

992. *Complexes of Ruthenium, Rhodium, Iridium, and Platinum with Tin(II) Chloride.*

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The interaction of platinum-metal salts with tin(II) chloride leads to complex anions of ruthenium, rhodium, iridium, and platinum which have been isolated as salts of large cations. The anions are formulated $[\text{RuCl}_2(\text{SnCl}_3)_2]^{2-}$, $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$, $[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]^{4-}$, and *cis*- and *trans*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, where the trichlorostannate(II) ion is considered to be acting as a donor anionic ligand of strength comparable to chloride ion.

Neutral complexes of rhodium, iridium, and platinum have been prepared which have an SnCl_3 group bound to the metal together with ligands such as di-olefins, and triphenyl-phosphine and -arsine, examples being $(\text{C}_7\text{H}_8)_2\text{RhSnCl}_3$ and $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$.

It has long been known that the interaction of tin(II) chloride with solutions of platinum and other platinum-metal salts gives coloured species,¹ which have been utilised analytically,² but until recently³ the nature of the species present in solution was uncertain. We now give details of our studies^{3b} and their extensions.

Complex Tin-containing Anions of Ruthenium, Rhodium, Iridium, and Platinum.—In dilute hydrochloric acid solution, tin(II) chloride reacts at room temperature with rhodium(III) chloride and with sodium chloroplatinate(II) to give dark red solutions. Ruthenium(III) chloride and sodium hexachloroiridate(IV) require heating on a water-bath and give orange-red and amber solutions, respectively. Other water-soluble compounds of the metals such as hexachloroplatinate(IV) or sodium hexachlororhodate(III) behave similarly and give the same resultant species as indicated by the similarity in the electronic absorption spectra of the solutions (Table 1) and the identity of the isolated salts (Table 2). Palladium forms an unstable complex with tin(II) chloride but no detailed study has yet been made.

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—we have usually employed tetramethylammonium chloride—gives precipitates under conditions where neither tin(II) nor tin(IV) complex chloro-anions are precipitated. The salts can be crystallised from mixtures of ethanol with 3M-hydrochloric acid. They are moderately soluble in acetone, nitromethane, and dimethylformamide, in which they give conducting solutions; they are insoluble in non-polar organic solvents and also in ethanol, diethyl ether, or tetrahydrofuran. The solid are air-stable and the aqueous acid solutions of the anions are also stable with the exception of the platinum solutions, which are moderately air-sensitive and are best handled under nitrogen.

¹ For extensive references see Shukla, *Ann. Chim. (France)*, 1961, **6**, 1383.

² See "Treatise on Analytical Chemistry," The Platinum Metals, ed. Kolthoff and Elving, Interscience-Wiley, New York and London, 1963, Part II, Vol. 8.

³ (a) Cramer, Jenner, Lindsay, and Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691; (b) Davies, Wilkinson, and Young, *ibid.*, p. 1692.

TABLE 1.

Electronic spectra of anionic tin(II) chloride complexes of Ru, Rh, Ir, and Pt.

Metal	$\lambda_{\max.}$ (m μ) (ϵ in parentheses)		Ref.
	NMe ₄ ⁺ salts *	Anionic species †	
Ruthenium	439 (1.1 × 10 ³), 306 (1.5 × 10 ⁴)	438 (1.7 × 10 ³), 305 (2.7 × 10 ⁴)	‡
		441 (2.5 × 10 ³), 303 (4.0 × 10 ⁴)	(a)
Rhodium	425 (1.1 × 10 ³), 303 (6.8 × 10 ⁴)	206.5 (6.3 × 10 ⁴)	
		462 (4.0 × 10 ³)	
		419 (3.3 × 10 ³), 310 (2.8 × 10 ⁴)	‡
		470	(b)
		475 330	(c)
		475 (3.9 × 10 ³)	(d)
Iridium	326 (1.0 × 10 ⁴)	473 (~5.0 × 10 ³), 330—340 (~2.5 × 10 ³)	(e)
		418	‡ (e)
		321 (3.6 × 10 ⁴)	‡
		355	‡
Platinum (red isomer)	401 (1.6 × 10 ³), § 310 (1.2 × 10 ⁴) 254 (1.6 × 10 ⁴)	403 (8.0 × 10 ³), 310 (~3.5 × 10 ³)	
		403 310	(g)
Platinum (yellow isomer)	310sh, ¶ 278 (1.2 × 10 ⁴), 254 (1.3 × 10 ⁴)	403 (7.8 × 10 ³), 310 (4.0 × 10 ⁴)	(h)

* 1 : 1 HCl solutions. † HCl solutions at least 0.5M in SnCl₂. ‡ 3M-HCl solutions. § Acetone solution. ¶ May be due to presence of red isomer in solution.

(a) Okuno *et al.*, Proc. 7th U.C.C.S. (Stockholm), 1962, Abstr. 4 E3; (b) Maynes and McBryde, *Analyst*, 1954, **79**, 230; (c) Ayres *et al.*, *Analyt. Chem.*, 1955, **27**, 1742; (d) Berman and Ironside, *Canad. J. Chem.*, 1958, **36**, 1151; (e) Shukla, *Ann. Chim. (France)*, 1961, **6**, 1383; (f) Berman and McBryde, *Analyst*, 1956, **81**, 566; (g) Ayres and Meyer, *Analyt. Chem.*, 1951, **23**, 299; (h) Berman and Goodhue, *Canad. J. Chem.*, 1959, **37**, 370.

TABLE 2.

Salts of anionic platinum-metal-tin(II) chloride complexes.

Salt	Colour	M. p.	$\Lambda_m(10^{-3}M)$ *		Type
			DMF	MeNO ₂	
(Me ₄ N)[RuCl ₂ (SnCl ₃) ₂]	Orange	d. >200°	125	113	1 : 2
(Ph ₃ PH)[RuCl ₂ (SnCl ₃) ₂]	Yellow	177—180	80	87	1 : 2
(Me ₄ N) ₄ [Rh ₂ Cl ₂ (SnCl ₃) ₄]	Orange	d. >250	244	—	1 : 4
(Ph ₃ PH) ₄ [Rh ₂ Cl ₂ (SnCl ₃) ₄]	Yellow-orange	137—138	119	—	1 : 4
(Me ₄ N) ₂ [RhCl(CO)(SnCl ₃) ₂]	Orange	d. >200	151	135	1 : 2
(Me ₄ N) ₄ [Ir ₂ Cl ₆ (SnCl ₃) ₄]	Yellow-orange	d. >300	240	244	1 : 4
(Ph ₃ PH) ₄ [Ir ₂ Cl ₆ (SnCl ₃) ₄]	Yellow	112—117	165	162	1 : 4
(Me ₄ N) ₂ [PtCl ₂ (SnCl ₃) ₂]	Red	d. >250	133	128	1 : 2
(Ph ₃ MeP) ₂ [PtCl ₂ (SnCl ₃) ₂]	Yellow	d. 195—200	140	—	1 : 2
(Ph ₃ MeP) ₂ [PtCl ₂ (SnCl ₃) ₂]	Yellow	50	—	—	—

* Conductivity ranges for electrolyte types in both dimethylformamide (DMF) and nitromethane (MeNO₂) are, in ohm⁻¹ cm.² mol.⁻¹: 1 : 1, 55—80; 1 : 2, 110—150; 1 : 3 (extrapolated), 175—220; 1 : 4, >230.

