Oxidative Addition of Triorganotin Halides to Platinum(0) Complexes †

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Triorganotin chlorides react with complexes of Pt^0 to give products of insertion into the Sn–C rather than the Sn–Cl bond as reported previously. Products of the type *cis*-$[PtR(PPh_3)_2(SnR'_2X)]$ (R = Ph, R'_2X = Ph_2Cl, MePhCl, Me_2Cl, $BrPh_2$, Ph_2I, $Ph_2(OH)$, $Ph_2(ONO_2)$, or Ph_3) have been obtained from $[Pt(C_2H_4)(PPh_3)_2]$ and $SnPhR'_2X$, *cis*-$[PtMe(PPh_3)_2(SnMe_2Cl)]$ from $[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_3Cl$, and *cis*-$[PtMe(PEt_3)_2(SnMe_3)]$ from $[Pt(PEt_3)_4]$ and $SnMe_4$. Various reactions reported to give complexes with Cl and SnR_3 ligands have been re-investigated and shown to give complexes with R and SnR_2Cl ligands or complexes derived from them. The reported transformation of the $SnPh_3$ ligand into a Ph ligand and $SnPh_2$ has not been substantiated. Complexes and product-mixtures have been characterised by ^{31}P-$\{^1H\}$ spectra. An approximate thermochemical analysis suggests that M–C insertion may be favoured relative to M–Cl insertion for M = Sn, Ge, and Si, with reactivity decreasing in that order. The known complex *cis*-$[PtPh\{GePh_2(OH)\}(PEt_3)_2]$ may be formed *via* insertion of $[Pt(PEt_3)_2]$ into a Ge–Ph bond.

PREVIOUS reports of complexes $[PtClL_2(SnR_3)]$ (R = Ph or Me; L = unidentate phosphine) are summarised in Table 1.[1-5] Complexes formulated as $[PtCl(PPh_3)_2(SnPh_3)]$ or $[PtCl(PPh_3)_2(SnMe_3)]$ have been obtained by oxidative addition of SnR_3Cl to platinum(0) complexes or from platinum(II) complexes. However, in each instance there are significant differences in the reported physical properties of the materials obtained by the different routes, which could possibly imply the existence of *cis* and *trans* isomers. With the exception of $[PtCl(PMePh_2)_2(SnMe_3)]$, for which the reported ^1H n.m.r. parameters of the P–Me groups clearly imply a *trans* configuration,[5] the reported physical parameters are an inadequate basis for assignment of isomeric structure. Since determination of the ^{31}P n.m.r. spectra would be expected to establish their structures and to provide values of ^1J(Pt–P) for comparison with those available for complexes with SiR_3 and GeR_3 ligands,[6] we decided to repeat the reported synthetic procedures for $[PtCl(PPh_3)_2(SnPh_3)]$ and to examine the products by ^{31}P-$\{^1H\}$ Fourier-transform spectroscopy.

RESULTS AND DISCUSSION

Reaction of $[Pt(PPh_3)_4]$ *with* $SnPh_3Cl$.—A benzene solution containing equimolar quantities of $[Pt(PPh_3)_4]$ and $SnPh_3Cl$ deposited a white solid (I: m.p. 205 °C, i.r. band at 299 cm^{-1}) which gave a satisfactory analysis for $[PtCl(PPh_3)_2(SnPh_3)]$. This complex is presumably identical to that obtained by Layton *et al.*[1] The kinetics of the reactions between $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(PPh_3)_3]$ and $SnPh_3Cl$ have been studied, but no attempt was made to isolate the products.[7]

The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (I) in dichloromethane comprised two doublets each with ^{195}Pt satellites, characteristic of a *cis*-bis(phosphine) complex

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† No reprints available.

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with a different ligand *trans* to each phosphine. The coupling constant ^2J(PPtP) 15 Hz is typical for a *cis* complex, but the values ^1J(Pt–P) 2 137 and 2 689 Hz are very different from those we expected for *cis*-[PtCl(PPh$_3$)$_2$(SnPh$_3$)]. Since values of ^1J(Pt–P) are known to depend largely on the nature of the phosphine and of the *trans* ligand in complexes of Pt^{II},[8] we expected a value of ^1J(Pt–P) *ca.* 2 000 Hz for PPh$_3$ *trans* to Sn by analogy with *cis*-[Pt(PMe$_2$Ph)$_2$(SiMePh$_2$)] [^1J(Pt–P) 1 559 Hz] [6] and making allowance for an increase in ^1J(Pt–P) resulting from increasing phenyl substitution in the phosphine.[9] Although this could reasonably account for the smaller coupling constant ^1J(Pt–P) for (I), it implies that ^1J(Pt–P) 2 689 Hz for (I) derives from the PPh$_3$ *trans* to Cl. This coupling was very considerably smaller than for P *trans* to Cl in *cis*-[PtCl$_2$(PPh$_3$)$_2$] (3 679 Hz) or *cis*-[PtPh(Cl)(PPh$_3$)$_2$] (4 500 Hz).[10] One instance of a small coupling constant for P *trans* to Cl is known, namely for the platinum(IV) complex *cis*-[PtCl$_4$(PBu$_3$)$_2$] (2 065 Hz), but since values of ^1J(Pt–P) in Pt^{IV} are reduced by a factor of 0.6 from those in similar complexes of Pt^{II}, the estimated value for P *trans* to Sn in Pt^{IV} was *ca.* 1 200 Hz, too small to account for the other value of ^1J(Pt–P) in (I). Furthermore, there was no indication in the i.r. spectrum of (I) of formation of a platinum(IV) complex by *ortho*-metallation of a phenyl ring.

TABLE 1

Reported properties of [PtClL$_2$(SnR$_3$)] (L = unidentate phosphine)

Formula	Method of synthesis	M.p. (θ_c/°C)	$\tilde{\nu}$(Pt–Cl)/ cm^{-1}	Configuration [a]	Ref.	Other data
[PtCl(PPh$_3$)$_2$(SnPh$_3$)]	[Pt(PPh$_3$)$_4$] + SnPh$_3$Cl	205			1	
	trans-[PtCl(H)(PPh$_3$)$_2$] + SnPh$_3$(NO$_3$)	278—282 (decomp.)	298	*trans*	2	Found: C, 58.7; H, 4.20; Cl, 5.20%
	cis-[PtCl$_2$(PPh$_3$)$_2$] + Li(SnPh$_3$)				2	Details not reported
[PtCl(PPh$_3$)$_2$(SnMe$_3$)]	[Pt(C$_2$H$_4$)(PPh$_3$)$_2$] + SnMe$_3$Cl	280 (decomp.)	296	*trans*	3	τ(SnMe) 9.32 (in CDCl$_3$) Found: C, 50.55; H, 4.00%; Cl, unsatisfactory
	trans-[PtCl(H)(PPh$_3$)$_2$] + SnMe$_3$(NMe$_2$)	234	278	*trans*	4	τ(SnMe) 9.6, τ(Ph) 2.78
[PtCl(PMePh$_2$)$_2$(SnMe$_3$)]·2C$_6$H$_6$	[Pt(PMePh$_2$)$_4$] + SnMe$_3$Cl (*a*) [b]	113—117 (decomp.)		*trans*	5	Found: C, 48.55; H, 4.55% τ(SnMe) 9.42, τ(PMe) 8.37, $\lvert {}^2J(\text{PPtPCH}) + {}^2J(\text{PCH}) \rvert$ 6,[c] ^3J(PtPCH) 32 Hz (in CH$_2$Cl$_2$)
[PtCl(PMePh$_2$)$_2$(SnMe$_3$)]·C$_6$H$_6$	[Pt(PMePh$_2$)$_4$] + SnMe$_3$Cl (*b*) [b]	128—130		*trans*	5	Found: C, 52.0; H, 5.00; P. 6.5% (I.r. and ^{1}H n.m.r. similar to above complex)

[a] Assignments are usually only tentative. [b] Methods (*a*) and (*b*) of ref. 5. [c] The value quoted was 3 Hz, which probably refers to the separation of the triplet components.

