Mercuric Halide Adducts of Tertiary Phosphine or Tertiary Arsine Complexes of Palladium(II) and Platinum(II) †

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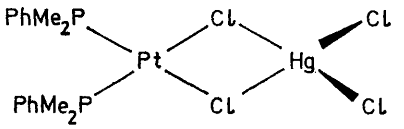
Certain complexes of the type $[MX_2L_2]$ (M = Pd or Pt; X = Cl, Br, or I; L = tertiary phosphine or tertiary arsine) react with mercuric halides to give adducts of the type $[MX_2L_2HgX_2]$, having a double halide bridge between the metal atoms. A di-adduct $[PtCl_2(PMe_3)_2(HgCl_2)_2]$ is also reported. The adducts are often easily dissociated. Adducts of the same formula are also obtained by the action of mercuric halides on some complexes of the type *trans*-$[PtHXL_2]$. The formation of these adducts, their structure and their reactivity, have been followed by a variety of physico-chemical techniques, far-i.r. spectroscopy proving exceptionally useful.

THE reaction of mercuric halides with transition metal complexes has been shown to give compounds with transition metal–mercury bonds, either by (*a*) addition to low oxidation state complexes, *e.g.* the oxidation of *trans*-$[IrCl(CO)(PPh_3)_2]$ to $[IrCl_2(HgCl)(CO)(PPh_3)_2]$,[1] or by (*b*) formation of metal donor–acceptor complexes, *e.g.* $[Co(CO)_2(\pi\text{-}C_5H_5)]$ can apparently act as a Lewis base to give $[Co(CO)_2(\pi\text{-}C_5H_5),HgCl_2]$, the crystal structure[2] of which shows it to contain a cobalt–mercury bond. It has come to our attention that the crystal structure of a third type of product, involving increase of the co-ordination number of mercury, with halogen bridge formation, has been determined: the compound studied was $[PtCl_2(PMe_2Ph)_2HgCl_2]$.[3] Mann and Purdie[4] very briefly reported the formation of a 1 : 1 adduct from equivalent quantities of *trans*-$[PdBr_2(AsPr^n_3)_2]$ and mercuric bromide in ethanol solution;[4] we prepared some 29 adducts of this type in 1968,[5] but were not sure of their structure, until we became aware of the *X*-ray work.[3] We now describe these new complexes.

When complexes of the type *cis* or *trans*-$[MX_2L_2]$ (M = Pd or Pt; X = Cl, Br, or I; L = tertiary phosphine or tertiary arsine) are treated with mercuric halides, HgX_2, highly crystallised 1 : 1 adducts $[MX_2L_2HgX_2]$ are obtained. The crystal structure of a typical adduct $[PtCl_2(PMe_2Ph)_2HgCl_2]$[3] is as shown in configuration (I); the co-ordination is square-planar about platinum and distorted tetrahedral about mercury. Bond lengths suggest that the mercuric chloride is only weakly co-ordinated. We consider the structure of the other adducts to be analogous. The structure shows that the compound is the *sym-cis* isomer, *i.e.* both ligands L remain attached to the transition metal. If the ligand L is not strongly bonded to palladium, as is the case for certain ligands, this type of product is not obtained, since the ligand L becomes bonded to mercury (see below).



(I)

A typical procedure to give a product of configuration (I) is that between a solution of *trans*-$[PdCl_2(PEt_2Ph)_2]$ in methanol–chloroform and a methanolic solution of mercuric chloride. On admixture of these solutions yellow needles of the 1 : 1 adduct are formed immediately. The molecular weight of this product in chloroform solution is that expected for $[PdCl_2(PEt_2Ph)_2HgCl_2]$: commonly however the molecular weight data indicate considerable dissociation in solution. Molecular weights and other data for the various compounds are given in the Table. It is noteworthy that dissociation depends

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† No reprints available.

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

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

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

[4] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1940, 1230.

[5] P. R. Brookes, Ph.D. Thesis, University of Leeds, 1968.

on the halide ligand present such that dissociation increases in the other $Cl < Br < I$: we cannot explain this trend, since it might be expected that (since the iodide is the best bridging ligand) an iodo-complex of configuration (I) would be more stable to dissociation than its bromo- or chloro-analogues.