The reaction of platinum-metal salts with tin(II) chloride also proceeds in organic solvents such as ethanol and acetone. It has also long been known that the red platinum and rhodium complex can be extracted from aqueous acid solutions by solvents such as ethyl acetate.² In organic solutions we consider that species similar to (I)—(IV) are present but with the SnCl₃⁻ replaced by solvated SnCl₂ so that the species are neutral. Attempts to isolate solids from organic solutions have failed and only red gums remain on removal of solvent. The addition of tetramethylammonium chloride to the ethanolic solutions for rhodium and platinum gives salts identical with those obtained from 3M-hydrochloric acid solutions. On heating solutions of hydrated ruthenium(III) chloride with tin(II) chloride in ethanol dark blue solutions, which appear to contain ruthenium(II) and not a tin-containing complex, are obtained.

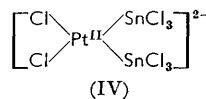
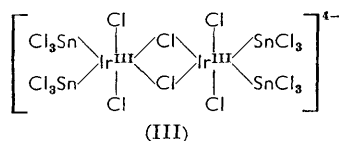
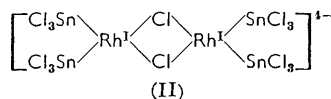
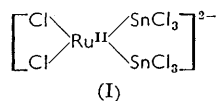
The salts and some of their properties are summarised in Table 2 and the complex anions formulated as (I)—(IV). This is on the basis of analyses, conductivities, diamagnetism, and the fact that if we regard^{3b} the trichlorostannate(II) ion as a donor ligand using its

lone-pair electrons,⁴ the usual common formal oxidation states and stereochemistries of the platinum metals can be preserved. While it is possible to regard the complex ions as having tin(IV) bound to the platinum-metal atom, as appears to be the case in some other transition-metal-tin complexes such as $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{SnCl}_3$,⁵ we believe that it is more realistic to regard the present complexes as containing the trichlorostannate(II) ion acting as a donor. The ruthenium complex may be polymeric in the solid state through chlorine bridges giving octahedral co-ordination, as is the case for $\text{Ru}(\text{CO})_2\text{I}_2$ and $\text{C}_7\text{H}_8\text{RuCl}_2$, but it is undoubtedly a discrete ion in solution, where the remaining co-ordination sites could be occupied by solvent molecules.

A study of the rhodium(III) chloride-tin(II) chloride reaction in either 3*M*-hydrochloric acid or in ethanol, using the Job method, shows that three molecules of tin(II) are required per molecule of rhodium(III), indicating the utilization of one molecule of tin(II) for reduction of rhodium(III) to rhodium(I) and two molecules of tin(II) for complexation. Further, as discussed below, stronger π -bonding ligands such as triphenylphosphine or carbon monoxide will displace tin from the complexes as tin(II); conversely, tin(II) will displace the volatile carbon monoxide from carbonyl complexes, or other weakly bound ligands such as mesityl oxide which is displaced from its complex with platinum(II) chloride. In certain cases it can be shown that the displacement reactions are reversible.

Platinum complexes. *cis-trans* Isomerism is possible in the planar complexes of ruthenium and platinum. In the case of platinum, we have been able to isolate two isomers of $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ as the tetramethylammonium salts, one of which is red and the other yellow. The *cis*- and the *trans*-ion both exist in solutions at Sn : Pt ratios of 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. We discuss first the ions and salts derived from solutions where the ratio is low.

The addition of anhydrous stannous chloride to a solution of sodium chloroplatinite in ethanol so that the Pt : Sn ratio is 1 : 2 gives an orange-red solution which on standing under nitrogen at room temperature (*ca.* 15 min.) slowly changes colour, becoming orange-yellow. Addition to this solution of a slight excess of tetramethylammonium chloride quantitatively precipitates a yellow crystalline salt. The salt, when dissolved in



acetone, is re-precipitated as yellow needles by the addition of ethanol; it analyses as $(\text{Me}_4\text{N})_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$. When tetramethylammonium chloride, in a calculated deficiency sufficient to precipitate 60% of the platinum, is added to the red solution immediately after mixing, a red crystalline precipitate is obtained quantitatively. Dissolution in acetone followed by re-precipitation with ethanol gives red needles whose analysis also corresponds to $(\text{Me}_4\text{N})_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$. The solution after precipitation of the red salt is still yellow, and the addition of excess of tetramethylammonium chloride precipitates yellow crystals, in *ca.* 40% yield, identical with those obtained from the aged solutions. The same red-yellow isomerism occurs in 3*M*-hydrochloric acid solutions, and both yellow and red tetramethylammonium salts, identical with those obtained from ethanol solutions, can be precipitated in the same way.

⁴ Grdenic and Kamenar, *Proc. Chem. Soc.*, 1961, 304; *J. Inorg. Nuclear Chem.*, 1962, **24**, 1039.

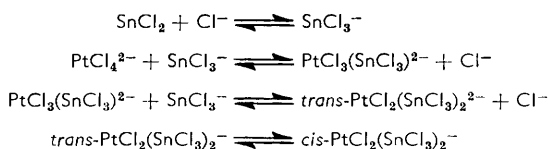
⁵ (a) Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486; (b) Bonati and Wilkinson, *J.*, 1964, 179.

We consider these red and yellow anionic species to be *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 different, and no lines due to the yellow isomer were observed in the red crystals obtained on immediate precipitation as above. The red isomeric anion appears to be the predominant form in fresh solutions with Pt : Sn = 1 : 2, at room temperature, 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 ratios 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.* -70° . This solid is presumably a mixture of yellow $(\text{NMe}_4)_2[\text{PtCl}_2(\text{SnCl}_3)_2]$ and $(\text{NMe}_4)(\text{SnCl}_3)$, 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. However, even when the yellow precipitate is collected and thoroughly washed at this low temperature, it isomerises rapidly on warming, probably through occluded stannous chloride or $(\text{NMe}_4)(\text{SnCl}_3)$ even though the X-ray powder pattern of the isomerised material showed no lines due to these substances.

The observations above 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 1) are sufficiently different to enable the equilibrium shifts to be observed. The addition of trichlorostannate(II) ion to a solution of the yellow salt in 6M-hydrochloric acid promotes the growth of peaks at 400 and 310 μ at the expense of the one at 278 μ . In 3M-hydrochloric acid solutions of Pt : Sn ratio 1 : 2, the peaks due to the red isomer at 400 and 310 μ predominate initially, but decrease in intensity with time while a new peak at 280 μ 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 310 μ , as was observed for solutions of the yellow salt above.

