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Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. Part II.¹ Reactivity of Co-ordinated Ligands

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The reactions with bromine of square planar platinum(II) complexes of the isomeric styryldimethylarsines, o-, mand p-CH₂·CH·CH·C₆H₄·AsMe₂ have been studied. The complexes PtBr₂(*m*-arsine)₂ and PtBr₂(*p*-arsine)₂ add successively 3 equivalents of bromine. The first equivalent oxidises the metal atom giving orange, octahedral platinum(IV) complexes of general formula PtBr₄(arsine)₂ in both cases. The second and third equivalents of bromine then add to the double bonds of the ligands. The complex PtBr₂(o-arsine)₂ also adds successively 3 equivalents of bromine, but the mode of addition is different. The product of reaction with one equivalent of bromine is a yellow complex PtBr₄(o-arsine)₂, which is formulated as an octahedral platinum(IV) complex containing a metal-carbon σ -bond to the vinyl group of one of the ligands. The second equivalent of bromine adds to the remaining double bond of this complex, leaving the metal-carbon bond intact. An excess of bromine breaks this bond, giving the orange, octahedral platinum(\overline{IV}) complex PtBr₄(o-arsine Br₂)₂.

Similar reaction sequences are observed in the bromination of the corresponding platinum(II) complexes of the isomeric allylphenyldimethylarsines, o-, m-, and p-CH₂·CH·CH₂·C₆H₄·AsMe₂. Steric hindrance of bromine addition at the platinum atom alone cannot account for the unusual behaviour of the complexes of the ortho-substituted ligands, because the platinum(II) complexes of o- and p-propyldimethylarsine, Prⁿ⁺C₆H₄+AsMe₂, are both oxidised by bromine at the metal atom, giving the usual orange octahedral platinum(IV) complexes.

By contrast, the three octahedral rhodium(III) complexes of general formula RhBr₃(arsine)₃ (arsine = o, m-, and p-CH₂:CH·C₆H₄·AsMe₂) react similarly with bromine, with addition across the double bonds of the ligands. Bromine also adds to the double bonds of the methiodides of the isomeric allylphenyldimethylarsines, the order of reactivity being meta > para > ortho.

Alcoholysis and reduction of the platinum(IV) complexes of the ortho-substituted olefinic ligands are discussed, and the formation of chelate complexes of general formula PtBr₂(o-arsine) is described.

SQUARE planar platinum(II) complexes of tertiary phosphines and arsines are readily oxidised by halogens to octahedral platinum(IV) complexes.²

$$Pt \times_2 L_2 + \times_2 \longrightarrow Pt \times_4 L_2$$

$$(L = tertiary phosphine or arsine; X = CI, Br, or I)$$

We have studied the reaction with bromine of square planar complexes of the type PtBr₂(arsine)₂, the arsines being the isomeric styryldimethylarsines, o-, m-, and p-CH₂:CH·C₆H₄·AsMe₂, and the isomeric allylphenyldimethylarsines, o-, m-, and p-CH2:CH•CH2•C6H4•AsMe2, hereafter denoted by oS, mS, pS, and oA, mA, and pA, respectively. These complexes contain three potential reaction centres for bromine: the platinum atom and two double bonds. We wished to know if the reactivity of the double bonds in the complexes of the o-arsines could be affected by interaction either with the vacant $6p_z$ orbital or the filled $5d_{z^2}$ orbital of square-coordinated platinum(II). For comparison we studied the reaction with bromine of the octahedral rhodium(III) complexes of the isomeric styryldimethylarsines, $RhBr_{3}(arsine)_{3}$, and the reaction with bromine of the methiodides of the isomeric allylphenyldimethylarsines. In both cases, only the double bonds can be attacked by bromine. In order to investigate possible steric effects of ortho-substituents in the tertiary arsine, we also studied

the bromination of platinum(II) complexes of the type $PtBr_2(arsine)_2$ derived from o- and p-propylphenyldimethylarsine, $Pr^{n} \cdot C_6 H_4 \cdot AsMe_2$, denoted by oP and pP, respectively.

Preparation of Ligands and Complexes.—The isomeric tertiary arsines are prepared by reaction of the Grignard reagent of the appropriate bromostyrene or allylchlorobenzene with dimethyliodoarsine:

 $CH_2:CH \cdot C_6H_1 \cdot MgBr + Me_2Asl \longrightarrow CH_2:CH \cdot C_6H_1 \cdot AsMe_2 + MgBrI$ CH2:CH·CH2·C6H4·MgX + Me2Asl ----> $CH_2:CH\cdot CH_2\cdot C_6H_4\cdot AsMe_2 + MgXI (X = CI or Br)$

The complexes $PtBr_2(arsine)_2$ can be prepared by the reaction of the ligands (2 mols.) with acidified, alcoholic potassium bromoplatinate(II) solution (1 mol.), or, more conveniently, with anhydrous platinum(II) bromide (1 mol.) suspended in chloroform. The complexes are vellow, monomeric, and non-conducting in nitrobenzene. Their infrared spectra show a band at ca. 1630-1640 cm.⁻¹ due to an unco-ordinated C=C stretching frequency, and bands characteristic of a vinvl group (Table 1). o-Styryldimethylarsine gives two isomeric complexes of formula $PtBr_2(oS)_2$, which differ in colour (pale yellow and yellow) and in their solubility in organic

¹ Part I, M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, J. Chem. Soc., 1964, 4570. ² R. S. Nyholm, J. Chem. Soc., 1950, 843; J. Chatt, *ibid.*, p.

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solvents; they are presumably *cis* and *trans* isomers.^{2,3} Only the *trans* isomer of $PtBr_2(oA)_2$ can be isolated, but the dipole moment of 4.08D in benzene may indicate partial isomerisation in the solvent. All the other

TABLE 1

C=C stretching, C-Br stretching, and vinyl group frequencies (cm.⁻¹)

