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Reactions of Organotin(IV) Compounds with Platinum Complexes. Part IV*: Mechanisms of Reactions between SnR_3Cl Compounds and Pt(0) Complexes

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The reaction of SnR_3Cl (R = alkyl) with platinum(0) complexes in dichloromethane is found to initiate *via* insertion of Pt(0) into Sn-R bonds forming complexes containing the $Pt(R)(SnR_2Cl)$ species. The mechanism of formation of Pt-R bonds is believed to proceed *via* two intermediates containing Pt(II) and Pt(IV) complexes, respectively. Several reactions between SnR_3Cl and $[Pt(C_2H_4)(PPh_3)_2]$ alone and between SnR_3Cl and $[Pt(C_2H_4)(PPh_3)_2]$ in the presence of SnR'_4 compounds, have been carried out to trace the intermediates by using ^{31}P-NMR spectroscopy. The ^{119}Sn-NMR spectra of some of the so formed complexes and other related complexes have been recorded.

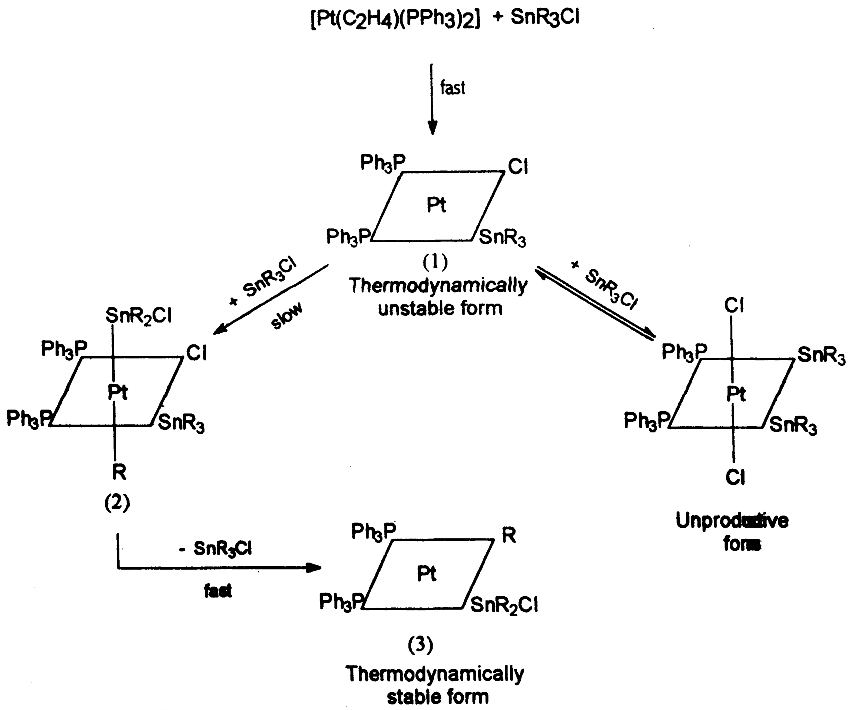
Key Words: SnR_3Cl Compounds, Pt(0) complexes, Oxidative-addition, Mechanisms.

INTRODUCTION

Earlier workers have reported the reaction of SnR_3Cl (R = alkyl or aryl) with $[Pt(C_2H_4)(PPh_3)_2]$ in CH_2Cl_2 proceeds *via* insertion of Pt(0) into Sn-R bonds to give the complexes *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$[2] and not into Sn—Cl bonds to give $[PtCl(SnR_3)(PPh_3)_2]$ as it was believed before[3]. Later we suggested[4] that formation of *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$ is initiated through two intermediates, the first one being the thermodynamically unstable complex, *cis*-$[Pt^{(II)}Cl(SnR_3)(PPh_3)_2]$ **(1),** which ultimately reacts with a further SnR_3Cl molecule to give the second intermediate, $[Pt^{(IV)}R(Cl)(SnR_3)(SnR_2Cl)(PPh_3)^2]$ **(2)** and this in turn loses SnR_3Cl to give the thermodynamically stable complex *cis*-$[Pt^{(II)}R(SnR_2Cl)(PPh_3)]$ **(3) (Scheme 1).** The intermediate complex **(1)** has been obtained by treatment of $[PtCl(SnR_3)(COD)]$ {from $[Pt(COD)_2]$ and SnR_3Cl; COD = 1,5-cyclooctadiene} with PPh_3 at –70°C in CH_2Cl_2[5]. Complex **(1)** slowly forms the *trans-* isomer and the mixture of isomers is rapidly converted into complex **(3)** in the presence of SnR_3Cl at temperatures above –30°C.

