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OXIDATIVE ADDITION OF TRIORGANOSTANNANES TO AMINE, PHOSPHITE AND PHOSPHINE COMPLEXES OF PLATINUM *

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Summary

Triarylstannanes $SnHR_3$ react with the platinum(0) complexes $[PtL_4]$ [L = $P(OR')_3$, R' = Ph, C_6H_4Me-3 or -4] and $[Pt(PPh_3)L_3]$ [L = $P(OC_6H_4Me\text{-}3)_3$] to give *trans*-$[Pt(SnR_3)_2L_2]$, with the oxalato-platinum(II) complexes $[Pt(C_2O_4)LL']$ [L = L' = $P(OPh)_3$; L = PMe_2Ph, L' = $P(OPh)_3$; L = PEt_3, L' = $P(OPh)_3$] to give *trans*-$[Pt(SnR_3)_2LL']$, with $[Pt(CO_3)(BIPY)]$ (BIPY = 2,2'-bipyridyl) to give stable platinum(IV) complexes *cis-trans*-$[PtH_2(SnR_3)_2(BIPY)]$, with $[PtMe_2(BIPY)]$ to give *cis-trans*-$[PtH(Me)(SnR_3)_2(BIPY)]$, and with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give *trans*-$[Pt(SnR_3)_2(PMe_2Ph)_2]$ or $[PtH(Me)(SnR_3)_2(PMe_2Ph)_2]$, and with *cis*-$[PtMe_2(PY)(PPh_3)]$ (PY = pyridine) to give *trans*-$[Pt(SnPh_3)_2(PPh_3)(PY)]$. The results indicate that the stability of the platinum(IV) complexes increases with the 'hardness' of the bases L: $P(OR)_3 <$ phosphines $<$ BIPY. The reaction mixtures of $SnHPh_3$ and $[PtMe_2(BIPY)]$ or $[PtMe_2(PMe_2Ph)_2]$ catalyse homogeneously the formation of Sn_2Ph_6. The starting complexes and product complexes were characterised by elemental analysis, IR, ^1H and ^{31}P-$\{^1H\}$ NMR spectroscopy.

Introduction

Platinum(IV) complexes containing triorganotin ligands tend to decompose easily to platinum(II) complexes. Thus, the complexes $[PtHCl(SnMe_3)_2(DPPE)]$ (DPPE = 1,2-bis(diphenylphosphino)ethane), $[PtH(SnMe_3)_3(DPPE)]$ [1] and $[PtH_2(SnR_3)_2L_2]$ (R = benzyl, aryl; L = $AsEt_3$, phosphine) [2] decompose on attempted recrystallisation, and it has been suggested that the rapid precipitation of these complexes is a significant feature of their synthesis [2]. In many instances, reactions between triorganostannanes and platinum(0) or

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platinum(II) complexes give only platinum(II) products, but the involvement of platinum(IV) intermediates is often implied, for example, by the presence of two triorganotin ligands in the products. The factors governing the stability of the platinum(IV) complexes are not well-understood, and since the results reported hitherto have almost exclusively concerned complexes with phosphine ligands, the role of the neutral ligands has not been explored. We now report a study of oxidative addition reactions of triarylstannanes with platinum complexes containing amine (2,2'-bipyridyl, BIPY; pyridine, PY), phosphine and triaryl phosphite ligands. As well as being electronically different from the phosphines, the amine and triaryl phosphite ligands have different (smaller) steric requirements.

Results and discussion

Starting complexes

The platinum(IV) complexes $[PtH(SnMe_3)_3(DPPE)]$ and $[PtH_2(SnR_3)_2L_2]$ have been shown to be formed in reactions between triorganostannanes and platinum(0) complexes or platinum(II) carbonato-complexes $[Pt(CO_3)L_2]$ [1,2]. The carbonato-complexes are probably reduced to platinum(0) intermediates by the stannane, and in other reactions platinum(II) oxalato-complexes have been shown to behave in a similar manner [3]. For the triaryl phosphites we have used platinum(0) and oxalato-platinum(II) complexes as starting complexes; attempts to prepare carbonato complexes with triaryl phosphite ligands were unsuccessful. For 2',2'-bipyridyl, the carbonato complex was used, and since the complex $[PtMe_2(BIPY)]$ had been shown to give platinum(IV) complexes with a number of organo derivatives of Group IV element halides [4—6], the reactions of this and some related dimethyl complexes with triorganostannanes have been examined.

The complex $[PtL_4]$, L = $P(OPh)_3$, was prepared by reduction of *cis*-$[PtCl_2L_2]$ with hydrazine in presence of an excess of L in ethanol [7]; the new complexes $[PtL_4]$ [L = $P(OC_6H_4Me\text{-}3)_3$ and $P(OC_6H_4Me\text{-}4)_3$] were prepared similarly. In attempts to obtain the complex with L = $P(OC_6H_4Me\text{-}3)_3$ in better yield, we treated $[Pt(PPh_3)_4]$ and $[Pt(C_2H_4)(PPh_3)_2]$ with an excess of L in ben-

TABLE 1

PROPERTiES OF PLATINUM(0) COMPLEXES

Complex	m.p. (°C)	Analysis (Found (calcd.) (%))		$^{31}P\text{-}\{^1H\}$ NMR parameters [a]		
		C	H	−δ (ppm)	$^1J(PtP)$ (Hz)	$^2J(PP)$ (Hz)
$[Pt\{P(OC_6H_4Me\text{-}3)_3\}_4]$	48	62.7 (62.9)	5.1 (5.3)	42.8	5881	
$[Pt\{P(OC_6H_4Me\text{-}4)_3\}_4]$	134—135	63.3 (62.9)	5.4 (5.3)	40.9	5835	
$[Pt(PPh_3)\{P(OC_6H_4Me\text{-}3)_3\}_3]$	118—120	64.5 (64.2)	5.2 (5.2)	42.3 [b] 126.0 [c]	6064 3470	66