It appeared possible that the presence of nine phenyl groups in [PtCl(PPh$_3$)$_2$)(SnPh$_3$)] could cause distortion of the complex and give rise to anomalous values of the coupling constants. We therefore prepared complexes containing nine phenyl groups, [PtCl(PPh$_3$)$_3$][BF$_4$] and *cis*-[PtCl(PPh$_3$)$_2$(SbPh$_3$)][BF$_4$] (the cation of which is isoelectronic with the tin complex), and examined the reactions of triphenylphosphine complexes of Pt^0 with SnMe$_n$Ph$_{3-n}$Cl (n = 1—3) in order to obtain complexes with a smaller number of phenyl groups in the tin ligand. The coupling constants for the cationic complexes were not anomalous. Values obtained for ^1J(Pt–P) in [PtCl(PPh$_3$)$_3$]$^+$, 2 481 (intensity 2) and 3 643 Hz (intensity 1), were as expected for P *trans* to P and for P *trans* to Cl, and in *cis*-[PtCl(PPh$_3$)$_2$(SbPh$_3$)]$^+$ the couplings were 3 118 and 3 584 Hz, which indicates that we may have underestimated ^1J(Pt–P) for P *trans* to Sn, but does not resolve the anomaly of the small coupling for P *trans* to Cl in the tin complex. During the course of other work, we found a value ^1J(Pt–P) 2 290 Hz for P *trans* to Sn in [Pt(SnPh$_3$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)].[11] The assignment of the smaller coupling in (I) to P *trans* to Sn could not therefore be regarded as completely reliable.

Reactions of Platinum(0) *Complexes with* SnMe$_n$Ph$_{3-n}$Cl (n = 1—3).—The reaction between [Pt(PPh$_3$)$_4$] and SnMePh$_2$Cl in benzene–diethyl ether gave a white solid (II), with an analysis corresponding to the expected product of oxidative addition and a band in the i.r. at 293 cm^{-1}. A similar reaction of SnMe$_2$PhCl gave a mixture of products, which was shown by ^{31}P-{^{1}H} n.m.r. to contain *cis*-[PtCl$_2$(PPh$_3$)$_2$] as well as a complex analogous to (I); by use of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] in place

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of [Pt(PPh$_3$)$_4$], we obtained a white crystalline product, (III), which gave an analysis corresponding to the expected tin complex and an i.r. absorption at 292 cm^{-1}. Complexes (I) and (II) were also prepared by this route. From the reaction between SnMe$_3$Cl and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] we obtained a white crystalline complex (IV), m.p. 240—242 °C and an i.r. band at 278 cm^{-1}, which gave an analysis corresponding to the expected oxidative-addition product. From a similar reaction, Akhtar and Clark[3] reported the isolation of [PtCl(PPh$_3$)$_2$(SnMe$_3$)], but with different physical properties from (IV) (Table 1). The physical properties of the complex obtained from *trans*-[PtCl(H)(PPh$_3$)$_2$] and SnMe$_3$(NMe$_2$) (Table 1)[4] correspond fairly closely with those of (IV), and it is reasonable to assume that the slightly lower m.p. is due to a different degree of purity.

The ^{31}P-{^{1}H} spectra of products (I)—(IV) were qualitatively similar, with ^2J(PPtP) 15—16 Hz, and values of ^1J(Pt–P) of 2 689 and 2 137 (I), 2 598 and 2 122 (II), 2 489 and 2 131 (III), and 2 474 and 2 092 Hz (IV). Thus the replacement of phenyl by methyl groups on tin [which increases from (I) to (IV)] caused a reduction in the magnitudes of the coupling constants rather than an increase towards the expected value of 3 700—4 500 Hz for PPh$_3$ *trans* to Cl, which, with the results for the cationic complexes, indicates that the coupling constants are not appreciably affected by steric factors.

In order to identify positively the coupling constants ^1J(Pt–P) derived from the bonds *trans* to Sn, sufficient spectra were accumulated for the ^{117}Sn and ^{119}Sn satellites to be observed. The coupling constants ^2J(SnPtP) are known to be in the range 100—200 Hz for Sn *cis* to P,[11] and, by analogy with the coupling constants ^2J(PPtP),[9] the values for *trans*-related ligands were expected to be much larger. For complexes (I)—(IV) satellite lines corresponding to ^2J(SnPtP) were observed with magnitudes *ca.* 150 Hz (Sn *cis* to P) for phosphorus with ^1J(Pt–P) *ca.* 2 100 Hz, and *ca.* 2 100—2 400 Hz (Sn *trans* to P) for phosphorus with the larger J(Pt–P) *ca.* 2 500—2 700 Hz. That a coupling constant ^1J(Pt–P) as low as *ca.* 2 100 Hz could derive from a phosphine *trans* to chloride now appeared exceedingly improbable. The magnitude of this coupling implies that the PPh$_3$ ligand must be *trans* to a group of high *trans* influence, and from the methods of synthesis and the coupling constant ^1J(Pt–P) 1 763 Hz for *cis*-[PtPh$_2$(PPh$_3$)$_2$][10] it is likely that the *trans* ligand is Ph or Me. Complexes containing these ligands could result from oxidative addition of SnMe$_n$Ph$_{3-n}$Cl involving Sn–C rather than Sn–Cl bonds.

The magnitude of the coupling constants can be accounted for in a very satisfactory manner in terms of this hypothesis. Complex (I) obtained from SnPh$_3$Cl is formulated as *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)], and the coupling for P *trans* to Ph is 2 137 Hz. Since couplings of closely similar magnitudes are observed for complexes (II) (2 122) and (III) (2 131 Hz), they also have P *trans* to Ph, and are formulated as *cis*-[PtPh(PPh$_3$)$_2$(SnMePhCl)], (II), and *cis*-[PtPh(PPh$_3$)$_2$(SnMe$_2$PhCl)], (III). However, complex (IV), obtained from SnMe$_3$Cl must be formulated as *cis*-[PtMe(PPh$_3$)$_2$(SnMe$_2$Cl)] with P *trans* to Me, and indeed the appropriate coupling constant (2 092 Hz) is significantly different from those in (I)—(III). Furthermore, the coupling constants now definitely assigned to P *trans* to Sn decrease in the sequence (I) (2 689) > (II) (2 598) > (III) (2 489 Hz), corresponding to increasing methyl substitution in the tin ligand, SnPh$_2$Cl (I), SnMePhCl (II), and SnMe$_2$Cl (III), and the coupling in (IV) (2 474 Hz) is very similar to that in (III) because the ligand *trans* to P is SnMe$_2$Cl in both (III) and (IV).

The new formulae of the complexes were unequivocally established from ^{1}H n.m.r. spectra of deuteriodichloromethane solutions. Under conditions of high spectrometer gain, the spectrum of (IV) comprised a low-intensity 1 : 1 : 1 : 1 quartet centred at τ 9.35 due to PtCH$_3$ coupled to two non-equivalent ^{31}P nuclei,[11] together with an intense sharp peak at τ 10.1 with tin satellites due to SnCH$_3$, and a multiplet at low field from phenyl groups. The integrated spectrum was also in agreement with the new formula. Since the presence of two kinds of phenyl group in complexes (I) and (II) could not be detected from the ^{1}H spectra, we obtained the spectrum of the product of the reaction between [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and Sn(C$_6$H$_4$Me-*m*)$_3$Cl. The spectrum contained two peaks attributable to methyl groups at τ 7.8 (six protons) and 8.3 (three protons) and the ^{31}P-{^{1}H} spectrum was very similar to that of (I). The complex must therefore be formulated as *cis*-[Pt(C$_6$H$_4$Me-*m*)(PPh$_3$)$_2${Sn(C$_6$H$_4$Me-*m*)$_2$Cl}] and the new formulation of complexes (I)—(III) is established by inference. Full details of the characterisation of the complexes are given in Table 2, and the reactions involved in the synthesis of these complexes are represented by equations (1) and (2).

$$[\mathrm{Pt(C_2H_4)(PPh_3)_2}] + \mathrm{SnMe_3Cl} \longrightarrow \\ cis\text{-}[\mathrm{PtMe(PPh_3)_2(SnMe_2Cl)}] + \mathrm{C_2H_4} \quad (1)$$

$$[\mathrm{Pt(C_2H_4)(PPh_3)_2}] + \mathrm{SnMe}_n\mathrm{Ph}_{3-n}\mathrm{Cl} \longrightarrow \\ cis\text{-}[\mathrm{PtPh(PPh_3)_2(SnMe}_n\mathrm{Ph}_{2-n}\mathrm{Cl)}] + \mathrm{C_2H_4} \quad (2)$$

