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Journal of Organometallic Chemistry 654 (2002) 21–28

Journal of Organometallic Chemistry

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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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Received 10 December 2001; received in revised form 8 February 2002; accepted 8 February 2002

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

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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.

☆ For Part II of this work, see Ref. [J. Organomet. Chem. 590 (1999) 25].

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PII: S0022-328X(02)01331-1

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.

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

$$[PtX(Cl)L_2] + R_2Sn \rightarrow [PtX(SnR_2Cl)L_2] \tag{2}$$

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):

$$\begin{aligned}&[PtX(Cl)L_2] + R_2Sn \rightarrow [PtX(SnR_2Cl)L_2]\\&\quad \rightarrow [PtL_2] + R_2SnXCl \xrightarrow{\text{fast}} [PtX(SnR_2Cl)L_2]\end{aligned} \tag{3}$$

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

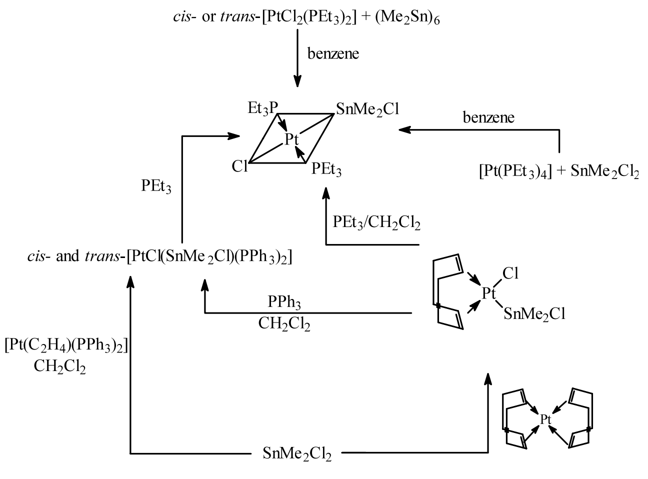
A) When a mixture of *trans*-$[PtCl_2(PBu_3)_2]$ and $(Et_2Sn)_9$ in toluene was stirred with a five-fold excess of $SnMe_2Cl_2$ at room temperature, the ^{31}P-NMR spectrum showed the presence of, in addition to some unreacted platinum starting material, only