[a] In benzene. Positive shifts are to high frequency of the reference $(MeO_3)P$ in C_6D_6. [b] Phosphite ligand. [c] PPh_3 ligand.

zene. In each case the product obtained after concentration of the solution and addition of hexane was the mixed complex $[Pt(PPh_3)L_3]$. The ^{31}P-$\{^1H\}$ NMR spectrum of this complex comprised a doublet at δ —40.6 ppm from the phosphite ligands L and a 1 : 3 : 3 : 1 quartet at δ —126 ppm for the PPh_3 ligand. The coupling constant $^1J(PtP)$ for the phosphite ligand is somewhat larger for the mixed complex (6064 Hz) than for the tetrakis(phosphite) complex (5881 Hz), and this trend has also been noted for the couplings to the tridentate phosphine ligand $CH_3C(CH_2PPh_2)_3$ (TRIPHOS) in the complexes [Pt(TRIPHOS)L] ($L = PPh_3$, $^1J(PtP)$ 3096 Hz; $L = P(OPh)_3$, $^1J(PtP)$ 2883 Hz) [8]. The ratio of the coupling constants $^1J(PtP)_{phosphite}/^1J(PtP)_{phosphine}$ is almost exactly the same for the complexes $[Pt\{P(OC_6H_4Me\text{-}3)_3\}_3L]$ [$L = P(OC_6H_4Me\text{-}3)_3$, PPh_3]. This is to be expected in such closely related complexes, since the changes induced in the platinum orbitals as well as those induced in the phosphorus orbitals are likely to be very similar.

Carbonato-complexes of platinum can be obtained by treatment of dichlorobis(phosphine) complexes with freshly prepared silver carbonate [9], or by displacement of the SEt_2 ligands of $[Pt(CO_3)(SEt_2)_2]$ by phosphine [10]. Both methods appeared to fail for $P(OPh)_3$: treatment of *cis*-$[PtCl_2\{P(OPh)_3\}_2]$ with silver carbonate resulted in deposition of platinum, and addition of $P(OPh)_3$ to a benzene solution of $[Pt(CO_3)(SEt_2)_2]$ led only to the platinum(0) complex $[Pt\{P(OPh)_3\}_4]$. However, the oxalato complex $[Pt(C_2O_4)\{P(OPh)_3\}_2]$ and the related complexes $[Pt(C_2O_4)L\{P(OPh)_3\}]$ ($L = PMe_2Ph$, PEt_3) were easily obtained from reactions between silver oxalate and the corresponding dichloro complexes. The bipyridyl complex $[Pt(CO_3)(BIPY)]$ was obtained from the slow reaction of BIPY with $[Pt(CO_3)(SEt_2)_2]$ in dichloromethane.

The dimethyl complexes $[PtMe_2L_2]$ ($L = \frac{1}{2}$ BIPY, PMe_2Ph, $\frac{1}{2}$ DPPE) were obtained from reactions between $[PtMe_2(COD)]$ (COD = cyclo-octa-1,5-diene) or $[Pt_2Me_4(SEt_2)_2]$ and L. Although the COD ligand of $[PtMe_2(COD)]$ is not displaced by pyridine, we found that pyridine enters the reaction if used as the solvent when $[PtMe_2(COD)]$ is treated with an equimolar proportion of PPh_3. The product was shown to be *cis*-$[PtMe_2(PY)(PPh_3)]$ by elemental analysis and by the ^1H NMR spectrum, in which there were resonances from the non-equivalent $PtCH_3$ groups, each displaying coupling to one ^{31}P nucleus and ^{195}Pt. This complex is probably formed by displacement of one olefinic donor group by PPh_3 followed rapidly by displacement of the second olefinic group by pyridine. It is known from kinetic studies that the second olefinic group of COD is displaced more rapidly by a nucleophile [11], and it is reasonable to assume that the high concentration of pyridine enables pyridine to compete effectively with the PPh_3 in this less-discriminating stage of the displacement.

Reactions with triorganostannanes

Reactions between the starting complexes and triorganostannanes were carried out at room temperature. Starting complexes with triaryl phosphite ligands gave *trans*-platinum(II) products containing two stannio ligands and two phosphorus donors; the products were isolated and characterised by elemental analysis and ^{31}P-$\{^1H\}$ NMR spectroscopy (Table 2). The configuration of the complexes is shown to be *trans* by the simple form of the Sn satellite resonances, and additionally for the complexes containing phosphine and phosphite ligands

TABLE 2

PROPERTIES OF COMPLEXES *trans*-$[Pt(SnR_3)_2L_2]$

Complex	m.p. (°C)	Analysis (Found (calcd.) (%))		^{31}P-$\{^1H\}$ NMR parameters [a]			
		C	H	−δ (ppm)	$^1J(PtP)$ (Hz)	$^2J(SnP)$ (Hz)	$^2J(PP)$ (Hz)
trans-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2\{P(OPh)_3\}_2]$	152	58.2	4.8	23.9	4814	171	
		(58.6)	(4.5)				
trans-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2\{P(OC_6H_4Me\text{-}3)_3\}_2]$				25.8	4819	166	
trans-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2\{P(OC_6H_4Me\text{-}4)_3\}_2]$				24.2	4741	168	
trans-$[Pt(SnPh_3)_2\{P(OC_6H_4Me\text{-}4)_3\}_2]$		57.0	4.6				
		(56.0)	(4.3)				
trans-$[Pt(SnPh_3)_2(PEt_3)\{P(OPh)_3\}]$	144	54.3	4.4	24.7	4443	190	557
		(54.5)	(4.6)	134	2527	161	
trans-$[Pt(SnPh_3)_2(PMe_2Ph)\{P(OPh)_3\}]$	105	55.7	4.1	23.7	4609	n.o. [b]	579
		(55.4)	(4.2)	157.1	2544	n.o. [b]	
trans-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2(PMe_2Ph)\{P(OPh)_3\}]$	151	58.5	4.9				
		(57.2)	(4.8)				