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Compound	v(C=C)	δ(CH)	ν(C-Br)
»S	1630	990	
mS	1631	990	<i>·</i>
¢S	1629	994	
•A	1635	993	
<i>m</i> A	1639	663	
<i>b</i> A	1639	992	
$\operatorname{RhBr}_{\mathfrak{g}}(oS)_{\mathfrak{g}}$	1623	1019, 1010	
$\operatorname{RhBr}_{\mathfrak{g}}(mS)_{\mathfrak{g}}$	1626	988	
$\operatorname{RhBr}_{3}(pS)_{3}$	1631	988	
$\operatorname{RhBr}_{3}(o\operatorname{SBr}_{2})_{3}$			599
$\operatorname{RhBr}_{3}(m\operatorname{SBr}_{2})_{3}$			598
$\operatorname{RhBr}_{3}(p\operatorname{SBr}_{2})_{3}$			599
$cis-PtBr_2(oS)_2$	1630	996, 990	
$rans-PtBr_2(oS)_2$	1627	1000, 984	
PtBr ₂ oS	1488		
$PtBr_2(mS)_2$	1631	991, 982sh	
$PtBr_{2}(pS)_{2}$	1634	991	
$PtBr_2(oA)_2$	1633	992	
PtBr ₂ 0A	1500	1002	
$\operatorname{PtBr}_{2}(mA)_{2}\ldots\ldots\ldots\ldots$	1640	995, 989	
$PtBr_2(pA)_2$	1639	997	
$PtBr_{3}(oSBr)(oS)$	1638	998, 992	600,ª 577 ª
$PtBr_{3}(oSBr)(oSBr_{2})$	<u> </u>		595,ª 573 ª
$PtBr_4(oSBr_2)_2$	<u> </u>		594, 572
PtBr ₃ (oSOMe)(oS)	1632	b	<u> </u>
$PtBr_2(oSBr_2)_2$			596
$PtBr_4(mS)_2$	1631	990	
$PtBr_4(mSBr_2)_2$			600
$PtBr_4(pS)_2$	1640	988	
$PtBr_4(pS)(pSBr_2)$	1634	996	599
$PtBr_4(pSBr_2)_2\dots\dots$			592
$PtBr_{3}(oABr)(oA)$	1634	993	601 a
$PtBr_{3}(oABr)(oABr_{2}) \dots$			601,ª 561 ª
PtBr ₃ (oAOMe)(oA)	1639	996	
$PtBr_4(oABr_2)_2$			561
$PtBr_2(oABr_2)_2$			570, 547
$PtBr_4(mA)_2$	1640	996	
$PtBr_4(mABr_2)_2$			560
$PtBr_4(pA)_2$	1640	996	
$PtBr_4(pA)(pABr_2)$	1641	991	561
$PtBr_4(pABr_2)_2$			560

^a May be v(Pt-C). ^b Could not be identified.

bis(arsine) complexes are obtained in the *trans* form, as judged by colour and solubility. They are formulated as in (I), the double bonds being unco-ordinated to the metal.

o-Styryldimethylarsine (oS) (1 mol.) also reacts with platinum(II) bromide (1 mol.) to give a colourless complex PtBr₂oS, which is monomeric and non-conducting in nitrobenzene. The infrared spectrum shows no band at *ca*. 1640 cm.⁻¹, and a new band appears at *ca*. 1490 cm.⁻¹ (Table 1) which is characteristic of a C=C stretching frequency modified by co-ordination to platinum(II).⁴ We therefore formulate PtBr₂oS as a chelate complex (II) similar to those obtained with pent-4-enyldimethylarsine and related ligands.¹ The corresponding complex of *o*-allylphenyldimethylarsine,

PtBr₂oA (III), is formed readily by a similar reaction between platinum(II) bromide (1 mol.) and the ligand (1 mol.) and, surprisingly, is also formed on heating the bis(arsine) complex PtBr₂ $(oA)_2$ in dilute solutions of primary alcohols. The C=C stretching frequency of



PtBr₂oA occurs at 1500 cm.⁻¹. The fact that PtBr₂oA forms more readily than PtBr₂oS may be due to the ease with which the double bond of the allyl group can be oriented at right-angles to the plane of the metal and the other ligands, as is generally found in mono-olefin complexes of platinum(II).⁵ Molecular models suggest that this is not so readily achieved with the vinyl group of oS.

The rhodium(III) complexes $RhBr_3(arsine)_3$ are obtained from the ligands (3 mols.) and rhodium(III) chloride (1 mol.) with excess of lithium bromide.⁶ They are orange crystalline solids whose infrared spectra resemble those of the bis(arsine)platinum(II) complexes (Table 1); they probably have the *trans* configuration.

Bromination Studies.—(a) Tertiary arsines. Spectrophotometric titration of dilute solutions of the olefinic tertiary arsines in carbon tetrachloride solution with bromine shows an initial, rapid absorption of 1 mol. of bromine per mol. of ligand, followed by a slower uptake of a further mol. of bromine. The first step is evidently due to bromination of the arsenic atom ($As^{III} \longrightarrow As^{V}$), since it is also observed with phenyldimethylarsine, and the second step is the addition of bromine to the double bond, as shown in Scheme 1. There is no evident difference in reactivity between the isomeric styryldimethylarsines or between the isomeric allylphenyldimethylarsines (Scheme 1).

$$CH_2:CH+C_6H_4+AsMe_2 \xrightarrow{Br_4} CH_2:CH+C_6H_4+AsMe_2Br_2 \xrightarrow{Br_4} CH_2Br+CHBr+C_6H_4AsMe_2Br_2$$

$$Scheme \ I$$
Bromination of tertiary arsines

(b) *Tertiary arsine methiodides*. The bromination of the methiodides of the isomeric allylphenyldimethylarsines was studied spectrophotometrically to see if a

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³ K. A. Jensen, Z. anorg. Chem., 1936, **229**, 225; J. Chatt, J. Chem. Soc., 1951, 652.

⁴ J. Chatt and L. A. Duncanson, J. Chem. Soc., 1953, 2939.

⁵ J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, 1954, 7, 130; P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *ibid.*, 1960, 13, 149.

 ^{13, 149.} J. Chatt, N. P. Johnson, and B. L. Shaw, J. Chem. Soc., 1964, 2508.

positively charged metal-free substituent could affect the reactivity of the double bond to addition of bromine. The reaction is complex, because the absorption maximum for bromine in chloroform (411 m μ) shifts to 385 $m\mu$ in the methiodide solutions, probably owing to the formation of species such as [IBr₂]⁻. The order of reactivity of the methiodides with bromine is $mAMe^+I^->$ $pAMe^{+}I^{-} \gg oAMe^{+}I^{-}$. The reduced reactivity of the o-arsine methiodide is consistent with electrostatic repulsion of an attacking species, such as Br⁺, by the positively charged ortho substitutent.

(c) Rhodium(III) complexes. The rhodium(III) complexes of the isomeric styryldimethylarsines react with an excess (>6 mols.) of bromine giving complexes of general formula RhBr₃(arsine Br₂)₃ (arsine = oS, mS, or pS), whose infrared spectra show no band at ca. 1630 cm.⁻¹ and no characteristic vinyl frequencies (Table 1). In these three cases, bromine adds to the free double bonds in the complexes of the isomeric ligands, and no difference in reactivity between them is evident.

Platinum(II) complexes. The complexes (\mathbf{d}) $PtBr_2(mS)_2$, $PtBr_2(mA)_2$, $PtBr_2(\phi S)_2$, and $PtBr_2(\phi A)_2$ react with 1 equivalent of bromine in carbon tetrachloride or benzene giving orange crystalline complexes of general formula PtBr₄(arsine)₂, which can be reduced to the original complexes with ethanolic tin(II) chloride. Their infrared spectra show a band at ca. 1640 cm.⁻¹ and their ultraviolet absorption spectra (Table 2) show a band

