Mercury(II) Halide Adducts of Transition-metal Complexes. Part II.[1] Tertiary-phosphine and -arsine Complexes of Rhodium(III) and Iridium(III)†

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Treatment of mercury(II) halides with complexes $[MX_3(L)_3]$ (both isomers) or $[IrX_{3-n}(H)_nL_3]$ (M = Rh or Ir; X = Cl, Br, or I; $1 \leqslant n \leqslant 3$) gives adducts of the types $[MX_3(L)_3(HgY_2)]$ (I: M = Rh, X = Y = Cl, L = $AsMe_2Ph$ or PMe_2Ph; M = Ir, X = Y = Cl, L = PEt_3, PPr^n_3, Bu^n_3, PMe_2Ph, $AsEt_3$, $AsMe_2Ph$, or $AsEt_2Ph$; M = Ir, X = Y = Br, L = PMe_2Ph or $AsMe_2Ph$; M = Ir, X = Cl, Y = Br or I, L = PEt_3), (II: M = Ir, X = Cl, Y = Cl or Br, L = PEt_3), or (III: M = Ir, X = Br, Y = Cl, L = PEt_3), and $[MH(X)_2(L)_3(HgY_2)]$ (IV: M = Ir, X = Y = Cl, L = PMe_2Ph or PEt_2Ph; X = Y = I, L = PMe_2Ph; X = Y = Br, L = PEt_2Ph), respectively, believed to have a double halide bridge between the metal atoms, often easily dissociated. Hydride ligands in certain stereochemistries in the precursors can act as reductants towards mercury(II) halides. A bis-$HgCl_2$ adduct $[IrCl_3(PEt_3)_3(HgCl_2)_2]$, (V), is also reported. $SnCl_2$ Reacts with the adduct $[IrCl_3(PEt_3)_3(HgCl_2)]$ to give $[IrCl_2(SnCl_3)(PEt_3)_3]$, (XI); the reaction is reversed by the action of $HgCl_2$. The configuration of the complexes and their reactivity have been studied mainly using i.r. (4 000—200 cm^{-1}) and ^1H(methyl) n.m.r. spectroscopies.

Mercury(II) halides have been shown to react with transition-metal complexes in three distinct ways.[2-4] We recently described[1] the formation of adducts of mercury(II) halides with complexes $[MX_2(L)_2]$ (M = Pd or Pt; X = Cl, Br, or I; L = tertiary phosphine or arsine), which involves increase of the co-ordination number of mercury to four with halide bridge formation. The crystal structure of the adduct $[PtCl_2(PMe_2Ph)_2(HgCl_2)]$ is known.[4] We now report on adduct formation between mercury(II) halides and octahedral tertiary phosphine and arsine (L) complexes of rhodium(III) and iridium(III), $[MX_3(L)_3]$ (both isomers) and $[MX_{3-n}(H)_nL_3]$ (M = Rh or Ir; X = Cl, Br, or I; $1 \leqslant n \leqslant 3$).

RESULTS AND DISCUSSION

In certain stereochemistries some of the $[MX_3(L)_3]$ complexes lose ligand L to mercury, and some of the hydrido-complexes $[MX_{3-n}(H)_nL_3]$ can act as reducing agents toward mercury(II) halides, but in general we find that complexes of the above two formula types give 1 : 1 adducts with double halide bridges between the metal M and mercury, the co-ordination remaining octahedral around the transition metal atom and being approximately tetrahedral about mercury; an example is (I).

Although some rhodium–mercury(II) halide adducts were prepared, they were often present only as constituents of mixtures. Tertiary phosphines and arsines appear to be less strongly bonded to rhodium(III) than to iridium(III), and even under mild conditions some of the ligand L was lost to mercury from rhodium(III) complexes, giving products such as $[Hg_2Cl_4(AsMe_2Ph)_2]$ (see Experimental section). Similar behaviour was noted with some palladium(II) complexes.[1] For a labile ligand L (*e.g.* $AsEt_3$) no adduct $[RhCl_3(AsEt_3)_3(HgCl_2)]$, configuration (I), could be isolated from the complex *mer*-$[RhCl_3(AsEt_3)_3]$ and mercury(II) chloride, since all the ligand L was lost to the mercury atom to give $[Hg_2Cl_4(AsEt_3)_2]$.

In general adducts formed between rhodium(III) or iridium(III) are soluble only in polar solvents. The molar conductivities of some representative adducts were determined in 10^{-3}M-nitrobenzene solution at 22 °C and found to be 1—2 Ω^{-1} cm^2 mol^{-1}, *i.e.* considerably higher than those of the parent transition-metal complexes but far less than that required for a 1 : 1 electrolyte in this solvent. This conductivity may be associated, as with similar palladium(II) and platinum(II) complexes, with slight ionic dissociation according to equation (1),

$$[MX_3(L)_3(HgY_2)] \rightleftharpoons [MX_3(L)_3(HgY)]Y \qquad (1)$$

involving a three-co-ordinate mercury(II) species. The molecular weights of adducts in (chloroform) solution were often low, indicating simple dissociation of the adduct to its constituents, as was also shown for certain adducts by ^1H n.m.r. spectroscopy and by analytical evidence, *e.g.* attempted recrystallization of $[IrBr_3(AsMe_2Ph)_3(HgBr_2)]$, (I), from methanol led to complete dissociation.

N.m.r. spectra (methyl resonances) of adducts $[MX_3(L)_3(HgY_2)]$ (L = PMe_2Ph or $AsMe_2Ph$) should indicate the stereochemistry. The spectra of the five adducts investigated were, however, within the limits of experimental error identical with their precursors, indicating extensive dissociation in (chloroform) solution. Hence most of the adducts were obtained by precipitation from the reaction mixture by suitable choice of solvent and cooling in the presence of excess of mercury(II) halide in order to suppress any dissociation.