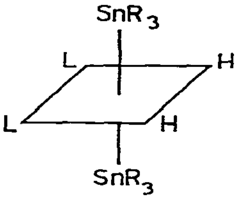
[a] In dichloromethane. Positive shifts are to high frequency of the reference $(MeO)_3P$ in C_6D_6. [b] Not observed.

by the large value of ^2J(PP), which is invariably associated with *trans* related ligands in platinum(II) complexes [12]. Reactions in benzene between [PtL$_4$] and SnHR$_3$ (L = P(OPh)$_3$, P(OC$_6$H$_4$Me-3)$_3$, P(OC$_6$H$_4$Me-4), R = C$_6$H$_4$Me-4; L = P(OC$_6$H$_4$Me-4)$_3$, R = Ph) gave *trans*-[Pt(SnR$_3$)$_2$L$_2$] and the reaction between the mixed phosphine-phosphite complex [Pt(PPh$_3$){P(OC$_6$H$_4$Me-3)}$_3$] and SnH-(C$_6$H$_4$Me-4)$_3$ gave only the phosphite complex *trans*-[Pt{Sn(C$_6$H$_4$Me-H)$_3$}$_2$-{P(OC$_6$H$_4$Me-3)$_3$}$_2$]. The reactions of the platinum(0) complexes [PtL$_4$] are believed to involve the initial dissociation of one ligand L [13]. Since phosphine complexes [PtL$_4$] are more dissociated than the corresponding phosphite complexes, it is probable that the mixed phosphine-phosphite complex loses the larger ligand PPh$_3$ [14] to give [Pt{(POC$_6$H$_4$Me-3)$_3$}], which then reacts with the stannane to form the phosphite complex *trans*-[Pt(SnR$_3$)$_2$L$_2$].

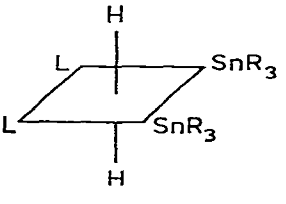
Platinum(II) complexes *trans*-[Pt(SnR$_3$)$_2$LL'] [R = C$_6$H$_4$Me-4, L = L' = P(OPh)$_3$; R = C$_6$H$_4$Me-4, L = PMe$_2$Ph, L' = P(OPh)$_3$; R = Ph, L = PEt$_3$, L' = P(OPh)$_3$; R = Ph, L = PMe$_2$Ph, L' = P(OPh)$_3$] were obtained by treatment of the oxalato complexes [Pt(C$_2$O$_4$)LL'] in ethanol with SnHR$_3$.

These results for phosphite-containing complexes contrast with those obtained previously, when platinum(IV) complexes [PtH$_2$(SnR$_3$)$_2$L$_2$] were obtained for L = phosphine from SnHR$_3$ and concentrated solutions of [PtL$_4$] in benzene or from SnHR$_3$ and [Pt(CO$_3$)L$_2$] in alcohols [2]. The presence of two SnR$_3$ ligands in the products from the phosphite complexes strongly implies that similar platinum(IV) complexes are intermediates in the reactions of both the platinum(0) phosphite complexes and the oxalato complexes. Since the platinum(IV) phosphine complexes were obtained as precipitates which readily lost H$_2$ on dissolution in benzene or dichloromethane, the intermediate platinum(IV) phosphite complexes are presumably of lower stability or greater solubility than the analogous phosphine complexes.

Treatment of [Pt(CO$_3$)(BIPY)}] in methanol with SnHR$_3$ (R = Ph, C$_6$H$_4$Me-2, C$_6$H$_4$Me-4) gave precipitates of [PtH$_2$(SnR$_3$)$_2$(BIPY)] which were characterised by elemental analysis, and by IR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra comprise a single resonance for Pt*H* coupled to ^{195}Pt and with unresolved ^{119}Sn and ^{117}Sn satellites. The intensity and the simple form of the Sn satellite spectra show that the complexes contain two magnetically equivalent Sn donor atoms, and the equivalence of the SnR$_3$ ligands is confirmed by the observation of a single Me resonance for the complexes with R = C$_6$H$_4$Me-2 or -4. Two structures, I and II (L = $\frac{1}{2}$ BIPY), are compatible with these results. The complexes with L = phosphine are known to have structure I with ν(PtH) 2080—2150 cm^{-1} and ^1J(PtH) 625—685 Hz [2]; these are of smaller magnitudes than ν(PtH) (2220—2260 cm^{-1}) and ^1J(PtH) (939—960 Hz) for the BIPY complexes.