Comparison with Previous Work.—Complex (IV), *cis*-[PtMe(PPh$_3$)$_2$(SnMe$_2$Cl)] (Table 2), has a similar m.p. and i.r. frequency to the complex obtained from *trans*-[PtCl(H)(PPh$_3$)$_2$] and SnMe$_3$(NMe$_2$) (in xylene at 145 °C for 2 h). To determine whether the complexes were identical, we repeated the reported procedure[4] and obtained a ^{31}P-{^{1}H} spectrum of a dichloromethane solution of the crude product. This indicated extensive decomposition and we were unable to identify any constituents of the mixture. An experiment with a shorter period of heating (15 min) gave a product with a satisfactory spectrum, which, however, showed the presence of at least three complexes. The major component had a spectrum which was virtually identical with that of complex (IV) except that the ^{195}Pt satellites were too weak to be observed. Also present were *cis*-[PtCl$_2$(PPh$_3$)$_2$] and *trans*-[PtCl(H)(PPh$_3$)$_2$] (unchanged starting material), identified by comparison of shifts and coupling constants with those of authentic samples. This result, together with the reported m.p., shows that the brown crystals previously obtained from *trans*-[PtCl(H)(PPh$_3$)$_2$] and SnMe$_3$(NMe$_2$) were a less pure form of complex (IV). The high purity of (IV) is indicated by the ^{31}P-{^{1}H} spectrum, in which $<5\%$ of the total intensity is attributable to impurities. One impurity was identified as *cis*-[PtCl$_2$(PPh$_3$)$_2$], but this may have been produced by slow elimination of SnMe$_3$Cl followed by reaction of the platinum(0) species with the solvent (CH$_2$Cl$_2$), since we showed in a separate experiment that the ^{1}H spectrum of (IV) in CDCl$_3$ changes with time, with SnMe$_3$Cl (peak at τ 9.35)[12] appearing in the solution and the gradual precipitation of *cis*-[PtCl$_2$(PPh$_3$)$_2$]. Since the compound SnMe$_3$(NMe$_2$) is known to be a powerful dehydrochlorination reagent,[13] the mechanism of formation of (IV) under these conditions is probably as in equations (3) and (4).

$$trans\text{-}[PtCl(H)(PPh_3)_2] + SnMe_3(NMe_2) \longrightarrow [Pt(PPh_3)_2] + SnMe_3Cl + NMe_2H \quad (3)$$

$$[Pt(PPh_3)_2] + SnMe_3Cl \longrightarrow cis\text{-}[PtMe(PPh_3)_2(SnMe_2Cl)] \quad (4)$$

Since our complex (IV) and that of Akhtar and Clark[3] (Table 1) were obtained from [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and SnMe$_3$Cl under similar conditions, it is most improbable that their complex was correctly formulated, and the differences in the physical parameters obtained are rather surprising. Since the high purity of (IV) is strongly indicated by its ^{31}P-{^{1}H} spectrum, it is unlikely that the higher m.p. for the other material was associated with a purer form of (IV). It is possible that the material obtained by Akhtar and Clark was a mixture of (IV) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] since the latter has m.p. 300—310 °C and ν(Pt–Cl) at 295 and 321 cm^{-1}, and a satisfactory chlorine analysis could not be obtained. Furthermore, they found τ(SnMe) 9.32 (CDCl$_3$ solution) which probably corresponds to the presence of SnMe$_3$Cl (τ 9.35[12]) in their solutions and this would prevent the observation of the very weak signals from the PtCH$_3$ group of (IV) (τ 9.35) if this were also present.

Complexes formulated as [PtCl(PPh$_3$)$_2$(SnPh$_3$)] have been described by Layton *et al.*[1] and by Baird,[2] and the former is clearly identical to (I) (Tables 1 and 2). Baird used two synthetic methods, but gave details only for the better route (Table 1), and he also reported that i.r. spectra indicated that his complex was converted into [PtPh(Cl)(PPh$_3$)$_2$] in acetone under reflux during 2 h [equation (5)].[2] We

$$trans\text{-}[PtCl(PPh_3)_2(SnPh_3)] \longrightarrow trans\text{-}[PtPh(Cl)(PPh_3)_2] + SnPh_2 \quad (5)$$

found that complex (I) did not change on refluxing in acetone or tetrahydrofuran, and there was no indication of formation of *trans*-[PtPh(Cl)(PPh$_3$)$_2$] after prolonged heating in toluene. It therefore appears probable that Baird's complex is different from (I), so we repeated the synthesis as described from *trans*-[PtCl(H)(PPh$_3$)$_2$] and SnPh$_3$(NO$_3$). We obtained a white crystalline product, m.p. 280—285 °C (turned brown at *ca.* 200 °C), i.r. bands at 299, 311, and 323 cm^{-1}, and analytical results (Found: C, 58.05; H, 4.15%) close to the reported values (Table 1). Apart from the additional bands at 311 and 323 cm^{-1}, this product is exactly as described by Baird. The ^{31}P-{^{1}H} spectrum in dichloromethane showed the presence of three complexes, (A)—(C). One of these [(A), *ca.* 40% of the total spectrum intensity] had parameters in precise agreement with those found for (I) (tin satellites were too weak to be observed in the mixture). Another complex [(B), *ca.* 35%] was identified as *trans*-[PtPh(Cl)(PPh$_3$)$_2$] by comparison

TABLE 2

Data for the complexes *cis*-[PtR(PPh$_3$)$_2$L] (L = SnR′$_2$X, SnRR′Cl, or SnR′$_3$)

Complex	M.p. (θ_c/°C)	$\tilde{\nu}$(Sn–Cl) cm^{-1}	Analysis (%)				τ(SnCH$_3$)[a]	^2J(SnCH) Hz	δ(P)[b,c] p.p.m.	^1J(Pt–P)[c]	^2J(^{117}SnPtP)[c]	^2J(^{119}SnPtP)[c]	^2J(PPtP)
			Found		Calc.					Hz			
			C	H	C	H							
cis-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] (I)	205	299	59.2	4.40	58.7	4.10			113.8	2 689	2 291	2 398	15
	(decomp.)								117.5	2 137	145	151	
cis-[PtPh(PPh$_3$)$_2$(SnMePhCl)] (II)	170—200	293	55.9	4.35	56.4	4.15	9.9	39	113.8	2 598	2 205	2 310	15
	(decomp.)								117.3	2 122	149[d]		
cis-[PtPh(PPh$_3$)$_2$(SnMe$_2$Cl)] (III)	240—250	292	53.65	4.10	53.85	4.20	10.1	39	113.8	2 489	2 107	2 205	15
	(decomp.)								118.2	2 131	148[d]		
cis-[PtMe(PPh$_3$)$_2$(SnMe$_2$Cl)]	240—242	278	50.75	4.15	51.0	4.30	10.1[e]	34	107.9	2 474	2 174	2 274	16
	(decomp.)								118.4	2 092	175[d]		
cis-[Pt(C$_6$H$_4$Me-*m*)(PPh$_3$)$_2$-{Sn(C$_6$H$_4$Me-*m*)$_2$Cl}]	176—181	291	55.7	4.30	56.55	4.35[f]	[g]		112.9	2 671	[h]		15
	(decomp.)								116.4	2 148			
cis-[PtPh(PPh$_3$)$_2$(SnBrPh$_2$]	195—205		55.85	4.00	56.4	4.00			114.1	2 717	[h]		15
	(decomp.)								116.1	2 140			
cis-[PtPh(PPh$_3$)$_2$(SnPh$_2$I)]	200—210		54.2	3.95	54.2	3.80			115.9	2 748	[h]		15
	(decomp.)								115.2	2 126			
cis-[PtPh(PPh$_3$)$_2${SnPh$_2$(OH)}]	205—208		60.1	4.70	59.7	4.25			112.9	2 463	[h]		15
	(decomp.)								118.7	2 095			
cis-[PtPh(PPh$_3$)$_2${SnPh$_2$(ONO$_2$)}]	200—205		53.45	4.10[i]	54.3	3.90[f,i]			113.9	2 810	[h]		16
	(decomp.)								124.3	1 990			
cis-[PtPh(PPh$_3$)$_2$(SnPh$_3$)]	195—200		59.65	4.30	59.5	4.25[f]			114.2	2 344	[h]		17
	(decomp.)								119.3	2 036			

[a] Relative to CH$_2$Cl$_2$ or SiMe$_4$ as internal standard in CD$_2$Cl$_2$ solutions. Multiplets due to aromatic protons occurred at τ 2.5—3.0. [b] Shifts of CH$_2$Cl$_2$ solutions to high field of external P(OMe)$_3$ in C$_6$D$_6$. [c] Upper value refers to P *trans* to Sn. [d] Separate ^{117}Sn and ^{119}Sn satellites were not resolved. [e] Parameters of Pt–Me: τ 9.35, ^3J(PPtCH) 7 and 11 Hz. [f] Includes 1 mol of CH$_2$Cl$_2$ of crystallisation. [g] Parameters of aryl C*H*$_3$: τ 7.8 (6 H) and 8.3 (3 H). [h] Signal to noise ratio insufficient for observation of Sn satellites. [i] N, 1.20 (Calc.: 1.15%).