*For Part(III), see ref. 1.

In the present study, we have investigated several reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and SnR_3Cl alone and in the presence of SnR'_4 ($R = R'$ or $R \neq R'$ = Me, Et, Bu) in order to trace both the intermediates suggested in the mechanism of the reaction.



Scheme 1

EXPERIMENTAL

All the solvents were dry and oxygen-free, and reactions were carried out under nitrogen or dry argon. The ^{31}P-$\{^1H\}$ NMR spectra were recorded on a Jeol PFT-100 spectrometer at 40.486 MHz (usually in CH_2Cl_2) using trimethylphosphite (TMP) or trimethylphosphate (TMPO) as external references. The ^{119}Sn-$\{^1H\}$NMR spectra were performed at City of London Polytechnic, London, UK, on a Jeol FX-90Q spectrometer (with multinuclear probe) at 33.34 MHz using CH_2Cl_2 as solvent.

Starting Materials

K_2PtCl_4 and the organotin(IV) compounds, $SnMe_3Cl$, $SnEt_3Cl$, $SnBu_3Cl$, $SnMe_4$, $SnEt_4$, $SnPr^i_4$ and $SnBu_4$ were either obtained commercially or prepared by standard methods. The platinum complexes used in this study were prepared by standard methods, $[Pt(C_2H_4)(PPh_3)_2]$[5], *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$ (R = Me, Bu) and *cis*- and *trans*-$[PtCl(SnMe_2Cl)(PPh_3)_2]$[6], $[PtCl(SnMe_3)(DPPE)]$ and $[PtCl(SnMe_2Cl)(DPPE)]$[7].

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with a mixture of SnR_3Cl and SnR'_2

In a typical procedure, the complex $[Pt(C_2H_4)(PPh_3)_2]$ (0.15g, 0.2 mmol) was dissolved in CH_2Cl_2 (5 mL) and a mixture of SnR_3Cl (R = Bu) (0.033g, 0.1 mmol) and SnR'_4 (R′ = Me) (0.18g, 1.0 mmol) was added. The solution was allowed to stand for *ca.* 90 min at room temperature and then reduced in volume for recording the ^{31}P-NMR spectrum.

The corresponding reactions were carried out for R = Me, Et, Bu and R′ = Me, Pr^i, Bu.

A similar procedure was carried out for the reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and a mixture of SnR_2Cl_2 (R = Me, Bu) and $SnMe_4$.

Reaction of *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ with $SnMe_4$ in the presence of $[Pt(C_2H_4)(PPh_3)_2]$

The complex *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ {prepared from the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnBu_3Cl$}[6] (0.14 g, 0.1 mmol), together with the complex $[Pt(C_2H_4)(PPh_3)_2]$ (0.075 g, 0.1 mmol) were dissolved in CH_2Cl_2 (5 mL) and a large excess of $SnMe_4$ was added. After *ca.* 90 min at room temperature the volume was reduced for the recording of the ^{31}P-NMR spectrum.

A similar procedure was carried out for the reaction between *cis-* and *trans-* $[PtCl(SnMe_2Cl)(PPh_3)_2]$ and $SnMe_4$ in the presence of $[Pt(C_2H_4)(PPh_3)_2]$.

Reaction of $[PtCl(SnMe_3)(DPPE)]$ with $SnMe_3Cl$

A solution of the complex $[PtCl(SnMe_3)(DPPE)]$[7] (0.1 g, 0.13 mmol) in CH_2Cl_2 (0.7 mL) was placed into an NMR tube and $SnMe_3Cl$ (0.06 g, 0.3 mmol) was added at ambient temperature. The yellow solution was allowed to stand for *ca.* 2 h and the ^{31}P-NMR spectrum was recorded.

A similar sample was prepared in CD_2Cl_2 for recording of the ^{1}H-NMR spectrum.