(I)



(II)

TABLE 3

2,2′-BIPYRIDYL-PLATINUM(IV) COMPLEXES

Complex	M.p. [a] (°C)	Analysis (Found (calcd.) (%))			IR (cm^{-1})		^1H NMR parameters [b]				
		C	H	N	ν(PtH)	ν(PtC)	δ(Pt*H*) (ppm)	^1J(PtH) (Hz)	^2J(SnH) (Hz)	δ(PtC*H*$_3$) (ppm)	^2J(PtH) (Hz)
cis-trans-[PtH$_2$(SnPh$_3$)$_2$(BIPY)]	145	51.5	4.5	2.6	2220		−18.1	948	26		
		(52.3)	(3.8)	(2.7)							
cis-trans-[PtH$_2${Sn(C$_6$H$_4$Me-2)$_3$}$_2$(BIPY)]	170−175	55.8	4.7	2.6	2250		−17.7	939	28		
		(54.9)	(4.6)	(2.5)							
cis-trans-[PtH$_2${Sn(C$_6$H$_4$Me-4)$_3$}$_2$(BIPY)]	135−140	53.8	4.5	2.5	2260		−17.8	960	29		
		(54.9)	(4.6)	(2.5)							
cis-trans-[PtH(Me)(SnPh$_3$)$_2$(BIPY)] [c,d]	134	53.0	4.1	2.0	2218	570	−16.4	1033	25.4	1.17	66
		(52.9)	(4.0)	(2.6)							
cis-trans-[PtH(Me){Sn(C$_6$H$_4$Me-2)$_3$}$_2$(BIPY)] [d]	137−138	55.0	4.8	2.4	2225	540	−15.8	984	18	1.21	66
		(55.3)	(4.7)	(2.4)	(broad)						
cis-trans-[PtH(Me){Sn(C$_6$H$_4$Me-4)$_3$}$_2$(BIPY)] [e]	128−131	55.3	4.8	2.5	2210	575	−16.4	1037	25.4	1.15	64
		(55.3)	(4.7)	(2.4)							

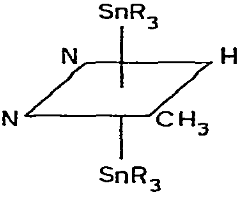
[a] With decomposition. [b] Solutions in $CDCl_3$; positive shifts are to high frequency of internal $SiMe_4$. [c] ^{119}Sn-{^{1}H} NMR (CH_2Cl_2 solution): δ −74.2 ppm, ^1J(PtSn) 6641 Hz. [c] Obtained from a reaction in methanol. [e] Obtained from a reaction in benzene.

The well-established dependence of the magnitudes of these parameters on the nature of the *trans* ligand, therefore, implies that for L = BIPY H is *trans* to N (structure I) and not *trans* to H (structure II). In contrast to the complexes I (L = phosphine), the complexes I (L = BIPY) show no tendency to lose H_2 and may be recrystallised without decomposition from benzene/pentane. It is probable, therefore, that the tendency of complexes I to lose H_2 varies with L in the order BIPY < phosphines, arsines [2] < phosphites, which is the order of increasing "softness" of the ligands [15], but does not correspond with the order of increasing steric effect of L, for which models (Corey—Pauling—Kolthum) indicate the order BIPY < phosphites < phosphines [14]. Since the dissociation of H_2 from the phosphine complexes can be reversed by passing H_2 through the solutions [2], the stability order may well be controlled by the dependence of the equilibrium constant for equation 1 on L, and it is reasonable that the relatively hard BIPY ligand should be associated with a smaller equilibrium constant than the phosphite ligands.

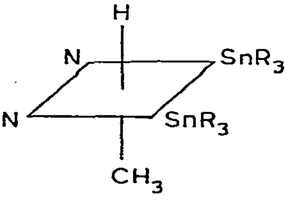
$$\textit{cis-trans}\text{-}[PtH_2(SnR_3)_2L_2] \rightleftharpoons [Pt(SnR_3)_2L_2] + H_2 \qquad (1)$$

Although the platinum(II) product is *trans* for L = unidentate phosphines or phosphites whereas the BIPY complex is *cis*, the extra stability this imparts to the phosphine and phosphite products is probably insufficient to affect the qualitative order of equilibrium constants, since solutions of complex I with R = Ph and L = $\frac{1}{2}$ DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane) also lose H_2 easily to form $[Pt(SnPh_3)_2(DPPE)]$ [2].

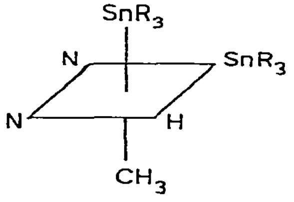
Addition of $SnHR_3$ (R = Ph, C_6H_4Me-2, C_6H_4Me-4) (4—5 mol) to a solution of $[PtMe_2(BIPY)]$ in methanol caused vigorous gas evolution and the solution changed from red to purple. A similar solution was formed by treatment of a suspension of $[PtMe_2(BIPY)]$ in benzene with $SnHR_3$ and the completion of the reaction after ca. 1 h was indicated by the complete dissolution of the starting complex. The volume of the solvent was reduced by evaporation and the complexes, which were obtained in high yield after the addition of hexane, had elemental analyses consistent with the formula $[PtH(Me)(SnR_3)_2(BIPY)]$ (Table 3). The integrated ^1H NMR spectrum also agreed with this formula and the intensities of the Sn satellites of the hydride resonance showed that two Sn donor atoms were present. The equivalence of the SnR_3 ligands was evident from the observation of a single resonance for the Me groups of R (R = C_6H_4Me-2 or -4) in the ^1H NMR spectra and in the ^{119}Sn-$\{^1H\}$ NMR spectrum for R = Ph (Table 3). Two structures, III and IV, are consistent with these results, but the magnitudes of the NMR and IR parameters, which are sensitive



(III)



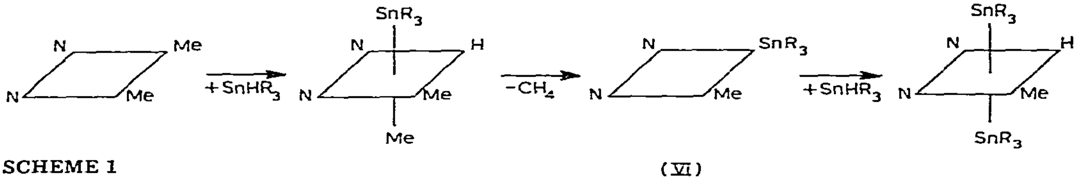
(IV)