It has not been possible to determine unequivocally the configurations of the two isomers. However, we consider the yellow form to be the *cis*-isomer. We expect some $d_{\pi}-d_{\pi}$ bonding between platinum and tin which would cause the *cis*-isomer to be more stable than the *trans*-, because in the latter configuration there will be competition between the two SnCl_3^- groups for the same d -orbitals of platinum and hence weaker π -bonding. Our results 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. We would expect the *cis*-isomer 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. We cannot, however, be certain of the true intensities of the spectral bands of the yellow form because (a) we are dealing with allowed intensities which are temperature dependent, (b) we do not know the exact conditions under which the yellow isomer only is present in solution, and (c) complex-formation may be incomplete at these necessary conditions. It is probable that several interdependent equilibria exist simultaneously in solution, of the type:



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 initial formation of the *trans*-isomer which is what is observed. The stabilization of the *trans*-isomer by excess SnCl_3^- can be interpreted as the suppression of a dissociation mechanism through which isomerization probably occurs. The presence of so many species in solution at equilibrium will make determination of accurate thermodynamic constants for the system very difficult. We have not yet found a suitable method to determine these quantities reliably.

With the concentration of tin above Pt : Sn of 1 : 2, the absorption of $(\text{SnCl}_3)^-$ or solvated stannous chloride obscures the region below 290 $m\mu$, so that the presence or absence of the yellow species cannot be detected. Using the band at 400 $m\mu$, it appears that Beer's Law is not obeyed until the Sn : Pt ratio is above 8 : 1; above this ratio, Beer's Law is obeyed. Addition of tetramethylammonium chloride to solutions in ethanol or 3M-hydrochloric acid with ratios of Pt : Sn from 1 : 2 up to 1 : 10 gives red precipitates. The solids after dissolution in acetone and re-precipitation by ethanol have variable compositions. We have, indeed, obtained samples whose analyses correspond quite well to $(\text{NMe}_4)_3[\text{Pt}(\text{SnCl}_3)_5]$. 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 6.

No lines due to $(\text{NMe}_4)(\text{SnCl}_3)$ or other free tin species appear in 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-ordinate ion, $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$, but it is surprising that the X-ray powder patterns of the "high tin" solids are identical with that of the red $(\text{NMe}_4)_2[\text{PtCl}_2(\text{SnCl}_3)_2]$ salt, and that there is no change in the line pattern in spite of variable analyses.

It is conceivable that further co-ordination of tin to form a 5 : 1 species in solution might occur. However, there is no appreciable change in the electronic spectrum for high tin ratios. For ethanol and 3M-hydrochloric acid solutions, Job plots of the platinum-tin system using the band at 400 $m\mu$ rise to a maximum at a Pt : Sn ratio of 1 : 2 ($5 \times 10^{-3}\text{M}$ -Pt) but show little change with additional tin concentration up to *ca.* 1 : 6 ratio, confirming that more than one species is present, as is also indicated by the failure of the band at 400 $m\mu$ to obey Beer's Law, referred to above. This may be explained by *cis-trans*-isomerisation of the 1 : 2 species.

Although the fine needle-shaped red crystals obtained from solutions with high tin concentrations, which give analytical data for $(\text{NMe}_4)_3[\text{Pt}(\text{SnCl}_3)_5]$, appear to be quite homogeneous under the polarising microscope, dissolution in acetone and crystallisation on a slide gives a mixture of approximately equal amounts of red and white crystals. The solubilities of $(\text{NMe}_4)(\text{SnCl}_3)$ in ethanol and 3M-hydrochloric acid are extremely similar to those of red $(\text{NMe}_4)_2[\text{PtCl}_2(\text{SnCl}_3)_2]$, so that it is not unexpected that we have been unable to separate the components by normal crystallization procedures or by elution from anion-exchange resins.

Another argument against the existence of a complex ion in solution containing five tin species co-ordinated to each platinum is that the red salt (apparently 5 : 1) 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 is performed at -70° , however, a yellow solid is obtained which, even after collection and washing, becomes red again when allowed to warm to room temperature.

However, in agreement with other studies,^{3a} it seems to be reasonably certain that a quinqueco-ordinated ion, $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$, is stabilized in the crystals by large cations and that the solids of intermediate analyses are mixtures of salts of this ion and of $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$. Intercomparison of our high-tin crystals and the American material indicates that they are identical. The only well authenticated example of quinqueco-ordinated platinum(II) involves a multidentate ligand. Platinum(II) appears to have a limited affinity for strongly π -bonding ligands, as in such compounds as $(\text{R}_3\text{P})_2\text{PtCl}_2$, $(\text{R}_3\text{Sb})_2\text{PtCl}_2$, and $(\text{CO})_2\text{PtCl}_2$.

Using triphenylmethylphosphonium ion as precipitant, we have found that there is a

more facile interconversion between the crystalline forms than with the tetramethylammonium salts, and consequently it is more difficult to obtain the pure isomers. It was possible to obtain the yellow isomer as an amorphous solid by precipitating it at -70° from solutions with Pt : Sn ratios of 1 : 2.5 and washing it thoroughly with ethanol at this temperature. The salt rapidly changes into a mixture when heated to 50° . When precipitated at room temperature from aged ethanolic solutions with a Pt : Sn ratio of 1 : 2 it isomerises to an orange oil too rapidly to be isolated. Precipitation with a deficiency of triphenylphosphonium chloride from such solutions immediately on mixing 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 close to $(\text{Ph}_3\text{MeP})_2[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]$. On cooling (to -70°) or heating (to 80°) the ethanolic suspensions of these solids after precipitation, there is a reversible, but incomplete, shift to the yellow and red forms, respectively. We do not know if these orange solids contain the pure red isomer; the colour is very different from that of the red tetramethylammonium salt.

Other Ligand-replacement Reactions.—Using platinum and rhodium complexes we find that tin(II) chloride can displace other ligands in addition to the chloride ion as in the previous section. Thus, the interaction of tin(II) chloride with potassium ethylenetrichloroplatinate(II), (mesityl oxide)dichloroplatinum(II), and cyclo-octa-1,5-dienedichloroplatinum(II) gives the ion $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, whilst the rhodium complex ion (II) can be obtained from bis(norbornadiene)- $\mu\mu'$ -dichlorodirrhodium(I). In absolute ethanol anhydrous tin(II) chloride and tetracarbonyl- $\mu\mu'$ -dichlorodirrhodium(I) interact, leading to bridge-cleavage and partial carbon monoxide displacement. On addition of tetramethylammonium chloride, the salt of the ion $[\text{RhClCO}(\text{SnCl}_3)_2]^{2-}$ is obtained.

In a number of cases the reverse reaction, namely the displacement of the tin(II) chloride ligand, can be achieved; the displaced tin can be shown to be in the (II)-state by standard chemical tests such as the cacotheline reaction. The tetramethylammonium salts can be substituted only with difficulty, but with amines the ruthenium and rhodium salts gave, respectively, $\text{Ru py}_4 \text{Cl}_2$ and $\text{Rh}(p\text{-toluidine})_3\text{Cl}_3$. The platinum salt in ethanol suspension at room temperature reacts readily with triphenylphosphine to give $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ while the chlorine bridge in the rhodium salt is readily cleaved by carbon monoxide to give the salt of the ion $[\text{RhClCO}(\text{SnCl}_3)_2]^{2-}$.

