991. *Metal–Metal Bonds. Part III.* Formation of Rhodium–Mercury Bonds from Complex Rhodium Hydrides*

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Complexes of the general formula $L_3X_2Rh{-}HgY$ (where $L = Ph_2AsMe$; $X = Cl$ or Br; $Y = F$, Cl, Br, I, and OAc), in which there is a direct rhodium–mercury bond, have been prepared by a new method involving the reaction of the appropriate monohydride $L_3X_2Rh{-}H$ with mercuric, mercurous, or organomercury compounds.[1] In addition to these monomeric derivatives, complexes of the approximate formulæ $L_3X_2Rh{-}HgCN$ and $L_3X_2Rh{-}HgCNS$ have been prepared, but for these compounds it is difficult to avoid some displacement of X by CN or CNS; the CN and CNS derivatives are dimeric, probably because of pseudo-halogon bridging between two mercury atoms. Evidence for the presence of direct (covalent) rhodium–mercury bonds has been provided by spectrophotometric titration with solutions of bromine, reactions with hydrogen chloride, the diamagnetism, and the fact that the derivatives are non-electrolytes in solution.

The visible spectra indicate that in all cases the rhodium atom has a normal d_ϵ^6 configuration; the shift of the observable long-wavelength *d*–*d* transition for the $L_3X_2Rh{-}Z$ complexes (to shorter wavelengths) is in the order $Z = Br < Cl < H < HgI < HgBr < HgCl < HgF < HgOAc$. A possible reason for this increase in ligand-field strength in terms of metal–metal double bonding is discussed.

A study of the reactions between the hydrides of Ru(II), Os(II), Ir(III), Rh(I), and Pt(II) has led to the isolation of Os–Hg and Ir–Hg bonded complexes.

Covalent bonds between transition and post-transition metal atoms occur in a number of complexes in which the transition metal is co-ordinated to one or more carbon monoxide ligands. In only a few cases, however, have compounds been prepared in which there is a metal–metal bond between second- and third-row transition metals and post-transition metals; examples include $Cl_3Sn{-}Ir(cyclo{-}octa{-}1,5{-}diene)_2$,[2] and $(Ph_3P)_2Pt(GePh_3)_2$.[3] The formation of metal–metal bonds by reduction is more limited, *e.g.*, the preparation of mercurous chloride from mercuric chloride. The most common method involves a metathesis between the sodium salt of a carbonyl anion and a metal halide:[4]

$$(CO)_5MnNa + ClSnPh_3 \longrightarrow (CO)_5MnSnPh_3 + NaCl$$

Compounds containing transition-metal–gold bonds, *e.g.*, $Ph_3P \longrightarrow Au{-}Mn(CO)_5$ have been prepared similarly.[5]

In this investigation compounds containing bonds between some later transition metals and post-transition metals have been prepared by a different reaction in which hydrogen halide is evolved:

$$L_nM{-}H + Cl{-}M'L'_m \longrightarrow L_nM{-}M'L'_m + HCl$$

By this method the compounds L_3X_2RhHgY (where $L = Ph_2AsMe$; $X = Cl$ or Br; $Y = F$, Cl, Br, I, or OAc) were prepared in low yield by treating L_3X_2RhH[6] with HgY_2 in hot ethanol, hydrogen halide being eliminated. Mercurous halides and mercurous acetate also

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* Part II, A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1965, 3407.

[1] Preliminary communication, R. S. Nyholm and K. Vrieze, *Proc. Chem. Soc.*, 1963, 138.

[2] H. M. Powell, K. Mannan, B. T. Kilbourn, and P. Porta, Proc. 8th Internat. Conf. Co-ord. Chem., 1964, p. 155, 1B3.

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

[4] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1960, **82**, 3833.