(V)

to the nature of the *trans* ligand, provide strong support for structure III. Thus, ν(PtH) and ^1J(PtH) for [PtH(CH_3)(SnR_3)$_2$(BIPY)] have magnitudes similar to those for [PtH_2(SnR_3)$_2$(BIPY)] (Table 3) and larger than those for *cis-trans*-[PtH_2(SnR_3)$_2$$L_2$] (L = phosphines, As$Et_3$) [2], so H is probably *trans* to N rather than Me, which has a much higher *trans* influence. The coupling constants ^2J(PtCH) for [PtH(Me)(SnR_3)$_2$(BIPY)] (64—66 Hz) are slightly larger than for [PtMe_2(Cl)(SnR_nCl_{3-n})(BIPY)] (56—61 Hz [4]), where the Me ligands are *trans* to N. This also indicates structure III (CH_3 *trans* to N) rather than structure IV (CH_3 *trans* to H).

Analysis of the gas evolved during the formation of [PtH(Me)(SnR_3)$_2$(BIPY)] showed it to consist of H_2 and CH_4, whereas equation 1 and Scheme 1



SCHEME 1

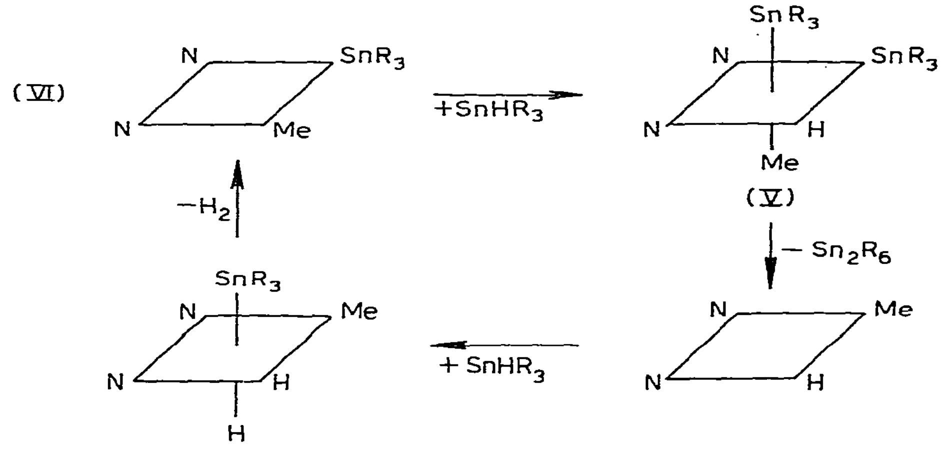
show only the formation of CH_4. For R = Ph, Sn_2Ph_6 was isolated from the

$$[PtMe_2(BIPY)] + 2\ SnHR_3 \rightarrow [PtH(Me)(SnR_3)_2(BIPY)] + CH_4 \qquad (1)$$

reaction mixtures, so it appears that this and the H_2 are formed catalytically from $SnHR_3$ (equation 2).

$$2\ SnHR_3 \rightarrow Sn_2R_6 + H_2 \qquad (2)$$

Neither the complex [PtH(Me)($SnPh_3$)$_2$(BIPY)] (III, R = Ph), BIPY, nor *cis-trans*-[PtH_2($SnPh_3$)$_2$(BIPY)], which could be formed from III (R = Ph) by elimination of CH_4 followed by addition of $SnHPh_3$, were significantly active in the catalysis of reaction 2. When the reaction between [PtMe_2(BIPY)] and $SnHPh_3$ was carried out with equimolar proportions of reagents, a mixture of the starting complex, complex III (R = Ph) and some decomposition products was formed, and when an excess of $SnHPh_3$ was used the IR spectrum of the prod-



SCHEME 2

uct mixture showed no band for ν(SnH), indicating that the stannane had been completely converted into III (R = Ph) or Sn_2Ph_6. A mixture from which the $SnHPh_3$ had disappeared was shown not to convert added $SnHPh_3$ into Sn_2Ph_6. Since the complexes III are formed in very high yields from [$PtMe_2$(BIPY)] and $SnHR_3$, it appears that the effective catalyst system is present in small concentrations in the reaction mixtures, and that the active complexes decompose or form III (R = Ph) in the absence of $SnHPh_3$. It is possible that the catalytic system involves an isomer of III (R = Ph) (e.g., V, R = Ph, Scheme 2) which readily loses Sn_2Ph_6. This isomer could be formed to a small extent from VI (Scheme 2) and $SnHPh_3$, and reductive elimination of Sn_2Ph_6 would generate [PtH(Me)(BIPY)]. This is expected to be a highly reactive complex which would rapidly undergo oxidative addition in presence of $SnHPh_3$, eventually forming IV and H_2 (Scheme 2), but which would probably decompose rapidly in the absence of $SnHPh_3$.

There was no indication of any reaction when [$PtMe_2$(BIPY)] was heated in benzene under reflux with Sn_2Ph_6, $Sn_2Bu^n{}_6$ or $SnMe_3(C_6H_4Me\text{-}4)$. Platinum(0) complexes react with compounds containing Sn—H [2], Sn—Sn or Sn—C bonds [16], but it appears that [$PtMe_2$(BIPY)] does not react with Sn—Sn or Sn—Ar bonds.