TABLE 2

Ultraviolet absorption spectra in benzene

Compound	$\lambda_{max.}$ (m μ)	ε
$PtBr_{o}(oS)$,	296	6800
$PtBr_{o}(oA)$,	296	5200
$PtBr_{\bullet}(oSBr_{\bullet})$,	295	11,700
$PtBr_{o}(oABr_{o})$,	296	12,400
PtBr.(oP).	297	13,300
$PtBr_{A}(pA)_{2}$	342	19,600
$PtBr_{\bullet}(mS)$,	345	19,600
PtBr (AsMe,Ph),	347	24,600
PtBr (oSBr,),	343	24,700
$PtBr_{4}(oABr_{2})_{2}$	346	19,500
PtBr _s (oSBr)(oS)	$270 \mathrm{sh}$	22,000
	360	6400
$PtBr_{a}(oABr)(oA)$	269 sh	20,400
	367	4600
$PtBr_{a}(oSBr)(oSBr_{2})$	264 sh	25,000
	354	5800
$PtBr_{3}(oABr)(oABr_{2})$	$270 \mathrm{sh}$	25,000
	363	6800
PtBr ₃ (oSOEt)(oS)	270 sh	19,300
	360	5100
PtBr ₃ (oAOEt)(oA)	$268 \mathrm{sh}$	21,500
/	367	6700

at ca. 350 mµ similar to that found in the spectrum of $PtBr_4(PhMe_2As)_2$. Spectrophotometric titration of the complexes $PtBr_2(PhMe_2As)_2$, $PtBr_2(mS)_2$, $PtBr_2,(mA)_2$, $PtBr_2(pS)_2$, and $PtBr_2(pA)_2$ with bromine shows a rapid rise in optical density at 418 mµ (the absorption maximum for bromine) until one equivalent of bromine has been added, owing to the tail of the absorption band at ca. $350 \text{ m}\mu$ in the products. The first step in the bromination of the complexes of the meta and para ligands is, therefore, oxidation of the metal $(Pt^{II} \longrightarrow Pt^{IV})$

giving octahedral platinum(IV) complexes PtBr₄(arsine)₂.

Addition of an excess (>3 equivalents) of bromine to the original complexes, or of 2 equivalents of bromine to the platinum(IV) complexes, gives orange complexes of general formula PtBr₈(arsine)₂, which show none of the characteristic vinyl frequencies in their infrared spectra (Table 1), and are clearly the platinum(IV) complexes of the fully brominated ligands, PtBr₄(arsine Br_2 ₂. Their infrared spectra show a band at *ca*. 609 cm.⁻¹ which may be due to a carbon-bromine stretching frequency ^{7a} since it also appears in the corresponding rhodium(III) complexes RhBr₃(arsine Br₂)₃.

Products of formula $PtBr_4(pS)(pSBr_2)$ and $PtBr_{4}(pA)(pABr_{2})$, in which only one of the olefinic ligands has been brominated, can be isolated from the reaction of one equivalent of bromine with $PtBr_4(pS)_2$ and $PtBr_4(pA)_2$, respectively. Attempts to obtain similar complexes with the meta-arsines give mixtures of unchanged $PtBr_4(arsine)_2$ and $PtBr_4(arsineBr_2)_2$. The reaction sequences are shown in Scheme 2.



Bromination of $PtBr_2(arsine)_2$ (arsine = mS, mA, pS, pA)

The complexes of the ortho ligands, $PtBr_2(oS)_2$ and $PtBr_2(oA)_2$, also react with an excess (>3 equivalents) of bromine to give orange complexes PtBr₈(arsine)₂, whose infrared and ultraviolet absorption spectra resemble those of the corresponding complexes of the *m*- and p-arsines. They are therefore formulated as $PtBr_4(o-arsineBr_2)_2$. The intervening stages of the bromination are, however, different.

The action of one equivalent of bromine in carbon tetrachloride or benzene on the complexes $PtBr_2(oS)_2$ and PtBr₂(oA)₂ gives yellow crystalline complexes of empirical formula $PtBr_4(o-arsine)_2$ which are monomeric and non-conducting in nitrobenzene. Their ultraviolet absorption spectra show only a weak band at ca.350 mµ, with an additional strong band at 270 m μ which appears as a shoulder on absorption rising into the ultraviolet region. Spectrophotometric titration of $PtBr_2(oS)_2$ and $PtBr_2(oA)_2$ with bromine in benzene or carbon tetrachloride shows a rise in optical density at 418 m μ until one equivalent of bromine has been added, but this increase is much less marked than in the case of the corresponding complexes of the m- and p-arsines owing to the reduced intensity of the band at $350 \text{ m}\mu$ in the product. The complex $PtBr_4(oS)_2$ is reduced by ethanolic tin(II) chloride to a mixture of the starting

⁷ L. J. Bellamy, "The Infra-red Spectra of Complex Mole-cules," Methuen, 1958, (a) p. 331; (b) p. 116.

complex $PtBr_2(oS)_2$ and the chelate complex $PtBr_2oS$. Similar reduction of $PtBr_4(oA)_2$ gives only the chelate complex PtBr_ooA. The complexes of formula $PtBr_4(o-arsine)_2$ show the characteristic C=C frequency as a very weak band at ca. 1640 cm.⁻¹, and the characteristic vinyl frequencies are either shifted, or appear with reduced intensity, compared with the initial platinum(II) complexes of formula PtBr₂(o-arsine)₂. The complexes of formula $PtBr_4(o-arsine)_2$ react with a further equivalent of bromine to give yellow complexes of empirical formula PtBr₆(o-arsine)₂, which are monomeric and non-conducting in nitrobenzene. The ultraviolet absorption spectra of these complexes resemble those of $PtBr_4(o-arsine)_2$ but the infrared spectra show no band assignable to C=C stretching or vinyl CH deformation frequencies. This second stage of bromination cannot be followed by spectrophotometric titration, because the reaction does not occur readily at the concentrations of complex (ca. 3×10^{-4} M) required for the technique.

The spectroscopic evidence suggests that the compounds $PtBr_4(o-arsine)_2$ are not simple platinum(IV) complexes like their isomers $PtBr_4(m-arsine)_2$ and $PtBr_4(p-arsine)_2$. The compounds $PtBr_4(o-arsine)_2$ and $PtBr_6(o-arsine)_2$ could obviously be formulated as platinum(II) complexes containing one and two molecules, respectively, of the brominated ligand, i.e., $PtBr_2(o-arsine)(o-arsineBr_2)$ and $PtBr_2(o-arsineBr_2)_2$. We find, however, that the end-product of the bromination of $PtBr_2(oS)_2$, the platinum(IV) complex PtBr₄(oSBr₂)₂, is reduced by tin(II) chloride to the corresponding platinum(II) complex PtBr₂(oSBr₂)₂, which is not identical with the complex $PtBr_6(oS)_2$ obtained by adding two equivalents of bromine to $PtBr_2(oS)_2$. Similarly, the complex $PtBr_2(oABr_2)_2$ is not identical with $PtBr_6(oA)_2$ obtained by brominating $PtBr_2(oA)_2$. Also, the complexes $PtBr_4(oS)_2$ and $PtBr_6(oS)_2$, but not PtBr₂(oSBr₂)₂, react with primary alcohols on heating to give yellow complexes of empirical formula $PtBr_3OR(oS)_2$ and $PtBr_5OR(oS)_2$ (R = Me, Et, Prⁿ, or Bun), respectively, which are monomeric and nonconducting in nitrobenzene. Reaction with secondary, tertiary, or longer-chain primary alcohols gives mainly the chelate complex PtBr₂oS. The action of alcohols on $PtBr_4(oA)_2$ and $PtBr_6(oA)_2$ produces mainly the chelate complex PtBr, oA, and only methoxy- and ethoxyderivatives of the type $PtBr_3OR(oA)_2$ can be isolated. The infrared spectra of the alkoxy-substituted complexes show characteristic strong bands in the 1070-1100 cm.⁻¹ region characteristic of C-O-C stretching vibrations,^{7b} but are otherwise similar to the spectra of the starting bromo-compounds. The ready metalassisted solvolysis of a halogen atom by alcohols has been observed previously in the alcoholysis of the chloromethyl-substituted allyl complex $Pd_2Cl_2(\pi-Cl\cdot CH_2\cdot C_3H_4)_2$ obtained from the reaction of butadiene with palladium(II) chloride.8 The behaviour seems to be characteristic of any negative group (e.g., halide, acetate) attached to a CH2. or CHMe. group, which, on ionis-

