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OXIDATIVE ADDITION OF TIN(IV) COMPOUNDS TO ETHYLENE BIS(TRIPHENYLPHOSPHINE)PLATINUM *

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Summary

Reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and organotin halides have been investigated. With $SnPh_2Cl_2$ the product of insertion into the Sn—C bond, *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$, was obtained, whereas $SnMe_2Cl_2$, $SnPhCl_3$, $SnMeCl_3$ and $SnCl_4$ gave products of insertion into the Sn—Cl bond, viz. *cis*- and *trans*-$[PtCl(SnCl_nR_{3-n})(PPh_3)_2]$. The products were characterised by ^{31}P-$\{^1H\}$ NMR spectroscopy. Compounds of similar stoichiometry $[PtR(SnCl_3)(PPh_3)_2]$ were examined for purposes of comparison and were obtained from $SnCl_2$ and the corresponding chloro complexes. The compounds *cis*- and *trans*-$[PtCl(SnCl_3)(PPh_3)_2]$ were obtained both by the oxidative-addition reaction and the $SnCl_2$ insertion route. A wide variety of similar products were obtained with organotin chlorides and bromides. Competition experiments indicated an order of reactivity in the oxidative addition reaction $SnMe_4 < SnPh_4 < SnMe_3Cl <$ $SnPh_3Cl$, $SnMeCl_2 < SnPh_2Cl_2$, $SnMeCl_3 < SnPhCl_3 < SnCl_4$. The presence of radicals in the reaction mixture was not detected by radical transfer or spin-trapping experiments.

Introduction

An attempt to compare the *trans* influence of SnR_3 and Cl ligands by measurement of the NMR coupling constants $^1J(PtP)$ in complexes *cis*-$[PtCl(SnR_3)(PPh_3)_2]$ led us to repeat the reported procedures for the synthesis of these complexes. All the methods, and in particular the oxidative addition of R_3SnCl

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* In dedicating this paper to Professor Joseph Chatt, our colleague at the University of Sussex, on the occasion of his 65th birthday, we wish to acknowledge his contribution to our research efforts over many years. The discovery [1] of the very large and variable coupling constants ^1J(Pt—P) was made with complexes obtained from a sample of n-Bu_3P given by him to A.P., and the entry of C.E. into the field of Group IV element derivatives of transition metals was greatly facilitated by his collaboration [2].

to platinum(0) complexes, were found, in fact, to form the complexes *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$ (R = alkyl or aryl), which are formally the result of insetion of platinum into the Sn—R rather than the Sn—Cl bond [3]. Insertion of platinum(0) into Sn—R bonds has subsequently been demonstrated for a variety of triorgano- and tetraorganotin compounds [4]. Since the insertion of low-valent transition elements into Sn—Cl bonds is well-known for $SnCl_4$ it appeared probable that a changeover from Sn—R insertion (for SnR_4 and SnR_3Cl) to Sn—Cl insertion would occur for SnR_nCl_{4-n} ($n = 1, 2$), and the reactions of such compounds and $SnCl_4$ with $[Pt(C_2H_4)(PPh_3)_2]$ are reported here.

Results and discussion

Reactions of diorganotin(IV) compounds

The reaction of $SnPh_2Cl_2$ with $[Pt(C_2H_4)(PPh_3)_2]$ in dry dichloromethane gives *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$. This was established by elemental analysis of the product and from the ^{31}P-$\{^1H\}$ NMR spectrum of the product or the product mixture examined in situ in the NMR tube. The spectrum comprises a pair of strong doublets from the coupled ($^2J(PPtP)$ 15 Hz) non-equivalent PPh_3 ligands, each of which is associated with satellites due to coupling to ^{117}Sn, ^{119}Sn and ^{195}Pt nuclei. The coupling constants to the Sn nuclei permit unambiguous assignment of the P nuclei *trans* and *cis* to Sn, since indirect coupling

TABLE 1

^{31}P NMR PARAMETERS OF COMPLEXES FORMED FROM $[Pt(C_2H_4)(PPh_3)_2]$ AND SnR_2X_2 [a]

