Oxidative-addition and Reductive-elimination Reactions involving Platinum Complexes and Tetraorganotin Compounds †

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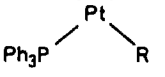
Tetraorganotin compounds $SnMe_{4-n}R_n$ (R = aryl, n = 1—3) react with $[Pt(C_2H_4)(PPh_3)_2]$ to form *cis*-$[PtR(SnMe_{4-n}R_{n-1})(PPh_3)_2]$ [n = 1(1) or 2(2)], but with an excess of $SnMe_3R$ (if R has no 2-substituents) the complex *cis*-$[PtR(SnMe_2R)(PPh_3)_2]$ (2) is also formed by insertion of (1) into an Sn–Me bond of a second molecule of $SnMe_3R$ and elimination of $SnMe_4$. Complex (1) reacts with $SnMe_2R_2$ to form (2) and $SnMe_3R$ and both of these reactions are reversible: (1) and $SnMe_3R$ are formed from (2) and $SnMe_4$, and (1) and $SnMe_2R_2$ are formed from (2) and $SnMe_3R$. The system catalyses the redistribution $2SnMe_3R \rightleftharpoons SnMe_2R_2 + SnMe_4$, and (2) catalyses redistribution of aryl groups (R,R′) between $SnMe_2R_2$ and $SnMe_2R'_2$. Mechanisms involving platinum(IV) intermediates are proposed for these and several related reactions. Reactions of (1) and (2) (R = Ph) with a number of oxidative-addition reagents are reported. With organotin chlorides $SnMe_3Cl$, $SnMe_2Cl_2$, and $SnPh_2Cl_2$, (1) and (2) form bis(triphenylphosphine)platinum(II) complexes in which a Pt–Ph bond is retained and in which the number of chlorine atoms on the stannio-ligand is less than or equal to that in the tin(IV) reagent. The mechanism of these processes also appears to involve platinum(IV) intermediates and to be consistent with the normal order of reactivity Sn–Cl > Sn–R > Sn–Me. Some complexes (1) and (2) have been isolated and characterised and ^{31}P-{^1H} n.m.r. parameters are reported for all complexes.

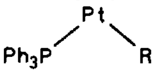
REACTIONS between $[Pt(C_2H_4)(PPh_3)_2]$ and the tin compounds $SnPh_4$, $SnPh_3Cl$, $SnMe_3Cl$, and $SnPh_2Cl_2$ give platinum(II) complexes, which are formally products of insertion into the Sn–C bonds, *e.g.* equation (i), whereas products of insertion into Sn–Cl bonds, *e.g.* equation (ii), are formed by $SnMe_2Cl_2$, $SnMeCl_3$, $SnPhCl_3$, and $SnCl_4$.[1-3] Tin compounds such as $SnMe_2PhCl$, which contain both Sn–alkyl and Sn–aryl bonds, have been found to form exclusively products of insertion into the Sn-aryl bonds.[1]

$$[Pt(C_2H_4)(PPh_3)_2] + SnPh_3Cl \longrightarrow [PtPh(SnPh_2Cl)(PPh_3)_2] + C_2H_4 \quad \text{(i)}$$

$$[Pt(C_2H_4)(PPh_3)_2] + SnMe_2Cl_2 \longrightarrow [PtCl(SnMe_2Cl)(PPh_3)_2] + C_2H_4 \quad \text{(ii)}$$

In contrast to these reactions, we have found that tetraorganotin compounds of the type $SnMe_3R$, where R is an aryl group, usually react with $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane or benzene to form two platinum(II) complexes, *cis*-$[PtR(SnMe_3)(PPh_3)_2]$ (1) and *cis*-$[PtR(SnMe_2R)(PPh_3)_2]$ (2). Some of these complexes were isolated in a pure state, and they can be interconverted by use of appropriate tin compounds as detailed below.


(1)


(2)

RESULTS AND DISCUSSION

Our results for mixtures obtained by addition of excesses of aryltrimethyltin compounds $SnMe_3R$ to solutions of $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane and for a number of other experiments are consistent with the sequence of reactions shown in Scheme 1. The evidence for the structures of complexes (1) and (2) and for other aspects of Scheme 1 is as follows [(*a*)—(*g*)].

(*a*) The tin compounds $SnMe_3R$ (R = C_6H_4Me-2, C_6H_4OMe-2, or $C_6H_2Me_3$-2,4,6) each gave only a single complex even when used in excess. The complexes for R = C_6H_4Me-2 and C_6H_4OMe-2 were isolated and had elemental analyses and ^1H and ^{31}P-{^1H} n.m.r. spectra consistent with structure (1) (Tables 1—3). Thus, resonances from methyl groups on Sn and from the phenyl-ring substituents were present in the ^1H n.m.r. spectrum and they integrated in the ratio 3 : 1 (Table 3), and the ^{31}P-{^1H} n.m.r. spectra comprised two equally intense doublets with ^{195}Pt satellites and with ^{117}Sn and ^{119}Sn satellites of intensity corresponding to the presence of one ligand with an Sn donor atom (Table 2). Satisfactory elemental analyses and a similar ^{31}P-{^1H} n.m.r. spectrum were also obtained for the compounds *cis*-$[PtR(SnMe_3)(PPh_3)_2]$ (R = $C_6H_4NO_2$-4 or 2-furyl) which were obtained from equimolar proportions of the platinum(0) complex and $SnMe_3R$ (Tables 1 and 2). It is probable that only a single complex is formed when R = C_6H_4Me-2, C_6H_4OMe-2, or $C_6H_2Me_3$-2,4,6 because of inhibition of subsequent reactions by the steric effect of the 2-substituent on the phenyl group. When a 2-

$$\begin{aligned} &[Pt(C_2H_4)(PPh_3)_2] + SnMe_3R \longrightarrow \\ &\qquad \underset{(1)}{cis\text{-}[PtR(SnMe_3)(PPh_3)_2]} + C_2H_4 \quad \text{(iii)} \\ &cis\text{-}[PtR(SnMe_3)(PPh_3)_2] + SnMe_3R \rightleftharpoons \\ &\qquad \underset{(2)}{cis\text{-}[PtR(SnMe_2R)(PPh_3)_2]} + SnMe_4 \quad \text{(iv)} \\ &\underset{(2)}{cis\text{-}[PtR(SnMe_2R)(PPh_3)_2]} + SnMe_3R \rightleftharpoons \\ &\qquad \underset{(1)}{cis\text{-}[PtR(SnMe_3)(PPh_3)_2]} + SnMe_2R_2 \quad \text{(v)} \end{aligned}$$

SCHEME 1

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† No reprints available.

TABLE 1

Melting points and elemental analyses

Complex	R	M.p. (θ_c/°C)	Elemental analysis (%) Found C	Found H	Calc. C	Calc. H
(1)	C_6H_4Me-2	132	57.0	4.7	56.7	4.7
	C_6H_4OMe-2	126—128	54.7	5.1	55.8	4.6
	$C_6H_4NO_2$-4 [a]	140	53.3	4.8	53.7	4.3
	2-furyl	112—114	54.3	4.8	54.3	4.4
(2)	Ph	134—136	58.5	5.0	58.7	4.5
	C_6H_4Me-3	126	59.4	4.9	59.4	4.8
	C_6H_4OMe-4	112—114	57.9	5.0	57.7	4.6
	C_6H_4OMe-2	116	57.4	4.6	57.7	4.6
	2-furyl	152—154 [b]	55.4	4.4	55.1	4.2
cis-[PtPh($SnPh_3$)($(PPh_3)_2$)] [c]		158 [c]	62.5	4.9	62.8	4.4

[a] N, 1.4; Calc. 1.4%. [b] Melts with decomposition. [c] Reported previously [1] with 1 mol of CH_2Cl_2 of crystallisation.

