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Reactions of organotin(IV) compounds with platinum complexes. Part(III). Reactions of $(R_2Sn)_n$, (R = Me or Ph, $n = 6$; R = Et, $n = 9$) with platinum complexes☆

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Abstract

The R_2Sn moieties formed when the cyclic compounds $(R_2Sn)_n$, R = Me or Ph, $n = 6$; R = Et, $n = 9$, are exposed to light, react with the platinum(II) complexes $[PtCl_2L_2]$, $L = PEt_3$, PPr_3, PBu_3, $PEtPh_2$, PPh_3 to give new complexes of the general formula $[PtCl(SnR_2Cl)L_2]$. Similarly, Et_2Sn from $(Et_2Sn)_9$ reacts with $[PtMe(Cl)L_2]$ to give $[PtMe(SnEt_2Cl)L_2]$ and Ph_2Sn from $(Ph_2Sn)_6$ reacts with $[PtPh(Cl)L_2]$ or $[PtPh_2L_2]$ to give $[PtPh(SnPh_2Cl)L_2]$ or $[PtPh(SnPh_3)L_2]$ ($L = PEt_3$), respectively. Reactions involving $(R_2Sn)_n$ and the bridged complex $[\{Pt(\mu\text{-}Cl)ClL\}_2]$ give a mixture of $[PtCl(SnR_2Cl)L_2]$ and $[PtCl(SnRCl_2)L_2]$, R = Me or Et, L = PBu_3. It is suggested that these reactions initially involve insertion of R_2Sn moieties into Pt–Cl bonds of the complexes $[PtX(Cl)\ L_2]$ or $[\{Pt(\mu\text{-}Cl)ClL\}_2]$ then generate R_2SnXCl (X = Cl, Me, Ph) and the Pt(0)complex $[PtL_2]$, which undergoes oxidative-addition of the formed tin(IV) species to give complexes containing Pt–Sn bonds. With $(Ph_2Sn)_6$ and $[PtPh_2L_2]$, the mechanism takes a different course. Reactions under similar conditions involving the Pt(0) complexes $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(COD)_2]$, (COD = 1,5-cyclooctadiene) and $(R_2Sn)_6$, R = Me or Ph, gave no detectable complexes containing Pt–Sn bonds. The complex $[Pt(PEt_3)_4]$ and $(MeSn)_6$ likewise gives no species containing Pt–Sn bonds but with $(Ph_2Sn)_6$, two complexes, tentatively identified as *trans*-$[PtPh(Sn_2Ph_5)(PEt_3)_2]$ and *trans*-$[PtPh(Sn_6Ph_{11})(PEt_3)_2]$, were detected in the solution. In all cases, the products were identified by ^{31}P-NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organotin compounds; Stannylenes; Platinum complexes; ^{31}P-NMR studies

1. Introduction

The cyclic tin compounds $(R_2Sn)_n$ are known to generate the stannylenes R_2Sn in solution upon exposure to light at room temperature [2,3].These species can be also formed by thermal disproportionation of 1,2-disubstituted distannanes $(R_2SnX)_2$, which gives SnR_2X_2 and R_2Sn [4]. The transient R_2Sn species can undergo insertion into C-halogen, O–O, Sn–H, Sn–C and Sn–Sn bonds [5,6], the reactions being carried out by exposing a mixture of the substrate and $(R_2Sn)_n$ to light. Corresponding insertions into Si–H, Si–O, and Si–Cl bonds take place with the transient silylene Me_2Si [7]. Stannylenes R_2Sn (R = alkyl or aryl) generated in solution can co-ordinate to transition metals (M), M = Cr, W and Fe [8–10], in the presence of an electron donating solvent such as pyridine or THF, to form complexes containing M–Sn bonds. Several articles dealing with the formation of complexes containing Pt–M bonds (M = Sn, Ge, Si) have been reported recently [11]. As an extention to our ongoing interest in the synthesis of new platinum complexes containing Pt–Sn bonds, we present here the reaction of the cyclic tin compounds $(R_2Sn)_n$, (R = Me or Ph, $n = 6$; R = Et, $n = 9$) with several platinum complexes, which to the best of our knowledge is novel.

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2. Experimental

2.1. General

All the solvents were dry and oxygen-free, and reactions were carried out under dry nitrogen or dry argon. The proton-decoupled FT ^{31}P-NMR spectra were recorded at 40.48 MHz on a JEOL PFT-100 spectrometer with trimethylphosphite (TMP) or trimethylphosphate (TMPO) as external reference and chemical shifts were corrected to H_3PO_4 as a reference standard.

2.2. Starting materials

The metal complexes were prepared by standard methods: $[PtCl_2L_2]$, L = PEt_3, PPr_3, PBu_3, $PEtPh_2$, PPh_3; $[\{Pt(\mu\text{-}Cl)Cl(PBu_3)\}_2]$; *trans*-[PtCl R$(PEt_3)_2$], R = Me, Ph [12–16]; *cis*-$[PtPh_2(PEt_3)_2]$ [17]; $[PtCl_2(COD)]$ [18]; $[Pt(C_2H_4)(PPh_3)_2]$ [19]; $[Pt(COD)_2]$ [20]; and $[Pt(PEt_3)_4]$ [21]. The organotin compounds were also prepared by standard methods: SnR_2Cl_2, R = Me, Et, Ph [22,23]; $(R_2Sn)_n$, R = Me, Ph, $n = 6$ and R = Et, $n = 9$ [2,24].