Tin reagent	Complex	Isomer [b] (%)	−δ *trans* to Sn (ppm)
$SnPh_2Cl_2$	$[PtPh(SnPhCl_2)(PPh_3)_2]$	*cis* 100	114.2
$SnPh_2Br_2$	$[PtPh(SnPhBr_2)(PPh_3)_2]$	*cis* 100	116.3
$SnPh_2BrCl$ [d]	$[PtPh(SnPhBrCl)(PPh_3)_2]$ [d]	*cis* 100	115.3
$SnMe_2Cl_2$	$[PtCl(SnMe_2Cl)(PPh_3)_2]$ [f]	*cis* 42	107.4
		trans 58	—
$Sn\text{-}n\text{-}Bu_2Cl_2$	$[PtCl(Sn\text{-}n\text{-}Bu_2Cl)(PPh_3)_2]$	*cis* 69	107.1
		trans 31	—
$Sn(CH_2Ph)_2Cl_2$	$[PtCl\{Sn(CH_2Ph)_2Cl\}(PPh_3)_2]$	*cis* 95	107.1
		trans 5	—
$Sn(C_2H_4CO_2Me)_2Cl_2$	$[PtCl\{Sn(C_2H_4CO_2Me)_2Cl\}(PPh_3)_2$	*cis* 85	108.1
		trans 15	—
$(SnMe_2Br)_2O$	$[PtBr(SnMe_2OSnMe_2Br)(PPh_3)_2]$	*cis* 40	110.9
		trans 60	—
$(SnEt_2Br)_2O$	$[PtBr(SnEt_2OSnEt_2Br)(PPh_3)_2]$	*cis* 80	110.4
		trans 20	—
$(Sn\text{-}n\text{-}Bu_2Br)_2O$	$[PtBr(Sn\text{-}n\text{-}Bu_2OSn\text{-}n\text{-}Bu_2Br)(PPh_3)_2]$	*cis* 80	110.6
		trans 20	—
$\{Sn(C_6H_{13})_2Cl\}O$ [g]	$[PtCl\{Sn(C_6H_{13})_2OSn(C_6H_{13})_2Cl\}(PPh_3)_2]$	*cis* 72	107.1
		trans 28	—
$\{Sn(CH_2Ph)_2Cl\}_2O$	$[PtCl\{Sn(CH_2Ph)_2OSn(CH_2Ph)_2Cl\}(PPh_3)_2]$	*cis* 100	105.8

[a] In dichloromethane. [b] Relative abundance (%) of isomers as determined from the peak heights in the ^{31}P $\{^1H\}$ NMR spectra. [c] Separate ^{119}Sn and ^{117}Sn satellites were not usually resolved. [d] Mixture of $SnPh_2Br_2$ and $SnPh_2Cl_2$; complex present in 50% abundance with 25% each of complexes from $SnPh_2Br_2$ and $SnPh_2Cl_2$. [e] Signal to noise ratio insufficient for the observation of Sn satellites. [f] ^1H

between ligand atoms in platinum(II) complexes is known to be much larger for *trans* than *cis* related ligands [5]. The phosphorus *trans* to Sn ($^{2}J(^{119}$SnPtP) 2961 Hz) is associated with ^{1}J(PtP) 3105 Hz and that *cis* to Sn (^{2}J(SnPtP) 193 Hz; ^{117}Sn and ^{119}Sn satellites are not resolved) with ^{1}J(PtP) 2053 Hz. The well-established dependence of ^{1}J(PtP) on the nature of the ligand *trans* to phosphorus [5] can now be used to infer that the PPh_3 ligand with ^{1}J(PtP) 2053 Hz is *trans* to a Ph ligand derived from $SnPh_2Cl_2$ and not, for example, a Cl ligand in which case ^{1}J(PtP) would be ca. 4000 Hz [3]. The stoichiometry of the reaction then indicates that the stannio ligand is $SnPhCl_2$, and this is confirmed by the smooth change in ^{31}P parameters for PPh_3 *trans* to the stannio ligand in *cis*-$[PtPh(SnPh_3)(PPh_3)_2]$ (^{1}J(PtP) 2354 Hz, $^{2}J(^{119}$SnPtP) 1938 Hz, ref. 3), *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (^{1}J(PtP) 2688 Hz, $^{2}J(^{119}$SnPtP) 2400 Hz, ref. 3) and in the complex under consideration *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ (^{1}J(PtP) 3105 Hz, $^{2}J(^{119}$SnPtP) 2961 Hz) (Table 1). From the spectrum of the products of a reaction carried out in the NMR tube, formation of a small amount of *cis*-$[PtCl_2(PPh_3)_2]$ was detected. It is presumed that this derives from HCl formed from the tin compound by accidental hydrolysis; this dichloro complex and the product of oxidative addition account for all the lines in the ^{31}P-{^{1}H} spectrum.

The product from the reaction between the ethylene complex and $SnBr_2Ph_2$ has a ^{31}P-{^{1}H} spectrum very similar to that of the product from $SnPh_2Cl_2$, and

^{1}J(Pt—P) (Hz)	^{2}J (^{119}SnP) (Hz)	^{2}J (^{117}SnP) (Hz)	—δ *cis* to Sn (ppm)	^{1}J (Pt—P) (Hz)	^{2}J(SnP)^{c} (Hz)	^{2}J(PP) (Hz)
3105	2961	2844	120.1	2053	193	15
3145	2954	2822	118.6	2064	193, 183	15
3125	*e*	*e*	119.4	2058	*e*	15
2201	2265		120.8	4358	59	13
—	—	—	115.6	2793	132	—
2166	2045	1960	120.4	4468	56	13
—	—	—	114.6	2793	117	—
2332	2460	2280	123.2	4319	68	12
—	—	—	115.7	2715	*e*	—
2219	*e*	*e*	122.5	4341	63	13
—	—	—	116.3	2720	138	—
2290	*e*	*e*	117.7	4465	*e*	—
—	—	—	117.5	2734	117	—
2259	2044	1953	118.7	4448	117	15
—	—	—	116.8	2787	117	—
2219	*e*	*e*	118.8	4450	*e*	14
—	—	—	116.6	2586	*e*	—
2144	2038	1980	120.3	4475	*e*	15
—	—	—	114.7	2769	120	—
2036	1719	1641	120.9	4458	102	15

