

THE INTERACTION OF TIN(II) CHLORIDE WITH SOME ALLYL COMPLEXES OF PLATINUM AND PALLADIUM AND DIENE COMPLEXES OF RHODIUM

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SUMMARY

The interaction of tin(II) chloride with $\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2\text{Cl}$ gives the ionic and covalent complexes, $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2][\text{SnCl}_3]$ and $\text{PtSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$ respectively. Palladium complexes analogous to the latter have also been prepared. The reaction of tin(II) chloride with chloro(norbornadiene)rhodium(I) dimer in the presence of a tertiary phosphine or arsine ligand L leads to a variety of five coordinate monomers of the type $\text{RhSnCl}_3(\text{NBD})\text{L}_2$ and the five coordinate rhodium(I) complexes, $\text{RhSnCl}_3(\text{butadiene})_2$ and $\text{RhSnCl}_3(\text{CO})(\text{SbPh}_3)_3$ have also been prepared. The structures of the complexes have been investigated by ^1H NMR and IR spectroscopy.

INTRODUCTION

The reactions of tin(II) chloride with low valent transition metal complexes containing metal chlorine bonds usually result in the formation of complexes containing covalently bonded SnCl_3^- ligands¹. However, in certain instances ionic compounds are formed as typified by the reaction of tin(II) chloride with $\pi\text{-C}_5\text{H}_5\text{NiCl}(\text{PPh}_3)$ which has been shown² to give $\pi\text{-C}_5\text{H}_5\text{NiSnCl}_3(\text{PPh}_3)$ together with a small amount of an ionic complex, $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PPh}_3)_2][\text{SnCl}_3]$. Clearly the formation of a covalent or ionic complex will depend on a number of factors which will include the nucleophilicity of the SnCl_3^- ligand, the electronic configuration of the transition metal atom and the nature of the other ligands present. Herein we describe the reaction of tin(II) chloride with chloro(π -allyl)bis(triphenylphosphine)platinum(II) which yields both ionic and covalent products together with the preparation and properties of a number of norbornadiene complexes of the type $\text{RhSnCl}_3(\text{NBD})\text{L}_2$ and related complexes of rhodium(I).

RESULTS AND DISCUSSION

Chloro(π -allyl)bis(triphenylphosphine)platinum(II) has a conductivity in nitromethane which is typical of a 1/1 electrolyte but in non-polar solvents and in the solid state it appears to be five-coordinate^{3,4}. In methylene chloride/methanol

solution we find that tin(II) chloride reacts with $\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2\text{Cl}$ to give yellow crystals of $\text{Pt}(\text{C}_3\text{H}_5)(\text{PPh}_3)_2\text{SnCl}_3$, (I) together with a minor product $\text{Pt}(\text{C}_3\text{H}_5)(\text{PPh}_3)\text{SnCl}_3$, (II). The far-IR spectrum of (II) contains two Sn-Cl stretching frequencies at 354 and 325 cm^{-1} which are typical of a coordinated SnCl_3 group (Table 1)

TABLE 1

INFRARED SPECTRA (400–200 cm^{-1}) OF THE COMPLEXES

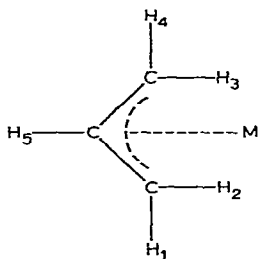
Compound	$\nu(\text{SnCl})$		Other bands
	Sym.	Asym.	
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2][\text{SnCl}_3]$	293 m	259 s	
$\text{PtSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$	354 m	325 s (br)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$	335 m	325 s	
		320 (sh)	
		297 vs	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3)$	335 m	325 s	342 m
		317 s	
		297 vs	
$\text{RhSnCl}_3(\text{NBD})_2$	314 s	299 s	
		281 s	
$\text{RhSnCl}_3(\text{NBD})(\text{PPh}_3)_2$	305 s	280 s	
$\text{RhSnCl}_3(\text{NBD})(\text{AsPh}_3)_2$	307 s	284 s	331 m, 323 (sh)
$\text{RhSnCl}_3(\text{NBD})(\text{SbPh}_3)_2$	311 s	296 s	277 m, 267 m
			261 (sh), 254 w
$\text{RhSnCl}_3(\text{NBD})(\text{PBU}_3)_2$	302 s	278 s	
$\text{RhSnCl}_3(\text{NBD})(\text{PMePh}_2)_2$	306 s	287 s	
		273 m	
$\text{RhSnCl}_3(\text{NBD})(\text{AsEt}_3)_2$	305 s	295 s	
		276 s	
$\text{RhSnCl}_3(\text{C}_6\text{H}_6)_2$	328 s	303 s	376 m, 209 m
$\text{RhSnCl}_3(\text{CO})(\text{SbPh}_3)_3$	321 s	300 s	279 s, 269 s
			264 (sh)
$[\text{Et}_4\text{N}][\text{Rh}(\text{SnCl}_3)_3\text{CO}]$	312 s	297 (sh)	348 m
$[\text{Ph}_4\text{As}][\text{SnCl}_3]$	289 ms	252 s	