TABLE 2

^{31}P-{^1H} N.m.r. parameters for the products of reaction between [Pt(C_2H_4)($(PPh_3)_2$)] and $SnMe_3R$

R	−δ/p.p.m. (*trans* to Sn)	^1J(PtP)/Hz	^2J(^{119}SnP)/Hz	^2J(^{117}SnP)/Hz	−δ/p.p.m. (*trans* to R)	^1J(PtP)/Hz	^2J(SnP)/Hz [b]	^2J(PP)/Hz
	cis-[PtR($SnMe_3$)($(PPh_3)_2$)] (1) [a]							
Ph	114.3	2 060	1 718	1 640	115.2	2 129	145	13
C_6H_4Me-4	115.1	2 053	1 731	1 654	114.7	2 148	159	12
C_6H_4Me-3	113.9	2 068	[c]	[c]	115.0	2 126	[c]	15
C_6H_4Me-2	115.3	2 092	1 698	1 618	115.8	2 129	[c]	12
$C_6H_2Me_3$-2,4,6	116.4	2 104	1 721	1 643	116.4	2 146	[c]	15
C_6H_4Ph-4	114.9	2 051	1 697	1 621	115.0	2 153	[c]	14
C_6H_4OMe-4	114.7	2 026	[c]	[c]	114.7	2 175	[c]	12
C_6H_4OMe-3	114.1	2 059	1 708	1 632	115.2	2 148	160	13
C_6H_4OMe-2	114.8	2 106	1 719	1 642	114.8	2 345	137	15
C_6H_4SMe-4	114.6	2 036	1 653	1 575	115.0	2 165	[c]	15
C_6H_4Cl-4	114.8	2 029	1 688	1 612	115.3	2 190	[c]	15
C_6H_4Br-4	115.1	2 031	1 658	1 584	115.1	2 192	142	15
C_6H_4F-4	114.4 [d]	2 019	1 721	1 646	115.1	2 189	142	13
C_6H_4F-3	113.9 [e]	2 039	1 676	1 600	115.4 [f]	2 183	138	15
$C_6H_3Br_2$-3,5	113.0	2 026	1 606	1 538	116.0	2 271	122	15
$C_6H_3(CF_3)_2$-3,5	113.7	1 997	1 597	1 528	116.1	2 253	132	15
$C_6H_4NO_2$-4	114.5	2 051	[c]	[c]	116.0	2 187	[c]	17
$C_6H_4SnMe_3$-4	114.1	2 070	1 704	1 626	115.2	2 124	149	12
$C_6H_4SnMe_3$-3	114.3	2 044	1 702	1 624	114.6	2 136	147	13
$C_6H_4C{\equiv}CSiMe_3$-4	114.8	2 046	1 660	1 587	115.4	2 161	142	15
$C_6H_4C{\equiv}CSiMe_3$-3	113.8	2 031	1 680	1 604	115.4	2 173	142	14
$C_6H_4NMe_2$-4	114.4	2 024	[c]	[c]	114.4	2 168	[c]	12
($C_6H_4NMe_3$-4)I	113.9	2 026	1 621	1 548	116.3	2 212	137	15
2-Furyl	116.7	1 899	1 726	1 648	115.5	2 432	127	15
	cis-[PtR($SnMe_2R$)($(PPh_3)_2$)] (2) [g]							
Ph	114.1	2 060	[h]	[h]	116.2	2 092	[h]	13
	114.1	*2 169*	*1 793*	*1 713*	*116.3*	*2 091*	*153*	*13*
C_6H_4Me-4	114.9	2 144	[h]	[h]	115.6	2 087	[h]	12
C_6H_4Me-3	113.8	2 160	[h]	[h]	116.0	2 095	[h]	12
	113.8	*2 167*	*1 790*	*1 711*	*116.1*	*2 093*	*155*	*13*
C_6H_4Me-2	[i]							
$C_6H_2Me_3$-2,4,6	[i]							
C_6H_4Ph-4	[j]							
C_6H_4OMe-4	114.4	2 114	[h]	[h]	115.6	2 139	[h]	15
	114.5	*2 125*	*1 834*	*1 752*	*115.7*	*2 139*	*144*	*13*
C_6H_4OMe-3	113.9	2 175	[h]	[h]	116.4	2 109	[h]	15
C_6H_4OMe-2	*114.7* [i]	*2 189*	*1 843*	*1 761*	*116.9*	*2 292*	*148*	*15*
C_6H_4SMe-4								
C_6H_4Cl-4	114.6	2 166	[h]	[h]	116.9	2 141	[h]	15
C_6H_4Br-4	114.8	2 167	[h]	[h]	116.7	2 144	[h]	15
C_6H_4F-4	114.2 [d]	2 142	[h]	[h]	116.5	2 146	[h]	15
C_6H_4F-3	113.7 [k]	2 178	[h]	[h]	117.2 [f]	2 133	[h]	15
$C_6H_3Br_2$-3,5	[j]							
$C_6H_3(CF_3)_2$-3,5	[j]							
$C_6H_4NO_2$-4	[j]							
$C_6H_4SnMe_3$-4	[j]							
$C_6H_4SnMe_3$-3	[j]							
$C_6H_4C{\equiv}CSiMe_3$-4	[j]							
$C_6H_4C{\equiv}CSiMe_3$-3	[j]							
$C_6H_4NMe_2$-4	114.4	2 102	[h]	[h]	115.0	2 134	[h]	12
($C_6H_4NMe_3$-4)I	[j]							
2-Furyl	116.4	2 078	[h]	[h]	117.2	2 366	[h]	15

[a] From solutions obtained from equimolar proportions of reagents. [b] Separate satellites from ^{119}Sn and ^{117}Sn were not resolved. [c] Signal-to-noise ratio insufficient for the observation of tin satellites. [d] ^6J(PF) 5 Hz. [e] ^5J(PF) 2 Hz. [f] ^5J(PF) 6 Hz. [g] From solutions obtained from an excess of $SnMe_3R$. Solutions also contained complex (1). Results in italics pertain to solutions obtained after treatment of [Pt(C_2H_4)($(PPh_3)_2$)] with $SnMe_2R_2$. [h] Overlap with resonances of complex (1) precluded the observation of tin satellites. [i] Complex not formed from [Pt(C_2H_4)($(PPh_3)_2$)] and an excess of $SnMe_3R$. [j] Reactions with an excess of $SnMe_3R$ not examined. [k] ^5J(PF) obscured.

TABLE 3

Proton n.m.r. parameters for complexes (1) and (2) [a]

Complex	R	δ(SnMe)/ p.p.m.	δ(aryl *Me* or O*Me*)/ p.p.m.	^3J(PtSnCH) [b]/ Hz	^2J(SnCH) [b]/ Hz
(1)	Ph	−0.66		7	39
	C_6H_4Me-3	−0.66	1.80	7	39
	C_6H_4Me-2	−0.67	2.19	8	40
	C_6H_4OMe-3	−0.62	3.52	7	40
	C_6H_4OMe-2	−0.69	3.47	8	40
	C_6H_4F-4	−0.65		7	40
	C_6H_4F-3	−0.63		7	40
	2-Furyl	−0.58		8	40
(2)	Ph	−0.50		7	39
	C_6H_4Me-3	−0.39, −0.57	1.77, 2.17	7	39
	C_6H_4OMe-4	−0.51	3.61, 3.71	7	38
	C_6H_4OMe-3	−0.42, −0.56	3.33, 3.68	7	39
	C_6H_4OMe-2	−0.42, −0.58	3.17, 3.70	8	39
	C_6H_4F-4	−0.48		7	40
	2-Furyl	−0.40		8	43

[a] In $CDCl_3$; shifts are quoted relative to $SiMe_4$; positive shifts are to high frequency of the reference. [b] Separate satellites from ^{119}Sn and ^{117}Sn were not resolved.

substituent is present on R the further reactions are completely inhibited only when a 2-substituent is present in both (1) and $SnMe_3R$. Thus, whereas there was no detectable reaction between (1; R = C_6H_4OMe-2) and $SnMe_3(C_6H_4Me$-2) or between (1; R = C_6H_4Me-2) and $SnMe_3(C_6H_4OMe$-2), complex (1; R = C_6H_4OMe-2) with $SnMe_3Ph$ gave a product with ^{31}P-{^1H} n.m.r. parameters different from (1) or (2) (R = Ph or C_6H_4OMe-2) and which is probably *cis*-[$Pt(C_6H_4OMe$-2)$(SnMe_2Ph)(PPh_3)_2$] (see Experimental section), and (1; R = Ph) gave (1; R = C_6H_4OMe-2) when treated with an excess of $SnMe_3$-(C_6H_4OMe-2).