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ation, forms a carbonium ion which can be stabilised by interaction with filled orbitals in a transition-metal complex.^{8,9} On this basis we formulate the complexes $PtBr_4(o-arsine)_2$ and $PtBr_6(o-arsine)_2$ (o-arsine = oS, oA) as octahedral platinum(IV) complexes which contain metal-carbon σ -bonds to the side-chains of the ligands, and we write them as PtBr₃(oSBr)(oS), PtBr₃(oABr)(oA), $PtBr_3(oSBr)(oSBr_2)$, and $PtBr_3(oABr)(oABr_2)$, respectively. Attempts to obtain direct evidence for the presence of platinum-carbon bonds by examining the n.m.r. spectra for ¹⁹⁵Pt isotopic splitting of proton resonances have been frustrated by the low solubility of the complexes and by the complexity of the spectra shown by all the bis(arsine) complexes and their bromination products. We also do not know which carbon atom of the side-chains of the ligands is attached to the platinum atom. Some possible structures for PtBr₃(oSBr)(oS) are shown in (IV)--(VI). We consider structure (VI) less probable, since it contains a bond between the transition metal and a secondary carbon atom, examples of which are rare. A similar uncertainty exists for the complexes $PtBr_{a}(oSBr)(oSBr_{a}),$ PtBr₃(oABr)(oA), and PtBr₃(oABr)(oABr₂).



The alkoxy-substituted derivatives could be formulated as metal alkoxides, *e.g.*,

PtBr₂OR(o-arsineBr)(o-arsine), in which a bromine atom attached to the metal has been replaced by an alkoxy-However, the n.m.r. spectrum group. of PtBr₃OMe(oS)₂ shows a sharp signal at τ 6.85 due to the methoxyl protons, which is not observably split into a 1:4:1 triplet by ¹⁹⁵Pt, as would be expected if the methoxyl group were directly attached to the metal. Further, the strong band at 1087 cm.⁻¹ in the infrared spectra of $PtBr_3OMe(oS)_2$ and $PtBr_3OMe(oA)_2$ is reasonably assigned as the C-O-C stretching frequency of an ether group, rather than as the C-O stretching frequency

⁸ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806. ⁹ (a) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, 1959, **81**, 3484; E. A. Hill and J. H. Richards, *ibid.*, 1961, **83**, 3840, 4216; E. A. Hill, *J. Org. Chem.*, 1963, **28**, 3586; (b) D. S. Trifan and R. Backsai, *Tetrahedron Letters*, 1960, No. 13, 1; (c) C. Jutz, *Tetrahedron Letters*, 1959, 1.

of a metal methoxide, which occurs at ca. 1033 cm $^{-1.10}$ We therefore formulate the alkoxy-complexes as PtBr₃(o-arsoneOR)(o arsine) and PtBr₃(o-arsineOR)-(o-arsineBr₂), the bromine atoms attached to carbon being replaced by OR.

The suggested sequence of bromination of the bis(o-arsine) complexes PtBr₂(o-arsine)₂ is: (1) Attack on one double bond, with formation of a metal-carbon σ -bond to the vinvl or allyl side-chain. (2) Addition of bromine to the remaining double bond, leaving the metalcarbon σ -bond intact. (3) Attack by bromine on the metal-carbon σ -bond, forming finally the tetrabromoplatinum(IV) complex of the fully brominated ligand. This sequence is summarised in Scheme 3.

PtBr₂(o-arsineBr)(o-arsine) The complexes and PtBr₃(o-arsineBr)(o-arsineBr₂) also show bands in this region, but they cannot be distinguished from bands due to carbon-bromine stretching modes, and are therefore of no diagnostic value.

Assuming the correctness of our suggested structures for the complexes, we tentatively assign the band at ca. 270 mµ in the electronic spectra of the complexes PtBr₃(o-arsineBr)(o-arsine) and PtBr_a(o-arsineBr)-(o-arsineBr₂) as a ligand-field band corresponding to the band at ca. 350 mµ in the spectra of the tetrabromoplatinum(IV) complexes, the shift to higher energy being caused by the higher ligand-field strength of carbon than of bromine.14



Bromination of $PtBr_2(oS)_2$ [a similar reaction sequence can be written for $PtBr_2(oA)_2$]

The isomeric complexes $PtBr_2P_2$ (P = o- and p-propylphenyldimethylarsine, $Pr^{n} \cdot C_6 H_4 \cdot AsMe_2$) are oxidised by bromine to the corresponding orange platinum(IV) complexes PtBr₄P₂, there being no obvious qualitative difference in the reactivity of the two starting complexes. Therefore, the oxidation by bromine of platinum(II) to platinum(IV) is not seriously hindered by ortho substituents in the aromatic ring of the ligand, and the effect of the ortho vinyl and ortho allyl groups must be primarily electronic.

The complexes $PtBr_3(o arsineBr)(o - arsine)$ and PtBr₃(o-arsineBr)(o-arsineBr₂), and the alkoxy-derivatives, in benzene solution are unaffected by hydrogen and by carbon monoxide, and the only reaction with hydrogen chloride is to replace the reactive bromine atom by chlorine. The stability of the platinum-carbon bonds in these complexes is also shown by the fact that they are formed in a reaction involving bromine, and are only broken by bromine in the last stage of that reaction. Platinum(IV) alkyls containing tertiary phosphine ligands readily decompose to platinum(II) alkyls,¹¹ e.g.,

and the stability of our complexes seems to be comparable with that of the platinum(IV) alkyls which contain no other ligand, such as $[PtMe_3I]_4$.¹²

Both platinum(II) and platinum(IV) alkyls show bands in their infrared spectra at ca. 600 cm.⁻¹ which have been assigned to metal-carbon stretching frequencies.13

Attempts to brominate the complexes $PtBr_2(oS)_2$ and PtBr₂(oA)₂ in chloroform, dichloromethane, nitromethane, and acetonitrile lead to considerable decomposition; the only identifiable products are the chelate complexes $PtBr_2(o-arsine)$.

DISCUSSION

We can explain the reactions of the platinum(II) complexes of the ortho-substituted olefinic ligands, if we assume that Br^+ is the attacking entity in addition reactions of bromine (Scheme 4). This assumption



is certainly an over-simplification especially for reactions of bromine in non-polar solvents such as benzene and carbon tetrachloride.¹⁵

¹³ D. M. Adams, J. Chatt, and B. L. Shaw, J. Chem. Soc., 1960, 2047.