2.3. Reaction procedure

The reactions involved $(R_2Sn)_n$,(R = Me, Ph; $n = 6$ or R = Et; $n = 9$) and various platinum complexes. A typical procedure was as follows: the compound $(Me_2Sn)_6$ (0.18 g, 1.2 mmol) was suspended in benzene or toluene (20 cm^3) and $[PtCl_2\ L_2]$ (L = PEt_3, PPr_3, PBu_3, $PEtPh_2$, PPh_3) (2.1 mmol) was added. The mixture was stirred at room temperature (r.t.) for 24 h (L = PEt_3, PBu_3, PPh_3); 12 h (L = $PEtPh_2$) or 50 h (L = PPr_3). A yellow–orange solution was obtained, except in the case of L = PPh_3 which gave a coloured suspension owing to the insolubility of the starting material *cis*-$[PtCl_2\ (PPh_3)_2]$. The clear supernatant liquid was reduced in volume and used for recording of the ^{31}P-NMR spectrum. Details of the reactions between $(R_2Sn)_n$ and platinum complexes are summarised in Table 1.

3. Results and discussion

3.1. Reactions of $(R_2Sn)_n$ with platinum(II) complexes

Reactions of $(R_2Sn)_n$, (R = Me, Ph; $n = 6$ and R = Et; $n = 9$), in slight excess, with Pt(II) complexes were carried out in benzene or toluene. Chlorinated solvents react with $(R_2Sn)_n$ upon exposure to daylight by insertion of R_2Sn into C–Cl bonds [5,6]. For R = Me or Et the mixtures were exposed to daylight at room temperature whereas for R = Ph they were exposed to light from a tungsten lamp at ca. 90 °C. The results of these reactions are summarised in Table 1. The ^{31}P-NMR spectrum of the concentrated solution obtained from the reaction between *trans*-$[PtCl_2(PEt_3)_2]$ and $(Me_2Sn)_6$ in benzene after ca. 24 h comprised a ca. 1:4:1 triplet with tin satellites (94%) together with the signals from a small amount of the starting complex. The values of δ 15.0 ppm and J(PtP) 2390 Hz associated with tin- 119 and -117 satellites (Table 2) were identical to those for the complex *trans*-$[PtCl(SnMe_2Cl)(PEt_3)_2]$, which has been prepared by three different methods [1,25] (Scheme 1).

Similarly, the reaction of *trans*-$[PtCl_2(PEt_3)_2]$ and $(Et_2Sn)_9$ gave the complex *trans*-[PtCl $(SnEt_2Cl)(PEt_3)_2]$, which was also obtained by the routes shown in Scheme 1.

In contrast when a mixture of $(Ph_2Sn)_6$, and *trans*-$[PtCl_2(PEt_3)_2]$ in toluene was stirred in daylight at room temperature, the ^{31}P-NMR spectrum showed that no reaction had taken place even after ca. 3 days. This may due to the lower tendency of $(Ph_2Sn)_6$ compared with $(Me_2Sn)_6$ and $(Et_2Sn)_9$ to dissociate to R_2Sn moieties. However, when the mixture was exposed to tungsten light at ca. 90 °C for ca. 100 h, the ^{31}P-NMR spectrum revealed the presence of (in addition to a small amount of the starting platinum complex) three complexes, all having the *trans*-configuration. Two of them were identified as *trans*-[PtCl $(SnPh_2Cl)(PEt_3)_2]$ (separately prepared by reaction of $[Pt(PEt_3)_4]$ with $SnPh_2Cl_2$ [25]) and *trans*-[PtCl $(SnPhCl_2)(PEt_3)_2]$ (Tables 1 and 2), the latter being formed by reaction of the starting platinum complex with the decomposition products of $(Ph_2Sn)_6$ formed upon prolonged heating (see latter). The third complex (10%) was identified as *trans*-$[PtPhCl(PEt_3)_2]$ [26].

Analogous results were obtained from the reactions between *cis*- or *trans*-$[PtCl_2L_2]$, L = PBu_3, PPr_3, $PEtPh_2$ and $(R_2Sn)_n$ (Tables 1 and 2). However, neither $(R_2Sn)_6$ (R = Me, Ph) nor $(Et_2Sn)_9$ reacted with the *cis*-$[PtCl_2(PPh_3)_2]$ in toluene or benzene at room temperature or at higher temperatures, because of the extreme insolubility of *cis*-$[PtCl_2(PPh_3)_2]$. The more soluble *trans*-isomer, *trans*-$[PtCl_2(PPh_3)_2]$, was thus prepared [27]. The reactions between this complex and $(Me_2Sn)_6$ or $(Et_2Sn)_9$ were not examined, because, the expected products *trans*-$[PtCl(SnR_2Cl)(PPh_3)_2]$ (R = Me, Et) were already known, having been prepared by the oxidative-addition reaction between $[Pt(C_2H_4)(PPh_3)_2]$ and SnR_2Cl_2 (R = Me, Et), in contrast to that with $SnPh_2Cl_2$, which gave *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$. The reaction between *trans*-$[PtCl_2(PPh_3)_2]$ and $(Ph_2Sn)_6$ was examined since the expected product *cis*- or *trans*-$[PtCl(SnPh_2Cl)(PPh_3)_2$ had not been previously prepared. When the ^{31}P-NMR spectrum was recorded after UV irradiation for 1 h of a mixture of *trans*-$[PtCl_2(PPh_3)_2]$ and $(Ph_2Sn)_6$ in benzene, it revealed the