(*b*) The products of a large number of reactions between [$Pt(C_2H_4)(PPh_3)_2$] and tin compounds $SnMe_3R$ were examined *in situ* in dichloromethane by ^{31}P-{^1H} n.m.r. spectroscopy. With equimolar proportions of reagents and a reaction time of 2 h at room temperature a single complex was formed in all instances [R = Ph or 2-furyl; C_6H_4X, X = Me-4, Me-3, OMe-4, OMe-3, SMe-4, Cl-4, Br-4, F-4, F-3, NO_2-4, $SnMe_3$-4, $SnMe_3$-3, C≡C$SiMe_3$-4, C≡C$SiMe_3$-3, NMe_2-4, or NMe_3^+-4; $C_6H_3Br_2$-3,5 or $C_6H_3(CF_3)_2$-3,5]. These products are assigned structure (1) on the basis of the similarity of their ^{31}P-{^1H} n.m.r. parameters to those whose structure was established as described under (*a*) above (Table 2), and since complex (1) contains one group R whereas complex (2) contains two, the former is the expected initial product of the reaction between [$Pt(C_2H_4)(PPh_3)_2$] and $SnMe_3R$. The ^{31}P-{^1H} n.m.r. spectrum of complexes (1) were sufficiently intense for the ^{117}Sn and ^{119}Sn satellites to be observed, and the PPh_3 ligand *trans* to the Sn ligand is assigned on the basis of the large coupling ^2J(PPtSn) *ca.* 1 650 Hz.[1,4] With the exception of R = 2-furyl and the bulky $C_6H_2Me_3$-2,4,6, C_6H_4Me-2, and C_6H_4OMe-2, the coupling constants ^1J(Pt–P) for PPh_3 *trans* to Sn are closely similar, reflecting the invariance of the ligand in *trans* relationship, namely $SnMe_3$. There is significantly greater variation in ^1J(Pt–P) *trans* to the varying R ligand.

The complex (1; R = $C_6H_2Me_3$-2,4,6) was formed to the extent of *ca.* 27% from $SnMe_3R$ (*ca.* 1 mol dm^{-3}) after 10 h, where the other products (1) were formed to the extent of 50—100% after 2 h from $SnMe_3R$ (*ca.* 0.1 mol dm^{-3}). The low rate for R = $C_6H_2Me_3$-2,4,6 is presumably due to steric hindrance.

The presence of the aryl ligand in (1; R = C_6H_4F-3 or -4) was confirmed by the observation of long-range P–F coupling in the ^{31}P-{^1H} n.m.r. spectrum (see Table 2, footnotes *d*—*f*) and this same coupling and also coupling to ^{195}Pt found in the ^{19}F n.m.r. spectra (R = C_6H_4F-3 or -4) (Table 4). The magnitudes of the couplings ^2J(PPtSn) associated with the P coupled to F showed that F was more strongly coupled to the *trans*-phosphorus nucleus for R = C_6H_4F-3, but for R = C_6H_4F-4 the only coupling large enough to be resolved was to the phosphorus in *cis* relationship. Since the couplings between nuclei in *trans*-related ligands are normally the larger in platinum(II) complexes,[4] the coupling observed for the *cis*-related ligands in (1; R = C_6H_4F-4) may occur by the 'through-space' mechanism.

TABLE 4

Fluorine-19 n.m.r. parameters for complexes (1) and (2)

Complex	R	−δ(PtR) [a]/ p.p.m.	^4J(PF) [b]/Hz *trans* P	^4J(PF) [b]/Hz *cis* P	J(PtF) [c]/ Hz	−δ(SnR) [a]/ p.p.m.
(1)	C_6H_4F-4	127.0		4	27	
	C_6H_4F-3	118.2	5	1	43	
(2)	C_6H_4F-4	127.0		4	27	117.8
	C_6H_4F-3	118.0	5		43	116.9

[a] Solutions in CH_2Cl_2; positive shifts are to high frequency of internal $CFCl_3$. [b] For R = C_6H_4F-4, ^6J(PF); for R = C_6H_4F-3, ^5J(PF). [c] For R = C_6H_4F-4, ^5J(PtF); for R = C_6H_4F-3, ^4J(PtF).

(*c*) Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with an excess of $SnMe_3R$ [R = 2-furyl or C_6H_4X (X = H, Me-4, Me-3, OMe-4, OMe-3, Cl-4, Br-4, F-4, F-3, or NMe_2-4)] gave a product mixture, the ^{31}P-{^1H} n.m.r. spectrum of which showed the presence of complex (1) and a second complex (2). The spectrum of (2) comprised two doublets from *cis*-PPh_3 ligands with coupling to ^{195}Pt (Table 2), but the intensity of the spectra and overlap with the resonances of (1) precluded the observation of any tin satellites.

Complexes with ^{31}P-{^1H} n.m.r. parameters identical to those of (2) were prepared by treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with $SnMe_2R_2$ (R = Ph, C_6H_4Me-3, C_6H_4OMe-4, or 2-furyl) [equation (vi)], and the spectra of these were sufficiently intense for the detection of tin satellites

$$[Pt(C_2H_4)(PPh_3)_2] + SnMe_2R_2 \longrightarrow \textit{cis}\text{-}[PtR(SnMe_2R)(PPh_3)_2] + C_2H_4 \quad \text{(vi)}$$

(Table 2, footnote *g*). The intensities of the tin satellites showed that the complexes contained one Sn donor atom, and the assignment of the PPh_3 *trans* to the Sn (Table 2) was based on the magnitude of ^2J(PPtSn) as described previously. The elemental analyses agreed with those expected for structure (2) (Table 1), and the ^1H n.m.r. spectra of the complexes with R = C_6H_4Me-3 or C_6H_4OMe-4 displayed resonances for the methyl groups of $Pt(C_6H_4X)$ and $Sn(C_6H_4X)$ (X = Me-3 or OMe-4) and $SnMe_2$ moieties with an intensity ratio of 1 : 1 : 2 (Table 3). Confirmation that the products from $[Pt(C_2H_4)(PPh_3)_2]$ and an excess of $SnMe_3R$ are mixtures of complexes (1) and (2) was obtained from the ^1H n.m.r. spectra of the product mixtures after removal of the excess of $SnMe_3R$. For R = C_6H_4X (X = Me-3 or OMe-3), three resonances for Me groups of C_6H_4X were present, two of which were equally intense, as expected for (2), and the third resonance being the single resonance expected for (1). The ratios of the concentrations of (1) and (2) implied by the intensities of these resonances were in agreement with those determined from the ^{31}P-{^1H} n.m.r. spectra of the mixture.

By means of the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_2R_2$ we prepared the complex (2) containing the sterically hindered R group C_6H_4OMe-2; this complex was not formed in detectable amounts from $SnMe_3R$ [see (*b*) above]. The complex was characterised by elemental analysis and by ^1H and ^{31}P-{^1H} n.m.r. spectroscopy (Tables 1—3). In the reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_2R_2$ (R = Ph, C_6H_4Me-3, C_6H_4-OMe-4, C_6H_4OMe-2, or 2-furyl) in no instance was any product other than (2) detected by ^{31}P-{^1H} n.m.r. spectroscopy.

In the ^1H n.m.r. spectra of complexes (2; R = C_6H_4-OMe-2, C_6H_4OMe-3, or C_6H_4Me-3) at 30 °C the $SnMe_2$ groups gave rise to two equally intense broad resonances instead of the sharp *ca.* 1 : 4 : 1 resonances observed for other R (Table 3). Further broadening occurred at higher temperatures and at *ca.* 90 °C the resonance appeared as a single broad band. It is probable that at the lower temperatures the two Me groups of the $SnMe_2$ group are non-equivalent and for 2- or 3-substituted phenyl groups this could arise from restricted rotation about either or both of the Pt–C or Pt–Sn bonds.

