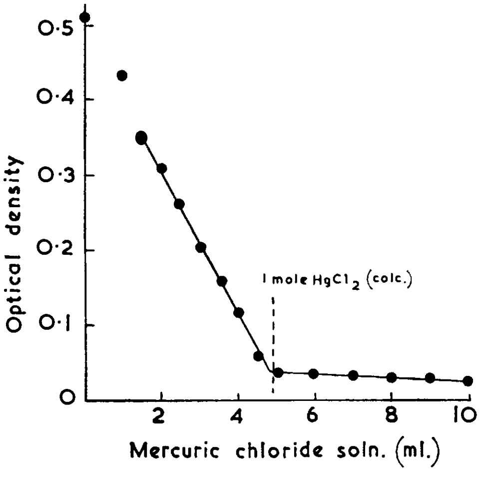


FIGURE 1. Spectrophotometric titration (λ = 4500 Å) of $(Ph_3P)_2(CO)IrCl$ ($\sim 10^{-3}$M) in benzene with mercuric chloride ($\sim 6 \times 10^{-3}$M) in ethanol

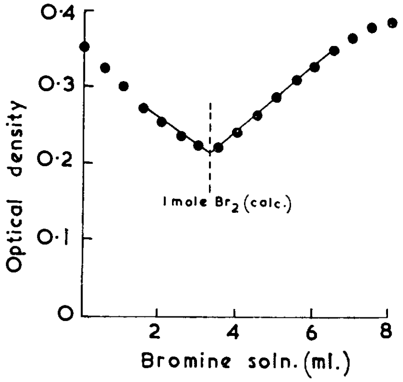


FIGURE 2. Spectrophotometric titration (λ = 4000 Å) of $(Ph_3P)_2(CO)ClBrIr{-}HgBr$ ($\sim 0{\cdot}8 \times 10^{-3}$M) with bromine ($\sim 6 \times 10^{-3}$M) in dichloromethane

Reactions with Oxidising Agents.—Oxidation of the Ir–Hg compounds with halogens (in dichloromethane) and with gaseous hydrogen chloride (in ether suspension) proceeded as in the following examples:

$$\underset{\text{yellow}}{(Ph_3P)_2(CO)ClIIr{-}HgI} + I_2 \longrightarrow \underset{\text{orange}}{(Ph_3P)_2(CO)ClIIrI} + \underset{\text{red}}{HgI_2}$$

$$(Ph_3P)_2(CO)ClBrIr{-}HgBr + Br_2 \longrightarrow (Ph_3P)_2(CO)ClBrIr{-}Br + HgBr_2$$

$$(Ph_3P)_2(CO)Cl_2Ir{-}HgCl + HCl \longrightarrow (Ph_3P)_2(CO)Cl_2IrH + HgCl_2$$

Spectrophotometric titration at 4000 Å showed that exactly 1 mole of $(Ph_3P)_2(CO)ClBrIrHgBr$ reacted with 1 mole of bromine (see Figure 2). The iridium compounds isolated from the three reactions were identical with the products obtained from the reactions of $(Ph_3P)_2(CO)ClIr$ with iodine, bromine, and gaseous hydrogen chloride, respectively, as was shown from colours, mixed melting points, infrared spectra, and elemental analyses.

TABLE 2

Properties of products of oxidation of $(Ph_3P)_2(CO)IrCl$

Oxidant	Compound formed	Colour	M. p.	ν(C–O) (cm.$^{-1}$)	ν(Ir–H) (cm.$^{-1}$)
I_2	$(Ph_3P)_2(CO)ClIIr–I$	Orange	277°	2070 *	—
Br_2	$(Ph_3P)_2(CO)ClBr\ Ir–Br$	Deep yellow	272	2070 *	—
HCl	$(Ph_3P)_2(CO)Cl_2Ir–H$	White	317	2030 †	2245

* Nujol mull. † 2045 cm.$^{-1}$ in chloroform solution, see ref. 2.

The reaction of the complex $(Ph_3P)_2(CO)Cl_2Ir–HgCl$ in benzene with molecular hydrogen is of special interest; even in the absence of a catalyst at room temperature, reaction occurred (20—30 hr.) which yielded metallic mercury, some mercurous chloride, and the hydride $(Ph_3P)_2(CO)Cl_2Ir–H$. The latter was slightly contaminated with $(Ph_3P)_2(CO)Cl_2Ir–Cl$. This uncatalysed splitting of a metal–metal bond with hydrogen has also been observed [4] in the case of $(Ph_3P)_2Pt(GePh_3)_2$; in this instance one of the Pt–Ge bonds is broken.