 ¹⁰ R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.
 ¹¹ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.
 ¹² G. E. Coates, "Organometallic Compounds," Methuen, 1960, 2nd edn., p. 325 et seq.

¹⁴ J. Chatt and R. G. Hayter, J. Chem. Soc., 1961, 772.

¹⁵ P. B. D. de la Mare, *Quart. Rev.*, 1949, **3**, 126; P. W. Robertson, *Rev. Pure Appl. Chem. (Australia)*, 1957, **7**, 155.

In the first step, Br^+ attacks $PtBr_2(o-arsine)_2$ at the platinum atom, giving the platinum(IV) species (VII), which is stabilised by electron donation from the double bond to the vacant $6p_z$ orbital of the metal, giving the carbonium ion (VIII). Attack by Br^- on this species completes the sequence. An alternative mechanism in which Br^+ initially attacks one of the free double bonds of $PtBr_2(o-arsine)_2$ is also possible. The resulting carbonium ion could be stabilised by electron donation from the filled $5d_{z_2}$ orbital of platinum(II), and attack by Br^- on the metal would complete the sequence.

The ready alcoholysis of $PtBr_3(o\text{-arsineBr})(o\text{-arsine})$ may proceed by initial loss of Br^- , giving the same carbonium ion (VIII), which can be stabilised by electron donation from filled non-bonding orbitals (d_{xy}, d_{xz}, d_{yz}) on octahedrally co-ordinated platinum(IV). Attack on this species by alkoxide ions OR^- from the alcohol gives the alkoxy-substituted product (Scheme 4). A similar mechanism can be envisaged for the alcoholysis of $PtBr_3$ (o-arsine) (o-arsineBr_2). The formation of the chelate complexes $PtBr_2(o\text{-arsine})$ in these reactions presumably arises from elimination of bromine (which may oxidise the alcohol) and one of the ligands, together with a nucleophilic attack by the remaining double bond on the metal.

At present we have no direct evidence for carboniumion participation in these reactions. The carbonium ions derived from cyclic and acyclic diene iron tricarbonyl complexes,¹⁶ and the ferrocenylcarbonium ion,^{9c} can be isolated, and the intermediate in our system may show comparable stability.

The structure of $PtBr_3(oAOEt)(oA)$, which has been determined recently by X-ray study,¹⁷ confirms the presence of a metal-carbon σ -bond in this compound with octahedral stereochemistry about platinum(IV). It is of interest that the side-chain containing the carbon atom attached to the metal is branched, *i.e.*, the complex contains the ring system

 $Pt \cdot CH_2 \cdot CH(CH_2OEt) \cdot C_6H_4 \cdot AsMe_{2^{-0}}$. We do not know whether the branching occurs in the bromination of $PtBr_2(oA)_2$ or in the ethanolysis of $PtBr_3(oABr)(oA)$, although the similarity to a Wagner-Meerwein rearrangement, for which carbonium-ion intermediates have been postulated, suggests that the second possibility is more likely.

EXPERIMENTAL

Light petroleum had b. p. 60—80°. o-, m-, and p-Bromostyrenes were commercial. m- and p-Allylbromobenzenes were obtained by treating the mono-Grignard reagent of the appropriate dibromobenzene with allyl bromide. o-Allylbromobenzene was first prepared by treating the diazonium salt of o-allylaniline hydrochloride (Aldrich) with cuprous bromide. More conveniently, o-allylchlorobenzene was obtained by treating the mono-Grignard reagent of o-bromochlorobenzene with allyl bromide.

Olefinic Tertiary Arsines.—A Grignard reagent prepared from magnesium turnings (0.1 g.-atom) and the appro-

¹⁶ R. Pettit and G. F. Emerson, Adv. Organometallic Chem., 1964, 1, 1, and references therein. priate bromostyrene or allylbromobenzene (0.1 mol.) in dry ether (*m*- and *p*-compounds) or tetrahydrofuran (*o*-compound) was treated with dimethyliodoarsine (0.1 mol.) in dry benzene. The mixture was worked up as previously described,¹ and the ligands isolated in *ca*. 60%yield by vacuum distillation. They were characterised as their *methiodides*. Analyses are in Tables 3 and 4.

o- and p-Propylphenyldimethylarsines.—The appropriate allylbromobenzene (19.7 g., 0.1 mol.) in absolute ethanol (100 ml.) was hydrogenated with platinum oxide (0.1 g.) as catalyst. Distillation at $56^{\circ}/2$ mm. gave the bromopropylbenzene (17 g.). Treatment with magnesium and dimethyliodoarsine as above gave the required ligands. Analyses are in Table 4.

Complexes.—(a) Rhodium(III) complexes, RhBr₃(oS)₃, RhBr₃(mS)₃, and RhBr₃(pS)₃. Rhodium trichloride trihydrate (0.42 g., 1 mol.), lithium bromide (2 g., ca. 20 mols.), and the appropriate styryldimethylarsine (1 g., 4 mols.) were heated in ethanol (50 ml.) for 1 hr. The solution was evaporated to dryness at 15 mm., and the residue extracted with chloroform (3 \times 15 ml.). Solvent was removed at 15 mm., and the solid recrystallised from 1:1 benzene-light petroleum to give the complex (ca. 50% yield). Analyses are in Table 3.

complexes. PtBr₂(oS)₂. Potassium (b) Platinum(11) tetrabromoplatinate(II) (1.66 g., 1 mol.) in water (50 ml.) was treated with o-styryldimethylarsine (1.2 g., 2 mol.) and the mixture shaken for 1 hr. The pale yellow solid was extracted with 1:1 ethanol-ether $(2 \times 15 \text{ ml.})$. The residue was recrystallised slowly from benzene to give crystals of the cis-complex (40%). The ethanol-ether extract was evaporated to dryness at 15 mm., and the residue recrystallised from hot benzene-light petroleum to give crystals of the trans-complex. Similarly obtained were PtBr₂(mS)₂, recrystallised from ethyl methyl ketoneether, only the trans-complex being isolated, and $PtBr_2(pS)_2$, recrystallised from benzene-light petroleum, only the trans-complex being isolated. Analyses are in Table 3.

PtBr₂(oA)₂. o-Allylphenyldimethylarsine (3·13 g., 2 mols.) in chloroform (10 ml.) was added slowly to a stirred suspension of anhydrous platinum(II) bromide (2·5 g., 1 mol.) in chloroform (30 ml.). The mixture was stirred for 30 min., filtered, evaporated to dryness at 15 mm., and the residue recrystallised from benzene to give needles of the *complex* (85%). Similarly obtained were PtBr₂(mA)₂, flakes from ethanol (80%), PtBr₂(pA)₂, needles from ethanol (70%), PtBr₂oS (a 2:1 mole ratio of platinum(II) bromide to *o*-styryldimethylarsine was used), recrystallised from dichloromethane-light petroleum (70%).

PtBr₂oA. This was obtained as above, a 1:1 mol. ratio of o-allylphenyldimethylarsine to platinum(II) bromide being used, as needles from ethanol (80%). Recrystallisation from benzene gave a *hemisolvate*, whose infrared spectrum showed an intense band at 698 cm.⁻¹; this disappeared when the solvate was recrystallised from ethanol. The presence of benzene in the ethanol was confirmed by comparing the ultraviolet spectrum with that of pure ethanol. Bands characteristic of benzene appeared at 243, 249, 255, and 261 m μ .