NMR parameters: *cis* isomer δ 1.76 ppm, ^{2}J(SnH) 18 Hz; *trans* isomer δ 1.4 ppm, ^{2}J(SnH) 19 Hz. ^{13}C NMR parameters (see text): *cis* isomer δ 2.3 ppm (doublet), ^{3}J(PC) 13 Hz; *trans* isomer δ 3.22 ppm, ^{2}J(PtC) 111 Hz. [g] C_6H_{13} = *n*-hexyl.

so is assigned the structure *cis*-[PtPh(SnBr$_2$Ph)(PPh$_3$)$_2$] (Table 1). The presence of two Br atoms on Sn in this complex is confirmed by the observation of two infrared bands at 226 and 257 cm^{-1}; Sn—Br stretching vibrations are normally in the region 200—280 cm^{-1} (e.g. 240, 250 cm^{-1} for SnBr$_2$Me$_2$ [6]), whereas the Pt—Br stretching frequency is nearly always below 200 cm^{-1}.

With SnMe$_2$Cl$_2$ the ^{31}P-{^{1}H} NMR spectrum showed that the reaction had taken a different course. Two complexes were clearly present. The spectrum of one comprised two doublets (^2J(PPtP) 13 Hz) from a *cis* complex with non-equivalent PPh$_3$ ligands, but in contrast to the products from SnPh$_2$X$_2$ (X = Cl, Br), the PPh$_3$ ligand *cis* to Sn (^2J(SnPtP) 59 Hz) was associated with a large coupling constant ^1J(PtP) 4356 Hz indicating that the ligand in *trans* relationship to PPh$_3$ was Cl. The formulation *cis*-[PtCl(SnMe$_2$Cl)(PPh$_3$)$_2$] satisfies this requirement and is consistent with the other ^{31}P parameters. In particular, for PPh$_3$ *trans* to SnMe$_2$Cl the value of ^2J(^{119}SnPtP) in this complex (2265 Hz) is very similar to that in *cis*-[PtMe(SnMe$_2$Cl)(PPh$_3$)$_2$] (2274 Hz) [3], and this coupling is known to be sensitive to the nature of the groups on the tin atom.

The spectrum of the second complex comprises a single resonance with satellites from ^{195}Pt (^1J(PtP) 2793 Hz) and Sn (^2J(SnPtP) 132 Hz; ^{119}Sn and ^{117}Sn satellites were not resolved). The intensity of the Sn satellites is such that there must be one Sn atom per molecule and the magnitudes of both coupling constants establish that two PPh$_3$ ligands are mutually *trans* (for example, in *trans*-[PtPh(Cl)(PPh$_3$)$_2$], ^1J(PtP) 2800 Hz) and a stannio ligand is in *cis*-relationship to them. Further inference about the nature of the ligands *cis* to PPh$_3$ cannot be made on the basis of the magnitudes of the coupling constants since their dependence on the *cis* ligands is relatively small and poorly understood at present. The spectrum is, however, consistent with the formula *trans*-[PtCl(SnMe$_2$Cl)(PPh$_3$)$_2$], and it is reasonable to expect both *cis* and *trans* isomers to be present, since *cis*—*trans* equilibration of chloroplatinum complexes in the presence of traces of phosphine is well known from the work of Chatt et al. [7]. This formula rather than, for example, *trans*-[PtMe(SnMeCl$_2$)(PPh$_3$)$_2$], is also supported by the ^{1}H NMR spectrum of the product mixture recorded under very favourable conditions of signal to noise with a Fourier transform spectrometer. The spectrum comprises two sharp lines in the SnCH$_3$ region (each with Sn satellites, see Table 1) with a relative intensity corresponding to that expected from the ^{31}P-{^{1}H} spectrum, and with no evidence for the presence of a Pt—CH$_3$ group. The ^{13}C-{^{1}H} NMR spectrum is also consistent with the formula (Table 1, footnote *f*), but such prolonged accumulation of the spectrum was required that we cannot exclude the possibility that some of the observed lines are due to decomposition products.

