Reactions of Organotin (IV) Compounds with Platinum Complexes Part (I): Oxidative-Addition Reactions of SnR_xCl_{4-x} with $[Pt(PR_3')_n]$, R' = Et, n = 3 or 4 and R' = Cyc, n = 2

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The complex $[Pt(PEt_3)_n]$ (n = 3 or 4) reacts oxidatively with SnR_2Cl_2 (R = Me, Et) to give *trans*-$[PtCl(SnR_2Cl)(PEt_3)_2]$ which may also be obtained by treatment of $[Pt(C_2H_4)(PPh_3)_2]$ and SnR_2Cl_2 followed by addition of two molar equivalents of PEt_3. The corresponding reaction of $SnPh_2Cl_2$ likewise gives the product of insertion of Pt(0) into Sn-Cl bonds when the reaction was carried out at –30°C, but at room temperature the product of insertion into the Sn-Ph bond is obtained. Tin compounds SnR_3Cl (R = Me, Ph) give product of insertion into Sn-R bonds at room temperature, but only $SnMe_3Cl$ gives product of insertion into Sn-Cl bonds at –30°C. The compounds $SnPh_4$ and $SnPh_3Me$ undergo insertion into Sn-Ph bonds to form both the *cis*- and *trans*- isomers. The dinuclear tin compound Sn_2Ph_6 reacts with $[Pt(PEt_3)_4]$ to give the complexes *trans*-$[Pt(SnPh_3)_2(PEt_3)_2]$ and *cis*- and *trans*-$[PtPh(SnPh_3)(PEt_3)_2]$, while its reaction with $[Pt(C_2H_4)(PPh_3)_2]$ followed by addition of an equimolar quantity of PEt_3 gives *cis*- and *trans*-$[PtPh(Sn_2Ph_5)(PEt_3)_2]$ along with the breakdown products *cis*- and *trans*-$[PtPh(SnPh_3)(PEt_3)_2]$. Similar observations were made for the reaction of $[Pt(PCyc_3)_2]$ with SnR_2Cl_2 (R = Me, Et, Bu, Ph) to give *trans*-$[PtCl(SnR_2Cl)(PCyc_3)_2]$, with SnR_3Cl (R = Me, Bu, Cl) to give *trans*-$[PtCl(SnR_3)(PCyc_3)_2]$, and with $SnPh_3Cl$ to give *cis*- and *trans*-$[PtPh(SnPh_2Cl)(PCyc_3)_2]$. The reactions of the lead compounds PbR_3Cl (R = Me, Ph) with $[Pt(PCyc_3)_2]$ were found to proceed analogously. The compound $PbMe_3Cl$ gives the product of insertion into Pb-Cl bonds whereas $PbPh_3Cl$ gives product of insertion into Pb-Ph bonds as SnR_3Cl compounds do. The complexes and their decomposition products were identified by ^{31}P NMR spectroscopy.

INTRODUCTION

Oxidative-addition reactions of organotin(IV) compounds with platinum(0) complexes containing phosphine ligands have been described by several research groups[1, 2]. Eaborn *et al.*[3, 4] re-examined all the previous work and studied the structures of the products in detail, mainly by ^1H and ^{31}P NMR spectroscopy, using the more convenient platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$. They showed

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that the products formed depend markedly on the nature of the organotin compound, e.g., SnR_4 and SnR_3Cl (R = alkyl or aryl) undergo insertion of Pt into Sn-R bonds while SnR_2Cl_2 (R = alkyl) and $SnRCl_3$ (R = alkyl or aryl) and $Sn_2R_2Cl_2$ (R = aryl) undergo insertion of Pt into Sn-Cl bonds. Lappert et al.[5, 6] had previously observed that in reaction of $SnMe_3R$ (R = $F_2C=CF_2$, PhC•CPh) with $[Pt(PPh_3)_4]$ insertion of Pt into the Sn-R bond occurred. Similar observations were found by Cotton et al.[7].

In a short communication, we[8] discussed the reaction mechanisms of the oxidative-addition of $SnMe_3Cl$ with Pt(0) complexes, in which insertion of Pt into Sn-Cl first occurs, to give the rather unstable complex cis- $[PtCl(SnMe_3)PPh_3)_2]$, the latter then being converted into the thermodynamically more stable complex cis-$[PtMe(SnMe_2Cl)(PPh_3)_2]$, via an unidentified platinum(IV) complex.*

Oxidative-addition reactions of organotin(IV) compounds with Pt(0) complexes containing phosphine ligands other than PPh_3, i.e., PEt_3 and $PCyc_3$ (Cyc = cyclohexyl) have been relatively little studied because of the high sensitivity of $[Pt(PEt_3)_n]$ (n = 3 or 4) and $[Pt(PCyc_3)_2]$ towards air and mositure. We decided to investigate products formed in the reactions of SnR_xCl_{4-x} with $[Pt(PR_3')_n]$, R′ = Et, n = 3 or 4 and R′ = Cyc, n = 2, which to the best of our knowledge have not been previously studied[9, 10]

EXPERIMENTAL

All the solvents were dry and oxygen-free, and reactions were carried out under dry nitrogen or dry argon. The ^1H NMR spectra were recorded on a 90 MHz Perkin-Elmer R32 spectrometer using $SiMe_4$ as internal reference where necessary. The ^{31}P NMR spectra were recorded at 40.48 MHz on a Jeol PFT 100 instrument using trimethylphosphine (TMP) or trimethylphosphate (TMPO) as external references.

