STUDIES ON TIN COMPOUNDS AND COMPLEXES OF THE PLATINUM GROUP METALS

A Thesis submitted

by

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ABSTRACT

Stannous chloride interacts with platinum-metal compounds to form complex anions of ruthenium, rhodium, iridium and platinum which have been isolated as salts of large cations. The anions are formulated as $[RuCl_2(SnCl_3)_2]^{2-}$, $[Rh_2Cl_2(SnCl_3)_4]^{4-}$, $[Ir_2Cl_6(SnCl_3)_4]^{4-}$ and cis- and trans- $[PtCl_2(SnCl_3)_2]^{2-}$ where the trichlorostannate(II) ion is considered to be acting as a donor anionic ligand.

Neutral complexes of rhodium, iridium and platinum have been prepared which have an $SnCl_3$ group bound to the metal atom together with ligands such as di-olefins, and phosphine and arsine ligands; examples are: (norbornadiene)$_2$MSnCl$_3$(M=Rh,Ir), $(Ph_3P)_2PtCl(SnCl_3)$, $(Ph_3P)_3RhSnCl_3$ and $(Ph_2MeAs)_3RhCl_2(SnCl_3)$.

Carbonyl chlorides of ruthenium and rhodium react with stannous chloride to give new complex anions as tetramethylammonium salts: $[Ru(CO)_2Cl_2(SnCl_3)_2]^{2-}$ and $[Rh(CO)Cl(SnCl_3)_2]^{2-}$. A similar iridium carbonyl anion, $[Ir(CO)Cl_3(SnCl_3)_2]^{2-}$ is prepared by a different route through the interaction of $[Ir_2Cl_6(SnCl_3)_4]^{4-}$ with an alkanolic solvent.

Stannous chloride has also been used in the preparation of new hydrides of rhodium and iridium, or as a new route to hydrides that have previously been prepared. In this way the following have been isolated and characterized: a new isomer of $(Ph_2MeAs)_3RhHCl_2$, $(Ph_3P)_3IrHCl(SnCl_3)$, $(Ph_3P)_3IrH_2(SnCl_3)$, $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$.

ABSTRACT (contd.)

acetone, $(Ph_3P)_2Ir(CO)HCl_2$ and $(Ph_3P)_3IrHCl_2$.

The reaction of stannic chloride with $(Ph_3P)_2Ir(CO)Cl$ has lead to the formation of a new compound containing the $SnCl_3$ group; viz.: $(Ph_3P)Ir(CO)Cl_2(SnCl_3)$.

Aspects of stannous chloride as a donor ligand, and its possible role as a reducing agent for transition metal compounds are discussed.

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INTRODUCTION

It has been known for a long time that salts of platinum metals react with stannous chloride in hydrochloric acid solutions to give intensely coloured solutions (1-3). These reactions have been utilized quite frequently for the detection and estimation of platinum (4-6), rhodium (5-7) and also for the estimation of palladium (4,8), although the coloured solutions are much less stable. Iridium was recognised to interfere with the determinations of the other platinum metals; but its reaction with stannous chloride was not demonstrated until much later (9).

Detailed spectrophotometric studies have now been made on the colour reactions with platinum (10-14), rhodium (15,16), palladium (17) and iridium (18); and they have been successfully applied to accurate, quantitative determinations of the metals. Furthermore stannous bromide and iodide have been shown to give related colour reactions which can also be used for quantitative estimation of the metals (19-21).

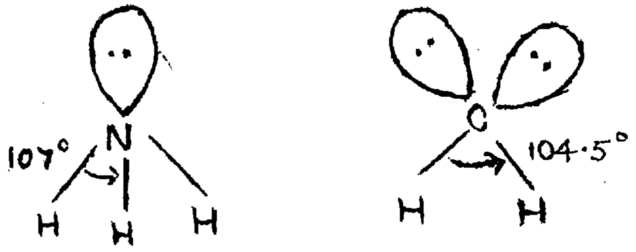
Ruthenium does not appear to react readily with stannous chloride, but it has been reported that amyl alcohol extracts a violet colour from mixtures of ruthenium trichloride and stannous chloride in hydrochloric acid media (22). It is known that the coloured species formed with platinum will extract into a variety of organic solvents such as alcohols (23), ketones (23), ethers (24) and acetate esters. (10,24,25). Such extractions have also been used in the spectrophotometric determination of the metal as the visible spectrum is the same as in aqueous solution. The colour developed with palladium can also be extracted (17); but no mention has been made of the behaviour of the rhodium and iridium reactions in this respect.

Hitherto most interest has been in the spectrophotometric aspects of these reactions and relatively little attention has been paid to the nature of the chemical species in solution. Ayres and Meyer (23) concluded from spectral studies that a range of complexes of varying platinum: tin ratios were in solution. They claimed to have isolated a cationic species $[Pt\ Sn_4Cl_4]^{4+}$ as the phenylarsonate. On the other hand Shukla (26) demonstrated the anionic nature of the coloured species for platinum, palladium and rhodium, using electrophoresis and paper chromatography. A recent report (27) on the existence of an anionic ruthenium -tin complex formulated as $[Ru(SnCl_3)_2Cl_2]^{2-}$ was in agreement with Shukla's findings.

Other reports of complexes between stannous chloride and transition metals are comparatively few. Dwyer and Nyholm (28) prepared compounds of rhodium with stannous chloride and diphenylmethylarsine; but some of their starting materials have since been reformulated and the structures they proposed need re-examining. Gorsich (29) reacted stannous chloride with certain metal carbonyls. The compounds he obtained are similar to those previously prepared by reactions between metal carbonyls and stannic chloride (30,31) and it appears that such compounds are better regarded as covalent compounds of tin(IV) rather than tin(II). More recent work by Bonati and Wilkinson (32,33) has confirmed this view. A report by Russian workers (34,35) has indicated a reaction between ferrous iron, stannous chloride and dimethylglyoxime.

A consideration of the structural features of stannous compounds can provide a clue to the nature of the interaction between stannous chloride and the platinum metals. The outer electronic structure of tin is $5s^2$,$5p^2$ and the divalent state can be assumed to arise through the 5s electrons forming an 'inert pair' with only the p electrons involved in chemical bonding. This is in contrast to the predominately covalent tetravalent state where all the outer electrons are utilized for bonding by means of sp^3 hybridization. The simple view of inert electrons in a pure s-orbital has now been modified to fit in with modern ideas of the importance of 'lone pairs' of electrons in determining inorganic stereochemistries (36,37).

The concept of considering an inert pair to occupy a directed non-bonding orbital of the same hybridisation as the bonding orbitals has successfully led to the explanation of donor properties in compounds like NH_3 or H_2O. Structural determinations in the vapour state show them to have pyramidyl or angular configurations with bond angles intermediate between 90° and 109·5° (the **tetrahedral** angle). These stereochemistries are best considered to arise from distorted tetrahedral configurations (sp^3 hybridization), the observed bond angles being due to different electron pair repulsions. (Fig.1.)



Bond repulsions: lone pair -lone pair > Lone pair- bonding pair > bonding pair- bonding pair.

Fig.1. Standard stereo-chemistries of Groups V & VI compounds.

The bond angles are further reduced in homologues of lower members of the groups (Table 1) because bond repulsions are altered due to changes in bond polarities arising from electronegativity differences. Thus although bond angles in AsH_3, SbH_3, SeH_2 are close to those expected for pure p-bonding, they are still best regarded as a distorted tetrahedral with the 'lone pair' occupying one site.

In the same way the structure of $SnCl_2$ in the vapour state as determined by Lister and Sutton (38) (Fig.2a) is best regarded as a distorted plane-trigonal structure involving the lone pair in an sp^2 hybrid orbital. The low electronegativity of tin would account for the large angular distortion similar to those in compounds of the adjacent elements in Group V.

TABLE I

Bond angles (Angle XMX in degrees) in hydrides and chlorides of Groups IV, V and VI
(Taken from "Tables of Interatomic Distance and Configurations in Molecules and Ions" Chem.Soc.Spec.Pub. No.11, 1958)

CH_4	109·5	NH_3	107	OH_2	104·5
CCl_4	109·5			OCl_2	110·8
		PH_3	93·5	SH_2	92·1
		PCl_3	100·1	SCl_2	102
		AsH_3	91·8	SeH_2	91
		$AsCl_3$	98·4		
$SnCl_4$	109·5				
		SbH_3	91·3		
$SnCl_2$	95	$SbCl_3$	99·5		
$PbCl_2$	95	$BiCl_3$	100		

TABLE II

Electronegativities of elements of Groups IV, V and VI
(Values expressed on Pauling's scale of electronegativities)

	N 3.05	O 3.50
	P 2.15	S 2.60
Ge 1.90	As 2.10	Se 2.55
Sn 1.90	Sb 2.05	Te 2.30

Recent structural investigations of crystalline divalent tin compounds have shown that, in the solid state at least, stannous tin shows a preference for three-fold coordination with a pyramidal structure analogous to MX_3 in Group V. Therefore they are better regarded as distorted tetrahedral sp^3 hybridization with one orbital occupied by the lone pair, two orbitals in covalent bond, and the fourth used in a dative covalent bond by some donor atom or molecule. (see Fig.2). Hence crystalline, anhydrous stannous chloride (39) has chloride bridges maintaining the desired stereochemistry; while hydrated stannous chloride $SnCl_2.2H_2O$, should be formulated as $SnCl_2(OH_2)H_2O$ (40) which explains why one water molecule is tightly held. $K_2SnCl_4.H_2O$ has recently shown to be a double salt $KCl.KSnCl_3.H_2O$ where the $SnCl_3^-$ ion has a pyramidyl structure (41).

Similar structures probably exist in solution also. Solvent coordination through lone pairs on the oxygen atoms explains the solubility of stannous chloride in such solvents as ether, acetone, ethylacetate, etc. In hydrochloric acid solution $SnCl_3^-$ should be present besides other species; <u>viz</u>: Sn^{2+},$SnCl^+$, $SnCl_2$ and $SnCl_4^{2-}$. Heavy cations (e.g. Me_4N^+, Ph_4As^+) precipitate $MSnCl_3$ from acid solutions. Woodward and Taylor (42) have shown by Raman spectra that ether extracts of hydrochloric acid solution of stannous chloride contain only $SnCl_3^-$ with the same stereochemistry as its isoelectronic analogue $SbCl_3$. But they concluded that other species are present in acid solutions. A thorough study of the equilibrium constants for the

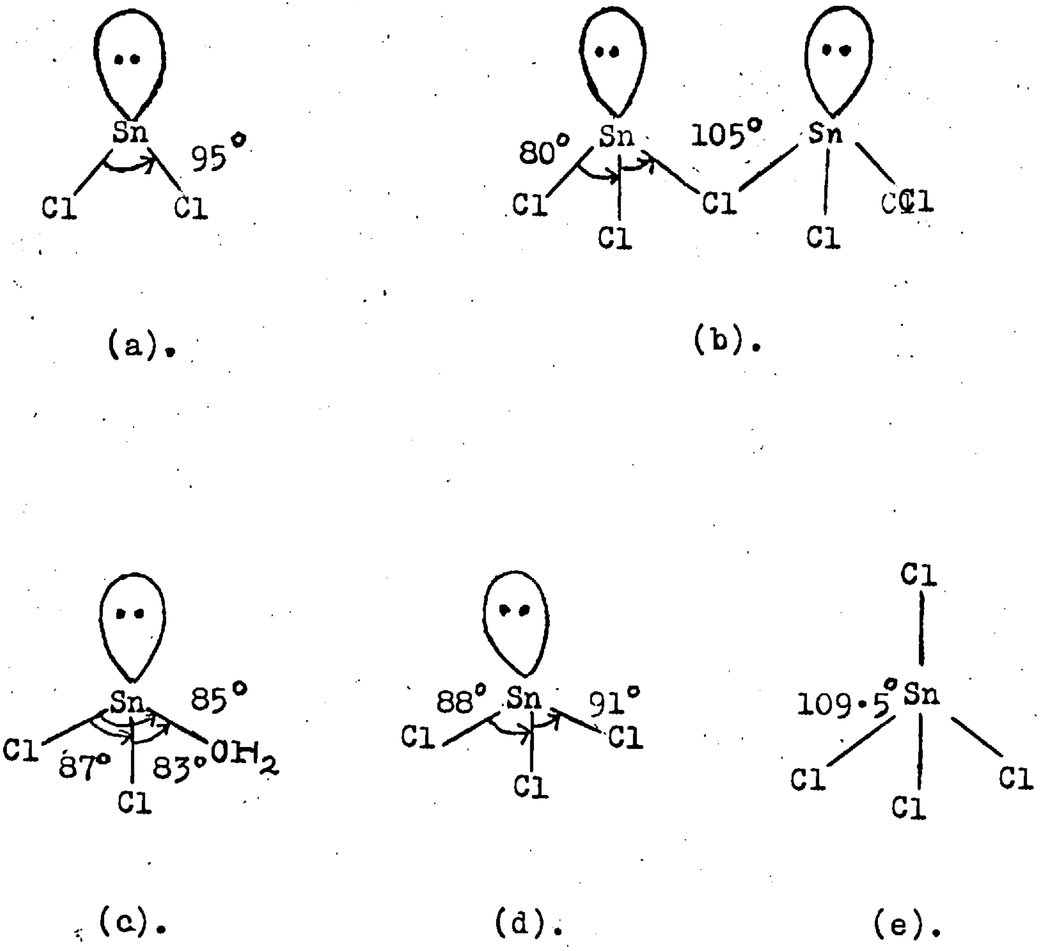


Fig.2 Crystal structures of some tin(II) compounds. (a) anhydrous $SnCl_2$ (vapour). (b) anhydrous $SnCl_2$ (crystal). (C) $SnCl_2.2H_2O$. (d) $SnCl_3$ in $K_2SnCl_4.H_2O$. (e) $SnCl_4$ (vapour).

system $SnCl_2$-HCl-H_2O by Vanderzee and Rhodes (43) agrees on all these points. They show that $SnCl_3^-$ is the predominant species in 2M-hydrochloric acid solutions and that $SnCl_4^{2-}$ is not present in appreciable quantities even at strong acid concentrations. Furthermore hydrolysis of stannous chloride is suppressed by the addition of hydrochloric acid and is very small at concentrations above 2M.

Thus the species reacting with platinum metals on hydrochloric acid media must be the $SnCl_3^-$ ion, which has a directed lone pair of electrons capable of forming a coordinate link with transition metals. Furthermore tin has vacant 5d orbitals which would be capable of forming d_π- d_π bonds with the metal and thereby strengthening σ-bonding. The same would be true of solvated stannous chloride in an organic solvent. Thus in either case stannous chloride appears to be capable of acting as a donor ligand (either neutral or anionic) capable of forming normal co-ordination complexes with the platinum metals.

DISCUSSION

1. Complex Tin-containing Anions of the Platinum Metals

In dilute hydrochloric acid solutions, stannous chloride is found to react with rhodium trichloride and sodium chloroplatinate(II) at room temperature to give dark red solutions. Ruthenium trichloride and sodium hexachloroiridate(IV) will react on a water bath to give orange-red and amber solutions respectively. Other halogeno-complexes such as chloroplatinic acid, platinous chloride, sodium hexachlororhodate and iridium trichloride behave similarly as shown by the electronic spectra of the solutions (Table III) and the identity of the isolated salts (Table IV). Addition of stannous chloride to a solution of sodium chloropalladate(II) gives a series of colour changes suggesting that there is probably a complex series of equilibria in solution. The system has not been studied in detail as the solutions are also air unstable and palladium metal is eventually deposited.

It is possible to show by simple ion-exchange experiments that the coloured complexes in aqueous acid solutions are anionic. The addition of solutions of salts of large cations - aqueous tetramethylammonium chloride is convenient - gives precipitates under conditions where neither tin(II) or tin(IV) complex chloro-anions appear to be precipitated. The salts can be recrystallized from mixtures of ethanol and 3M-hydrochloric acid solutions. They are moderately soluble in acetone, nitromethane and dimethylformamide in which they give conducting

TABLE III

Electronic Spectra of anionic stannous chloride complexes of Ru, Rh, Ir and Pt

	λ max(mμ) (ε in parentheses)		
Metal	NMe_4^+ salts$^{(a)}$	Anionic species$^{(b)}$	Ref.
Ruthenium	$439(1\cdot1 \times 10^3)$	$438(1\cdot7 \times 10^3)$,$305(2\cdot7 \times 10^4)$	(c)
	$306(1\cdot5 \times 10^4)$	$441(2\cdot5 \times 10^3)$,$303(4\cdot0 \times 10^4)$	27
		$206\cdot5(6.3 \times 10^4)$	27
Rhodium	$425(1\cdot1 \times 10^3)$	$462(4\cdot0 \times 10^3)$	(c)
	$310(6\cdot8 \times 10^4)$	$419(3\cdot3 \times 10^3)$,$310(2\cdot8 \times 10^4)$	
		470	16
		475 330	15
		$475(3\cdot9 \times 10^3)$	19
		$473(\sim 5\cdot0 \times 10^3)$,330-340 $(\sim 2\cdot5 \times 10^3)$	26a
		418	(c)
Iridium	$326(1\cdot0 \times 10^4)$	$321(3\cdot6 \times 10^4)$	(c)
	$278(4\cdot0 \times 10^3)$	355	18
Platinum	$401(1\cdot6 \times 10^3)$	$403(8\cdot0 \times 10^3)$,$310(\sim 3\cdot5 \times 10^4)$	
(red isomer)	$310(1\cdot2 \times 10^4)$	403 ,310	10
	$254(1\cdot6 \times 10^4)$	$403(7\cdot8 \times 10^3)$,$310(4\cdot0 \times 10^4)$	13
Platinum	310 sh. (d)	310 sh.(d)	(c)
(yellow isomer)	$278(1\cdot2 \times 10^4)$	278 ,254	(c)
	$254(1\cdot3 \times 10^4)$		

(a) This work. Measured in 1:1 HCl solutions (b) HCl solutions at least 0·5M in $SnCl_2$ (c) 3M-HCl solutions (d) May be due to the presence of red isomer in solution.