A number of other compounds SnR$_2$XY (R = alkyl or substituted alkyl; X = Cl, Br; Y = Cl, OSnR$_2$Cl, see Table 1) were available to us, and the ^{31}P-{^{1}H} NMR spectra of the products of their reactions with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] were qualitatively similar to that of the product from SnMe$_2$Cl$_2$, and the magnitudes of the coupling constants were also closely similar. In one instance, with {Sn(CH$_2$Ph)$_2$Cl}$_2$O, only the *cis* product was detected, but for the other compounds both *cis* and *trans* isomers were observed, with signal intensities generally indicating a prepondrance of the *cis* isomer (Table 1).

The products of the reactions with SnMe$_2$Cl$_2$ and Sn-n-Bu$_2$ were isolated and gave satisfactory analyses; it is not clear whether the solid samples contain a single isomer or are mixtures of isomers.

The results for the diorganotin compounds may be summarized by eqs. 1 and 2.

$$[Pt(C_2H_4)(PPh_3)_2] + SnPh_2X_2 \rightarrow cis\text{-}[PtPh(SnPhX_2)(PPh_3)_2] + C_2H_4 \ (X = Cl, Br) \qquad (1)$$

$$[Pt(C_2H_4)(PPh_3)_2] + SnR_2XY \rightarrow cis\text{- and } trans\text{-}[PtX(SnR_2Y)(PPh_3)_2] + C_2H_4$$
$$(X = Cl, Br; R = \text{alkyl, for Y see Table 1}) \qquad (2)$$

Reactions of organotin trichlorides and tribromides

The products of the reactions of organotin trichlorides and tribromides with $[Pt(C_2H_4)(PPh_3)_2]$ are less soluble in dichloromethane than those from the diorganotin(IV) compounds, so we were unable to detect Sn-satellites in several of the spectra. A complete set of parameters was, however, obtained for the products from $SnMeCl_3$ (Table 1), and it is clear by analogy with the results for $SnMe_2Cl_2$ that they are formulated *cis*- and *trans*-$[PtCl(SnMeCl_2)(PPh_3)_2]$. The analytical results for the isolated product agree with this formula, and a possible alternative product *trans*-$[PtMe(SnCl_3)(PPh_3)_2]$, prepared from *trans*-$[PtMe(Cl)(PPh_3)_2]$ and $SnCl_2$, has ^{31}P parameters (δ — 125.8 ppm, $^1J(PtP)$ 2493 Hz, $^2J(SnPtP)$ 120 Hz, Table 3) which are clearly different from those of the *trans* product of the oxidative-addition reaction (Table 2).

Although the Sn-satellites could not be observed for the products from $SnPhCl_3$, the ^{31}P parameters are similar to those of the products from $SnMeCl_3$, and the parameters of the *trans* isomer are also clearly different from those of *trans*-$[PtPh(SnCl_3)(PPh_3)_2]$ (δ —120.7 ppm, $^1J(PtP)$ 2844 Hz, $^2J(SnPtP)$ 242 Hz, Table 3). The products are, therefore, formulated *cis*- and *trans*-$[PtCl(SnPhCl_2)(PPh_3)_2]$, and this is consistent with the analytical results for the isolated product. The parameters of the remaining products listed in Table 2 are very similar to those for the $SnMeCl_3$ product, so for both phenyl- and alkyl-tin trihalides the oxidative-addition proceeds as in eq. 3.

$$[Pt(C_2H_4)(PPh_3)_2] + SnRX_3 \rightarrow cis\text{- and } trans\text{-}[PtX(SnRX_2)(PPh_3)_2]$$
$$(X = Cl, Br; R = \text{alkyl, Ph}) \qquad (3)$$

The $^{31}P\text{-}\{^1H\}$ parameters of a number of complexes obtained by reactions between chloroplatinum(II) complexes and an excess of $SnCl_2$ are given in Table 3, in all instances the coupling constants $^1J(PtP)$ are significantly different from those of the starting materials *trans*-$[PtR(Cl)L_2]$.

Reactions of tin tetrahalides

The products of the reactions of SnX_4 (X = Cl, Br, I) with $[Pt(C_2H_4)(PPh_3)_2]$ are very insoluble in CH_2Cl_2 and considerable difficulty was experienced in obtaining good $^{31}P\text{-}\{^1H\}$ NMR spectra. For $SnCl_4$ and $SnBr_4$ it was found that satisfactory spectra could be obtained after prolonged accumulation from reactions in the NMR tube between dilute solutions in CH_2Cl_2. For SnI_4 this procedure was ineffective, because the product precipitated too rapidly from CH_2Cl_2,

TABLE 2

^{31}P NMR PARAMETERS OF COMPLEXES *cis*- AND *trans*-[PtX(SnRX$_2$)(PPh$_3$)$_2$] [a]