The molar conductivities of some representative adducts were determined in 10^{-3}M nitrobenzene solution at 26°: $[PdCl_2(PEt_2Ph)_2HgCl_2]$ and $[PtCl_2(PMe_2Ph)_2HgCl_2]$ gave values of 1·71 and 2·86 Ω^{-1} cm^2 mol^{-1}, respectively. These values are considerably higher than those of the parent transition-metal complexes (*ca.* 3 × 10^{-2} Ω^{-1} cm^2 mol^{-1}), although less than that required for a 1 : 1 electrolyte in this solvent (*e.g.* for $PMePh^+I^-$, 19·1 Ω^{-1} cm^2 mol^{-1}). Since the conductivity of mercuric chloride is very low, simple dissociation to the precursors cannot explain the appreciable conductivity values of the adducts. We suggest that the conductivity may be associated with slight ionic dissociation according to equation (1) involving a three co-ordinate

$$MX_2L_2HgX_2 \rightleftharpoons MX_2L_2HgX^+X^- \qquad (1)$$

mercury(II) species: the species HgX_3^- is established, and for its congener cadmium it is known that an 0·5M $CdBr_2$ solution contains twice the concentration (0·043M) of $CdBr_3^-$ as of the four-co-ordinate $CdBr_4^{2-}$.[6]

Analytical, molecular weight, melting point, and far-i.r.[a] data for complexes of the type $[MX_2L_2,nHgY_2]$ (M = Pd or Pt; X and Y = Cl, Br, or I; L = tertiary-phosphine or -arsine; n = 1 or 2)

Compound	Yield (%)	Colour	Analytical data[b] C	H	Other	M[b,c]	M.p.	ν(M–Cl–Hg)	ν(Hg–Cl)	ν(Hg–Br)†	Frequencies of other bands
$PdCl_2(PMe_2Ph)_2HgCl$	74	Yellow	26·45 (26·5)	2·9 (3·05)		723 (725)	159—161[c]	282vs, 259s	347s		429m, 325m, 253m
$PdBr_2(PMe_2Ph)_2HgBr_2$	69	Yellow	21·45 (21·3)	2·45 (2·45)		667 (903)	141—146			233s	443s, 420m, 357w, 341m, 299w
$PdCl_2(PEt_2Ph)_2)HgCl_2$	98	Yellow	30·55 (30·75)	3·8 (3·85)	Hg: 25·3(25·65)	758 (781)	153—156	282s, 250s	340vs		394m, 219m
$PdCl_2(Ph_2PCH_2\cdot)_2HgCl_2$	34	Cream	36·65 (36·85)	3·1 (2·85)			287—290[d]	295vs, 278vs	331s		430m, 392w, 361vw
$PdCl_2(AsMe_2Ph)_2HgCl_2$	94	Orange	23·5 (23·65)	2·65 (2·75)			170—174	286vs, 251s	335s		314m, 207m
$PdBr_2(AsMe_2Ph)_2HgBr_2$	88	Orange	20·8 (19·4)	2·4 (2·25)			144—146			238s	318s, 307m, 289w, 275m, 263w
$PdI_2(AsMe_2Ph)_2HgI_2$	91	Brown	16·65 (16·3)	2·0 (1·9)		616 1179)	112—116	283vs, 244s			
$PdCl_2(PMe_2Ph)_2HgBr_2$	85	Yellow	23·1 (23·6)	2·6 (2·75)			175—177				444s, 424m, 350m, 319m * 304m, 224m 319m,* 304m, 224
$PdCl_2(PMe_2Ph)_2HgI_2$	90	Yellow	21·4 (21·15)	2·6 (2·45)			172—174[d]	279vs, 254s			444s, 428m, 384m, 306m, 221m
$PdCl_2(PEt_2Ph)_2HgBr_2$	95	Yellow	27·7 (27·6)	3·3 (3·5)	1·64 (1·68)[e]		156—159	279vs, 241vs			391m, 323m
$PdCl_2(PEt_2Ph)_2HgI_2$	84	Yellow	24·7 (24·9)	2·95 (3·15)			150—153	279vs, 248vs			408vw, 393w, 324w, 296m
$PdCl_2(AsMe_2Ph)_2HgBr_2$	74	Orange	21·4 (21·3)	2·4 (2·45)			147—149·5	287vs, 277s		238vs	320m, 313m
$PtCl_2(PMe_3)_2HgCl_2$	36	Colourless	10·9 (10·45)	2·5 (2·65)			212—230[d]	278vs, 263vs	320vs		394m, 373s
$PtBr_2(PMe_3)_2HgBr_2$	88	Cream	8·75 (8·3)	2·0 (2·1)			200—204[d,f]			229vs	394m, 373s
$PtCl_2(PEt_3)_2HgCl_2$	93	Colourless	18·7 (18·6)	3·9 (3·9)		593 (774)	170—172·5	283vs, 268vs	330vs		424s, 379w, 291s,* 254m
$PtBr_2(PEt_3)_2HgBr_2$	71	Colourless	15·65 (15·15)	3·5 (3·2)			151—154			226m	437w, 423m, 377w, 330w
$PtCl_2(PMe_2Ph)_2HgCl_2$	95	White	23·75 (23·6)	2·7 (2·7)	Pt: 25·0 (23·95)		190—193	291vs, 271s	340vs		450s, 431m, 359m, 313m
$PtBr_2(PMe_2Ph)_2HgBr_2$	82	Cream	19·45 (19·35)	2·2 (2·25)	Pt: 19·9 (19·65)		149—151			231s	432m, 362m, 353m, 307w, 291w
$PtI_2(PMe_2Ph)_2HgI_2$	43	Brown	16·5 (16·3)	2·15 (1·9)	Pt: 17·05 (16·55)	687 (1180)	167—173·5				446s, 431s, 372m, 273w
$PtCl_2(PEt_2Ph)_2HgCl_2$	52	Colourless	27·35 (27·6)	3·55 (3·5)			178—181	294vs, 264s	347s		433s,* 498w, 329m, 288s
$PtCl_2(PPh_3)_2HgCl_2$	73	Cream	41·1 (40·7)	3·15 (2·85)	Pt: 19·0 (18·35)		290—295[d]	294s, 277s	345s		443m, 418m, 313m, 222m
$PtCl_2(AsMe_2Ph)_2HgCl_2$	94	Cream	21·35 (21·3)	2·5 (2·45)	Pt: 22·1 (21·65)	707 (902)	174—176·5	296vs, 279s	340s		325m, 313m,* 255s
$PtBr_2(AsMe_2Ph)_2HgBr_2$	85	Yellow	17·8 (17·8)	2·15 (2·05)		721 (1080)	144—146			238s	319s, 313m *
$PtCl_2(PEt_3)_2HgBr_2$	82	Colourless	17·0 (16·7)	3·4 (3·5)	2·73 (2·80)[e]		159—164	290vs, 279vs		234vs	437m*, 422s, 380w, 329w
$PtCl_2(PEt_3)_2HgI_2$	79	Colourless	15·0 (15·05)	3·25 (3·15)			160—164	283vs, 263s			431s, 382m
$PtCl_2(PMe_2Ph)_2HgBr_2$	50	Cream	20·95 (21·3)	2·5 (2·4)			147—148	293s, 278m		239s	446s, 431m, 357m, 313m
$PtCl_2(AsMe_2Ph)_2HgBr_2$	65	Yellow	18·85 (19·4)	2·2 (2·25)			138—140	292vs, 286s		242vs	320s, 315m, 208m
$PtCl_2(AsMe_2Ph)_2HgI_2$	62	Cream	17·75 (17·7)	2·05 (2·05)			133—135	305s, 287s			325m, 263m, 250m
$PtCl_2(PMe_3)_2(HgCl_2)_2$[g]	46	White	9·25 (9·05)	2·3 (2·1)	Cl: 26·7 (26·75) Pt: 18·7 (18·4)		218—242[f]		376vs		397m, 301vs,[h] 289vs,[e] 276vs[h]