For the complexes (2) which were isolated the ^{31}P-{^1H} n.m.r. parameters of the PPh_3 ligands *trans* and *cis* to Sn were assigned on the basis of the relative magnitudes of ^2J(PPtSn). For these complexes the PPh_3 ligand *trans* to Sn gave a resonance at higher frequency ($-\delta$ smaller) than PPh_3 *trans* to R, and this feature has been used to assign the spectra of the complexes (2) where tin satellites were not observed. This assignment was also consistent with the long-range P–F couplings observed for the Pt–R groups in (2; R = C_6H_4F-3 or -4), assuming that the relative magnitudes of the couplings between *cis*- and *trans*-related compounds were similar to those established for complexes (1) [(*b*) above, Table 4]. The ^{19}F n.m.r. spectra were recorded for the mixtures of (1) and (2) obtained by use of an excess of $SnMe_3R$, and the spectra for complexes (2) comprised the expected equally intense resonances for the fluorine substituents in the PtR and SnR groups (R = C_6H_4F-3 or -4).

(*d*) A sample of complex (1; R = C_6H_4OMe-3) which contained no impurities detectable by ^{31}P-{^1H} n.m.r. spectroscopy was dissolved in dichloromethane and set aside at room temperature. After 8 h the spectrum showed the presence of small amounts of unidentified impurities, but complex (2) was not present in a detectable amount. This shows that (2) is not formed by disproportionation or decomposition of (1). Addition of an excess of $SnMe_3(C_6H_4OMe\text{-}3)$ led to the formation of (2), the ratio of the concentrations of (2) : (1) being 2 : 1 after 4 h at room temperature. When a reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and an equimolar proportion of $SnMe_3(C_6H_4OMe\text{-}3)$ was monitored at intervals by ^{31}P-{^1H} n.m.r. spectroscopy, the ratio of concentrations (2) : (1) determined from the intensities was 0 after 2 h, 0.4 : 1 after 5 h, and 0.5 : 1 after 7 h. This behaviour is consistent with the reactions for the formation of (1) and (2) as represented in Scheme 1.

(*e*) That $SnMe_4$ is formed when $[Pt(C_2H_4)(PPh_3)_2]$ is treated with an excess of $SnMe_3R$ (R = Ph or 2-furyl) was verified from the ^1H n.m.r. spectra of reaction mixtures (see below). This process corresponds to reaction (iv) of Scheme 1, and its reverse has been demonstrated by treating solutions of pure (2; R = Ph, C_6H_4OMe-2, or 2-furyl) or an approximately equimolar mixture of (1) and (2) (R = C_6H_4OMe-3) with an excess of $SnMe_4$. After several hours at room temperature, ^{31}P-{^1H} n.m.r. spectra of the solutions showed at least 50% conversion of (2) into (1) for R = Ph, C_6H_4OMe-2, C_6H_4OMe-3, or 2-furyl and for R = C_6H_4OMe-3 only (1) was detected after 6 h.

(*f*) Although reactions (iii) and (iv) account for the formation of the product complexes (1) and (2) and $SnMe_4$, reaction (v) is required to account for the formation of $SnMe_2R_2$ when $[Pt(C_2H_4)(PPh_3)_2]$ is treated with a large excess of $SnMe_3R$. The formation of $SnMe_2R_2$ in this way has been detected for R = Ph or 2-furyl by ^1H n.m.r. spectroscopy, and since in reactions

(iv) and (v) the complexes (1) and (2) are essentially catalysts for the redistribution reaction of the organotin compounds [equation (vii)], the $SnMe_2R_2$ was formed in

$$2SnMe_3R \rightleftharpoons SnMe_4 + SnMe_2R_2 \qquad \text{(vii)}$$

larger concentrations than (1) and (2) when sufficient $SnMe_3R$ was provided. Thus, when $[Pt(C_2H_4)(PPh_3)_2]$ (4×10^{-5} mol) was treated with $SnMe_3Ph$ (2.7×10^{-4} mol) the integrated ^1H n.m.r. spectrum after 36 h showed the presence of $SnMe_2R_2$, $SnMe_3R$, and $SnMe_4$ in the ratio $5 : 20 : 7$. Starting from $[Pt(C_2H_4)(PPh_3)_2]$ (6.7×10^{-5} mol), $SnMe_2Ph_2$ (2×10^{-4} mol), and $SnMe_4$ (2×10^{-4} mol) gave a corresponding ratio of $3 : 6 : 4$ after 70 h. Since the equilibrium ratio should be the same in both instances, it is clear that equilibrium (vii) is reached rather slowly for R = Ph. Although equation (vii) requires that equimolar amounts of $SnMe_4$ and $SnMe_2R_2$ should be formed from $SnMe_3R$ (or from initially equimolar amounts of $SnMe_4$ and $SnMe_2R_2$) the amount of $SnMe_4$ exceeds that of $SnMe_2R_2$ in our reaction mixtures because some of the latter is consumed in the formation of (2). We showed by ^1H n.m.r. spectroscopy that solutions of $SnMe_3R$ (R = aryl) in CH_2Cl_2 remain unchanged after several weeks at room temperature; redistribution of tetraorganotin compounds has been observed previously at 50 °C in the presence of Friedel Crafts catalysts.[5]

Reaction (v) has also been demonstrated by $^{31}P-\{^1H\}$ n.m.r. spectroscopy for R = Ph or 2-furyl. For R = Ph, treatment of (2) in dichloromethane with an excess of $SnMe_3R$ at room temperature gave after 7 h an approximately equimolar mixture of (1) and (2). A similar experiment with R = 2-furyl gave a mixture of complexes (1) and (2) in the ratio *ca.* 1 : 4. The reverse of reaction (v) was also demonstrated for R = Ph and 2-furyl. For R = Ph a mixture of (1) (57%) and (2) (43%) was converted into (2) by treatment with an excess of $SnMe_2Ph_2$ in dichloromethane at room temperature for 6 h, and for R = 2-furyl an excess of $SnMe_2R_2$ converted (1) into (2) after 12 h.

(*g*) A brief study was made of reactions between complexes (1) and (2) and tin compounds $SnMe_3R$, with R different from that of the complex. A mixture of (1) and (2) (R = Ph, 1 mol) was treated with $SnMe_3$(2-furyl) (1 mol). The $^{31}P-\{^1H\}$ n.m.r. spectrum after 2 h showed the presence of the single complex (1; R = 2-furyl), and when an excess of $SnMe_3$(2-furyl) was used a mixture of (1) and (2) (R = 2-furyl) was formed. With an excess of $SnMe_3(C_6H_4OMe\text{-}2)$, the mixture of (1) and (2) (R = Ph) was converted into (1; R = $C_6H_4OMe\text{-}2$) and it was also shown that (2; R = $C_6H_4OMe\text{-}4$) gave (1; R = 2-furyl) after treatment with an equimolar amount of $SnMe_3$(2-furyl) for 2 h. These results indicate reactions corresponding to equations (viii) and (ix) for which the equilibrium positions must depend on R and R′; evidently, for R = Ph and R′ = 2-furyl, both equilibria lie well to the right. It should be noted, however, that the reaction between (1; R = $C_6H_4OMe\text{-}2$) and $SnMe_3Ph$ was found to follow a different course [equation (x), see (*a*) above], which is analogous to reaction (iv).

$$cis\text{-}[PtR(SnMe_3)(PPh_3)_2] + SnMe_3R' \rightleftharpoons cis\text{-}[PtR'(SnMe_3)(PPh_3)_2] + SnMe_3R \qquad \text{(viii)}$$

$$cis\text{-}[PtR(SnMe_2R)(PPh_3)_2] + SnMe_3R' \rightleftharpoons cis\text{-}[PtR'(SnMe_3)(PPh_3)_2] + SnMe_2R_2 \qquad \text{(ix)}$$

$$cis\text{-}[Pt(C_6H_4OMe\text{-}2)(SnMe_3)(PPh_3)_2] + SnMe_3Ph \rightleftharpoons cis\text{-}[Pt(C_6H_4OMe\text{-}2)(SnMe_2Ph)(PPh_3)_2] + SnMe_4 \qquad \text{(x)}$$