Starting materials

K_2PtCl_4 and $PtCl_2$ were commercial products. The tert. phosphines PEt_3, PPh_3 and $PCyc_3$ and other neutral ligands were either purchased or prepared by standard methods. The organotin(IV) compounds SnR_xCl_{4-x}, R = Me, Et, Bu,Ph ; x = 4-0, Sn_2Ph_6, $Sn_2Et_4Cl_2$ and organolead(IV) compounds $PbMe_3Cl$ and $PbPh_3Cl$, were either commercial products or prepared by standard methods. The platinum complexes $[Pt(PEt_3)_n]$ (n = $3,4^{[11,12]}$), trans-$[PtCl_2(PCyc_3)_2]^{[13]}$, $[Pt(PCyc_3)]^{[14,15]}$ and $[Pt(C_2H_4)(PPh_3)_2]^{[16]}$ were prepared by standard methods.

Reactions between $[Pt(PEt_3)_n]$ (n = 3 or 4) and SnR_xCl_{4-x}

(a) [Pt(PEt_3)_4] and SnPh_4: The platinum(0) complex (0.5 g, 0.75 mmol) was dissolved in toluene (10 mL) and $SnPh_4$ (0.3 g, 0.70 mmol) was added. The mixture was heated gently until complete dissolution of S_nPh_4. After ca. 30 min, the yellow-orange solution became paler, but it was set aside for a further 2 h,

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* More details will be given later in a separate paper.

then filtered through Celite. The clear solution was reduced in volume and the ^{31}P NMR spectrum was recorded.

A similar procedure was used with other tin reagents, *i.e.*, $SnPh_3Cl$, $SnMe_3Cl$, $Sn_2Et_4Cl_2$ and Sn_2Ph_6, but no heating was necessary since they are soluble in toluene. In the reaction of Sn_2Ph_6 with $[Pt(PEt_3)_4]$ a white crystalline material came out of solution. The crystals were filtered off, washed with n-hexane (3×5 mL) and dried in *vacuo*; they had melting points of 184–186°C (lit.175°C).[3] (Found: C, 51.4; H, 5.4%. Required for $C_{48}H_{60}P_2 \cdot Sn_2Pt$: C, 51.0; H, 5.3%). The ^{31}P NMR spectrum of the crystals in dichloromethane was recorded, and revealed the presence of *trans*-$[Pt(SnPh_3)_2(PEt_3)_2]$. The ^{31}P NMR spectrum of the mother liquor showed it to contain *cis*- and *trans*- $[PtPh (SnPh_3)(PEt_3)_2]$.

(b) *[Pt(PEt₃)₃] and SnMe₂Cl₂*:   A 0.3 M toluene solution of $[Pt(PEt_3)_3]$ (2 mL) [prepared by dissolution of the oil $[Pt(PEt_3)_3]$ (2.5 g, 4.55 mmol) in toluene (15 mL) under argon] was added to a solution of $SnMe_2Cl_2$ (0.15 g, 0.68 mmol) in toluene (3 mL) and the mixture was stirred at room temperature for *ca.* 2 h, then filtered through celite. The clear solution was reduced in volume and the ^{31}P NMR spectrum recorded.

A similar procedure was used for $SnPh_3Cl$, $SnMe_3Cl$, $SnPh_2Cl_2$, $Sn_2Et_4Cl_2$, $SnPh_4$ and $SnMe_4$, but in the case of $SnPh_4$ the mixture was heated gently until the $SnPh_4$ just dissolved .

Reaction between [Pt(PCyc₃)₂] and SnRₓCl₄ ₋ₓ

(a) *General procedure*:   The complex $[Pt(PCyc_3)_2]$ (0.12 g, 0.15 mmol) was dissolved in benzene (8 mL) and the ogranotin reagent [SnR_2Cl_2 (R = Me, Et, Bu, Ph), SnR_3Cl (R = Me, Bu, Ph) or $SnCl_4$] (0.2 mmol) was added under nitrogen. The mixture was stirred for *ca.* 30 min, then filtered through celite. The clear filtrate was reduced in volume and the ^{31}P NMR spectra recorded.