[a] In cm^{-1}, over the range 450—200 cm^{-1}, Nujol mulls, error $< \pm 2$ cm^{-1}. * = shoulder. [b] Theoretical values given in parentheses. [c] Chloroform solution. [d] With decomp. [e] $AgNO_3$ titre, ml. [f] With some sublimation. [g] Compound contains 1·0 mol of 1,2-dichloroethane per platinum atoms. [h] Pt–Cl–Hg and Hg–Cl–Hg bridging absorptions.

† Tentative assignments.

Adducts of the type $[MX_2L_2HgX_2]$ have been obtained from complexes of the type *trans*-$[MX_2L_2]$ as precursors as well as from various *cis*-compounds. In the former case a change in stereochemistry is necessary to form the product with configuration (I). Some of the adducts of type $[PdCl_2L_2HgCl_2]$ are yellow (see Table). This is not incompatible with a *cis* arrangement of the ligands L about Pd. Although some early papers indicate otherwise,[7] not all yellow complexes $[PdCl_2L_2]$ have the *trans*-configuration. Thus $[PdCl_2(PPh_2CH_2\cdot)_2]$ is mononuclear and a non-conductor and must be the *cis*-isomer, but its colour is yellow.[8] In general the adducts $[MX_2L_2HgX_2]$ are the same colour as the parent complexes $[MX_2L_2]$. They are air-stable, again like the parent complexes.

I.r. spectra of the adducts (2500—450 cm^{-1}) are

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[6] J. W. Macklin and R. A. Plane, *Inorg. Chem.*, 1970, **9**, 821 and references therein.

[7] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1953, 70 and references therein.

[8] M. J. Hudson, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 1968, 40.

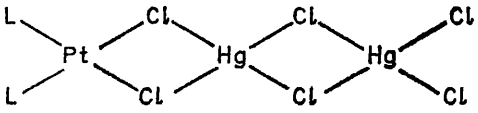
closely comparable with their precursors. The far-i.r. spectra (450—200 cm^{-1}) show important differences however, especially in the region associated with metal–chlorine stretching vibrations. Study of the far-i.r. spectra (Table) was facilitated by the preparation of complexes of the type $[MCl_2L_2HgY_2]$ (Y = Br or I), from $[MCl_2L_2]$ and HgY_2. Complexes of the type $[MY_2L_2HgCl_2]$ could not be prepared, the appropriate reactants yielding only $[MCl_2L_2HgCl_2]$ even under very mild conditions, presumably because of exchange of chloride ion derived from the (comparatively) ionic mercuric chloride.