Mechanism.—It is probable that reactions (iv) and (v) proceed *via* oxidative-addition and reductive-elimination steps involving transitory platinum(IV) intermediates, but these intermediates were not formed in sufficient quantities to be observable in the $^{31}P-\{^1H\}$ n.m.r. spectra; reaction (iii) is an oxidative addition involving insertion of platinum(0) into the Sn–R bond. Preferential insertion of platinum(0) into the Sn–R rather than the Sn–Me bonds of compounds $SnMe_nR_{3-n}Cl$ (R = aryl, n = 1 or 2) has been established previously,[1-3] but the presence of the ligand $SnMe_2R$ in (2) shows that, if (2) is formed from (1) by oxidative addition of $SnMe_3R$ and reductive elimination of $SnMe_4$, the platinum(II) complex (1) must insert into the Sn–Me rather than the Sn–R bond of $SnMe_3R$. However, it is clear from the fact that $SnMe_4$ reacts with (2) [reverse of (iv)] that the Sn–Me bonds are capable of oxidative addition to platinum(II) complexes. It is important to note that the suggested mechanism (Scheme 2) does not require that insertion of (1) into the Sn–Me bond of $SnMe_3R$ [equation (xii)] is faster than insertion into the Sn–R bond [equation (xi)]. Indeed, the reverse is likely to be true, but insertion of (1) into Sn–R is presumably followed by elimination of $SnMe_3R$ to reform (1) [reverse of (xi)]; insertion of (1) into Sn–Me, although slower, can result in the formation of the new complex (2) by elimination of $SnMe_4$ [equation (xiii)]. Exchange of R groups between different molecules of $SnMe_3R$ is a probable consequence of these reactions [Scheme 2, reaction (xi) and its reverse] and strong evidence for the insertion of (1) into Sn–R bonds of $SnMe_3R$ was obtained from the reaction between (1; R = Ph) and $SnMe_3$(2-furyl) [equation (viii)]. The only detectable product, (1; R = 2-furyl), is presumably formed by insertion of (1; R = Ph) into the Sn–(2-furyl) bond, followed by elimination of $SnMe_3Ph$; the fact that $cis\text{-}[PtPh\{SnMe_2(2\text{-furyl})\}(PPh_3)_2]$ was not formed in a detectable amount indicates that insertion of (1; R = Ph) into the Sn–(2-furyl) bond is much more rapid than the insertion into an Sn–Me bond. This is to be expected since the Sn–(2-furyl) bond is amongst the most reactive of Sn–R bonds. Further evidence for insertion of com-

$$\underset{(1)}{cis\text{-}[PtR(SnMe_3)(PPh_3)_2]} \xrightleftharpoons{R\text{–}SnMe_3,\ \text{fast}} [PtR_2(SnMe_3)_2(PPh_3)_2] \qquad \text{(xi)}$$

$$(1)\ [PtMe(R)(SnMe_3)(SnMe_2R)(PPh_3)] \xrightleftharpoons{Me\text{–}SnMe_2R} \qquad \text{(xii)}$$

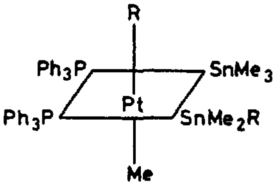
$$[PtMe(R)(SnMe_3)(SnMe_2R)(PPh_3)] \xrightleftharpoons{-SnMe_4} \underset{(2)}{cis\text{-}[PtR(SnMe_2R)(PPh_3)_2]} \qquad \text{(xiii)}$$

Scheme 2

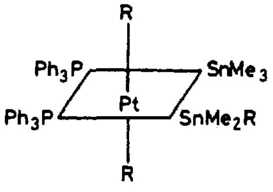
plexes (1) into Sn–R bonds was obtained from the reaction between *cis*-[PtPh(SnEt$_3$)(PPh$_3$)$_2$] {obtained from [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and an equimolar proportion of SnEt$_3$Ph} and an excess of SnMe$_3$Ph, which gave a product mixture comprising (1) and (2) (R = Ph) and no complexes containing Sn–Et groups remained.

That the reaction between (1; R = C$_6$H$_4$OMe-2) and SnMe$_3$Ph [equation (x)] forms *cis*-[Pt(C$_6$H$_4$OMe-2)-(SnMe$_2$Ph)(PPh$_3$)$_2$] can also be rationalised in terms of this mechanism, since after insertion into the Sn–Ph bond the reverse elimination of SnMe$_3$Ph [which only exchanges SnMe$_3$ groups between (1; R = C$_6$H$_4$OMe-2) and SnMe$_3$Ph] would probably be faster than the sterically hindered elimination of SnMe$_3$(C$_6$H$_4$OMe-2), whereas after insertion into the Sn–Me bond of SnMe$_3$Ph, reductive elimination of SnMe$_4$ would occur readily to give the observed product.

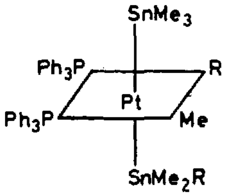
Although complexes (1) undergo no observable change on treatment with SnMe$_4$, the mechanism suggests that exchange occurs between SnMe$_3$ groups of (1) and SnMe$_4$ [Scheme 2, equation (xii) and its reverse]. This type of process has been demonstrated by treatment of *cis*-[PtPh(SnEt$_3$)(PPh$_3$)$_2$] with an excess of SnMe$_4$ when the only platinum(II) complex detected after 15 h was *cis*-[PtPh(SnMe$_3$)(PPh$_3$)$_2$].



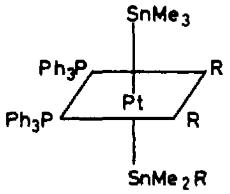
(3)



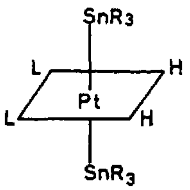
(4)



(5)



(6)



(7)

Our results do not establish the structures of the platinum(IV) intermediates, but on the assumptions that the PPh$_3$ ligands remain *cis* throughout, that the oxidatively added and reductively eliminated moieties are *cis*, and that the tin ligands are symmetrically placed in the platinum(IV) complexes the structures of the intermediates for reactions (iv) and (v) can be written as (3) and (4) or (5) and (6). The symmetry of the complexes would allow the possible exchange processes mentioned above to occur with microscopic reversibility and analogues of these intermediates are similarly plausible for reactions (vi), (viii), and (ix). As far as we are aware, platinum(IV) complexes with *cis* phosphines (or neutral ligands), two alkyl or aryl ligands, and two triorganotin (or silicon) ligands have not been isolated or detected, so a choice between the possible intermediates (3) and (4) or (5) and (6) cannot be based on a closely analogous system. Complexes in which hydride ligands are present instead of aryl ligands are known with configuration (7; L = PEt$_3$ or PMe$_2$Ph; R = Ph, C$_6$H$_4$Me-2, -3, or -4), and they were obtained by oxidative addition of SnR$_3$H to a transient platinum(0) species,[6] so the balance of evidence perhaps favours structures (5) and (6) for the intermediates in equations (iv) and (v).

A brief study was made of the rates of formation of complexes (1) and (2). The reaction between [Pt(C$_2$H$_4$)-(PPh$_3$)$_2$] and SnMe$_3$(C$_6$H$_4$OMe-2) gives only complex (1) and it was shown by monitoring the ^{31}P-{^{1}H} n.m.r. spectra that the rate of formation of (1) approximately doubled when the initial concentration of SnMe$_3$(C$_6$H$_4$OMe-2) was increased from 1 to 2 mol dm^{-3}. The rate of formation of (2) from (1) (R = C$_6$H$_4$OMe-3) also increased on doubling the concentration of SnMe$_3$(C$_6$H$_4$OMe-3), but by a factor much smaller than 2, and this is consistent with Scheme 1, since (2) is both formed and destroyed by reaction with SnMe$_3$R.