A similar procedure was used with organolead reagents PbR_3Cl (R = Me, Ph).

(b) *Preparation of trans-[PtCl(SnCl₃)(PCyc₃)₂]:*   A benzene solution of a slight excess of $SnCl_4$ was added dropwise to a benzene solution of the complex $[Pt(PCyc_3)_2]$ (0.4 g, 0.53 mmol) under nitrogen, and the mixture was stirred for *ca.* 30 min. The solution was reduced to *ca.* 30% of the original volume and n-hexane was then added to precipitate any trace of the side product $[Pt_2Cl_4(PCyc_3)_2]$. The mixture was filtered through celite and the filtrate evaporated to dryness. The crude yellow residue was redissolved in hot hexane and filtered hot through Celite. Yellow crystals of *trans*-$[PtCl(SnCl_3)(PCyc_3)_2]$ were obtained after leaving the solution in the freezer overnight, m.p. 180°C (decomp.). (Found: C, 42.3; H, 6.8%. Required for $C_{36}H_{66}P_2Cl_4SnPt$: C, 42.5; H, 6.5%) .

## RESULTS AND DISCUSSION

The oxidative-addition reactions of $[Pt(PEt_3)_n]$ (n = 3,4) and $[Pt(PCyc_3)_2]$ with organotin compounds (in slight excess) were carried out in distilled, dried and degassed toluene or benzene with careful precautions to exclude air and moisture. The ^{31}P NMR spectra of the reaction mixtures were recorded *ca.* 30

min after mixing the reactants unless otherwise stated. The values of δ ppm and $^1J(^{195}Pt\text{-}^{31}P)$ Hz were measured and the ^{119}Sn and ^{117}Sn satellites detected and the value of $^2J(^{195}Pt\text{-}P\text{-}^{119/117}Sn)$ were measured (Tables 1 and 2).

Reactions of [Pt(PEt₃)ₙ] (n = 3 or 4)

(a) *With SnR$_x$Cl$_{4-x}$:* The reactions of [Pt(PEt₃)ₙ] (n = 3 or 4) with SnR₂Cl₂ (R = Me, Et) gave products of insertion of Pt(0) into Sn-Cl bonds, and only the *trans-* isomers were formed, *i.e., trans-*[PtCl(SnR₂Cl)(PEt₃)₂]. The values of δ ppm and $^1J(Pt\text{-}P)$ Hz for the products were identical with those for a complex prepared by treating the mixture of *cis-* and *trans-*[PtCl(SnR₂Cl)(PPh₃)₂] (prepared from [Pt(C₂H₄)(PPh₃)₂] with SnR₂Cl₂)[4] with PEt₃. In the case where R = Ph, the reaction with [Pt(PEt₃)₄] carried out at ambient temperature and at −30°C and the results obtained in both cases compared to those obtained from [Pt(C₂H₄)(PPh₃)₂] and SnPh₂Cl₂ followed by addition of PEt₃ are summarized in the following Scheme:
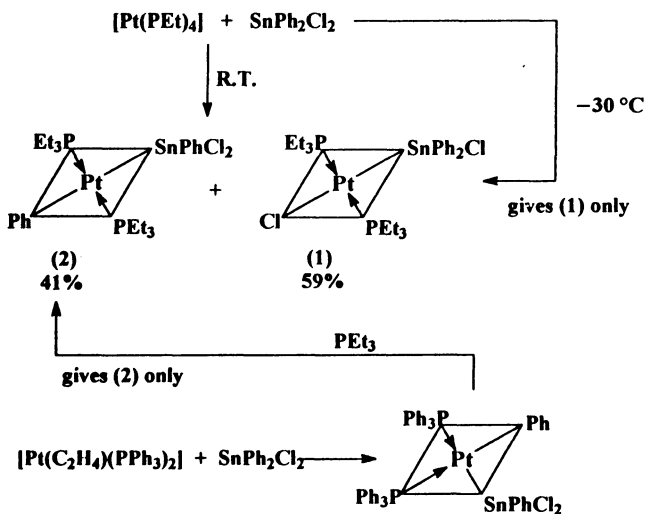
It seems likely that the reaction of [Pt(PEt₃)₄] with SnPh₂Cl₂ at room temperature probably initially gives the *cis-* [PtCl(SnPh₂Cl)(PEt₃)₂] as a product of an insertion of Pt(0) into the Sn-Cl bond, and in the presence of traces of free highly basic PEt₃ this initial product isomerizes to the *trans-* isomer (probably via formation of the cationic complex [Pt(SnPh₂Cl)(PEt₃)₃]⁺Cl⁻ as an intermediate[17]) which undergoes an oxidative- addition reaction of Pt into Sn-Ph

bonds of $SnPh_2Cl_2$. Reductive-elimination of $Cl-SnPh_2Cl$ from the $Pt^{(IV)}$ intermediate would then form *trans*- $[PtPh(SnPhCl_2)(PEt_3)_2]$ as summarized in the following Scheme :