TABLE IV

Salts of anionic stannous chloride complexes of platinum metals

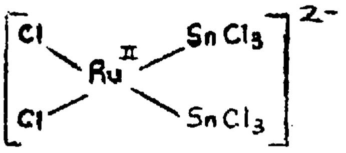
			Λ_m (10^{-3}M)*		Electrolyte
Salt	Colour	M.p.	DMF	$MeNO_2$	Type
$(NMe_4)_2[RuCl_2(SnCl_3)_2]$	Orange	d > 200°	125	113	1:2
$(PHPh_3)_2[RuCl_2(SnCl_3)_2]$	Yellow	177-180	80^+	87	
$(NMe_4)_4[Rh_2Cl_2(SnCl_3)_4]$	Orange	d > 250	244	> 200	1:4
$(PHPh_3)_4[Rh_2Cl_2(SnCl_3)_4]$	Yellow-orange	137-138	119^+	Insol	
$(NMe_4)_4[Ir_2Cl_6(SnCl_3)_4]$	Yellow-orange	d > 300	240	244	1:4
$(PHPh_3)_4[Ir_2Cl_6(SnCl_3)_4]$	Yellow	112-117	165^+	162	
$(NMe_4)_2[PtCl_2(SnCl_3)_2]$	Red	d > 250	133	128	1:2
	Yellow	d 195-200	140	-	1:2
$(PMePh_3)_2[PtCl_2(SnCl_3)_2]$	Yellow	50 (isomerizes)	-	-	-

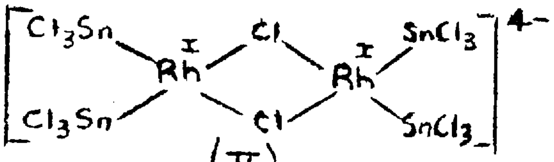
* Conductivity ranges for electrolyte types in both dimethylformamide (DMF) and nitromethane ($MeNO_2$) are, in ohms^{-1} cm.^{2} moles^{-1}: 1:1, 55-80; 1:2, 110-150; 1:3 (extrapolated), 175-220; 1:4, > 230.

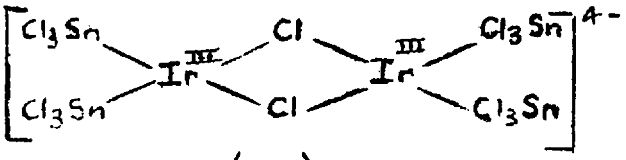
\+ The low values are probably due to incomplete dissociation of the phosphonium salts.

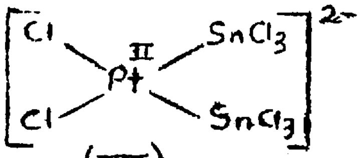
solutions; but are insoluble in non-polar organic solvents and also in ethanol, diethyl ether and tetrahydrofuran. The solids are all air-stable as are the aqueous acid solutions of the anions with the exception of the platinum solutions, which are moderately air-sensitive and are best handled under nitrogen.

The reaction of platinum-metal salts with stannous chloride also proceeds in organic solvents such as ethanol or acetone. It is probable that neutral species exist in such solutions due to the association of solvated $SnCl_2$ rather than the $SnCl_3^-$ ion. Attempts to isolate solids directly from the organic solutions have failed and only red gums remain on removal of the solvent. The addition of tetramethylammonium chloride to the ethanolic solutions of rhodium and platinum gives salts identical with those obtained from 3M hydrochloric acid solutions.


(I)


(II)


(III)


(IV)

Sodium hexachloroiridate(IV) and stannous chloride likewise form a neutral complex in hot ethanolic solutions which interacts with the solvent to form a carbonyl complex which will be considered later. On heating solutions of hydrated ruthenium(III) chloride with stannous chloride in ethanol, dark blue solutions are obtained, which appear to contain ruthenium(II), but not a tin-containing complex.

The salts and some of their properties are summarised in Table 2 and the complex ions formulated as (I)-(IV). If the trichlorostannate (II) ion ($SnCl_3^-$) is considered to be acting as a donor ligand using its lone pair of electrons, the usual common formal oxidation states and stereochemistries of the platinum metals can be preserved. Analyses, conductivities and diamagnetism confirm this formulation and the consideration of stannous tin stereochemistry shows the feasibility of electron donation by $SnCl_3^-$. Complexes in organic solutions would then be regarded as neutral solvated species, e.g.$Rh_2Cl_2(SnCl_2.EtOH)_4$. The ruthenium complex may be polymeric in the solid state, achieving octahedral coordination through chloride bridges as is the case for $Ru(CO)_2I_2$ and $C_7H_8RuCl_2$; but it is undoubtedly a discrete ion in solution, where the remaining co-ordination sites could be occupied by solvent molecules.

It is possible to regard the complex ions as having tin(IV) bound to the platinum-metal ion, as appears to be the case in some other transition-metal tin complexes such as $(\pi\text{-}C_5H_5)W(CO)_3SnCl_3$ (29). However the behaviour of these complexes is more consistent with the presence of stannous tin, and no reaction with stannic chloride has been observed under similar conditions. A spectrophotometric study of the rhodium(III) chloride-stannous chloride reaction in either 3M hydrochloric acid or ethanol, using the Job method of continuous variations, shows that three molecules of stannous chloride are required per molecule of rhodium indicating the utilization of one molecule of

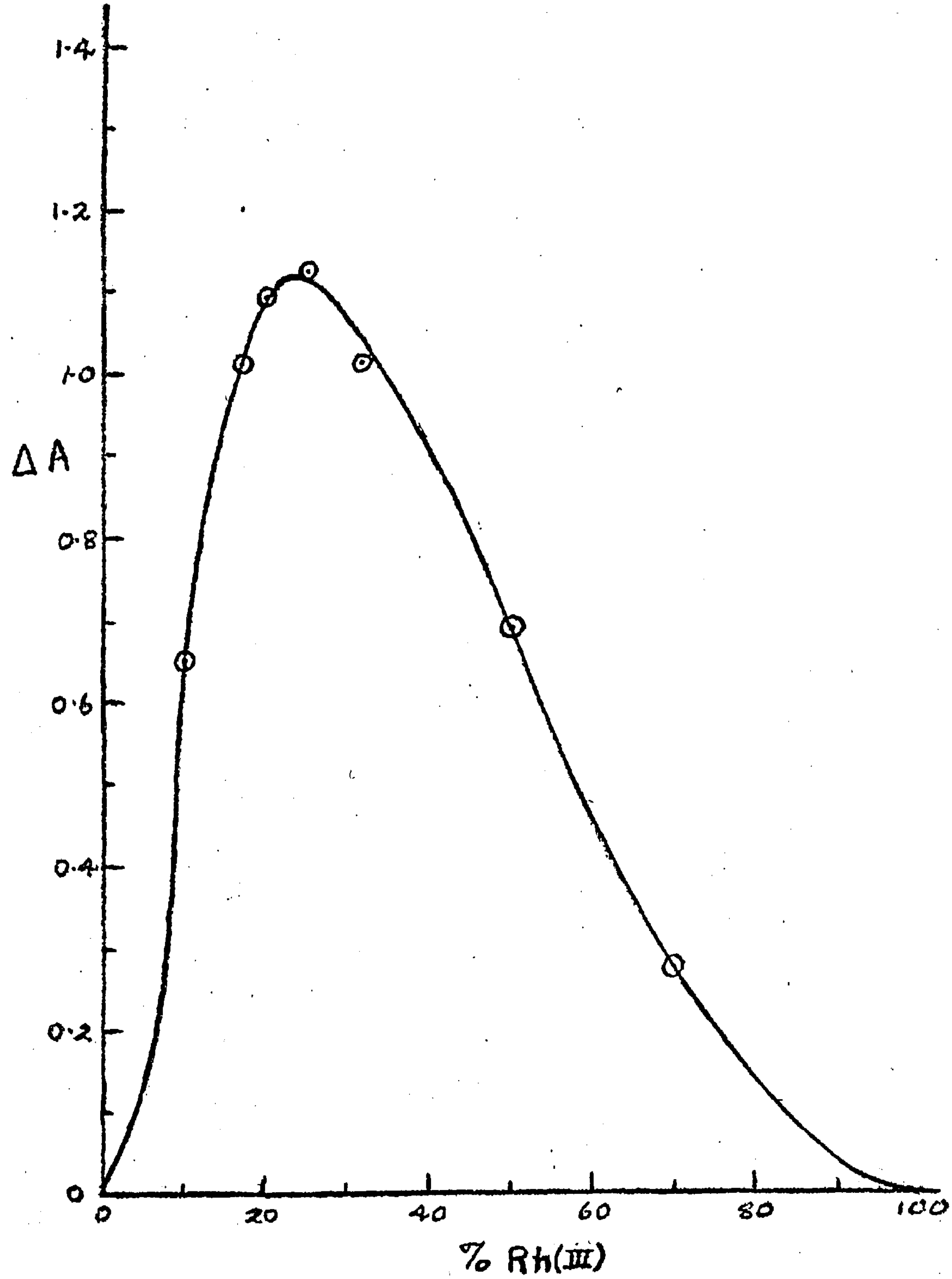


Fig. 3 Typical Job plot of $RhCl_3$-$SnCl_2$ system. Measured at 400mμ.

tin(IV) for the reduction of rhodium(III) to rhodium(I) and two molecules of tin(II) for complexation.

Further it is possible to displace tin from the complexes as stannous chloride, which can be identified by standard chemical tests. In this respect the use of the colour reaction with cacotheline (44) has been shown to be both sensitive and reliable and has the advantage of being equally effective in organic solvents. Thus triphenylphosphine or arsine reacts with bis(tetramethylammonium)dichlorobis(trichlorostannato)platinate(II) in ethanol suspension at room temperature to give bis(triphenylphosphine)dichloroplatinum(II). But generally the tetramethylammonium salts can be substituted only with difficulty; with amines the ruthenium and rhodium salts gave low yields of $Ru(pyridine)_4Cl_2$ and $Rh(p\text{-}toluidine)_3Cl_3$ with the liberation of free stannous chloride. Simple bridge-cleaving reactions do not appear to take place, with the exception of CO (see later).

The tin complexes in ethanolic solution undergo displacement reactions much more readily, however. Thus at room temperature and pressures, carbon monoxide displaces stannous chloride from its rhodium complex to give good yields of $[Rh(CO)_2Cl]_2$. Cycloöcta-1, 5-diene, 4-vinycyclohexene and dicyclopentadiene give complexes $(diene)_2Rh_2Cl_2$, but norbornadiene gives $(C_7H_8)_2RhSnCl_3$ (see below). In the same way (cycloöcta-1,5-diene)dichloroplatinum(II) could be prepared and the formation of Zeise's salt has also been achieved.(45)

Conversely it is found that stannous chloride can displace other ligands besides the chloride ion. Thus the interaction of stannous chloride with potassium ethylenetrichloroplatinate(II) (Zeise's salt) and (cycloöcta-1,5-diene)dichloroplatinum(II) gives the ion $[PtCl_2(SnCl_3)_2]^{2-}$, demonstrating the reversibility of the replacement reactions in some cases. Mesityl oxide, ammonia and pyridine are also displaced, apparently irreversibly, from their neutral, platinum(II) complexes. Similarly the rhodium and ruthenium complex ions can be obtained from $(norbornadiene)_2Rh_2Cl_2$ and $(norbornadiene)_2RuCl_2$ respectively.

2. Platinum-tin complexes

cis-*trans*- Isomerism is possible in the planar complexes of ruthenium and platinum. No isomerism has been observed with the former; but in the case of platinum it has been possible to isolate two isomers of $[Pt(SnCl_3)_2Cl_2]^{2-}$ as the tetramethylammonium salts one of which is red and the other yellow. The *cis*- and *trans*- ions both exist in solutions at Sn:Pt ratios 2:1, but at higher concentrations of tin, precipitation with tetramethylammonium chloride gives red salts which appear to contain higher ratios up to 5:1. The ions and salts derived from solutions where the ratio is low are discussed first.

The addition of anhydrous stannous chloride to a solution of sodium chloroplatinite in ethanol, so that the Sn:Pt ratio is 2:1, gives an orange-red solution which on standing under nitrogen at room temperature (*ca* 15 min.) slowly changes colour, becoming orange-yellow. Addition of a slight excess of tetramethylammonium chloride to this solution quantitatively precipitates a yellow, crystalline salt. The salt is re-precipitated as yellow needles from acetone solution by the addition of ethanol; it analyses as $(NMe_4)_2\left[PtCl_2(SnCl_3)_2\right]$. If tetramethylammonium chloride is added to the platinum-tin solution immediately after mixing a red, crystalline salt is precipitated in a quantitative yield. Dissolution in acetone, followed by re-precipitation with ethanol gives red needles whose analysis also corresponds to $(NMe_4)_2\left[PtCl_2(SnCl_3)_2\right]$. When tetramethylammonium chloride, in a calculated quantity sufficient to precipitate 60% of the platinum, is added to the red solution immediately after mixing, then the red, crystalline salt is obtained quantitatively. The solution after filtration is still yellow and addition of excess of the precipitant gives yellow crystals, in ca 40% yield, identical with those obtained from aged solutions. The same red-yellow isomerism occurs in 3M hydrochloric acid solutions and both red and yellow tetramethylammonium salts identical to those obtained from ethanol solutions, can be precipitated in the same way, although recovery of the latter is more difficult because of its solubility (see below).

These red and yellow ionic species are presumably cis- trans- isomers. The yellow salt is the more soluble in 3-6M hydrochloric acid, in which the red salt is soluble only with difficulty. X-ray powder patterns of the two salts are quite distinct, and no lines due to the yellow isomer were observed in the pattern of the red crystals obtained on immediate precipitation as above. The red isomeric anion appears to be the predominant form at room temperature in fresh solutions with Pt:Sn=1:2, in both 3M-hydrochloric acid and ethanol, and, according to the electronic spectra of the solutions, it is the predominant form in all solutions with higher tin ratios. Above Sn:Pt of 8:1 it appears to be the only form at room temperature, on the basis of absorption spectra. However, a yellow solid can be precipitated from ethanol solutions with Sn:Pt ratios up to 5:1 if the solutions are cooled to ca -78°C. However, even when the yellow precipitate is collected and thoroughly washed at this low temperature it isomerises rapidly on warming, probably through the presence of occluded stannous chloride or $(NMe_4)(SnCl_3)$, even though the X-ray powder pattern of the isomerized material showed no lines due to these substances. The initial precipitate could well be a mixture of yellow $(NMe_4)_2[Pt(SnCl_3)_2Cl_2]$ and $(NMe_4)(SnCl_3)$, since the solubilities of tetramethylammonium trichlorostannate(II) in hydrochloric acid or ethanol are very similar to the solubilities of the tetramethylammonium platinum complex salts at all temperatures used here.

The above observations show that the equilibrium between the two isomers is dependent upon temperature and the concentration of stannous chloride. The electronic spectra of the two forms (Table III) are sufficiently different to enable the equilibrium shifts to be observed spectrophotometrically. The addition of stannous chloride to a solution of the yellow salt in 6M-hydrochloric acid promotes the growth of peaks at 400 - 310 mμ at the expense of the one at 278 mμ. In 3M-hydrochloric acid or ethanol solutions of Pt:Sn ratio 1:2, the peaks due to the red isomer at 400 & 310 mμ predominate initially, but

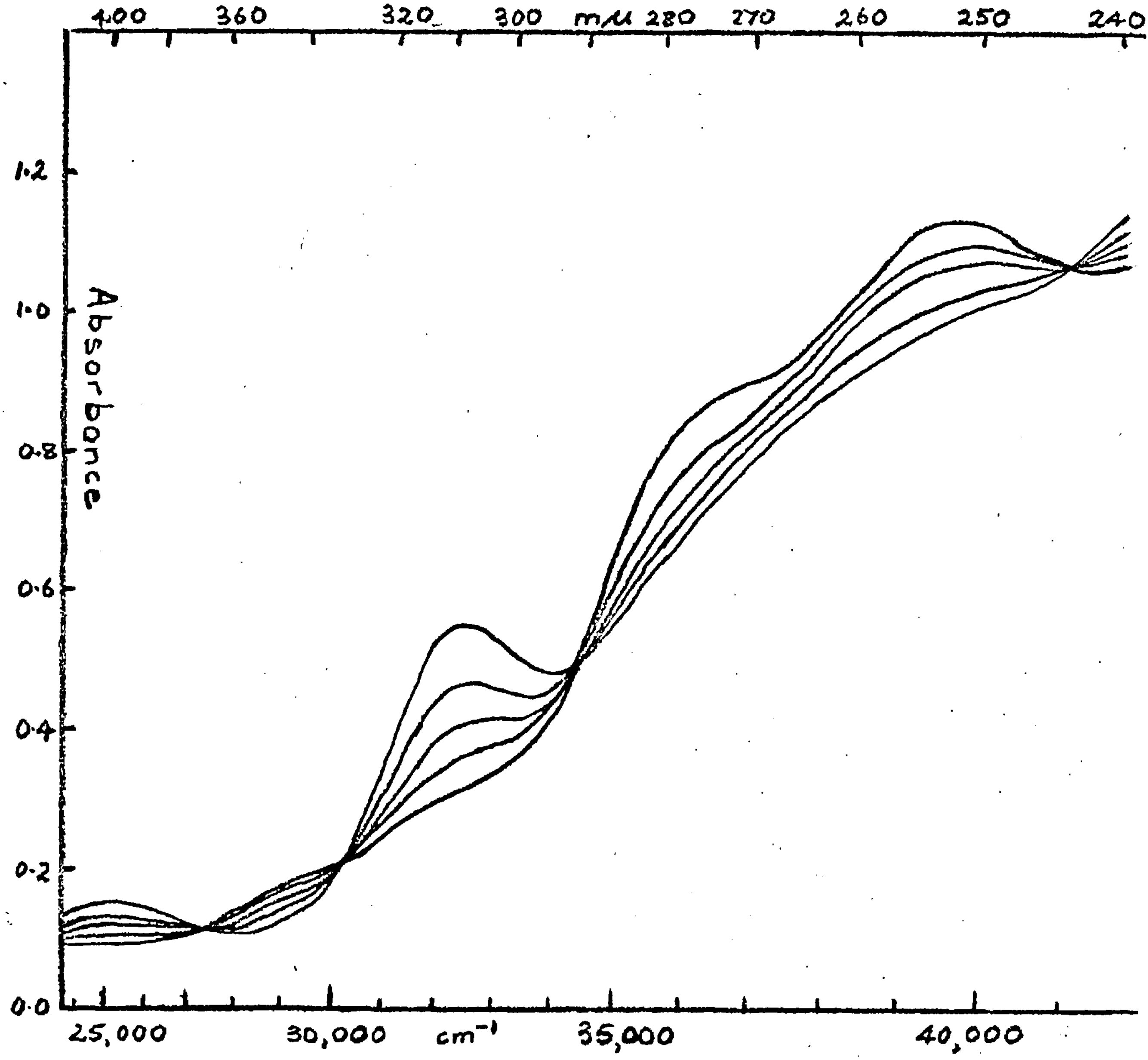


FIG. 4 Spectrum of ethanol solutions with Pt:Sn = 1:2 Variation with time.

decrease in intensity with time while a new peak at 280mμ appears simultaneously. A series of isosbestic points accompanying this change indicates that only the two isomeric anions contribute to the spectra, thus confirming the precipitation experiments. Addition of stannous chloride again restores the peaks at 400 and 310mμ , as was observed for solutions of the yellow salt.