The preparation of some of the adducts is indicated in the Scheme. Thus addition of an ethanolic solution of several molar equivalents of mercury(II) chloride to an ethanolic solution of *mer*-$[IrCl_3(PEt_3)_3]$ immediately gave a crystalline, bright yellow, precipitate of composition $[IrCl_3(PEt_3)_3(HgCl_2)]$, with a conductivity of 0·91 Ω^{-1} cm^2 mol^{-1} in nitrobenzene at 22 °C. The i.r. spectrum (4 000—450 cm^{-1}) was virtually the same as that of *mer*-$[IrCl_3(PEt_3)_3]$ suggesting a *mer*-arrangement of the triethylphosphine ligands. The far-i.r. spectrum (450—200 cm^{-1}) showed several differences, and is compatible with the suggested structure of the adduct, (I). The

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† No reprints available.

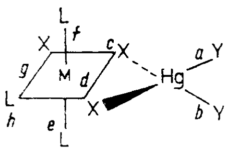
[1] Part I, P. R. Brookes and B. L. Shaw, *J.C.S. Dalton*, 1973, 783.

[2] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.

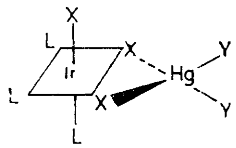
[3] I. N. Nowell and R. D. Russell, *Chem. Comm.*, 1967, 817.

[4] R. W. Baker, M. J. Braithwaite, and R. S. Nyholm, *J.C.S. Dalton*, 1972, 1924.

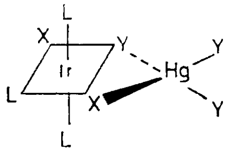
precursor *mer*-[$IrCl_3(PEt_3)_3$] shows [5] in the far-i.r. region a band at 313 cm^{-1} due to ν(Ir–Cl) *trans* to Cl and one at 262 cm^{-1} due to ν(Ir–Cl) *trans* to PEt_3 (of higher *trans*-influence). The 1 : 1 adduct showed three strong bands, in the region associated with ν(M–Cl), at 323, 298, and 223 cm^{-1} (Table 1). We derived a consistent set of data if the band at 323 cm^{-1} was assigned to ν(Hg–Cl) of the terminal $>HgCl_2$ moiety: only a single band is observed in complexes of the type [$HgCl_2(L)_2$] and [$MCl_2(L)_2(HgCl_2)$] (see ref. 1 and refs. therein), and the value is comparable with that found in the present complexes. Of the remaining two bands, that at 298 cm^{-1} is assigned to ν(Ir–Cl) *trans* to a (bridging) chlorine atom [see configuration (I)], and is compatible with the range established for ν(Ir–Cl) *trans* to a chloride ligand.[5] The band at 223 cm^{-1} is then associated with the $IrCl_2Hg$ bridge. Only one absorption band was commonly found in the complexes described here, except in cases where considerable asymmetry of the bridge is anticipated (see below).



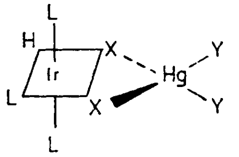
(I) M=Rh, X=Y=Cl, L=$AsMe_2Ph$ or PMe_2Ph
M=Ir, X=Y=Cl, L=PEt_3, PPr^n_3, Bu^n_3, PMe_2Ph, $AsEt_3$, $AsMe_2Ph$, or $AsEt_2Ph$;
X=Y=Br, L=PMe_2Ph or $AsMe_2Ph$;
X=Cl, Y=Br or I, L=PEt_3



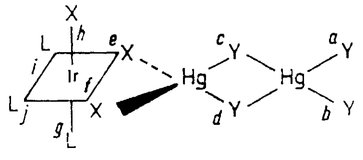
(II) X=Cl, Y=Cl or Br
L=PEt_3



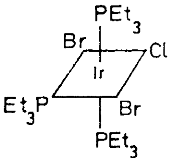
(III) X=Br, Y=Cl, L=PEt_3



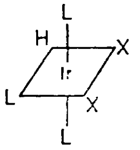
(IV) X=Y=Cl, L=PMe_2Ph or PEt_3
X=Y=I, L=PMe_2Ph
X=Y=Br, L=PEt_2Ph



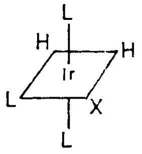
(V) X=Y=Cl, L=PEt_3



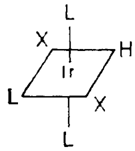
(VI)



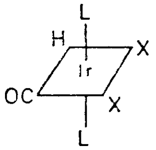
(VII)



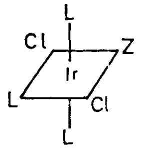
(VIII)



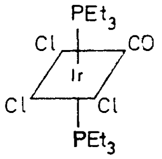
(IX)



(X)

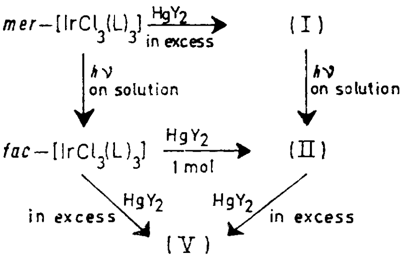


(XI)
Z=$SnCl_3$, I,
H, or Br



(XII)

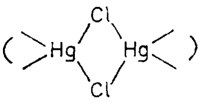
(VII)–(XI) X=Halide, L=tertiary phosphine or arsine



SCHEME Preparation of mercury(II) halide adducts of complexes [$IrCl_3(L)_3$]. X = Y = Halide, L = tertiary phosphine or arsine

In order to confirm many of the assignments of metal–chlorine stretching frequencies we prepared other adducts where bromine or iodine replace some or all of the chlorine ligand atoms, *e.g.* the action of HgY_2 (Y = Br or I) on complexes *mer*-[$IrCl_3(L)_3$] gives [$IrCl_3(L)_3(HgY_2)$], configuration (I). Here the spectra (Table 1) were similar to those of the adducts [$IrCl_3(L)_3(HgCl_2)$], configuration (I), but the band previously assigned to ν(Hg–Cl) was missing and (for Y = Br) an additional band at low frequency and possibly due to ν(Hg–Br) was observed. Such mixed-halide complexes were prepared under mild conditions, and there was no evidence for halide metathesis. Complexes of the type *fac*-[$IrCl_3(L)_3$] gave with mercury(II) halides analogous isomeric adducts [$IrCl_3(L)_3(HgY_2)$] whose far-i.r. spectra were compatible with configuration (II). The i.r. spectra, colour, and comparative insolubility of these adducts all indicate the *fac*-arrangement of ligands L is retained in the adducts.