The far-i.r. spectra of the 1 : 1 adducts are compatible with the overall stereochemistry (I). Comparison of the spectra of the complexes $[PdX_2(PMe_2Ph)_2HgX_2]$ (X = Cl or Br; see Table) shows that three strong bands are associated with the chloride ligands, at 347, 282, and 259 cm^{-1}, in the chloro-complex. We assign the latter two bands to the bridging chloride ligands, by analogy with $[PdCl_2(PMe_2Ph)_2HgBr_2]$ which shows now two absorptions compared with the tetrabromo-adduct, at 283 and 244 cm^{-1}, and $[PdCl_2(PMe_2Ph)_2HgI_2]$ which shows a similar pair of bands at 279 and 254 cm^{-1}. These values are comparable with a pair of absorptions at 310—300 and 280—250 cm^{-1} in complexes of the type $[Pd_2Cl_4L_4]$ and assigned [9] to the bridging chloro-ligands. The remaining significant absorption in the spectrum of $[PdCl_2(PMe_2Ph)_2HgCl_2]$, at 347 cm^{-1}, is then assignable to terminal ν(Hg–Cl). Mercuric chloride itself gives a very strong absorption in the far-i.r. region at 374 cm^{-1} [10] (and also weaker bands at 331 and 311 cm^{-1}), but the structure of the solid is very distorted octahedral about the mercury atom.[11]

Terminal $>HgCl_2$ groups in all our adducts give only one ν(Hg–Cl) absorption (Table). This we attribute to accidental overlap: compare the single band due to ν(Hg–Cl) assignable to $[HgCl_2(pyridine)_2]$ [12,13] and comparable complexes, where two bands are expected, and the very poor or non-resolution of $>SnCl_2$ and $-SnCl_3$ groups, which similarly often give only one band.[14]

For the 1 : 1 adducts of the platinum complexes, assignments of the far-i.r. spectra can be made as discussed above for palladium (see Table). The results given in this Table show that terminal ν(Hg–Cl) is comparable for all complexes of the type $[MCl_2L_2HgCl_2]$ configuration (I); for M = Pd, the range for ν(Hg–Cl) is 347—335 cm^{-1} and for M = Pt, ν(Hg–Cl) the range is 347—320 cm^{-1}. The bridging chlorine ligands give rise to absorption which is lower for M = Pd in complexes of the type $[MCl_2L_2HgX_2]$ (X = Cl, Br, or I), configuration (I) than for M = Pt. For the Pd complexes, the two bridging frequencies fall in the (overlapping) ranges 295—279 and 278—241 cm^{-1}; for the Pt complexes, the corresponding ranges are 305—278 and 287—263 cm^{-1}. This behaviour parallels that of bridging ν(M–X) absorption of complexes of the type $[M_2X_4L_2]$.[9] In such complexes for M = Pd, the chlorine bridging modes were assigned as two bands in the range 310—300 and 280—250 cm^{-1}, again lower than the range established for the corresponding complexes where M = Pt (335—310 and 295—250 cm^{-1}).

The di-adduct $[PtCl_2(PMe_3)_2(HgCl_2)_2]$, to which by analogy with the mono-adducts we assign configuration (II) shows four new very strong bands in the far-i.r.



(II)

region compared to *cis*-$[PtCl_2(PMe_3)_2]$, at 376, 301, 289, and 276 cm^{-1}. The first band we can assign to terminal ν(Hg–Cl): the position of this band is very similar to that at 374 cm^{-1} in mercuric chloride, as described above, and demonstrates the extremely weak bonding of the 'second' $HgCl_2$ molecule. The other three bands are then associated with the two double chlorine bridges: we cannot assign these bands specifically. The di-adduct is formed under vigorous conditions (see Experimental section): its formation may be associated with the comparative insolubility of trimethylphosphine complexes in most solvents.

^{1}H N.m.r. studies have been made on the complexes $[MX_2(PMe_2Ph)_2HgX_2]$ (X = Cl or Br). The adducts were insufficiently soluble in chloroform for spectra to be obtained: however, they were soluble in liquid sulphur dioxide. The spectrum of the palladium complex (spectra were obtained from sealed tubes) was identical with that of $[PdCl_2(PMe_2Ph)_2]$ in the same solvent,[15] showing that complete dissociation of the adduct must occur. In liquid sulphur dioxide as solvent the methyl resonance pattern consists of two doublets ^2J(P–H) 12·1, ^4J(P–H) 0·9 Hz (coupling of the methyl group to the remote phosphorus is not observed in other commonly used n.m.r. solvents, C_6H_6, $CDCl_3$, CH_2Cl_2, *etc.*).