The tin complexes prepared in ethanolic solution undergo displacement reactions much more readily, however. Thus, at room temperature and pressure, carbon monoxide displaces tin(II) chloride from the red complex to give high yields of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. Cyclo-octa-1,5-diene, 4-vinylcyclohexene, and dicyclopentadiene give complexes $(\text{diene})_2\text{Rh}_2\text{Cl}_2$, whereas norbornadiene gives $(\text{C}_7\text{H}_8)_2\text{RhSnCl}_3$ (see below). In the same way we could prepare cyclo-octa-1,5-dienedichloroplatinum(II); the formation of Zeise's salt by tin-displacement has also been achieved.^{2a}

Tin-containing Olefin Complexes.—Although the interaction of ethanolic solutions of

TABLE 3.

Trichlorostannato-complexes of Rh, Ir, and Pt with olefin and triphenyl-phosphine, -arsine, and -stibine ligands.

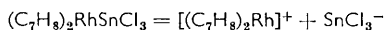
Compound *	Colour	M. p.	Λ_m †
$(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$	Red-brown	130—132°	9
$(\text{NBD})_2\text{RhSnCl}_3$	Yellow	decomp. 170—177	3.3
$(\text{Ph}_3\text{P})_2(\text{NBD})\text{RhSnCl}_3$	Orange	134—135	8.7
$(\text{Ph}_3\text{As})_2(\text{NBD})\text{RhSnCl}_3$	Orange	decomp. 177—179	5.1
$(\text{Ph}_3\text{Sb})_2(\text{NBD})\text{RhSnCl}_3$	Orange	decomp. ~200	5.0
$(\text{NBD})_2\text{IrSnCl}_3$	Pale yellow	decomp. 230—240	Insol.
$(\text{COD})_2\text{IrSnCl}_3$	Yellow	decomp. 178—180	..
$(\text{Ph}_3\text{P})_2(\text{COD})\text{IrSnCl}_3$	Yellow	decomp. 127—130	30
$(\text{Ph}_3\text{As})_2(\text{COD})\text{IrSnCl}_3$	Yellow	171—174	16
$(\text{Ph}_3\text{P})_2\text{ClPtSnCl}_3$	Orange	—	62
$(\text{Ph}_3\text{As})_2\text{ClPtSnCl}_3$	Orange	150—151	54

* NBD = norbornadiene; COD = cyclo-octa-1,5-diene. † In nitromethane at 10^{-3}M .

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rhodium(III) chloride and tin(II) chloride with cyclo-octa-1,5-diene and other poly-olefins gave the well known halogen-bridged binuclear olefin complexes, norbornadiene, as noted above, gives a compound $(C_7H_8)_2RhSnCl_3$, whilst corresponding reactions with iridium salts give the olefin complexes $(di-olefin)_2IrSnCl_3$ in all cases. The crystalline complexes (Table 3) are precipitated from solutions slowly at room temperature and more rapidly on warming. Although the initially amber iridium-tin solutions become yellow, we have been unable to isolate crystalline products using cyclohexa-1,3-diene, cyclohexa-1,4-diene, 1,5-dimethylhexa-2,5-diene, or butadiene. It is noteworthy that for the iridium complexes isomerisation of the olefin appears to occur on complex-formation. Thus, cycloheptatriene gives a complex identical with the one from norbornadiene, whilst cyclo-octa-1,3-diene and 4-vinylcyclohexene appear to give the same 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 olefinic group which would be expected if it were acting as a diene. The compounds and their phosphine-substituted derivatives are too insoluble to allow unequivocal characterisation by n.m.r. studies. The formation of the complexes where isomerisation occurs is considerably slower than with norbornadiene and cyclo-octa-1,5-diene.

The olefin complexes are only sparingly soluble in polar organic solvents and are insoluble in benzene and petroleum. Attempts to increase the solubility of the complexes by direct alkylation of the $SnCl_3$ groups by Grignard reagents, alkyl-lithiums, dimethyl-, and diethyl-mercury, and tetraethyl-lead were unsuccessful. However, more soluble compounds of similar type can be obtained by interaction of the complexes with triphenylphosphine, which displaces one di-olefin molecule to give complexes of the stoichiometry $(diene)(Ph_3P)_2IrSnCl_3$. The norbornadiene-iridium complex did not react with triphenylphosphine, in accord with its greater thermal stability. The molecular weights of the triphenylphosphine-substituted complexes show that they are monomeric, and this fact, coupled with the non-conductance of nitromethane solutions of the compounds $(di-olefin)_2MSnCl_3$, suggests that in all cases we have quinqueco-ordinate structures. The complex $(C_7H_8)_2RhSnCl_3$ is appreciably soluble in water, and the solutions give precipitates with large anions, suggesting the dissociation:



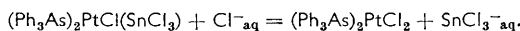
A white tetraphenylborate salt has been characterised and the aqueous solution contains tin(II). Although a similar reaction does not occur with the more stable norbornadiene-iridium complex, the cyclo-octa-1,5-diene complex ion, $(C_8H_{12})_2Ir^+$, can be obtained as its tetraphenylborate from aqueous dimethylformamide solutions.

Other Triphenyl-phosphine and -arsine Complexes.—The interaction of ethanolic solutions of platinum-metal salts and tin(II) chloride with triphenyl-phosphine and -arsine leads to complexes similar to the above olefin-containing species (Table 3). Thus, from ethanolic platinum-tin solutions we obtain 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 solutions. However, the latter complex dissolves in acetone containing excess of tin(II) chloride to re-form the orange tin complex. It appears therefore that we have an equilibrium:



Under no conditions tried have we been able to isolate the reported^{3a} complex $(Ph_3P)_2Pt(SnCl_3)_2$ even from solutions saturated with tin(I) chloride.

Triphenylarsine gives a similar platinum complex which appears to be more stable towards dissociation in acetone solutions than the triphenylphosphine complex; however, it can be converted into $(Ph_3As)_2PtCl_2$ on treatment with dilute hydrochloric acid:



Again, the aqueous solution contains tin(II).

The interaction of rhodium-tin solutions in ethanol with triphenylphosphine gives brown-red crystals of $(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$, which, like the above platinum complexes, are presumably square planar. No clean product could be isolated from iridium solutions treated in the same manner.

The addition of triphenylphosphine to aqueous acid solutions containing the complex ions merely precipitated the triphenylphosphonium salts which were recognised by the characteristic P-H stretching frequency at *ca.* 2400 cm^{-1} , except for solutions containing $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ which again gave $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$ as an orange precipitate.