Table 1
Formation of complexes containing R_2Sn (R = Me, Ph, Et) moieties

Reactants	Reaction conditions	Product	L	Configuration	Proportion (%)[a]
trans-$[PtCl_2L_2]+(Me_2Sn)_6$	Benzene, daylight, room temperature,24 h	$[PtCl(SnMe_2Cl)L_2]$	PEt_3	*trans*-	94
trans-$[PtC1_2L_2]+(Et_2Sn)_9$	Benzene, daylight, room temperature,50 h	$[PtCl(SnEt_2Cl)L_2]$	PEt_3	*trans*-	100
trans-$[PtCl_2L_2]+(Ph_2Sn)_6$	Toluene, tungsten light, 90 °C, 100 h	$[PtCl(SnPh_2C1)L_2]$	PEt_3	*trans*-	37
		$[PtCl(SnPhCl_2)L_2]$		*trans*-	23
cis- or *trans*-$[PtCl_2L_2]+(Me_2Sn)_6$	Benzene, daylight, room temperature,24 h	$[PtCl(SnMe_2C1)L_2]$	PBu_3	*trans*-	34
cis- or *trans*-$[PtCl_2L_2]+(Et_2Sn)_9$	Benzene, daylight, room temperature,12 h	$[PtCl(SnEt_2Cl)L_2]$	PBu_3	*trans*-	10
cis- or *trans*-$[PtCl_2L_2]+(Ph_2Sn)_6$	Toluene, tungsten light, 90 °C, 100 h	$[PtCl(SnPh_2Cl)L_2]$	PBu_3	*trans*-	31
		$[PtCl(SnPhCl_2)L_2]$		*trans*-	31
cis-$[PtC1_2L_2]+(Me_2Sn)_6$	Benzene, daylight, room temperature,50 h	$[PtCl(SnMe_2Cl)L_2]$	PPr_3	*trans*-	85
cis-$[PtC1_2L_2]+(Me_2Sn)_6$	Toluene, daylight, room temperature,12 h	$[PtCl(SnMe_2Cl)L_2]$	$PEtPh_2$	*trans*-	61
cis-$[PtCl_2L_2]+(Et_2Sn)_9$	Benzene, daylight, room temperature, 12 h	$[PtCl(SnEt_2Cl)L_2]$	$PEtPh_2$	*trans*-	34
		$[PtCl(SnEt_2Cl)L_2]$		*cis*-	29
trans-$[PtMe(C1)L_2]+(Et_2Sn)_9$	Benzene, daylight, room temperature,40 h	$[PtMe(SnEt_2Cl)L_2]$	PEt_3	*trans*-	6.0
trans-$[PtPh(Cl)L_2]+(Ph_2Sn)_6$	Toluene, tungsten light, 90 °C, 100 h	$[PtPh(SnPh_2Cl)L_2]$	PEt_3	*trans*-	15.5
trans-$[PtCl_2L_2]+(Ph_2Sn)_6$	Benzene, UV light, reflux, 1 h	$[PtPh(SnPhCl_2)L_2]$	PPh_3	*cis*-	42
		$[PtPh(SnPh_2Cl)L_2]$		*cis*-	24.5
cis-$[PtPh_2L_2]+(Ph_2Sn)_6$	Toluene, tungsten light, 90 °C, 168 h	$[PtPh(SnPh_3)L_2]$	PEt_3	*trans*-	4.0
cis- $[PtPh_2L_2]+SnPh_4$	Toluene, tungsten light, 90 °C, 168 h	$[PtPh(SnPh_3)L_2]$	PEt_3	*trans*-	10
$[Pt_2Cl_4L_2]+(Me_2Sn)_6$	Toluene, daylight, room temperature, 24 h	$[PtCl(SnMe_2Cl)L_2]$	PBu_3	*trans*-	2.5
		$[PtCl(SnMeCl_2)L_2]$		*trans*-	26
$[Pt_2Cl_4L_2]+(Et_2Sn)_9$	Toluene, daylight, room temperature, 1 h	$[PtCl(SnEt_2Cl)L_2]$	PBu_3	*trans*-	19
		$[PtCl(SnEtCl_2)L_2]$		*trans*-	17.5
cis-$[PtCl_2L_2]+(Et_2ClSn)_2$	Toluene, sealed tube, 130 °C, 30 h	$[PtCl(SnEtCl_2)L_2]$	PBu_3	*trans*-	44
cis-$[PtCl_2L_2]+SnCl_4$	Toluene, room temperature, soon	$[PtCl(SnC1_3)L_2]$	PBu_3	*trans*-	10
$[PtL_4]+(Ph_2Sn)_6$	Toluene, room temperature, 2 h	$[PtPh(Sn_2Ph_5)L_2]$	PEt_3	*trans*-	22
		$[PtPh(Sn_6Ph_{11})L_2]$		*cis*-	30
trans-$[PtMe(C1)L_2]+(Me_2Si)_6$	Cyclohexane, UV light,13 h	$[PtCl(SiMe_3)L_2]$	PBu_3	*trans*-	35.5

[a] Proportions of complexes were inferred directly from the relative peak heights in the $^{31}P\{^1H\}$-NMR spectra.

presence of *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ (42%), *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (24%), *trans*-$[PtPhCl(PPh_3)_2]$ (24.5%), as well as a small amount of the starting complex. There was no evidence for the presence of *cis*- or *trans*-$[PtCl(SnPh_2Cl)(PPh_3)_2$ in the spectrum (see below for the suggested mechanism).