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with an authentic spectrum. The remaining complex [(C), *ca.* 25%] had a spectrum characteristic of a *cis*-bis(phosphine) complex with non-equivalent phosphines [^1J(Pt–P) 2 052 and 3 108, ^2J(PPtP) 16 Hz]. The coupling of magnitude 2 052 Hz indicates the presence of a Ph ligand *trans* to PPh_3, but the coupling 3 108 Hz is larger than expected for *trans* ligands $SnPh_3$ or $SnPh_2X$, and too small to imply a *trans* ligand such as chloride or nitrate.[14] Large values of ^1J(Pt–P) are associated with more ionic bonds to the *trans* ligands,[14] so the unidentified ligand in (C) may be SnPhXY (X, Y = Cl, OH, or ONO_2). There is thus no evidence for the formation of $SnPh_3$ complexes in the reactions reported by Baird (Table 1), but complex (I) is formed in both reactions, and its presence explains the slight decomposition observed on heating the product mixture above *ca.* 200 °C. A plausible mechanism for the formation of (I) in the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and $Li(SnPh_3)$ is represented by equations (6) and (7); the mechanism for formation of (I) in the reaction of the hydride complex with $SnPh_3(NO_3)$ presumably involves formation of $SnPh_3Cl$ and a complex of Pt^0, but the details are not clear. A complex with two electronegative groups on tin could be formed *via* acid cleavage of a Ph group from Sn.[15] The mechanism of formation of *trans*-$[PtPh(Cl)(PPh_3)_2]$, (B), is discussed below.

$$cis\text{-}[PtCl_2(PPh_3)_2] + Li(SnPh_3) \longrightarrow [Pt(PPh_3)_2] + SnPh_3Cl + LiCl \quad (6)$$

$$[Pt(PPh_3)_2] + SnPh_3Cl \longrightarrow cis\text{-}[PtPh(PPh_3)_2(SnPh_2Cl)] \quad (7)$$

Our failure to obtain *trans*-$[PtPh(Cl)(PPh_3)_2]$ from a sample of (I) (known from the ^{31}P-{^1H} spectrum to contain <0.5% of observable phosphorus-containing impurity), together with its presence as *ca.* 35% of component (B) in Baird's starting material, suggested that his report of its formation in refluxing acetone could have been derived from selective precipitation of this component by the procedure adopted to obtain samples for examination of their i.r. spectra. Although we could not demonstrate this for our sample of mixture (A)—(C), selective precipitation of component (B) could depend critically on the concentrations and other variables involved. Alternatively it is possible that Baird's observations on the effects of heating in acetone may have been affected by the presence of HCl resulting from hydrolysis of Sn–Cl bonds. Addition of a slight excess of HCl in diethyl ether to (I) in dichloromethane gave a yellow solution from which a white precipitate was obtained on addition of ethanol. From the ^{31}P-{^1H} spectrum this was shown to be composed of *cis*-$[PtPh(Cl)(PPh_3)_2]$ (*ca.* 55%), *trans*-$[PtPh(Cl)(PPh_3)_2]$ (30%), and *cis*-$[PtCl_2(PPh_3)_2]$ (15%), indicating that the Pt–Sn bond is more readily cleaved than the Pt–Ph bond by HCl. It is very probable that the component (B), *trans*-$[PtPh(Cl)(PPh_3)_2]$, in the mixture (A)—(C) is formed by acid cleavage of Sn from (A) (≡I) during the reaction or work-up.

In view of the formation of complexes with SnR_2Cl ligands in reactions of SnR_3Cl with platinum(0) complexes of PPh_3, it would be surprising if the reaction between $SnMe_3Cl$ and $[Pt(PMePh_2)_4]$ gave a product containing the $SnMe_3$ ligand (Table 1).[5] Repetition of this reaction by the procedure described (method *b* of ref. 5) gave a light brown material with analysis for C and H close to that reported (Found: C, 52.3; H, 5.05%). This material appeared to melt at 110—112 °C, but resolidified and melted again at 172 °C. As reported previously,[5] this complex probably contains benzene of crystallisation, and a second form, which was off-white [(V), m.p. 172 °C], was obtained after recrystallisation from dichloromethane–hexane. This material gave analytical results (Found: C, 49.65; H, 5.00%) similar to those reported for the product of a reaction with stoicheiometric quantities of reagents (Table 1; method *a* of ref. 5). The ^{31}P-{^1H} spectrum of this material in dichloromethane comprised a triplet and a doublet of relative intensities 1 : 2 together with ^{195}Pt satellites. There were no observable phosphorus-containing impurities. The spectrum shows that (V) is a tris(phosphine) complex and the values of ^1J(Pt–P) [2 924 (intensity 2), 1 880 Hz (intensity 1)] are similar to those in $[PtMe(PPh_3)_3][SFO_3]$ (2 925 and 1 919 Hz)[16] and significantly different from those in $[PtH(PEt_3)_2(PPh_3)][ClO_4]$ (2 480 and 2 094 Hz).[17] Analytical results and the method of preparation of (V) then suggest the formulation $[PtMe(PMePh_2)_3][SnMe_3Cl_2]$, and this is partially confirmed by the similarity of ^1H shift for the Sn–Me group in (V) (τ 9.24) and in a mixture of $SnMe_3Cl$ and $[NEt_4]Cl$ (τ 9.29) (both samples in dichloromethane). The observation of a virtually coupled P–Me triplet [τ 8.2, $|^2J(PCH) + {}^4J(PPtPCH)|$ 6, ^3J(PtPCH) 32 Hz] and a P–Me doublet [τ 8.4, ^2J(PCH) 7 Hz] is consistent with the formulation as a tris(phosphine) complex, but lines attributable to the Pt–Me group could not be identified, presumably because the coupling to 3P and Pt causes extensive splitting of the resonance, which is also expected to be situated in a region obscured by Sn and Pt satellites of the SnMe and PMe resonances. A possible mechanism for the formation of (V) is represented in equations (8)—(10); the first step, (8), is presumed to be similar to (1) and the HCl is probably formed by hydrolysis of $SnMe_3Cl$.

$$[Pt(PMePh_2)_4] + SnMe_3Cl \longrightarrow [PtMe(PMePh_2)_2(SnMe_2Cl)] + 2PMePh_2 \quad (8)$$

$$[PtMe(PMePh_2)_2(SnMe_2Cl)] + HCl \longrightarrow [PtMe(Cl)(PMePh_2)_2] + SnMe_2ClH \quad (9)$$

$$[PtMe(Cl)(PMePh_2)_2] + PMePh_2 + SnMe_3Cl \longrightarrow [PtMe(PMePh_2)_3][SnMe_3Cl_2] \quad (10)$$

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[15] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542.

[16] C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J.C.S. Dalton*, 1976, 58.

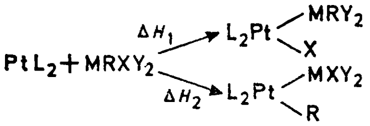
[17] T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846.