R	X	Isomer (%) [b]	−δ *trans* to Sn(ppm)	^1J(Pt—P) (Hz)	^2J(^{119}SnP) (Hz)	^2J(^{117}SnP) (Hz)	−δ *cis* to Sn(ppm)	^1J(Pt—P) (Hz)	^1J(SnP) [c] (Hz)	^2J(PP) (Hz)
Ph	Cl	*cis* 80	109.3	2637	*d*	*d*	125.4	3950	*d*	15
		trans 20	—	—	—	—	118.7	2483	98	—
Me	Cl	*cis* [e] 55	109.1	2551	3105	2965	125.9	3987	124	14
		trans [e] 45	—	—	—	—	119.0	2528	159	—
$C_2H_4CO_2Me$	Cl	*cis* 70	111.2	2512	3286	3140	127.4	4038	114	15
		trans 30	—	—	—	—	119.3	2539	171	—
$C_2H_4CO_2Me$	Br	*cis* 88	116.4	2595	*d*	*d*	125.8	4060	*d*	15
		trans 12	—	—	—	—	121.7	2542	*d*	—
$C_2H_4CO_2Et$	Cl	*cis* 70	111.4	2507	*d*	*d*	127.7	4038	*d*	15
		trans 30	—	—	—	—	119.3	2544	146	—

[a] In dichloromethane; obtained in situ from [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and SnRX$_3$. [b] See Table 1 footnote *b*. [c] See Table 1 footnote *c*. [d] See Table 1 footnote *e*. [e] ^{1}H NMR parameters: *cis* isomer δ −0.56 ppm, ^3J(PtH) 8 Hz, ^2J(SnH) 47.2 Hz; *trans* isomer δ 0.12 ppm, ^2J(SnH) 43.9 Hz.

TABLE 3

^{31}P NMR PARAMETERS FOR COMPLEXES OBTAINED BY $SnCl_2$ INSERTION IN SITU

Complex [a]	−δ (ppm)	$^1J(PtP)$ (Hz)	$^2J(SnP)$ [b] (Hz)
trans-$[PtPh(SnCl_3)(PPh_3)_2]$	120.7	2844	242
trans-$[PtMe(SnCl_3)(PPh_3)_2]$	125.8	2493	*c*
trans-$[PtH(SnCl_3)(PPh_3)_2]$	112.6	2688	*c*
trans-$[PtPh(SnCl_3)(PEt_3)_2]$	130.3	2493	234
trans-$[PtH(SnCl_3)(PEt_3)_2]$	119.6	2490	*c*
trans-$[PtPh(SnCl_3)(PMe_2Ph)_2]$	149.4	2576	*c*
trans-$[Pt(4\text{-}FC_6H_4)(SnCl_3)(PMe_2Ph)_2]$	150.0	2527	*c*
trans-$[Pt(SiPh_3)(SnCl_3)(PMe_2Ph)_2]$	146.0	2666	*c*

[a] Complex *trans*-$[PtR(SnCl_3)L_2]$ obtained from *trans*-$[PtRClL_2]$ and $SnCl_2$ in CH_2Cl_2. [b] See Table 1 footnote *c*. [c] See Table 1 footnote *e*.

but it was slightly more soluble in $CHCl_3$ and quite soluble in pyridine, so ^{31}P-$\{^1H\}$ NMR results were obtained using those solvents (Table 4).

The principal product from $SnCl_4$ is a *cis* complex with non-equivalent PPh_3 ligands and is formulated *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$. The ^{31}P-$\{^1H\}$ spectra of this and related $SnCl_3$-containing complexes have been reported recently in a thorough study of systems containing dichloroplatinum complexes and $SnCl_2$ [8]. The parameters reported for *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$ in CH_2Cl_2 at −50° C (for example $^1J(PtP)$ 3083, 3637 Hz) are slightly different from those obtained by us at 25° C (Table 5), but differences of this magnitude can arise from differences in the temperature and concentration of the samples [9]. This was confirmed by recording the spectrum of a solution of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of $SnCl_2$ in CH_2Cl_2 at 25° C; the spectrum was nearly identical to that obtained from the oxidative-addition reaction. The spectra obtained from the $SnCl_4$ and $SnCl_2$ routes also implied the presence of a small amount of a complex with mutually *trans* PPh_3 ligands ($^1J(PtP)$ 2330 Hz). The parameters for the *trans* complex in a CH_2Cl_2 solution of $[PtCl(SnCl_3)(PPh_3)_2]$ at −50° C were not reported [8], but the *trans* complex in our solutions can be assigned the formula *trans*-$[PtCl(SnCl_3)(PPh_3)_2]$ by comparison of $^1J(PtP)$ with that obtained for *trans*-$[PtCl(SnCl_3)\{P(C_6H_4Cl\text{-}p)_3\}_2]$ (2334 Hz) in $CHCl_3$ at −50° C [8]; *trans*-bis(phosphine) complexes containing two $SnCl_3$ ligands have coupling constants $^1J(PtP) < 1900$ Hz [8].