When *trans*-$[PtMeCl(PEt_3)_2]$ was treated with $(Et_2Sn)_9$ with exposure to daylight in benzene at room temperature for ca. 40 h, the ^{31}P-NMR spectrum revealed the presence of a complex with δ 14.8 ppm and J(PtP) 2600 Hz, which was judged to be *trans*-$[PtMe(SnEt_2Cl)(PEt_3)_2]$. These parameters are identical to those for *trans*-$[PtMe(SnMe_2Cl)(PEt_3)_2]$ prepared by oxidative-addition of $SnMe_3Cl$ to $[Pt(PEt_3)_3]$, {J(PtP) 2583 Hz} [25]. Similarly *trans*-$[PtPhCl(PEt_3)_2]$ when treated with $(Ph_2Sn)_6$ in toluene under tungsten light irradiation at 90 °C for ca. 100 h, the ^{31}P-NMR spectrum revealed the presence of *trans*-$[PtPh(SnPh_2Cl)(PEt_3)_2]$ (Tables 1 and 2), authentic samples of which were prepared from $SnPh_3Cl$ by the three methods shown in Scheme 1.

3.2. Suggested mechanism for reactions of $(R_2Sn)_n$ with platinum(II) complexes

We consider two possible mechanisms for the reactions of $(R_2Sn)_n$ with platinum(II) complexes:

1) The stannylenes R_2Sn generated in aromatic solvents from $(R_2Sn)_n$, upon exposure to light, undergo direct insertion into Pt–Cl bonds to form $Pt(SnR_2Cl)$ species.

$$(R_2Sn)_n \xrightarrow{h\nu} nR_2Sn \quad (1)$$

$$[PtX(Cl)L_2] + R_2Sn \rightarrow [PtX(SnR_2Cl)L_2] \quad (2)$$

2) The R_2Sn moieties generated in solution first inserted into Pt–Cl bonds to form $Pt(SnR_2Cl)$ species followed by generation of R_2SnXCl, with reduction of the platinum(II) complex to $[PtL_2]$. The latter, which is highly reactive, undergoes oxidative-addition of R_2SnXCl to give $[PtX(SnR_2Cl)L_2]$ Eq. (3):

$$[PtX(Cl)L_2] + R_2Sn \rightarrow [PtX(SnR_2Cl)L_2]$$
$$\rightarrow [PtL_2] + R_2SnXCl \xrightarrow{fast} [PtX(SnR_2Cl)L_2] \quad (3)$$

We favour the second mechanism for the reasons set out below:

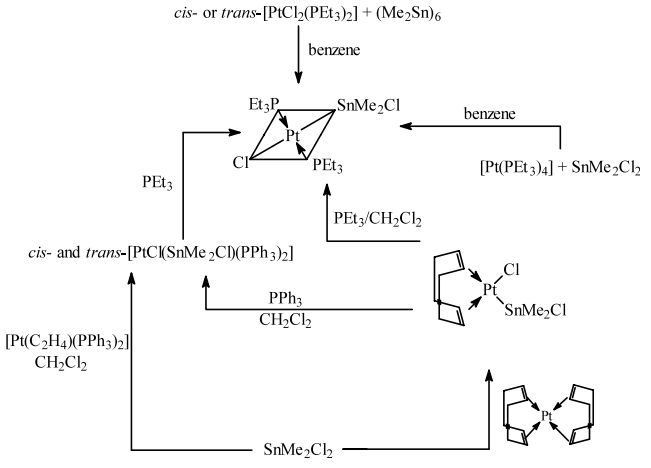
A) When a mixture of *trans*-$[PtCl_2(PBu_3)_2]$ and $(Et_2Sn)_9$ in toluene was stirred with a five-fold excess of $SnMe_2Cl_2$ at room temperature, the ^{31}P-NMR spectrum showed the presence of, in addition to some unreacted platinum starting material, only

Table 2
$^{31}P\{^{1}H\}$-NMR data of complexes obtained from the reaction between platinum(II) complexes and $(R_2Sn)_n$, R = Me, Ph, $n = 6$; R = Et, $n = 9$

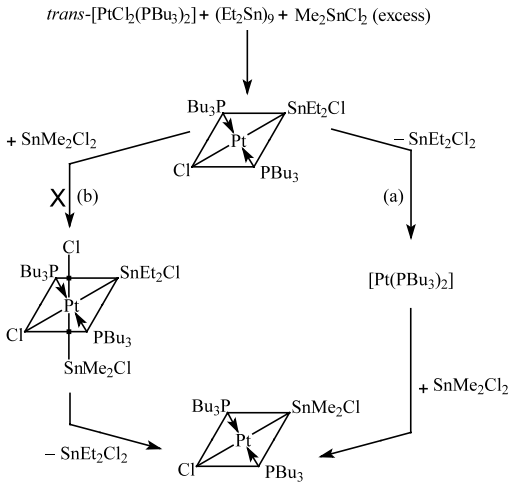
Complex	L	δ (ppm)	^{1}J(PtP) (Hz)	^{2}J(SnP) (Hz)		^{2}J(PP) (Hz)
				^{119}Sn	^{117}Sn	
trans-(PtCl(SnMe$_2$Cl)L$_2$] [a]	PEt$_3$	16.0	2390	137 [f]		
		16.5 [g]	2387	139	133	
	PBu$_3$	7.3	2376	140	134	
	PPr$_3$	6.6	2368	137 [f]		
	PEtPh$_2$	19.8	2651	137 [f]		
trans-(PtCl(SnEt$_2$Cl)L$_2$] [a]	PEt$_3$	16.8 [g]	2420	127 [f]		
	PBu$_3$	8.3	2398	128	123	
	PEtPh$_2$	20.1	2681	127 [f]		
cis-[PtCl(SnEt$_2$Cl)L$_2$]	PEtPh$_2$	25.7 [c]	2134	2076	1987	
		16.3 [d]	4312	[e]	[e]	12
trans-[PtMe(SnEt$_2$Cl)L$_2$] [a]	PEt$_3$	14.8	2600	[e]	[e]	
trans-[PtCl(SnPh$_2$Cl)L$_2$] [a]	PEt$_3$	14.6 [g]	2318	150	143	
	PBu$_3$	5.6	2300	149	144	
trans-[PtPh(SnPh$_2$Cl)L$_2$] [a]	PEt$_3$	7.7 [g]	2539	195	186	
trans-[PtPh(SnPh$_3$)L$_2$] [a]	PEt$_3$	6.3 [g]	2580	[e]	[e]	
trans-[PtPh(Sn$_2$Ph$_5$)L$_2$] [a]	PEt$_3$	9.7 [g]	2544	204	195	
cis-[PtPh(Sn$_6$Ph$_{11}$)L$_2$] [a]	PEt$_3$	10.5 [c]	2264			17
		5.3 [d]	1966			
cis-[PtPh(SnPhCl$_2$)L$_2$] [b,h]	PPh$_3$	26.1 [c]	3107			
		20.4 [d]	2054	[e]	[e]	16
cis-[PtPh(SnPh$_2$Cl)L$_2$] [b,h]	PPh$_3$	27.2 [c]	2637			
		23.5 [d]	2138	[e]	[e]	15
trans-[PtCl(SnPhCl$_2$)L$_2$] [a]	PEt$_3$	14.4	2208	180	172	
	PBu$_3$	5.6	2192	180	171	
trans-[PtCl(SnMeCl$_2$)L$_2$] [a]	PBu$_3$	6.2	2223	172	165	
trans-[PtCl(SnEtCl$_2$)L$_2$] [a]	PBu$_3$	6.9	2240	165	158	
trans-[PtCl(SnCl$_3$)L$_2$] [a]	PBu$_3$	6.0	2053	234	223	
trans-[PtCl(SiMe$_3$)L$_2$]	PBu$_3$	12.7	2820			