The presence of the Pt–Me group in (V) is a very strong indication that [PtMe($PMePh_2$)$_2$($SnMe_2Cl$)] rather than [PtCl($PMePh_2$)$_2$($SnMe_3$)] is formed from [Pt($PMePh_2$)$_4$] and $SnMe_3Cl$, but it is not clear whether the products obtained by Clark and Itoh[5] contained [PtMe($PMePh_2$)$_2$($SnMe_2Cl$)] or were essentially identical to the products we obtained. Both Clark and Itoh and ourselves obtained two products whose formulae differ by one molecule of benzene of crystallisation, and the ^1H parameters of the principal resonances (Sn–Me and *trans* P–Me groups) are rather similar. The ^1H shift of the Sn–Me group reported by Clark and Itoh is also somewhat different from the value obtained for the $SnMe_2Cl$ ligand in (IV), so we incline to the view that the two sets of complexes are similar. However, the m.p.s of the complexes are substantially different and the phosphorus analysis reported by Clark and Itoh (Table 1) is lower than required for the formulation [PtMe($PMePh_2$)$_3$][$SnMe_3Cl_2$]·C_6H_6 (P, 8.25%).

Reaction of Organotin Compounds with Platinum(0) *Complexes.*—The most straightforward route to complexes [PtR(PPh_3)$_2$(SnRR′Cl)] (R, R′ = Me or Ph) is the oxidative-addition reaction of the appropriate triorganotin chloride with [Pt(C_2H_4)(PPh_3)$_2$]. We have made a brief investigation of the scope of this type of reaction. The tin compounds $SnPh_3X$ (X = Br, I, OH, or ONO_2) reacted with [Pt(C_2H_4)(PPh_3)$_2$] in benzene to form white precipitates which had ^{31}P-{^1H} parameters similar to those of *cis*-[PtPh(PPh_3)$_2$($SnPh_2Cl$)] (Table 2), so they are assigned formulae *cis*-[PtPh(PPh_3)$_2$($SnPh_2X$)] (X = Br, I, OH, or ONO_2). The iodo-complex is also formed in the reaction between (I) and sodium iodide in dichloromethane–acetone. As expected, the i.r. band at *ca.* 290 cm^{-1} is absent in the spectra of these complexes, supporting its assignment to ν(Sn–Cl).

The electronegativity of iodine is relatively low, and on the Pauling scale it has the same value (2.5) as carbon,[18] so the reactivity of $SnPh_3I$ indicates that the presence of a Sn–X bond of high polarity is not a requirement in this reaction. Furthermore, since the Sn–C bond breaks in these reactions, the group X may not be significantly involved. Accordingly we examined the reactions of compounds containing only Sn–C bonds. Under fairly vigorous conditions (50 °C for 1 h), *cis*-[PtPh(PPh_3)$_2$($SnPh_3$)] was obtained from $SnPh_4$ and [Pt(C_2H_4)(PPh_3)$_2$], but when this platinum(0) complex was treated with $SnMe_4$ under a variety of conditions, a red colouration characteristic of polynuclear complexes developed, and there were no indications in the ^{31}P-{^1H} spectra of formation of tin-containing complexes of Pt^{II}. However, treatment of the more reactive platinum(0) complex [Pt(PEt_3)$_4$][19] with $SnMe_4$ in benzene under reflux for 5 h led to the isolation of an oil, the ^{31}P-{^1H} spectrum of which clearly indicated the presence of *cis*-[PtMe(PEt_3)$_2$($SnMe_3$)] [δ 128.6 p.p.m., ^1J(Pt–P) 1 598 Hz (*trans* to Me); δ 131.4 p.p.m., ^1J(Pt–P) 2 233 Hz (*trans* to Sn), ^2J(PPtP) 18 Hz] contaminated with PEt_3 and PEt_3O.

Comparison of Carbon and Tin Compounds.—The oxidative-addition reactions of alkyl and aryl halides RX with phosphine complexes of Pt^0 may be regarded as insertions of the PtL_2 (L = phosphine) moiety into C–X bonds. With triorganotin halides SnR'_3X the Sn–C rather than the Sn–X bond undergoes insertion. The mode of reaction is probably determined by kinetic rather than thermodynamic factors, but at present there is no information concerning the mechanism of the reaction of the tin compounds; some, at least, of the reactions of alkyl halides have been shown to involve abstraction of halogen by Pt^0 with formation of R· radicals.[20] Although an analysis of the thermodynamic factors related to the mode of reaction is hampered by the paucity of appropriate heats of formation and bond energies, an approximate treatment in terms of the Scheme is possible. The Group 4 halide is represented by $MRXY_2$ (M = Group 4 element; X = halogen; R bonds to M or Pt *via* a carbon atom; Y = H, alkyl, or aryl) and ΔH_1 and ΔH_2 are heats of reaction for the formalised insertions into the M–X and M–C bonds. For a given M (C or Sn), factors which make ($\Delta H_2 - \Delta H_1$) more negative may favour insertion into the M–C bond. If it is assumed that the Pt–M bond energy is the same for the ligands MRY_2 and MXY_2, then ($\Delta H_2 - \Delta H_1$) is given in terms of bond energies (E) by equation (11).



SCHEME

$$\Delta H_2 - \Delta H_1 = -(E_{\mathrm{PtX}} - E_{\mathrm{PtR}}) - (E_{\mathrm{MR}} - E_{\mathrm{MX}}) \quad (11)$$

If we compare ($\Delta H_2 - \Delta H_1$) for M = C with M = Sn, the terms involving bonds to platinum cancel, and the comparison reduces to the difference in the terms ($E_{\mathrm{MR}} - E_{\mathrm{MX}}$) for C and Sn. For carbon the terms take values 29, 71, and 143 kJ mol^{-1} for X = Cl, Br, or I, and for tin the terms are −94 and −47 kJ mol^{-1} for X = Cl and Br.[21] The approximate analysis is therefore in agreement with experiment to the extent that, for a given X, tin compounds have a much greater tendency than carbon compounds to react by insertion into M–C rather than M–X.

For M = Si or Ge, the values of the terms ($E_{\mathrm{MR}} - E_{\mathrm{MX}}$) (X = Cl, Br, and I) are −90, −9, and +60 kJ mol^{-1} (M = Si), and −87, −21, and +42 kJ mol^{-1} (M = Ge),[21] which are rather similar to the values for M = Sn. This suggests that when carbon and tin compounds undergo different modes of insertion the silicon and germanium compounds would probably resemble tin

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[18] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Hala, New York, 1960.

[19] G. W. Parshall, *J. Amer. Chem. Soc.*, 1974, **96**, 2360.

[20] M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.

[21] M. C. Ball and A. H. Norbury, 'Physical Data for Inorganic Chemists,' Longmans, London, 1974.

rather than carbon compounds. However, in view of the greater strength of M–X and M–C bonds for M = Si and Ge compared with M = Sn, it is probable that silicon and germanium compounds would be of lower reactivity than tin compounds in oxidative-addition reactions.

Reactions of Germanium Compounds.—Although the thermochemical analysis is approximate and incomplete, it suggests that if GeR_3X underwent an oxidative-addition reaction with a phosphine complex of Pt^0 the product would be $[PtR(GeR_2X)L_2]$ rather than $[PtX(GeR_3)L_2]$ (L = phosphine). From a brief examination it appeared that $[Pt(C_2H_4)(PPh_3)_2]$ and $[Pt(PEt_3)_4]$ were insufficiently active to give oxidative-addition products with $GeMe_3Ph$ or (2-benzo[*b*]furyl)trimethylgermane; with $GeBrMe_3$ or $GeBrPh_3$ and $[Pt(C_2H_4)(PPh_3)_2]$, small amounts of platinum(II) bromo-complexes were identified in the ^{31}P-{^1H} spectra of the products, but they are probably formed from HBr produced by hydrolysis of the Ge–Br bonds. However, the complex *cis*-$[PtPh\{GePh_2(OH)\}(PEt_3)_2]$ has been known for some time, having been obtained after hydrolysis of a mixture of $[PtI_2(PEt_3)_2]$ and $Li(GePh_3)$.[22] Originally formulated as $[Pt(GePh_3)(OH)(PEt_3)_2]$, its structure was later established by *X*-ray methods, and it was suggested, by analogy with the reaction (5) described by Baird, that the mechanism of its formation might involve rearrangement of the hydroxo-complex.[23] In view of the formation of *cis*-$[PtPh(PPh_3)_2\{SnPh_2(OH)\}]$ from $SnPh_3(OH)$ and $[Pt(C_2H_4)(PPh_3)_2]$ and the lack of confirmation in our results for reaction (8), it appears probable that the germanio-complex was formed by insertion of a platinum(0) complex into a Ge–Ph bond. A possible mechanism is summarised in equations (12)—(14), where