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

[6] J. Lewis, R. S. Nyholm, and G. K. N. Reddy, *Chem. and Ind.*, 1960, 1386.

yield similar complexes, again in low yield, with the precipitation of mercury and the elimination of hydrogen halide:

$$L_3Cl_2RhH + Hg_2Y_2 \longrightarrow L_3Cl_2RhHgY + Hg + HY$$

The use of phenylmercury halides PhHgY (Y = Cl, Br, or I) unexpectedly gave the following reaction:

$$L_3Cl_2RhH + PhHgY \longrightarrow L_3Cl_2RhHgY + C_6H_6$$

The binuclear compounds prepared by these reactions did not show the characteristic Rh–H stretching frequency, which is observed at 2077 and 2073 cm.$^{-1}$ for $L_3Cl_2Rh{-}H$ and $L_3Br_2Rh{-}H$, respectively.[6]

Several attempts to prepare the corresponding organomercury derivatives, L_3Cl_2RhHgR, by using HgR_2 (R = Et or Ph) were unsuccessful. In this context it is interesting to observe that the complexes $RHg{-}M(CO)_n$ (M = transition metal) have been isolated only in the case of $(CH_3Hg)_2Fe(CO)_4$,[7] whilst in other cases compounds of the type $HgM^{II}(CO)_n$ [8] or $Hg[M^{I}(CO)_n]_2$ [9,10] only have been prepared.

Physical Properties.—The complexes are stable to air and moisture, readily soluble in organic solvents like benzene and chloroform, but only slightly soluble in ethanol, acetone, and ether. They are diamagnetic, and non-electrolytes in nitrobenzene. Molecular-weight measurements in chloroform or benzene (Table 1), by means of a vapour-pressure osmometer, showed that the complexes are monomeric when Y is halogen and acetate, and approximately dimeric when Y is CN and SCN.

TABLE 1

Properties of $L_3X_2Rh{-}HgY$ and related complexes

Compound (L = Ph_2AsMe)	Colour	M. p.	Molecular weight § Found	Calc.
L_3RhCl_3	Orange	208°	953	942
L_3Cl_2RhH	Yellow	172—175	980	907
$L_3Cl_2Rh{-}HgF$ *	Yellow	195	1126	1125
$L_3Cl_2Rh{-}HgCl$ *	Yellow	205	1144	1142
$L_3Cl_2Rh{-}HgBr$ †	Orange-yellow	165	1203	1186
$L_3Cl_2Rh{-}HgI$ †	Orange	155	1248	1233
$L_3Cl_2Rh{-}HgOAc$ ‡	Yellow	172	1150	1165
$L_3Br_2Rh{-}HgF$	Yellow	154	1217	1214
$L_3Br_2Rh{-}HgCl$	Yellow	202	1225	1231
$L_3Br_2Rh{-}HgBr$	Yellow-orange	187	1270	1275
$L_3Br_2Rh{-}HgI$	Orange	148	1307	1322
$L_3Br_2Rh{-}HgOAc$	Pale yellow	190	1262	1254

* Isomorphous. † Isomorphous. ‡ Infrared bands characteristic of CO_2^- at 1550 and 1333 cm.$^{-1}$. § Concentration *ca.* 5—25 × 10^{-3}M (benzene) or 10 × 10^{-3}M (chloroform).

Irradiation of several of the compounds in the solid state *in vacuo* with ultraviolet light (mercury lamp) caused blackening. The rate of decomposition is rapid when Y is F or Cl, slow when Y is Br or OAc, and imperceptible when Y is I, CN, or SCN; thus the tendency to decompose in ultraviolet light seems to be least when Y is a more polarisable ligand. Ultraviolet irradiation of a number of mercury compounds caused the yellow compounds Hg_2F_2 and Hg_2I_2 to blacken rapidly; the white complexes Hg_2Cl, Hg_2Br_2, HgY_2, and PhHgY are quite stable. Physical properties of the compounds L_3X_2RhHgY are listed in Table 1. [Compounds approximating to the formulæ $L_3Cl_2Rh{-}HgCN$, $L_3Cl_2Rh{-}Hg(CNS)$, $L_3Br_2Rh{-}HgCN$, and $L_3Br_2Rh{-}Hg(CNS)$ have also been prepared. It is difficult to obtain them pure probably because some replacement of the halogen (on the Rh atom) by CN or CNS occurs. Surprisingly, these complexes are all dimeric,