The rate of formation of (1) from [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and SnMe$_3$(C$_6$H$_4$X) increased with the electron-withdrawing power of the substituent X: under similar conditions the reaction was fast for X = NO$_2$-4 and slow for X = NMe$_2$-4 and competition experiments indicated that the reaction was *ca.* 2.5 times faster for X = F-3 than for X = H which in turn was *ca.* 2.5 times faster than for X = OMe-4. Although the results for the competition experiments could be influenced by exchange of aryl groups [equation (viii)] the order of reactivity of tin compounds SnMe$_3$(C$_6$H$_4$X) appears to be X = NO$_2$-4 $>$ F-4 $>$ H $>$ OMe-4 $>$ NMe$_2$-4 and the reaction with SnMe$_3$(2-furyl) was also fast.

The sequence of decreasing reactivity of the SnMe$_3$R (R = aryl) compounds agrees with that of the decreasing acidity of the corresponding arene species, RH, and also with the decreasing ease of base cleavage of Me$_3$Si–R bonds, which is thought to involve nucleophilic attack at silicon and separation of R$^-$.[7] We suggest that the insertions into the Sn–R bond also involve predominant nucleophilic attack at tin and generation of significant carbanionic character in R in the transition state, but in the medium used the carbanion is most unlikely to separate, and will attach to the forming Pt$^+$ centre either synchronously in a three-centre process or (less likely) subsequently within an ion pair. The synchronous process would show an analogy with cleavage of Me$_3$Sn–R (R = aryl) bonds by Na[OMe]–MeOH, in which substantial anionic character is developed in the aryl group in the rate-determining step, but synchronous proton transfer from the solvent to the leaving carbon atom prevents actual separation of the anion.[7] Although other mechanisms are known for oxidative-addition reactions of platinum(0) complexes, the three-centre insertion seems to be the most probable for a relatively non-polar tetraorganotin substrate and a similar mechanism is likely also for reactions (ii)—(iv) and (vi)—(viii) which involve insertion of platinum(II).

It is noteworthy that, although $SnMe_4$ reacts with platinum(II) complexes (2) [reverse of equation (iii)], mixtures of $SnMe_4$ and the platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ do not form *cis*-$[PtMe(SnMe_3)(PPh_3)_2]$ or other platinum(II) products. Since, however, $SnMe_4$ is rapidly eliminated from platinum(IV) complexes [for example, equation (xiii)], it is possible that elimination from platinum(II) complexes is also rapid and that formation of *cis*-$[PtMe(SnMe_3)(PPh_3)_2]$ is thus prevented by thermodynamic factors.

TABLE 5

Variations of $^1J(PtP)$ with X for complexes $[Pt(C_6H_4X\text{-}4)(SnMe_3)(PPh_3)_2]$

X	ΔJ */Hz		σ_I
	trans	*cis*	
$SnMe_3$	−5		0.0
H	0	0	0.00
Me	19	−7	−0.08 to +0.02
Ph	24	−9	0.08—0.15
SMe	36	−24	0.13—0.31
NMe_2	39	−36	0.06—0.19
OMe	46	−34	0.23—0.34
NO_2	58	−9	0.68—0.76
F	60	−41	0.50—0.54
Cl	61	−31	0.46—0.50
Br	63	−29	0.44—0.49
$NMe_3^+I^-$	83	−34	0.93

* $^1J(PtP)$ for X = X minus that for X = H.

^{31}P *N.M.R. Parameters of* (1).—Some pattern can be discerned in the variations of the coupling constants $^1J(PtP)$ with X in the complexes $[Pt(C_6H_4X\text{-}4)(SnMe_3)(PPh_3)_2]$. In Table 5 are given two sets of ΔJ values, *i.e.* of the difference between $^1J(PtP)$ for X = X and that for X = H, one for the PPh_3 *trans* and the other for the PPh_3 *cis* to C_6H_4X. Also shown are the values of the inductive constants σ_I for the X groups.[8] It will be seen that for the *trans* set ΔJ increases roughly in line with the value of σ_I (*i.e.* with increasing inductive electron withdrawal by X); only the data for X = NO_2 fall significantly out of sequence, although, in addition, the effect of the Me group seems surprisingly large in relation to those of the more polar groups. A related but more precise correlation between $^1J(PtP)$ and σ_I was noted previously for the complexes *cis*-$[Pt(C_6H_4X\text{-}4)_2(PPh_3)_2]$.[9] For the *cis* set, the *J* values change in the opposite direction as X is varied, *i.e.* the *negative* ΔJ values tend to increase with increasing inductive electron withdrawal by X, but the parallel is poorer than for the *trans* set and the small ΔJ for X = NO_2 is especially anomalous. This is an example, albeit imprecise, of the coupling constants *cis* and *trans* to a series of related ligands varying in opposite senses.[10]

Reactions of Complexes (1) *and* (2).—The products of several reactions of complexes (1) and (2) (Table 6) are the same as those obtained from reactions of platinum(0) complexes such as $[Pt(C_2H_4)(PPh_3)_2]$, which has, for

TABLE 6

Products of reactions of complexes (1) or (2) in dichloromethane at room temperature

Starting complex	Reagent (time, *t*/h)	Products *
(1; R=Ph)	O_2(1)	$[PtO_2(PPh_3)_2]$
	$SnMePh_3$ (5)	*cis*-$[PtPh(SnMePh_2)(PPh_3)_2]$
(2; R = Ph)	MeI (6)	*trans*-$[PtMe(I)(PPh_3)_2]$
	PhI (6)	*cis*- and *trans*-$[PtPh(I)(PPh_3)_2]$
(2; R = C_6H_4OMe-4)	$SnMePh_3$ (5)	*cis*-$[PtPh(SnMePh_2)(PPh_3)_2]$
	$SnPh_4$ (5)	*cis*-$[PtPh(SnPh_3)(PPh_3)_2]$

* Identified by $^{31}P\text{-}\{^1H\}$ n.m.r. spectra recorded *in situ*; parameters of *cis*-$[PtPh(SnMePh_2)(PPh_3)_2]$ and *cis*-$[PtPh(SnPh_3)(PPh_3)_2]$ are given in the Experimental section.

TABLE 7

Products of reactions between *cis*-$[PtPh(SnMe_3)(PPh_3)_2]$ (1) or *cis*-$[PtPh(SnMe_2Ph)(PPh_3)_2]$ (2) and organotin chlorides in dichloromethane at room temperature