From *fac*-[$IrCl_3(PEt_3)_3$] it was possible to prepare an adduct with two moles of mercury(II) chloride. This is assigned configuration (V); mercury(II) halides commonly show this type of structure with repeating bridges, *e.g.* [$Hg_2Br_4(AsBu^n_3)_2$] and related complexes.[6] The far-i.r. spectrum, in agreement with the suggested structure, included an absorption at higher wavenumber



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[5] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789.

[6] A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., Clarendon Press, Oxford, 1962, pp. 894—895.

TABLE 1

Analytical and far-i.r. (450—200 cm^{-1}) [a] data for the adducts

Adduct	Yield (%)	Colour	Analyses (%) [b]				M [b,c]	M.p. (t/°C)	ν(M–Cl–Hg)	ν(Hg–Cl)	ν(Hg–Br) [d]	ν (M–Cl) *trans*-Ligand atom		Other bands
			C	H	Halogen	Hg						Cl	P or As	
[$RhCl_3(PMe_2Ph)_3(HgCl_2)$],$HgCl_2$ (I)	23	Orange	24·5 (24·7)	2·9 (2·85)	20·6 (21·25)			127—130	*c*	325s		340s		433s, 417m, 411m, 375s,[f] 356w, 334s 312s,[f] 288m, 210s
[$RhCl_3(AsMe_2Ph)_3(HgCl_2)$] (I)	36	Red	27·8 (28·05)	3·3 (3·25)				156—165 [g]	242s	310s		345vs		320m, 279s
[$IrCl_3(PEt_3)_3(HgCl_2)$] (I)	93	Yellow	23·6 (23·4)	4·85 (4·9)	18·85 (19·2)	21·8 (21·7)		108—110	223s	323vs		298s		442m, 427m, 382w
[$IrCl_3(PEt_3)_3(HgCl_2)$] (II)	74	Colourless	23·3 (23·4)	4·55 (4·9)				186—189 [g]	244s	303s *			292vs	437s, 385w
[$IrCl_3(PEt_3)_3(HgCl_2)_2$] (V)	91	Colourless	18·0 (18·1)	3·7 (3·8)	21·05 (20·75)			175—184 [g]	*c*	366s [h]			277vs	438s, 290s, 287s,* 240s
[$IrCl_3(PEt_3)_3(HgBr_2)$] (I)	77	Yellow	21·25 (21·35)	4·4 (4·5)	1·61 (1·64) [i]			107—111	288s		221vs	334s		443vs, 384m, 245m
[$IrCl_3(PEt_3)_3(HgBr_2)$] (II)	87	Colourless	21·25 (21·35)	3·9 (4·5)				184—188	245s				289vs	431m, 385w
[$IrCl_3(PEt_3)_3(HgI_2)$] (I)	72	Yellow	19·85 (19·55)	4·2 (4·1)				107—111	293s			331s		442vs, 383m, 240m
[$IrBr_2(Cl)(PEt_3)_3(HgCl_2)$] (III)	57	Yellow	21·4 (21·35)	4·65 (4·5)	1·40 (1·44) [i]			104—107	252s	309s				440m, 382w
[$IrCl_3(PPr^n_3)_3(HgCl_2)$] (I)	86	Yellow	30·0 (30·85)	5·75 (6·05)				124—127	240s	318vs		292s		439s, 415m, 379m
[$IrCl_3(PBu^n_3)_3(HgCl_2)$] (I)	21	Yellow	36·8 (36·75)	6·9 (6·95)				107—109	236s	315s		295s		455m, 4032, 393w *
[$IrCl_3(PMe_2Ph)_3(HgCl_2)$] (I)	71	Yellow	29·15 (29·3)	3·4 (3·4)				171—175	228s	326vs		297s		437s, 422m, 409m, 347m, 252m,* 245m
[$IrBr_3(PMe_2Ph)_3(HgBr_2)$] (I)	70	Orange	23·95 (23·9)	2·85 (2·75)				164—167						438s, 423m, 412s, 350m, 339w, 317m, 245m, 217w
[$IrCl_3(AsEt_3)_3(HgCl_2)$] (I)	84	Orange	20·35 (20·55)	4·2 (4·3)		18·9 (19·0)	940 (1 056)	115—118	220s	322vs		395s		438s, 444m,* 380w
[$IrCl_3(AsMe_2Ph)_3(HgCl_2)$] (I)	65	Yellow	26·2 (25·85)	3·25 (3·0)				179—180	253s	317s		304s		333s, 304s, 280m
[$IrBr_3(AsMe_2Ph)_3(HgBr_2)$] (I)	55	Orange	21·75 (21·55)	2·5 (2·5)				200—204			223s			314s, 303s, 278w, 258m, 242m
[$IrCl_3(AsEt_2Ph)_3(HgCl_2)$] (I)	69	Orange	30·7 (30·0)	4·4 (3·8)				166—169	263vs	328vs		301s		
[$IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)$] (IV)	91	Colourless	30·5 (30·35)	3·55 (3·6)	14·8 (14·95)	21·5 (21·1)	870 (950)	285—296	269s, 246s	320s				443s, 428s, 418s, 360m, 340m, 225m
[$IrH(I)_2(PMe_2Ph)_3(HgI_2)$ (IV)	70	Yellow	21·3 (21·9)	2·75 (2·6)				108—113						443s, 418s, 352m, 320w
[$IrH(Cl)_2(PEt_2Ph)_3(HgCl_2)$] IV)	87	White	34·55 (34·85)	4·4 (4·5)				135—138	265vs, 253s *	301vs				499s, 407m, 327m, 286m, 206m
[$IrH(Br)_2(PEt_2Ph)_3(HgBr_2)$] (IV)	96	Cream	29·55 (29·75)	3·8 (3·85)				152—155						453s, 388m, 323w, 242w

* Shoulder.