The reactions of stannanes with [$PtMe_2$(DIPHOS)] have been examined (DIPHOS = DPPE or bis(diphenylphosphino)methane) by Glocking et al. [1]. We found that treatment of *cis*-[$PtMe_2(PMe_2Ph)_2$] with $SnHPh_3$ in benzene or methanol led to the evolution of gas and formation of Sn_2Ph_6 and the complex *trans*-[$Pt(SnPh_3)_2(PMe_2Ph)_2$], which was identified by elemental analysis, the absence of a ν(PtH) band in the IR spectrum, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum (δ —154.6 ppm, ^1J(PtP) 2436, ^2J(SnP) 185 Hz) [2]. The complex *trans*-[$Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2(PMe_2Ph)_2$] was obtained in a similar manner. In one experiment, in which a solution of [$PtMe_2(PMe_2Ph)_2$] in methanol was treated with $SnHPh_3$, an off-white precipitate formed immediately. The IR spectrum showed a ν(PtH) band (at 2045 cm^{-1}) in the region expected for H *trans* to P in a platinum(IV) complex and at a higher frequency than that expected for H *trans* to Sn [1,2]. The spectrum also displayed a strong band at 450 cm^{-1} attributable to ν(Pt—C). These results and the elemental analysis are consistent with the formula *cis-trans*-[$PtH(Me)(SnPh_3)_2(PMe_2Ph)_2$]. An attempt to record the $^{31}P\text{-}\{^1H\}$ NMR spectrum of a benzene solution of the complex led to decomposition and only resonances for *trans*-[$Pt(SnPh_3)_2(PMe_2Ph)_2$] were detected.

Since the platinum(IV) complexes containing BIPY appear to be more stable than those containing phosphines, we examined the reaction of the mixed ligand complex *cis*-[$PtMe_2(PY)(PPh_3)$] with $SnHR_3$ in benzene. A precipitate of Sn_2Ph_6 was formed and addition of pentane gave a complex, believed to be *trans*-[$Pt(SnPh_3)_2(PY)(PPh_3)$] on the basis of its $^{31}P\text{-}\{^1H\}$ NMR spectrum (δ —111.6 ppm, ^1J(PtP) 3036, ^2J(SnP) 246 Hz), and there was no indication of the presence of a platinum(IV) complex.

Experimental

General

Reactions were carried out under dry nitrogen. Dichloromethane was distilled from phosphorus pentoxide and methanol was distilled from magnesium methoxide. Melting points were determined with a Kofler block or a Gallenkamp Electrothermal apparatus. Infrared spectra were recorded as Nujol mulls. The ^{1}H NMR spectra were recorded on a Perkin Elmer R32 instrument at 90 MHz or a Varian T60 spectrometer at 60 MHz; tetramethylsilane was used as the internal standard in deuteriochloroform solutions. The ^{31}P-{^{1}H} NMR spectra were recorded at 40.48 MHz with a JEOL PFT-100 Fourier Transform spectrometer using a solution of $P(OMe)_3$ in deuteriobenzene as the ^{2}H-lock and external standard. Positive shifts are to high frequency of the reference. Elemental analyses were carried out in the Microanalytical Laboratory of this School.

Starting complexes

[Pt{P(OPh)$_3$}$_4$]. This complex was prepared with m.p. 148—154°C by the method of Levison and Robinson [17].

[PtL$_4$] L = P(OC$_6$H$_4$Me)$_3$, P(OC$_6$H$_4$Me)$_3$. A suspension of *cis*-$[PtCl_2L_2]$ (0.5 g, obtained from $[PtCl_2(COD)]$ (COD = cyclo-octa-1,5-diene) and L) and L (0.5 g) in ethanol (10 cm^3) was treated with a 10% (by volume) solution of anhydrous hydrazine in butanol (1 cm^3) and the mixture was maintained at 50°C for 0.5 h. The pale yellow precipitate was filtered off and recrystallised from benzene/hexane to give the product as yellow crystals (yield: L = P(OC$_6$H$_4$Me-3)$_3$, 43%; L = P(OC$_6$H$_4$Me-4)$_3$, 23%). The low yields were due to the high solubility of these complexes.

[Pt(PPh$_3$){P(OC$_6$H$_4$Me-3)$_3$}$_3$]. A solution of $[Pt(PPh_3)_4]$ (0.59 g) in benzene was treated with P(OC$_6$H$_4$Me-3)$_3$ (0.84 g) and the solution put aside for 2 h at room temperature. The solution was then filtered, partially evaporated under reduced pressure, and treated with hexane to give the product as colourless crystals (72%). This complex was also obtained after treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with an excess of the phosphite in benzene under reflux.

[Pt(CO$_3$)(SEt$_2$)$_2$]. A solution of *cis*-$[PtCl_2(SEt_2)_2]$ (5.3 g) in dichloromethane (200 cm^3) was stirred for 3 h with an excess of freshly prepared silver carbonate (20 g) and filtered through Celite, and the filtrate was reduced in volume to ca. 20 cm^3 by evaporation under reduced pressure. Addition of diethyl ether (200 cm^3) gave a yellow oil which crystallised when set aside in the refrigerator. The crystals were washed with diethyl ether and with a 1/1 benzene/diethyl ether (to remove *cis*-$[PtCl_2(SEt_2)_2]$), to give the light brown product. (4.5 g, 85%), m.p. 72—74°C (Found: C, 24.7; H, 4.6. $C_9H_{20}O_3PtS_2$ calcd.: C, 24.8; H, 4.6%); ^{1}H NMR, δ 1.47 (CH_3), 3.0 (CH_2) ppm, ^3J(HH) 7.5 Hz; IR, ν(CO) 1680, 1615 cm^{-1}.

[Pt(CO$_3$)(BIPY)]. A solution of $[Pt(CO_3)(SEt_2)_2]$ (0.12 g) in dichloromethane (1 cm^3) was treated with BIPY (0.25 g) and the solution was put aside at room temperature. A red-brown precipitate began to form after 2 days. This was removed by filtration after 10 days and washed with benzene and diethyl ether to give the product as the monohydrate. (0.11 g, 89%), m.p. 270—280°C (decomp.) (Found: C, 30.6; H, 2.3; N, 6.3. $C_{11}H_{10}N_2O_4Pt$ calcd.: C, 30.8; H, 2.3; N, 6.5%); IR, ν(CO) 1650, ν(OH) 3430 cm^{-1}.