RESULTS AND DISCUSSION

It was originally reported that the triorganotin halides, *i.e.*, $SnMe_3Cl$ were added oxidatively to platinum(0) complexes by insertion into the Sn-Cl bonds[3]. However, earlier workers[2] showed this was incorrect, and that the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_3Cl$ in fact proceeded by insertion into Sn-Me bonds. No firm mechanism for this reaction was suggested at the time, but latter we suggested a mechanism involving platinum(IV) intermediates **(Scheme 1)**. Above *ca.* 10°C, the complex $[Pt(C_2H_4)(PPh_3)_2]$ reacts with SnR_3Cl to give *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$ **(3)** [R = Me, ^1J(PtP) 2474 Hz (P *trans-* to Sn) and 2092 Hz (P *trans-* to Me)], but we suggested that the initial product is *cis*-$[PtCl(SnMe_3)(PPh_3)_2]$ **(1)**, which is rapidly converted into *cis*-$[PtR(SnR_2Cl)(PPh_3)_2]$ **(3)** by insertion of **(1)** into the Sn-R bond of SnR_3Cl. The presumably faster reaction of **(1)** with the Sn-Cl bond of SnR_3Cl is the unproductive complex $[PtCl_2(SnR_3)_2(PPh_3)_2]$ and neither **(1)** nor the platinum(IV) intermediate **(2)** are detectable in reaction mixture by ^{31}P-NMR spectroscopy.

It should be noted that low temperature (–70°C) reaction between

$[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_3Cl$ in CH_2Cl_2 was carried out in order to trap the intermediate **(1)** but the ^{31}P-NMR spectrum showed that no reaction had occurred. A number of spectra were recorded at 10°C intervals up to 10°C, and at this temperature, a very small amount of an additional species appeared in the spectrum. At room temperature the peaks of this product had increased and the values of δ and J were identical to those of *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$, no signals attributable to the intermediate *cis*-$[PtCl(SnMe_3)(PPh_3)_2]$ could be detected.

Attempts to trap the intermediate *cis*-$[PtCl(SnR_3)(PPh_3)_2]$ (1)

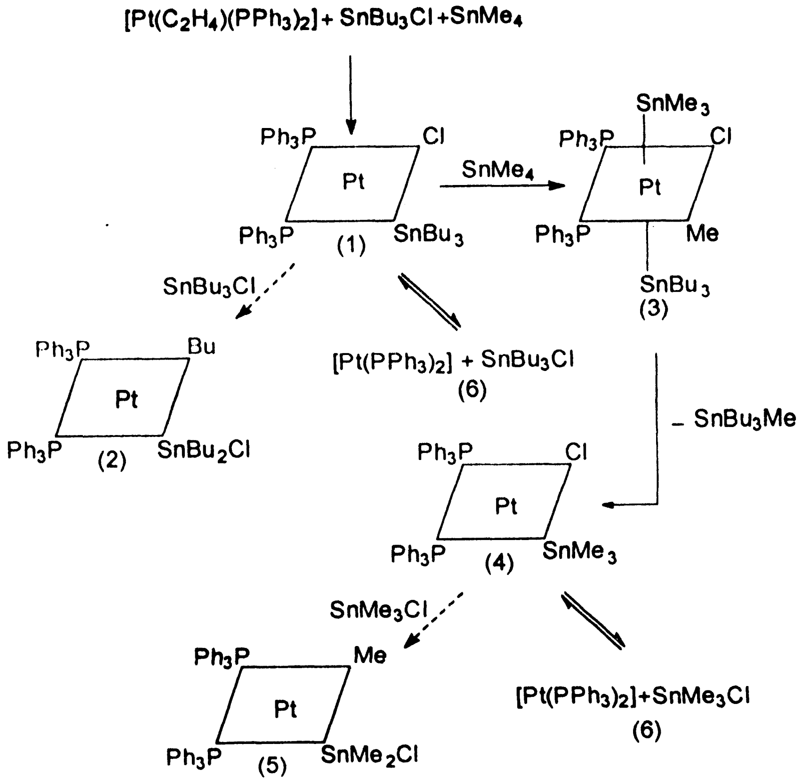
Initially the experiments below were carried out with the objective of trapping the proposed intermediate *cis*-$[PtCl(SnR_3)(PPh_3)_2]$ in the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and SnR_3Cl . Subsequently such a species, with R = Me, was prepared by another route from the reaction between $[PtCl(SnMe_3)(COD)]$ and PPh_3 in CH_2Cl at –70°C [$^1J(PtP)$ 1946 Hz (P *trans*- to Sn) and 4516 Hz (P *trans*- to Cl)][7]. A large number of reactions were studied *in situ* by ^{31}P-NMR spectroscopy as described below.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with SnR_3Cl in the presence of SnR'_4:

The ^{31}P-NMR spectrum showed that there was no reaction between $SnMe_4$ and $[Pt(C_2H_4)(PPh_3)_2]$ or *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ {prepared from the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnBu_3Cl$}[2] in CH_2Cl_2 or benzene during 48 h at room temperature. However, a mixture of $SnBu_3Cl$ (0.1 mmol) and $SnMe_4$ (1.0 mmol) reacted with $[Pt(C_2H_4)(PPh_3)_2]$ (0.2 mmol) in CH_2Cl_2 during *ca.* 1.5 h at room temperature to give (in addition to unchanged platinum starting materials), a mixture of two *cis*-complexes assigned to be *cis*-$[PtBu(SnBu_2Cl)(PPh_3)]$ (13.5% proportion) and *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ (35% proportion) and the decomposition product *cis*-$[PtCl_2(PPh_3)_2)]$ (8.5% proportion).

We thought that this reaction involved initial insertion of platinum(0) into the Sn-Cl bond of $SnBu_3Cl$ **(Scheme-2)** to give *cis*-$[PtCl(SnBu_3)(PPh_3)_2]$ **(1)**, which the latter was then either following the course shown in **Scheme-1** to give *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ **(2)**, or reacting with $SnMe_4$ to give the platinum(IV) intermediate **(3)**. Complex **(3)** would then lose $SnBu_3Me$ to give *cis*-$[PtCl(SnMe_3)(PPh_3)_2]$ **(4)** which would enter the sequence shown in Scheme 1 to give *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ **(5)**. We found in separate experiments that complex (4) readily loses $SnMe_3Cl$ in the presence of PPh_3 to give $[Pt(PPh_3)_3]$.

As mentioned above, neither *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ nor $[Pt(C_2H_4)(PPh_3)_2]$ reacted separately with $SnMe_4$, but the ^{31}P-NMR spectrum of a mixture obtained from the reaction between cis-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ (0.1 mmol){prepared from the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ and $SnBu_3Cl$ in equimolar ratio and isolated as described in ref. 2}, $[Pt(C_2H_4)(PPh_3)_2]$ (0.1 mmol), and excess of $SnMe_4$ in CH_2Cl_2 or benzene at room temperature for 1.5 h, revealed (in addition to unchanged platinum(0) starting material) the presence of two *cis*-complexes, **(2)** and **(5)** **(Scheme -)** in 14.5 and 37% proportions, respectively and the decomposition product *cis*-$[PtCl_2(PPh_3)_2]$.