 $PtBr_2(oP)_2$. This was obtained as above, a 2:1 mol. ratio of ligand to platinum(II) bromide being used, as needles from ethanol (70%).

¹⁷ M. A. Bennett, G. J. Erskine, J. Lewis, R. Mason, R. S. Nyholm, G. B. Robertson, and A. D. C. Towl, *Chem. Comm.*, 1966, 395.

Metal

M

577

799

799

799

959

959

959

1120

1120

1280

1280

1280

924

803

803

963

963

856

806

805

875

875

24.3

24.3

20.3

20.3

24.8 23.8

20.5

20.3

^d EtO, Found: 5.9; Reqd.: 4.8%.

Colours, m. p., analyses (%), and molecular weights of the ligands oS , mS , pS , and their metal complexes														
			(0	н		A	s	Hal	ogen	${\rm Me}$	tal	1	М
Compound	Colour	M. p.	Found	Reqd.	Found l	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.
<i>o</i> S	White oil	$70^{\circ}/0.5 \mathrm{mm}.$	• 57.5	57.7	6.5	$6 \cdot 3$	35.7	36.0						
mS	White oil	64/0·3 mm. 4	57.8	57.7	$6 \cdot 3$	$6 \cdot 3$	35.4	36.0						
⊅S	White oil	8890/1 mm. ª	58.0	57.7	$6 \cdot 3$	$6 \cdot 3$	36.0	36.0						
oSMe+I	White	218-220 dec.	37.7	37.7	4 ·7	4.6								
mSMe+I	White	185	37.7	37.7	$4 \cdot 2$	4.6								
<i>∕</i> SMe+I	White	197 - 200	37.9	37.7	4.7	4.6								
RhBr ₃ (oS) ₃	Orange	135—140 dec.	37.2	37.3	$4 \cdot 3$	$4 \cdot 1$	$23 \cdot 3$	23.2						
$RhBr_{3}(mS)_{3}$	Orange	100—110 dec.	37.7	37.3	$4 \cdot 0$	4.1								
$RhBr_{3}(pS)_{3}$	Orange	172 dec.	37.7	37.3	$4 \cdot 2$	4.1			$25 \cdot 1$	$24 \cdot 8$				
$RhBr_3(oSBr_2)_3$	Orange	103-105 dec.	$24 \cdot 9$	24.9	$2 \cdot 6$	2.7			$49 \cdot 3$	49.7				
$RhBr_3(mSBr_2)_3$	Orange	105-110 dec.	25.1	$24 \cdot 9$	$3 \cdot 0$	2.7	15.4	15.5						
$RhBr_{3}(\rho SBr_{2})_{3}$	Orange	110125 dec.	25.2	24.9	$2 \cdot 8$	$2 \cdot 7$			49.2	4 9·7				
PtBr ₂ 0S	White	235 - 237	21.7	21.3	$2 \cdot 2$	$2 \cdot 3$			28.9	28.4	34.5	34.6	554	563 °
cis-PtBr ₂ (oS) ₂	Yellow	190192	30.7	$31 \cdot 1$	3.7	3.4			20.6	20.7			740	771
trans-PtBr ₂ (oS) ₂	Yellow	177-181	31.3	$31 \cdot 1$	3.6	$3 \cdot 4$			20.5	20.7	25.0	25.3		
$PtBr_2(mS)_2$	Yellow	164	30.7	$31 \cdot 1$	3.7	$3 \cdot 4$			20.8	20.7	$25 \cdot 3$	25.3		
$PtBr_{2}(pS)_{2}$	Yellow	153 - 156	30.8	$31 \cdot 1$	$3 \cdot 3$	$3 \cdot 4$	19.7	19.4	20.7	20.7	25.7	25.3		
$PtBr_{a}(oSBr)(oS) \dots$	Yellow	132	25.7	25.8	$2 \cdot 9$	$2 \cdot 8$	16.5	$16 \cdot 1$	33.9	34.3	21.0	21.0	850	931
$PtBr_{4}(mS)_{2}$	Orange	188	26.0	25.8	$2 \cdot 9$	$2 \cdot 8$			34.5	34.3				
$PtBr_4(pS)_2$	Orange	168-171	26.2	25.8	$2 \cdot 9$	$2 \cdot 8$	$16 \cdot 1$	16.1	33.9	34·3	21.2	21.0	902	931
$PtBr_{3}(oSBr)(oSBr_{2})$	Yellow	146 - 149	22.0	22.0	2.5	$2 \cdot 7$							980	1091
$PtBr_{4}(pS)(pSBr_{2})$	Orange	194195	$22 \cdot 6$	22.0	2.8	$2 \cdot 7$			44 ·4	44 ·0				
$PtBr_4(oSBr_2)_2$	Orange	181-183	19.4	19.2	$2 \cdot 3$	$2 \cdot 1$			50.6	51.1	15.3	15.6	1120	1251
$PtBr_{a}(mSBr_{a})_{2}$	Orange	180 dec.	19.2	19.2	1.9	$2 \cdot 1$			50.4	$51 \cdot 1$				
$PtBr_4(pSBr_2)_2$	Orange	209-211	19-1	19.2	$2 \cdot 2$	$2 \cdot 1$	$12 \cdot 4$	12.0	51.4	$51 \cdot 1$	15.9	15.6	1217	1251
PtBr ₂ (oSBr ₂),	Yellow	167 - 169	22.0	22.0	2.7	$2 \cdot 4$			44.5	44.0				
PtBr ₃ (oSOMe)(oS)	Yellow	176 - 178	28.6	28.6	3.5	$3 \cdot 3$	$2 \cdot 7$	1.8	27.2	27·2 ď				
$PtBr_5(oSOEt)(oS) \dots$	Yellow	175 - 176	29.5	29.5	$3 \cdot 8$	$3 \cdot 5$			27.5	26·8 °				
$PtBr_{3}(oSOPr^{n})(oS)$	Yellow	215	29.2	30.6	3.7	$3 \cdot 6$	1.6	1.8	c					
$PtBr_{3}(oSOBu^{n})(oS)$	Yellow	169-171	30.7	31.2	$4 \cdot 0$	$3 \cdot 8$	$1 \cdot 2$	1.7	c					
$PtBr_{3}(oSOMe)(oSBr_{2})$	Yellow	147 - 150	$25 \cdot 2$	$24 \cdot 2$	$3 \cdot 1$	$2 \cdot 8$			38.2	38.4				
^a Boiling point. ^b Found: 5.3; Reqd.;	Measured 5.0%.	osmometrically in	n aceto	one. °	Oxygen	anal	lysis. d	MeO,	Found	l: 3·4;	Reqd	.: 3.6	%. e	EtO,