[a] Spectra recorded on Nujol mulls (cm^{-1}), error ± 2 cm^{-1}. [b] Calculated values are given in parentheses. [c] Chloroform solution. [d] Tentative assignments. [e] Not assigned. [f] Due to lattice $HgCl_2$ (see ref. 7). [g] With decomposition. [h] End of terminal $HgCl_4$ moiety (see text). [i] $AgNO_3$ titre (cm^3).

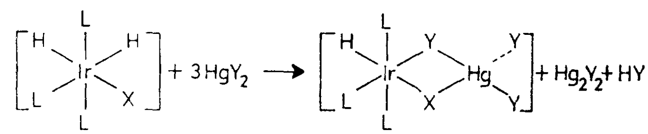
[366 cm^{-1}, assigned to ν(Hg–Cl)] than found for the 1 : 1 adducts, indicative of extremely weak bonding of the 'second' $HgCl_2$ molecule [mercury(II) chloride itself gives its highest absorption band at 374 cm^{-1}].[7] This behaviour parallels that shown by $[PtCl_2(PMe_3)_2(HgCl_2)_2]$.[1]

A mixed-halide complex, *mer*-$[IrBr_2(Cl)(PEt_3)_3]$, (VI), was used to prepare an adduct $[IrBr_2(Cl)(PEt_3)_3(HgCl_2)]$, with a far-i.r. spectrum in agreement with the assigned configuration (III).

By several methods (see below) it was possible to prepare adducts $[IrH(X)_2(L)_3(HgY_2)]$, assigned configuration (IV) on the basis of n.m.r. and far-i.r. spectra. In such adducts two bands assignable to bridging chloride ligand were found, possibly because the hydride ligand is of such high *trans*-influence that a considerable degree of asymmetry is induced in the $IrCl_2Hg$ bridging moiety.

The two adducts of rhodium complexes prepared showed ν(Rh–Cl) at higher values than shown by ν(Ir–Cl) in complexes of the same geometry, as anticipated.[8] The complex *mer*-$[RhCl_3(PMe_2Ph)_3]$ gave an adduct shown by analysis to contain two molar equivalents of mercury(II) chloride, but the far-i.r. spectrum clearly showed this to be a 1 : 1 adduct with one molecule of lattice mercury(II) chloride {compare the complex $[Hg_3Br_6(AsBu^n_3)_2]$ [6]}.

Preparation of Adducts (IV).—Complexes $[IrH(X)_2L_3]$, (VII), react with mercury(II) halides to give 1 : 1 adducts in which the hydride ligand can be shown (*e.g.* by i.r. spectroscopy, or formation of HCl with chlorine) to be still present. For example, $[IrH(Cl)_2(PMe_2Ph)_3]$, (VII), reacted with mercury(II) chloride in ethanol solution at once; colourless plates of a 1 : 1 adduct, ascribed configuration (IV), precipitated out in 84% yield. This complex is diamagnetic, and its conductivity and molecular weight in chloroform solution are as expected for a non-conducting mononuclear species. 1 : 1 Adducts of the same configuration were also obtained from either the dihydrido-complex $[IrH_2(X)L_3]$, configuration (VIII), or *fac*-$[IrH_3(L)_3]$. In the precursor (VIII), one of the hydride ligands is *trans* to a ligand of very high *trans*-influence (tertiary phosphine) and is strongly hydridic in character; thus, for example, it is labile to dilute mineral acids.[9] We find that a hydride ligand in such a stereochemistry acts as a reductant to mercury(II) halides, so the overall reaction can be represented as in equation (2) (X = Y = Cl, Br, or I), the other hydrido-ligand (*trans* to X) being unaffected. The last two products of this reaction are readily detected, and the adduct has the stereochemistry (IV), identical with that obtained directly from (VII). The complex *fac*-$[IrH_3(PEt_2Ph)_3]$ gave a 61% yield of (IV) when treated with mercury(II) chloride in ethanol. Here two of the hydride ligands reduce $HgCl_2$ to Hg_2Cl_2 as before, but isomerization of the neutral ligands must occur simultaneously, since they have the *mer*-configuration in the adduct (see below).



(2)

The hydride ligand in complexes $[IrH(X)_2L_3]$, (IX), is also *trans* to the ligand L of very high *trans*-influence. Thus complexes of this configuration also act as reductants to mercury(II) chloride, in contrast to the isomers of (VII), giving $[IrCl_3(L)_3(HgCl_2)]$, (I), as obtainable directly from *mer*-$[IrCl_3(L)_3]$. When a reaction mixture including $[IrH(Cl)_2L_3]$, (IX) (L is comparatively labile, *e.g.* $AsEt_3$), was heated, some of the ligand L was lost to mercury(II) halide present in solution, and the products of reaction included complexes $[(HgY_2)_nL_2]$. Presumably the hydride ligand in complexes (IX) exerts some labilizing effect on the ligand L *trans* to itself. In complexes (VII) the hydride ligand is *trans* to halide, and is not labile to dilute acid;[9] rather, it is neutral in character. In $[IrH(X)_2(CO)L_2]$, (X), introduction of the poor σ-donor ligand carbon monoxide in place of tertiary phosphine or arsine causes the hydride ligand to show acidic character: thus HX can be eliminated from the complex even by weak bases,[10] and Nyholm and Vrieze have shown [2] that the action of mercury(II) halides gives complexes $[Ir(HgY)X_2(CO)L_2]$, with loss of HX. The configuration of the hydrides $[RhH(X)_2(AsMePh_2)_3]$ (X = Y = Cl or Br), from which the same authors prepared [11] complexes of the type $[Rh(HgY)X_2(AsMePh_2)_3]$, was not known: however, it is clear that the hydride ligand has acidic character, since (effectively) HX is lost and HgY_2 adds to the square-planar complex $[RhX(AsMePh_2)_3]$. Other hydridorhodium complexes have been shown [12] to react with mercury(II) halides to give products $[Rh(HgY)(X)_2L_3]$ (X = Y = Cl, Br, or I; L = tertiary phosphine), but again the stereochemistry of both the reactants and products was unknown.