It has not been possible to determine unequivocally the configurations of the two isomers: however it is likely that the yellow form is the *cis*- isomer. Some d_π -d_π bonding is to be expected between platinum and tin which would cause the *cis*- isomer to be more stable than the *trans*-, because in the latter configurations there will be competition between two $SnCl_3^-$ groups for the same *d*-orbitals of platinum and hence weaker π-bonding. The experimental observations show that, while the red form is favoured kinetically, the yellow is more stable thermodynamically. Furthermore, the yellow form has bands in the electronic spectrum at a lower wavelength which is indicative of greater stability. The *cis*- isomer might be expected to be more soluble in polar solvents, and the yellow form is indeed more soluble in hydrochloric acid than the red, as noted above.

Spectrophotometric evidence shows that only the red isomer is present at Sn:Pt ratios 8:1 and that it obeys Beer's law. However the true intensities of the spectral bands of the yellow form are uncertain because (a) these are allowed bands which will be temperature dependent, (b) the exact conditions under which only the yellow isomer is present in solution are not known, and (c) complex formation

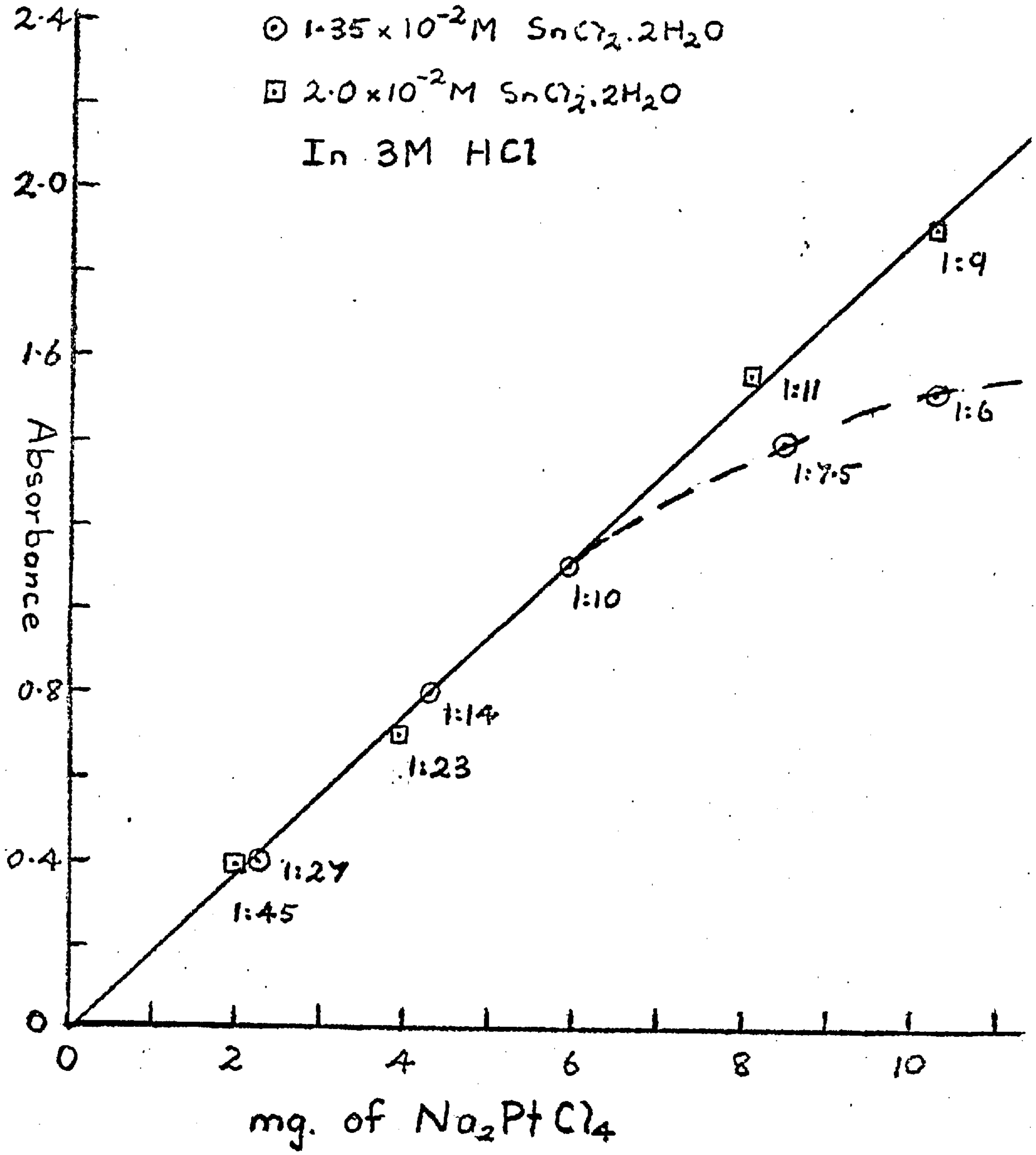


FIG. 5 Variation in intensity of the 400mμ peak with concentration of Pt, at constant Sn concn. (Pt : Sn ratios are given)

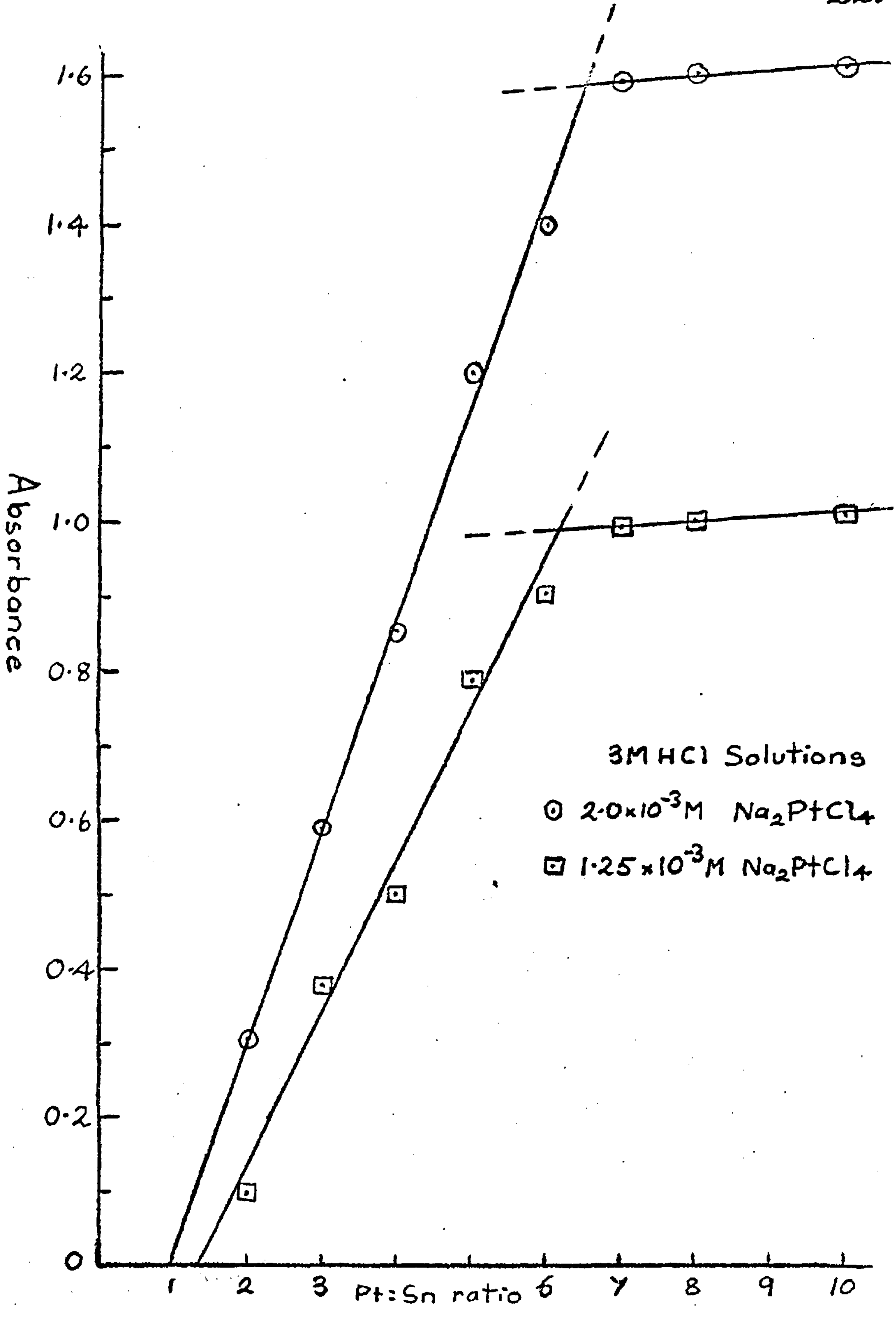


FIG. 6. Variation in intensity of 400mμ peak with concentration of Sn, at constant Pt concn.

may be incomplete at these necessary conditions. It is probable that several interdependent equilibria exist simultaneously in solution, of the type:

$$SnCl_2+Cl^- \rightleftharpoons SnCl_3^-$$

$$PtCl_4^{2-}+SnCl_3^- \rightleftharpoons PtCl_3(SnCl_3)^{2-}+Cl^-$$

$$PtCl_3(SnCl_3)^{2-}+SnCl_3^- \rightleftharpoons \underline{trans}\text{-}\ PtCl_2(SnCl_3)_2^{2-}+Cl^-$$

$$\underline{trans}\text{-}\ PtCl_2(SnCl_3)^{2-} \rightleftharpoons \underline{cis}\text{-}\ PtCl_2(SnCl_3)_2^{2-}$$

If substitution of $PtCl_4^{2-}$ by $SnCl_3^-$ takes place in two steps, we would expect a trans- effect from $SnCl_3^-$ stronger than Cl^- favouring the initial formation of the trans- isomer which is what is observed. The stabilization of the trans- isomer by excess $SnCl_3^-$ can be interpretated as the supression of a dissociation mechanism through which isomerization probably occurs.

With the concentration of tin above Pt:Sn of 1:2, the absorption of $SnCl_3^-$ or solvated stannous chloride obscures the region below 290mμ, so that the presence or absence of the yellow species cannot be detected. Using the band at 400mμ it appears that Beer's law is not obeyed until the Sn:Pt ratio is above 8:1.

The precipitates obtained by the addition of tetramethylammonium chloride to aged, ethanolic solutions of Pt:Sn ratios between 1:2 and 1:5 were studied by X-ray diffraction. The proportion of yellow isomer present decreases from pure yellow at Pt:Sn=1:2 to only small amounts at Pt:Sn=1:5. At an intermediate value (Pt:Sn=1:3), the quantities of red and yellow isomers were approximately equal. Although quantitative precipitation was achieved no $(NMe_4)(SnCl_3)$ was detected in the X-ray powder patterns.

The pure yellow salt can be re-precipitated from acetone solution with ethanol without isomerization occuring in the absence of any free tin(II) species. But if some $(NMe_4)(SnCl_3)$ or $SnCl_2$ is added, then isomerization occurs to an extent depending on the amount of extra tin. When the latter is present in a molar ratio of 2, the red isomer is predominant in the re-precipitated solid, and the yellow salt is found to be entirely absent when 3 or more moles are present during reprecipitation, i.e., full isomerization occurs under these conditions.

When tetramethylammonium chloride is added to fresh solutions, in ethanol or 3M-hydrochloric acid, with ratios of Pt:Sn from 1:2 up to 1:10, red precipitates are always obtained. The solids, after dissolution in acetone and re-precipitation by ethanol, have variable analyses. Samples have been obtained whose analyses correspond quite well to $(NMe_4)_3[Pt(SnCl_3)_5]$. However the X-ray powder patterns of materials obtained from solutions with different Pt:Sn ratios are identical despite their different analyses; the d spacings are given in Table V. No lines due to $(NMe_4)(SnCl_3)$ or other free tin species appear in powder patterns of the red crystals obtained from solutions with high Sn:Pt ratios. This suggests that the tin is co-ordinated to platinum to give a quinqueco-coordinated ion, $[Pt(SnCl_3)_5]^{3-}$ (45); but it is surprising that the X-ray powder

TABLE V

d spacings of platinum - tin complexes from different sources

Pt:Sn ratio of reactants	Yellow isomer 1:2	1:2	Red isomer 1:2	1:2	Red1:5* complex 1:5		
Solvent	EtOH	HCl	EtOH	HCl	-		
% Sn	26·6	-	27·9	-	-	$(NMe_4)_2PtCl_4$	Anhyd. $SnCl_2$
d-spacings	9·4s	9·4s	9·55vs	9·55vs	9·63vs	7·3s	15·5ms
	9·1vs	9·1vs	8·35s	8·35s	8·34ms	6·95vs	7·1ms
	6·15ms	6·15ms			6·93w	6·2m	4·87ms
	5·17m	5·19m	5·85m	5·90m	5·89m	4·45m	4·28m
	5·05vs	5·05vs	5·05mw	5·02vw	5·02w	4·38ms	3·93ms
	4·15w	4·17w	4·18ms	4·18ms	4·16m	4·18ms	3·73m
			3·82mw	-	-		
	3·09mw	3·08w	3·40vw	3·40vw	3·40w	3·70m	3·58m
	2·90m	2·90m	3·20ms	3·20ms	3·20m	3·10m	3·53ms
	2·26w	2·26w	2·77mw	2·77mw	2·77mw	2·82m	2·77m
	2·07w	2·07vw	2·63w	2·62mw	2·63mw	2·77m	2·74m
	1·935w	1·935w	2·33mw	2·33mw	2·33mw	2·37ms	2·51m
	1·875w	1·875w	1·92w	-	-	2·08m	

* G.W. Parshall, personal communication

TABLE V (con.)

Red precipitates

Pt:Sn ratio of reactants	1:3	1:5	1:5	1:5	1:10		
Solvent	EtOH	EtOH	EtOH	HCl	HCl		
% Sn	-	31·4	36·3	32·3	26·6	$(NMe_4)(SnCl_3)$	$(NMe_4)_2SnCl_6$
d-spacings	9·50vs	9·50vs	9·50vs	9·50vs	9·50vs	6·06s	7·4s
	8·30s	8·25s	8·25s	8·25s	8·25s	6·04vs	7·3m
	5·90m	5·85m	5·85m	5·85m	5·85m	4·58vs	6·45ms
	5·01vw	5·00vw	5·02vw	-	5·02mw	4·48ms	6·3vw
	4·18ms	4·18ms	4·18ms	4·17ms	4·16ms	3·29ms	4·29s
	3·83vw	3·80vw	3·82vw	-	3·81vw	3·19s	4·27w
	3·40vw	3·40vw	3·40vw	3·40vw	3·40w	2·92ms	3·9m
	3·20ms	3·20ms	3·20ms	3·20ms	3·20ms	2·87s	3·85w
	2·77mw	2·77mw	2·77mw	2·77mw	2·77mw	2·29m	3·23ms
	2·63w	2·63w	2·63w	2·62w	2·63w	2·13m	3·18vw
	2·33mw	2·32mw	2·33m	2·33mw	2·33m	2·07m	2·90mw
	1·92vw	1·915vw	1·92w	1·91w	1·92w	2·02m	2·50m

patterns of the "high tin" solids are identical with that of the red $(NMe_4)_2[PtCl_2(SnCl_3)_2]$ salt, and that there is no change in the line patterns in spite of variable analyses.

Although the needle-shaped crystals obtained from solutions with high tin concentrations, which give analytical data for $(NMe_4)_3[Pt(SnCl_3)_5]$, appear to be quite homogeneous under the polarizing microscope, dissolution in acetone and crystallization on a slide gives a mixture of approximately red and white crystals. The solubilities of $(NMe_4)(SnCl_3)$ in ethanol and 3M-hydrochloric acid are similar to those of red $(NMe_4)_2[PtCl_2(SnCl_3)_2]$ and it may be a mixture of these two compounds. It has not proved possible to separate the components by normal crystallization, neither have attempts to separate the compounds by use of anion-exchange resins been successful.

Furthermore the red salt (apparently 5:1 complex) dissolves in acetone to give a red solution, which, treated with ethanol at room temperature, re-precipitates the red needles unchanged. When this re-precipitation procedure is carried out at $-78^{\circ}C$ a yellow solid is obtained, which, even when filtered, washed and dried at the same temperature becomes red again when allowed to warm to room temperature.