Formation of a 1 : 1 adduct does not always occur between $[PdX_2L_2]$ and HgX_2. We have confirmed that reaction of the type

$$2[PdX_2L_2] + nHgX_2 \longrightarrow [Pd_2X_4L_2] + [(HgX_2)_nL_2] \quad (n = \geqslant 1)$$

occurs when L is a comparatively weakly bonded tertiary phosphine or tertiary arsine ligand with respect to palladium; thus we have repeated Mann's work [4] with PEt_3 and $AsEt_3$, and also shown that the above reaction similarly occurs when L = $P(allyl)_3$ or PMe_3 (using X = Cl). In the latter case, the novel complex

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[9] D. M. Adams and P. J. Chandler, *Chem. Comm.*, 1966, 69.

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

[11] D. Grdenic, *Arkiv Kem.*, 1950, **22**, 14.

[12] R. J. H. Clark and C. S. Williams, *Chem. and Ind.*, 1964, 1317.

[13] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

[14] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 45.

[15] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

$[Pd_2Cl_4(PMe_3)_2]$ was isolated. The far-i.r. spectrum of this bright orange complex has strong bands at 254 and 293 cm^{-1} assignable to the stretching frequency of the bridging chloro-ligands,[9] and one at 344 cm^{-1} assignable to terminal ν(Pd–Cl).

Nyholm and Vrieze[16] reported that $[PtHCl(PPh_3)_2]$ when treated with mercuric halides gave 'mostly reduction to metallic mercury and no complexes could be isolated.' Allen and Baird[17] showed that at 0° $HgCl_2$ and *trans*-$[PtHCl(PPh_3)_2]$ gave metallic mercury and *trans*-$[PtCl_2(PPh_3)_2]$. We now find that with *trans*-$[PtHX(PR_3)_2]$ (X = Cl, Br, or I; $PR_3 = PEt_3$ or PEt_2Ph) HgX_2 react as follows:

$$[PtHX(PR_3)_2] + 3HgX_2 \longrightarrow [PtX_2(PR_3)_2HgX_2] + Hg_2X_2 + HX$$

Attempted metathesis of the adducts of type $[MCl_2(PR_3)_2HgCl_2]$ (M = Pd or Pt) with lithium bromide or sodium iodide caused loss of mercuric halide and gave only complexes of type $[MX_2(PR_3)_2]$ (see Experimental section). Similarly $[PtCl_2(PMe_2Ph)_2HgCl_2]$ with chlorine in chloroform gave *cis*-$[PtCl_4(PMe_2Ph)_2]$.

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage apparatus and are corrected. All reactions involving the heating of solutions under reflux were carried out under nitrogen. Percentage yields, m.p.s, analytical and molecular-weight data for the mercuric halide adducts are given in the Table. Analysis of halide ion in the presence of mercuric ion was as by Fernandez *et al.*[18] Mercury was determined (by Mr. A. Hedley) by heating the compounds in an atmosphere of nitrogen at *ca.* 800—850° and absorbing the resultant mercury vapour on finely-divided gold foil at *ca.* 120°. Molecular weights were determined on a Mecrolab Osmometer at 37° in *ca.* 1% *w/v* solutions.

All the adducts described below, with the exception of the unique di-mercuric chloride adduct, are considered to have the configuration (I) as shown in the discussion above, *i.e.*, the *sym-cis* isomer.

Di-μ-chloro-[dichloromercury(II)*]bis(dimethylphenylphosphine)palladium*(II), $[PdCl_2(PMe_2Ph)_2HgCl_2]$.—A solution of mercuric chloride (0·20 g) in methanol (3 ml) was added to one of dichlorobis(dimethylphenylphosphine)palladium(II) (0·13 g) in chloroform–methanol (4 : 1, 5 ml). After 6 h at ambient temperature, the required *product* (0·15 g) had deposited from the reaction mixture as prisms.