Reactions with Donor Compounds.—When triphenylphosphine was added to a colourless solution of $(Ph_3P)_2(CO)Cl_2Ir–HgCl$ in benzene at room temperature, the colour instantly changed to lemon yellow. Concentration of the solution yielded initially a white crystalline product, and subsequently the lemon yellow compound $(Ph_3P)_2(CO)IrCl$. The latter compound was identified from its *X*-ray powder pattern, melting point, infrared spectra, and by oxidation with mercuric chloride. Comparison of *X*-ray powder patterns of $(Ph_3P)_2HgCl_2$ and $(Ph_3P,HgCl_2)_2$ * with the powder pattern of the white powder formed indicated that this product contained a mixture of the 2 : 1 and 1 : 1 adducts of Ph_3P and $HgCl_2$. The reaction apparently proceeded as follows:

$$(Ph_3P)_2(CO)Cl_2Ir–HgCl + Ph_3P \longrightarrow (Ph_3P)_2(CO)ClIr + (Ph_3P)_2HgCl_2 + (Ph_3P,HgCl_2)_2$$

The other binuclear compounds showed the same reaction, but the products were not investigated in detail. Ammonia and pyridine also caused a change in colour of a solution of $(Ph_3P)_2(CO)Cl_2Ir–HgCl$ to lemon yellow; surprisingly, neither triphenylarsine nor methyldiphenylarsine gave any reaction even at higher temperatures.

In this connection it is of interest to note that Ph_3P,NH_3 [5] and pyridine reduce Hg(I) in mercurous compounds (*e.g.*, Hg_2Cl_2) to mercury, probably with formation of mercury(II) adducts, while Ph_2AsMe and Ph_3As do not react.

The physical and chemical properties of these mercury–iridium compounds clearly indicate that they contain a normal covalent iridium–mercury bond, analogous to the rhodium–mercury bonds in $(Ph_2AsMe)_3X_2RhHgY$ discussed in Part I.[6]

The configuration (III) had previously been assigned [2] to the square-planar iridium(I) complex $(Ph_3P)_2(CO)IrCl$, in which the Cl and CO groups are *trans*.

The configuration of the ligands in the hydride, trichloride, and the mercury compounds is not known. Chatt *et al.*[7] isolated two of the six possible isomers of $(PhEt_2P)_2(CO)Cl_2IrH$; these were characterised by dipole moments and infrared spectra. Comparison of the Ir–H and C–O stretching frequencies of these hydrides with those of $(Ph_3P)_2(CO)Cl_2IrH$ appears to indicate that the latter has the configuration (I), with the carbonyl group and the hydrogen atom both *trans* to chlorine atoms; this is possible for only one of the six geometrical isomers.

* The 1 : 1 and 1 : 2 adducts of $HgCl_2$ and Ph_3P were kindly provided by Dr. G. B. Deacon.

[4] R. J. Cross and F. Glocking, *Proc. Chem. Soc.*, 1964, 143.

[5] K. Broderson and L. Kunkel, *Chem. Ber.*, 1958, **91**, 2698.

[6] E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.

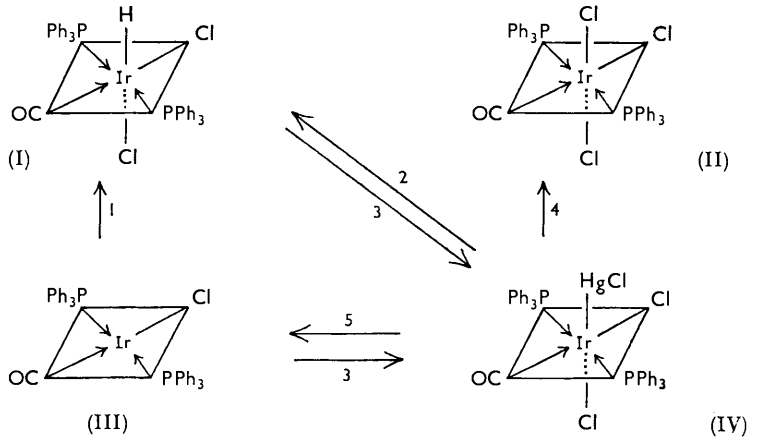
[7] J. Chatt, N. P. Johnson, and B. L. Shaw, *J.*, 1964, 1625.