(not observed)
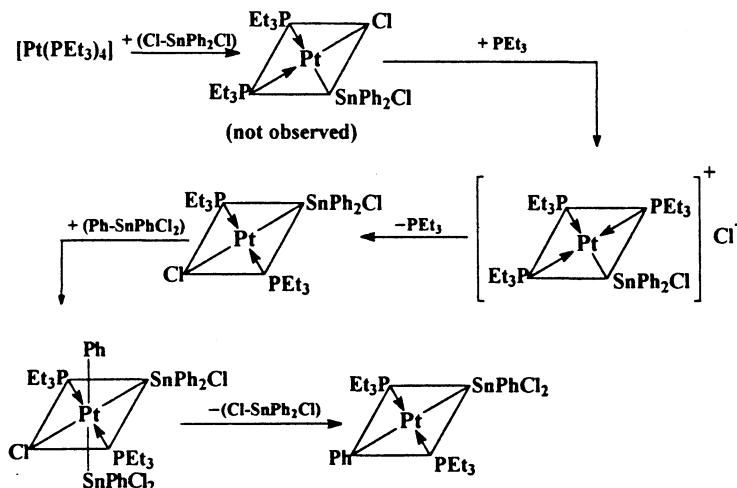
* More details will be given latter in a separate article.

In contrast, the reaction of $[Pt(PEt_3)_n]$ with $SnPh_3Cl$ leads to the formation of *trans*-$[PtPh(SnPh_2Cl)(PEt_3)_2]$ as revealed by ^{31}P NMR spectroscopy. The values of δ and J(Pt-P) for the product were closely similar to those for the complex *trans*-$[PtPh(SnPhCl_2)(PEt_3)_2]$, and identical to those for the complex prepared by treating the known complex *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (obtained as described in ref. 3) with PEt_3. The suggested mechanism for the reaction is similar to that outlined above. The related reaction between $[Pt(PEt_3)_3]$ and $SnMe_3Cl$ was carried out in toluene both at ambient temperature and at −40°C . In both cases, the ^{31}P NMR spectra revealed the presence of *trans*- complex with the parameters δ-117.2 ppm and J(Pt-P) 2728 Hz (toluene); identified as *trans*-$[PtHCl(PEt_3)_2]$: δ-117.8 ppm and J(PtP) 2723 Hz (CHCl$_3$)[18], and a small amount of the cationic complex $[PtMe(PEt_3)_3]^+Cl^-$ (*vide infra*). In addition to those, the reaction at room temperature gives a complex with δ-122.7 ppm and J(PtP) 2583 Hz, which was judged to be *trans*-$[PtMe(SnMe_2Cl)(PEt_3)_2]$, since the value of 2583 Hz is in the range generally observed for complexes having alkyl or aryl group attached to platinum in *cis*- relationship to phosphorus. In contrast the reaction at −40°C gives a complex with δ-123.7 ppm and J(PtP) 2347 Hz, which was judged to be *trans*-$[PtCl(SnMe_2Cl)(PEt_3)_2]$, since the value 2347 Hz is in the range for complexes having chlorine attached to platinum in *cis*- relationship to phosphorus (PEt$_3$ or PCyc$_3$) (Tables 1 and 2).

However, all attempts to obtain *trans*-$[PtMe(SnMe_2Cl)(PEt_3)_2]$ by the method described, *i.e.*, treatment of *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ with PEt_3, using various solvents at room temperature or even at −80°C, failed. In all cases, the cationic complex $[PtMe(PEt_3)_3]^+Cl^-$ was observed as a major product, together with free PPh_3. The failure to obtain *trans*-$[PtMe(SnMe_2Cl)(PEt_3)_2]$ by this