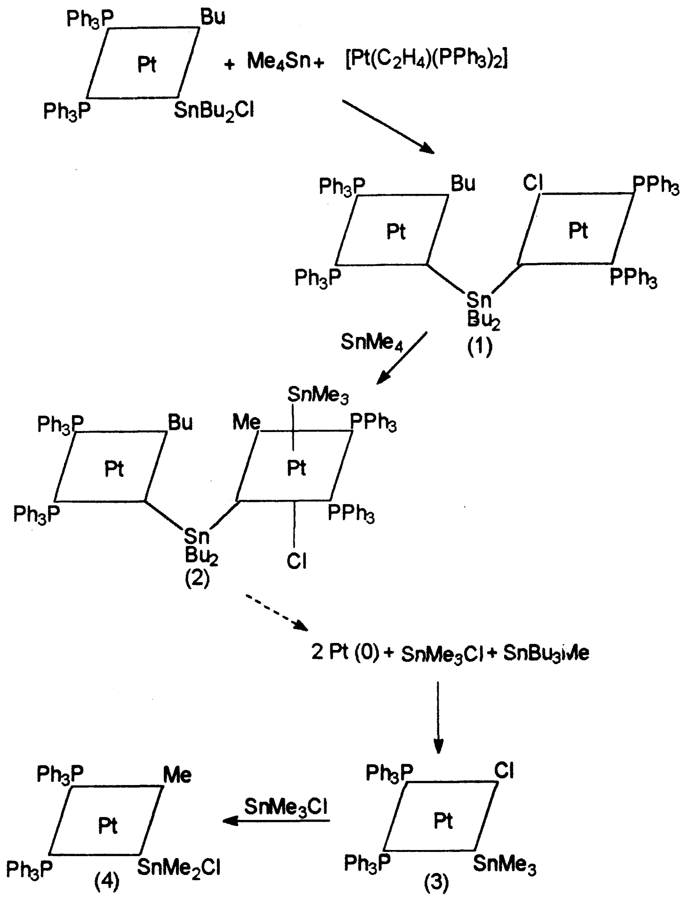


Scheme 2

We thought that this reaction might have involved initial insertion of platinum(0) into the Sn-Cl bond of *cis*-[PtBu($SnBu_2Cl$)(PPh_3)$_2$] to give complex **(1)** **(Scheme 3).**

Cis-addition of $SnMe_4$ to complex **(1)** would then probably occur in the part of the molecule containing the Pt-Cl species, which would be the more reactive, to give complex **(2)**. However, complex **(2)** would rapidly lose both $SnMe_3Cl$ and $SnBu_3Me$ to give [Pt(PPh_3)$_2$], which would again react with $SnMe_3Cl$ by the route shown in **Scheme-1**, to form the thermodynamically stable complex **(4)** **(Scheme-3)**, *viz, cis*-[PtMe($SnMe_2Cl$)(PPh_3)$_2$] at room temperature. However, since $SnMe_4$ in fact reacts with *cis*-[PtBu($SnBu_2Cl$)(PPh_3)$_2$] in the presence of [Pt(C_2H_4)(PPh_3)$_2$], the earlier reaction between [Pt(C_2H_4)(PPh_3)$_2$], $SnBu_3Cl$ and $SnMe_4$ cannot necessarily be attributed to the intermediate *cis*-[PtCl($SnBu_3$)(PPh_3)$_2$] and the very similar product distribution from the two experiments indicates a common origin for the mechanism depicted in **Scheme-3.**

Similar results were obtained when the reaction was carried out using [Pt(C_2H_4)(PPh_3)$_2$] with $SnEt_3Cl$ and $SnMe_4$ in one experiment and with $SnBu_3Cl$ and $SnEt_4$ in another experiment.



Scheme-3

When a similar procedure was carried out for the reaction between $[Pt(C_2H_4)(PPh_3)_2]$, $SnBu_3Cl$ and $SnPr^i_4$ in CH_2Cl_2 for 2 h, the $^{31}P-\{^1H\}$ NMR spectrum revealed (in addtion to the unreacted platinum starting material) the presence of *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$ and a small amount of *cis*-$[PtCl_2(PPh_3)_2]$, and none of the expected product *cis*-$[PtPr^i(SnPr^i_2Cl)(PPh_3)_2]$. It seems that $SnPr^i_4$ does not enter into the reaction.

Similar results were obtained from a mixture of $[Pt(C_2H_2)(PPh_3)_2]$, $SnMe_3Cl$, and an excess of $SnBu_4$ in CH_2Cl_2. After 2 h the ^{31}P-NMR spectrum showed (in addition to the unreacted platinum starting material) the presence of *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ as the major component and a small amount of *cis*-$[PtCl_2(PPh_3)_2]$, and none of the expected product *cis*-$[PtBu(SnBu_2Cl)(PPh_3)_2]$. This shows that like $SnPr^i_4$, $SnBu_4$ does not enter the reaction.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with SnR_2Cl_2 in the presence of $SnMe_4$

We showed above that no reaction occurred between $[Pt(C_2H_4)(PPh_3)_2]$ and

$SnMe_4$. ^{31}P-NMR spectroscopy showed that there was no reaction between (mixed) *cis-* and *trans-* $[PtCl(SnR_2Cl)(PPh_3)_2]$ {prepared as described in ref. 6 from the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with SnR_2Cl_2 (R = Me, Bu)} and $SnMe_4$ in CH_2Cl_2 at room temperature even after 4 h.