It was not possible to determine the geometrical arrangements of the ligands in the iridium–mercury compounds, as only one isomer was isolated for each complex [note that six isomers may exist for $(Ph_3P)_2(CO)Cl_2IrHgCl$, and eight for $(Ph_3P)_2(CO)ClYIrHgY$].

Infrared Spectra.—The carbonyl stretching frequencies of the single CO group were observed in the range 2030—2070 cm.$^{-1}$ (see Table 1), which is characteristic for tervalent iridium compounds of the type $L_2(CO)IrX_3$ and $L_2(CO)X_2IrH$.[2,7]

The complex $(Ph_3P)_2(CO)Cl(CN)IrHgCN$ shows two C–N stretching frequencies (see Table 1), which may be due to the fact that the two cyanide groups are bonded to different metal atoms (*i.e.*, Ir and Hg). Infrared measurements do not permit one to distinguish between sulphur–metal bonding and nitrogen–metal bonding in the analogous thiocyanate compound $(Ph_3P)_2(CO)Cl(CNS)Ir$–HgSCN, because the C–S frequencies, which can indicate the mode of bonding,[8] could not be observed owing to ligand (Ph_3P) absorptions.

Reactions of $(Ph_3P)_{21}(CO)Cl_2Ir$–HgCl



Reagents: 1, +HCl; 2, +HCl + H_2; 3, +$HgCl_2$ or +Hg_2Cl_2; 4, +Cl_2; 5, Ph_3P

The asymmetric and symmetric stretching frequencies of the acetate groups in the complex $(Ph_3P)_2(CO)Cl(OAc)IrHgOAc$ (see Table 1) are similar to those of $Hg(OAc)_2$ and CF_3S·HgOAc.[9] In view of the complexity of the asymmetric band system of the latter two compounds it was tentatively proposed [9] that the acetate group may act as a bidentate ligand. However, the method of attachment of the acetate groups to a mercury atom which can be two-, three-, or four-co-ordinate is still not absolutely certain, and in our Ir–HgOAc compounds the question is still undecided. It is of interest to recall that in the complexes $L_3X_2RhHgOAc$ (X = Cl or Br) only one asymmetric and one symmetric acetate band was observed (in Nujol) (see Part II).

Miscellaneous Reactions.—In view of the ease with which $(Ph_3P)_2(CO)IrCl$ formed complexes with mercury salts, we have attempted to apply these reactions to other post-transition metal compounds of the Cu, Zn, Ga, and Ge Groups. We have not yet succeeded in isolating metal–metal bonded compounds. In the case of tin, it was claimed [10] that the complex $(Ph_3P)_2(CO)Cl_2Ir$–$SnPh_2Cl$ had been prepared by treatment of $(Ph_3P)_2(CO)ClIr$ with Ph_2SnCl_2.

The complexes $(Ph_3P)_2(CO)RhCl$ [isomorphous with $(Ph_3P)_2(CO)IrCl$] and L_2PtCl_2 (L = Ph_3P, Ph_3As, or Ph_2AsMe) did not add mercuric compounds to form octahedral complexes. In the case of platinum(II) compounds, *e.g.*, $(Et_3P)_2Pt(H)Cl$ [11] and

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[8] J. Lewis, R. S. Nyholm, and P. W. Smith, *J.*, 1961, 4590.
[9] A. J. Downs, E. A. V. Ebsworth, and H. J. Emeléus, *J.*, 1962, 1254.
[10] J. P. Collman, personal communication.
[11] J. Chatt and B. L. Shaw, *J.*, 1962, 5075.

$(Et_3P)_2Pt(GePh_3)_2$,[4] the addition of hydrogen chloride gave rise to the formation of octahedral platinum compounds. It is relevant to note that the univalent rhodium compound $(Ph_3P)_2(CO)RhCl$ is much more stable to oxidation, as only halogens gave oxidation,[12,13] but not hydrogen chloride, hydrogen, or silver nitrate, whereas the isomorphous iridium complex reduced silver nitrate to metallic silver.