[a] Data obtained with toluene as solvent and H_3PO_4 as external reference.
[b] Data obtained by dichloromethane as solvent.
[c] Parameters for P *trans*- to Sn.
[d] Parameters for P *cis*- to Sn.
[e] Signal to noise ratio insufficient for observation of Sn satellites.
[f] Tin satellites for Sn(119) and Sn(117) were not very well resolved.
[g] Closely similar to those reported [25].
[h] These were already reported and their data are closely similar to those reported [37].

trans-[PtCl(SnMe$_2$Cl)(PBu$_3$)$_2$] and no *trans*-[PtCl(SnEt$_2$Cl)(PBu$_3$)$_2$].This is what would be expected for the mechanism above (Eq. (3)), in which Et$_2$Sn first inserts into Pt–Cl bonds of [PtCl$_2$(PBu$_3$)$_2$] to form Pt(SnEt$_2$Cl) species and the latter then generates Et$_2$SnCl$_2$ with the formation of [Pt(PBu$_3$)$_2$], then since SnMe$_2$Cl$_2$ is more reactive than SnEt$_2$Cl$_2$, it would selectively add to the Pt(0) complex to give the observed product (Scheme 2a). However, in another experiment, when the complex *trans*-[PtCl(SnEt$_2$Cl)(PBu$_3$)$_2$], prepared as described earlier, was treated with an excess of SnMe$_2$Cl$_2$ in toluene for 4 h the ^{31}P-NMR spectrum of the solution revealed the presence of only *trans*-[PtCl(SnMe$_2$Cl)(PBu$_3$)$_2$]. It is possible that SnMe$_2$Cl$_2$ added oxidatively to *trans*-[PtCl(SnEt$_2$Cl)(PBu$_3$)$_2$] to give a Pt(IV) intermediate (Scheme 2b) which underwent reductive-elimination of SnEt$_2$Cl$_2$ to form the Pt(II) complex *trans*-[PtCl(SnMe$_2$Cl)(PBu$_3$)$_2$]. Thus, it is also possible that the reaction between *trans*-[PtCl$_2$(PBu$_3$)$_2$] and a



Scheme 1. Methods of preparing *trans*-[PtCl(SnMe$_2$Cl)(PEt$_3$)$_2$].



Scheme 2. The suggested mechanism for the reaction of stannylenes R_2Sn with $[PtCl_2L_2]$ complexes.

mixture of $(Et_2Sn)_9$ and $SnMe_2Cl_2$ did not form $[Pt(PBu_3)_2]$ but instead gave *trans*-$[PtCl(SnEt_2Cl)(PBu_3)_2]$, which reacted with $SnMe_2Cl_2$ as in Scheme 2b. This ambiguity was resolved as described under (B), below.