method might possibly be due to its destruction by adventitiously formed HCl, which would cleave the Pt-Sn bond to form the cationic complex. The ^{31}P NMR parameters of the latter were: δ for P *trans*- to P is −128.5 ppm [J(PtP) 2617 Hz] and δ for P *trans*- to Me is −133.6 ppm [J(PtP) 1866 Hz; ^{2}J(PP) 22 and 213.7 Hz (toluene)]. To validate our suggestion concerning the cationic complex, an analogue complex, *i.e.*, [PtMe(PEt$_3$)$_3$]$^+$ClO$_4^-$ was prepared in acetone by the established method[19] with slight modification, *i.e.*, by treatment of the acetone solution of *cis*-[PtMeCl(DMSO)$_2$] with PEt$_3$ in the presence of NaClO$_4$. The ^{31}P NMR parameters of the complex so prepared were: δ for P *trans*- to P is −128.5 ppm, J(PtP) 2607 Hz and δ for P *trans*- to Me is −133.8 ppm, J(PtP) 1807 Hz; ^{2}J(PP) 22 and 213.7 Hz (acetone).
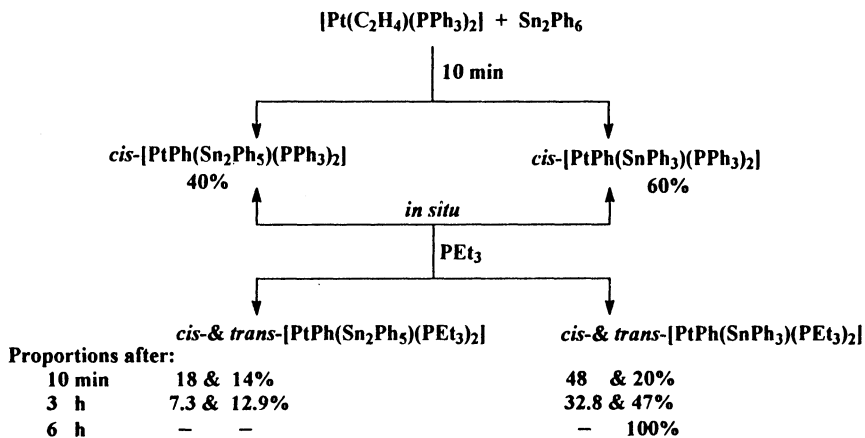
The ^{31}P NMR spectrum of the mixture obtained from the reaction between [Pt(PEt$_3$)$_3$] and SnPh$_4$ in toluene showed, in addition to *trans*-[PtPh$_2$(PEt$_3$)$_2$] (δ-132.1 ppm and J(PtP) 2830 Hz) (in 33% proportion), the presence of two complexes, identified as *trans*- and *cis*-[PtPh(SnPh$_3$)(PEt$_3$)$_2$] (in 35% and 32% proportions, respectively) (Table-1). The reaction of *cis*-[PtPh(SnPh$_3$)(PPh$_3$)$_2$] (obtained as described in ref. 3) with PEt$_3$ gave only the *trans*-[PtPh(SnPh$_3$)(PEt$_3$)$_2$] with ^{31}P NMR parameters identical to that obtained directly from [Pt(PEt$_3$)$_3$] and SnPh$_4$.

Similarly the reaction of [Pt(PEt$_3$)$_4$] with SnMe$_3$Ph in toluene gave both *trans*- and *cis*-[PtPh(SnMe$_3$)(PEt$_3$)$_2$] (19/6 ratio), as revealed by ^{31}P NMR spectroscopy (Table-1).

It has been reported that [Pt(PEt$_3$)$_4$] reacts with SnMe$_4$ in benzene under reflux for 5h to give *cis*-[PtMe(SnMe$_3$)(PEt$_3$)$_2$] as an oil[3]. The ^{31}P NMR parameters of the complex were reported, but tin satellites were not observed, and so in an attempt to complete the series of the complexes produced by this method, we repeated this reaction under various conditions. In all cases, the ^{31}P NMR spectra showed no complexes containing Pt-Sn bonds. (The complex mentioned has been prepared by another method: by treating [Pt(COD)$_2$] with SnMe$_4$ followed by addition of PEt$_3$ at *ca.* -40°C; this will be reported later.)

(b) *With dinuclear organotin compounds*: The reaction between [Pt(PEt$_3$)$_4$] and Sn$_2$Ph$_6$ in toluene after *ca.* 30 min led to precipitate of white crystals from a yellow solution. The crystals were filtered off and judged from its analytical studies to be *trans*-[Pt(SnPh$_3$)$_2$(PEt$_3$)$_2$]; its ^{31}P NMR parameters recorded in CH$_2$Cl$_2$ were identical to those for the same complex prepared previously[3] by treating [PtCO$_3$(PEt$_3$)$_2$] with SnPh$_3$H in benzene. The ^{31}P NMR spectrum of the concentrated yellow filtrate indicated the presence of two complexes, identified as *cis*- and *trans*-[PtPh(SnPh$_3$)(PEt$_3$)$_2$]. In order to throw light on this reaction more, the reaction of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] with Sn$_2$Ph$_6$ was carried out since it has been reported[4] to give *cis*-[PtPh(Sn$_2$Ph$_5$)(PPh$_3$)$_2$] and its decomposition product *cis*-[PtPh(SnPh$_3$)(PPh$_3$)$_2$], which was also formed directly in the reaction between [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and SnPh$_4$[3]. However, treatment of the mixture containing both the complexes with PEt$_3$ gave *cis*- and *trans*-[PtPh(Sn$_2$Ph$_5$)(PEt$_3$)$_2$], which we did not observe in the direct reaction between [Pt(PEt$_3$)$_4$] and Sn$_2$Ph$_6$ (above), and *cis*- and *trans*-[PtPh(SnPh$_3$)-(PEt$_3$)$_2$].