$$trans\text{-}[PtI_2(PEt_3)_2] + Li(GePh_3) \longrightarrow [Pt(PEt_3)_2] + GePh_3I + LiI \quad (12)$$

$$[Pt(PEt_3)_2] + GePh_3I \longrightarrow cis\text{-}[PtPh(GePh_2I)(PEt_3)_2] \quad (13)$$

$$cis\text{-}[PtPh(GePh_2I)(PEt_3)_2] + [OH]^- \longrightarrow cis\text{-}[PtPh\{GePh_2(OH)\}(PEt_3)_2] + I^- \quad (14)$$

the basic solution formed at the hydrolysis stage is presumed to result in replacement of iodide on Ge by hydroxide. The complex $[Pt(PEt_3)_2]$, which is postulated as an intermediate in this reaction, would be more reactive than $[Pt(PEt_3)_4]$, so the failure to observe oxidative addition by Ge–C bonds using $[Pt(PEt_3)_4]$ is not inconsistent with the proposed mechanism, (12)—(14).

Conclusions.—Our results have not confirmed earlier reports of the preparations of the complexes $[PtClL_2(SnR_3)]$ summarised in Table 1. Although there is not always exact correspondence between the properties of our complexes and those reported for complexes obtained by similar methods, the generality found for the oxidative addition involving Sn–C rather than Sn–Cl bonds leads us to conclude that the formulae previously assigned are incorrect, even when our complexes may not be identical to those previously obtained. The approximate thermochemical analysis suggests that the behaviour of compounds of Si and Ge in oxidative addition to Pt^0 should resemble that of tin rather than carbon compounds, but that reactivity may well be lower for compounds of Si and Ge. This indicates a mechanism for the reaction between $Li(GePh_3)$ and *trans*-$[PtI_2(PEt_3)_2]$ which appears to be much more plausible than the previously suggested interchange of hydroxo- and phenyl groups in *cis*-$[Pt(GePh_3)(OH)(PEt_3)_2]$.[23]

Some reactions between nickel(0) complexes and SnR_3Cl[24] and between nickel(0) and cobalt(0) and SiR_3Cl[25] have been found to give chloro-complexes of Ni or Co. None of the products contained transition metal–Group 4 element bonds, although it was suggested that compounds formed by abstraction of Cl from Si–Cl bonds were intermediates in some of the reactions. Although this would not be incompatible with our thermochemical analysis, both that analysis and analogy with the Pt^0–SnR_3Cl system would suggest that insertion into the Si–C bonds would be preferred. It is difficult to exclude the possibility that the chloro-complexes obtained as products were formed from HCl resulting from hydrolysis of the Si–Cl bonds; it is known, for example, that $[CoCl(PPh_3)_3]$ and $[CoCl_2(PPh_3)_2]$, the products of the reaction between $[Co(N_2)(PPh_3)_3]$ and $SiCl_3H$, are also formed when the dinitrogen complex is treated with HCl.[26]

This work illustrates the power of ^{31}P-{^1H} spectroscopy in the study of the co-ordination chemistry of phosphine complexes, particularly where the central metal has an abundant isotope with nuclear spin of $\frac{1}{2}$. The revision of the formulae of the tin complexes was derived from the observation of the coupling constants ^1J(Pt–P) and the fact that certain correlations in their magnitudes are now well established.[8] It is noteworthy, however, that, if the complexes $[PtRL_2(SnR_2Cl)]$ had adopted *trans* configurations, the spectra and coupling constants would have appeared compatible with the formulae originally proposed. It is now evident that the activity of the Sn–R bonds in oxidative-addition reactions extends over a wide range of organic radicals R.[27]

EXPERIMENTAL

General.—All reactions were made under dry nitrogen. Solvents were dried and degassed before use.

Infrared spectra were recorded as liquid films or Nujol mulls between CsI plates on a Perkin-Elmer 457 grating spectrometer. The ^1H n.m.r. spectra were obtained from

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[24] R. E. Garrou and G. E. Hartwell, *J.C.S. Chem. Comm.*, 1972, 881; 1973, 100.

[25] M. F. Lappert and G. Speier, *J. Organometallic Chem.*, 1974, **80**, 329.

[26] J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Fergusson, *Nature*, 1969, **221**, 551.

[27] B. Cetinkaya, M. F. Lappert, J. McMeeking, and D. E. Palmer, *J.C.S. Dalton*, 1973, 1202; C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometallic Chem.*, 1973, **60**, C70.

CD_2Cl_2 solutions with CH_2Cl_2 or $SiMe_4$ as internal reference on Varian A60 or HA100 spectrometers. The $^{31}P-\{^1H\}$ spectra were obtained for CH_2Cl_2 solutions in 8-mm tubes with $P(OMe)_3$ or $PO(OMe)_3$ in C_6D_6 or CD_2Cl_2 as external reference, using a JEOL PFT-100 Fourier-transform spectrometer. Elemental analyses were by Mrs. G. Olney of this laboratory.

Tin and Germanium Compounds.—The compounds $SnPh_4$ and $SnPh_3Cl$ were purchased; $GeBrMe_3$, $GeBrPh_3$, $GeMe_3Ph$, and (2-benzo[*b*]furyl)trimethylgermane were available in this laboratory. The following compounds were obtained by methods described in the literature: $SnMe_4$;[28] $SnMe_3Cl$;[29] $SnMe_2PhCl$;[30] $SnMePh_2Cl$;[31] and $Sn(C_6H_4Me\text{-}m)_3Cl$.[32] The compounds $SnBrPh_3$, $SnPh_3I$, $SnPh_3(OH)$, and $SnPh_3(ONO_2)$ were prepared from $SnPh_3Cl$.

Platinum Complexes.—The following complexes of Pt^0 were prepared by established methods: $[Pt(PPh_3)_4]$;[33] $[Pt(C_2H_4)(PPh_3)_2]$;[33] $[Pt(PMePh_2)_4]$;[5] and $[Pt(PEt_3)_4]$.[19] The hydrido-complex *trans*-$[PtCl(H)(PPh_3)_2]$ was obtained by hydrazine reduction of *cis*-$[PtCl_2(PPh_3)_2]$[34] and had no impurities detectable in the $^{31}P-\{^1H\}$ spectrum [δ 111.7 p.p.m., J(Pt–P) 3 008 Hz]. The $^{31}P-\{^1H\}$ parameters for *cis*-$[PtCl_2(PPh_3)_2]$[10] [δ 126.3 p.p.m., ^1J(Pt–P) 3 679 Hz] and *trans*-$[PtPhCl(PPh_3)_2]$[10] [δ 115.6 p.p.m., ^1J(Pt–P) 3 157 Hz] were obtained from authentic samples and the parameters for *cis*-$[PtPhCl(PPh_3)_2]$ [δ 119.7 p.p.m., ^1J(Pt–P) 1 562.5 Hz; δ 122.8 p.p.m., ^1J(Pt–P) 3 594 Hz, ^2J(PPtP) 15 Hz] were obtained from a sample prepared by treatment of a benzene solution of $[Pt(C_2H_4)(PPh_3)_2]$ with a stoicheiometric quantity of HgPhCl. Removal of solvent and recrystallisation from dichloromethane–diethyl ether gave *cis*-$[PtPhCl(PPh_3)_2]$ as colourless crystals, m.p. 285—288 °C (Found: C, 60.4; H, 4.10. Calc. for $C_{42}H_{35}ClP_2Pt$: C, 60.6; H, 4.25%), ν(Pt–Cl) at 310 cm^{-1}. The complex $[PtCl(PPh_3)_3][BF_4]$ [δ 117.2 p.p.m., ^1J(Pt–P) 2 481 Hz, intensity 2; δ 128.0 p.p.m., ^1J(Pt–P) 3 643 Hz, intensity 1; ^2J(Pt–P) 19.5 Hz] was prepared as previously described.[35] In a similar procedure $SbPh_3$ (0.05 g) was added to $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$[16] (0.1 g) in $MeNO_2$ (5 cm^3) and the solution stirred at room temperature for 0.5 h. Addition of diethyl ether (50 cm^3) gave a white precipitate which was washed with diethyl ether and recrystallised from dichloromethane–ether to give *cis*-chlorobis(triphenylphosphine)(triphenylstibine)platinum(II) tetrafluoroborate containing one mol equiv. of CH_2Cl_2 of crystallisation (0.12 g), m.p. 237—239 °C, ν(Pt–Cl) 325 cm^{-1} [δ 114.1 p.p.m., ^1J(Pt–P) 3 118 Hz; δ 130.7 p.p.m.; ^1J(Pt–P) 3 584 Hz; ^2J(PPtP) 15 Hz] (Found: C, 51.7; H, 3.80. $C_{55}H_{47}BCl_3F_4P_2PtSb$ requires C, 51.6; H, 3.7%).