TABLE 3

Found Reqd. Found Reqd. Found Reqd. Found Reqd. Found Reqd. Compound Colour М. р. 72—77°/1 mm.ª 70—74/2 mm.ª 59.359.56·8 $6 \cdot 8$ 33.9 33.8 White oil oA White oil 59.959.56.6 6·8 33.7 33.8 *m*A 33.8 76/2 mm.ª 59.66·4 6·8 33.6 *p*A..... White oil 59.57.6*o*P White oil 90-92/6 mm.ª 59.558.97.433.533.57.7White oil 100-102/6 mm." 58.758.97.6 $33 \cdot 2$ 33.5*p*T oAMe+I⁻ *m*AMe+I⁻ White 134-136 39.6 39.6 $5 \cdot 3$ $5 \cdot 0$ 147-151 White 39.8 39.6 $5 \cdot 0$ 18.4 20.634.7 34.9 4.9 $pAMe^+I^-$ $pPMe^+I^-$ $5 \cdot 0$ $5 \cdot 0$ 20.6 144 - 14639.339.618.3 $33 \cdot 2$ 34.9 White 120 - 123White 39.439.3 5.8 $5 \cdot 6$ *φ*PMe⁺I⁻ White 145 - 14839.3 39.3 $5 \cdot 8$ 5.6 $\begin{array}{c} PtBr_2 oA \\ PtBr_2 oA \frac{1}{2}C_6H_6 \end{array}$ dec. > 225dec. > 22523.1 22.9 2.82.6 27.427.7 $34 \cdot 2$ 34.8 White 3.1 White 27.527.32.9 25.826.0 31.9 31.6 146-149119-121 131-133 $24 \cdot 2$ PtBr₂(oA)₂ 33.3 $32 \cdot 9$ 4.1 20.420.124.5Yellow 3.819.218.8 $PtBr_2(mA)_2$ Yellow 32.632.9 $3 \cdot 8$ $3 \cdot 8$ 24.724.5 $\begin{array}{c} PtBr_2(\phi A)_2 \\ PtBr_3(oABr)(oA) \\ \dots \\ \end{array}$ 32.832.93.6 $3 \cdot 8$ 18.218.8 19.920.124.724.5Yellow 140 27.927.4 $3 \cdot 3$ $3 \cdot 2$ 33.1 33.4 20.420.4Yellow $140 \\ 135 - 139 \\ 129 - 131 \\ 142 - 148 \\ 118 - 122 \\ 107$ 27.0 27.43.2 $3 \cdot 2$ 33.4 33.420.020.4 $PtBr_4(mA)_2$ Orange $\begin{array}{c} PtBr_4(pA)_2 & \dots \\ PtBr_3(oABr)(oABr_2) \end{array}$ $27 \cdot 2$ 27.43.3 3.1 33.8 33.4 20.520.4910 Orange Yellow 23.823.5 $3 \cdot 1$ 2.7 $43 \cdot 2$ 42.81050 $PtBr_4(pA)(pABr_2)$... Orange 24.1 23.53.0 2.7**43**·0 42.8 1080 20.320.52.9 $2 \cdot 4$ 51.7**50**·0 1280 $PtBr_4(oABr_2)_2$ Orange 107 130-135159-162171-174 $PtBr_4(mABr_2)_2$ 2.721.1 20.52.450.050.0 1040 Orange 20.3 $3 \cdot 1$ 2.4**49**·8 1160 20.550.0 $PtBr_4(pABr_2)_2$ Orange $22 \cdot 8$ 23.5 $2 \cdot 5$ 2.742.7 $PtBr_2(oABr_2)_2$ Yellow 42.8

573750 774 796 940 910

TABLE 4 Colours, m. p., analyses (%), and molecular weights of the ligands oA, mA, pA, oP, and pP and their metal complexes

н

As

1.8 %

1.70

26.7

 $25 \cdot 9$

36.6

26.4 °

26·0 d

37.4

 $2 \cdot 9$

 $2 \cdot 0$

Halogen

С

 $168 - 170 \\ 165 - 167$ 32.632.6 $4 \cdot 2$ Yellow $33 \cdot 1$ $4 \cdot 3$ PtBr4(0P)2 Red 192 - 19527.327.43.73.527.4

30.3

31.1

25.8

3.8

4.1

3.4

4.4

3.7

3.5

 $3 \cdot 8$

3.1

 $4 \cdot 2$

3.5

30.8

31.4

26.3

 $33 \cdot 2$

 $27 \cdot 4$

 $PtBr_4(pP)_2$ Red ^a Boiling point. ^b Oxygen analysis. ^c MeO, Found: 5.9; Reqd.: 3.4%

Yellow

PtBr₃(oAOMe)(oA) ... Yellow

PtBr₃(oAOMe)(oABr₂) Yellow

PtBr₂(oP)₂ Yellow

PtBr₃(oAOEt)(oA) ...

 $PtBr_2(pP)_2$

166—167

160

157-161

167-170

pΡ

J. Chem. Soc. (A), 1967

 $PtBr_2(pP)_2$. This was obtained as above, as fine needles from ethanol (70%).

Bromination Studies.—(a) Tertiary arsines. Approximately 3×10^{-3} M solutions of the tertiary arsines in carbon tetrachloride or benzene were titrated with 0·1M-bromine in the same solvent in a 1 cm. silica cell shielded from light, and after each drop of bromine had been added, the optical density at 418 mµ (λ_{max} for bromine in CCl₄ and C₆H₆) was measured. Optical density at 418 mµ was then plotted against mols. of bromine added, allowance being made for the progressive dilution of the solution. The bromination products of the ligands were intractable oils which were not further characterised.

(b) Tertiary arsine methiodides. The above procedure was followed, except that chloroform was used as solvent. The absorption maximum for bromine in chloroform (411 m μ) was shifted to 385 m μ on addition to the methiodide solutions. No band at 520 m μ appeared, showing that iodine was not formed. One equivalent of 0.01M-bromine in chloroform was added in one portion to the methiodide solutions, and the relative rates of disappearance of bromine were determined by measuring the optical density at 385 m μ at set time intervals. The methiodide of *m*-allyl-phenyldimethylarsine reacted completely after 4 days, the para-isomer after 5 days, while the ortho-isomer failed to react completely even after several days.

(c) Rhodium(III) complexes.

(S = oS, mS, pS). The rhodium(III) complex (0.24 g., 1 mol.) in carbon tetrachloride (75 ml.) was treated with an excess of bromine (15 ml. of 0.1M) at room temperature for 24 hr. A light buff precipitate formed slowly. Solvent and bromine were removed at 15 mm., and the residue was recrystallised from 1:1 benzene-light petroleum to give the brominated *complex*.

(d) Platinum(II) complexes. Spectrophotometric titrations were carried out as in (a) above, with $ca.3 \times 10^{-4}$ M-complex and 0.01M- bromine solutions.

The general preparative procedure was as follows. The platinum(II) complex (ca. 0.5 g.) in carbon tetrachloride or benzene was treated with the calculated volume of 0.1Mbromine in the same solvent during 30 min., and left at room temperature for 24 hr. Solvent was evaporated off at 15 mm. from the solution, and the residue was recrystallised from a suitable solvent. The yield of recrystallised product and the solvent are in parentheses. Analyses are in Table 3 and 4.