The rates of decomposition of *cis*- and *trans*-[PtPh(Sn$_2$Ph$_5$)(PEt$_3$)$_2$] were then studied and the results are summarized in the following Scheme:

$[Pt(C_2H_4)(PPh_3)_2]$ + Sn$_2$Ph$_6$

| 10 min |

cis-[PtPh(Sn$_2$Ph$_5$)(PPh$_3$)$_2$]   *cis*-[PtPh(SnPh$_3$)(PPh$_3$)$_2$]
40%   60%

in situ

PEt$_3$

cis-& *trans*-[PtPh(Sn$_2$Ph$_5$)(PEt$_3$)$_2$]   *cis*-& *trans*-[PtPh(SnPh$_3$)(PEt$_3$)$_2$]

Proportions after:
10 min	18 & 14%	48 & 20%
3 h	7.3 & 12.9%	32.8 & 47%
6 h	— —	— 100%

It follows from the observations that *cis*- and *trans*-[PtPh(Sn$_2$Ph$_5$)(PEt$_3$)$_2$] are unstable in solution, and decompose at room temperature by losing SnPh$_2$ species, either initially to give only *cis*-[PtPh(SnPh$_3$)(PEt$_3$)$_2$], which then isomerizes to the more stable *trans*- isomer, or directly to give both *cis*- and *trans*- isomers.

The reaction of [Pt(PEt$_3$)$_n$] (n = 3 or 4) with Sn$_2$Et$_4$Cl$_2$ in toluene was found to give *trans*-[PtCl(SnEt$_2$Cl)(PEt$_3$)$_2$] which was also obtained directly from the reaction between [Pt(PEt$_3$)$_4$] and SnEt$_2$Cl$_2$ and by treating *cis*- and *trans*-[PtCl(SnEt$_2$Cl)(PPh$_3$)$_2$] with PEt$_3$. It is possible that the reaction of Sn$_2$Et$_4$Cl$_2$ proceeds via insertion into Sn-Cl bonds to form the intermediate complex *trans*-[PtCl(Sn$_2$Et$_4$Cl)(PEt$_3$)$_2$] and this in turn loses SnEt$_2$ to form the final product *trans*-[PtCl(SnEt$_2$Cl)(PEt$_3$)$_2$].

Reaction of [Pt(PCyc$_3$)$_2$]

(a) *With SnR$_x$Cl$_{4-x}$*: The ^{31}P NMR spectrum of a mixture obtained from the reaction between [Pt(PCyc$_3$)$_2$] and SnR$_2$Cl$_2$ (R = Me, Et, Bu, Ph) in benzene at ambient temperature revealed the presence of one main product which was identified to be *trans*-[PtCl(SnR$_2$Cl)(PCyc$_3$)$_2$]. The ^{31}P NMR parameters of these complexes were closely similar to those for the complexes *trans*-[PtCl(SnR$_2$Cl)(PEt$_3$)$_2$] (R = Me, Et) (Tables 1 and 2).

TABLE 1 ^{31}P NMR DATA FOR COMPLEXES HAVING PT-S
BONDS AND L=PEt$_3$

Complex	δ ppm	^{1}J(PtP) Hz	^{2}J(SnP) Hz	
			^{119}Sn	^{117}Sn
trans-[PtCl(SnMe$_2$Cl)L$_2$]^a	124	2386.5	139	133
trans-[PtCl(SnEt$_2$Cl)L$_2$]^a	123.1	2416	127	122
trans-[PtCl(SnPh$_2$Cl)L$_2$]^a	125.1	2305	148	142.8
trans-[PtPh(SnPhCl$_2$)L$_2$]^a	132	2506	213.6	204
trans-[PtCl(SnMe$_3$)L$_2$]^a	123.7	2374	141.6^g	
trans-[PtMe(SnMe$_2$Cl)L$_2$]^a	122.7	2583	125.5^g	
trans-[PtPh(SnPh$_2$Cl)L$_2$]^a	132.7	2538	195	185.5
trans-[PtPh(SnPh$_3$)L$_2$]^b	133.5	2583	186.8	178.2
cis-[PtPh(SnPh$_3$)L$_2$]^b	119.4	2075^c	174.5	166
	129.0	2317^d	1862.8	1795.6
trans-[PtPh(SnMe$_3$)L$_2$]^b	130.1	2654	188	179.5
cis-[PtPh(SnMe$_3$)L$_2$]^b	130.5	2073^c	158.6	152.6
	131.3	2015^d	1811.5	1762.7
trans-[PtPh(Sn$_2$Ph$_5$)L$_2$]^b	130.4	2540	200.2	193.4
cis-[PtPh(Sn$_2$Ph$_5$)L$_2$]^b	120.3	2027^c	e	
	129.2	2242^d	e	
trans-[PtPh (SnPh$_3$)$_2$L$_2$]^b	135.1	2351	172.1	164.8
	135.1^f	2349	171	

^{a} Spectra recorded in toluene at room temperature.
^{b} Spectra recorded in CH$_2$Cl$_2$ at room temperature.
^{c} ^{1}J(PtP) for P in cis- relationship to Sn.
^{d} ^{1}J(PtP) for P in trans- relationship to Sn, ^{2}J(pp) = 16 Hz.
^{e} Tin satellites were obscured by the principal signals of the mixture.
^{f} Data taken from reference 3.
^{g} Tin 119, 117 satellites were not well resolved.