This investigation of the formation of metal–metal bonds perhaps raises as many questions as have been answered. Whereas it is clear that the d^8, iridium(I) compound $(Ph_3P)_2(CO)IrCl$ can be oxidised by mercuric chloride (or indeed mercurous chloride with simultaneous deposition of mercury), the same reaction has not yet been observed with d^8 metal atoms in the Periodic Table vertically above it (*e.g.*, Rh^I or Co^I), to the left (Os^0), or to the right (Pt^{II} or Au^{III}). This might be a kinetic problem, but we believe that the difficulty is more likely to arise from thermodynamics. If we consider the oxidation of a square d^8 complex to a d_ϵ^6 complex, by use of a molecule R–X (which could be ClHg–Cl, Cl_2, HCl, etc.), three energy quantities are involved: (*a*) promotion of the d^8 (diamagnetic) atom, in the square complex, from the $nd_\epsilon{}^6nd_{z^2}{}^2$ to the $nd_\epsilon{}^6nd_{z^2}{}^1$ $(n + 1)$ p-configuration [this increases rapidly with formal charge, and since the $(n + 1)$ p-orbital is in a different quantum shell from the nd-orbital the increase in promotion energy $nd \longrightarrow (n\mathrm{H})p$ is not linear with charge *]; (*b*) the dissociation energy of the ClHg–Cl bond (~81 kcal./mole); this is obviously constant for the sequence of atoms under consideration; (*c*) the energy of formation of the two bonds to the metal atom, *viz.*, M–HgCl and M–Cl. These are expected to increase in strength as the formal charge rises, but certainly not so rapidly as does the increase in promotion energy.

It is observed experimentally that, as we move to the left from the d^8 atoms Au^{III} to Os^0, the tendency to form compounds in which the oxidation state of the central metal atom is 2 higher increases. Thus, the $Au^{III} \longrightarrow Au^V$ oxidation is unknown; $Pt^{II} \longrightarrow Pt^{IV}$ occurs with the halogens, in certain special cases with the hydrogen halides, and in one or two cases with hydrogen to form unstable products. However, $(Ph_3P)_2(CO)IrCl$ is oxidised by halogens, hydrogen halides, and by hydrogen. In the case of Os^0 the tendency to increase the valency is so marked that $Os(CO)_4$ is in fact a trimer with Os–Os bonds which give the osmium atom a formal valency of 2.

The ease with which the $M^{(x)} \longrightarrow M^{(x+2)}$ valency change occurs for the sequences Os^0, Ir^I, Pt^{II}, and Au^{III} is thus highly sensitive to the formal (initial) valency. For the vertical sequence Co, Rh, and Ir, comparative data are more difficult to obtain; however, for the somewhat similar promotion process $(n)d^{10} \longrightarrow nd^9(n + 1)p^1$ for Zn^{2+}, Cd^{2+}, and Hg^{2+} the promotion energies (ΔE) are, respectively, 137,876, 133,813, and 103,549 cm.$^{-1}$. The marked increase in ΔE in passing from the third to the first and second transition series strongly suggests that it will be even more difficult to oxidise (with mercuric chloride) either $(Ph_3P)_2(CO)RhCl$ or a cobalt(I) derivative than the iridium(I) complex, as is observed. It must be emphasised, however, that a variation in the nature of the attached ligands would normally alter this promotion energy, and the use of different ligands from those in $(Ph_3P)_2(CO)IrCl$ could lead to the formation of Rh–M and Co–M bonds. We believe that the ligands required for this purpose are those which reduce the formal charge on the metal atom. Experimental work aimed at achieving this objective is in progress.

EXPERIMENTAL

Preparation of Complexes with Iridium–Mercury Bonds.—(a) *From a hydride.* The preparation of $(Ph_3P)_2(CO)Cl_2Ir–HgCl$ from the hydrides $(Ph_3P)_2(CO)Cl_2IrH$ and $(Ph_3P)_2(CO)ClIrH_2$ was carried out in the same way as for the analogous rhodium complexes in the preceding paper.

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* Thus, for the transition $nd^{10} \longrightarrow nd^9$ $(n + 1)p^1$, the promotion for Pt^0, Au^+, Hg^{2+}, and Tl^{3+} are, respectively, 27,982, 63,053, 103,549, and 147,635 cm.$^{-1}$.

[12] L. Vallarino, *J.*, 1957, 2287.

[13] L. Vallarino, *J. Inorg. Nuclear Chem.*, 1958, **8**, 288.

(b) *Oxidation with* HgY_2 *or* Hg_2Y_2. A solution of HgY_2 (0·2 g., excess) in ethanol (50 ml.) was added to a lemon yellow solution of $(Ph_3P)_2(CO)IrX$ (X = Cl, Br) (0·2 g.) in benzene (100 ml.) at room temperature. The solution became colourless, except when Y = I when it remained yellow, and then evaporated to dryness. The resulting crystalline powder was thoroughly washed with hot ethanol and dried *in vacuo*. By use of suspensions of Hg_2Y_2 (Y = Cl, Br, I, or OAc), the same compounds were formed, mercury also being precipitated. In all cases the yield was quantitative.