Reactions of $[Pt(PPh_3)_4]$.—A mixture of $SnPh_3Cl$ (0.155 g, 0.4 mmol) and $[Pt(PPh_3)_4]$ (0.5 g, 0.4 mmol) in benzene was set aside for 12 h. The white solid formed was washed with benzene and recrystallisation from dichloromethane–ethanol gave colourless crystals of cis-(*chlorodiphenylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II), (I) (0.29 g, 45%). By a similar procedure using $SnMePh_2Cl$ and benzene–diethyl ether solvent, cis-[(*chloro*)(*methyl*)*phenylstannio*)]*phenylbis*(*triphenylphosphine*)*platinum*(II), (II), was obtained as colourless crystals (39%). The reaction of $[Pt(PPh_3)_4]$ with $SnMe_2PhCl$ under similar conditions gave a white solid, shown from the $^{31}P-\{^1H\}$ spectrum to be a mixture of (III) and *cis*-$[PtCl_2(PPh_3)_2]$, δ 126.3 p.p.m., ^1J(Pt–P) 3 680 Hz [lit.,[10] δ 126.3 p.p.m., ^1J(Pt–P) 3 679 Hz].

Reactions of $[Pt(C_2H_4)(PPh_3)_2]$.—Addition of $SnMe_3Cl$ (0.053 g, 0.27 mmol) in diethyl ether (1 cm^3) to $[Pt(C_2H_4)(PPh_3)_2]$ (0.2 g, 0.27 mol) in benzene (1 cm^3) gave during 2 h a white deposit, which was filtered off and washed with diethyl ether. Recrystallisation from dichloromethane–ethanol gave cis-(*chlorodimethylstannio*)*methylbis*(*triphenylphosphine*)*platinum*(II), (IV), as white crystals (0.12 g, 53%). Use of an excess of $SnMe_3Cl$ (*ca.* 1.8 molar proportion) gave the same product (69%). Similarly obtained from $SnMe_2PhCl$ was cis-(*chlorodimethylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II), (III), as colourless crystals (73%). With $Sn(C_6H_4Me\text{-}m)_3Cl$ in benzene–diethyl ether a white solid was obtained. Recrystallisation from dichloromethane–ethanol gave cis-[*chlorobis*(m-*tolyl*)*stannio*](m-*tolyl*)*bis*(*triphenylphosphine*)*platinum*(II) (57%) containing one molecule of dichloromethane of crystallisation. Similarly obtained were (I) (81%, from $SnPh_3Cl$) and (II) (72%, from $SnMePh_2Cl$).

To $SnBrPh_3$ (0.058 g, 0.13 mmol) in benzene (1 cm^3) was added $[Pt(C_2H_4)(PPh_3)_2]$ (0.1 g, 0.13 mmol) in benzene (1 cm^3). Mild gas evolution was observed and a white precipitate formed. After 24 h at room temperature this was filtered off and recrystallised from dichloromethane–ethanol to give cis-(*bromodiphenylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II) as colourless crystals (0.09 g, 61%). Similarly obtained were cis-(*iododiphenylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II) as pale yellow crystals (72%, from $SnPh_3I$), cis-(*hydroxydiphenylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II) [76%, ν(OH) at 3 180br, 3 290br, 3 595, and 3 680 cm^{-1}, from $SnPh_3(OH)$], and cis-(*nitratodiphenylstannio*)*phenylbis*(*triphenylphosphine*)*platinum*(II) containing one molecule of dichloromethane of crystallisation [56%, from $SnPh_3(ONO_2)$ in benzene–diethyl ether].

A mixture of $[Pt(C_2H_4)(PPh_3)_2]$ (0.2 g, 0.27 mmol) and $SnPh_4$ (0.12 g, 0.27 mmol) in benzene was kept at 50 °C for 1 h. After removal of solvent from the red solution obtained, the residue was recrystallised from dichloromethane–hexane to give cis-*phenylbis*(*triphenylphosphine*)(*triphenylstannio*)*platinum*(II) as an off-white solid (0.2 g, 65%).

Reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and an excess of $GeMe_3Ph$ in benzene (at room temperature for 30 d or under reflux for 4 h) gave brown solids after removal of solvent. There were no indications of phosphine complexes of Pt in the $^{31}P-\{^1H\}$ spectra of these products. A benzene solution of $[Pt(C_2H_4)(PPh_3)_2]$ was treated with an excess of (2-benzo[*b*]furyl)trimethylgermane and the solution was heated under reflux for 3 h. Addition of hexane gave a pale brown solid which was shown by the $^{31}P-\{^1H\}$ spectrum to be composed mainly of $[Pt(C_2H_4)(PPh_3)_2]$. Products of reactions between $GeBrPh_3$ or $GeBrMe_3$ and $[Pt(C_2H_4)(PPh_3)_2]$ indicated contamination of reaction mixtures with HBr. In an attempt to reduce this contamination, NEt_3 (dried over $Li[AlH_4]$) was used in further experiments (described as follows), but no Pt–Ge complexes were detectable by $^{31}P-\{^1H\}$ n.m.r. in the products. A

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benzene solution of GeBrPh$_3$ (0.10 g), NEt$_3$ (4 cm^3), and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.2 g) was stirred at room temperature for 1.5 h. A white precipitate formed and was identified (i.r. spectrum) as [NEt$_3$H]Br. The solution was reduced in volume and the ^{31}P-{^{1}H} spectrum indicated the presence of *cis*-[PtBr$_2$(PPh$_3$)$_2$] [δ 126.9 p.p.m., ^1J(Pt–P) 3 621 Hz] and *trans*-[PtBr(H)(PPh$_3$)$_2$] [δ 111.5 p.p.m., ^1J(Pt–P) 2 976 Hz]. A similar reaction mixture containing GeBrMe$_3$ was heated under reflux for 2 h. After removal of solvent the residue was extracted with benzene. Addition of hexane gave a pale yellow powder identified (i.r. spectrum) as *trans*-[PtBr(H)(PPh$_3$)$_2$] [ν(Pt–H) at 2 280 cm^{-1}; lit.,[36] 2 280 cm^{-1}].

Reactions of [Pt(PEt$_3$)$_4$].—A solution of [Pt(PEt$_3$)$_4$] (0.37 g) in benzene (10 cm^3) was treated with SnMe$_4$ (1 cm^3) and the mixture was heated under reflux for 5 h. Removal of volatiles left a brown oil which could not be crystallised. The ^{31}P-{^{1}H} spectrum of the oil in dichloromethane indicated that it was comprised of *cis*-methylbis(triethylphosphine)(trimethylstannio)platinum(II) [δ 128.6 p.p.m., ^1J(Pt–P) 2 233, ^2J(PPtP) 18 Hz] and PEt$_3$O (δ 94.0 p.p.m.) The ^{31}P-{^{1}H} spectrum of the oil obtained by a similar procedure from [Pt(PEt$_3$)$_4$] and (2-benzo[*b*]furyl)trimethylgermane gave no clear indication of the presence of (phosphine)platinum complexes.