For adducts (IV), i.r. spectra in the region 2 000—500 cm^{-1} were virtually identical with those of the present complexes, suggesting that the *mer*-arrangement of tertiary phosphine ligands is retained. This was confirmed by the n.m.r. spectra (see below). I.r. spectra in the hydride region were only slightly altered from those of the parent complexes, and ν(Ir–H) appeared at *ca.* 220 cm^{-1}. Chatt *et al.* showed [9] that ν(Ir–H) *trans* to chloride is commonly high, values in the range 2 220—2 195 cm^{-1} being usually observed. The far i.r. spectra of these adducts were discussed earlier and are contained in Table 1. N.m.r. spectra (methyl resonances) of the dimethylphenylphosphine-containing adducts are given in Table 2. The spectra for both the complexes studied showed two overlapping 1 : 2 : 1 triplets due to dimethylphenylphosphine ligands in mutual *trans*-position, there being no plane of symmetry through the P–Ir–P bond,

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[7] D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228.

[8] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

[9] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.

[10] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 1887.

[11] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5331.

[12] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc.* (*A*), 1966, 1670.

Table 2

^{1}H N.m.r. data for mercury(II) halide adducts $[IrH(X)_2(PMe_2Ph)_3HgX_2]$ (X = Cl or I) in chloroform solution, τ values ±0·01, *J* values ±0·1 Hz

Aduct	Phosphine methyl resonances			
	1 : 1 Doublet		Triplet[a]	
	τ	'*J*'[b]	τ	'*J*'[b]
$[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$ (IV)	8·79	11·0	8·06	3·8
$[IrH(I)_2(PMe_2Ph)_3(HgI_2)]$ (IV)	8·66	10·2	7·59	*ca.* 3·5

[a] Resonance appears as two overlapping 1 : 2 : 1 triplets: central τ value as shown; $J_1 = J_2$, values as shown. [b] Complexes containing two PMe_2Ph ligands may be analysed as $X_6AA'X'_6$ systems (R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275); the values quoted for '*J*' are separations of the outer peaks for the triplets, *i.e.* $|^2J(P\text{–}H) + {}^4J(P\text{–}H)|$, and the separation of the two peaks for the doublets.

and a 1 : 1 doublet for the other phosphine, in agreement with configuration (IV). The adducts were insufficiently soluble for observation of resonances due to the hydride ligands.

Table 3

Preparation of the adducts (see Experimental section)

Precursor	Reaction conditions		Product	Notes
	Solvent	Reaction time		
mer-$[IrCl_3(PEt_3)_3]$, $HgCl_2$	*a*	2 h[b]	$[IrCl_3(PEt_3)_3(HgCl_2)]$ (I)	
fac-$[IrCl_3(PEt_3)_3]$, $HgCl_2$[c]	*d*	1 min[e]	$[IrCl_3(PEt_3)_3(HgCl_2)]$ (II)	Also prepared by photoisomerization of (I) (see text)
fac-$[IrCl_3(PEt_3)_3]$, $HgCl_2$	*d*	30 s[e]	$[IrCl_3(PEt_3)_3(HgCl_2)_2]$ (V)	Also prepared by the action of $HgCl_2$ on $[IrCl_3(PEt_3)_3(HgCl_2)]$, (II)
mer-$[IrCl_3(PEt_3)_3]$, $HgBr_2$	*f*	2 h[b]	$[IrCl_3(PEt_3)_3(HgBr_2)]$ (I)	
fac-$[IrCl_3(PEt_3)_3]$, $HgBr_2$	*d*	1 min[e]	$[IrCl_3(PEt_3)_3(HgBr_2)]$ (II)	Also prepared by photoisomerization of (I) (see text)
mer-$[IrCl_3(PEt_3)_3]$, HgI_2	*f*	1 h[b]	$[IrCl_3(PEt_3)_3(HgI_2)]$ (I)	Also prepared by reaction of $HgCl_2$ adduct with HgI_2 in acetone
$[IrBr_2(Cl)(PEt_3)_3]$ (VI), $HgCl_2$	*a*	1 h[b]	$[IrBr_2(Cl)(PEt_3)_3(HgCl_2)]$ (III)	
mer-$[IrCl_3(PPr^n{}_3)_3]$, $HgCl_2$	*d*	30 s, 45 °C	$[IrCl_3(PPr^n{}_3)(HgCl_2)]$ (I)	
mer-$[IrCl_3(PBu^n{}_3)_3]$, $HgCl_2$	*d*	1 h[b]	$[IrCl_3(PBu^n{}_3)(HgCl_2)]$ (I)	
mer-$[IrCl_3(PMe_2Ph)_3]$, $HgCl_2$	*d*	18 h[e]	$[IrCl_3(PMe_2Ph)_3(HgCl_2)]$ (I)	
mer-$[IrBr_3(PMe_2Ph)_3]$, $HgBr_2$	*d*	14 h[e]	$[IrBr_3(PMe_2Ph)_3(HgBr_2)]$ (I)	
mer-$[IrCl_3(AsEt_3)_3]$, $HgCl_2$	*d*	1 h[b]	$[IrCl_3(AsEt_3)_3(HgCl_2)]$ (I)	
mer-$[IrCl_3(AsMe_2Ph)_3]$, $HgCl_2$	*d*	30 h[e]	$[IrCl_3(AsMe_2Ph)_3(HgCl_2)]$ (I)	
mer-$[IrBr_3(AsMe_2Ph)_3]$, $HgBr_2$	*d*	27 h[e]	$[IrBr_3(AsMe_2Ph)_3(HgBr_2)]$ (I)	
mer-$[IrCl_3(AsEt_2Ph)_3]$, $HgCl_2$	*g*	26 h[e]	$[IrCl_3(AsEt_2Ph)_3(HgCl_2)]$ (I)	
$[IrH(Cl)_2(PMe_2Ph)_3]$ (VII), $HgCl_2$	*a*	10 s, 50 °C	$[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$ (IV)[h]	
$[IrH_2(Cl)(PMe_2Ph)_3]$ (VIII), $HgCl_2$	*a*	10 min[b]	$[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$ (IV)	Reaction mixture filtered from precipitated Hg_2Cl_2 (see text)
fac-$[IrH_3(PMe_2Ph)_3]$, $HgCl_2$	*f*	2 min[e]	$[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$ (IV)	Reaction mixture filtered as above
$[IrH(I)_2(PMe_2Ph)_3]$ (VII), HgI_2	*d*	10 min[e]	$[IrH(I)_2(PMe_2Ph)_3(HgI_2)]$ (IV)[i]	
$[IrH(Cl)_2(PEt_2Ph)_3]$ (VII), $HgCl_2$	*a*	10 s[e]	$[IrH(Cl)_2(PEt_2Ph)_3(HgCl_2)]$ (IV)[j]	
fac-$[IrH_3(PEt_2Ph)_3]$, $HgCl_2$	*a*	1 min[e]	$[IrH(Cl)_2(PEt_2Ph)_3(HgCl_2)]$ (IV)	Reaction mixture filtered as above
$[IrH(Br)_2(PEt_2Ph)_3]$ (VII), $HgBr_2$	*a*	10 s[e]	$[IrH(Br)_2(PEt_2Ph)_3(HgBr_2)]$ (IV)[k]	
$[IrH_2(Br)(PEt_2Ph)_3]$ (VIII), $HgBr_2$	*f*	10 s[e]	$[IrH(Br)_2(PEt_2Ph)_3(HgBr_2)]$ (IV)	