Analytical Data.—(I) *Dichloromonocarbonylbis(triphenylphosphine)monochloromercury*(I)-*iridium*(II) (Found: C, 42·9; H, 3·8; Cl, 10·0; Hg, 19·0; Ir, 18·5. $C_{37}H_{30}Cl_3HgIrOP_2$ requires C, 42·3; H, 2·9; Cl, 10·1; Hg, 19·0; Ir, 18·3%).

(II) *Monobromomonochloromonocarbonylbis(triphenylphosphine)monobromomercury*(I)*iridium*(II) (Found: C, 38·8; H, 3·3; Cl, 3·0; Hg, 17·6; Ir, 16·7; Br, 13·7. $C_{37}H_{30}Br_2ClHgIrOP_2$ requires C, 39·0; H, 2·6; Cl, 3·1; Hg, 17·7; Ir, 16·8; Br, 14·0%).

(III) *Monochloromonoiodomonocarbonylbis(triphenylphosphine)monoiodomercury*(I)*iridium*(II) (Found: C, 35·6; H, 3·1; Cl, 2·8; I, 21·2; Hg, 16·5; Ir, 15·4. $C_{37}H_{30}ClHgIrI_2OP_2$ requires C, 36·0; H, 2·4; Cl, 2·8; I, 20·6; Hg, 16·3; Ir, 15·5%).

(IV) *Monoacetatomonochloromonocarbonylbis(triphenylphosphine)monoacetatomercury*(I)*iridium*(II) (Found: C, 45·1; H, 4·5; Cl, 3·1; Hg, 17·8; Ir, 17·3. $C_{41}H_{36}ClHgIrO_5P_2$ requires C, 44·8; H, 3·3; Cl, 3·2; Hg, 18·3; Ir, 17·5%).

(V) *Monochloromonocyanomonocarbonylbis(triphenylphosphine)monocyanomercury*(I)*iridium*(II) (Found: C, 45·3; H, 3·6; Cl, 3·2; Hg, 18·8; Ir, 18·7. $C_{39}H_{30}ClHgIrN_2OP_2$ requires C, 45·4; H, 3·0; Cl, 3·4; Hg, 19·4; Ir, 18·6%).

(VI) *Dibromomonocarbonylbis(triphenylphosphine)monomercury*(I)*iridium*(II) (Found: C, 37·8; H, 2·7; Br, 19·9; P, 5·3; Hg, 16·9; Ir, 16·1. $C_{37}H_{30}Br_3HgIrOP_2$ requires C, 37·5; H, 2·5; Br, 20·3; P, 5·2; Hg, 17·0; Ir, 16·2%).

(VII) *Monochloromonothiocyanatomonocarbonylbis(triphenylphosphine)monothiocyanatomercury*(I)*iridium*(II) (Found: C, 42·0; H, 4·1; Cl, 1·6; Hg, 18·6; Ir, 17·5. $C_{39}H_{30}ClHgIrN_2OP_2S_2$ requires C, 42·7; H, 2·7; Cl, 3·2; Hg, 18·3; Ir, 17·6%).

Conductance Measurements.—These were carried out at 25° with a Wayne Kerr Universal bridge type B 221, using dip-type bright platinum electrodes.

Molecular Weights.—These were determined with a Vapor Pressure Osomometer, model 301 A (Mechrolab) in benzene or chloroform.

Magnetic Susceptibilities.—These were measured by the Gouy method at room temperature. The corrected molar susceptibilities are of the order of +60 c.g.s.u. for the iridium compounds. These values were temperature-independent from 80°K to room temperature (measured by Mr. P. R. Woolliams).

Absorption Spectra.—Infrared spectra were recorded on a Grubb–Parsons double-beam grating instrument, type 2A, from 2 to 20 μ, using NaCl and KBr plates. Visible and ultraviolet spectra were measured with a Perkin-Elmer spectrophotometer, model 137 UV, from 2500 to 7500 Å. A Unicam S.P. 500 spectrophotometer was used for the spectrophotometric titrations.

Estimation of the Elements.—Carbon and hydrogen were determined in the microanalytical laboratory of this department, while C, H, Hg, As, P, and, in some cases, halogen were determined at the Max Planck Institut, Mühlheim, Germany. Analyses of Rh, Ir (as metal), and, in some cases, halogen (potentiometrically) were carried out in this department.

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