The following compounds were similarly prepared from the appropriate precursors, with the time for essentially complete precipitation of the product given in parentheses: *di-μ-chloro-[dichloromercury*(II)*]bis(diethylphenylphosphine)palladium*(II), $[PdCl_2(PEt_2Ph)_2HgCl_2]$, as needles (50 min); *di-μ-chloro-[dichloromercury*(II)*]bis(dimethylphenylarsine)palladium*(II), $[PdCl_2(AsMe_2Ph)_2HgCl_2]$, as prisms (14 h); *di-μ-chloro-[dibromomercury*(II)*]bis(dimethylphenylphosphine)palladium*(II), $[PdCl_2(PMe_2Ph)_2HgBr_2]$, as prisms (2 h); *di-μ-chloro-[di-iodomercury*(II)*]bis(dimethylphenylphosphine)palladium*(II), $[PdCl_2(PMe_2Ph)_2HgI_2]$, as prisms (1 h); *di-μ-chloro-[dibromomercury*(II)*]bis(diethylphenylphosphine)palladium*(II), $[PdCl_2(PEt_2Ph)_2HgBr_2]$, as prisms (1 h); *di-μ-chloro-[di-iodomercury*(II)*]bis(diethylphenylphosphine)palladium*(II), $[PdCl_2(PEt_2Ph)_2HgI_2]$, as prisms (3 h); *di-μ-chloro-[dibromomercury*(II)*]bis(dimethylphenylarsine)palladium*(II), $[PdCl_2(AsMe_2Ph)_2HgBr_2]$, as prisms (1 h); *di-μ-chloro-[dichloromercury*(II)*]bis(dimethylphenylphosphine)platinum*(II), $[PtCl_2(PMe_2Ph)_2HgCl_2]$, as prisms (1 h).

Di-μ-bromo-[dibromomercury(II)*]bis(dimethylphenylphosphine)palladium*(II), $[PdBr_2(PMe_2Ph)_2HgBr_2]$.—A solution of mercuric bromide (0·30 g) in methanol (3 ml) was added to one of dibromobis(dimethylphenylphosphine)palladium(II) (0·32 g) in chloroform–methanol (2 : 1, 9 ml). The mixture was heated under reflux for 4 h. Removal of about half the solvent under reduced pressure gave the required *product* as prisms (0·37 g).

The following compounds were similarly prepared from the appropriate precursors, the time of heating under reflux being given in parentheses: *di-μ-chloro-[dichloromercury*(II)*][1,2-bis(diphenylphosphino)ethane]palladium*(II), $[PdCl_2(Ph_2PCH_2CH_2PPh_2)HgCl_2]$, as plates (10 min) [reaction carried out in chloroform–acetone (2 : 1)]; *di-μ-bromo-[dibromomercury*(II)*]bis(dimethylphenylarsine)palladium*(II), $[PdBr_2(AsMe_2Ph)_2HgBr_2]$, as prisms (19 h); *di-μ-iodo-[di-iodomercury*(II)*]bis(dimethylphenylarsine)palladium*(II), $[PdI_2(AsMe_2Ph)_2HgI_2]$, as prisms (30 h); *di-μ-chloro-[dichloromercury*(II)*]bis(trimethylphosphine)platinum*(II), $[PtCl_2(PMe_3)_2HgCl_2]$, as prisms (10 min) [reaction carried out in dichloroethane–methyl isopropyl ketone (2 : 1)]; *di-μ-bromo-[dibromomercury*(II)*]bis(trimethylphosphine)platinum*(II), $[PtBr_2(PMe_3)_2HgBr_2]$, as prisms (4 h) (reaction carried out in acetone); *di-μ-chloro-[dichloromercury*(II)*]bis(triethylphosphine)platinum*(II), $[PtCl_2(PEt_3)_2HgCl_2]$, as plates (5 min) {reaction carried out in acetone using *cis*-$[PtCl_2(PEt_3)_2]$ as precursor; also obtained from the *trans*-isomer under more vigorous conditions}; *di-μ-bromo-[dibromomercury*(II)*]bis(triethylphosphine)platinum*(II), $[PtBr_2(PEt_3)_2HgBr_2]$, as plates (5 h); *di-μ-bromo-[dibromomercury*(II)*]bis(dimethylphenylphosphine)platinum*(II), $[PtBr_2(PMe_2Ph)_2HgBr_2]$, as prisms (70 h) (reaction carried out in acetone); *di-μ-iodo-[di-iodomercury*(II)*]bis(dimethylphenylphosphine)platinum*(II), $[PtI_2(PMe_2Ph)_2HgI_2]$, as prisms (16 h) (reaction carried out in chloroform); *di-μ-chloro-[dichloromercury*(II)*]bis(triphenylphosphine)platinum*(II), $[PtCl_2(PPh_3)_2HgCl_2]$, as prisms (3 h) [reaction carried out in acetone–chloroform (2 : 1)]; *di-μ-chloro-[dichloromercury*(II)*]bis(dimethylphenylarsine)platinum*(II), $[PtCl_2(AsMe_2Ph)_2HgCl_2]$, as plates (2 min) (reaction carried out in acetone); *di-μ-bromo-[dibromomercury*(II)*]bis(dimethylphenylarsine)platinum*(II), $[PtBr_2(AsMe_2Ph)_2HgBr_2]$, as prisms (22 h); *di-μ-chloro-[dibromomercury*(II)*]bis(triethylphosphine)platinum*(II), $[PtCl_2(PEt_3)_2HgBr_2]$, as plates (30 s); *di-μ-chloro-[di-iodomercury*(II)*]bis(triethylphosphine)platinum*(II), $[PtCl_2(PEt_3)_2HgI_2]$, as prisms (2 min); *di-μ-chloro-[dibromomercury*(II)*]bis(dimethylphenylphosphine)platinum*(II), $[PtCl_2(PMe_2Ph)_2HgBr_2]$, as prisms (3 min); *di-μ-chloro-[dibromomercury*(II)*]bis(dimethylphenylarsine)platinum*(II), $[PtCl_2(AsMe_2Ph)_2HgBr_2]$, as prisms (10 s); *di-μ-chloro-[di-iodomercury*(II)*]bis(dimethylphenylarsine)platinum*(II), $[PtCl_2(AsMe_2Ph)_2HgI_2]$, as needles (3 min).