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[7] F. Hein and E. Heuser, *Z. anorg. Chem.*, 1942, **249**, 293.
[8] F. Hein and H. Pobloth, *Z. anorg. Chem.*, 1941, **248**, 84.
[9] W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 43.
[10] W. Hieber and W. Schropp, *Chem. Ber.*, 1960, **93**, 455.

presumably owing to bridging through CN[11] or CNS[12] groups between three-co-ordinate mercury atoms. Data in these are not given here pending further detailed investigation of their preparation, purification, and structure.]

Reactions with Oxidising Agents.—All the complexes undergo a quantitative reaction with the halogens and with hydrogen chloride. Titration of $L_3Cl_2RhHgBr$ with bromine in dichloromethane, followed spectrophotometrically at 4900 Å, shows an end-point after the addition of two equivalents of bromine (see Figure 1). The reaction is:

$$L_3Cl_2RhHgBr + Br_2 \longrightarrow L_3Cl_2RhBr + HgBr_2$$

The spectrum (2800—7500 Å) of the compound produced is identical with that of the 1 : 1 reaction mixture of L_3Cl_2RhH and bromine in dichloromethane in which the species L_3Cl_2RhBr is known to be formed.[13]

The compound $L_3Cl_2RhHgCl$ reacted in ether suspension with dry hydrogen chloride. The complex rhodium hydride was formed quantitatively after a few minutes, and was identified by elemental analysis, mixed melting point with the original hydride (173°), and by the presence of the Rh–H stretching frequency at 2077 cm.$^{-1}$ in the infrared spectrum (Nujol mull).[6]

The stability of the rhodium–mercury bond towards oxidation is similar to that of the Pb–Mn bond in $Ph_3PbMn(CO)_5$[4] and the Au–Mn bond in $Ph_3PAuMn(CO)_5$,[5] both of which are broken by halogens and hydrogen chloride; however, the Fe–Sn bond in $C_5H_5(CO)_2FeSnPh_3$ is broken only by halogens, and the Mn–Sn bond in $(CO)_5MnSnPh_3$ is stable to halogens and hydrogen chloride.[4]

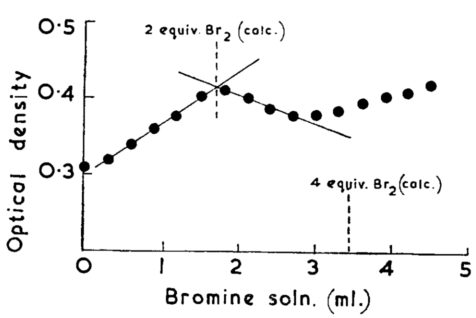

FIGURE 1. Spectrophotometric titration ($\lambda = 4900$ Å) of $(Ph_2AsMe)_3Cl_2Rh{-}HgBr$ with bromine in dichloromethane solution. (The increase in optical density after three equivalents of bromine had been added is believed to be due to polybromide formation.)

No reaction was observed between any of the rhodium–mercury bonded complexes in benzene solution and molecular hydrogen; this is in contrast to the reaction of $(Ph_3P)_2(CO)Cl_2IrHgCl$ with hydrogen (see following Paper) in which the hydride $(Ph_3P)_2(CO)Cl_2IrH$ is formed.

All the foregoing data are consistent with the explanation that the complexes contain a direct metal–metal bond between (formally) Rh(II) and Hg(I), the bonding being effected by normal electron-pair sharing. The geometrical arrangements of the ligands in the trihalides L_3RhX_3, L_3X_2RhH, and L_3X_2RhHgY is unknown. Two isomers are possible for the trihalides, whilst, for the latter two types of compound, three isomers may in principle arise. Pending *X*-ray studies speculation is unwarranted. However, the *X*-ray powder patterns show that the complexes L_3X_2RhHgY are isomorphous when X is Cl or Br and Y is F, Br, or I, and $L_3Cl_2RhHgCl$ and $L_3Cl_2RhHgOAc$ are isomorphous with $L_3Cl_2RhHgCl$ and $L_3Cl_2RhHgOAc$, respectively.*

Electronic Absorption Spectra.—(a) *Visible spectra*. All metal–metal bonded compounds studied, as well as the simple and the monohydrides,[6] are diamagnetic; hence, the rhodium

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* In ref. 1 the complex L_3Cl_2RhHgF was reported to be isomorphous with $L_3Cl_2RhHgCl$. Since then, however, this compound has been obtained in the above mentioned form.