It is conceivable that further co-ordination of tin to form a 5:1 species in solution might occur. In ethanol and 3M-hydrochloric acid Job plots of platinum-tin solutions, using the 400mμ peak, rise to a maximum at Pt:Sn ratio of 1:2, but show little change with additional tin concentration up to <u>ca</u> 1:6 ratio, confirming that more than one

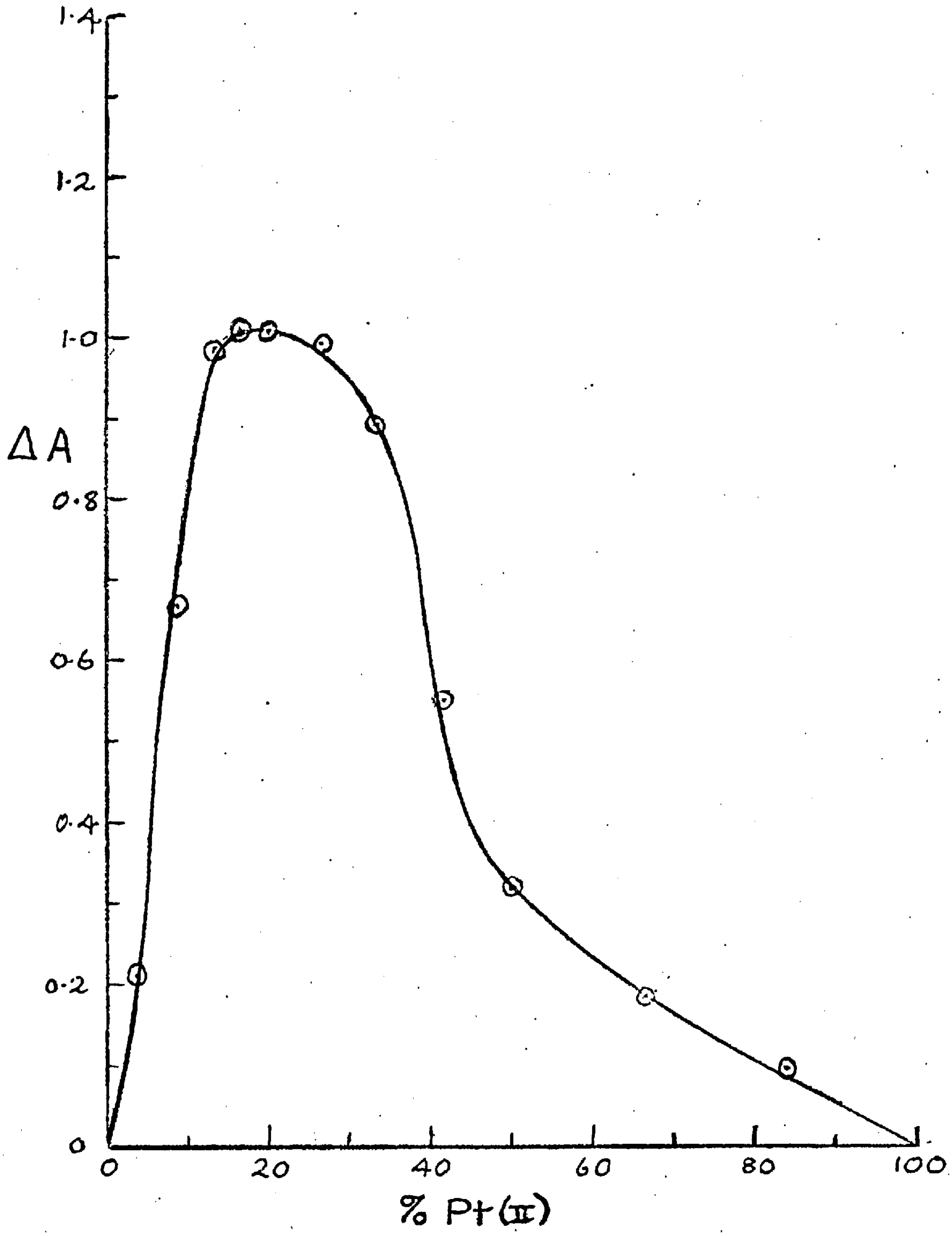


Fig. 7 Typical Job plot of the $Na_2PtCl_4-SnCl_2$ system. Measured at 400mμ.

species is present in solution. This is indicated also by the failure of this peak to obey Beer's law at these lower ratios and it may be explained by cis- trans- isomerization of the 1:2 species. The increase in intensity of the 400mμ peak as the Sn:Pt ratio increases from 2:1 to 5:1 has been shown to be due to increasing amounts of the red isomer. The very small variation in intensity with increasing tin concentration above these ratios would not be expected if further coordination of stannous chloride were to occur.

Nevertheless the existence of salts of the complex anion, $[Pt(SnCl_3)_5]^{3-}$ has been reported (45). It is possible that the presence of a large cation might stabilize a 5:1 species in the solid state, but it is doubtful whether it has a real existence in solution. A preliminary X-ray crystal structural determination by Cramer, et al. has shown $(NMe_4)_3[Pt(SnCl_3)_5]$ to have a trigonal tripyramidyl arrangement of $SnCl_3^-$ groups around the central platinum atom, and their findings have been reinforced by the preparation of other 5-coordinated complexes containing the $SnCl_3^-$ ligand (46). Solids of intermediate analyses could thus be mixtures of salts of the $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$ anions; but it has not been possible to resolve the discrepancies between the two sets of data.

When the triphenylmethylphosphonium cation is used as the precipitant for the 2:1 complexes there is a more facile interconversion between the two isomers than with the tetramethyl ammonium salts, and consequently it is more difficult to obtain pure isomers. It was possible to obtain the yellow isomer as an amorphous solid by precipitating it at -78°C from solutions with Pt:Sn ratios of 1:2·5, and washing it thoroughly with ethanol at this temperature. The salt changes rapidly into a mixture of the isomers when heated to 50°C. When it is precipitated at room temperature from aged ethanolic solutions, with a Pt:Sn ratio of 1:2, it isomerizes to an orange oil too rapidly to be isolated. Precipitation with a deficiency of triphenylmethylphosphonium chloride immediately on mixing sodium chloroplatinite and stannous chloride gives orange, crystalline solids. Similar solids were precipitated from solutions with Pt:Sn ratios of 1:5 and 1:10; their compositions were all close to $(Ph_3MeP)_2[PtCl_2(SnCl_3)_2]$. On cooling (to -78°C) or heating (80°C) ethanolic suspensions of these solids after precipitation, there is a reversible, but incomplete, shift to the yellow and red forms respectively. These orange solids are thus probably mixtures; the colour is very different from that of the red tetramethylammonium salt.

3. Olefin Complexes containing tin

Although the interaction of ethanolic solutions of rhodium(III) chloride and tin(II) chloride with cyclo-octa-1, 5-diene and other di-olefins gave the well known halogen-bridged, binuclear, olefin complexes, norbornadiene gives a compound $(C_7H_8)_2RhSnCl_3$. Corresponding reactions with the neutral iridium-tin complex in ethanol solution gives the olefin complexes $(\text{di-olefin})_2IrSnCl_3$ in all cases.

The crystalline complexes (Table VI) are precipitated from solutions slowly at room temperature and more rapidly on warming. Although the initially amber iridium-tin solutions become yellow no crystalline products have been isolated using cyclohexa-1,3-diene, cyclohexa-1,4-diene, 1,5-dimethylhexa-2,5-diene, or butadiene.

TABLE VI

Olefin complexes of rhodium and iridium containing tin

			$\Delta m(10^{-3}M)$	
Compound*	Colour	M.p.	$MeNO_2$	DMF
$(NBD)_2RhSnCl_3$	Yellow	decomp.170-177	3·3	75
$(Ph_3P)_2(NBD)RhSnCl_3$	Orange	134-135	7·3	9·1
$(Ph_3As)_2(NBD)RhSnCl_3$	Orange	decomp.177-179	5·1	7·7
$(Ph_3Sb)_2(NBD)RhSnCl_3$	Orange	decomp. > 200	5·0	-
$(NBD)_2IrSnCl_3$	Pale yellow	decomp.230-240	Insol.	65
$(COD)_2IrSnCl_3$	Yellow	decomp.178-180	9·7	68
$(Ph_3P)_2(COD)IrSnCl_3$	Yellow	decomp.127-130	21	30
$(Ph_3As)_2(COD)IrSnCl_3$	Yellow	171-174	11	16

* NBD = norbornadiene; COD = cyclo-octa-1,5-diene.

It is noteworthy that for the iridium complexes, isomerization of the olefin appears to occur on complexing in some cases. Thus cycloheptatriene gives a complex identical with the one from norbornadiene, whilst cyclo-octa-1,3-diene and 4-vinyl-cyclohexene appear to complex as cyclo-octa-1,5-diene. The identity of the complexes is shown by the similarity in infrared spectra and the complex obtained from cycloheptatriene does not show a C=C stretch for an unco-ordinated olefin group which would be expected if it were acting as a diene. The formation of the complexes where isomerization occurs is considerably slower than with norbornadiene and cyclo-octa-1,5-diene. Unfortunately the compounds and their phosphine-substituted derivatives are too insoluble to allow unequivocal characterization by n.m.r. studies; however this type of isomerization during complexing has been observed by Rinehart and Lasky in rhodium and iridium complexes (47).

The olefin complexes are only sparingly soluble in polar organic solvents and are insoluble in benzene and petroleum. Several attempts to increase the solubility of the complexes by direct alkylation of the $SnCl_3$ groups, using a variety of reagents: alkyl-lithiums, Grignard Reagents, diethyl mercury and tetraethyl lead, were unsuccessful. However more soluble complexes of a similar type can be obtained by the interaction of the complexes with triphenyl-phosphine and -arsine which displace one olefin molecule to give complexes of the stoicheiometry $(diene)(Ph_3P)_2MSnCl_3$. The norbornadiene-iridium complex did not react with triphenyl-phosphine in accord with its greater thermal stability. The molecular weights of these substituted complexes show that they are monomeric and this fact, coupled with the non-conductance of the complexes in nitromethane solutions (and also of $(diene)_2MSnCl_3$) suggests that in all cases these are neutral five-coordinate compounds.

However the complex $(norbornadiene)_2RhSnCl_3$ is slightly soluble in hot water and the solutions give precipitates with large anions, suggesting dissociation of the type:

$$(C_7H_8)_2RhSnCl_3 \rightleftharpoons (C_7H_8)_2Rh^+ + SnCl_3^-$$

A white tetraphenylborate salt has been characterized and tin(II) detected in the aqueous solution. Stannous chloride can be extracted from the initial tetraphenylborate precipitate by treatment with hot, dilute hydrochloric acid. Ion exchange experiments indicate that there is not complete ionization as attempts to remove $SnCl_3^-$ to give $(C_7H_8)_2RhCl$, by treatment with an anion-exchange resin, were not successful. If the equilibrium lay well to the left no appreciable exchange would take place; but the tetraphenylborate would still be precipitated. Although similar ionization does not occur with the more stable (norbornadiene)$_2$IrSnCl$_3$, the cyclo-octa-1,5-diene complex ion, $(C_8H_{12})_2Ir^+$, can be obtained as its tetraphenylborate from aqueous dimethylformamide solutions. However the salt is not as well characterized as in the case of the rhodium analogue.

Conductivity measurements on dimethylformamide solutions of (diene)$_2$MSnCl$_3$ suggest complete ionization to a 1:1 electrolyte takes place. It is possible that the formation of (diene)$_2$M$^+$ is now complete, but the high co-ordinating power of dimethylformamide could lead to ionization of another type:

$$(C_7H_8)_2RhSnCl_3 + DMF \rightleftharpoons \left[(C_7H_8)_2RhSnCl_2DMF\right]^+ \quad Cl^-$$

Both cation- and anion- exchange were carried out on dimethylformamide solutions, but no conclusive results were obtained. Cation exchange apparently does not take place, and anion-exchange is incomplete and not repeatable. Sometimes no exchange was detected, while at the best only a partial exchange of $SnCl_3^-$ took place. It was not possible to precipitate an insoluble salt because of the good solvent properties of dimethylformamide. It is possible that both types of ionization occur as lack of exchange may well be due to inefficient action of the exchange resins in non-aqueous solvents.

4. Phosphine and arsine complexes containing tin

The addition of triphenyl-phosphine to ethanolic platinum-tin solutions precipitates the complex $(Ph_3P)_2PtCl(SnCl_3)$ as an orange solid. This dissolves and disproportionates in acetone to give $(Ph_3P)_2PtCl_2$ which can be recovered from the solution. However the latter complex dissolves in acetone containing excess stannous chloride to reform the orange tin complex. It appears therefore that there is an equilibrium:

$$(Ph_3P)_2PtCl(SnCl_3) + \text{acetone} \rightleftharpoons (Ph_3P)_2PtCl_2 + SnCl_2(\text{acetone})$$

Under no conditions tried was the reported complex $(Ph_3P)_2Pt(SnCl_3)_2$ (45) isolated even from solutions saturated in tin(II) chloride. It seems probable that the sample was contaminated with free stannous chloride.

Triphenylarsine gives a similar platinum complex which is more stable towards dissociation in acetone solution, then the triphenylphosphine analogue. It can be converted into $(Ph_3As)_2PtCl_2$ on treatment with dilute hydrochloric acid.

$$(Ph_3As)_2PtCl(SnCl_3) + Cl^- \rightleftharpoons (Ph_3As)_2PtCl_2 + SnCl_3^-$$

and free stannous chloride can be detected in solution. Again treatment of $(Ph_3As)_2PtCl_2$ with stannous chloride in acetone restores the tin complex.

The interaction of rhodium-tin solutions in ethanol with triphenylphosphine gives an intermediate yellow-orange precipitate, which on refluxing changes to brown-red crystals of $(Ph_3P)_3RhSnCl_3$. This compound must be related to the recently reported, square planar, chloro-complex $(Ph_3P)_3RhCl$ (48), from which it can be derived. Like $(Ph_3P)_3RhCl$ the tin complex dissociates in solution and cannot be recovered. It has not been possible to identify the orange solids obtained from its solution. Nor has the initial, intermediate precipitate been identified as it has always been contaminated with crystals of $(Ph_3P)_3RhSnCl_3$. On treatment with solvents the yellow solid usually turns dark orange and dissolves to give an orange solution. It has not proved possible to recover a solid from the solution; only sticky gums are produced by removal of the solvent or by precipitation with ethyl ether or petroleum ether. It is likely that this initial precipitate is $(Ph_3P)_2RhCl(SnCl_2EtOH)$, analagous to the reaction between triphenylphosphine and rhodium carbonyl chloride, which will probably undergo changes in solution; e.g. dissociation and dimerization.

No clean product could be isolated from ethanolic iridium-tin solutions treated in the same manner.

The addition of triphenylphosphine to hydrochloric acid solutions of the complex anions, merely precipitates the triphenylphosphonium salts, which are recognized by the characteristic P-H stretching frequency at ca $2400cm^{-1}$ in their infra-red spectra.

TABLE VII

Stannous chloride complexes of Rh and Pt with phosphine and arsine ligands

Compound	Colour	M.p.	Λm *
$(Ph_3P)_2PtCl(SnCl_3)$	Orange	decomp.> 100	62
$(Ph_3As)_2PtCl(SnCl_3)$	Orange	150-151	54
$(Ph_3P)_3RhSnCl_3$	Red-brown	130-132	9
$(Ph_2MeAs)_3RhCl_2(SnCl_3)$	Orange-brown	173-176	12·5

* In nitromethane at $10^{-3}M$

Solutions of the platinum-tin anion $[PtCl_2(SnCl_3)_2]^{2-}$ are an exception giving $(Ph_3P)_2PtCl(SnCl_3)$ again as an orange precipitate.

A brief re-examination of the rhodium-tin-diphenylmethylarsine system, investigated previously by Dwyer and Nyholm (28), was undertaken as a result of this present work. All of the structures proposed by Dwyer and Nyholm can be reformulated as octohedral complexes of rhodium(III) if stannous chloride is considered to be acting as a donor ligand (Table VIII).

TABLE VIII

A reformulation of Dwyer and Nyholm's rhodium-tin complexes

Original Formulation	Possible Structures
$RhCl_2.SnCl_2.3As$	$RhHCl(SnCl_3)As_3$
$RhCl_3.SnCl_2.3As^1$	$RhCl_2(SnCl_3)As^1_3$
$(RhCl_3.3As)_2SnCl_2$	$[RhCl_4As_2][RhCl(SnCl_3)As_4]$

As = Ph_2MeAs As^1 = $(o\text{-}Me.Ph)Me_2As$.

Refluxing a mixture of rhodium trichloride and diphenylmethylarsine in ethanol with excess stannous chloride precipitates an orange-brown powder which analyses as $(Ph_2MeAs)_3RhCl_2(SnCl_3)$. If aqueous ethanol is used instead, orange solids are precipitated whose analyses correspond to no particular composition, and which are probably mixtures.

Refluxing the same mixture in ethanol containing hydrochloric acid gives orange crystals (m.p. 185-188°C) which analyse as $(Ph_2MeAs)_3RhHCl_2$. The crystals have an Rh-H stretching frequency at $2070 cm^{-1}$ in their infrared spectrum, and the n.m.r. spectrum of a solution shows the presence of a high-field doublet (τ=26·1, J=10·2 c.p.s.). The compound appears to be a different isomer from the hydride described by Nyholm (49). The reduction of $(Ph_2MeAs)_3RhCl_3$ with hypophosphorous acid gave a yellow hydride (m.p.174-176°C) of the same stoicheiometry. Its appearance, melting point and infrared spectrum (ν Rh-H: $2079 cm^{-1}$) suggest it is another isomer, although the n.m.r. spectrum is very similar (δ Rh-H: τ=26·3, J=10·2 c.p.s.). This latter hydride is probably the same isomer as was prepared by Nyholm.

5. Carbonyl and Hydride Complexes Containing Stannous Chloride

Stannous chloride and rhodium carbonyl chloride react together rapidly in ethanol at room temperature. A spectrophotometric study of the system, using the Job method of continuous variations, shows that 4 moles of stannous chloride per mole of carbonyl are required

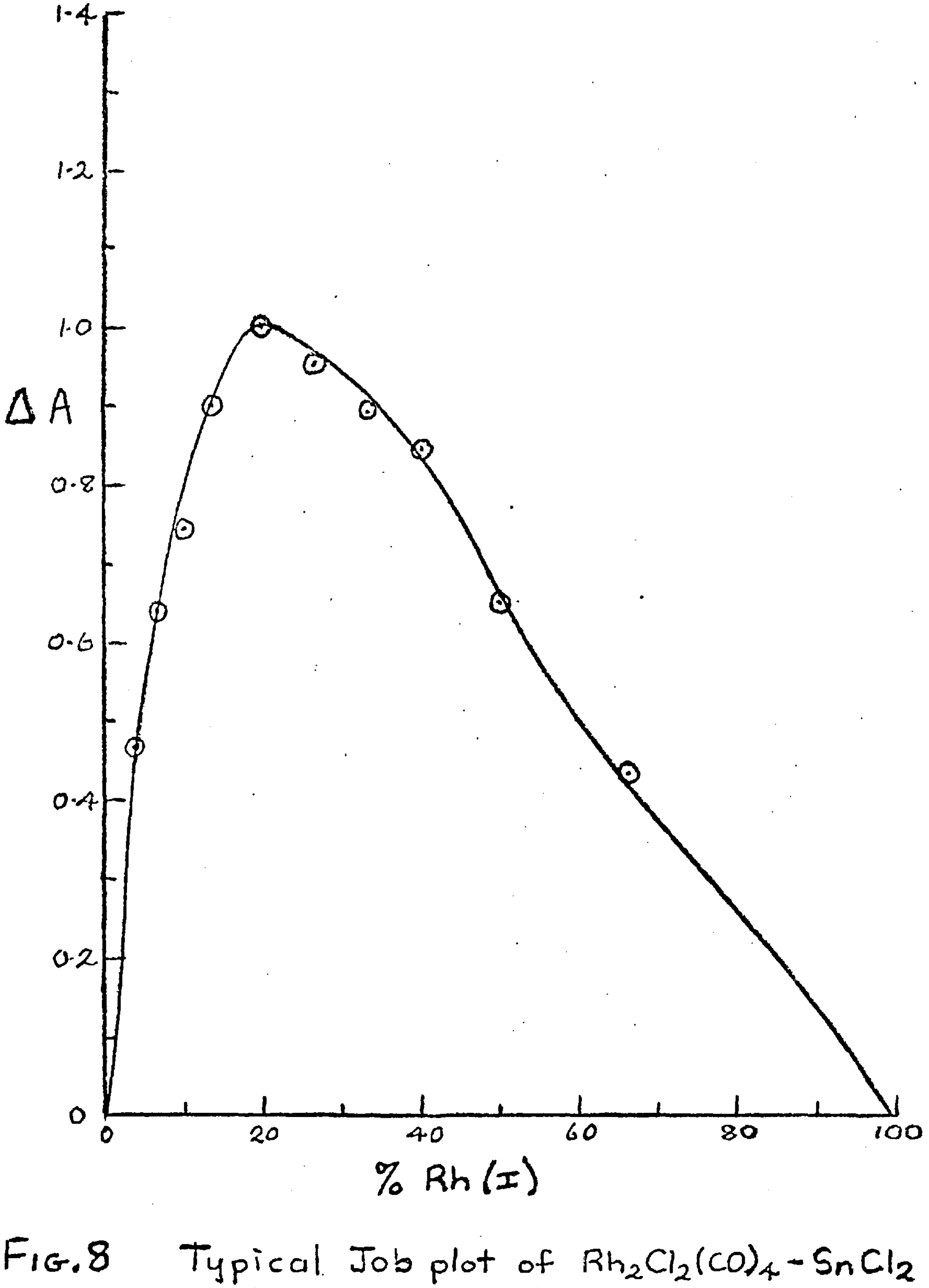


FIG. 8 Typical Job plot of $Rh_2Cl_2(CO)_4 - SnCl_2$ system. Measured at 400 mμ.

for complex formation, suggesting that bridge cleavage and partial carbon monoxide replacement occurs. The addition of tetramethylammonium chloride does precipitate the ion $[Rh(CO)Cl(SnCl_3)_2]^{2-}$ as expected. This same compound is obtained also by the cleavage of the chlorine bridge in $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ with carbon monoxide.