However, when a mixture of $SnMe_2Cl_2$ (0.1 mmol) and $SnMe_4$ (1.0 mmol) was added to $[Pt(C_2H_4)(PPh_3)_2]$ (0.2 mmol) in CH_2Cl_2 and the solution was kept at room temperature for 3 h, the ^{31}P-NMR spectrum revealed (in addition to the unchanged platinum starting material) the presence of a mixture of complexes, *cis-* and *trans-* $[PtCl(SnMe_2Cl)(PPh_3)_2]$ (19 and 33% proportions, respectively), *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ (16.5 proportion %) and the decomposition product *cis*-$[PtCl_2(PPh_3)_2]$ (10% proportion). These results also support the mechanism outlined in **Scheme 3**; *i.e.*, it can be assumed that $[Pt(C_2H_4)(PPh_3)_2)]$ reacted initially with $SnMe_2Cl_2$ to give *cis-* and *trans-* $[PtCl(SnMe_2Cl)(PPh_3)_2)]$, and the latter then reacted with $SnMe_4$ in the presence of $[Pt(C_2H_4)(PPh_3)_2]$ to give the complex *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$. This was shown clearly to be the case by the following experiment. A mixture of *cis-* and *trans-* $[PtCl(SnMe_2Cl)(PPh_3)_2]$ {prepared as in ref. 6 from the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $SnMe_2Cl_2$} (0.1 mmol), $SnMe_4$ (0.1 mmol) in CH_2Cl_2 was set aside for 3 h. The ^{31}P-NMR spectrum revealed (in addition to the unchanged platinum starting material) the presence of the same complex as mentioned above and in almost the same proportions.

It is evident that the amount of unreacted $[Pt(C_2H_4)(PPh_3)_2]$ is less in the case of $SnMe_2Cl_2$ than in the case of SnR_3Cl as can be seen from the proportion of the unreacted $[Pt(C_2H_4)(PPh_3)_2]$, suggesting that the extent of reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and $SnMe_2Cl_2$ (as inferred from the relative intensities in the ^{31}P-NMR spectrum of the Pt(0) complex and the products) is somewhat larger than could be obtained from the known amounts of Pt(0) + SnR_2Cl_2 used. This might be a misleading observation, since the intensities of the ^{31}P signals obtained by ^{31}P-NMR spectroscopy depend on the relaxation times and other factors and not simply on the concentration of the complex.

Additional information was provided by three experiments below:

(A) When a solution of $[Pt(C_2H_4)(PPh_3)_2]$ in CH_2Cl_2 was kept for 48 h at room temperature, the ^{31}P-NMR spectrum showed that no decomposition to *cis*-$[PtCl_2(PPh_3)_2]$ had occurred, and no other product was detected.

(B) The ^{31}P-MNR spectrum of the mixture obtained from the reaction between $[Pt(C_2H_4)(PPh_3)_2]$ (0.2 mmol) and a mixture of $SnBu_2Cl_2$ (0.1 mmol) and $SnMe_4$ (1.0 mmol) in CH_2Cl_2 (with complete exclusion of air and moisture), revealed after *ca.* 3 h (in addition to the unreacted platinum starting material in 39% proportion), the presence of the complexes shown in the following equation .

$$\underset{0.2\text{ mmol}}{[Pt(C_2H_4)(PPh_3)_2]} + \underset{0.1\text{ mol}}{SnBu_2Cl_2} + \underset{1.0\text{ mmol}}{SnMe_4} \rightarrow \underset{\mathbf{I}\ (11\%)}{cis\text{-}[PtMe(SnMe_2Cl)(PPh_3)_2]}$$

$$\underset{\mathbf{II}\ (cis\text{-},\ 29\%,\ trans\text{-},\ 13.5\%)}{cis\text{- and } trans\text{-}[PtCl(SnBu_2Cl)(PPh_3)_2]} + \underset{\mathbf{III}\ (7\%)}{cis\text{-}[PtCl_2(PPh_3)_2]}$$

When the mixture was set aside for a further 15 h, the ^{31}P-NMR spectrum showed that complex **(II)** had been totally converted into complexes **(I)** and **(III)** [as shown from the observed proportion **(I)**, 34; **(II)**, 0; **(III)**, 32%] and the proportion of [$Pt(C_2H_4)(PPh_3)_2$] had fallen by only 5%. Since CH_2Cl_2 had little effect on [$Pt(C_2H_4)(PPh_3)_2$], the decomposition product *cis*- [$PtCl_2(PPh_3)_2$] must therefore have been produced from the decomposition of complex **(II)** and not from [$Pt(C_2H_4)(PPh_3)_2$].