TABLE 4

^{31}P NMR PARAMETERS OF COMPLEXES $[PtX(SnX_3)(PPh_3)_2]$ [a]

X	Isomer (%) [b]	−δ *trans* to Sn(ppm)	$^1J(PtP)$ (Hz)	−δ *cis* to Sn(ppm)	$^1J(PtP)$ (Hz)	$^2J(PP)$ (Hz)
Cl	*cis* 95	113.0	3047	129.7	3662	15
	trans 5	—	—	121.0	2329	—
Br	*cis* 100	121.1	3052	127.0	3716	15
I	*trans* [c] 100	—	—	128.1	2493	—
	trans [d] 100	—	—	127.5	2498	—

[a] From SnX_4 and $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane. [b] See Table 1 footnote *b*. [c] In chloroform. [d] In pyridine.

TABLE 5

^{31}P NMR PARAMETERS OF COMPLEXES OBTAINED BY $SnCl_2$ INSERTION IN SITU [a]

Complex	Isomer (%) [b]	$-\delta$ *trans* to Sn (ppm)	$^1J(PtP)$ (Hz)	δ *cis* to Sn (ppm)	$^1J(PtP)$ (Hz)	$^2J(SnP)$ [c] (Hz)	$^2J(PP)$
$[PtCl(SnCl_3)(PPh_3)_2]$ [d]	*cis* 95	113.0	3050	129.7	3660	*e*	15
	trans 5	—	—	121.0	2330	*e*	—
$[PtCl(SnCl_3)\{P(OPh)_3\}_2]$ [f]	*cis* 80	63.3	4739	67.8	5759	*e*	30
$[Pt(SnCl_3)_2\{P(OPh)_3\}_2]$ [f]	*trans* 20	—	—	44.4	3965	239	—
$[PtCl(SnCl_3)(PEt_3)_2]$ [g]	*trans* 100	—	—	125.9	2073	232	—
$[PtCl(SnCl_3)(PEt_2Ph)_2]$ [h]	*trans* 100	—	—	128.3	2156	*e*	—

[a] At 25°C in dichloromethane; for analogous results at −50°C see ref. 8. [b] Relative abundance (%) of product as determined from the peak heights in the $^{31}P\{^1H\}$ NMR spectra. [c] See Table 1 footnote c. [d] From *cis*-$[PtCl_2(PPh_3)_2]$. [e] See Table 1 footnote c. [f] From *cis*-$[PtCl_2\{P(OPh)_3\}_2]$. [g] From *cis*-$[PtCl_2(PEt_3)_2]$. [h] From *cis*-$[PtCl_2(PEt_2Ph)_2]$.

The products obtained from $[Pt(C_2H_4)(PPh_3)_2]$ and SnX_4 (X = Br, I) gave satisfactory analyses for $[PtX(SnX_3)(PPh_3)_2]$ and the $^{31}P\text{-}\{^1H\}$ NMR spectra show that for X = Br the complex has the *cis* configuration (in CH_2Cl_2) and for X = I the complex is *trans* (in $CHCl_3$ and pyridine).

Satellites due to Sn were not observed in the spectra of the products from $SnBr_4$ or SnI_4, or in the spectrum of *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$ at 25 or −50°C. At the higher temperature this may be due to exchange processes involving dissociation of SnX_2; at −50°C the insolubility of the PPh_3 complexes with $SnCl_3$ ligands presumably prevents their detection, but satellites have been observed at −50°C in spectra of complexes of other phosphines where the solubility is greater [8].

Course of oxidative addition reactions

Combining these observations with our earlier results [3], it is now clear that the pattern of oxidative addition reactions of organotin chlorides to $[Pt(C_2H_4)(PPh_3)_2]$ is as indicated in Scheme 1.

Product *cis*-$[PtR(PPh_3)_2(SnR_{n-1}Cl_{4-n})]$	$SnPh_4$	$(SnMe_4)$[a]
	$SnPh_3Cl$	$SnMe_3Cl$
	$SnPh_2Cl_2$	$SnMe_2Cl_2$
Products *cis*- and *trans*-$[PtCl(PPh_3)_2(SnR_nCl_{3-n})]$	$SnPhCl_3$	$SnMeCl_3$
	$SnCl_4$	

SCHEME 1. Products of reaction of SnR_nCl_{4-n} with $[Pt(C_2H_4)(PPh_3)_2]$.

[a] Reacts only with more active Pt^0 complex $[Pt(PEt_3)_4]$ [3].