Reaction of [Pt(CO$_3$)(SEt$_2$)$_2$] with P(OPh)$_3$. Addition of $P(OPh)_3$ (0.5 cm^3) to a solution of $[Pt(CO_3)(SEt_2)_2]$ (0.2 g) in dichloromethane (2 cm^3) caused an exothermic reaction and gas was evolved. The cooled solution was treated with diethyl ether to give a white precipitate. Recrystallisation from hexane gave colourless crystals of $[Pt\{P(OPh)_3\}_4]$. (0.36 g, 54%), m.p. 153—155°C (Found: C, 59.5; H, 4.3. $C_{72}H_{60}O_{12}P_4Pt$ calcd.: C, 60.2, H, 4.2%).

$[Pt(C_2O_4)L\text{-}\{P(OPh)_3\}]$, $L = PMe_2Ph$, PEt_3, $P(OPh)_3$. The complex $[Pt(C_2O_4)(PMe_2Ph)\ \{P(OPh)_3\}]$ was prepared as follows. A solution of *cis*-$[PtCl_2(PMe_2Ph)\{P(OPh)_3\}]$ (0.49 g, prepared from *sym-trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ and two molar equivalents of $P(OPh)_3$) in dichloromethane was treated with silver oxalate (1.21 g) and the mixture was stirred at room temperature for 7 h. The suspension was then filtered and the filtrate concentrated by evaporation. Addition of diethyl ether gave the products as colourless crystals. (0.4 g, 78%), m.p. 188°C (Found: C, 46.1; H, 3.8. $C_{28}H_{26}O_7P_2Pt$ calcd.: C, 46.0; H, 3.6%); $^{31}P\text{-}\{^1H\}$ NMR, PMe_2Ph: δ —152.5 ppm, $^1J(PtP)$ 3438 Hz; $P(OPh)_3$: δ —83.8 ppm, $^1J(PtP)$ 6248, $^2J(PP)$ 46 Hz; IR, $\nu(CO)$ 1710, 1670 cm^{-1}. Similarly prepared were $[Pt(C_2O_4)(PEt_3)\{P(OPh)_3\}]$ and $[Pt(C_2O_4)P(OPh)_3]_2$ (Found: C, 50.4; H, 3.3. $C_{38}H_{30}O_{10}P_2Pt$ calcd.: C, 50.5; H, 3.3%), $^{31}P\text{-}\{^1H\}$ NMR, δ —36.4 ppm, $^1J(PtP)$ 5862 Hz; IR, $\nu(CO)$ 1690, 1720 cm^{-1}.

$[PtMe_2L_2]$ $L = \frac{1}{2}BIPY$, PMe_2Ph, $\frac{1}{2}DPPE$. The complex L = $\frac{1}{2}$BIPY was obtained by treatment of a warm benzene solution of $[PtMe_2(SEt_2)_2]$ with BIPY [5], and the complexes with L = PMe_2Ph, $\frac{1}{2}$ DPPE were obtained by treatment of $[PtMe_2(COD)]$ in benzene with a slight excess of the phosphine.

$[PtMe_2(PY)(PPh_3)]$. A solution of PPh_3 (0.082 g, 3.1×10^{-4} mol) in anhydrous PY (1.5 cm^3) was added dropwise to a solution of $[PtMe_2(COD)]$ (0.1 g, 3.1×10^{-4} mol) in anhydrous PY (2 cm^3) and the mixture was stirred at room temperature for 2 h. Most of the PY was then evaporated under reduced pressure and pentane (5 cm^3) added. The white precipitate was removed by filtration, washed with pentane (3×5 cm^3) and dried in vacuo to give $[PtMe_2(PY)(PPh_3)]$ (0.13 g, 72%), m.p. 158—159°C (decomp.). (Found: C, 53.6; H, 4.9; N, 2.2. $C_{25}H_{26}NPPt$ calcd.: C, 53.0; H, 4.6; N, 2.5%); $^{31}P\text{-}\{^1H\}$ NMR, δ —111.2 ppm, $^1J(PtP)$ 1954 Hz; ^1H NMR, δ 1.28 ppm ($PtCH_3$), $^2J(PtH)$ 84.6, $^3J(PH)$ 7.7 Hz, δ 1.24 ppm ($PtCH_3$), $^2J(PtH)$ 69.3, $^3J(PH)$ 7.3 Hz.

Reactions between phosphite-platinum(0) complexes and $SnHR_3$

A solution of $[Pt\{P(OPh)_3\}_4]$ (0.2 g) in benzene (5 cm^3) was treated with $SnH(C_6H_4Me\text{-}4)_3$ (0.12 g). After 0.5 h at room temperature the solvent was removed under vacuum and the residue washed with hexane and recrystallised from benzene/hexane to give *trans*-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2\{P(OPh)_3\}_2]$ as green-yellow needles (0.13 g, 67%). Similarly obtained were *trans*-$[Pt(SnR_3)_2L_2]$ R = Ph, L = $P(OC_6H_4Me\text{-}4)_3$ (63%); R = $C_6H_4Me\text{-}4$, L = $P(OC_6H_4Me\text{-}3)_3$, L = $P(OC_6H_4Me\text{-}4)_3$.