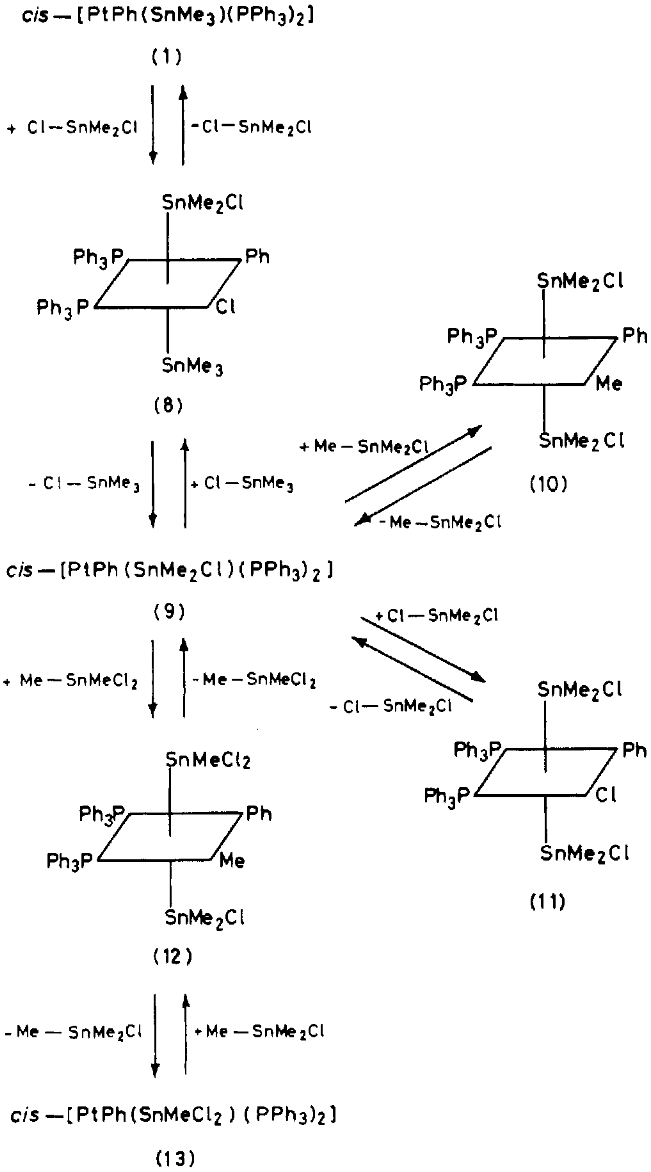
Starting complex	Organotin chloride [a]	t [b]/h	Product complexes [c]
(1)	$SnMe_2Cl_2$ (1)	3	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (100)
	$SnMe_2Cl_2$ (2.5)	3.5	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (90), *cis*-$[PtPh(SnMeCl_2)(PPh_3)_2]$ (10)
	$SnPh_3Cl$ (1)	5	*cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (90), *cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (10)
	$SnPh_3Cl$ (2·5)	5.5	*cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (70), *cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (30)
	$SnPh_2Cl_2$ (1)	4	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (100)
	$SnPh_2Cl_2$ (2.5)	4.5	*cis*-$[PtPh(SnMeCl_2)(PPh_3)_2]$ (100)
(2)	$SnMe_3Cl$ (1)	7	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (100)
	$SnMe_3Cl$ (2.5)	8	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (30), *cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (70)
	$SnMe_2Cl_2$ (1)	5	*cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (65), *cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (35)
	$SnMe_2Cl_2$ (2.5)	4.5	*cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (60), *cis*-$[PtPh(SnMeCl_2)(PPh_3)_2]$ (40)
	$SnPh_3Cl$ (1)	6	*cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (50), *cis*-$[PtPh(SnMe_2Cl)(PPh_3)_2]$ (50)
	$SnPh_3Cl$ (2.5)	6	*cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (50), *cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (50)
	$SnPh_2Cl_2$ (1)	4.5	*cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (100)
	$SnPh_2Cl_2$ (2.5)	4	*cis*-$[PtPh(SnMePhCl)(PPh_3)_2]$ (45), *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ (36), *cis*-$[PtPh(SnMeCl_2)(PPh_3)_2]$ (18)

[a] Molar proportion of tin reagent is given in parentheses. [b] Period between mixing of reagents and commencement of acquisition of $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. [c] Composition (%) of product mixture as determined from the intensities of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum is given in parentheses.

example, been shown to form *cis*-[PtPh(SnMePh$_2$)(PPh$_3$)$_2$] with SnMePh$_3$ and *cis*-[PtPh(SnPh$_3$)(PPh$_3$)$_2$] with SnPh$_4$ (see Experimental section; neither of these complexes reacts with SnMe$_4$). In the absence of any indication from the n.m.r. spectra of dissociation of (1) and (2), it is probable that the reagents add to (1) and (2) to form platinum(IV) intermediates which then eliminate a tetraorganotin compound. This mechanism is certainly implied by the fact that [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (6.7 × 10^{-5} mol) catalyses the exchange of aryl groups between SnMe$_2$(C$_6$H$_4$OMe-4)$_2$ (1.67 × 10^{-4} mol) and SnMe$_2$Ph$_2$ (1.67 × 10^{-4} mol). After 72 h at room temperature the ^{1}H n.m.r. spectrum of this mixture showed that the three tin compounds SnMe$_2$(C$_6$H$_4$OMe-4)$_2$, SnMe$_2$Ph(C$_6$H$_4$OMe-4), and SnMe$_2$Ph$_2$ were present in a molar ratio of *ca.* 1 : 2 : 1, which is that expected for statistical redistribution of the aryl groups Complexes (2) are clearly undergoing oxidative addition with Sn–R bonds and SnMe$_2$Ph(C$_6$H$_4$OMe-4) is formed by elimination from [PtPh(C$_6$H$_4$OMe-4)(SnMe$_2$Ph){SnMe$_2$(C$_6$H$_4$-OMe-4)}(PPh$_3$)$_2$].

The products of a number of reactions between complexes (1) and (2) and organotin chlorides SnMe$_3$Cl, SnMe$_2$Cl$_2$, SnPh$_3$Cl, and SnPh$_2$Cl$_2$ were examined *in situ* by ^{31}P-{^{1}H} n.m.r. spectroscopy (Table 7). The product complexes were identified by their chemical shifts and coupling constants ^1J(PtP), which have been reported previously, except for *cis*-[PtPh(SnMeCl$_2$)(PPh$_3$)$_2$].[1-3] The chemical shifts and coupling constants ^1J(PtP), ^2J(SnP), and ^2J(PP) for this complex (see Experimental section) agree well with those expected from trends in the magnitude of the parameters for *cis*-[PtPh(SnX$_3$)(PPh$_3$)$_2$] (SnX$_3$ = SnPh$_3$,[1] SnPh$_2$Cl,[1,3] SnPhCl$_2$,[2] or SnMe$_2$Cl [1,3]).

The formation of all the product complexes can be rationalised in terms of oxidative-addition and reductive-elimination steps in which the two PPh$_3$ ligands and one Pt–Ph bond are retained throughout. Since the nature of several of the products and the results described earlier in this paper show that Sn–Me bonds are reactive in these systems, the retention of one Pt–Ph bond in all the products probably derives from thermodynamic factors, which may also be responsible for the formation of aryl- rather than methyl-platinum complexes in reactions between chloroplatinum(II) complexes and an equimolar quantity or an excess of SnMe$_3$R (R = aryl).[11] A mechanism, which is simplified by the exclusion of processes resulting in the loss of all Pt–Ph bonds, is given in Scheme 3 for the reaction between (1) and SnMe$_2$Cl$_2$. Initial addition of SnMe$_2$Cl$_2$ *via* the Sn–Cl bond is expected to be much faster than that *via* the Sn–Me bond, so with equimolar proportions of (1) and SnMe$_2$Cl$_2$ an equimolar mixture of *cis*-[PtPh(SnMe$_2$Cl)(PPh$_3$)$_2$] (9) and SnMe$_3$Cl should form rapidly. Scheme 3 shows that, provided one Pt–Ph bond is retained, the platinum(IV) intermediates (8) and (10) that can be formed by addition of SnMe$_3$Cl to (9) can then only revert to (9) on elimination of a tin(IV) compound. In the presence of an excess of SnMe$_2$Cl$_2$ the fast addition of the Sn–Cl bond of this reagent to (9) is unproductive, but the presumably slower addition of the Sn–Me bond can lead to the formation of *cis*-[PtPh(SnMeCl$_2$)(PPh$_3$)$_2$] (13) *via* (12). Scheme 3 thus accounts satisfactorily for the products we found, and although addition of SnMe$_2$Cl$_2$ *via* the Sn–Cl bond to (8) can result in formation of SnMeCl$_3$ and thence *cis*-[PtPh(SnCl$_3$)(PPh$_3$)$_2$] (not shown in Scheme 3), the absence from the list of products given in Table 6 of complexes containing a greater number of chlorine atoms than the starting tin compound suggests that their formation may also be prevented by thermodynamic factors. Although (13), which was formed when an excess of SnMe$_2$Cl$_2$ was used, could derive from a reaction between (1) and SnMe$_2$Cl$_2$ *via* an insertion into the Sn–Me bond (not shown in Scheme 3), this is improbable in view



SCHEME 3 The structure of the platinum(IV) intermediates has not been established

of the fact that no (13) was detectable in the products when equimolar amounts of reagents were used. The relative proportions of (9) and (13) formed *via* addition of $SnMe_2Cl_2$ to (1) cannot vary with the initial concentration of $SnMe_2Cl_2$ if, as seems probable, the insertions into the Sn–Me and Sn–Cl bonds of $SnMe_2Cl_2$ have the same dependence on the concentration of that reagent. In the reactions between (1) and $SnPh_2Cl_2$, the complex *cis*-[PtPh($SnMe_2Cl$)(PPh_3)$_2$] was formed from equimolar proportions of the reagents, and *cis*-[PtPh($SnMeCl_2$)(PPh_3)$_2$] was the only complex formed when an excess of $SnPh_2Cl_2$ was used. We also showed that treatment of a solution of *cis*-[PtPh($SnMe_2Cl$)(PPh_3)$_2$] (1 mol) with $SnPh_2Cl_2$ (2 mol) resulted in complete formation of *cis*-[PtPh($SnMeCl_2$)(PPh_3)$_2$], so it is probable that the extra or new products formed by use of an excess of tin(IV) reagent result from further reactions of complexes formed initially from (1) or (2) and not by new pathways involving direct reaction with (1) or (2).