For some of the product mixtures small amounts of other complexes were also detected in the $^{31}P\text{-}\{^1H\}$ spectra. For tin compounds containing more than one Sn—Cl bond it was difficult on the small scale of our experiments to avoid some formation of *cis*-$[PtCl_2(PPh_3)_2]$ via hydrolysis of the tin compounds. Also, in the reaction of $SnPhCl_3$, despite repeated distillation of the tin compound, the product mixture always contained some *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$, the product of reaction of the platinum(0) complex with $SnCl_4$. The $SnCl_4$ was presumably formed by the redistribution reaction shown in eq. 4, and significant quantities of the $SnCl_3$ complex arise because the tin compound was used in excess in our experiments and $SnCl_4$ reacts more rapidly than $SnPhCl_3$ with the platinum(0) complex (vide infra).

$$2\,SnPhCl_3 \rightleftharpoons SnPh_2Cl_2 + SnCl_4 \qquad (4)$$

Competition experiments

In order to obtain some information about the relative reactivities of organotin compounds towards $[Pt(C_2H_4)(PPh_3)_2]$ we carried out a number of competition experiments in which equimolar amounts (2.5×10^{-4} mol) of two tin compounds in CH_2Cl_2 were mixed with the platinum complex (2.5×10^{-4} mol) in CH_2Cl_2 and the $^{31}P\text{-}\{^1H\}$ spectrum of the product mixture was recorded after complete reaction of the complex (ca. 30 min). Although the product mixtures contained small amounts of such complexes as $[PtCl(X)(PPh_3)_2]$ (X = Cl, H, Me, Ph), probably because of reactions of the tin complexes with HCl formed by hydrolysis, and repetition of particular experiments showed that the quantitative accuracy was low, analysis of the intensities of the $^{31}P\text{-}\{^1H\}$ lines led to the order of reactivity shown in Scheme 2. The reactivity of the tin compounds

$$(SnMe_4) < SnPh_4, SnMe_3Cl < SnPh_3Cl, \mathrm{SnMe_2Cl_2} < SnPh_2Cl_2,$$

$$\mathrm{SnMeCl_3} < \mathrm{SnPhCl_3} < \mathrm{SnCl_4}$$

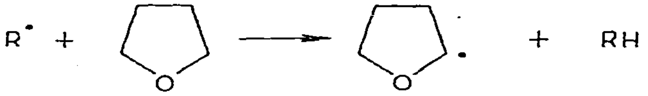
SCHEME 2. Reactivity order towards $[Pt(C_2H_4)(PPh_3)_2]$; compounds in italics react via insertion into Sn—C bonds, and $SnMe_4$ reacts only with the more active platinum(0) complex $[Pt(PEt_3)_4]$ [3].

increases with decreasing n in SnR_nCl_{4-n} for insertion into Sn—C or Sn—Cl bonds. The greater reactivity of Sn—Ph compared with Sn—Me bonds is consistent with the observation that $SnMe_nPh_{4-n}$ (n = 1—3) and $SnMe_nPh_{3-n}Cl$ (n = 1, 2) form products of insertion into Sn—Ph rather than Sn—Me bonds [3].

Comparison of the rates of reaction of $SnPh_2Cl_2$ and $SnPh_2Br_2$ is not possible because of redistribution between Cl and Br which may involve the organotin halides and the product complexes. Thus, when an equimolar mixture of these tin compounds was used, the $^{31}P\text{-}\{^1H\}$ spectrum indicated the formation of the complexes *cis*-$[PtPh(SnPhXY)(PPh_3)_2]$ X, Y = Cl, Cl; Cl, Br; Br, Br) in approximately statistical proportions (1/2/1); the ^{31}P parameters for the complex containing the SnBrPhCl ligand are close to the average of those for the dichloro and dibromo analogues (Table 1).

Mechanisms

The reactions of certain alkyl halides with platinum(0) complexes have been shown to involve production of alkyl radicals by means of spin trapping experiments with t-BuNO and nitrosodurene [10]. In similar experiments using nitrosodurene and reaction mixtures containing $[Pt(C_2H_4)(PPh_3)_2]$ with $SnMe_3Cl$, $SnMe_2Cl_2$ or $SnPh_2Cl_2$ only very weak ESR signals were detected, and these were similar to those obtained from mixtures of nitrosodurene and the products of the oxidative addition reactions. Also, the products of the reactions of $[Pt(C_2H_4)(PPh_3)_2]$ with $SnMe_3Cl$, $SnMe_2Cl_2$ and $SnPh_2Cl_2$ were the same in tetrahydrofuran as in CH_2Cl_2, and there were no indications of the presence of complexes containing the $2\text{-}C_4H_7O$ moiety formed by via radical transfer reactions (eq. 5). However, these experiments do not exclude the pres-



(5)

ence of carbon-centred radicals as intermediates and they would not reveal the presence of tin-centred radicals, should they be produced. At present we have no direct evidence concerning the mechanisms of these reactions, but the changeover from formal Sn—C to Sn—Cl insertion contrasts with the uniform Sn—Cl insertion found in the reactions of $[PtMe_2(bipy)]$ (bipy = 2,2'-bipyridyl) with SnR_nCl_{4-n} (n = 0—3) [11]. The changeover of product form could result