However the reaction of polymeric $Ru(CO)_2Cl_2$ with stannous chloride does not displace carbon monoxide and only bridge cleavage occurs to give the discrete, octohedral anion $[Ru(CO)_2Cl_2(SnCl_3)_2]^{2-}$. Stannous chloride also reacts with the air-sensitive iridium carbonyl, $Ir(CO)_3Cl$, at room temperature giving air-stable solutions. However it was not possible to isolate any definite stannous chloride - carbonyl complex; the addition of tetramethylammonium chloride appears to precipitate mixtures which depend on the amount of stannous chloride added.

Nevertheless it is possible to form an iridium-tin-carbonyl complex by interaction with an alkanolic solvent. When stannous chloride is added to an ethanolic solution of sodium hexachloroiridate(IV), in the cold, a precipitate is formed which is presumably insoluble sodium hexachloroiridate(III). On heating the suspension, the solid immediately dissolves and at this point precipitation with tetramethylammonium chloride gives the complex salt(IV). However if the solution is refluxed for <u>ca</u> one hour before precipitation, then a carbonyl complex $[Ir(CO)Cl_3(SnCl_3)_2]^{2-}$ can be isolated. A purer product is obtained when 2-methoxyethanol is used

TABLE IX

Anionic carbonyl complexes of Ru, Rh and Ir
containing stannous chloride

A Electronic spectra *

Compound	λ max (mμ) (ε in parentheses)
$(NMe_4)_2Rh(CO)Cl(SnCl_3)_2$	419 ($1{\cdot}9 \times 10^3$), 311 ($1{\cdot}4 \times 10^3$), 260 sh.
$(NMe_4)_2Ir(CO)Cl_3(SnCl_3)_2$	294 sh , 325 sh , 262 sh.
$(NMe_4)_2Ru(CO)_2Cl_2(SnCl_3)_2$	360 ($4{\cdot}9 \times 10^4$), 274 ($4{\cdot}2 \times 10^5$)

B Properties

Compound	Colour	M.p.	Λm^+	$\nu C{=}O^{**}(cm^{-1})$
$(NMe_4)_2Rh(CO)Cl(SnCl_3)_2$	Orange	d.> 200°	151	2005
$(NMe_4)_2Ir(CO)Cl_3(SnCl_3)_2$	Yellow	d.> 250°	114	2058
$(NMe_4)_2Ru(CO)_2Cl_2(SnCl_3)_2$	Yellow	d.> 230°	97	2058, 2000

* Measured in 1:1 HCl solutions. + in dimethylformamide at 10^{-3}M. In $ohms^{-1}.\ cm.^2\ mol.^{-1}$. ** in Nujol mulls.

as the solvent. Reduction of the solvent by stannous chloride probably produces carbon monoxide, which then splits the chlorine bridge; but bridge cleavage by carbon monoxide appears to be slow and incomplete in the cold. The formation of carbonyl complexes by solvent reaction is already well known for both iridium and ruthenium (50,51) in the presence of triphenylphosphine, and the mechanisms may well be related.

It might be expected, therefore, that ruthenium-tin solutions in alkanols will also react with the solvent and this has been observed. If ethanolic solutions of ruthenium trichloride and excess stannous chloride are refluxed together for several hours the initially blue solution slowly turns yellow. The solution apparently contains carbonyl species, but the excess of stannous chloride precludes the isolation of any pure complex because of the co-precipitation of $(NMe_4)(SnCl_3)$. Similar behaviour is observed using 2-methoxyethanol as solvent, but if the stannous chloride content is allowed to drop too low, metallic ruthenium is also precipitated. Thus hydrido-carbonyls may be formed in this case (*cf*. ref.51).

The interesting example of the formation of a rhodium hydride catalysed by stannous chloride has already been mentioned. The facile formation of iridium hydrides through the interaction of alcohols in the presence of triphenylphosphine has been investigated by Vaska (52), and it was of interest to ascertain whether stannous chloride would also catalyse their preparation. Vaska prepared $(Ph_3P)_3IrHCl_2$ by refluxing a chloroiridate(IV) solution with excess triphenylphosphine in aqueous ethanol, but preferably in aqueous 2-methyoxyethanol, for a few hours. Refluxing sodium hexachloroiridate(IV) in ethanol (in a nitrogen atmosphere) with excess triphenylphosphine and stannous chloride for half an hour gives a yellow solution, which on cooling precipitates $(Ph_3P)_3IrHCl(SnCl_3)$. The infra-red spectrum shows a very broad hydride peak at ca $2000cm^{-1}$, but triphenylphosphine oxide is also present. The stannous chloride is labile in solution because successive recrystallizations from methylene chloride - ethanol result in gradual loss of tin with the eventual formation of $(Ph_3P)_3IrHCl_2$; the same isomer as is obtained from Vaska's method (52).

If the reaction is repeated under the same conditions, but with 2-methoxyethanol as the solvent, white crystals are obtained in good yield. The infra-red spectrum shows two sharp Ir-H stretching frequencies and elemental analyses confirm a dihydride species, $(Ph_3P)_3IrH_2(SnCl_3)$. It appears to be another example of a dihydride series, $(Ph_3P)_3IrH_2X$, many of which have been prepared by Angoletta(53). Evaporation of the residual solution, after removal of the dihydirde, gives a yellow solid, which contains tin, but gives $(Ph_3P)_3IrHCl_2$ again after several recrystallizations.

The n.m.r. spectra of the iridium hydride complexes are given in Table XI. $(Ph_3P)_3IrHCl_2$ shows the high-field line expected for a hydrogen atom attached directly to a transition metal. The resonance is split by interaction with three equivalent phosphorous nuclei into a symmetrical quartet with relative intensities 1:3:3:1 and coupling constant $J = 14$ c.p.s.,

TABLE X

Properties of iridium hydride and carbonyl complexes

Compound	Colour	M.p.	ν Ir-H(cm^{-1})(a)	ν C=O(cm^{-1})(a)
$(Ph_3P)_3IrHCl(SnCl_3)$	Orange-yellow	132-134	2155(br)	
$(Ph_3P)_3IrHCl_2$	Pale cream	144-146	2228	
$(Ph_3P)_3IrH_2(SnCl_3)$	White	206-207	2262,2210	
$(Ph_3P)_3IrH_2Cl$ (b)			2290,2210	
$(Ph_3P)_2Ir(CO)Cl$	Yellow			1975
$(Ph_3P)_2Ir(CO)HCl(SnCl_3)$-acetone			2150(c)	2055(c)
	V. Pale yellow	199-201	2193,2155	2058,2051
$(Ph_3P)_2Ir(CO)HCl(SnCl_3)$			2148(d)	2052(d)
$(Ph_3P)_2Ir(CO)HCl_2$	White		2237	2022
$(Ph_3P)Ir(CO)Cl_2(SnCl_3)$	Lemon-yellow	270-275		2077,2072
$(Ph_3P)_2Ir(CO)Cl_3$ (b)				2079

(a) In Nujol mulls (b) R.C. Taylor, private communication

(c) in methylene chloride solutions (d) estimated from I.R. spectra of mixtures.

TABLE XI

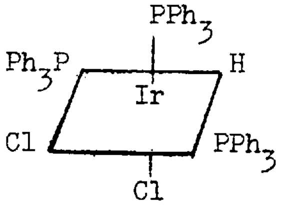
N.m.r. spectra of iridium hydrides

Compound	τH (J_{PH} (c.p.s.) in parentheses)$^{(a,b)}$
$(Ph_3P)_3IrHCl(SnCl_3)$	31·4(T, 10) , 30·3(Q,13) 24·7(D,14)
$(Ph_3P)_3IrH_2Cl$	29·2(Q,14)
$(Ph_3P)_3IrH_2(SnCl_3)$	21·3(T ,~10), 23·0(T ,~10),24·7(Q ,~20)
$(Ph_3P)_3IrH_2Cl$	19·9(T, 20), 22·2(T,20), 30·2(Q, 15)
$(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ .acetone.	19·9(T,20)
$(Ph_3P)_2Ir(CO)HCl_2$	insoluble

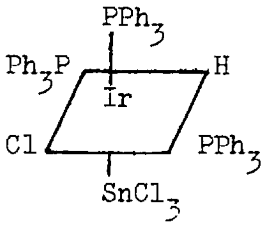
(a) in methylene chloride solutions (b) Line splittings.

D = doublet, T = triplet, Q = quartet.

which is the magnitude of splitting expected for a cis- arrangement of the phosphine ligands relative to the hydrogen (54), structure(V) . The n.m.r. spectrum of $(Ph_3P)_3IrHCl(SnCl_3)$ is more complex. A weak



(V)

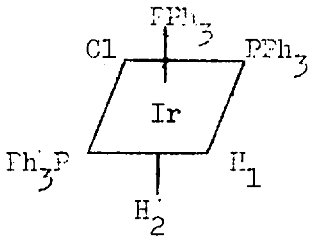


(VI)

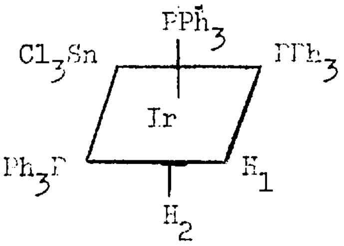
1:3:3:1 quartet at $\tau = 30{\cdot}3$ would be expected for structure (VI) since the environment of the hydrogen atom is not very different from that in (V). Stannous chloride behaves as a <u>trans</u>- directing ligand (see later) and if it were <u>trans</u>- to the hydride ligand we would expect the peak to be shifted to much lower τ values as found for platinum hydrides (54). However the 1:2:1 triplet at $\tau = 31{\cdot}4$ is the most intense peak (about 3-4 times the intensity of the quartet) and must therefore be attributed to the predominant species. The high τ value of the triplet is not consistent with the $SnCl_3^-$ being <u>trans</u>- to the hydrogen and furthermore the splitting can only arise from the interaction of two <u>cis</u>- phosphorous nuclei. This can be explained if it is assumed that the phosphine <u>trans</u>- to $SnCl_3^-$, sufficiently labilized by a strong <u>trans</u>- effect, is caused to dissociate readily and thus effectively not couple. Addition of excess triphenylphosphine should therefore depress dissociation and change the triplet into the quartet;this has been observed in part. Excess phosphine ($\sim$ 5 moles) decreases the triplet to about half its original intensity, while the other resonance grows to approximately equal intensity, with a broadened quartet structure (J_{PH} $\sim$20 c.p.s.).

The addition of a greater excess of triphenylphosphine does not appear to alter the spectrum appreciably. The low field doublet is very weak and not well defined; it may be due to a contaminating phosphine oxide species.

The n.m.r. spectrum of $(Ph_3P)_3IrH_2Cl$ shows two 1:2:1 triplets of equal intensity and a 1:3:3:1 quartet (approximately twice the intensity) at higher field. Structure (VII) is most consistent with the spectrum if interactions by adjacent hydrogens are assumed to be negligible. The hydrogen cis- to all phosphine ligands (H_1) will give a symmetrical quartet at high-field (cf. $(Ph_3P)_3IrHCl_2$). H_2 should have a lower chemical shift since it is trans- to a trans-directing ligand. N.m.r. studies on $(PR_3)_2PtHX$ complexes have shown that phosphorous nuclei couple with hydrogen much more strongly when they are in the trans- position: J_{PH}(trans) = 80-150 c.p.s.; J_{PH}(cis)= 12-24 c.p.s. (55). Therefore the H_2 resonance should be split first to a 1:2:1 triplet by the cis- phosphines and then into a doublet by the trans- phosphine. If the two low field triplets are interpretated this way they lead to coupling constants (J_{PH}(cis)= 20 c.p.s.; J_{PH}(trans) = 130 c.p.s.) of the right order.



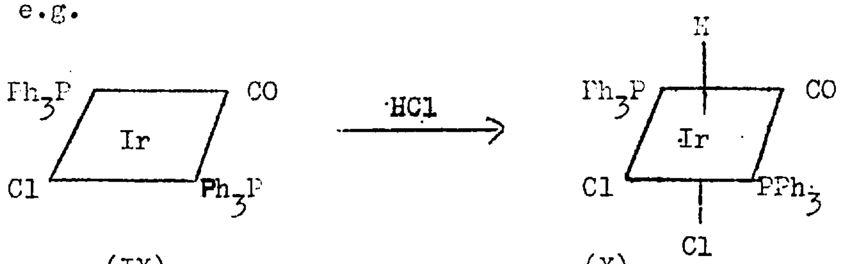
(VII)



(VIII)

$(Ph_3P)_3IrH_2(SnCl_3)$ should have the same structure with the chloride ion replaced by $SnCl_3^-$ (VIII), and the n.m.r. spectrum is consistent with this view. The quartet of H_1 is shifted to a lower field value under the influence of the trans- directing $SnCl_3^-$ group; but the double triplet remains essentially unchanged except for a small shift up-field.

The square planar iridium carbonyl complex trans-$(Ph_3P)_2Ir(CO)Cl$ (50) is well known for the ease with which it can form octohedral iridium(III) complexes through addition by HCl (50), Cl_2, H_2 (56), and RX (57): e.g.



(IX) (X)

The reaction of (IX) with stannous chloride also forms an octohedral complex, but in an unusual way. (IX) dissolves in acetone containing stannous chloride to give a yellow solution from which slowly crystallizes $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$.acetone. This is another interesting example of stannous chloride reacting with the solvent and thereby promoting the formation of a hydride complex. The hydrogen must clearly come from the acetone as no reaction occurs in ethanol even under reflux.

The presence of acetone is indicated both by the infra-red spectrum and by analysis. The ketonic C=O stretching frequency at $1709cm^{-1}$ and the C-H assymetric stretching frequency at $1218cm^{-1}$ in the infra-red spectrum are both indicative of uncoordinated acetone(58).

Moreover the acetone is not retained on recrystallization and infra-red spectra of solutions no longer show frequencies characteristic of acetone.

The infra-red spectrum also shows two Ir-H stretching frequencies and two C=O stretching frequencies (Table X). It seems most likely that these doublets are due entirely to solid state splittings as in solution each pair becomes a single peak. Furthermore the n.m.r. spectrum has only one high-field line, so that the hydride ligand must be in a single environment. The 1:2:1 triplet structure is due to cis-phosphines, and its low τ value suggests that the hydrogen is trans- to $SnCl_3^-$ (structure X with Cl replaced by $SnCl_3^-$).

On attempted recrystallization from methylene chloride-ethanol mixtures, breakdown of the complex occurs and instead of obtaining $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ a mixture of compounds results. The infra-red spectra show the presence of $(Ph_3P)_2Ir(CO)HCl_2$ and sometimes traces of $(Ph_3P)_2Ir(CO)Cl$. Two unidentified bands can be attributed to $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ as their values are close to the acetone adduct. Further extraction with methylene chloride leaves the expected residue of insoluble $(Ph_3P)_2Ir(CO)HCl_2$, but recrystallization with ethanol again gives the same mixture as before. Thus a progressive loss of stannous chloride occurs on repeated recrystallizations and thus it has not so far proved possible to isolate pure $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$.

It would be expected that the interaction of stannous chloride and $(Ph_3)_2Ir(CO)HCl_2$ (X) in acetone should lead to the same stannous chloride complex. A suspension of (X), in acetone will dissolve in the presence of stannous chloride, but crystals are not precipitated in this case. However evaporation of the solvent and extraction of excess stannous chloride with ethanol leaves a solid which contains predominately $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ but small amounts of $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ acetone and $(Ph_3P)_2Ir(CO)Cl$ also. Recrystallization of this mixture from methylene chloride-methanol gives progressive loss of tin in the same way as outlined above.

The reaction with stannic chloride with (IX) was also investigated to see if the tendency to form iridium(III) complexes could induce stannic chloride to add as $SnCl_3$ and Cl. Refluxing in benzene, under dry nitrogen, for 24 hours gives a partial reaction as evidenced by the appearance of a new carbonyl band at higher frequencies. To get complete reaction it was necessary to heat (IX) in refluxing stannic chloride for 24 hours. A pale yellow powder was obtained which analyses as $(Ph_3P)Ir(CO)Cl_2(SnCl_3)$. Thus it appears that one phosphine molecule has been lost to give an apparently 5-coordinate iridium(III) complex. It may well achieve octohedral coordination through chlorine bridging, but the compound is completely insoluble and it has not been possible to make any physical measurements on it. $(Ph_3P)_2Ir(CO)HCl_2$ reacted under the same conditions gives exactly the same complex.

6. Aspects of Stannous Chloride as a Ligand

The reactions of stannous chloride with platinum metal compounds suggests that it behaves as a stronger ligand than chlorine with appreciable π-acceptor properties; but that it is much more labile in solution. If $SnCl_3^-$ is analogous to the MR_3 ligands of Group V, then σ-bonding would be expected to be relatively weak and that the strength of the metal-tin bond should be due to considerable $d_\pi - d_\pi$ bonding. Vacant 5d orbitals on the tin atom should overlap with filled d orbitals on the transition metal atom. There appears to be no co-ordination, at room temperature, between stannous chloride and boron trichloride where only σ-bonding could occur.