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Action of Mercuric Chloride on cis-*Dibromobis(triethylphosphine)platinum*(II).—A mixture of mercuric chloride (0·44 g) and the dibromoplatinum(II) complex (0·17 g) was dissolved in methanol–chloroform (2 : 1, 15 ml), and the reaction mixture was set aside for 48 h: *di-μ-chloro-[dichloromercury*(II)*]bis(triethylphosphine)platinum*(II) (0·18 g) separated out, identified by its far-i.r. spectrum. A similar reaction between mercuric chloride and dibromobis(dimethylphenylphosphine)platinum(II) (reaction time 30 s) gave di-μ-chloro-[dichloromercury(II)]bis(dimethylphenylphosphine)platinum(II), identified by its m.p. and far-i.r. spectrum.

Di-μ-chloro-dichloromercury(II)*[di-μ-chloro-mercury*(II)*]bis(trimethylphosphine)platinum*(II)*–1,2-Dichloroethane*, $[PtCl_2(PMe_3)_2(HgCl_2)_2]C_2H_4Cl_2$, *Configuration* (II).—A solution of mercuric chloride (0·905 g) in methylisopropyl ketone (10 ml) was added to a solution of the dichloroplatinum(II) complex (0·33 g) in 1,2-dichloroethane (20 ml) and the reaction mixture was heated under reflux for 4 h. On cooling, the solution deposited the *product* as prisms (0·37 g).

Action of Mercuric Chloride on cis-*Dichlorobis(trimethylphosphine)palladium*(II).—A solution of mercuric chloride (0·52 g) in acetone (5 ml) was added to one of the palladium(II) complex (0·19 g) in acetone–1,2-dichloroethane (1 : 1, 17 ml) at *ca.* 45°. The reaction mixture became dark yellow, and deposited a mixture of white and yellow crystals. After cooling the solution to 0°, the mixed product (0·34 g) was filtered off, and extracted with boiling ethanol (10 ml), leaving a residue. The yellow extract on cooling gave *di-μ-chloro-dichlorobis(trimethylphosphine)palladium*(II) (0·025 g) as needles. The residue was extracted with boiling acetone (10 ml). On cooling the extract it gave *hexachlorobis(trimethylphosphine)trimercury*(II) (0·04 g) as colourless needles, m.p. 267—273° (decomp.) (Found: C, 7·35; H, 1·75. $C_6H_{18}Cl_6Hg_3P$ requires C, 7·45; H, 1·9%). A similar reaction between mercury chloride and *trans*-dichlorobis(triallylphosphine)palladium(II) gave di-μ-chloro-dichlorobis(triallylphosphine)dipalladium(II) (identified by comparison of its ^1H n.m.r. spectrum with that of an authentic sample,[19] and *tetrachlorobis(triallylphosphine)dimercury*(II) as colourless prisms, m.p. 139—141·5° (Found: C, 25·1; H, 3·45. $C_{18}H_{30}Cl_4Hg_2P_2$ requires C, 25·4; H, 3·55%). ν(C=C) 1631 cm^{-1} (s); C–H deformation of CH_2 group 1410 cm^{-1} (s); C–H deformation of $RC\mathit{H}{=}CH_2$ 990 cm^{-1} (vs); C–H deformation of $RCH{=}\mathit{CH_2}$ 919 cm^{-1} (vs).