(1)
$$PtBr_2(oS)_2 + Br_2 \longrightarrow$$

 $PtBr_3(oSBr)(oS)$ (acetone, 50%)

(2)
$$PtBr_2(oA)_2 + Br_2 \longrightarrow$$

 $PtBr_3(oABr)(oA)$ (acetone, 50%)

(3)
$$PtBr_2(oS)_2 + 2Br_2 \longrightarrow PtBr_3(oSBr)(oSBr_2)$$

 $2{\cdot}5\,mols.\,of$ bromine were used per mol. of complex (benzene-light petroleum 60%). The same complex was obtained from $PtBr_3(oSBr)(oS)$ and 1 mol. of bromine

(4)
$$PtBr_2(oA)_2 + 2Br_2 \longrightarrow PtBr_3(oABr)(oABr_2)$$

(dichloromethane-light petroleum, 75%)

(5)
$$PtBr_2(oS)_2 + 3Br_2 \longrightarrow PtBr_4(oSBr_2)_2$$

A large excess (ca. 6 mols.) of bromine was added per mol. of complex, and the mixture heated for 1 hr. (benzene, 60%)

(6)
$$PtBr_2(oA)_2 + 3Br_2 \longrightarrow PtBr_4(oABr_2)_2$$

As in (5) (dichloromethane-light petroleum, 83%)

(7)
$$PtBr_2(mS)_2 + Br_2 \longrightarrow$$

 $PtBr_4(mS)_2$ (benzene-light petroleum, 65%)
(8) $PtBr_2(mA)_2 + Br_2 \longrightarrow$

(8)
$$PtBr_2(mA)_2 + Br_2 \longrightarrow$$

PtBr₄(mA)₂ (carbon tetrachloride, 60%)

(9)
$$PtBr_2(mS)_2 + 2Br_2 \longrightarrow$$

 $PtBr_4(mS)_2 + PtBr_4(mSBr_2)_2$ (see below)

(10)
$$PtBr_2(mA)_2 + 2Br_2 \longrightarrow$$

 $PtBr_4(mA)_2 + PtBr_4(mABr_2)_2$ (see below)

(11)
$$PtBr_2(mS)_2 + 3Br_2 \longrightarrow PtBr_4(mSBr_2)_2$$

- As in (5) (benzene, 50%)
- (12) $PtBr_2(mA)_2 + 3Br_2 \longrightarrow PtBr_4(mABr_2)_2$
- As in (5) (benzene-light petroleum, 45%)
- (13) $PtBr_2(pS)_2 + Br_2 \longrightarrow$ $PtBr_4(pS)_2$ (benzene-light petroleum, 55%)

(14)
$$PtBr_2(pA)_2 + Br_2 \longrightarrow$$

 $PtBr_4(pA)_2$ (carbon tetrachloride, 60%)

(15)
$$PtBr_2(pS)_2 + 2Br_2 \longrightarrow$$

 $PtBr_4(pS)(pSBr_2)$ (acetone, 10%)

(16)
$$PtBr_2(pA)_2 + 2Br_2 \longrightarrow$$

 $PtBr_4(pA)(pABr_2)$ (carbon tetrachloride, 60%)

(17)
$$PtBr_2(\rho S)_2 + 3Br_2 \longrightarrow PtBr_4(\rho SBr_2)_2$$

As in (5) (benzene, 25%)

- (18) $PtBr_2(pA)_2 + 3Br_2 \longrightarrow PtBr_4(pABr_2)_2$
- As in (5) (benzene-light petroleum, 30%)

(19)
$$PtBr_2(oP)_2 + Br_2 \longrightarrow$$

 $PtBr_4(oP)_2$ (carbon tetrachloride, 70%)

(20)
$$PtBr_2(pP)_2 + Br_2 \longrightarrow$$

 $PtBr_4(pP)_2$ (carbon tetrachloride, 60%)

(e) Alcoholysis of bromination products of $PtBr_2(oS)_2$ and $PtBr_2(oA)_2$. The platinum complex (ca. 0.5 g.) was heated in the appropriate alcohol for 30 min. The product crystallised from the reaction medium.

(1)
$$PtBr_3(oSBr)(oS) + MeOH \longrightarrow$$

 $PtBr_3(oSOMe)(oS)$ (methanol, 63%)
(2) $PtBr_2(oSBr)(oS) + EtOH \longrightarrow$

(2)
$$PtBr_3(oSBr)(oS) + EtOH \longrightarrow$$

 $PtBr_3(oSOEt)(oS)$ (ethanol, 50%)

(3)
$$PtBr_3(oSBr)(oS) + Pr^n OH \longrightarrow$$

 $PtBr_3(oSOPr^n)(oS)$ (n-propanol, 35%)

(4)
$$PtBr_3(oSBr)(oS) + Bu^nOH \longrightarrow$$

 $PtBr_3(oSOBu^n)(oS)$ (n-butanol, 30%)

(5)
$$PtBr_3(oSBr)(oSBr_2) + MeOH \longrightarrow$$

 $PtBr_3(oSOMe)(oSBr_2)$ (methanol, 25%)

(6)
$$PtBr_3(oABr)(oA) + MeOH \longrightarrow PtBr_3(oAOMe)(oA)$$

separated from chelate complex $PtBr_2oA$ also produced by extraction with cold benzene and recrystallisation from acetone (40%)

(7) $PtBr_{3}(oABr)(oA) + EtOH \longrightarrow PtBr_{3}(oAOEt)(oA$

As in (6) (ethanol, $35^{0/}_{0}$)

(8) $PtBr_3(oABr)(oABr_2) + MeOH \longrightarrow PtBr_3(oAOMe)(oABr_2)$

As in (6) (methanol, 43%)

(f) Reduction of platinum(IV) complexes to platinum(II) complexes. The complex PtBr₄($oSBr_2$)₂ (ca. 0.3 g.) in acetone (30 ml.) was treated with a slight excess of tin(II) chloride dihydrate in acetone to give crystals of PtBr₂($oSBr_2$)₂ (methanol, 65%). The complex PtBr₄($oABr_2$)₂ was converted into PtBr₂($oABr_2$)₂ by the same method, or by heating in ethanol (ethanol, 67%). Both complexes were unaffected by prolonged heating in alcohols.

Physical Measurements.—Molecular weights were determined on ca. 0.02 μ solutions in chloroform on a Mechrolab vapour-pressure osmometer. Infrared spectra were recorded in Nujol and hexachlorobutadiene mulls on a GrubbParsons GS2A spectrometer in the range 4000-500 cm.⁻¹ Ultraviolet and visible spectra were determined on a Unicam S.P. 500 spectrophotometer. The dipole moment of PtBr₂(oA)₂ was determined in benzene by Mrs. Caradine, Imperial Chemical Industries Limited Petrochemicals and Polymers Research Laboratory, Runcorn, Cheshire, whom we thank.

Analysis.—Carbon and hydrogen analyses were by Mr. W. Winter of this Department and by Alfred Bernhardt, Microanalytical Laboratory of the Max-Planck Institut für Kohlenforschung, Mülheim, Germany. The latter also carried out methoxyl and ethoxyl determinations. Oxygen analyses were by the Microanalytical Department, Imperial College. Halogen was determined by fusing the complexes with sodium, extracting with water, and titrating the halide ion potentiometrically with silver nitrate after acidifying with dilute nitric acid. Platinum was determined by direct ignition.

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