EXPERIMENTAL

Microanalyses and molecular-weight measurements (at 37° using a Mechrolab Osmometer unless otherwise specified) are by the Microanalytical Laboratory, Imperial College. *M. p.s* were determined with a Kofler hot-stage microscope. Infrared spectra were determined in Nujol mulls (unless otherwise specified) using a Grubb-Parsons grating Spectromaster instrument, electronic spectra on a Perkin-Elmer model 350 recording spectrophotometer, and n.m.r. spectra on a Varian Model 43100 at 56.5 Mc./sec. X-Ray powder photographs were taken on a Guinier powder camera.

It was shown that tin(II) can be detected by the standard cacotheline reagent in non-aqueous media.

Molar conductivities (Λ_m) are given in $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ with the medium in parentheses. DMF = dimethylformamide; $\text{SnCl}_2 = \text{anhydrous tin(II) chloride}$; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is the dihydrate (reagent grade). Ethanol is absolute. The platinum-metal starting materials usually employed were hydrated RuCl_3 (Ru 40%), $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$, all from Johnson, Matthey and Co. Ltd.

TABLE 4.
Analytical data on platinum-metal-tin complexes.

	Compound	Found					Required				
		C	H	Cl	N	Sn	C	H	Cl	N	Sn
A1	$(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$	13.2	2.9	34.0	3.7	32.0	13.4	3.4	34.6	3.9	32.0
A2	$(\text{Ph}_3\text{PH})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$	36.2	2.9	23.1	—	22.8	38.7	2.9	22.3	—	21.3
A3a	$(\text{Me}_4\text{N})_2[\text{PtCl}_2(\text{SnCl}_3)_2]$	11.2	3.1	32.8	3.4	26.6	11.1	2.8	32.8	3.3	27.5
A3b	$(\text{Me}_4\text{N})_2[\text{PtCl}_2(\text{SnCl}_3)_2]$	11.4	2.6	32.9	2.9	27.5	11.1	2.8	32.8	3.3	27.5
A4a	$(\text{Ph}_3\text{MeP})_2[\text{PtCl}_2(\text{SnCl}_3)_2]$	31.8	2.4	24.3	—	18.7	35.0	2.9	22.5	—	18.7
A5	$(\text{Me}_4\text{N})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$	12.1	3.1	36.4	3.2	28.1	12.8	3.2	37.8	3.7	31.6
A6	$(\text{Ph}_3\text{PH})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$	36.7	2.8	24.5	—	20.0	37.6	2.8	24.7	—	20.6
A7	$(\text{Me}_4\text{N})_4[\text{Ir}_2\text{Cl}_4(\text{SnCl}_3)_4]$	10.7	2.8	33.4	3.0	27.1	10.7	2.7	35.5	3.1	27.0
A8	$(\text{Ph}_3\text{PH})_4[\text{Ir}_2\text{Cl}_4(\text{SnCl}_3)_4]$	33.9	3.0	25.2	—	18.8	33.9	2.5	25.0	—	18.6
A9	$(\text{Me}_4\text{N})_2[\text{RhCOCl}(\text{SnCl}_3)]$	13.6	3.0	34.3	3.5 *	35.6	14.5	3.2	33.2	2.2 *	31.1
D1	$(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$	44.4	3.2	14.0	—	11.9	44.1	3.1	14.5	—	12.1
D2	$(\text{Ph}_3\text{As})_2\text{PtCl}(\text{SnCl}_3)$	40.0	3.2	13.2	—	11.1	40.5	2.8	13.6	—	11.1
D3	$(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$	54.9	3.9	10.4	—	10.6	58.2	4.1	9.5	—	10.6
E1	$(\text{C}_7\text{H}_8)_2\text{RhSnCl}_3$	32.5	3.4	21.9	—	24.9	32.8	3.2	20.8	—	23.2
E2	$(\text{C}_7\text{H}_8)_2\text{Rh}(\text{BPh}_4)$	71.6	5.8	<1	—	—	75.5	6.0	—	—	—
E3	$(\text{C}_7\text{H}_8)_2\text{IrSnCl}_3$	27.6	2.7	18.2	—	19.1	27.9	2.7	17.7	—	19.7
E4	$(\text{C}_8\text{H}_{12})_2\text{IrSnCl}_3$	29.9	3.8	16.3	—	17.8	30.3	3.8	16.8	—	18.7
E5	$(\text{C}_8\text{H}_{12})_2\text{IrBPh}_4$	56.8	5.1	1.0	—	—	66.5	6.1	—	—	—
E6	$(\text{Ph}_3\text{P})_2\text{C}_6\text{H}_5\text{RhSnCl}_3$	54.3	4.2	11.2	—	12.8	54.7	4.0	11.3	—	12.6
E7	$(\text{Ph}_3\text{As})_2\text{C}_7\text{H}_8\text{RhSnCl}_3$	49.9	4.0	10.4	—	11.7	50.0	3.7	10.3	—	11.5
E8	$(\text{Ph}_3\text{Sb})_2\text{C}_7\text{H}_8\text{RhSnCl}_3$	44.9	3.4	10.1	—	8.5	45.8	3.4	9.5	—	10.5
E9	$(\text{Ph}_3\text{P})_2\text{C}_8\text{H}_{12}\text{IrSnCl}_3$	49.0	4.0	11.6	—	11.3	48.0	3.5	10.1	—	11.3
E10	$(\text{Ph}_3\text{As})_2\text{C}_8\text{H}_{12}\text{IrSnCl}_3$	45.2	4.2	9.8	—	11.8	44.3	3.7	9.3	—	10.4

Molecular weights: E6, *M* (benzene) 914 (944); E7, *M* (acetone) 1016 (1032); E8, *M* (chloroform) 1102 (1126); E9, *M* (benzene) 910 (1050).

* Oxygen %.

A. *Complex-anion Studies* (analyses in Table 4).—1. *Tetrakis(tetramethylammonium)tetrakis(trichlorostannato)-μμ'-dichlorodirrhodate(I)*. (a) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.9 g.) in 3*M*-hydrochloric acid (50 ml.) was treated with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.9 g.). The addition of Me_4NCl (0.5 g.) in water (10 ml.)

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gives an orange precipitate of the salt (2.0 g., 85%). Contamination with the salt of the hexachlorostannate(IV) ion can be avoided by using a deficiency of the precipitant. The salt is recrystallised from 3M-hydrochloric acid-ethanol (1 : 10). It decomposes above 250°.

(b) Bis(norbornadiene)- $\mu\mu'$ -dichlorodirhodium(I) (0.3 g.) in ethanol (30 ml.) was treated with SnCl_2 (0.8 g.). Addition of Me_4NCl (0.2 g.) in water (9 ml.) gave an orange precipitate whose infrared 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%).

2. *Tetrakis(triphenylphosphonium)tetrakis(trichlorostannato)- $\mu\mu'$ -dichlorodirhodium(I)*. To a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 g.) and SnCl_2 (0.45 g.) in 3M-hydrochloric acid (40 ml.) was added triphenylphosphine in ethanol (5 ml.). The precipitate yellow salt was washed with ethanol (in which it is moderately soluble) and dried *in vacuo* (0.6 g., 70%); $\nu(\text{P-H})$ 2392 cm^{-1} .