Action of Mercuric Chloride on trans-*Hydridochlorobis(triethylphosphine)platinum*(II).—A solution of mercuric chloride (0·50 g) in methanol (10 ml) was added to a solution of the hydrido-complex (0·20 g) in methanol (20 ml). The reaction mixture was heated to b.p., then put aside at 20° for 6 h. Its pH had decreased to *ca.* 3. A grey precipitate (identified as mercurous chloride) was filtered off. On removal of about half the bulk of the solvent under reduced pressure, the residual solution gave *di-μ-chloro-[dichloromercury*(II)*]bis(triethylphosphine)platinum*(II) as plates (0·19 g) identified by comparison of its far-i.r. spectrum with that of an authentic sample (see above). The residual mother-liquors, on spontaneous evaporation at ambient temperature, gave yellow prisms (0·02 g) of *trans*-dichlorobis(triethylphosphine)platinum(II), m.p. 141—143° (lit.,[20] 142—143°) (Found: C, 29·15; H, 6·15. Calc. for $C_{12}H_{30}Cl_2P_2Pt$: C, 28·7; H, 6·0%). A similar reaction between mercuric chloride and *trans*-hydridochlorobis(diethylphenylphosphine)platinum(II) gave a precipitate shown to contain mercurous bromide and mercury, and a solution from which *di-μ-chloro-[dichloromercury*(II)*]bis(diethylphenylphosphine)platinum*(II) was isolated as prisms.

Action of Mercuric Bromide on trans-*Hydridobromobis(triethylphosphine)platinum*(II).—A solution of mercuric bromide (0·30 g) in methanol (4 ml) was added to a solution of the hydrido-complex (0·16 g) in methanol (10 ml). A flocculant yellow precipitate appeared, and the pH of the solution fell to *ca.* 2. The reaction mixture was maintained at b.p. for 1 min, cooled, and a grey precipitate (identified as mercurous bromide) was filtered off. The mother-liquor at 0° deposited *cis*-dibromobis(triethylphosphine)platinum(II) (0·12 g) as white prisms (identified by analysis and by its m.p.). A similar reaction between mercuric iodide and *trans*-hydridoiodobis(triethylphosphine)platinum(II) gave an insoluble greyish-yellow solid and an acidic solution from which *trans*-di-iodobis(triethylphosphine)platinum(II) was isolated as yellow prisms (68%), identified by analysis, m.p., and its far-i.r. spectrum.[21]

Action of Sodium Iodide on Di-μ-chloro-[dichloromercury(II)*]bis(diethylphenylphosphine)palladium*(II).—Sodium iodide (0·40 g) was added to a solution of the mercuric chloride adduct (0·20 g) in acetone (10 ml). After being put aside for 30 min, the reaction mixture was evaporated to about half its bulk under reduced pressure, water (0·4 ml) and ethanol (10 ml) were added, and the solution put aside at −20° trans-*di-iodobis(diethylphenylphosphine)palladium*(II) crystallised out as dark orange-red prisms (0·16 g, 93%), m.p. 123—125·5° (Found: C, 34·5; H, 4·35; Pd, 16·4. $C_{20}H_{30}I_2P_2Pd$ requires C, 34·7; H, 4·35; Pd, 15·35%). A similar reaction between lithium bromide and di-μ-chloro-[dichloromercury(II)]bis(diethylphenylphosphine)platinum(II) gave cis-*dibromobis(diethylphenylphosphine)platinum*(II) as very pale cream prisms, m.p. 190—193° (Found: C, 35·1; H, 4·3. $C_{20}H_{30}Br_2P_2Pt$ requires C, 34·95; H, 4·4; Pt, 28·4%). A similar reaction between sodium iodide and di-μ-chloro-[dichloromercury(II)]bis(dimethylphenylarsine)platinum(II) gave di-iodobis(dimethylphenylarsine)platinum(II) (80%), identified by its m.p. (158·5—160·5°) (lit.,[22] 155—157°) and by analysis. A similar reaction between sodium iodide and [dichloromercury(II)-di-μ-chloromercury(II)di-μ-chloro]bis(trimethylphosphine)platinum(II)–1,2-dichloroethane gave *trans*-di-iodobis(trimethylphosphine)platinum(II) (70%), identified by its m.p. (192—194°) (lit.,[21] 194°) and by analysis and comparison of far-i.r. spectrum.[21]

Action of Chlorine on Di-μ-chloro-[dichloromercury(II)*]bis(dimethylphenylphosphine)platinum*(II).—The mercuric chloride adduct (0·058 g) was suspended in chloroform (7 ml), and a rapid stream of chlorine was passed through the suspension for some minutes. Partial removal of the solvent under reduced pressure gave cis-*tetrachlorobis(dimethylphenylphosphine)platinum*(IV) as yellow prisms (0·028 g, 65%), m.p. 194—196° (Found: C, 31·3; H, 3·85. $C_{16}H_{22}Cl_4P_2Pt$ requires C, 31·35; H, 3·6%).

Nuclear Magnetic Resonance Spectra.—^1H N.m.r. spectra were recorded at *ca.* 34° at 60 MHz on a Perkin-Elmer R.10

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spectrometer, using tetramethylsilane as an internal reference standard.

Infrared Spectra.—These spectra were recorded on a Grubb-Parsons G.S.4 spectrometer (2500—400 cm^{-1}) and a Grubb-Parsons D.B.3/D.N.2 spectrometer (450—200 cm^{-1}).

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