[a] EtOH. [b] Ambient temperature. [c] 1·00 Molar equivalent $HgCl_2$ per Ir atom only. [d] $MeOH\text{–}CHCl_3$ (1 : 1 v/v). [e] Heated under reflux. [f] MeOH. [g] $EtOH\text{–}CH_2Cl_2$ (1 : 1 v/v). [h] ν(Ir–H) at 2 219 cm^{-1} (Nujol). [i] ν(Ir–H) at 2 183 cm^{-1} (Nujol). [j] ν(Ir–H) at 2 275 cm^{-1} (Nujol). [k] ν(Ir–H) at 2 215 cm^{-1} (Nujol).

Some Reactions of Adducts (I)—(IV).—The yellow complex $[IrCl_3(PEt_3)_3(HgCl_2)]$, (I), in dilute solution in benzene gave the white isomer, (II), when exposed to light of normal laboratory intensity over a few days. We have already reported[13] facile photoisomerization of the complexes *mer*-$[IrX_3(L)_3]$. Similarly it was possible to photoisomerize the adduct $[IrCl_3(PEt_3)_3(HgBr_2)]$, (I), to its isomer, (II). Treatment of the adduct $[IrCl_3(PEt_3)_3(HgCl_2)]$, (II), with further mercury(II) chloride gave (V), as already described. If the adduct $[IrCl_3(AsEt_3)_3(HgCl_2)]$, (I) (prepared under mild conditions), was treated with a large excess of mercury(II) chloride under vigorous conditions triethylarsine was lost to mercury, with the production of $[(HgCl_2)_4(AsEt_3)_2]$. On shaking in benzene in the presence of hydrogen (1 atm, 3 days), the same adduct gave *mer*-$[IrCl_3(AsEt_3)_3]$ together with the reduction products Hg_2Cl_2 and HCl: *i.e.* the double chloro-bridge is broken by molecular hydrogen at ambient temperature. Although some mercury(II) chloride may be present by dissociation, this alone is not reduced by hydrogen in benzene solution. Similarly the action of hydrogen on $[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$, (IV), in refluxing benzene over 7 h gives $[IrH(Cl)_2(PMe_2Ph)_3]$, (VII), together with Hg_2Cl_2 and HCl.

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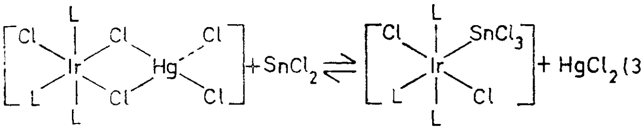
[13] P. R. Brookes, C. Masters, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3756.

In addition the double chloro-bridge in the adducts $[IrCl_3(L)_3(HgCl_2)]$, (I), could also be broken by reagents such as sodium iodide, sodium methoxide, or the ligand L (*e.g.* L = triethylarsine). The products in each case were of configuration (XI; Z = I, H, or Cl, respectively). Similarly the action of dimethylphenylphosphine on $[IrH(Cl)_2(PMe_2Ph)_3(HgCl_2)]$, (IV), gave $[IrH(Cl)_2(PMe_2Ph)_3]$, (VII). The other product, presumably of the type $[(HgCl_2)_nL_2]$, was not isolated from the reaction mixture. The action of carbon monoxide on a refluxing solution of $[IrCl_3(PEt_3)_3HgCl_2]$, (I), in 2-methoxyethanol gave $[IrCl_3(CO)(PEt_3)_2]$, (XII).

Tin(II) chloride in large excess with $[IrCl_3(PEt_3)_3(HgCl_2)]$, (I), gave *mer*-$[IrCl_2(SnCl_3)(PEt_3)_3]$, (XI; Z = $SnCl_3$). This reaction presumably involves equilibrium (3), since the Ir–Sn complex, on treatment with an excess of mercury(II) chloride, gave back $[IrCl_3(PEt_3)_3(HgCl_2)]$, (I). The irreversible redox reaction (4) occurs

$$2Hg^{2+} + Sn^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+} \qquad (4)$$

at the same time, starting either from the mercury(II) halide adduct [which provides mercury(II) ion to react with the excess of tin(II)] or from the Ir–Sn complex [which provides tin(II) ion to react with the excess of mercury(II)].