(C) When solutions of the mixed *cis*- and *trans*-[$PtCl(SnBu_2Cl)(PPh_3)_2$] complexes in CH_2Cl_2, with or without the presence of [$Pt(C_2H_4)(PPh_3)_2$], were kept for 15 h at room temperature, the ^{31}P-NMR spectra showed that no changes had occurred.

It is concluded from these observations that the complex [$Pt(C_2H_4)(PPh_3)_2$] was not affected by the solvent, by the complex [$PtCl(SnBu_2Cl)(PPh_3)_2$], or by $SnMe_4$ on its own, but that reaction took place in a mixture of all three reagents to give the complex *cis*-[$PtMe(SnMe_2Cl)(PPh_3)_2$] and a small amount of the decomposition product *cis*-[$PtCl_2(PPh_3)_2$]. This is good support for the mechanism outlined in **Scheme 3** above.

Reaction between [$PtCl(SnMe_3)(DPPE)$] and $SnMe_3Cl$

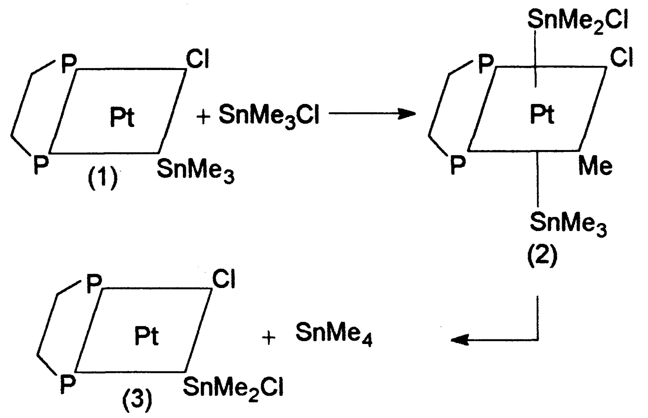
In order to prevent the possiblility of *cis*- and *trans*- isomerization, we used the chelating ligand 1,2-bis(diphenylphosphino) ethane (DPPE) in the following reactions.

The reaction of [$PtCl(SnMe_3)(DPPE)$] with $SnMe_3Cl$ was carried out in CH_2Cl_2 at room temperature in order to compare the results with those obtained earlier from the reaction of $SnMe_3Cl$ with the corresponding PPh_3 complex.

Thus the complex [$PtCl(SnMe_3)(DPPE)$], prepared as described in our previous work[7], was dissolved in CH_2Cl_2 at room temperature and $SnMe_3Cl$ was added (see Experimental). The solution was set aside for *ca.* 2 h; then its ^{31}P-NMR spectrum was recorded; this revealed the presence of [$PtCl(SnMe_2Cl)(DPPE)$ formed in approximately 100% yield.

The ^{1}H-NMR spectrum was also recorded for the mixture obtained from the reaction of [$PtCl(SnMe_3)(DPPE)$] and a slight excess of $SnMe_3Cl$ in CD_2Cl_2 at room temperature; the ^{1}H NMR spectrum was recorded after *ca.* 15 min and showed a resonance at δ 0.07 ppm, assigned to the protons of $SnMe_4$. The assignment was confirmed by addition of $SnMe_4$ which gave no new signal. The spectrum also showed resonances for PtSn-Me which indicated the presence of starting material [$PtCl(SnMe_3)(DPPE)$] and the product [$PtCl(SnMe_2Cl)(DPPE)$, as well as free $SnMe_3Cl$. No resonance from the protons of free $SnMe_2Cl_2$ was observed, which means that the complex [$PtCl(SnMe_3)$ (DPPE) does not behaves as a catalyst for the disproportionation of $SnMe_3Cl$ into $SnMe_2Cl_2$ and $SnMe_4$. The course of the reaction is represented by **Scheme-4.** The product must clearly be derived from a platinum(IV) complex containing two moles of $SnMe_3Cl$.