B) We mentioned above that treatment of *trans*-$[PtCl_2(PPh_3)_2]$ with $(Ph_2Sn)_6$ gave a mixture of *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ and *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ (Tables 1 and 2) and not the expected $[PtCl(SnPh_2Cl)(PPh_3)_2]$, which would be produced by insertion of Ph_2Sn into Pt–Cl bonds. It is quite likely that decomposition of $(Ph_2Sn)_6$ to various species occurred and that these insert into Pt–Cl bonds of *trans*-$[PtCl_2(PPh_3)_2]$ (Eq. (3))to give finally $[Pt(PPh_3)_2]$ and $SnPh_2Cl_2$ as well as $SnPh_3Cl$, and both of these tin compounds reacted with the Pt(0) complex to give a mixture of *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ and *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$, respectively. It is possible that insertion of Ph_2Sn moieties into Pt–Cl bond had initially occurred to give *cis*-or *trans*-$[PtCl(SnPh_2Cl)(PPh_3)_2]$ as an intermediate, and that the latter then reacted with another molecule of $SnPh_2Cl_2$ to give the thermodynamically stable *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ [1].The question then arises of how the complex *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ could be formed in solution if the reaction involved insertion of Ph_2Sn moieties? One possibility is that UV irradiation of *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ in solution somehow formed *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$, and so we examined the behaviour of *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$ (prepared as described in ref. [28]) when subjected to UV irradiation in toluene. After 1 h, the ^{31}P-NMR spectrum of the solution revealed the presence of *trans*-$[PtPhCl(PPh_3)_2]$ {δ 24.9 ppm and J(PtP) 3158 Hz (CH_2Cl_2)} as well as *trans*-$[PtCl_2(PPh_3)_2]$ {δ 20.0 ppm, J(PtP) 2672 Hz (CH_2Cl_2)}, and no complexes containing Pt–Sn bonds were detected. This showed that the formation of *cis*-$[PtPh(SnPh_2Cl)(PPh_3)_2]$ in the reaction involving $(Ph_2Sn)_6$ was not due to the effect of the UV light on the *cis*-$[PtPh(SnPhCl_2)(PPh_3)_2]$.

C) i) The reaction of *cis*-$[PtPh_2(PEt_3)_2]$ and $(Ph_2Sn)_6$ in toluene gave *trans*-$[PtPh(SnPh_3)(PEt_3)_2]$ and some $SnPh_4$ was also formed.
ii) The reaction of *cis*-$[PtPh_2(PEt_3)_2]$ with $SnPh_4$ in toluene gave *trans*-$[PtPh(SnPh_3)(PEt_3)_2]$ as shown by ^{31}P-NMR spectroscopy (Tables 1 and 2). These experiments provide good evidence that the first step is the formation of Pt(0) complex which is followed by oxidative-addition of $SnPh_4$ [produced by decomposition of $(Ph_2Sn)_6$] [3]. To confirm this, we exposed a stirred suspension of $(Ph_2Sn)_6$ in toluene under nitrogen at 90 °C to tungsten light for ca. 12 days. The mixture was then allowed to cool to room temperature and $[Pt(C_2H_4)(PPh_3)_2]$ was added and the toluene evaporated off. The residue was dissolved in dichloromethane (in which it is more soluble) and the ^{31}P-NMR spectrum of the solution revealed the presence of two *cis*-complexes as the major products along with a little of the starting complex. One of these *cis*-complexes was judged to be *cis*-$[PtPh(SnPh_3)(PPh_3)_2]$ [28] (Table 2) and the other gave parameters of δ 27.7 ppm; J(PtP) 2446 Hz (P *trans*- to Sn) and δ 22.1 ppm; J(PtP) 2097 Hz (P *trans*- to Ph) (the tin satellites could not be observed, because of the low signal to noise ratio). These parameters are closely similar to those for *cis*-$[PtPh(SnPh_2OSnPh_3)(PPh_3)_2]$ and *cis*-$[PtPh(SnPh_2OH)(PPh_3)_2]$ [29]. The results provide good evidence that $(Ph_2Sn)_6$ decomposes in solution under the conditions used to give organotin compounds that can react with Pt(0) complexes in the usual way. It is noteworthy that $(Ph_2Sn)_6$ does not react with $[Pt(C_2H_4)(PPh_3)_2]$ under normal conditions (vide infra).

D) It should be noted that double insertions of R_2Sn moieties into both Pt–Cl bonds in the reaction between $[PtCl_2L_2]$ and $(R_2Sn)_n$ to give $[Pt(SnR_2Cl)_2L_2]$ did not occur in any of the experiments, which provides further support for the mechanism shown in Scheme 2a.

The reaction of $(Me_2Si)_6$ with platinum(II) complexes was carried out in the hope of obtaining complexes formed by insertion of the Me_2Si moiety into Pt–Cl bonds. Due to the low reactivity of $(Me_2Si)_6$, UV light was used, and the quartz reaction vessel was irradiated at a distance of ca. 10 cm with a Hanovia medium pressure Hg lamp, model UVS. 500. The ^{31}P-NMR spectrum of a mixture obtained from *cis*-or *trans*-$[Pt\ Cl_2\ L_2]$ (L = PBu_3 or PEt_3) and $(Me_2Si)_6$ in 1:1 or 6:1 molar

ratio in cyclohexane after 16 h of irradiation revealed the presence of a complex with the parameters δ 14.4 ppm, J(PtP) 2715 Hz (L = PBu_3) and δ 23.3 ppm, J(PtP) 2726.5 Hz (L = PEt_3) which was identified as *trans*-[PtCl(H)L_2] [30]. It seems that Me_2Si moiety initially inserts into Pt–Cl bonds of [$PtCl_2L_2$] followed by generation of $SiMe_2Cl_2$ and [PtL_2]; the former would then undergo hydrolysis very readily to give HCl, which would add to [PtL_2]. When a mixture of *trans*-[PtMe(Cl)$(PBu_3)_2$] and a slight excess of $(Me_2Si)_6$ in cyclohexane was UV irradiated for ca. 13 h, the ^{31}P-NMR spectrum revealed the presence of three complexes, two of which were identified as *trans*-[$PtCl_2(PBu_3)_2$)] (22%) and *trans*-[PtCl(H)$(PBu_3)_2$] (20%). The third complex (36%), with parameters δ 12.7 ppm and J(PtP) 2820 Hz, was tentatively identified as *trans*-[PtCl$(SiMe_3)(PBu_3)_2$] since its coupling constant is very similar to that for e.g. *trans*-[PtCl$(SiPh_3)L_2$], *trans*-[PtCl$(SiPh_2Me)L_2$], *trans*-[PtCl$(SiCl_3)L_2$], L = PMe_2Ph; for which the values of J(PtP) are 2772, 2842 and 2873 Hz, respectively [31]. This favours the mechanism suggested for the analogous reactions with $(R_2Sn)_n$ compounds (Eq. (3) and Scheme 2a).