Similarly, SnR$_3$Cl (R = Me, Bu) gave products of an insertion of Pt(0) into
Sn-Cl bonds, i.e., trans-[PtCl(SnR$_3$)(PCyc$_3$)$_2$] which is rather surprising, since it
is known that such complexes are only unstable intermediates in the reaction
between [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and SnR$_3$Cl (R = Me, Bu, Ph)[8]. It is thus possible that
in the case of PCyc$_3$, the reactions proceed via insertion of Pt(0) into Sn-Cl
bonds to give initially cis-[PtCl(SnR$_3$)(PCyc$_3$)$_2$], which isomerizes to the trans-
isomer (see above), which does not undergo reaction with another molecule of
SnR$_3$Cl (to give finally [PtR(SnR$_2$Cl)(PCyc$_3$)$_2$]) such as in the case where the
ligand PPh$_3$ proceeds[8]. On the other hand, most of the PCyc$_3$ products had trans-
rather than cis- configuration; this could be due to the steric effects of the
cyclohexyl groups on the phosphine atoms which precludes formation of the cis-
isomer. In contrast, the reaction between [Pt(PCyc$_3$)$_2$] and SnPh$_3$Cl in benzene
gave cis- and trans- [PtPh(SnPh$_2$Cl)(PCyc$_3$)$_2$] (3/2 ratio), a product of and
insertion of Pt(0) into Sn-Ph bonds. The ^{31}P NMR parameters of both isomers

(Table 2) were typical of complexes having a phenyl group, rather than chloride, attached to platinum in *cis-* relationship to phosphorus for the *trans-* isomer and in *trans-* relationship to phosphorus for the *cis-* isomer.

TABLE 2

^{31}P NMR DATA FOR COMPLEXES HAVING Pt-Sn

BONDS AND L = PCyc$_3$[a]

Complex	$-\delta$ ppm	^{1}J (PtP) Hz	^{2}J (SnP)Hz	
			^{119}Sn	^{117}Sn
trans-[PtCl(SnMe$_2$Cl)L$_2$]	116	2384	123.3	118.4
trans-[PtCl(SnEt$_2$Cl)L$_2$]	115.5	2434	110	105
trans-[PtCl(SnBu$_2^n$Cl)L$_2$]	115.7	2440	110	105
trans-[PtCl(SnPh$_2$Cl)L$_2$]	117	2318	130.6	125.7
trans-[PtCl(SnMe$_3$)L$_2$]	115.7	2390	123.3	117.2
trans-[PtCl(SnBu$_3^n$)L$_2$]	115.7	2442.6	108.6	103.8
trans-[PtCl(SnCl$_3$)L$_2$]	118	2113	206.3	196.5
trans-[PtPh(SnPh$_2$Cl)L$_2$]	118.3	2452	125.7	118.4
cis-[PtPh(SnPh$_2$Cl)L$_2$]	109.4	2231.5[b]	163.6	140.4
	119.5	2655[c]	2434	2326.7
trans-[PtCl(PbMe$_3$)L$_2$]	117.5	2374.3	178.2[d]	
trans-[PtPh(PbPh$_2$Cl)L$_2$]	120.0	2460	197.7[d]	

[a] Spectra recorded in benzene at room temperature using TMP as a reference.
[b] ^{1}J(PtP) for P in *cis-* relationship to Sn.
[c] ^{1}J(PtP) for P in *trans-* relationship to Sn, ^{2}J(PP) = 11 Hz.
[d] Number for ^{2}J(^{207}PbP) Hz.