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, $n = 9$

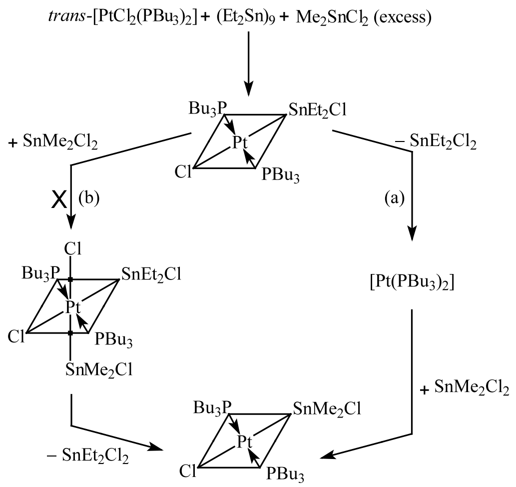
Complex	L	δ (ppm)	^{1}J(PtP) (Hz)	^{2}J(SnP) (Hz)		^{2}J(PP) (Hz)
				^{119}Sn	^{117}Sn	
trans-$(PtCl(SnMe_2Cl)L_2]$ [a]	PEt_3	16.0	2390	137 [f]		
		16.5 [g]	2387	139	133	
	PBu_3	7.3	2376	140	134	
	PPr_3	6.6	2368	137 [f]		
	$PEtPh_2$	19.8	2651	137 [f]		
trans-$(PtCl(SnEt_2Cl)L_2]$ [a]	PEt_3	16.8 [g]	2420	127 [f]		
	PBu_3	8.3	2398	128	123	
	$PEtPh_2$	20.1	2681	127 [f]		
cis-$[PtCl(SnEt_2Cl)L_2]$	$PEtPh_2$	25.7 [c]	2134	2076	1987	
		16.3 [d]	4312	[e]	[e]	12
trans-$[PtMe(SnEt_2Cl)L_2]$ [a]	PEt_3	14.8	2600	[e]	[e]	
trans-$[PtCl(SnPh_2Cl)L_2]$ [a]	PEt_3	14.6 [g]	2318	150	143	
	PBu_3	5.6	2300	149	144	
trans-$[PtPh(SnPh_2Cl)L_2]$ [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-$[PtPh(Sn_2Ph_5)L_2]$ [a]	PEt_3	9.7 [g]	2544	204	195	
cis-$[PtPh(Sn_6Ph_{11})L_2]$ [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-$[PtPh(SnPh_2Cl)L_2]$ [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-$[PtCl(SnMe_2Cl)(PBu_3)_2]$ and no *trans*-$[PtCl(SnEt_2Cl)(PBu_3)_2]$.This is what would be expected for the mechanism above (Eq. (3)), in which Et_2Sn first inserts into Pt–Cl bonds of $[PtCl_2(PBu_3)_2]$ to form $Pt(SnEt_2Cl)$ species and the latter then generates Et_2SnCl_2 with the formation of $[Pt(PBu_3)_2]$, then since $SnMe_2Cl_2$ is more reactive than $SnEt_2Cl_2$, it would selectively add to the Pt(0) complex to give the observed product (Scheme 2a). However, in another experiment, when the complex *trans*-$[PtCl(SnEt_2Cl)(PBu_3)_2]$, prepared as described earlier, was treated with an excess of $SnMe_2Cl_2$ in toluene for 4 h the ^{31}P-NMR spectrum of the solution revealed the presence of only *trans*-$[PtCl(SnMe_2Cl)(PBu_3)_2]$. It is possible that $SnMe_2Cl_2$ added oxidatively to *trans*-$[PtCl(SnEt_2Cl)(PBu_3)_2]$ to give a Pt(IV) intermediate (Scheme 2b) which underwent reductive-elimination of $SnEt_2Cl_2$ to form the Pt(II) complex *trans*-$[PtCl(SnMe_2Cl)(PBu_3)_2]$. Thus, it is also possible that the reaction between *trans*-$[PtCl_2(PBu_3)_2]$ and a



Scheme 1. Methods of preparing *trans*-$[PtCl(SnMe_2Cl)(PEt_3)_2]$.



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).

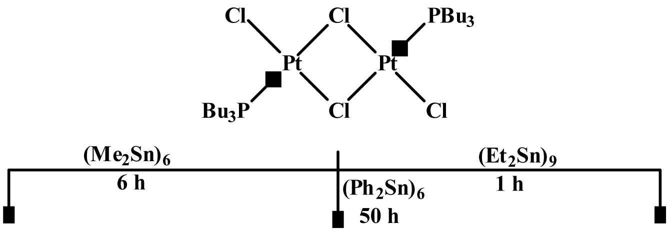
3.3. Reaction of $(R_2Sn)_n$ with bridged platinum complexes

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

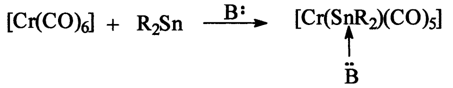
[{Pt(μ-Cl)Et(PBu_3)}$_2$] (30 %)
2.4 ppm, J(Pt-P) 5078 Hz
trans-[$PtCl_2(PBu_3)_2$] (33.5 %)
trans-[PtCl($SnEt_2Cl$)$(PBu_3)_2$] (19 %)
trans-[PtCl($SnEtCl_2$)$(PBu_3)_2$] (17.5 %)

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 $[\{Pt(\mu\text{-}Cl)Cl(PBu_3)\}_2]$ {*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*-$[\{Pt(\mu\text{-}Cl)Cl(PPh_3)\}_2]$ {*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).



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

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.

Acknowledgements

This work was carried out in the School of Molecular Sciences at Sussex University, Brighton BN1 9QJ, UK, in association with Professor C. Eaborn and Dr. A. Pidcock. The author is very grateful to them for their kind help and advice during the work.

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