Parshall (59) has used intramolecular F^{19} n.m.r. shielding to estimate the relative σ and π contributions in a metal-ligand bond in fluorophenyl complexes of platinum; viz.: trans-$(PEt_3)_2$Pt-(meta-fluorophenyl)X and the para-fluorophenyl analogue. The chemical shifts of the meta- are taken to measure the σ donor effect of the trans- ligand, and the para-fluorine to measure the combined σ and π effects. Hence the two contributions can be separated and have been measured for a variety of ligands. This approach has been used by Lindsay, et al. (60) to investigate the characteristics of $SnCl_3^-$ as a ligand. Their results suggest weak σ donation, but a strong π contribution to the M-Sn bond as expected.

$SnCl_3^-$ should therefore show a high trans- effect in common with other good π-acceptor ligands. A 'trans- effect' series has been made by Chatt (54,61) using the Pt-H stretching frequency in the infra-red spectra, or the chemical shift of the hydrogen atom in the n.m.r. spectra, of the hydride series trans-$(PEt_3)_2PtHX$. (Table XII). There is a good correlation between trans- effect and

TABLE XII

Trans- effect series for trans-$(PEt_3)_2PtHX$.

Ligand X	ν Pt-H$(cm^{-1})^{(a)}$	δ Pt-H $(\tau)^{(b)}$
Cl	2183	26·9
Br	2178	25·6
I	2156	22·7
NCS	2112	23·2
$SnCl_3^{-(c)}$	2105	19·2
CN	2041	17·8

Data from (a) ref.61 (b) ref. 54 (c) ref. 60

π-acceptor properties. An estimation of the trans- effect of $SnCl_3^-$ in this way shows it to be nearly as good a π-acceptor as cyanide. A high trans- effect is predicted from n.m.r. measurements on the fluorophenyl compounds and from results of this work.

Spectrophotometric studies have suggested that stannous bromide and iodide should also act as ligands (20,21). Recently the salts of the bromo-anionic tin complexes, $[Rh_2Br_2(SnBr_3)_4]^{2-}$ and $[Pt(SnBr_3)_5]^{3-}$ have been described (62). Far infra-red studies have been made on both the bromo- and chloro-anions. It appears that tin-halogen bond stretching frequencies can be distinguished from both bridging metal-halogen and metal-metal stretching frequencies. However it is doubtful whether unambiguous distinctions can be made between tin-halogen and terminal platinum metal-halogen stretching frequencies (Table XIII). Although Adams and Chandler assign bonds in the region $330-365 cm^{-1}$ to νSn-Cl, which is the range of frequencies expected for tin-chloride bonds (63-65), similar values are also found for νM-Cl (65-67). Therefore an assignment of bonds can only be made with any certainty where terminal metal chloride bonds are not likely to be present: <u>viz</u>. $[Rh_2Cl_2(SnCl_3)_4]^{4-}$; but in the case of the platinum salt such criteria are unlikely to unambiguously distinguish between $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$. The same comments apply to the bromo-complexes.

Stannous chloride is well known as a reducing agent and it has been suggested that in some cases reduction may proceed via an intermediate tin complex. During studies on the reduction of uranium(IV) to uranium(VI) by tin(II), (68) the formation of a weak 1:1 complex between uranium(IV) and stannous chloride has been detected spectrophotometrically in hydrochloric acid media. The kinetic first order dependance of both reagents suggests that the reduction may depend on such a complex. There is also a weak 1:1 complex between uranium(VI) and stannous chloride, although no further reduction takes place. Dye, et al. (69) have suggested that a similar complex of this type may contribute to the reduction of vanadium(V) by tin(II) in hydrochloric acid, although they have no direct evidence for this.

TABLE XIII

For infra red band assignments (Nujol Mulls)

Compound	νM-Cl	νM-Br	Refs.
$MeSnCl_3$	~360(br)		63
Me_2SnCl_2	~320(br)		63
$SnCl_4$.pyr.	374		63
K_2SnCl_6	313		65
$(NMe_4)(SnCl_3)$	242, 278, 286		64
$(AsPh_4)(SnCl_3)$	250, 256, 286		64
K_2PtCl_6	343		65
	344		66
K_2PtCl_4	320		66
	325		67
Cs_2PtCl_4	316		67
K_3RhCl_6	323		65
K_2PtBr_6		244	65
		240	66
K_2PtBr_4		233	66

Bands found by Adams and Chandler (62)

$(NEt_4)_3[Pt(SnCl_3)_5]$	336.6	
$(NEt_4)_3[Pt(SnBr_3)_5]$		264.1 253.9

Recently Smith (70) has reported the formation of a 1:1:1 complex with iron(III) or copper(II) with tin(II) and citrate or tartrate. Smith has suggested that a structure with the citrate or tartrate ion chelating both metals can be regarded as the stable intermediate of an electron transfer process between tin and the transition metal. He has observed the rapid photochemical reduction of iron(III) by tin(II) in tartrate media.

EXPERIMENTAL

General:

Most analyses and all molecular weight measurements (at 37° using a Mechrolab Osometer) are by the Microanalytical Laboratories, Imperial College. Some chloride determinations were made by potentiometric titrations with silver nitrate, using a silver electrode and a reference glass electrode. Platinum was analysed gravimetrically, by reduction to the metal with hypophosphorous acid (71), or spectrophotometrically using stannous chloride (10).

Infrared spectra were measured on a Grubb-Parsons "Spectromaster" grating spectrometer, in Nujol mulls unless otherwise stated. Absorption spectra were recorded on a Perkin Elmer model 350 recording spectrophotometer using silica cells.

All n.m.r. spectra were made with a Varian Model 43100 spectrometer at 56·5 Mc/sec., using 5-mm. (external diameter) non-spinning tubes. Line positions were determined by conventional side-band techniques and referred to tetramethylsilane as internal standard.

Conductivity measurements were made with a Mullard conductivity bridge using a Mullard "dipping" conductance cell with platinum-platinum black electrodes. Molar conductivities (Λm) are given in ohm^{-1} cm.^{2} mole^{-1} with the medium in parentheses: DMF = dimethylformamide.

Magnetic measurements were made on a converted two pan analytical balance using a permanent magnet of 43·6 x 10^{6} oersteds field-strength. X-ray powder patterns were taken on a Guinier powder camera using CuK(α) radiation. Melting points were determined on a Kofler hot-stage microscope.

It was shown that tin(II) can be detected by the standard cacotheline reagent in non-aqueous media. $SnCl_2$ = anhydrous stannous chloride; $SnCl_2,2H_2O$ is the dihydrate (reagent grade). Ethanol is absolute. The platinum metal starting materials usually employed were hydrated $RuCl_3$ (Ru 40%), $RhCl_3,3H_2O$, $Na_2IrCl_6,6H_2O$ and $Na_2PtCl_4,4H_2O$ all supplied by Johnson Matthey and Co. Ltd. Reagent grade chemicals are always employed, unless otherwise stated.

1. Complex tin-containing anions

Job plots. Absorption spectra for Job plots were measured on mixtures of solutions of $SnCl_2$ and $RhCl_3,3H_2O$ (10^{-3}M) in stoppered 10mm. silica cells. Measurements in 3M-hydrochloric acid or ethanol solutions gave similar results. Mixtures of solutions of $SnCl_2$ and $Na_2PtCl_4,4H_2O$ (5×10^{-3}M) were measured in 1mm. silica cells, in either 3M-hydrochloric acid or ethanol solutions. In one experiment all operations were carried out under nitrogen, but the results were not significantly different.

Tetrakis(tetramethylammonium)tetrakis(trichlorostannato)μ,μ'-dichlorodirhodate(I).

(a) $RhCl_3,3H_2O$ (0·9g.) in 3M-hydrochloric acid (50ml.) was treated with $SnCl_2,2H_2O$ (1·9g.). The addition of Me_4NCl (0·5g.) in water (10ml.) gives an orange precipitate of the *salt* (2·0g., 85%). Contamination with the salt of the hexachlorostannate$^{(IV)}$ ion can be avoided by using a deficiency of the precipitant. The salt is recrystallized from 3M-hydrochloric acid-ethanol (1:10). (Found: C, 13·2; H, 2·9; N, 3·7; Cl, 34·0; Sn, 32·0. $C_{16}H_{48}N_4Cl_{14}Sn_4Rh_2$ requires: C, 13·4; H, 3·4; N, 3·9; Cl, 34·6; Sn, 32·0 %).

(b) Bis(norbornadiene)-$\mu\mu'$-dichlorodirhodium(I) (0·3g.) in ethanol (30ml.) was treated with $SnCl_2$ (0·8g.). Addition of Me_4NCl (0·2g.) in water (9ml.) gave an orange precipitate whose infra-red spectrum showed the absence of olefin and whose electronic spectrum (in hydrochloric acid) was identical with that of the product obtained in (a) (Found: C, 12·4; H, 3·1 %).

Bis(tetramethylammonium)dichlorobis(trichlorostannato)platinate(II)

(a) Yellow isomer. To $Na_2PtCl_4,4H_2O$ (0·18g.) in ethanol (15ml.) in a nitrogen atmosphere was added anhydrous $SnCl_2$ (0·15g.) (Pt:Sn ratio = 1:2). The resulting red solution fades to yellow-orange on standing for 10-15 mins. Addition of Me_4NCl (0·10g.) in methanol (1ml.) precipitates the yellow, crystalline salt quantitatively. By dissolving in acetone and re-precipitating with ethanol, the compound was obtained as needles, decomp. 195-200° (Found: C, 11·2; H,2·9; N, 3·4; Cl, 32·8; Sn, 26·6; Pt, 22·0. $C_8H_{24}N_2Cl_8Sn_2Pt$ requires: C, 11·1; H, 2·8; N, 3·3; Cl, 32·8; Sn, 27·5; Pt, 22·6 %).

The reaction may also be carried out in methanol, but with 3M-hydrochloric acid as solvent isomerization is incomplete, even after standing 30 min., and a mixture of red and yellow isomers is obtained. The yellow salt can be obtained free of the red, in low yield, when the acid solutions are kept at -10°C.

(b) Red isomer. To $Na_2PtCl_4,4H_2O$ (0·20g.) in ethanol (10ml.) under nitrogen was added $SnCl_2$ (0·19g.) (Pt:Sn ratio = 1:2). On addition of Me_4NCl (0·06g.) in methanol (1ml.) immediately to the red solution, the red salt was obtained (0·23g., 60% corresponding to the amount of Me_4NCl added). This was purified by dissolving in acetone and reprecipitating as needles, decomp. 250° (Found: C, 11·4; H, 2·6; N, 2·9; Cl, 32·9; Sn, 27·5; Pt, 21·9. $C_8H_{24}N_2Cl_8Sn_2Pt$ requires: C, 11·1; H, 2·8, N, 3·3; Cl, 32·8; Sn, 27·5; Pt, 22·6%).

Not all the platinum is precipitated from solution, and addition of more Me_4NCl (0·05g.) in methanol (1ml.) to the yellow filtrate, after removal of the red isomer precipitates the yellow isomer identical with the previous sample (0·16g., 45% corresponding to the amount of platinum left in solution). When this reaction is carried out in 3M-hydrochloric acid, the red form is obtained initially as above, but the yellow form only slowly crystallizes in low yield on further addition of Me_4NCl owing to its solubility in hydrochloric acid.

(c) Precipitates from higher Pt:Sn ratios. To $Na_2PtCl_4,4H_2O$ in 3M-hydrochloric acid under nitrogen was added $SnCl_2,2H_2O$ in varying amounts to give Pt:Sn ratios of up to 1:10. Addition of Me_4NCl in water precipitates red solids as in (b). Re-precipitation in the same manner gives in every case red needles which appear homogeneous under the polarizing microscope. The electronic spectra and X-ray powder patterns of all these solids are identical and are the same

TABLE XIV

Analyses of red Pt-Sn solids from different sources

Initial	Reaction	Found.				
Pt:Sn ratio	Medium	C	H	Cl	Sn	Pt
1:5	HCl	11·4	2·6	32·9	27·4	-
1:5	HCl	-	-	33·5	32·3	14·2
1:10	HCl	9·7	2·0	33·8	30·7	12·0
1:5	EtOH	-	-	-	31·4	13·1
1:6 (Na_2PtCl_6)	EtOH	-	-	36·2	27·8	-
1:6 (H_2PtCl_6)	MeOH	9·8	2·7	36·9	36·3	14·3
1:5 *	EtOH	-	-	-	33·3	-
$(NMe_4)_3[Pt(SnCl_3)_5]$ requires		9·3	2·3	34·5	38·5	12·6
$(NMe_4)_2[PtCl_2(SnCl_3)_2]$ requires		11·1	2·8	32·7	27·4	22·6

* Precipitated at -78°C as the yellow form and isomerized on warming.

as those of the red isomer obtained in (b). If these reactions are carried out in ethanol similar results are made. However analyses of different samples vary considerably (Table XIV). If Pt:Sn ratios less than 1:5 are used, then the X-ray powder patterns show lines due to both the yellow and red isomers. The amount of yellow isomer decreases as the Pt:Sn ratio increases and at 1:5 only traces of the yellow salt are observed.

(d) (Mesityl oxide)dichloroplatinum(II) (0·16g.) in ethanol (25ml.) under nitrogen was treated with $SnCl_2,2H_2O$ (0·4g.). The resulting cherry-red solution had the same electronic absorption spectrum as that in (c) (Table XV) and gave an identical Me_4N^+ salt (Found: C, 11·0; H, 3·1 %).

(e) Potassium ethylenetrichloroplatinate(II) (0·37g.) in ethanol or 3M-hydrochloric acid (25ml.) was treated with $SnCl_2,2H_2O$ (0·45g.) with results as in (d) (Found: Cl, 34·8; Sn, 28·8 %).

(f) To (cyclo-octa-1, 5-diene)dichloroplatinum(II) (0·05g.) in acetone (20ml.) under nitrogen was added $SnCl_2$ (0·15g.); results as in (d).

(g) Platinum carbonyl chlorides, $Pt(CO)_2Cl_2$ and $Pt_2(CO)_2Cl_4$, were prepared according to Schutzenberger (72) and separated by sublimation. Both carbonyls were treated in ethanol or acetone solutions under nitrogen with excess $SnCl_2$. Carbon monoxide was evolved (identified by its gas infra-red spectrum) and gave the

TABLE XV

Electronic spectra of solutions of platinum complexes treated with excess stannous chloride

Obtained from	Solvent	λ max (mμ)		
$Na_2PtCl_4,4H_2O$	HCl	475 sh ,	402	, 310
$K[Pt(C_2H_4)Cl_3]$	HCl	475 sh ,	403	, 310
$(C_6H_{10}O)PtCl_2$ *	Acetone	475 sh ,	401	
$(C_8H_{12})PtCl_2$ **	Acetone	465 sh ,	403	
$Pt_2(CO)_2Cl_4$	Acetone	475 sh ,	400	
	Ethanol			310
$(CO)_2PtCl_2$	Acetone	460 sh ,	390	
cis-$(NH_3)_2PtCl_2$	HCl	460 sh ,	396	, 315
trans-$(NH_3)_2PtCl_2$	HCl	460 sh ,	396	, 315
cis-$(pyr)_2PtCl_2$	Acetone	465 sh ,	396	

* Mesityl oxide ** Cyclo-octa-1,5-diene

same cherry red solution as in (c) and a Me_4N^+ salt (Found: C, 11·4; H, 2·3 %) obtained.

(h) trans-diaminedichloroplatinum(II) (0·15g.) was suspended in acetone and treated with $SnCl_2$ (0·65g.). The amine dissolves to an orange red solution; the solvent was removed *in vacuo* and the sticky residue taken up in ethanol. Addition of Me_4NCl (0·15g.) in methanol (2ml.) precipitates the red salt (Found: C, 9·2; H, 2·8; Cl, 34·5 %) as in (c).

(i) cis-diaminedichloroplatinum(II) (0·10g.) was treated with $SnCl_2$ (0·50g.) as in (h) and the Me_4N^+ salt isolated (Found: C, 9·8; H, 2·4 %).

(j) cis-bispyridinedichloroplatinum(II) (0·22g.) was treated with $SnCl_2$ (0·95g.) as in (h) and the Me_4N^+ salt similarly isolated (Found: C, 11·4; H, 1·8; Cl, 32·3 %).

Bis(triphenylmethylphosphonium)dichlorobis(trichlorostannato)platinate(II)

(a) Yellow isomer. $Na_2PtCl_4,4H_2O$ (0·12g.) in methanol (10ml.) under nitrogen was allowed to react with $SnCl_2$ (0·13g.) (Pt:Sn ratio 1:2·5) at room temperature. The mixture was cooled in an acetone-solid carbon dioxide bath and allowed to equilibrate for 15 min. Ph_3MePCl (0·10g.) in methanol (1ml.) was added dropwise to the yellow solution. The yellow precipitate was quickly centrifuged and the mother-liquid decanted off without allowing it to warm up. The precipitate was washed in the same manner first with a small portion of methanol and then with several portions of diethyl ether to ensure the removal of all free stannous chloride. The suspension must not be allowed to warm up during these operations or rapid isomerization to an orange oil occurs. The precipitate is finally quickly transferred as a slurry in ether to a flask and the solvent removed rapidly in vacuo. Even by careful washing it is impossible to prevent a little isomerization, but the product is predominantly the yellow isomer. (Found: C, 31·8; H, 2·4; Cl, 24·3; Sn, 18·7. $C_{38}H_{36}P_2Cl_8Sn_2Pt$ requires: C, 35·0; H, 2·9; Cl, 22·4; Sn, 18·7 %). It is an amorphous powder which can be safely kept in a refrigerator, but it isomerizes slowly at room temperature and immediately at 50° to an orange oil.

Use of Pt:Sn ratios 1:2 makes it easier to isolate the yellow isomer free from the red form, but low tin analyses indicate contamination with $(Ph_3MeP)_2PtCl_4$ owing to incomplete reaction at low temperatures. It can be precipitated at 0°C, but isomerizes so rapidly in situ that it cannot be isolated.