The reaction of complex **(1) (Scheme-4)** probably proceeded *via* its insertion into the Sn-Me bond of $SnMe_3Cl$ to give the (undetected) platinum(IV) intermediate **(2)**. The latter, which contains two moles of $SnMe_3Cl$, for unknown reason eliminates $SnMe_4$ rather than $SnMe_3Cl$ (as suggested for the corresponding PPh_3 complex in the machanism shown in **Scheme-1** above).



Scheme-4

TABLE-1
$^{119}Sn-\{^1H\}$ NMR DATA, δ (ppm) AND J(Hz) FOR COMPLEXES CONTAINING Pt-Sn BONDS

Complex[a]	δ	$^1J(^{195}Pt-^{119}Sn)$	$^2J(^{119}Sn-^{31}P)$[b]	
			Sn *trans*- to P	Sn *cis*- to P
cis-$[PtCl(SnMe_2Cl)(PPh_3)_2]$	119	Obscured	2264 (2265)	70 (59)
trans-$[PtCl(SnMe_2Cl)(PPh_3)_2]$	43.7	14783	—	—
cis-$[PtMe(SnMe_2Cl)(PPh_3)_2]$	190	13831	2276 (2274)	177 (175)
cis-$[PtPh(SnPhCl_2)(PPh_3)_2]$	56.4	16881	2966 (2961)	195 (193)
cis-$[PtPh(SnPh_2Cl)(PPh_3)_2]$	33	14081	2393 (2400)	147 (146)
cis-$[PtPh(SnPh_3)(PPh_3)_2]$	–104.7	Obscured	1935 (1938)	165 (149)
$[Pt(SnMe_2)(DPPE)]$	–21.2	Obscured	1556 (1553)	140 (141)

[a]For the ^{31}P-NMR data of these complexes and other related ones, see refs. 2, 6, 7.
[b]Numbers in parentheses were obtained from ^{31}P-NMR spectra and are listed here for comparisons.

Although this reaction did not give the expected product $[PtMe(SnMe_2Cl)(DPPE)]$, it still offers very good support for the mechamism in **Scheme-1**, because:

1. the reaction proceeded *via* insertion of platinum(II) complexes into the Sn-Me bonds, as suggested for the mechanism in **Scheme-1.**
2. The reaction must involve a platinum(IV) intermediate, since the formation of $[PtCl(SnMe_2Cl)(DPPE)]$ could not be otherwise explained.

The reaction of $[PtCl(SnMe_3)(DPPE)]$ with $SnMe_3Cl$ was shown as follows to be irreversible. The complex $[PtCl(SnMe_2Cl)(DPPE)]$ was prepared and isolated[7]. The ^{31}P-NMR spectrum of a mixture obtained from the reaction between $[PtCl(SnMe_2Cl)(DPPE)]$ and a large excess of $SnMe_4$ in CH_2Cl_2 at room temperature for 2 h revealed the presence of the platinum starting material only. The reaction was repeated with benzene as solvent instead of CH_2Cl_2; the solution was kept at 50°C for 2 days then the solvent was removed and the residual yellowish solid was dissolved in CH_2Cl_2. The ^{31}P-NMR spectrum of the solution revealed (in addition to the platinum starting material) the presence of two complexes having the parameters δ –98.5 ppm, $^{1}J(PtP)$3623 Hz (29% proportion), identified as $[PtCl_2(DPPE)]$[8] and δ –96.2 ppm, $^{1}J(PtP)$ 1736 Hz; δ –97.0 ppm, $^{1}J(PtP)$ 4214 Hz (35% proportion) identified as [PtMe(Cl)(DPPE)][9]; the complex $[PtCl(SnMe_3)(DPPE)]$ was not detected.

Furthermore, in another experiment using Pt(0) with different phosphine we showed[10] that the reaction between $[Pt(PCyc_3)_2]$ and $SnMe_3Cl$ forms *trans*-$[PtCl(SnMe_3)(PCyc_3)_2]$. The latter does not go further to give $[PtMe(SnMe_2Cl)(PCyc_3)_2]$ either because the former does not add another molecule of $SnMe_3Cl$ to give Pt(IV) intermediate (**Scheme-1**) or the intermediate Pt(IV) cannot be formed at all because of the steric hindrance of the cyclohexyl groups.

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