[11] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[12] P. C. H. Mitchell and R. J. P. Williams, *J.*, 1960,, 1912.

[13] G. K. N. Reddy, Ph.D. Thesis, London, 1961.

atom has essentially a non-bonding spin-paired $4d^6$ (t_{2g}^6) electron configuration. The electronic transition $t_{2g}^6 \longrightarrow t_{2g}^5e_g^1$ gives rise to two spin-allowed, but Laporte forbidden, transitions, $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$, with the rhodium atom in an octahedral environment.[14]

Both transitions have been observed; for example, the $[\mathrm{RhX_6}]^{3}$ ion (X = Cl or Br),[14] *cis*-$(\mathrm{trienRhCl_2})^+$, and *cis*-$[\mathrm{trienRh(H)Cl}]^+$ have extinction coefficients between 100 and 200.[15] In other cases, *e.g.*, $\mathrm{K_3Rh(NO_2)_6}$ and $\mathrm{K_3Rh(CN)_6}$,[16] solely the long-wavelength transition $^1A_{1g} \longrightarrow {}^1T_{1g}$ is visible, and this only as a shoulder on the low-frequency side of the electron-transfer bands.

For the rhodium complexes discussed here the lower-wavelength transition can be observed either as a peak or as a shoulder (see Figure 2). No *d–d* absorption was observed for $\mathrm{L_3X_2RhHgY}$ (Y = CN or SCN) owing to strong electron-transfer. The extinction coefficients for these absorptions are of the order 200—400, when corrected for the electron transfer. It was observed that the peak (or shoulder) shifts to higher frequency for the complexes $\mathrm{L_3Cl_2RhZ}$ and $\mathrm{L_3Br_2RhZ}$ in the order: Z = Br < Cl < H < HgI < HgBr < HgCl < HgF < HgOAc (see also Table 2). The position of H relative to HgI has been decided from a study of the bromide compounds. In several cases, as for example for rhodium(III) [15] and ruthenium(II) [17] complexes it has already been established that hydrogen has a higher ligand-field than the halogens, and this appears to be true also for the $\mathrm{L_3X_2RhZ}$ series.

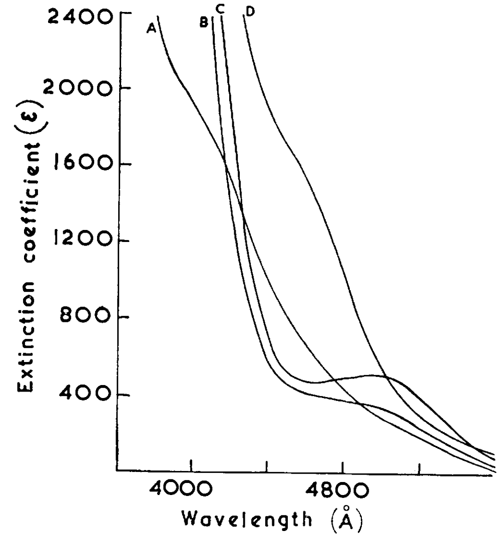

FIGURE 2. Absorption spectra of $\mathrm{(Ph_2AsMe)_3Br_2RhZ}$, where Z is (A) HgOAc, (B) H, (C) Br, (D) HgBr. (Only a selection of spectra is given, but the trend is clearly seen in Table 2.)