(b) Mixed isomers. To $Na_2PtCl_4,4H_2O$ (0·23g.) in methanol (15ml.) under nitrogen was added $SnCl_2$ (0·19g.) (Pt:Sn ratio 1:5) at room temperature. Addition of Ph_3MePCl (0·35g.) in methanol (3ml.) precipitates the orange solid (0·48g. 73%). The variable melting point indicates a mixture of two isomers. The same orange solid was precipitated at room temperature from any solutions with Pt:Sn ratios up to 1:10. (Found: Pt:Sn = 1·5; C, 33·8; H, 3·1; Cl, 24·6; Sn, 18·9;

Λ m(DMF), 119. Pt:Sn = 1:10; C, 34·4, H, 2·8; Cl, 24·3; Sn, 19·3; Λ m(DMF), 123. $C_{38}H_{36}P_2Cl_8Sn_2Pt$ requires: C, 35·0; H, 2·9; Cl, 22·5; Sn, 18·7 %). Attempts to prepare the pure red isomer by precipitation at higher temperatures, in the presence of excess stannous chloride, were unsuccessful.

Bis(tetramethylammonium)dichlorobis(trichlorostannato)ruthenate(II)

(a) To ruthenium trichloride hydrate (1g.) in 3M-hydrochloric acid (150ml.) was added $SnCl_2,2H_2O$ (6g.). On heating under nitrogen on a steam-bath the solution became orange-red (ca 1 hour). Addition of Me_4NCl (0·5g.) in water (10ml.) precipitated the salt (2·0g., 80%) which was recrystallized from 3M-hydrochloric acid-ethanol (1:4). The microcrystalline powder darkens above 200° (Found: C, 12·1; H, 3·1; N, 3·2; Cl, 36·4; Sn, 28·1. $C_8H_{24}N_2Cl_8Sn_2Ru$ requires: C, 12·4, H, 3·2; N, 3·7; Cl, 36·7; Sn, 30·8 %).

(b) Bis(norbornadiene)dichlororuthenium (0·21g.) was refluxed in 6M-hydrochloric acid (40ml.) under nitrogen for one hour with $SnCl_2,2H_2O$ (0·86g.). The yellow solution was filtered from unreacted starting material and Me_4NCl (0·30g.) in water (5ml.) added to precipitate a yellow salt, which has the same absorption spectrum as in (a). No olefin (free or coordinated) could be detected in the infrared spectrum; but the carbon and hydrogen analyses were consistently high (Found: C, 16·7; H, 3·1 %).

Tetrakis(tetramethylammonium)tetrachlorotetrakis(trichlorostannato)-$\mu\mu'$-dichlorodi-iridate(III)

To $Na_2IrCl_6,6H_2O$ (1g.) in 3M-hydrochloric acid (100ml.) was added excess $SnCl_2,2H_2O$ (4g.). After ca 1 hour on a steam-bath under nitrogen, Me_4NCl (0·5g. in 10ml. of water) precipitated the salt (1·5g., 90%), which re-crystallized from 3M-hydrochloric acid-ethanol (1:4) as hexagonal plates, decomp. $>250^\circ$ (Found: C, 10·7; H, 2·8; N, 3·0; Cl, 33·4; Sn, 27·1. $C_{16}H_{48}N_4Cl_{16}Sn_4Ir_2$ requires: C, 10·7; H, 2·7; N, 3·1; Cl, 35·5; Sn, 27·0 %).

2. Reaction of Ligands with Tetramethylammonium Salts

(a) To $(Me_4N)_2\,[PtCl_2(SnCl_3)_2]$ (0·5g.) in acetone (30ml.) was added triphenylphosphine (0·6g.); the solution quickly became colourless and free tin(II) was detected (cacotheline). Addition of dilute hydrochloric acid precipitated a white solid which, after washing with dilute acid, ethanol and diethyl ether, was identified as bis(triphenylphosphine)dichloroplatinum(II) by analysis (Found: C, 52·7; H, 4·4; Cl, 8·9. Calcd. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54·1; H,3·8; Cl, 8·9 %) and by its infrared spectrum.

(b) $(Me_4N)_2\,[RuCl_2(SnCl_3)_2]$ (0·3g.) was fused with triphenylphosphine (0·5g.) at 100° for 1 hour under nitrogen. Free tin(II) was detected, but no pure product was isolated. Under similar conditions the rhodium and iridium tetramethylammonium salts were unaffected.

(c) $(Me_4N)_2\,[RuCl_2(SnCl_3)_2]$ (0·3g.) was refluxed with dry pyridine (10ml.) for 1 hour under nitrogen. After filtration the solvent was removed and the residue leached with ethanol until no more tin(II) could be detected in the washings. After dissolution in chloroform the addition of petroleum ether (b.p. 40-60°) precipitated an orange solid with properties identical to those of $(pyridine)_4RuCl_2$ (73) (Found: C, 44·9; H, 3·2. Calcd. for $C_{20}H_{20}Cl_2N_4Ru$: C, 49·1; H, 4·1 %).

Under similar conditions the rhodium and iridium salts were attacked by pyridine, displacing $SnCl_2$; but no reaction products could be cleanly separated.

(d) $(NMe_4)_4\left[Rh_2Cl_2(SnCl_3)_4\right]$ (0·2g.) and p-toluidine (0·8g.) were treated in nitrogen for 30min. at 100°. The product contained free tin(II), identified by cacotheline and extraction with hot chloroform gave a yellow solution which yielded an orange solid on evaporation. Washing with diethyl ether left trichlorobis(p-toluidine)rhodium(III), m.p. 145-148°, in low yield (Found: C, 45·4; H, 5·0; Cl, 17·8. Calcd. for $C_{21}H_{27}N_3Cl_3Rh$: C, 47·7; H, 5·1; Cl 20·0 %).

Under the same conditions the ruthenium salt gave free tin(II) but no product could be isolated; the iridium salt is barely attacked.

3. Reaction of the complexes in organic solvents with ligands

(a) A solution of sodium chloroplatinate(II) (0·34g.) and $SnCl_2$ (0·6g.) in ethanol (25ml.) was shaken with cyclo-octa-1,5-diene (2ml.) under nitrogen. White needles slowly precipitated, which were removed after 2 days and shown to be $C_8H_{12}PtCl_2$, decomp 230-240° (0·1g., 35%) (Found: C, 25·0; H, 3·2; Cl, 19·1; M (benzene), 377. Calcd. for $C_8H_{12}Cl_2Pt$: C, 25·8; H, 3·2; Cl, 9·2 %; M, 374).

(b) To $RhCl_3,3H_2O$ (0·5g.) in ethanol (50ml.) was added $SnCl_2$ (1·2g.). The deep orange-red solution was treated with carbon monoxide at just above atmospheric pressure for 3 hours with agitation. After removal of the ethanol *in vacuo* the residue was extracted with petroleum (b.p. 30-40°) evaporation of which, followed by vacuum sublimation at 60-70° gave orange needles (0·2g., 65%) of $[Rh(CO)_2Cl]_2$ identical with an authentic specimen.

(c) The orange-red solution obtained in (b) was shaken with cyclo-octa-1,5-diene (2ml.). Within a few hours the yellow solid was collected, identical with authentic $(C_8H_{12})_2Rh_2Cl_2$, m.p. 247-249° (from acetic acid) (Found: C, 38·3; H, 5·2; Cl, 14·8; M (benzene) 500. Calcd. for $C_{16}H_{24}Cl_2Rh_2$: C, 39·0; H, 4·9; Cl, 14·4 %; M, 493).

(d) As in (c) using dicyclopentadiene, orange microcrystals m.p. 200-201° (Found: C, 42·1; H, 4·4; Cl, 13·6; M(benzene) 600. Calcd. for $C_{20}H_{24}Cl_2Rh_2$: C, 44·4; H, 4·5; Cl, 13·1 %; M, 541).

(e) As in (c) using 4-vinylhex-1-ene after 3 hours orange, microcrystalline powder of *bis(4-vinylhex-1-ene)-$\mu\mu'$- dichlorodirhodium(I)* decomp. 145-147° (Found: C, 36·1; H, 4;7; Cl, 13;5. $C_{16}H_{24}Cl_2Rh_2$ requires: C, 39·0; H, 4·9; Cl, 14·4 %; M, 493). The complex is identical with a sample prepared by the conventional method, *viz.*: $RhCl_3,3H_2O$ (1g.) in ethanol (150ml.) shaken with 4-vinylhex-1-ene (2ml.) for several weeks leads to an orange powder, decomp. 147-149° (Found: C, 38·9; H, 5·0; Cl, 14·7 %;

M(benzene) 487).

The complex is soluble in benzene and chloroform. However the solubility is too low to enable a reliable n.m.r. spectrum to be obtained; but the spectra were adequate enough to show that the compound was not identical with the cyclo-octa-1,5-diene complex. The infra-red spectra, colour and m.p.s. of these two compounds are all different.

4. Olefin complexes

Bis(norbornadiene)trichlorostannatorhodium(I). To $RhCl_3,3H_2O$ (0·4g.) and $SnCl_2$ (1·03g.) in ethanol (30ml.) was added norbornadiene (2ml.). After shaking for 1 hour at room temperature the yellow needles of the complex were collected, washed with ethanol and ether and dried (0·6g., 70%) (Found: C, 32·5; H, 3·4; Cl, 21·9; Sn,24·9. $C_{14}H_{16}Cl_3SnRh$ requires: C, 32·8; H, 3·2; Cl, 20·8; Sn, 23·2 %). The complex is slightly soluble in methylene chloride, dimethylformamide, nitromethane and hot water.

Bis(norbornadiene)rhodium(I) tetraphenylborate. To a hot, filtered, saturated solution of bis(norbornadiene)trichlorostannatorhodium(I) was added an aqueous solution of sodium tetraphenylborate. The flocculent precipitate was collected by centrifuging and washed by decantation with water (2x20ml.), 4M-hydrochloric acid (4x20ml.) and ethanol (4x20ml.). After drying, the solid was extracted with hot 4M-hydrochloric acid until no tin(II) chloride could be detected in the washings. Recrystallization from acetone gave the salt (Found:

C, 71·6; H, 5·8; Cl > 1, Λm(DMF), 25. $C_{38}H_{36}BRh$ requires: C, 75·5; H, 6·0 %).

Attempts to alkylate $(C_7H_8)_2RhSnCl_3$.

(a) A methyl Grignard reagent was prepared by reacting magnesium (0·6g.) and methyl iodide (1·5ml.) in Na-dried tetrahydrofuran (30ml.) in the usual manner. $(C_7H_8)_2RhSnCl_3$ (0·54g.) was added slowly as a suspension in tetrahydrofuran (5ml.) over 30 mins. The mixture was allowed to react overnight, but most of the rhodium complex did not react. The solution was worked up by normal procedures and an orange THF solution gave a small amount of orange material on evaporation of the solvent, which did not contain olefin.

(b) A solution of methyl lithium in diethyl ether was made by reacting metallic lithium (0·2g.) in ether (25ml.) with methyl iodide (0·7ml.) under reflux (external heat if necessary). A suspension of $(C_7H_8)_2RhSnCl_3$(0·8g.) in ether (25ml.) was added over 20 min. The complex changed from yellow to brown without dissolving. The solid is very deliquescent, only slightly soluble in methylene chloride and acetone and unstable in solution: it was not investigated further.

(c) $(C_7H_8)_2RhSnCl_3$ (0·3g.) was suspended in acetone (20ml.) with excess dimethyl mercury in a sealed tube overnight; no reaction took place. The reaction was repeated using diethyl mercury with benzene as the solvent, but with similar lack of success. If the reaction is carried out at higher temperatures complete or partial reduction to rhodium and mercury occurs.

(d) $(C_7H_8)_2RhSnCl_3$ (0·3g.) was suspended in benzene (70ml.) and treated with tetraethyl lead (1ml.). No reaction occurs at room temperature while at reflux temperatures complete reduction to rhodium occurs.

Ion-exchange experiments on bis(norbornadiene)trichlorostannatorhodium(I)

Anion exchange experiments were carried out using Permutit De-Acidite FF anion-exchange resin (14-52 mesh) in the chloride or nitrate form. The complex was dissolved in the appropriate solvent and passed through a glass column packed with resin at speeds up to 100ml./hr. The elutent was tested for qualitatively the presence of tin(II) to detect any appreciable exchange; quantitative analyses for tin and chlorine were carried out in doubtful cases. In only one experiment was any appreciable exchange observed. But full ion-exchange did not take place and the result could not be repeated so must be considered as spurious.

Cation exchange experiments were carried out similarly using Permutit Zeo-carb 225 cation exchange resin in the sodium form. No exchange was observed in any experiments.

Bis(norbornadiene)trichlorostannatoiridium(I) To a boiling solution of $Na_2IrCl_6,6H_2O$ (0·4g.) in ethanol (30ml.) under nitrogen was added $SnCl_2$ (0·8g.) in ethanol (10ml.). After 5 min. reflux the cooled solution was shaken with norbornadiene (2ml.). After 24 hours the pale yellow needles of the complex were collected, and washed with ethanol and diethylether (0·3g., 70%). (Found: C, 27·6; H, 2·7; Cl, 18·2; Sn, 19·1. $C_{14}H_{16}Cl_3SnIr$ requires: C, 27·9; H, 2·7; Cl, 17·7; Sn, 19·7 %). The complex is sparingly soluble in methylene chloride and dimethylformamide. Using cycloheptatriene a similar compound (Found: C, 27·6; H, 2·7; Cl, 17·4; Sn, 20·1%), with identical infrared spectrum, was obtained.

Attempts to alkylate bis(norbornadiene)trichlorostannatoiridium(I)

Alkylation of the complex was tried using methyl lithium, and dialkyl mercury using the same conditions as for the rhodium complex with similar results.

Bis(cyclo-octa-1,5-diene)trichlorostannatoiridium(I) As for the norbornadiene complex using cyclo-octa-1,5-diene (2ml.) hexagonal prisms (0·3g., 65%) (Found: C, 29·9; H, 3·8; Cl, 16·3; Sn, 17·8, $C_{16}H_{24}Cl_3SnIr$ requires: C, 30·3; H, 3·8; Cl, 16·8; Sn, 18·7 %). From cyclo-octa-1,3-diene a product with identical infrared spectrum (0·2g., 45%) (Found: C, 29·7; H, 3·7; Cl, 18·1; Sn, 16·8 %), was obtained. A similar complex was obtained from 4-vinylcyclohex-1-ene (0·22g., 50%) (Found: C, 30·0; H, 2·9; Cl, 17·2; Sn, 18·4 %). The same complex has been obtained (74) by the action of stannous chloride on chloroiridate solution in warm acetic acid containing cyclo-octa-1,5-diene.

Bis(cyclo-octa-1,5-diene)trichlorostannatoiridium(I)tetraphenylborate

The former complex (0·3g.) was dissolved in warm dimethylformamide (100ml.) and diluted with warm water (300ml.) A saturated aqueous solution of sodium tetraphenylborate was added slowly with stirring until the precipitate had coagulated. After centrifuging the precipitate was washed with water (2 x 20ml.) and bot 3M-hydrochloric acid (4 x 20ml.) to leave the salt, decomp. 225-230^{0} (Found: C, 56·8; H,5·1; Cl, 1·0. $C_{40}H_{44}BIr$ requires: C, 66·5; H, 6·1%).

Bis(triphenylphosphine)norbornadienetrichlorostannatorhodium(I)

Triphenylphosphine (0·84g.) was added to a suspension of $(C_7H_8)RhSnCl_3$ (0·40g.) in methylene chloride (50ml.); the solid immediately dissolved giving an orange solution. After 1 hour the solvent was removed and the orange complex was washed with diethyl ether to remove excess triphenylphosphine. (0·5g., 70%) (Found: C, 54·3; H, 4·2; Cl, 11·2; 12·8; M (benzene), 914; $C_{43}H_{38}P_2Cl_3SnRh$ requires: C, 54·7; H, 4·0; Cl, 11·3; Sn, 12·6 %; M, 944.). The complex is soluble in benzene, chloroform and methylene chloride and slightly soluble in acetone.

Prepared in exactly the same way were:

Bis(triphenylarsine)norbornadienetrichlorostannatorhodium(I).

Orange complex (0.55g., 70%) (Found: C, 49·9; H, 4·0; Cl, 10·4; Sn, 11·7; M (acetone) 1016. $C_{43}H_{38}As_2Cl_3SnRh$ requires: C, 50·0; H, 3·7; Cl, 10·3; Sn, 11·5%; M, 1032).

Bis(triphenylstibine)norbornadienetrichlorostannatorhodium(I).

Orange complex (0·7g., 85%) (Found: C, 44·9; H, 3·4; Cl, 10·1; Sn, 8·5; M (chloroform), 1102. $C_{43}H_{38}Sb_2Cl_3SnRh$ requires: C, 45·8; H, 3·4; Cl, 9·5; Sn, 10·5%; M, 1126).

Bis(triphenylphosphine)(cyclo-octa-1,5-diene)trichlorostannatoiridium(I)

Yellow complex (0·15g., 75%) (Found: C, 49·0; H, 4·0; Cl, 11·6; Sn, 11·3; M (benzene), 910. $C_{44}H_{42}P_2Cl_3SnIr$ requires: C, 48·0; H, 3·5; Cl, 10·1; Sn, 11·3%; M, 1050).

Bis(triphenylarsine)(cyclo-octa-1,5-diene)trichlorostannatoiridium(I)

Yellow complex (0·2g., 83%) (Found: C, 45·2; H, 4·2; Cl, 9·8; Sn, 11·8. $C_{44}H_{42}As_2Cl_3SnIr$ requires: C, 44·3; H, 3·7; Cl, 9·3; Sn, 10·4%).

5. Phosphine and arsine complexes

Bis(triphenylphosphine)(trichlorostannato)chloroplatinum(II)

(a) To a solution of $Na_2PtCl_4,4H_2O$ (0·5g.) and $SnCl_2$ (0·7g.)

in ethanol (40ml.) under nitrogen was added triphenylphosphine (0·6g.) in ethanol (10ml.). The orange precipitate of the complex was carefully washed with ethanol (3x5ml.) and diethyl ether (2x5ml.) containing a little $SnCl_2$. (Found: C, 44·4; H, 3·2; Cl, 14·0; Sn, 11·9. $C_{36}H_{30}P_2Cl_4SnPt$ requires: C, 44·1; H, 3·1; Cl, 14·5; Sn, 12·1%). The complex is soluble in acetone and dichloromethane; but recrystallization gives $(Ph_3P)_2PtCl_2$ (Found: C, 52·0; H, 4·3; Cl, 9·0. Calcd. for $C_{36}H_{30}P_2Cl_2Pt$: C, 54·1; H, 3·8; Cl, 8·9%).

(b) To a 3M-hydrochloric acid (50ml.) of a solution of $Na_2PtCl_4,4H_2O$ (0·5g.) and $SnCl_2$ (0·7g.) was added triphenylphosphine (0·6g.) in ethanol (10ml.). The orange complex is precipitated as washed as above (Found: Cl, 14·7%).