3. *Bis(tetramethylammonium)dichlorobis(trichlorostannato)platinate(II)*. (a) *Yellow isomer*. To $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.18 g.) in ethanol (15 ml.) in a nitrogen atmosphere was added anhydrous SnCl_2 (0.15 g.) (Pt : Sn ratio = 1 : 2). The resulting red solution fades to yellow-orange on standing for 10–15 min. Addition of Me_4NCl (0.10 g.) in methanol (1 ml.) precipitates the yellow crystalline salt quantitatively. By dissolving in acetone and re-precipitating with ethanol, the compound was obtained as needles, decomp. 195–200°. The reaction may also be carried out in methanol, but with 3M-hydrochloric acid as solvent; isomerisation is incomplete even after standing for 30 min., and a mixture of the red and yellow isomers is obtained.

(b) *Red isomer*. To $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.20 g.) in ethanol (10 ml.) under nitrogen was added anhydrous SnCl_2 (0.19 g.) (Pt : Sn ratio = 1 : 2). On addition of Me_4NCl (0.06 g.) in methanol (1 ml.) immediately to the red solution, the red salt was obtained (0.23 g., 60% corresponding to amount of Me_4NCl added). This was purified by dissolving in acetone and re-precipitating with ethanol as needles, decomp. 250°. Not all the platinum is precipitated from solution, and addition of more Me_4NCl (0.05 g.) in methanol (1 ml.) to the yellow filtrate, after removal of the red isomer, precipitates the yellow isomer identical with 3(a) above (0.16 g., 45% corresponding to 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 crystallises in low yield on further addition of NMe_4NCl owing to its solubility in hydrochloric acid.

(c) *Precipitates from higher Pt : Sn ratios*. To Na_2PtCl_4 in 3M-hydrochloric acid under nitrogen was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 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 polarising microscope. The electronic spectra and X-ray powder patterns of all these solids are identical and are the same as those of the red isomer obtained in (b). If these reactions are carried out in ethanol similar results are obtained.

Initial Pt : Sn ratio	Reaction medium	Found				
		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	—
1 : 5	EtOH	—	—	—	31.4	13.1
1 : 6 (from H_2PtCl_6)	EtOH	9.8	2.7	36.9	36.3	12.6

(NMe_4)₃[Pt(SnCl₃)₆] requires C, 9.3; H, 2.3; Cl, 34.5; Sn, 38.5; Pt, 12.6. (NMe_4)₂[Pt(SnCl₃)₂Cl₂] requires C, 11.1; H, 2.8; Cl, 32.7; Sn, 27.4; Pt, 22.6.

(d) (Mesityl oxide)dichloroplatinum(II) (0.16 g.) in ethanol (25 ml.) under nitrogen was treated with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.4 g.). The resulting cherry-red solution had the same electronic absorption spectrum as that in (c) (Table 5) and gave an identical Me_4N^+ salt (Found: C, 11.0; H, 3.1%).

(e) Potassium ethylenetrichloroplatinate(II) (0.37 g.) in ethanol or 3M-hydrochloric acid (25 ml.) was treated with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.45 g.) with results as in (d) (Found: Cl, 34.8; Sn, 28.8%).

(f) Platinum carbonyl chlorides, $\text{Pt}(\text{CO})_2\text{Cl}_2$ and $[\text{Pt}(\text{CO})\text{Cl}_2]_2$, were prepared according to Schutzenberger⁶ and were treated in ethanolic solution under nitrogen with excess of SnCl_2 . Carbon monoxide was evolved (identified by gas infrared spectrum), and a cherry-red solution as in (c) and a Me_4N^+ salt (Found: C, 11.4; H, 2.3%) obtained.

⁶ Schutzenberger, *Bull. Soc. chim. France*, 1870, **14**, 17 (*J. Chem. Soc. Abs.*, 1871, 1009).

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(g) To cyclo-octa-1,5-dienedichloroplatinum(II) (0.05 g.) in acetone (20 ml.) under nitrogen was added SnCl_2 (0.15 g.); results as in (d).

4. *Bis(triphenylmethylphosphonium)dichlorobis(trichlorostannato)platinate(II)*. (a) *Yellow isomer*. $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.12 g.) in methanol (10 ml.) under nitrogen was allowed to react with SnCl_2 (0.13 g.) (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 (0.10 g.) in methanol (1 ml.) was added dropwise to the yellow solution. The yellow precipitate was quickly centrifuged and the mother-liquor decanted off without allowing it to warm up. In the same manner the precipitate is washed with a small portion of methanol and then 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 isomerisation to 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 isomerisation, but the product is predominantly the yellow isomer. It is an amorphous powder which can be kept safely in a refrigerator but it isomerises more quickly at room temperature and immediately at 50° to an orange oil.

Use of Pt : Sn ratios 1 : 2 make it easier to isolate the yellow isomer free from the red form, but low tin analyses indicate contamination with $(\text{Ph}_3\text{MeP})_2\text{PtCl}_4$ owing to incomplete reaction at the low temperatures. It can be precipitated at 0° but isomerises so rapidly that it cannot be isolated.

(b) *Mixed isomers*. To $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.23 g.) in methanol (15 ml.) under nitrogen was added SnCl_2 (0.19 g.) (Pt : Sn ratio 1 : 5) at room temperature. Addition of Ph_3MePCl (0.35 g.) in methanol (3.5 ml.) precipitates the orange *solid* (0.48 g., 75%). 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, 19.3, 18.9; Λ_m , 119. Pt : Sn 1 : 10; C, 34.4; H, 2.8; Cl, 24.3; Sn, 19.3; Λ_m , 123. $\text{C}_{33}\text{H}_{36}\text{P}_2\text{Cl}_3\text{Sn}_2\text{Pt}$ 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 of stannous chloride were unsuccessful.

5. *Bis(tetramethylammonium)dichlorobis(trichlorostannato)ruthenate(II)*. (a) To ruthenium trichloride hydrate (1 g.) in 3M-hydrochloric acid (150 ml.) was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (6 g.). On heating under nitrogen on a steam-bath the solution became orange-red (*ca.* 1 hr.). Addition of Me_4NCl (0.5 g.) in water (10 ml.) precipitated the *salt* (2.0 g., 80%) which was recrystallised from 3M-hydrochloric acid–ethanol (1 : 4). The microcrystalline powder darkens above 200° .

6. *Bis(triphenylphosphonium)dichlorobis(trichlorostannato)ruthenate(II)*. Ruthenium trichloride hydrate (0.5 g.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3 g.) in 3M-hydrochloric acid (50 ml.) were heated on a steam-bath for *ca.* 1 hr. under nitrogen. Addition of triphenylphosphine (1.7 g.) in ethanol (20 ml.) gave a precipitate which, after drying and washing with ether to remove free triphenylphosphine, is the pure yellow *salt*, m. p. $177\text{--}180^\circ$ (1.5 g., 80%), $\nu(\text{P-H})$ 2398 cm^{-1} .