The exact spectrochemical sequence of the other ligands Z is less easy to determine because the microsymmetry in all the rhodium compounds investigated here is not known; unfortunately, only one ligand-field band is observed, whilst two are necessary for the simultaneous calculation of the ligand-field splitting parameter, $10Dq$, and the Racah interelectronic repulsion parameter, B.[16] The compounds $\mathrm{L_3X_2RhHgY}$, however, are isomorphous when X is Cl or Br and Y is F, Br, or I, and it is likely that the microsymmetry for $\mathrm{L_3X_2RhHgCl}$ and $\mathrm{L_3X_2RhHgOAc}$ is essentially the same. Furthermore, the rhodium atom in the $\mathrm{L_3X_2RhHgY}$ series is always surrounded by the same atoms (*i.e.*, three As, two X, and one HgY group), and it is therefore supposed that the interelectronic repulsion

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[14] C. K. Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, pp. 118, 149.

[15] R. D. Gillard and G. Wilkinson, *J.*, 1963, 3594.

[16] H. H. Schmidtke, *Z. phys. Chem. (Frankfurt)*, 1964, **40**, 96.

[17] J. Chatt and R. G. Hayter, *J.*, 1961, 772.

TABLE 2

Electronic spectra of the complexes L_3X_2RhZ

Compound (L = Ph_2MeAs)	Estimated $\lambda_{max.}$* ($\varepsilon_{estim.}$ ~200—400)	$\lambda_{max.}$ † (ε_ν 1 × 10^4—4 × 10^4)	Compound (L = Ph_2MeAs)	Estimated $\lambda_{max.}$* $\varepsilon_{estim.}$ ~200—400)	$\lambda_{max.}$ † (ε_ν 1 × 10^4—4 × 10^4)
L_3Cl_2RhBr	4700 (pk)	3400	L_3Br_2RhBr	4900 (pk)	3480
L_3Cl_2RhCl	4600 ,,	3350	L_3Br_2RhH	4800 (sh)	3050, 2570
L_3Cl_2RhH	4500 ,,	3320, 2930	L_3Br_2RhHgI	4700 ,,	3000
L_3Cl_2RhHgI	4500 (sh)	3280	$L_3Br_2RhHgBr$	4600 ,,	3350, 2730
$L_3Cl_2RhHgBr$	4450 ,,	3250	$L_3Br_2RhHgCl$	4300 ,,	3200
$L_3Cl_2RhHgCl$	4400 ,,	3220, 2700	L_3Br_2RhHgF	4200 ,,	3320
L_3Cl_2RhHgF	4350 ,,	3220	$L_3Br_2RhHgOAc$	4000 ,,	3120
$L_3Cl_3RhHgOAc$	4000 ,,	3200 (sh), 3050			

* Concn. about 10^{-3}M in CH_2Cl_2. † Concn. about 10^{-5}M in CH_2Cl_2.

parameter, *B*, of the 4*d*-electrons is about the same in each compound. We can thus safely deduce from the positions of the observable low-wavelength ligand-field band that the spectrochemical ligand-field sequence is the same as for this ligand-field band, *i.e.*, HgI < HgBr < HgCl < HgF < HgOAc. The exact position of the H atom and the HgY group is not known with certainty since compounds like L_3Br_2RhH and L_3Br_2RhHgI probably have slightly different structures. It is also not known how much H and HgI differ in their influence on the interelectronic repulsion parameter, *B*. The difference in energy, however, due to a difference in *B* in rhodium(III) compounds is in general small in comparison with the energy separation between the longer-wavelength *d–d* transitions of the series of rhodium(III) complexes discussed here. It is thus likely that, in particular, HgBr, HgCl, HgF, and HgOAc have a higher ligand-field than the hydrogen atom. This much greater ligand-field strength is intriguing and calls for comment.