(c) The addition of a 10M excess of $SnCl_2$ for $(Ph_3P)_2PtCl_2$ in acetone gives an orange solution which, after evaporation, careful eaching of free $SnCl_2$ with 3M-hydrochloric acid, followed by washing with ethanol and ether, leaves the complex (Found: Cl, 15·2; Sn,12·0%).

Bis(triphenylarsine)(trichlorostannato)chloroplatinum(II)

(a) To a solution in ethanol (40ml.) of $Na_2PtCl_4,4H_2O$ (0·5g.) and $SnCl_2$ (0·7g.) was added triphenylarsine (0·7g.) in ethanol (10ml.). The precipitated orange complex was collected and carefully washed with ethanol and diethyl ether (Found: C, 40·0; H, 3·2; Cl, 13·2; Sn, 11·1. $C_{36}H_{30}As_2Cl_4SnPt$ requires: C, 40·5; H, 2·8; Cl, 13·6; Sn, 11·1%).

The complex is soluble in acetone and chloroform in which it does not appear to be completely dissociated. The addition of dilute hydrochloric acid to the acetone solution precipitates $(Ph_3As)_2PtCl_2$ (Found: C, 48·8; H, 3·4; Cl, 8·1. Calcd. for $C_{36}H_{30}As_2Cl_2Pt$: C, 49·3; H, 3·5; Cl, 8·1 %).

(b) The complex is prepared exactly the same way using 3M-hydrochloric acid as solvent (Found: C, 41·5; H, 3·3; Cl, 13·7 %).

Tris(triphenylphosphine)(trichlorostannato)rhodium(I). To a solution of $RhCl_3,3H_2O$ (0·2g.) and $SnCl_2$ (1·5g.) in ethanol (40ml.) was added triphenylphosphine (6g.) in ethanol (15ml.) and the mixture boiled until the initial yellow precipitate changed to dark red-brown crystals of the *complex* (1·5g., 70%) (Found: C, 54·9; H, 3·9; Cl, 10·4; Sn, 10·6; M (chloroform), 435 (0·0045M), 331 (0·0035M). $C_{54}H_{45}P_3Cl_3SnRh$ requires: C, 58·2; H, 4·1; Cl, 9·5; Sn, 10·6; M, 1114). The complex is moderately soluble in acetone and chloroform, but sparingly soluble in benzene and ethanol. It cannot be recovered unchanged from solutions.

Tetrakis(triphenylphosphonium)tetrakis(trichlorostannato)-$\mu\mu$-dichlorodirhodate(I)

To a solution of $RhCl_3,3H_2O$ (0·2g.) and $SnCl_2$ (0·45g.) in 3M-hydrochloric acid (40ml.) was added triphenylphosphine (1g.) in ethanol (5ml.). The precipitated yellow *salt* was washed with ethanol (in which it is moderately sollible) and ether, and dried *in vacuo* (0·6g., 70%); ν(P-H) 2392cm^{-1} (Found: C, 36·2; H, 2·9; Cl, 22·3; Sn, 21·3 %).

Bis(triphenylphosphonium)dichlorobis(trichlorostannato)ruthenate(II)

Ruthenium trichloride hydrate (0·5g.) and $SnCl_2,2H_2O$ (3g.) in 3M-hydrochloric acid (50ml.) were treated on a steam-bath for *ca* 1 hour under nitrogen. Addition of triphenylphosphine (1·7g.) in ethanol (20ml.)

gave a precipitate which after washing with ether to remove excess triphenylphosphine, is the pure yellow salt, m.p. 177-180° (1·5g., 80%); ν(P-H) 2398cm^{-1}. (Found: C, 36·7; H, 2·8; Cl, 24·5; Sn, 20·0. $C_{36}H_{30}P_2Cl_8Sn_2Ru$ requires: C, 37·6; H, 2·8; Cl, 24·7; Sn, 20·6 %).

Tris(diphenylmethylarsine)(trichlorostannato)dichlororhodium(III)

$RhCl_3,3H_2O$ (0·2g.) and $SnCl_2$ (0·45g.) were dissolved in ethanol (50ml.) and diphenylmethylarsine (0·75ml., 0·9g.) added under nitrogen. A precipitate formed in the cold, which redissolved on warming. After refluxing for one hour under nitrogen an orange-brown powder was precipitated, on cooling, m.p. 173-176° (Found: C, 41·3; H, 4·0; Cl, 15·2; Sn, 10·7; M(chloroform), 821; Λ_M(DMF), 25. $C_{39}H_{39}As_3Cl_5$ SnRh requires: C, 41·3; H, 3·4; Cl, 15·7; Sn, 10·5 %; M, 1131).

The complex is soluble in benzene, chloroform, acetone and dimethylformamide. Free stannous chloride could be detected in the solutions, and the starting material could not be reprecipitated unchanged.

Tris(diphenylmethylarsine)dichlorohydridorhodium(III)

(a) To $RhCl_3,3H_2O$ (0·24g.) and $SnCl_2$ (1g.) in concentrated hydrochloric acid (15ml.) was added diphenylmethylarsine (0·75ml., 0·9g.) in ethanol (50mls.) under nitrogen. After refluxing for 30 min. the orange, crystalline complex was precipitated, m.p. 185-188°; ν(Rh-H) 2070cm^{-1}. (Found: C, 50·5; H, 4·3; Cl, 8·8; M(benzene), 790, Λ m(acetone), 4·8. $C_{39}H_{40}As_3Cl_2Rh$ requires: C, 51·6; H, 4·4; Cl, 7·8 %; M, 907).

(b) $(Ph_2MeAs)_3RhCl_3$ was prepared by refluxing $RhCl_3,3H_2O$ (0·52g.) and diphenylmethylarsine (1·5 ml., 2·0g.) in ethanol (50 ml.) for 15 mins. The complex precipitates on cooling, and was recrystallized from aqueous ethanol, m.p. 202-204° (Found: C, 49·6; H, 4·2; Cl, 11·3; M(benzene) 863. Calcd. for $C_{39}H_{39}As_3Cl_3Rh$. C, 49·7; H, 4·2; Cl, 11·3 %; M, 942).

$(Ph_2MeAs)_3RhCl_3$ (0·5g.) was dissolved in ethanol (50 ml.) and concentrated hydrochloric acid (2 ml.) with 30% hypophosphorous acid (3 ml.) added. The solution slowly turned yellow on refluxing for one hour and on cooling the yellow complex was precipitated, (0·15g., 30%); ν(Rh-H), 2079cm^{-1}. (Found: C, 51·4; H, 4·5; Cl, 8·3 %).

6. Carbonyl and hydride complexes

Bis(tetramethylammonium)chlorocarbonylbis(trichlorostannato)rhodate(I)

(a) Tetracarbonyl-$\mu\mu'$-dichlorodirhodium(I) (0·37g.) in ethanol (50 ml.) was treated with $SnCl_2$ (0·7g.) followed by Me_4NCl (0·05g.) in methanol (5 ml.), after evolution of carbon monoxide had ceased, to give the orange salt (1·3g., 85%) (Found: C, 13·6; H, 3·0; O, 3·5; Cl, 34·3; Sn, 35·6. $C_9H_{24}OCl_4SnRh$ requires: C, 14·5; H, 3·2; O, 2·2; Cl, 33·2; Sn, 31·1 %). The salt could not be satisfactorily recrystallized, but using a deficiency of Me_4NCl a reasonably pure product can be obtained. The second carbon monoxide cannot be replaced at reaction temperatures up to 100°.

(b) $(Me_4N)_2[Rh_2Cl_2(SnCl_3)_4]$ (0·54g.) in acetone (15 ml.) was treated with carbon monoxide for 8 hours at 100 atm. and 20°. After vacuum evaporation the residue was extracted with petroleum (B.p. 40-60°) which removed a small amount of $[Rh(CO)_2Cl]_2$ leaving the orange salt. (Found: C, 12·6; H, 3·1; O, 3·3; Cl, 35·7; Sn, 33·8 %). The reaction with carbon monoxide at room temperature and pressure is slow and incomplete in 2-3 days.

Bis(tetramethylammonium)dicarbonyldichlorobis(trichlorostannato)-ruthenate(II)

(a) Dicarbonyldichlororuthenium(II) (0·3g.) was refluxed in 3M-hydrochloric acid (25 ml.) with $SnCl_2,2H_2O$ (1·2g.) for one hour. Addition of Me_4NCl (0·5g.) in water (5 ml.) to the yellow solution precipitated the yellow complex (0·7g., 75%); recrystallized from 3M-hydrochloric acid-ethanol. (Found: C, 14·3; H, 2·8; O, 7.3; Cl, 32.4; Sn, 29·1. $C_{10}H_{24}O_2Cl_8Sn_2Ru$ requires: C, 14·2; H, 2·9; O, 3·8; Cl, 33·5; Sn, 28·0 %). The salt is soluble in acetone, nitromethane and dimethylformamide.

(b) $(Me_4N)_2[RuCl_2(SnCl_3)_2]$ (0·5g.) was suspended in acetone (15 ml.) and reacted with carbon monoxide at 85 atn. and 120° for 3 days. Most of the salt remained undissolved and unreacted, but evaporation of the acetone solution yielded a very small amount of solid showing carbonyl bonds in the infrared spectrum: it was not investigated further.

Reaction of $Ir(CO)_3Cl$ with stannous chloride

Carbon monoxide was bubbled through a refluxing solution of $Na_2IrCl_6,6H_2O$ in 2-methoxyethanol until the colour changed from brown to pale yellow (ca 2-3 hours). The solution at this stage is air sensitive and contains $Ir(CO)_3Cl$ (75). Addition of stannous chloride (8M excess) turns the solution yellow, which slowly becomes a deeper yellow on standing. When methanolic Me_4NCl is added gradually a white solid is first precipitated with no carbonyl absorption in the infrared spectrum, but subsequently a yellow solid slowly precipitates (ν C=O, 2040cm^{-1}). If the solution is refluxed, after the addition of stannous chloride, an orange solution is obtained from which the addition of Me_4NCl, in methanol, precipitates another yellow solid (ν C=O, 1985cm^{-1}). Neither of the solids give consistent analyses. Refluxing with less $SnCl_2$ (4M excess) gives a brown solution, from which no Me_4N^+ salt could be precipitated.

Bis(tetramethylammonium)carbonyltrichlorobis(trichlorostannato)-iridate(III)

$Na_2IrCl_6,6H_2O$ (0·32g.) was dissolved in ethanol (40ml.) in the cold. Addition of $SnCl_2$ (0·35g.) immediately precipitates all the iridium from solution as a light brown precipitate. On refluxing for 5 mins. the precipitate redissolves to an amber solution which precipitates $(NMe_4)_4[Ir_2Cl_6(SnCl_3)_4]$ on the addition of Me_4NCl. When the solution is refluxed for a longer period (ca 1 hour), the addition of Me_4NCl (0·12g.) in methanol (4 ml.) gives a fine yellow precipitate which is difficult to filter. It was collected by centrifuging and washed by decantation with alcohol and ether and finally dried on filter paper. Dissolution in dimethylformamide followed by re-precipitation with ethanol leaves the salt (0·4g., 75%) (Found: C, 11·1; H, 3·1; O, 2·0; Cl, 35·5; Sn, 24·7. $C_9H_{24}OCl_9Sn_2Ir$ requires

C, 11·6; H, 2·6; O, 1·7; Cl, 34·4; Sn, 25·6 %). The salt is insoluble in all common solvents except dimethylformamide. The same reaction takes place using 2-methoxyethanol as the solvent, and the initial precipitate is reasonably pure (Found: C, 10·5; H, 2·8; O, 1·9; Cl, 34·2%).

Treating the initial ethanolic solution of $Ir_2Cl_6(SnCl_2.solv.)_4$ with carbon monoxide at 50 atn. and room temperature does not react completely to form the carbonyl complex and mixtures of the two species appear to be present.

Reaction between ruthenium trichloride and stannous chloride in alkanolic solvents

Ruthenium trichloride hydrate (0·6g.) and an 8M excess of $SnCl_2$(3g.) were refluxed together in 2-methoxyethanol (30ml.) for 4 hours. The initially blue solution slowly turned yellow and a small amount of metallic ruthenium was also formed. The solution shows a carbonyl stretching frequency at $2070cm^{-1}$; but addition of Me_4NCl gave an almost white precipitate with only a weak carbonyl bond. This is attributed to the precipitation of a large excess of $(NMe_4)(SnCl_3)$, but attempts to remove the excess stannous chloride, before precipitation, by chromatography were not successful. If the reaction is repeated using less (4M excess) stannous chloride copious quantities of metallic ruthenium are formed while the blue solution turns brown, instead of yellow.

Tris(triphenylphosphine)hydridochloro(trichlorostannato)iridium(III)

A mixture of $Na_2IrCl_6,6H_2O$ (0·5g.), $SnCl_2$ (1g.) and triphenylphosphine (1·88g.) was refluxed im ethanol (40ml.) for 1½ hours under nitrogen. The orange solution was filtered hot and on cooling a yellow-orange solid separated (0·88g., 80%). (Found: C, 52·9; H, 4·1; Cl, 10·4; Sn, 8·2; M(chloroform), 1119; $C_{54}H_{46}P_3Cl_4SnIr$ requires: C, 52·1; H, 3·7; Cl, 11·4; Sn, 9·5 %; M, 1243). The presence of oxygen (2·6%) in the compound and bands in the infrared spectrum at 1115 and 723cm^{-1} indicate the presence of triphenylphosphine oxide in the molecule. However the complex cannot be purified since it dissociates somewhat in solution loosing stannous chloride. After several recrystallizations from methylene chloride-ethanol the pale cream chloro-complex, $(Ph_3P)_3IrHCl_2$, m.p. 150-152° (Found: C, 59·0; H, 4·5; Cl, 8·8. Calcd. for $C_{54}H_{46}P_3Cl_2Ir$: C, 61·5; H, 4·4; Cl, 6·7%) is recovered. Its colour, m.p., solubility and infrared and n.m.r. spectra are closely similar to those for the monohydride prepared by refluxing sodium chloroiridate(IV) with excess triphenylphosphine in 2-methoxyethanol.

Tris(triphenylphosphine)dihydrido(trichlorostannato)iridium(III)

$Na_2IrCl_6,6H_2O$ (0·20g.), $SnCl_2$ (0·40g.) and triphenylphosphine (0·75g.) were refluxed under nitrogen in 2-methoxyethanol (50 ml.) for 1½ hours. About half the solvent was removed by distillation under reduced pressure, during which white crystals began to form. These were collected and recrystallized from methylene-chloride-ethanol leaving the pure complex (Found: C, 53·8; H, 4·0; Cl, 9·0; Sn, 9·6. $C_{54}H_{47}P_3Cl_3SnIr$ requires: C, 53·7; H, 3·9; Cl, 8·7; Sn, 9·8 %). The complex is soluble in dichloromethane and chloroform.

Evaporation of the filtrate after removal of the dihydride, followed by treatment with ethanol, leaves a yellow solid, which on recrystallization from methylene chloride-ethanol gives $(Ph_3P)_3IrHCl_2$ as above.

Bis(triphenylphosphine)carbonylhydridodichloro(trichlorostannato)-iridium(III).acetonate

(a) Bis(triphenylphosphine)carbonylchloroiridium(I) (0·2g.) was suspended in acetone (10 ml.), and on treatment with $SnCl_2$ (0·4g.) dissolved to a yellow solution. This was filtered and left to stand under nitrogen. The solution slowly turns cloudy and on standing overnight crystals are deposited, leaving the supernatant liquor clear. The solution is left a further 24 hours in order to obtain a maximum yield of the crystals, which are then collected and washed with acetone (0·12g., 45%) (Found: C, 44·3; H, 3·4; O, 3·2; Cl, 14·6; Sn, 13·7. $C_{40}H_{37}P_2O_2Cl_4SnIr$ requires: C, 45·1; H, 3·5; O, 3·0; Cl, 13·3; Sn, 11·1 %). The pale off-white crystals become opaque at 166-170° and melt at 199-201°. On recrystallization from methylene chloride-ethanol the compound looses acetone and stannous chloride to give a mixture of $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ and $(Ph_3P)_2IrHCl_2(CO)$. Extraction with methylene chloride leaves an insoluble residue of the latter identified by its infrared spectrum (Found: C, 53·7; H, 4·0; Cl, 9·1. Calcd. for $C_{37}H_{31}P_2Cl_2OIr$: C, 58·4; H, 4·1; Cl, 9·3 %).

Evaporation of the filtrate, left after removal of the crystalline product, followed by extraction with ethanol to remove excess stannous chloride, leaves a very pale yellow solid whose infrared spectrum shows it to be predominately $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$ and $(Ph_3P)_2Ir(CO)HCl_2$ with small amounts of $(Ph_3P)_2Ir(CO)Cl$.

(b) Bis(triphenylphosphine)carbonylhydridodichloroiridium(III) (0·2g.) was refluxed with $SnCl_2$ (0·5g.) in acetone (25 ml.) for 2 hours under nitrogen. On cooling the yellow solution was filtered from a small amount of white solid and evaporated to dryness. Extraction with ethanol to remove excess stannous chloride leaves a pale yellow residue whose infrared spectrum shows the presence of predominately $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$.acetone contaminated with a smaller quantity of $(Ph_3P)_2Ir(CO)Cl$. Recrystallization gives the same behaviour as in (a).

<u>(Triphenylphosphine)carbonyldichloro(trichlorostannato)iridium(III)</u>

(a) Bis(triphenylphosphine)carbonylchloroiridium(I) (0·2g.) was refluxed in stannic chloride (5 ml.) under dry nitrogen for 18 hours. The solution was cooled and the excess stannic chloride was quickly poured off under dry nitrogen and the flask and its contents washed several times with dry benzene (4x10ml.) by decantation to remove all stannic chloride. During these operations the solid becomes sticky and adheres to the sides of the flask. Subsequent treatment with methylene chloride breaks it up to a pale yellow <u>powder</u> which is insoluble in all common solvents. (Found: C, 29·1; H, 2·0; Cl, 25·0; Sn, 15·8. $C_{19}H_{15}Cl_5SnIr$ requires: C, 29·2; H, 1·9; Cl, 22·7; Sn, 15·2%).

(b) Bis(triphenylphosphine)carbonylhydridodichloroiridium(III)

(0·23g.) was refluxed in stannic chloride (5 ml.) for 18 hours under dry nitrogen. Decantation of excess stannic chloride followed by washing with benzene (4x10 ml.) leaves a black mass, which on treatment with methylene chloride breaks up into a pale yellow powder identical to that in (a). The initial black colour may be due to a surface coating of metallic iridium, but the sample appears to be reasonably pure (Found: C, 28·4; H, 2·1; Cl, 24·9; Sn, 14·8 %).

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