(3)

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving heating solutions under reflux were carried out under a nitrogen atmosphere. Percentage yields, m.p.s, analytical and molecular-weight data for the novel mercury(II) halide adducts are given in Table 1. Analysis of halide ion and of mercury was as previously described.[1] Molecular weights were determined on a Mecrolab osmometer at 37 °C in *ca.* 1% (w/v) solutions. ^1H N.m.r. spectra were recorded at *ca.* 34 °C at 60 MHz on a Perkin-Elmer R.10 spectrometer, using tetramethylsilane as internal reference. I.r. spectra were recorded on Grubb–Parsons G.S.4 (2 500—400 cm^{-1}) and D.B.3/D.N.2 spectrometers (450—200 cm^{-1}).

Most of the iridium-containing mercury(II) halide adducts were prepared by reaction between the iridium complex and 1—2 times its own weight (*i.e.* several molar equivalents in excess) of the appropriate mercury(II) halide, in the minimum volume of solvent necessary to dissolve the reactants at ambient temperature. These preparations are summarized in Table 3. After the indicated time the reaction mixture was either set aside at −20 °C (room-temperature reaction) or evaporated to low bulk under reduced pressure (reactions at b.p.) and then set aside at *ca.* 0 °C. The product was filtered off and washed several times with methanol at −20 °C to remove excess of mercury(II) halide. The products could not always be recrystallized (see text): when they could be, the presence of an excess of the appropriate mercury(II) halide in solution was often necessary.

cd-*Di-μ-chloro*-abg-*trichloro*-efh-*tris(dimethylphenylarsine)-mercury*(II)*rhodium*(III) $[RhCl_3(AsMe_2Ph)_3(HgCl_2)]$, (I).—A solution of *mer*-trichlorotris(dimethylphenylarsine)rhodium(III) (0·33 g) and mercury(II) chloride (0·40 g) in methanol (45 cm^3) was heated under reflux for 40 min, then allowed to spontaneously evaporate to low volume at ambient temperature. The resultant mixture of red and white crystals was filtered off, washed, dried, and mechanically separated (the crystals being large and of different habit). The required *product* formed red prisms (0·16 g).

Action of Mercury(II) *Chloride on* mer-*Trichlorotris(dimethylphenylphosphine)rhodium*(III).—A solution of the trichloro-complex (0·385 g) and mercury(II) chloride (1·0 g) in methanol (10 cm^3) and chloroform (4 cm^3) was put aside at ambient temperature for 30 h. Filtration gave white needles (0·078 g) of octachlorobis(dimethylphenylphosphine)tetramercury(II), m.p. 205—207 °C (Found: C, 14·0; H, 1·75. Calc. for $C_{16}H_{22}Cl_8Hg_4P_2$: C, 14·1; H, 1·65%). The mother liquor was put aside for a further 60 h. The resulting product was filtered off and mechanically separated into further white needles (0·033 g), and large dark orange prisms (0·168 g) of cd-*di-μ-chloro*-abg-*trichloro*-efh-*tris(dimethylphenylphosphine)mercury*(II)*rhodium*(III)-*mercury*(II) *chloride* (1/1). The conductivity of this adduct (*ca.* 10^{-3}M-nitrobenzene solution, 22 °C) was 3·54 Ω^{-1} cm^2 mol^{-1}.

Action of Mercury(II) *Chloride on* mer-*Trichlorotris(triethylarsine)rhodium*(III).—A solution of mercury(II) chloride (0·65 g) in methanol (4 cm^3) was added to a solution of the trichlororhodium complex (0·47 g) in methanol (10 cm^3). The resultant orange-brown crystals were filtered off and shown to be tri-μ-chloro-trichlorotris(triethylarsine)dirhodium(III) by comparison of the far-i.r. spectrum with that of an authentic sample.[14] The mother liquor was evaporated to dryness under reduced pressure, and the residue, after washing with dichloromethane (10 cm^3), was recrystallized from acetone to give tetrachlorobis(triethylarsine)dimercury(II) as white prisms (0·23 g), m.p. 161—165 °C (lit.,[15] 162—163 °C) (Found: C, 16·9; H, 3·55. Calc. for $C_{12}H_{30}As_2Cl_4Hg_2$: C, 16·6; H, 3·4%).

Action of One Mole of Mercury(II) *Chloride on Dichlorohydridotris(triethylphosphine)iridium*(III), (IX).—A solution of mercury(II) chloride (0·108 g) in ethanol (10 cm^3) was added to a solution of the hydridoiridium(III) complex in ethanol (20 cm^3). The reaction mixture became cloudy and the pH fell to *ca.* 2. The solution was heated to boiling, cooled, and put aside at 0 °C. White *needles* (0·078 g) of tetrachlorobis(triethylphosphine)dimercury(II) separated, m.p. 155—164 °C, from dichloromethane–ethanol (Found: C, 18·5; H, 3·75. Calc. for $C_{12}H_{30}Cl_4Hg_2P_2$: C, 18·5; H, 3·9%). Similarly the action of mercury(II) chloride, (0·40 g) on dichlorohydridotris(triethylarsine)iridium(III), (IX), in ethanol gave white *microprisms* (0·294 g) of hexadecachlorobis(triethylarsine)octamercury(II), m.p. 157 °C (decomp.) (Found: C, 5·6; H, 1·1; Hg, 64·1. Calc. for $C_{12}H_{30}As_2Cl_{16}Hg_8$: C, 5·75; H, 1·2; Hg, 64·5%). The mother liquor, on spontaneous evaporation, deposited yellow crystals (0·125 g) of *cd*-di-μ-chloro-*abg*-trichloro-*efh*-tris(triethylarsine)mercury(II)iridium(III), (I). (The far-i.r. spectrum of the product was identical with that of an authentic sample, prepared as in Table 3.)