The orbitals available for σ-bonding between the rhodium atom and the mercury atom are the $4d_{z^2}$-orbital and the $6s6p_z$-hybrid, respectively, whilst π-bonding may occur through interaction of the filled $d_\epsilon(t_{2g})$ orbitals of the rhodium atom and the empty $6p_x$- and $6p_y$-orbitals of the mercury atom. Combined strong σ- and π-bonding is, in this case, conducive to a high ligand-field. It is interesting to note that the group Y, bonded to the mercury atom in L_3X_2RhHgY, seems to have a large influence on the position of the relevant energy levels, between which the ligand-field transitions take place, especially when bromine rather than chlorine atoms are bonded to the rhodium atom.

(b) *Ultraviolet spectra.* The electron-transfer absorptions (see Table 2) have a high extinction coefficient (larger than 10^4). The frequencies of these absorptions do not show any correlation with the redcing power of the ligands X when chlorine on the rhodium is replaced by bromine. Electron-transfer in these complexes is apparently not only due to ligand-to-metal electron transitions as is the case for $[RhX_6]^{3-}$ (X = Cl or Br).[14]

Miscellaneous Reactions.—Reactions between mercury compounds and the hydrides $(Ph_3P)_2(CO)Cl_2IrH$,[18] $(Ph_3P)_2ClIrH_2$,[18] $(Ph_3As)_3(CO)ClMH$ (M = Ru or Os),[19,20] $(Ph_3P)_2Pt(H)Cl$,[21] $(Ph_3P)_2PtH_2$,[22,23] and $(Ph_3P)_3(CO)RhH$ [24] are known to occur for the iridium hydrides. The complexes so formed were, however, more conveniently obtained by a different preparative method which is described in the following Paper. All other hydrides tried, with the exception of the osmium hydride, gave mostly reduction to metallic mercury, and no complexes could be isolated.

Treatment of the hydride of osmium with a series of mercury compounds yielded impure products. A dimeric impure thiocyanate compound was isolated from the reaction with

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[18] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784; 1962, **84**, 679.
[19] L. Vaska, *J. Amer. Chem. Soc.*, 1964, **86**, 1943.
[20] P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 1962, 333.
[21] J. Chatt and B. L. Shaw, *J.*, 1962, 5075.
[22] J. A. Chopoorian, J. Lewis, and R. S. Nyholm, *Nature*, 1961, **190**, 528.
[23] L. Malatesta, *J.*, 1963, 2080.
[24] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

mercuric thiocyanate. For this complex two C–N stretching frequencies were observed, at 2112 and 2150 cm.$^{-1}$, as in the case of the apparently dimeric thiocyanate compounds of rhodium. Repeated purification did not yield pure compounds and therefore no physical properties were determined.

Metal–mercury bonded compounds can thus be made by means of hydride reactions, but this type of reaction seems less generally applicable than the double decomposition reaction which involves the elimination of an alkali halide as already reported.[13]

EXPERIMENTAL

Preparation of $(Ph_2AsMe)_3X_2RhHgY$ *Complexes* (X = Cl or Br; Y = F, Cl, I, CN, or SCN).—To a hot solution of HgY_2 (0·1 g., excess) in ethanol (or methanol) 100 ml. the powdered hydride L_3X_2RhH (0·20 g.) was added. After a few minutes' shaking the mixture was cooled, filtered, and the cold filtrate set aside overnight; the required complex, which had crystallised out, was filtered off, washed with warm ethanol (or methanol), and dried *in vacuo*. The same compounds were also prepared by using, instead of the mercuric dihalides, a hot solution of PhHgY (Y = Cl, Br, or I) in hot ethanol, or a hot suspension of the mercurous halide (Hg_2Y_2) (Y = F, Cl, Br, I, or OAc). The yields were in all cases about 5—30%, considerable decomposition occurring.

Analytical Data.—(I) *Dichlorotris(methyldiphenylarsine)monofluoromercury*(I)*rhodium*(II) (Found: C, 41·8; H, 3·2; Rh, 9·0. $C_{39}H_{39}As_3Cl_2FHgRh$ requires C, 41·6; H, 3·5; Rh, 9·1%); isomorphous with (III) and (IV), below.