and although (II) is not sufficiently soluble for satisfactory ^1H NMR spectroscopy it almost certainly has a structure analogous to the corresponding palladium complex, $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$ which has been studied by single crystal X-ray techniques⁵.

The palladium complex, $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$ was originally prepared in acetone and it crystallises with half a molecule of solvent⁵. We also independently prepared this complex in methanol as solvent and recrystallisation from benzene/petroleum spirit gives a complex which contains a molecule of benzene, $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)\cdot\text{C}_6\text{H}_6$. However, if toluene is used in place of benzene then the unsolvated compound can be readily isolated. The action of SnCl_2 on $\text{PdCl}(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3)$ similarly leads to the complex $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3)\cdot\frac{1}{2}\text{C}_6\text{H}_6$. Recrystallisation in the presence of toluene gives the analogous product, $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3)\cdot\frac{1}{2}\text{PhMe}$. Attempts to isolate the corresponding triphenylstibine complex were not successful.

The ^1H NMR spectrum of $\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3)$ at room temperature is very similar to that of the triphenylphosphine analogue (Table 2) and the broadness of

TABLE 2

¹H NMR DATA FOR COMPLEXES^a

Complex	τ_5	$\tau_{1,4}$	$\tau_{2,3}$	$\tau_{1,2,3,4}$
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)\text{PPh}_3$	4.47 (qui)	5.4 (s, b)	6.6 (s, b)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)\text{AsPh}_3$	4.5 (m)	5.4 (s, b)	6.5 (s, b)	
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2]\text{Cl}^b$	4.31 (qui)			6.58 (4 bands)
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2][\text{SnCl}_3]^c$	4.32 (m)			6.56 (4 bands)

^a s = singlet, d = doublet, qui = quintet, m = unresolved multiplet, b = broad. ^b See ref. 4; $J(\text{H}_{1,2,3,4} - \text{H}_5) = 11$ Hz, $J(\text{H}_{1,2,3,4} - {}^{195}\text{Pt}) = 22$ Hz. ^c $J(\text{H}_{1,2,3,4} - \text{H}_5) = 11$ Hz, $J(\text{H}_{1,2,3,4} - {}^{195}\text{Pt}) = 22$ Hz.

the signals of the terminal protons of the allyl group may again be due to coupling effects⁵ since these signals remain broad even at -40° .

The conductivity of the complex (I), $\text{Pt}(\text{C}_3\text{H}_5)(\text{PPh}_3)_2\text{SnCl}_3$ in nitromethane indicates that in this solvent it behaves as a 1/1 electrolyte, and since the ¹H NMR spectrum of (I) and $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2]\text{Cl}^4$ are almost identical (see Table 2) the structure of (I) in solution is $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2][\text{SnCl}_3]$. However, since the far-IR spectrum of (I) contains two bands at 289 and 252 cm^{-1} typical of an uncoordinated SnCl_3^- group it would appear that unlike $[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2]\text{Cl}$, the complex (I) is also ionic in the solid state. This is somewhat surprising in view of the known tendency of the SnCl_3^- ligand to favour high coordination numbers as in the anion $\text{Pt}(\text{SnCl}_3)_3^{3-}$.

This observation consequently led us to investigate norbornadiene complexes of the type $\text{RhSnCl}_3(\text{NBD})\text{L}_2^1$ and related rhodium(I) complexes since although on going from platinum(II) to rhodium(I) there is an increase in tendency for the metal to become five coordinate⁶ it was felt that with certain ligands (L) the rhodium-tin bond might cleave to give ionic compounds in the solid state containing the SnCl_3^- anion.