The mechanisms required for the explanation of other reactions in Table 7 are more complicated than that in Scheme 3. In several instances a given product can be formed by more than one route and further studies are planned in which reaction mixtures at low temperatures are monitored by ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy. It is probable that platinum(II) complexes catalyse some redistribution reactions of organotin chlorides as well as those of the tetraorganotin compounds described above. If so, the results of some of our earlier experiments [2] in which [Pt(C_2H_4)(PPh_3)$_2$] was treated with mixtures of organotin compounds may require reinterpretation.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Solvents were dried and distilled before use. Melting points were recorded on a Gallenkamp Electrothermal melting-point apparatus and are uncorrected. The ^{1}H n.m.r. spectra were recorded on Varian T-60 or Perkin-Elmer R-32 spectrometers from samples in $CDCl_3$ with $SiMe_4$, CH_2Cl_2, or $CHCl_3$ used as internal reference. The ^{31}P-{^{1}H} n.m.r. spectra were obtained on a JEOL PFT-100 Fourier-transform spectrometer at 40.48 MHz. Samples were dissolved in CH_2Cl_2 and an external reference of P(OMe)$_3$ in C_6D_6 also provided the deuterium lock signal. Positive shifts are to high frequency of this reference. The ^{19}F n.m.r. spectra of $CDCl_3$ solutions were also recorded on this instrument. Elemental analyses were by the Micro-analytical Laboratory of this School.

Complexes.—The complex [Pt(C_2H_4)(PPh_3)$_2$] was prepared by the method of Cook and Jauhal,[12] and organotin compounds were available in this laboratory or were prepared by established procedures. The complexes (1) in Table 1 were prepared by treatment of [Pt(C_2H_4)(PPh_3)$_2$] in benzene or dichloromethane with $SnMe_3R$ in equimolar proportions (R = $C_6H_4NO_2$-4 or 2-furyl) or in excess. After *ca.* 5 h at room temperature, volatile components were removed under vacuum and the pure *products* were obtained after washing the residue with light petroleum (b.p. 30—40 °C). The complexes (2) in Table 1 were obtained in a similar manner from [Pt(C_2H_4)(PPh_3)$_2$] and an excess of $SnMe_2R_2$. No phosphorus-containing impurities were detected in the ^{31}P-{^{1}H} n.m.r. spectra of these samples. The complexes *cis*-[PtPh($SnMePh_2$)(PPh_3)$_2$] [^{31}P-{^{1}H} n.m.r.: P *trans* to Sn, δ −114.0 p.p.m., ^{1}J(PtP) 2 264, $^{2}J(^{119}$SnP) 1 865, $^{2}J(^{117}$SnP) 1 784 Hz; P *trans* to Ph, δ −117.4 p.p.m., ^{1}J(PtP) 2 058, ^{2}J(SnP) 155, ^{2}J(PP) 15 Hz] and *cis*-[PtPh($SnPh_3$)(PPh_3)$_2$] [for elemental analysis see Table 1. ^{31}P-{^{1}H} n.m.r.: P *trans* to Sn, δ −114.1 p.p.m., ^{1}J(PtP) 2 352, $^{2}J(^{119}$SnP) 1 936, $^{2}J(^{117}$SnP) 1 846 Hz; P *trans* to Ph, δ −119.4 p.p.m., ^{1}J(PtP) 2 036, ^{2}J(SnP) 149, ^{2}J(PP) 15 Hz] were obtained by treating [Pt(C_2H_4)(PPh_3)$_2$] with $SnMePh_3$ (in benzene) or an equimolar amount of $SnPh_4$ (in dichloromethane).

Reactions examined in situ.—A typical procedure was as follows. The complex [Pt(C_2H_4)(PPh_3)$_2$] (0.05 g) was placed in an n.m.r. tube and dissolved in CH_2Cl_2 (0.5 cm^3). An equimolar proportion of $SnMe_3Ph$ (0.016 g) was then added and the mixture set aside for 2 h at room temperature. The ^{31}P-{^{1}H} n.m.r. spectrum was then recorded and showed the presence of (1; R = Ph) and some [Pt(C_2H_4)(PPh_3)$_2$]. When the procedure was repeated with a 2.5 molar proportion of $SnMe_3Ph$ the spectrum showed the presence of (1) (*ca.* 45%) and (2) (*ca.* 55%) (R = Ph). Similar results were obtained for other $SnMe_3R$ except for sterically hindered R [see (*a*) above]. With $SnMe_3$(C_6H_4-NMe_2-4) the reaction was very slow; with a 10-fold excess of the tin compound a large amount of [Pt(C_2H_4)(PPh_3)$_2$] remained after 72 h.

The ^{31}P-{^{1}H} n.m.r. spectrum of the product from the reaction between (1; R = C_6H_4OMe-2) and an excess of $SnMe_3Ph$ comprised doublets [^{2}J(PP) 15 Hz] with platinum satellites at δ −114.5 [^{1}J(PtP) 2 207 Hz, *trans* to Sn] and −115.9 p.p.m. [^{1}J(PtP) 2 302 Hz, *trans* to aryl]. These parameters are different from those of (1) or (2) (R = Ph or C_6H_4OMe-2) (Table 2) and the value for ^{1}J(PtP) *trans* to R corresponds well with those *trans* to R in (1) and (2) (R = C_6H_4OMe-2), so the formula *cis*-[Pt(C_6H_4OMe-2)($SnMe_2Ph$)(PPh_3)$_2$] is indicated.

The products of reactions listed in Tables 6 and 7 were identified by comparison of their ^{31}P-{^{1}H} n.m.r. parameters with those of authentic samples: [PtO_2(PPh_3)$_2$], δ −125.3, ^{1}J(PtP) 4 083; *trans*-[PtMe(I)(PPh_3)$_2$], δ −112.6, ^{1}J(PtP) 3 072; *trans*-[PtPh(I)(PPh_3)$_2$], δ −118.7, ^{1}J(PtP) 3 090; *cis*-[PtPh(I)(PPh_3)$_2$], δ −123.9, ^{1}J(PtP) 4 300, δ −126.1 p.p.m., ^{1}J(PtP) 1 636, ^{2}J(PP) 16 Hz; complexes *cis*-[PtPh(SnX_3)(PPh_3)$_2$] [SnX_3 = $SnMe_2Cl$, SnMe(Ph)Cl, $SnPh_2Cl$, or $SnPhCl_2$], see refs. 2 and 3. The parameters for the complex *cis*-[PtPh($SnMeCl_2$)(PPh_3)$_2$] [P *trans* to Sn, δ −114.0, ^{1}J(PtP) 3 008, $^{2}J(^{119}$SnP) 2 871, $^{2}J(^{117}$SnP) 2 744; P *trans* to Ph, δ −120.6 p.p.m., ^{1}J(PtP) 2 058, ^{2}J(SnP) 184, ^{2}J(PP) 16 Hz] have not been reported previously.

We thank the Commonwealth Scholarship Commission (U.K.) for a Commonwealth Academic Staff Scholarship (for K. K.), and the Chugoku Marine Paints Co., Ltd., and the Shin Nihan Shoji Co., Ltd., for a gift of dichlorodimethyltin ('Nesstin Pure').

[0/1794 *Received, 20th November,* 1980]

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