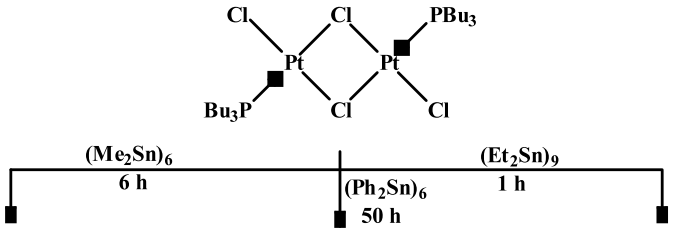
3.3. Reaction of $(R_2Sn)_n$ with bridged platinum complexes

Reactions of $(R_2Sn)_n$ with the bridged complex [{Pt(μ-Cl)Cl(PBu_3)}$_2$] were examined, these provide evidence of whether or not insertion of R_2Sn moieties occurs. The reactants and the products (with their proportions) of these reactions are indicated in Scheme 3.

When the ^{31}P-NMR spectrum of the mixture obtained from of [{Pt(μ-Cl)Cl(PBu_3)}$_2$] and $(Et_2Sn)_9$ was recorded again after 24 h at room temperatures, it showed that the [{Pt(μ-Cl)Et$(PBu_3)_2$}$_2$] had disappeared and the proportions of the other products had increased to 43, 29 and 28, respectively (Scheme 3). The disappearance of the [{Pt(μ-Cl)Et$(PBu_3)_2$}$_2$] is probably associated with the instability arising from the ease of β-elimination from the ethyl group attached to platinum. In contrast, the complex [{Pt(μ-Cl)Me$(PBu_3)_2$}$_2$], is fairly stable in solution. Furthermore, the complex *trans*-[PtCl$(SnEtCl_2)(PBu_3)_2$] (Scheme 3) was also detected by ^{31}P-NMR spectroscopy when a solution reaction of *cis*-[$PtCl_2(PBu_3)_2$] and $(Et_2ClSn)_2$ in toluene was heated at 130 °C in a sealed tube for 30 h in an attempt to produce Et_2Sn species [4] that might insert into Pt–Cl bonds to give, e.g. *trans*-[PtCl$(SnEt_2Cl)(PBu_3)_2$]. The ^{31}P-NMR spectrum of the mixture revealed the presence of, in addition to unchanged starting complex, only the *trans*-[PtCl$(SnEtCl_2)(PBu_3)_2$] (44%). The formation of *trans*-[PtCl$(SnRCl_2)(PBu_3)_2$] (R = Me, Et) in this reaction and the reactions listed in Scheme 3 can be understood in terms of a redistribution of organotin compounds in the presence of the extra chlorine in the bridge complex, to form $SnRCl_3$, with the latter, which has a high reactivity, reacting immediately with [$Pt(PBu_3)_2$] (Eq. (3), Scheme 2a) to give *trans*-[PtCl$(SnRCl_2)(PBu_3)_2$].

It is evident that none of the reactions of $(R_2Sn)_n$ with Pt(II) complexes that we examined proceeded via direct insertion of R_2Sn moieties into the Pt–Cl bonds. Furthermore we observed no formation of any bridge complex containing Pt–Sn bonds in the reaction between [{Pt(μ-Cl)Cl(PBu_3)}$_2$] and $(R_2Sn)_n$. In contrast, the stable divalent tin compounds R_2Sn, R = $N(SiMe_3)_2$ and $CH(SiMe_3)_2$ were found to undergo ready direct insertion into Pt–Cl bonds [32].

In order to complete the series of the complexes *trans*-[PtCl$(SnR_xCl_{3-x})(PBu_3)_2$] (X = 2, 3, 0), that with X = 0, i.e. *trans*-[PtCl$(SnCl_3)(PBu_3)_2$] [usually prepared by insertion of $SnCl_2$ into Pt–Cl bonds] was obtained from the reaction of *cis*-[$PtCl_2(PBu_3)_2$] with $SnCl_4$. When the



cis-[{Pt(μ-Cl)Me(PBu_3)}$_2$] (38 %)
0.4 ppm, J(Pt-P) 4809.5 Hz
trans-[{Pt(μ-Cl)Me(PBu_3)}$_2$] (15 %)
0.2 ppm, J(Pt-P) 4837 Hz
trans-[$PtCl_2(PBu_3)_2$] (14.5 %)
trans-[PtMe(Cl)$(PBu_3)_2$] (7 %)
trans-[PtCl$(SnMe_2Cl)(PBu_3)_2$] (2.5 %)
trans-[PtCl$(SnMeCl_2)(PBu_3)_2$] (26 %)

cis-[{Pt(μ-Cl)Ph(PBu_3)}$_2$] (10 %)
2.8 ppm, J(Pt-P) 4865 Hz
trans -[PtPh(Cl)$(PBu_3)_2$] (5 %)
Platinum starting material (85 %)
No platinum complex containing Pt-Sn bonds

[{Pt(μ-Cl)Et(PBu_3)}$_2$] (30 %)
2.4 ppm, J(Pt-P) 5078 Hz
trans-[$PtCl_2(PBu_3)_2$] (33.5 %)
trans-[PtCl$(SnEt_2Cl)(PBu_3)_2$] (19 %)
trans-[PtCl$(SnEtCl_2)(PBu_3)_2$] (17.5 %)

Scheme 3. The products formed from the reaction of *trans*-[{Pt(μ-Cl)Cl(PBu_3)}$_2$] and $(R_2Sn)_n$ in toluene. For ^{31}P-NMR data of the Pt–Sn complexes, see Table 2.