The complexes $\text{RhSnCl}_3(\text{NBD})\text{L}_2$, (L = Ph_3P , Ph_3As and Ph_3Sb) have previously been prepared⁷ by the action of L on the norbornadiene complex, $\text{RhSnCl}_3(\text{NBD})_2$. We find that the complexes $\text{RhSnCl}_3(\text{NBD})\text{L}_2$, [L = Ph_3P , Ph_3As , Ph_3Sb , $(n\text{-Bu})_3\text{P}$, Ph_2MeP and Et_3As] may also be readily obtained by the action of tin(II) chloride on a solution of $[\text{RhCl}(\text{NBD})]_2$ containing four moles of the ligand L. These reactions presumably proceed via intermediates of the type $\text{RhCl}(\text{NBD})\text{L}_2$ since similar five coordinate intermediates have been shown⁸ to be involved in exchange reactions of $\text{RhCl}(\text{NBD})(\text{PPh}_3)$. However, attempts to obtain complexes of the type $\text{RhSnCl}_3(\text{NBD})\text{L}_2$ with nitrogen donor ligands, e.g. *p*-toluidine, pyridine, have not

been successful.

Conductivity and molecular weight studies on the triphenylphosphine, -arsine, and -stibine complexes, have shown that these complexes are all five coordinate in solution⁷. Similarly we find that the new complexes prepared here are also non-conducting in nitrobenzene. Moreover the far-IR spectra of all the rhodium complexes (Table 1) contain bands typical of a coordinated SnCl_3^- ligand and hence are also five coordinate in the solid state. Thus, in none of these reactions has evidence for ionic products of the type $[\text{Rh}(\text{NBD})\text{L}_2][\text{SnCl}_3]$ been obtained. It is noteworthy, however, that in aqueous solution there is evidence that $\text{RhSnCl}_3(\text{NBD})_2$ dissociates into $\text{Rh}(\text{NBD})_2^+$ and SnCl_3^- ions⁷.

A single crystal X-ray study of $\text{IrSnCl}_3(\text{COD})_2$, (where COD is cycloocta-1,5-diene) has shown that the iridium atom is five coordinate⁹ and the norbornadiene rhodium complexes described here probably have a similar geometry.

The reaction of carbon monoxide with $[\text{RhCl}(\text{NBD})]_2$ in the presence of tin(II) chloride is different to that with the ligands L. Thus two compounds are formed, $\text{RhSnCl}_3(\text{NBD})_2$ together with the anionic species, $[\text{Rh}(\text{SnCl}_3)_3\text{CO}]^{2-}$ ¹⁰ which can be isolated as its tetraethylammonium salt.

The interaction of butadiene and an ethanolic rhodium(III) chloride/tin(II) chloride in a sealed glass tube gives buff coloured crystals of a complex of formula, $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$. This complex is not sufficiently soluble for molecular weight measurements but the far-IR spectrum contains two $\nu(\text{Sn}-\text{Cl})$ stretching frequencies (Table 1) typical of a coordinated SnCl_3^- ligand. Hence the complex is probably five coordinate in the solid state and probably has a similar structure to $\text{RhCl}(\text{C}_4\text{H}_6)_2$ ¹¹. In agreement with this the IR spectrum of $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$ is similar to that reported¹² for $\text{RhCl}(\text{C}_4\text{H}_6)_2$ in the region $1500-1350\text{ cm}^{-1}$. However, the trichlorotin derivative is considerably more stable than $\text{RhCl}(\text{C}_4\text{H}_6)_2$. The preparation of $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$ is analogous to that of $\text{RhSnCl}_3(\text{NBD})_2$ ⁷.

Norbornadiene reacts readily with $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$ to give $\text{RhSnCl}_3(\text{NBD})_2$ quantitatively. However, a similar reaction with 1,5-cyclooctadiene gives $[\text{RhCl}(1,5-\text{C}_8\text{H}_{12})]_2$ and it would appear that the unknown complex, $\text{RhSnCl}_3(1,5-\text{C}_8\text{H}_{12})_2$ is unstable with respect to $[\text{RhCl}(1,5-\text{C}_8\text{H}_{12})]_2$ and SnCl_2 . Previous attempts to obtain this complex have also failed⁷, and it is noteworthy that exchange reactions involving the complexes $\text{RhCl}(\text{NBD})\text{L}$ and $\text{RhCl}(\text{COD})\text{L}$ reveal that five coordinated rhodium(I) is more favoured by norbornadiene than by 1,5-cyclooctadiene⁸. We also find that only the cyclooctene complex, $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ ¹² can be isolated by treating an ethanolic solution of rhodium(III) chloride and tin(II) chloride with cyclooctene.