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[14] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

[15] R. C. Evans, F. G. Mann, H. S. Pieser, and D. Purdie, *J. Chem. Soc.*, 1940, 1209.

Action of Mercury(II) *Chloride on Dichloro*(*trichlorostannio*)*tris*(*triethylphosphine*)*iridium*(III), (XI).—The iridium–tin complex (0·165 g) was suspended in methanol–chloroform (2 : 1 v/v, 15 cm^3) and mercury(II) chloride (0·40 g) was added. A white precipitate appeared. The reaction mixture was shaken vigorously for $1\frac{1}{2}$ h, and the precipitate [shown to be mercury(I) chloride] was filtered off. The resulting yellow filtrate, on evaporation and addition of ethanol, gave yellow prisms (0·139 g, 77%), of *cd*-di-μ-chloro-*abg*-trichloro-*efh*-tris(triethylphosphine)mercury(II)iridium(III), (I). (The m.p. and far-i.r. spectrum of this product were identical with those of an authentic sample, prepared as in Table 3.)

Action of Tin(II) *Chloride on* cd-*Di*-μ-*chloro*-abg-*trichloro*-efh-*tris*(*triethylphosphine*)*mercury*(II)*iridium*(III), (I).—A solution of the adduct (0·122 g) in dichloromethane–ethanol (1 : 1 v/v, 14 cm^3) was treated with tin(II) chloride (0·49 g). The reaction mixture was vigorously shaken for 1 h, then centrifuged and decanted from mercury(I) chloride and mercury. The resulting yellow solution was evaporated under reduced pressure with the addition of ethanol: dichloro(trichlorostannio)tris(triethylphosphine)iridium(III), (XI), separated out as yellow prisms (0·077 g, 75%), m.p. 145—155 °C. (The far-i.r. spectrum of this product was identical with that of an authentic sample,[16] which had m.p. 155—160 °C.)

Action of Hydrogen on cd-*Di*-μ-*chloro*-abg-*trichloro*-efh-*tris*(*triethylarsine*)*mercury*(II)*iridium*(III), (I).—The adduct (0·198 g) was dissolved in benzene (15 cm^3) and shaken with hydrogen at 1 atm and ambient temperature for 3 days. The pH of the reaction mixture fell to *ca.* 3, and a precipitate of mercury(I) chloride appeared; after filtering this off, the filtrate was evaporated to dryness and the residue recrystallized from ethanol. The residue was shown to be *mer*-trichlorotris(triethylarsine)iridium(III) by far-i.r. spectroscopy.

Action of Triethylarsine on cd-*Di*-μ-*chloro*-abg-*trichloro*-efh-*tris*(*triethylarsine*)*mercury*(II)*iridium*(III), (I).—The adduct (0·194 g) was suspended in ethanol (15 cm^3) and triethylarsine (0·20 g) was added. The reaction mixture was set aside for 15 h, evaporated under reduced pressure to low bulk, and set aside at −20 °C. Pale orange plates (0·080 g, 55%) of *mer*-trichlorotris(triethylarsine)iridium(III) separated out, identified by far-i.r. spectroscopy.

Action of Potassium Hydroxide in Methanol on cd-*Di*-μ-*chloro*-abg-*trichloro*-efh-*tris*(*dimethylphenylphosphine*)*mercury*(II)*iridium*(III), (I).—The adduct (0·067 g) was suspended in methanol (10 cm^3) and potassium hydroxide (0·15 g) was added. The reaction mixture was vigorously shaken for 18 h and a precipitate, shown to be mercury(I) chloride, was filtered off. The filtrate, on evaporation and cooling, deposited yellow needles (0·040 g, 87%), identified as dichlorotris(dimethylphenylphosphine)hydridoiridium(III), (IX), by n.m.r. (in chloroform solution) and i.r. spectroscopy (in benzene).

Action of Hydrogen on cd-*Di*-μ-*chloro*-ab-*dichloro*-g-*hydrido*-efh-*tris*(*dimethylphenylphosphine*)*mercury*(II)*iridium*(III), (IV).—A suspension of the adduct (0·154 g) in benzene (15 cm^3) was heated under reflux, with hydrogen bubbling through the solution, for 7 h. A precipitate, shown to be mercury(I) chloride, was filtered off, and the filtrate evaporated to dryness to yield a residue, shown by i.r. spectroscopy in benzene solution to contain dichlorotris(dimethylphenylphosphine)hydridoiridium(III), (VII).

mer-*Dibromochlorotris*(*triethylphosphine*)*iridium*(III), (VI).—This complex was required in the above studies and has not been previously described. Concentrated hydrochloric acid (0·5 cm^3) was added dropwise to a solution of dibromohydridotris(triethylphosphine)iridium(III), (VII), (0·497 g), in methanol (3 cm^3). Water (0·5 cm^3) was added, and the reaction mixture set aside at −20 °C. The required *product* separated out as orange prisms (0·099 g), m.p. 116—121 °C (Found: C, 29·05; H, 6·2. Calc. for $C_{18}H_{45}Br_2ClIrP_3$: C, 29·15; H, 6·1%). A sample of the complex gave a titre of 2·12 cm^3 mercury(II) nitrate solution (calc. 2·18 cm^3 for the total halogen present), ν(Ir–Cl) *trans* to tertiary phosphine at 273 cm^{-1}.

We thank I.C.I. Ltd. for financial support and acknowledge the interest of (the late) Professor Sir Ronald Nyholm {who in 1947 characterised a 1 : 1 adduct of *mer*-[$RhCl_3(AsMePh_2)_3$] with mercury(II) chloride}.[17]

[3/2539 *Received, 13th December,* 1973]

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[16] J. Powell and B. L. Shaw, unpublished work.

[17] R. S. Nyholm, personal communication, 1967.