Complexes of the general formula *trans-* and *cis*-[PtCl(SnCl$_3$)L$_2$] were reported to be obtained from the reaction between *cis*-[PtCl$_2$L$_2$] (L = PEt$_3$, PPr$_3$, P(OPh)$_3$) and SnCl$_2$.[20] The present work indicates that a similar product can be formed by oxidative addition of SnCl$_4$ to [Pt(PCyc$_3$)$_2$]. The product *trans*-[PtCl(SnCl$_3$)(PCyc$_3$)$_2$] was demonstrated by ^{31}P NMR spectroscopy and the J(PtP) value, *i.e.*, 2113 Hz was consistent with those of similar complexes with PEt$_3$ (2042 Hz) and PPr$_3$ (2028 Hz). The latter was isolated as a pale yellow crystal (see Experimental section). It is noteworthy here that the ^{31}P NMR spectra of the mixtures obtained from the reaction between [Pt(PCyc$_3$)$_2$] and the halogenated tin reagents indicated, in addition to the products above, the presence of a small amount of a complex which had the ^{31}P NMR parameters of δ-125.8 ppm and J(PtP) 3564.4 Hz (benzene), and so was tentatively identified

as the dimer [Pt$_2$Cl$_4$(PCyc$_3$)$_2$]. It was precipitated from the benzene solution of the reaction mixture by concentration and addition of n-hexane. A fairly satisfactory elemental analysis was obtained.

Unsuccessful attempts were made to obtain products containing Pt-Sn bonds from the reaction between [Pt(PCyc$_3$)$_2$] and the non-halogenated organotin compounds SnMe$_4$, SnPh$_4$ and SnMe$_3$Ph. With SnMe$_4$ at ambient temperature, the ^{31}P NMR spectrum was recorded after *ca.* 20 h of mixing the reactants, and revealed that only the platinum starting material was present. When the mixture in benzene was refluxed for *ca.* 2 h the colour changed to brown and the ^{31}P NMR spectrum indicated the presence of the platinum starting matc.ial together with an unidentified complex having δ-78.7 ppm and J(PtP) 4190 Hz, which could be a platinum(0) cluster. With SnPh$_4$ and SnMe$_3$Ph at room temperature, the ^{31}P NMR spectrum recorded *ca.* 20 h after mixing the reactants revealed that only the starting material [Pt(PCyc$_3$)$_2$] was present. When the mixture was heated gently for few minutes, the spectrum revealed the presence of platinum starting material together with a product having δ-121.4 ppm and J(PtP) 2778 Hz, which was tentatively identified as *trans*-[PtPh$_2$(PCyc$_3$)$_2$]. In contrast, both SnPh$_4$ and SnMe$_3$Ph reacted fairly rapidly with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$][21] and rapidly with [Pt(PEt$_3$)$_4$]. The order of decreasing reactivity of these platinum(0) complexes towards organotin compounds is thus [Pt(PEt$_3$)$_4$] > [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] > [Pt(PCyc$_3$)$_2$] .

(b) *With PbR$_3$Cl (R = Me, Ph)*: In order to allow a comparison study between organotin compounds and their analogous organolead compounds the reaction between PbMe$_3$Cl and [Pt(PCyc$_3$)$_2$] in benzene at room temperature was examined. The ^{31}P NMR spectrum of the produced solution revealed the presence of two new complexes in addition to the platinum(0) starting complex. One of them (15% proportion) had the parameters δ-119.6 ppm and J(PtP) 2826 Hz (benzene) and so was tentatively identified as *trans*-[PtMeCl(PCyc$_3$)$_2$] . The other complex (58% proportion) had J(PtP) 2374 Hz (Table 2), identical to that for *trans*-[PtCl(SnMe$_3$)L$_2$] (L=PCyc$_3$,J(PtP) 2390 Hz; L=PEt$_3$, J(PtP) 2374 Hz). The complex must thus be *trans*-[PtCl(PbMe$_3$)(PCyc$_3$)$_2$], a product of insertion of Pt(0) into Pt-Cl bonds.

In contrast, the ^{31}P NMR of the mixture obtained from the reaction between [Pt(PCyc$_3$)$_2$] and PbPh$_3$Cl in benzene at room temperature indicated the presence of two complexes, both having the *trans*-configuration. One of them (70% proportion) had the parameters δ-123.4 ppm and J(PtP) 2793 Hz (benzene) which was tentatively identified as *trans*-[PtPhCl(PCyc$_3$)$_2$]. The other product (30% proportion) with J(PtP) 2460 Hz (Table-2) was identified as *trans*-[PtPh(PbPh$_2$Cl)(PCyc$_3$)$_2$] (compare the values for the tin analogue of J(PtP) 2452 Hz). Therefore, the reaction between [Pt(PCyc$_3$)$_2$] and PbPh$_3$Cl, proceeds *via* insertion of Pt(0) into Pb-Ph bonds. It should be noted that *cis*- and *trans*-[PtCl (PbMe$_3$)(PPh$_3$)$_2$] were formed from the reaction between [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and PbMe$_3$Cl in CH$_2$Cl$_2$ at −30°C, but the product was thermally unstable at room temperature[22]. Similarly, the complex *cis*-[PtPh(PbPh$_2$Br)-(PPh$_3$)$_2$] was formed in CH$_2$Cl$_2$ at −30°C from the reaction between [Pt(C$_2$H$_4$)-(PPh$_3$)$_2$] and PbPh$_3$Br.[22]

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