Reaction between trans-[PtCl(H)(PPh$_3$)$_2$] *and* SnMe$_3$(NMe$_2$).[4]—A solution of *trans*-[PtCl(H)(PPh$_3$)$_2$] (0.44 g) and SnMe$_3$(NMe$_2$) (0.18 g) in xylene (10 cm^3) was heated under reflux. A dark red-brown colour developed after 5 min, and heating was continued for 2 h. After allowing to cool, light petroleum (b.p. 40—60 °C) was added, and the light brown precipitate which formed was washed with light petroleum. The ^{31}P-{^{1}H} spectrum of a solution in dichloromethane was featureless. The experiment was repeated with a shorter period of reflux (15 min). After removal of solvent the oil remaining was dissolved in dichloromethane and the ^{31}P-{^{1}H} spectrum recorded. This showed the presence of three components: *cis*-[PtMe(PPh$_3$)$_2$(SnMe$_2$Cl)] [major component: δ 107.7 and 118.1 p.p.m., both doublets ^2J(PPtP) 15 Hz, ^{195}Pt satellites too weak to be observed], *cis*-[PtCl$_2$(PPh$_3$)$_2$] [δ 126.2 p.p.m., ^1J(Pt–P) 3 675 Hz], *trans*-[PtCl(H)(PPh$_3$)$_2$] (δ 111.7 p.p.m.), and a minor unidentified component (δ 113.4 p.p.m.).

Reaction between trans-[PtCl(H)(PPh$_3$)$_2$] *and* SnPh$_3$(ONO$_2$).[2]—The procedure described by Baird was followed. A solution of SnPh$_3$(ONO$_2$) (0.11 g, 0.26 mmol) and *trans*-[PtCl(H)(PPh$_3$)$_2$] (0.2 g, 0.26 mmol) in tetrahydrofuran (30 cm^3) was heated under reflux for 30 min. The mixture was allowed to cool. Water was added to the point of turbidity and the mixture set aside at 5 °C. Filtration of the solid and recrystallisation from dichloromethane–ethanol gave a white crystalline solid (0.11 g), m.p. 280—285 °C (turned brown at *ca.* 200 °C); ν(M–Cl) at 299, 311, and 323 cm^{-1} (Found: C, 58.05; H, 4.15%). The ^{31}P-{^{1}H} spectrum of the product in dichloromethane showed the presence of three components: *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] [*ca.* 40%; δ 117.5 p.p.m., ^1J(Pt–P) 2 138 Hz; δ 113.8 p.p.m., ^1J(Pt–P) 2 690 Hz, ^2J(PPtP) 15 Hz]; *trans*-[PtPh(Cl)(PPh$_3$)$_2$] [*ca.* 35%; δ 116.1 p.p.m., ^1J(Pt–P) 3 157 Hz]; and a third component, not positively identified [δ 120.7 p.p.m., ^1J(Pt–P) 2 052 Hz; δ 114.9 p.p.m., ^1J(Pt–P) 3 108 Hz, ^2J(PPtP) 16 Hz].

Reaction between [Pt(PMePh$_2$)$_4$] *and* SnMe$_3$Cl.[5]—A solution of SnMe$_3$Cl (0.2 g, 1.0 mmol) and [Pt(PMePh$_2$)$_4$] (0.356 g, 0.36 mmol) in benzene (3 cm^3) was heated at 80 °C in a sealed tube for 55 min. The mixture was set aside at 5° C. After 2 weeks, filtration gave [PtMe(PMePh$_2$)$_3$][SnMe$_3$Cl$_2$]·C$_6$H$_6$ as an off-white solid (0.3 g), m.p. 110—112 °C, solidifying and remelting at 165—170 °C. ^{1}H N.m.r. (in CH$_2$Cl$_2$): τ (PCH$_3$) 8.2, $|^2J(\mathrm{PCH}) + {}^4J(\mathrm{PPtCH})|$ 6 Hz; τ (Ph) 2.5; τ (SnCH$_3$) 9.27 (additional lines at τ 8.4 and 8.5 probably due to PCH$_3$) (Found: C, 52.3; H, 5.05. C$_{49}$H$_{57}$Cl$_2$P$_3$PtSn requires C, 52.4; H, 5.10%). Recrystallisation from dichloromethane–hexane gave [PtMe(PMePh$_2$)$_3$][SnMe$_3$Cl$_2$] as a white crystalline solid, m.p. 172—174 °C (Found: C, 49.65; H, 5.00. C$_{43}$H$_{51}$Cl$_2$P$_3$PtSn requires C, 49.4; H, 4.90%). To confirm the character of the anion, [NEt$_4$][SnMe$_3$Cl$_2$] was obtained (by treatment of SnMe$_3$Cl with an equimolar proportion of [NEt$_4$]Cl in ethanol) as white crystals, m.p. 191—193 °C. ^{1}H N.m.r.: τ (C*H*$_3$CH$_2$) 8.7 (t), τ (CH$_3$C*H*$_2$) 6.7 (q), τ (SnCH$_3$) 9.3 (Found: C, 36.7; H, 8.05; N, 3.95. Calc. for C$_{11}$H$_{29}$Cl$_2$NSn: C, 36.2; H, 8.00; N, 3.85%).

Reactions of cis-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)].—(a) *With* HCl. An excess of HCl in diethyl ether was added to a solution of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] in dichloromethane. After 5 min, ethanol was added to the yellow solution and a white precipitate formed, which was filtered off and washed with ethanol and diethyl ether. The ^{31}P-{^{1}H} spectrum of a dichloromethane solution showed the presence of *cis*-[PtPh(Cl)(PPh$_3$)$_2$] [*ca.* 50%; δ 119.7 p.p.m., ^1J(Pt–P) 1 562 Hz; δ 122.9 p.p.m., ^1J(Pt–P) 4 502 Hz, ^2J(PPtP) 15 Hz], *trans*-[PtPh(Cl)(PPh$_3$)$_2$] [*ca.* 35%; δ 115.5 p.p.m., ^1J(Pt–P) 3 154 Hz], and *cis*-[PtCl$_2$(PPh$_3$)$_2$] [δ 126.3 p.p.m., ^1J(Pt–P) 3 677 Hz].

(b) *With* NaI. A solution of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] (0.11 g) and *ca.* 5 molar proportions of NaI in dichloromethane–acetone was stirred overnight at room temperature. Filtration gave a white solid (0.07 g), m.p. 205—210 °C (decomp.), with a similar i.r. spectrum to the starting material except that the band at 299 cm^{-1} was absent. The analysis was unsatisfactory, but the ^{31}P-{^{1}H} spectrum [δ 115.4 and 115.9 p.p.m.] indicated the presence of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$I)].

Decomposition of cis-[PtMe(PPh$_3$)$_2$(SnMe$_2$Cl)].—The complex (0.05 g) was dissolved in deuteriochloroform (0.5 cm^3) and the ^{1}H n.m.r. spectrum was recorded at intervals during 1 week. A white solid deposited and was identified as *cis*-[PtCl$_2$(PPh$_3$)$_2$] [ν(Pt–Cl) at 296 and 323 cm^{-1} (authentic sample, 295 and 321 cm^{-1})]. The ^{1}H spectrum of the solution had resonances at τ 9.35 [SnMe$_3$Cl (lit.,[12] τ 9.35)] and 9.9.

cis-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] *in Refluxing Solvents*.—(a) A solution of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] (0.1 g) in acetone (15 cm^3) was heated under reflux for 3 h. The mixture was cooled, filtered, and the filtrate treated with ethanol. A white crystalline precipitate formed and was shown to have an identical i.r. spectrum (250—350 cm^{-1}) to that of the starting material. Prolonged reflux in acetone (15 h) gave a similar result.

(b) A solution of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] (0.1 g) in tetrahydrofuran (15 cm^3) was heated under reflux for 2 h. The solution became yellow. Addition of ethanol to the cooled solution gave a product whose i.r. spectrum was identical to that of starting material.

(c) A solution of *cis*-[PtPh(PPh$_3$)$_2$(SnPh$_2$Cl)] (0.1 g) in toluene was heated under reflux for 1 h. The brown solution was allowed to cool and diethyl ether was added.

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The brown solid obtained had no new i.r. absorption in the region 250—350 cm^{-1}. More prolonged reflux (2 h) gave a dark brown uncharacterisable solid.

(d) The mixture of complexes we obtained by Baird's method was heated under reflux in acetone for 3 h. Samples were taken at intervals, and treated with ethanol to give white precipitates which were examined by i.r. spectroscopy in the region 250—350 cm^{-1}. The absorption at 299 cm^{-1} was slightly broader in the later samples, but there were no other changes in the spectrum.

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