TABLE 6

COMPLEXES PREPARED FROM $[Pt(C_2H_4)(PPh_3)_2]$

Complex	Tin reagent	Solvent	Time (h)	M.p. (°C) (dec)	Yield (%)	Analysis (Found (calcd.)(%))		ν(SnX)(cm^{-1})
						C	H	
cis-$[PtPh(SnPhCl_2)(PPh_3)_2]$	$SnPh_2Cl_2$	PhMe	0.75	156	62	54.3 (54.2)	4.2 (3.8)	321, 309
cis-$[PtPh(SnPhBr_2)(PPh_3)_2]$	$SnPh_2Br_2$	PhMe	0.75	290	59	50.1 (50.0)	4.0 (3.5)	257, 226
$[PtCl(SnMe_2Cl)(PPh_3)_2]$	$SnMe_2Cl_2$	PhMe	5	182	55	48.8 (48.6)	4.1 (3.9)	325, 300, 288
$[PtCl(Sn\text{-}n\text{-}Bu_2Cl)(PPh_3)_2]$	$Sn\text{-}n\text{-}Bu_2Cl_2$	PhMe	5	200	63	52.0 (51.6)	4.5 (4.9)	332, 297, 282
$[PtCl(SnMeCl_2)(PPh_3)_2]$	$SnMeCl_3$	PhMe	5	238	58	45.2 (46.3)	3.8 (3.5)	329, 318, 299
cis-$[PtBr(SnBr_3)(PPh_3)_2$	$SnBr_4$	C_6H_6	0.1	228	80	37.7 (37.3)	2.8 (2.6)	248, 232
trans-$[PtI(SnI_3)(PPh_3)_2]$	SnI_4	C_6H_6	0.1	220	82	32.5 (32.1)	2.1 (2.2)	200

from different steps following a single initial process (such as transfer of an electron from Pt to the Sn compound), or from different initial processes. There are many possibilities involving three-centre, radical, polar and Sn^{II} intermediates and it is hoped that some definite conclusions may be reached as a consequence of work currently in progress.

Experimental

General

All the solvents were dry and oxygen-free, and reactions were carried out under nitrogen. The ^{31}P-$\{^1H\}$ NMR spectra were recorded at 40.48 MHz on a JEOL PFT100 instrument. Solutions in dichloromethane in 8-mm outside-diameter tubes were used. The field was locked to the ^2H resonance of a solution of trimethyl phosphite in deuteriobenzene which served as external reference; positive values of the chemical shift are to high frequency of the reference. Proportions of complexes were inferred directly from the relative peak heights in the ^{31}P-$\{^1H\}$ NMR spectra. The ^{13}C-$\{^1H\}$ NMR spectra were recorded on the same instrument at 25.15 MHz using dichloromethane as solvent and tetramethylsilane or chloroform as internal standard. The ESR spectra were obtained with a Varian E-line EPR spectrometer. The tin compounds $SnCl_4$, $SnBr_4$, SnI_4 were obtained from commerical sources; $SnPh_4$, $SnPh_3Cl$ $SnMe_4$ and $SnMe_3Cl$ were prepared by published methods; $SnMe_2Cl_2$ was a gift from Chugoku Marine Paints Co., and $Sn(CH_2CH_2CO_2Me)_2Cl_2$, $Sn(CH_2CH_2CO_2Me)Cl_3$, $Sn(CH_2CH_2CO_2Me)Br_3$, and $Sn(CH_2CH_2CO_2Et)Cl_3$ were a gift from Akzo Chemicals Ltd,; other tin compounds were available in this laboratory. The complex $[Pt(C_2H_4)(PPh_3)_2]$ was prepared by a published method [12].

Complexes

A solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.0050 mol) in toluene or benzene (5 cm^3) was treated with a solution of a tin compound (0.0053 mol) in the same solvent (5 cm^3) and the mixture stirred. After completion of the reaction the precipitate was washed with 3×5 cm^3 of hexane and the products from the organotin compounds were recrystallised from dichloromethane/hexane. Details of the compounds obtained in this way are given in Table 6.

Complexes prepared in situ

The following procedure was employed for the preparation of complexes for ^{31}P-$\{^1H\}$ NMR spectroscopy. The complex $[Pt(C_2H_4)(PPh_3)_2]$ (ca. 0.05 g) was dissolved in dichloromethane (1 cm^3) in an 8 mm NMR tube. An excess of tin compound was added and the mixture was shaken vigorously for ca. 5 min. during which period evolution of ethylene occurred. The mixture was then put aside for ca. 30 min. before being placed in the NMR probe.

Competition experiments

The competition experiments were carried out in a manner similar to the preparations in situ described above, but 2.4×10^{-4} mol of each of the complex $[Pt(C_2H_4)(PPh_3)_2]$ and the two tin compounds were used.

ESR experiments

The complex $[Pt(C_2H_4)(PPh_3)_2]$ was treated with tin compounds in dichloromethane in the presence of nitrosodurene under conditions that gave strong signals for the radicals 2,3,5,6-$Me_4C_6HN(O)R$ when alkyl halides RC(MeI, EtBr, n-PrBr, n-BuBr, $PhCH_2Br$) were used in place of the tin compounds [13].

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