(II) *Dichlorotris(methyldiphenylarsine)monochloromercury*(I)*rhodium*(II) (Found: C, 40·9; H, 3·6; Rh, 9·1; As, 17·9; Hg, 16·5; Cl, 9·4. $C_{39}H_{39}As_3Cl_3HgRh$ requires C, 40·9; H, 3·4; Rh, 9·0; As, 19·7; Hg, 17·6; Cl, 9·4%); isomorphous with (VII).

(III) *Dichlorotris(methyldiphenylarsine)monobromomercury*(I)*rhodium*(I) (Found: C, 38·4; H, 3·6; Rh, 8·4; As, 18·6; Hg, 16·7; Cl, 5·9; Br, 6·9. $C_{39}H_{39}As_3BrCl_2HgRh$ requires C, 39·5; H, 3·2; Rh, 8·6; As, 19·0; Hg, 16·9; Cl, 6·0; Br, 6·8%); isomorphous with (I) and (IV).

(IV) *Dichlorotris(methyldiphenylarsine)monoiodomercury*(I)*rhodium*(II) (Found: C, 37·8; H, 3·6; Rh, 8·5; As, 16·8; Hg, 16·5; Cl, 5·7; I, 10·2. $C_{39}H_{39}AsCl_2IHgRh$ requires C, 37·9; H, 3·3; Rh, 8·3; As, 18·2; Hg, 16·2; Cl, 5·8; I, 10·3%); isomorphous with (I) and (III).

(V) *Dichlorotris(methyldiphenylarsine)monoacetatomercury*(I)*rhodium*(II) (Found: C, 41·9; H, 3·9; Rh, 9·0; As, 18·6; Hg, 17·2; Cl, 6·2. $C_{41}H_{42}As_3Cl_2HgO_2Rh$ requires C, 42·2; H, 3·6; Rh, 8·9; As, 19·3; Hg, 17·2; Cl, 6·1%); isomorphous with (X).

(VI) *Dibromotris(methyldiphenylarsine)monofluoromercury*(I)*rhodium*(II) (Found: C, 38·5; H, 6·2; Rh, 8·3. $C_{39}H_{39}As_3Br_2FHgRh$ requires C, 38·5; H, 3·2; Rh, 8·3%); isomorphous with (I).

(VII) *Dibromotris(methyldiphenylarsine)monochloromercury*(I)*rhodium*(II) (Found: C, 38·2; H, 3·9; Rh, 8·3; Br, 12·9; Cl, 2·9. $C_{39}H_{39}As_3Br_2ClHgRh$ requires C, 38·0; H, 3·2; Rh, 8·4; Br, 13·0; Cl, 2·8%); isomorphous with (II).

(VIII) *Dibromotris(methyldiphenylarsine)monobromomercury*(I)*rhodium*(II) (Found: C, 36·7; H, 2·6; Rh, 8·0; Br, 18·9. $C_{39}H_{39}As_3Br_3HgRh$ requires C, 36·0; H, 3·1; Rh, 8·1; Br, 19·1%); isomorphous with (III).

(IX) *Dibromotris(methyldiphenylarsine)monoiodomercury*(I)*rhodium*(II) (Found: C, 35·0; H, 3·2; Rh, 7·7; Br, 12·0; I, 9·8. $C_{39}H_{39}As_3Br_2HgIRh$ requires C, 35·4; H, 3·0; Rh, 7·8; Br, 12·1; I, 9·6%); isomorphous with (IV).

(X) *Dibromotris(methyldiphenylarsine)monoacetatomercury*(I)*rhodium*(II) (Found: C, 40·3; H, 3·1; Rh, 8·4; Br, 12·7. $C_{41}H_{42}As_3Br_2HgO_2Rh$ requires C, 39·2; H, 3·3; Rh, 8·2; Br, 12·8%); isomorphous with (V).

The estimation of the elements in the complexes together with the methods used to measure molecular weights, conductances, magnetic susceptibilities, and spectra (ultraviolet, visible, and infrared) are mentioned in the Experimental section of Part II). The magnetic susceptibility values for the rhodium compounds are not quoted since all compounds described are diamagnetic.

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