The reaction of triphenylstibine with $[\text{RhCl}(\text{CO})_2]_2$ has recently been shown¹³ to give the five coordinate complex, $\text{RhCl}(\text{CO})(\text{SbPh}_3)_3$ and we find that this complex also readily reacts with tin(II) chloride to give the five coordinate monomer, $\text{RhSnCl}_3(\text{CO})(\text{SbPh}_3)_3$ which again contains a covalent SnCl_3^- ligand both in chloroform solution and in the solid state. Attempts to prepare the analogous triphenylphosphine derivative from *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, triphenylphosphine and tin(II) chloride have not been successful.

The reaction of tin(II) chloride with $[\text{RhCl}(\text{NBD})]_2$ in the presence of two moles of a ligand L gives no evidence for the formation of four coordinate complexes of the type $\text{RhSnCl}_3(\text{NBD})\text{L}$.

The IR data in Table 1 clearly show how useful this technique is differentiating

between ionic and covalent SnCl_3^- ligands. It is also noteworthy that some of the complexes contain three (Sn-Cl) stretching frequencies instead of the expected two. This has been observed previously¹⁴ and may be a consequence of the degeneracy of the antisymmetric stretching vibration being lifted by the influence of the site symmetry in the crystal. In agreement with earlier studies¹⁴ the symmetric and antisymmetric tin-chlorine stretching frequencies increase as the oxidation state of the transition metal in the complexes increases from +1 to +2.

EXPERIMENTAL

Analytical data, yields and melting points for all new complexes are given in Table 3. IR spectra were recorded on a Perkin-Elmer model 225 spectrophotometer.

TABLE 3
ANALYTICAL DATA FOR COMPLEXES

Compound	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			Mol. wt. found ^a (calcd.)
			C	H	Cl	
$[\text{Pt}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2][\text{SnCl}_3]$	50	165° dec.	48.0 (47.6)	3.61 (3.58)	11.7 (10.8)	
$\text{PtSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$	10	155-165° dec.	35.7 (35.0)	2.86 (2.80)	13.7 (14.7)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3) \cdot \text{C}_6\text{H}_6$	56	134-135° dec.	44.8 (45.5)	3.57 (3.67)	12.8 (14.9)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)$		138-140° dec.	40.2 (39.7)	3.25 (3.18)	16.7 (16.8)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3) \cdot \frac{1}{2}\text{C}_6\text{H}_6$	68	142-144° dec.	40.0 (40.2)	3.19 (3.22)	15.5 (14.8)	
$\text{PdSnCl}_3(\pi\text{-C}_3\text{H}_5)(\text{AsPh}_3) \cdot \frac{1}{2}\text{C}_7\text{H}_8$		145-147° dec.	40.3 (40.6)	3.23 (3.34)	15.8 (14.7)	
$\text{RhSnCl}_3(\text{NBD})(\text{PBU}_3)_2$	76	140-142°	45.1 (45.2)	7.25 (7.58)	12.3 (12.9)	812 (824)
$\text{RhSnCl}_3(\text{NBD})(\text{PMePh}_2)_2$	72	163-165°	47.9 (48.3)	4.31 (4.17)	13.9 (13.0)	800 (820)
$\text{RhSnCl}_3(\text{NBD})(\text{AsEt}_3)_2$	68	144°	30.8 (30.7)	5.17 (5.15)	14.3 (14.3)	714 (744)
$\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$	90	150-160° dec.	21.3 (22.0)	2.92 (2.78)	25.8 (24.4)	
$\text{RhSnCl}_3(\text{CO})(\text{SbPh}_3)_3$	60	186° dec.	46.2 (46.7)	3.19 (3.22)	7.90 (7.53)	1370 (1415)

^a Molecular weights were determined osmometrically in chloroform.

Proton NMR spectra were obtained in deuteriochloroform as solvent using a Varian Associates A60 spectrophotometer at 35°. Conductivities were determined in nitrobenzene using 10^{-3} molar solutions.