Reactions between oxalato-complexes and $SnHR_3$

A typical procedure was as follows. A solution of $[Pt(C_2O_4)(PEt_3)\{P(OPh)_3\}]$ (0.18 g) in ethanol was treated with $SnHPh_3$ (0.27 g) and the solution put aside for 1 h. Some of the solvent was then evaporated under vacuum and the solution treated with hexane to give *trans*-$[Pt(SnPh_3)_2(PEt_3)\{P(OPh)_3\}]$ as yellow crystals (0.19 g, 58%). Similarly prepared were *trans*-$[Pt(SnPh_3)_2(PMe_2Ph)\{P(OPh)_3\}]$ (51%), *trans*-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2(PMe_2Ph)\text{-}$

$\{P(OPh)_3\}]$ (63%) (Table 2), and *trans*-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2\{P(OPh)_3\}_2]$, which was identified from the $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 2).

Reactions between [Pt(CO₃)(BIPY)] and SnHR₃

The complex in methanol was treated with 4 molar proportions of $SnHR_3$ (R = Ph, $C_6H_4Me\text{-}2$, $C_6H_4Me\text{-}4$) and the solution put aside at room temperature for 1 h, during which time a red precipitate formed. Recrystallisation from benzene/hexane gave the product *cis-trans*-$[PtH_2(SnR_3)_2(BIPY)]$ as red crystals (Table 3).

Reactions between [PtMe₂(BIPY)] and SnHR₃

A mixture of $[PtMe_2(BIPY)]$ (0.1 g) and $SnHPh_3$ (0.5 cm^3) in benzene (5 cm^3) was stirred at room temperature for 1 h. There was an immediate reaction with gas evolution and the starting complex gradually dissolved. Most of the benzene was then removed under vacuum, and hexane (5 cm^3) was then added with stirring. The resulting purple precipitate was washed several times with hexane to give the pure complex (0.28 g, 99%). The hexane washings were combined and put aside for 12 h. White crystals of Sn_2Ph_6 identified by comparison of the IR spectrum and m.p. (227° C, lit. 232° C) with those of an authentic sample. In a separate experiment the gaseous products were collected and shown by GSC to be comprised of H_2 and CH_4. The product mixture obtained from $[PtMe_2(BIPY)]$ (0.1 g) and $SnHPh_3$ (2 cm^3) was divided into two portions. The solvent was evaporated from one portion and the IR spectrum of the residue indicated that no $SnHPh_3$ remained. The second portion was treated with $SnHPh_3$ (1 cm^3) and stirred for 24 h. There was no evolution of gas or colour change and the residue after removal of solvent showed a strong ν(SnH) band of $SnHPh_3$.

Mixtures of $SnHPh_3$ (0.5 cm^3) and $[PtH(Me)(SnPh_3)_2(BIPY)]$ (0.05 g) or *cis-trans*-$[PtH_2(SnPh_3)_2(BIPY)]$ (0.05 g) or BIPY (0.05 g) were stirred at room temperature for 24 h; there was no evolution of gas or colour change and the product mixtures gave IR spectra with a strong ν(SnH) band of $SnHPh_3$.

The complexes $[PtH(Me)(SnR_3)_2(BIPY)]$ were obtained from reactions in benzene for R = $C_6H_4Me\text{-}2$ (96%) and R = $C_6H_4Me\text{-}4$ (83%) and from reactions in methanol and a similar procedure for R = Ph (95%), $C_6H_4Me\text{-}2$ (83%) and $C_6H_4Me\text{-}4$ (93%). There were no significant differences in the properties of the complexes prepared from benzene or methanol solutions.

Reactions between cis[PtMe₂(PMe₂Ph)₂] and SnHR₃

Molten $SnHPh_3$ (0.5 cm^3) was added dropwise to a well stirred solution of *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.1 g) in methanol (5 cm^3) at room temperature. Gas evolution was observed and a pale yellow solid which precipitated was removed by filtration, washed with hexane (4 × 5 cm^3) and dried under vacuum to give $[Pt(SnPh_3)_2(PMe_2Ph)_2]$ (Analysis found: C, 53.4; H, 4.5. $C_{52}H_{47}P_2PtSn_2$ calcd.: C, 53.3; H, 4.5%) with $^{31}P\text{-}\{^1H\}$ NMR parameters similar to those reported previously (see above). Hexaphenyldistannane was recovered from the hexane washings.

On one occasion this procedure gave an immediate off-white precipitate with an IR spectrum (see above) and elemental analysis consistent with the formula

$[PtH(Me)(SnPh_3)_2(PMe_2Ph)_2]$ (Analysis found: C, 52.9; H, 4.4. $C_{53}H_{56}P_2PtSn_2$ calcd.: C, 53.6; H, 4.4%). The ^{31}P-$\{^1H\}$ NMR spectrum of a benzene solution of this complex showed the presence only of *trans*-$[Pt(SnPh_3)_2(PMe_2Ph)_2]$ (δ −154.6 ppm, ^1J(PtP) 2436, ^2J(SnP) 185 Hz) [2].

Treatment of *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.05 g) in benzene (5 cm^3) with $SnH(C_6H_4Me\text{-}4)_3$ (0.12 g) gave a white precipitate which was removed by filtration, washed with hexane and dried under vacuum to give *trans*-$[Pt\{Sn(C_6H_4Me\text{-}4)_3\}_2(PMe_2Ph)_2]$ (0.11 g, 86%) (Analysis found: C, 55.1; H, 5.6. $C_{58}H_{64}P_2PtSn_2$ calcd.: C, 55.5; H, 5.2%).

Reaction between $[PtMe_2(PY)(PPh_3)]$ and $SnHPh_3$

A suspension of $[PtMe_2(PY)(PPh_3)]$ (0.15 g) in benzene (2 cm^3) was treated with $SnHPh_3$ (0.46 g) and the mixture was stirred for 2 h at room temperature. Vigorous gas evolution occurred and a precipitate of Sn_2Ph_6 formed (0.12 g). Addition of pentane gave a pale yellow solid (0.15 g) which was examined in benzene solution by ^{31}P-$\{^1H\}$ NMR spectroscopy.

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