7. *Tetrakis(tetramethylammonium)tetrachlorotetrakis(trichlorostannato)- $\mu\mu'$ -dichlorodi-iridate(III)*. To sodium hexachloroiridate(IV) hexahydrate (1 g.) in 3M-hydrochloric acid (100 ml.) was added excess of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (4 g.). After *ca.* 1 hr. on a steam-bath under nitrogen, Me_4NCl (0.5 g. in 10 ml. of water) precipitated the *salt* (1.5 g., 90%) which crystallised from 3M-hydrochloric acid–ethanol (1 : 4) as hexagonal plates, decomp. $>300^\circ$.

8. *Tetrakis(triphenylphosphonium)tetrachlorotetrakis(trichlorostannato)- $\mu\mu'$ -dichlorodi-iridate(III)*. $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (0.5 g.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2 g.) in 3M-hydrochloric acid (50 ml.) were heated on a steam-bath for 1 hr. under nitrogen, and to the cooled solution was added triphenylphosphine (0.95 g.) in ethanol (15 ml.). The yellow precipitate was collected, dissolved in the minimum of acetone, and the *salt* reprecipitated with ethanol and dried, m. p. $112\text{--}117^\circ$ (0.7 g., 60%), $\nu(\text{P-H})$ 2398 cm^{-1} .

9. *Bis(tetramethylammonium)chlorocarbonyl(trichlorostannato)rhodate(I)*. (a) Tetracarbonyl- $\mu\mu'$ -dichlororhodium(I) (0.37 g.) in ethanol (50 ml.) was treated with SnCl_2 (0.7 g.), followed by Me_4NCl (0.05 g. in 5 ml. of water) after evolution of carbon monoxide ceased, to give the orange *salt* (1.3 g., 85%). The salt could not be satisfactorily recrystallised but with a deficiency of Me_4NCl the product is reasonably pure. It decomposes above 200° , $\nu(\text{C-O str.})$ 2000 cm^{-1} . The second carbon monoxide could not be replaced at reaction temperatures up to 100° .

(b) $(\text{Me}_4\text{N})[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$ (0.54 g.) in acetone (100 ml.) was treated with carbon monoxide for 8 hr. at 100 atm. and 20° . After vacuum-evaporation the residue was extracted with

petroleum (b. p. 40—60°) which removed a small amount of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ leaving the orange salt. The reaction with carbon monoxide at room temperature and pressure is slow and incomplete in 2—3 days.

B. Reactions of Other Ligands with Tetramethylammonium Salts.—(a) To $(\text{Me}_4\text{N})_2[\text{PtCl}_2(\text{SnCl}_3)_2]$ (0.5 g.) in acetone (30 ml.) was added triphenylphosphine (0.6 g.); 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 ether, was identified as bis(triphenylphosphine)dichloroplatinum(II) by analysis (Found: C, 52.7; H, 4.4; Cl, 9.0. Calc. for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pt}$: C, 54.1; H, 3.8; Cl, 8.9%) and infrared spectra.

(b) $(\text{Me}_4\text{N})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$ (0.3 g.) was fused with triphenylphosphine (0.5 g.) at 100° for 1 hr. under nitrogen. Free tin(II) was detected but no product was isolated pure. Under similar conditions $(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$ and $(\text{Me}_4\text{N})_4[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]$ were unaffected.

(c) $(\text{Me}_4\text{N})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$ (0.3 g.) was refluxed with dry pyridine for 1 hr. under nitrogen. After filtration the solvent was removed and the residue leached with ethanol (4 × 20 ml.) to remove SnCl_2 . After dissolution in chloroform the addition of petroleum (b. p. 40—60°) precipitated an orange solid with properties identical to those of py_4RuCl_2 ⁷ (Found: C, 44.9; H, 3.2. Calc. for $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_4\text{Ru}$: C, 49.1; H, 4.1%).

Under similar conditions the rhodium and iridium Me_4N^+ salts were attacked by pyridine, displacing SnCl_2 , but no reaction products could be cleanly separated.

(d) $(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$ (0.2 g.) and *p*-toluidine (0.8 g.) were heated in nitrogen for 30 min. at 100°. The product contained free tin(II), identified by cacotheline and other standard tests, and extraction with hot chloroform gave a yellow solution which yielded an orange solid on evaporation. Washing with diethyl ether left trichlorotris(*p*-toluidine)rhodium(III), m. p. 145—148°, in low yield (Found: C, 45.4; H, 5.0; Cl, 17.8. Calc. for $\text{C}_{21}\text{H}_{27}\text{Cl}_3\text{N}_3\text{Rh}$: C, 47.7; H, 5.1; Cl, 20.0%).

Under the same conditions, $(\text{Me}_4\text{N})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$ gave free tin(II) but no product could be isolated. The iridium salt is barely attacked under these conditions.

C. Reaction of Complexes in Organic Solvents with Ligands.—(a) A solution of sodium chloroplatinate(II) (0.34 g.) and SnCl_2 (0.6 g.) in ethanol (25 ml.) was shaken with cyclo-octa-1,5-diene (2 ml.) under nitrogen. After 2 days the white needles were removed and shown to be $\text{C}_8\text{H}_{12}\text{PtCl}_2$, decomp. 230—240° (0.1 g., 35%) [Found: C, 25.0; H, 3.2; Cl, 19.1%; *M* (benzene), 377. Calc. for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{Pt}$: C, 25.8; H, 3.2; Cl, 19.2%; *M*, 374].

(b) To rhodium trichloride trihydrate (0.5 g.) in ethanol (50 ml.) was added SnCl_2 (1.2 g.). The deep orange-red solution was treated with carbon monoxide at just above atmospheric pressure for 3 hr. with agitation. After removal of ethanol in a vacuum the residue was extracted with petroleum (b. p. 40—60°) evaporation of which followed by vacuum sublimation at 60—70° gave orange needles (0.2 g., 65%) of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, identical with authentic specimen.

(c) The orange-red solution obtained as in (b) was shaken with cyclo-octa-1,5-diene (2 ml.). Within a few hours the yellow solid was collected, identical with authentic $(\text{C}_8\text{H}_{12})_2\text{Rh}_2\text{Cl}_2$, m. p. 247—249° (from acetic acid) [Found: C, 38.3; H, 5.2; Cl, 14.8%; *M* (ebullioscopic in benzene), 500. Calc. for $\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{Rh}_2$: C, 39.0; H, 4.9; Cl, 14.4%; *M*, 493].

(d) As in (c) using dicyclopentadiene, orange microcrystals, decomp. 200—201° [Found: C, 42.1; H, 4.4; Cl, 13.6%; *M* (benzene), 600. Calc. for $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{Rh}_2$: C, 44.4; H, 4.5; Cl, 13.1%; *M*, 541].