The complexes $\text{PtCl}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2$ ^{4,5}, $\text{PdCl}(\pi\text{-C}_3\text{H}_5)\text{L}$, ($\text{L} = \text{Ph}_3\text{P}$, $\text{Ph}_3\text{-As}$)¹⁵, $[\text{RhCl}(\text{NBD})]_2$ ¹⁶, $\text{RhCl}(\text{CO})(\text{SbPh}_3)_3$ ¹³ and *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ¹⁷ were prepared as described in the literature.

Reaction of tin(II) chloride with $PtCl(\pi-C_3H_5)(PPh_3)_2$

A solution of $SnCl_2$ (1.2 g) in methanol was added to a stirred solution of $PtCl(\pi-C_3H_5)(PPh_3)_2$, (0.9 g) in methylene chloride/methanol. The resulting orange solution was stirred for 30 min and then evaporated to a small volume under reduced pressure to give an orange solid. The orange solid was filtered off and washed with methanol. Treatment of the solid with benzene gave a yellow solution and left a small amount of an insoluble orange solid. Recrystallisation of the orange solid from methylene chloride/methanol gave orange microcrystals of π -allyl(trichlorotin)(triphenylphosphine)platinum(II).

Addition of petroleum spirit (b.p. 100–120°) to the benzene solution gave yellow crystals of π -allylbis(triphenylphosphine)platinum(II) trichlorostannite(II).

Reaction of tin(II) chloride with $PdCl(\pi-C_3H_5)(PPh_3)$

A solution of tin(II) chloride (1.0 g) in methanol was added to a solution of $PdCl(\pi-C_3H_5)(PPh_3)$, (1.0 g) in warm methanol (25 ml). The dark coloured precipitate which formed was filtered off and was treated with hot benzene to give a yellow solution and a small quantity of a purple oil. Addition of petroleum spirit (b.p. 100–120°) to the filtered benzene solution and evaporation to a small volume gave pale yellow crystals of $PdSnCl_3(\pi-C_3H_5)(PPh_3) \cdot C_6H_6$. Recrystallisation of this product using toluene in place of benzene gave very pale yellow crystals of $PdSnCl_3(\pi-C_3H_5)(PPh_3)$.

Reaction of tin(II) chloride with $PdCl(\pi-C_3H_5)(AsPh_3)$

Addition of tin(II) chloride (0.5 g) in a minimum amount of a 1/1 methylene chloride/methanol solvent mixture to $PdCl(\pi-C_3H_5)(AsPh_3)$ in the same solvent mixture (15 ml) gave an immediate purple-red colouration. After 30 min the solution was evaporated under reduced pressure to a small volume and the resulting solid was treated in an analogous method to that described above to give off-white crystals of $PdSnCl_3(\pi-C_3H_5)(AsPh_3) \cdot \frac{1}{2}C_6H_6$. Recrystallisation from toluene-petroleum spirit gave $PdSnCl_3(\pi-C_3H_5)(AsPh_3) \cdot \frac{1}{2}C_7H_8$.

Preparation of complexes of the type $RhSnCl_3(NBD)L_2$

The complexes $RhSnCl_3(NBD)L_2$ were prepared by the same general method as described below for the triphenylphosphine derivative.

$[RhCl(NBD)]_2$ (0.23 g) and four moles of triphenylphosphine (0.5 g) were dissolved in a 1/1 mixture of methylene chloride/methanol (20 ml) to give a clear orange solution. Excess tin(II) chloride (0.4 g) was added and after shaking for a few minutes orange crystals of the product separated. The crystals were filtered off, washed with methanol and dried *in vacuo*.

Some of the products were more soluble than the triphenylphosphine complex and it was necessary to evaporate the solvent to small volume to induce crystallisation in these cases.

Reaction of carbon monoxide with a mixture of $[RhCl(NBD)]_2$ and tin(II) chloride

Carbon monoxide was passed into a solution of $[RhCl(NBD)]_2$ (0.4 g) in a 1/1 methylene chloride/methanol solvent mixture. After 15 min excess tin(II) chloride (0.8 g) in the same solvent was added. Carbon monoxide was bubbled into the resulting

deep red solution for a further 2–3 h, and as the methylene chloride was driven off yellow crystals were deposited. These were filtered off, washed with methanol, and dried and identified as $\text{RhSnCl}_3(\text{NBD})_2$ by m.p. and IR spectrum. (Found: C, 33.2; H, 3.01; Cl, 20.8. $\text{C}_{14}\text{H}_{16}\text{Cl}_3\text{RhSn}$ calcd.: C, 32.9; H, 3.14; Cl, 20.8%.)