$SnCl_4$ was added to *trans*-[$PtCl_2(PBu_3)_2$] in toluene a rapid reaction occurred and a white precipitate separated. The solid was dissolved in dichloromethane and the ^{31}P-NMR spectrum recorded to show that two complexes were present, with δ 5.5 ppm; J(PtP) 3657 Hz (78%) and δ 10.6 ppm; J(PtP) 3589 Hz (22%), neither associated with tin satellites. These may be related to a bridge complex present as both *cis*-and *trans*-isomers, but are not [{Pt(μ-Cl)Cl(PBu_3)}$_2$] {*cis*-, δ 0.2 ppm; J(PtP) 3702 Hz and *trans*-, δ 2.6 ppm; J(PtP) 3814 Hz (CH_2Cl_2)} [33]. The yellowish filtrate was shown by ^{31}P-NMR spectroscopy to contain *trans*-[PtCl($SnCl_3$)(PBu_3)$_2$] (Tables 1 and 2) as its parameters were identical to those for *trans*-[PtCl($SnCl_3$)L_2](L = PEt_3 [34] and L = $PCyc_3$ [25]). It is relevant to note that Baird [35] reported that *trans*-[PtH(Cl)(PPh_3)$_2$] and $SnCl_4$ in benzene gave an orange precipitate, which was identified as [$PtCl_2(SnCl_3)_2(PPh_3)_2$], i.e. a Pt(IV) complex. We repeated that reaction in order to examine the ^{31}P-NMR spectrum of the product. When the orange precipitate was isolated and dissolved in dichloromethane, the spectrum revealed the presence of two complexes with parameters: δ 12.9 ppm; J(PtP) 3884 Hz (63%) and δ 16.1 ppm; J(PtP) 3825 Hz (37%). None of the resonances showed tin satellites, although the signal to noise ratios were easily adequate for the detection of such satellites. The parameters could be for *cis*- and *trans*- isomers of a bridged complex, but not *cis*- and *trans*-[{Pt(μ-Cl)Cl(PPh_3)}$_2$] {*cis*-, δ 3.4 ppm; J(PtP) 4004 Hz and *trans*-, δ 5.2 ppm; J(PtP) 4099 Hz} [34]. We cannot account for Baird's results [35], and we could not detect the complex he suggested or, indeed, any complex containing Pt–Sn bonds.

3.4. Reaction of $(R_2Sn)_n$ with platinum(0) complexes

The reactions of $(R_2Sn)_n$ with platinum(0) complexes were examined in the hope of obtaining complexes arising either by ring opening of $(R_2Sn)_n$ to give bis-tin chelation to platinum or by insertion of platinum(0) into Sn–R bonds. It was reported that stable R_2Sn moieties (R = alkyl, aryl or halogen; M = Ge, Sn, Pb) can co-ordinate to Cr, W and Fe [8–10] in the presence of an electron donor solvent (B:), e.g. pyridine or THF (Equation 4).

$$[Cr(CO)_6] + R_2Sn \xrightarrow{B:} [Cr(\underset{\uparrow \atop \ddot{B}}{Sn}R_2)(CO)_5] \qquad (4)$$

Thus we carried out many reactions between platinum(0) complexes and $(R_2Sn)_n$ in various solvents. In the case of [$Pt(C_2H_4)(PPh_3)_2$] and $(Me_2Sn)_6$ or $(Ph_2Sn)_6$ in benzene, the ^{31}P-NMR spectrum recorded after 3 h at room temperature revealed the presence only of the platinum starting material, but when the mixture was heated at reflux for ca. 10 min or put aside for a further ca. 20 h, the ^{31}P-NMR spectrum revealed the presence of, in addition to the unchanged [$Pt(C_2H_4)(PPh_3)_2$], a complex with δ 49.9 ppm and J(PtP) 4463 Hz (30%), which was definitely identified as [$Pt(PPh_3)_3$] [36]; no complexes containing Pt–Sn bonds were observed. Similar results were obtained when either THF or pyridine was used instead of benzene.

When the more reactive complex [$Pt(PEt_3)_4$] was used with $(Me_2Sn)_6$ in toluene, an immediate decomposition, to give a dark brown mixture, occurred, but the ^{31}P-NMR spectrum showed that no complex containing Pt–Sn bonds was formed. When $(Ph_2Sn)_6$ was used instead of $(Me_2Sn)_6$, the ^{31}P-NMR spectrum revealed the presence of three complexes, the first one (17%) being the *trans*-[$PtPh_2(PEt_3)_2$] [26]. The second (22%) and third (30%) complexes (Tables 1 and 2) were identified as *trans*-[PtPh(Sn_2Ph_5)(PEt_3)$_2$] [25] and *cis*-[PtPh(Sn_6Ph_{11})(PEt_3)$_2$], respectively.

An attempt was made to bring $(Ph_2Sn)_6$ into reaction with the more active platinum(0) complex [$Pt(COD)_2$] in order to obtain complexes containing Pt–Sn bonds. A suspension of the reactants was stirred in toluene at room temperature for ca. 2 h, during which it turned yellow–brown. It was filtered through Celite and the filtrate evaporated to dryness. The residual solid was redissolved in dichloromethane and PPh_3 was added. The ^{31}P-NMR spectrum showed that no complex containing Pt–Sn bonds was present and only small singlet peaks (not associated with platinum satellites) were observed.

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