(e) As in (c) using 4-vinylhex-1-ene, after 3 hr. 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. $\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{Rh}$ 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.*, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 g.) in ethanol (150 ml.) shaken with 4-vinylhex-1-ene (2 ml.) for several weeks leads to 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. The solubility is too low to enable a reliable n.m.r. spectrum to be obtained but the spectra were adequate to show that the compound was not identical with the cyclo-octa-1,5-diene complex, and the infrared spectra of the two compounds were different.

D. Triphenylphosphine and -arsine Complexes (analytical data in Table 4).—1. *Bis*(triphenylphosphine)(trichlorostannato)chloroplatinum(II). (a) To a solution of $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.5 g.) and SnCl_2 (0.7 g.) in ethanol (40 ml.) under nitrogen was added triphenylphosphine (0.6 g.)

⁷ Abel, Bennett, and Wilkinson, *J.*, 1959, 3178.

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in ethanol (10 ml.). The orange precipitate of the *complex* was carefully washed with ethanol (3×5 ml.) and diethyl ether (2×5 ml.) containing a little SnCl_2 . The complex is soluble in acetone and dichloromethane, and crystallisation gives $(\text{Ph}_3\text{P})_3\text{PtCl}_2$ (Found: C, 52.0; H, 4.3; Cl, 9.0. Calc. for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pt}$: C, 54.1; H, 3.8; Cl, 8.9%).

(b) To a 3M-hydrochloric acid (50 ml.) solution of $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ (0.5 g.) and SnCl_2 (0.7 g.) was added triphenylphosphine (0.6 g.) in ethanol (10 ml.). The orange *complex* is precipitated and washed as above (Found: Cl, 14.7%).

(c) The addition of a 10M excess of SnCl_2 to $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ in acetone gives an orange solution which, after evaporation, careful leaching of SnCl_2 with m-hydrochloric acid, followed by washing with alcohol and ether, leaves the *complex* (Found: Cl, 15.2; Sn, 12.0%).

2. *Bis(triphenylarsine)(trichlorostannato)chloroplatinum(II)*. (a) To an ethanolic solution as in D1(a) was added triphenylarsine (0.7 g.) in ethanol (10 ml.), and the precipitated orange *complex* was collected and washed with ethanol and diethyl ether.

(b) As in D1(b) using triphenylarsine, the *complex* (Found: C, 41.5; H, 3.3; Cl, 13.7%).

The complex is soluble in acetone and chloroform in which it appears to be stable. The addition of dilute hydrochloric acid to the acetone solution precipitates $(\text{Ph}_3\text{As})_2\text{PtCl}_2$ (Found: C, 48.8; H, 3.4; Cl, 8.1. Calc. for $\text{C}_{36}\text{H}_{30}\text{AsCl}_2\text{Pt}$: C, 49.3; H, 3.5; Cl, 8.1%).

3. *Tris(triphenylphosphine)(trichlorostannato)rhodium(I)*. To a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 g.) and SnCl_2 (1.5 g.) in ethanol (40 ml.) was added triphenylphosphine (6 g.) in ethanol (15 ml.) and the mixture boiled until the precipitate of the salt (A2) changed in colour from yellow to dark red-brown crystals of the *complex* (1.5 g., 70%). The complex is moderately soluble in dichloromethane and acetone but sparingly soluble in benzene and ethanol. It cannot be recovered unchanged from solutions.

E. *Olefin Complexes*.—1. *Bis(norbornadiene)trichlorostannatorhodium(I)*. To $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.4 g.), SnCl_2 (1.03 g.) in ethanol (30 ml.) was added norbornadiene (2 ml.). After shaking for 1 hr. at room temperature the yellow needles of the *complex* were collected, washed with ethanol and ether, and dried (0.6 g., 75%). The complex is slightly soluble in dichloromethane, dimethylformamide, nitromethane, and hot water.

2. *Bis(norbornadiene)rhodium(I) tetraphenylborate*. To a hot filtered saturated solution of the complex E1 was added a saturated solution of sodium tetraphenylborate. The flocculent precipitate was collected (centrifuge), washed with water (2×20 ml.), 4M-hydrochloric acid (4×20 ml.), and ethanol (4×20 ml.). After drying, the solid was extracted with hot 4M-hydrochloric acid until no tin(II) chloride could be detected in the washings. Recrystallisation from acetone gave the *salt*, Λ_m (DMF), 25.

3. *Bis(norbornadiene)trichlorostannatoiridium(I)*. To a boiling solution of $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (0.4 g.) in ethanol (30 ml.) under nitrogen was added SnCl_2 (0.8 g.) in ethanol. After 5 min. reflux the cooled solution was shaken with norbornadiene (2 ml.). After 24 hr. the pale yellow needles of the complex were collected, and washed with ethanol and ether (0.3 g., 70%). The complex is sparingly soluble in hot water, 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.

4. *Bis(cyclo-octa-1,5-diene)trichlorostannatoiridium(I)*. As E3, using cyclo-octa-1,5-diene hexagonal prisms (0.3 g., 65%) were recovered. From cyclo-octa-1,3-diene a product with identical infrared spectrum (0.2 g., 45%) (Found: C, 29.7; H, 3.7; Cl, 18.1; Sn, 16.8%), was obtained. A similar product was obtained from 4-vinylcyclohexene (0.22 g., 50%) (Found: C, 30.0; H, 2.9; Cl, 17.2; Sn, 18.4%). This has also been obtained⁸ by the action of stannous chloride on chloroiridate solution in warm acetic acid containing cyclo-octa-1,5-diene.

5. *Bis(cyclo-octa-1,5-diene)iridium(I) tetraphenylborate*. Complex E3 (0.3 g.) was dissolved in warm dimethylformamide (100 ml.) and diluted with warm water (300 ml.). 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 (2×20 ml.) and hot 3M-hydrochloric acid (4×20 ml.) to leave the *salt*, decomp. 225–230°.

6. *Bis(triphenylphosphine)norbornadienetrichlorostannatorhodium(I)*. Triphenylphosphine (0.84 g.) was added to a suspension of $(\text{C}_7\text{H}_6)_2\text{RhSnCl}_3$ (0.40 g.) in dichloromethane (50 ml.); the solid immediately dissolved, giving an orange solution. After 1 hr. the solvent was removed and the orange crystals of the *complex* were washed with diethyl ether to remove unchanged triphenylphosphine (0.5 g., 70%), Λ_m (nitrobenzene), 1.75.

⁸ Venanzi, personal communication.

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7. *Bis(triphenylarsine)norbornadienetrichlorostannatorhodium(I)*. As E6 (0.55 g., 70%).
8. *Bis(triphenylstibine)norbornadienetrichlorostannatorhodium(I)*. As E6 (0.7 g., 85%).
9. *Bis(triphenylphosphine)cyclo-octa-1,5-dienetrichlorostannatoiridium(I)*. As E6 (0.15 g., 75%).
10. *Bis(triphenylarsine)cyclo-octa-1,5-dienetrichlorostannatoiridium(I)*. As E6 (0.2 g., 83%).

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