Tetrachthylammonium chloride (0.5 g) in methanol was added to the deep red filtrate. An orange precipitate of $[\text{Et}_4\text{N}]_2[\text{Rh}(\text{SnCl}_3)_3\text{CO}]$ formed immediately. (Found: C, 20.0; H, 4.04; Cl, 28.9; N, 2.73. $\text{C}_{17}\text{H}_{40}\text{Cl}_9\text{N}_2\text{ORhSn}$ calcd.: C, 19.3; H, 3.79; Cl, 29.9; N, 2.63%.)

(Trichlorotin)bis(1,3-butadiene)rhodium(I)

1,3-Butadiene (2 ml) was condensed onto a solution of hydrated rhodium trichloride (0.3 g) and tin(II) chloride (0.8 g) in absolute ethanol (20 ml) contained in a thick-walled glass tube cooled in liquid nitrogen. The tube was sealed, allowed to warm to room temperature, shaken mechanically for 1 h and left to stand overnight. The tube was then opened and the buff coloured crystals were filtered off, washed with ethanol, and dried under *vacuo*. IR (nujol mull) $\nu(\text{CH})$ 3076 (sh), 3059 m, 3050 (sh), 3004 w; CH_2 deformation 1478 m; $\nu(\text{C}=\text{C})$, 1425 s; CH rock 1377 ms; CH_2 rock 1226 w; $\nu(\text{C}-\text{C})$, 1209 w; CH wag 1187 wm; CH_2 wag 910 m; CH wag 775 m; CH_2 torsion 485 m; $\nu(\text{Rh}-\text{C})$ 434 m, 376 m; $\nu(\text{SnCl}_3)$ 328 s, 303 s; $\nu(\text{Rh}-\text{Sn})$ 209 m.

Reactions of $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$

(a). *With norbornadiene.* A suspension of $\text{RhSnCl}_3(\text{C}_4\text{H}_6)_2$ (0.1 g) in methylene chloride (10 ml) and norbornadiene (0.5 ml) were left to stand with occasional shaking. After about 1 h the solid gradually dissolved to give a yellow solution. Addition of methanol followed by rotary evaporation gave yellow crystals (0.12 g) of $\text{RhSnCl}_3(\text{NBD})_2$ identified by its m.p. and IR spectrum.

(b). *With 1,5-cyclooctadiene.* An identical reaction to that described above gave only $[\text{RhCl}(1,5\text{-C}_8\text{H}_{12})]$.

Reaction of cyclooctene with hydrated rhodium(III) chloride and tin(II) chloride

A mixture of cyclooctene (1 ml), hydrated rhodium(III) chloride and tin(II) chloride (0.8 g) was left to stand at room temperature for three weeks under an atmosphere of nitrogen. Rotary evaporation to a small volume and standing for a further two days gave orange crystals of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$. (0.05 g). M.p. 132° decompn. Lit. value 140°. (Found: C, 52.2; H, 7.66; Cl, 9.45. $\text{C}_{32}\text{H}_{56}\text{Cl}_2\text{Rh}_2$ calcd.: C, 53.5; H, 7.95; Cl, 9.89%.)

Reactions of tin(II) chloride

(a). *With $\text{RhCl}(\text{CO})(\text{SbPh}_3)_3$.* $\text{RhCl}(\text{CO})(\text{SbPh}_3)_3$ (0.44 g) and triphenylstibine (0.18 g) were dissolved in a 1/1 mixture of methylene chloride/methanol (25 ml). Excess tin(II) chloride (0.3 g) in the same solvent was added to the deep red solution whence a clear orange solution was obtained. Addition of methanol (25 ml) gave on standing orange crystals which were filtered off, washed with methanol, dried *in vacuo* and identified as $\text{RhSnCl}_3(\text{CO})(\text{SbPh}_3)_3$.

(b). *With $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and triphenylphosphine.* *Trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (0.69 g) and PPh_3 (0.26 g) were dissolved in warm tetrahydrofuran (30 ml). Excess tin(II) chloride (0.5 g) was added to the yellow solution in the minimum amount of the

same solvent. The mixture was refluxed for 3 h. The solution was then rotary evaporated to dryness and the resulting solid was washed with ethanol to give *trans*-RhCl(CO)-(PPh₃)₂.

A similar procedure using a solvent mixture of 1/1 methylene chloride/methanol gave an identical result.

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