SHORT PAPER

J. Chem. Research (S),
2003, 101-104

Reactions of the divalent tin compounds R_2M, R = $N(SiMe_3)_2$ or $CH(SiMe_3)_2$ with complexes of the platinum group metals[†]

Talal A.K. Al-Allaf*

Department of Chemistry, College of Basic Sciences, Applied Science University, Amman-11931, Jordan

The stannylenes R_2Sn, (R = $N(SiMe_3)_2$ or $CH(SiMe_3)_2$) insert into M–X bonds of complexes $[MX_2L_2]$ to give new complexes of the general formula $[MX(SnR_2X)L_2]$, (M = Pt, Pd, Ni; X = Cl, N_3, NO_2; L = PEt_3, PBu_3, DPPE). They also insert into Pt–Cl bonds of the bridged complexes $[\{Pt(\mu\text{-}Cl)Cl(L)\}_2]$, to give the new bridged complexes$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(L)\}_2]$, (R = $N(SiMe_3)_2$, L = PEt_3, PBu_3, PMe_2Ph, PPh_3), in which the bridge remained uncleaved. In one reaction of the stannylene R_2Sn, where R = $CH(SiMe_3)_2$, the bridged complex $[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]$ undergoes cleavage followed by migration of Cl to give $[PtCl(SnR_2Cl)(\eta^2\text{-}SnR_2)(PEt_3)]$. Further, the bridged complex $[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]$, (R = $N(SiMe_3)_2$), with the neutral ligands L′, (L′ = PPh_3, pyridine or $AsPh_3$), undergoes bridge cleavage to form the complexes $[PtCl(SnR_2Cl)(PEt_3)(L')]$. The reaction of the stannylene R_2Sn, (R = $N(SiMe_3)_2$) with the platinum(0) complexes $[Pt(C_2H_4)(PPh_3)_2]$ and $[Pt(COD)_2]$, COD = 1,5-cyclooctadiene is described. The complexes obtained have been characterised mainly by ^{31}P NMR spectroscopy and elemental analysis.

Keywords: stannylenes, platinum group complexes, ^{31}P NMR studies

Introduction

The stable stannylenes R_2Sn, (R = $N(SiMe_3)_2$) or $CH(SiMe_3)_2$), were previously shown to insert into the Pt–Cl bonds of the bridged complex *trans*-$[\{Pt(\mu\text{-}Cl)Cl(PEt_3)\}_2]$ to give *trans*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]$, (R = $N(SiMe_3)_2$ or $[PtCl(SnR_2Cl)(\eta^2\text{-}SnR_2)(PEt_3)]$, R = $CH(SiMe_3)_2$); these products were characterised by elemental analysis and Mössbauer spectroscopy, but their ^{31}P and ^{119}Sn NMR spectra were not recorded.[1-4] In a preliminary communication, we reported the crystal structures of platinum and palladium complexes derived from the reaction of R_2Sn, (R = $N(SiMe_3)_2$) and the complexes *trans*-$[\{Pt(\mu\text{-}Cl)Cl(PEt_3)\}_2]$, $[Pt(COD)_2]$[5] and $[PdCl_2(COD)]$.[6] In a further communication,[7] the crystal structures of the clusters obtained from the reaction of the homoleptic complexes $[M\{M`(NR_2)_2\}_3]$,( M = Pt or Pd, M`= Sn or Ge and R = $SiMe_3$) and CO were reported. These and other similar studies on R_2M, (M = Ge, Sn or Pb; R = $N(SiMe_3)_2$ or $CH(SiMe_3)_2$), were described in a comprehensive review.[8]

In continuation of our studies of complexes having group 14 elements attached to the noble metals,[4–10] we present here a full account consisting of the reactions of R_2Sn, (R = $N(SiMe_3)_2$ or $CH(SiMe_3)_2$), with various Pt(II), Pd(II), Ni(II) and Pt(0) complexes.

Experimental

General: Solvents were dry and oxygen–free. Manipulations were carried out under dry nitrogen gas or argon by standard Schlenk techniques. The NMR spectra were recorded using Bruker (^{119}Sn at 134 MHz with $SnMe_4$ as external reference) and Jeol (^{31}P at 40.5 MHz with TMP as external reference and chemical shifts were corrected to H_3PO_4 as a reference standard) instruments. The IR spectra were recorded as Nujol mulls between CsI discs on a Perkin-Elmer 457 or 597 instrument. Elemental analyses were carried out at the University of Sussex.

Starting materials: The stannylenes[2] R_2Sn, (R = $N(SiMe_3)_2$, $CH(SiMe_3)_2$) and the transition metal complexes $[PtCl_2L_2]$ (L = PEt_3, PBu_3, PMe_2Ph, PPh_3), cis-$[PtX_2(PBu_3)_2]$ (X = NO_2, N_3), $[MCl_2(DPPE)]$ (M = Ni, Pd, Pt), $[\{Pt(\mu\text{-}Cl)Cl(L)\}_2]$ (L = PEt_3, PBu_3, PMe_2Ph, PPh_3), $[PtCl_2(COD)]$, $[Pt(C_2H_4)(PPh_3)_2]$ and $[Pt(COD)_2]$ were prepared as previously reported.[11-19]

Preparation of complexes

cis-$[PtCl(Sn\{N(SiMe_3)_2\}_2Cl)(PEt_3)_2]$ **(1):** The stannylene $Sn\{N(SiMe_3)_2\}_2$ (0.3 g, 0.68 mmol) was added to a suspension of *cis*-$[PtCl_2(PEt_3)_2]$ (0.2 g, 0.40 mmol) in a mixture of *n*-hexane (20 ml) and benzene (10 ml). The mixture was stirred for *ca* 1 h then filtered through Celite and the filtrate evaporated to dryness. The residual yellow solid was recrystallised from benzene/*n*-hexane to give white crystals, which were washed with *n*-hexane and dried *in vacuo* for several hours.

The complex $[PtCl(Sn\{CH(SiMe_3)_2\}_2Cl)(PEt_3)_2]$ **(2)** was similarly prepared as a mixture of *cis*- and *trans*-isomers.

cis-$[PtN_3(Sn\{N(SiMe_3)_2\}_2N_3)(PBu_3)_2]$ **(3):** The stannnylene $Sn\{N(SiMe_3)_2\}_2$ (0.1 g, 0.23 mmol) was added to a solution of *cis*-$[Pt(N_3)_2(PBu_3)_2]$ (0.10 g, 0.15 mmol) in toluene (5 ml) and the mixture was allowed to stand for *ca* 30 min, then filtered through Celite. The pale yellow solution was reduced in volume to *ca*1 ml and *n*-hexane was added to the point of turbidity. Colourless crystals of the product separated after 12 h at –10 °C. These were washed with *n*-hexane and dried *in vacuo* for several hours.

White crystals of *cis*-$[Pt(NO_2)(Sn\{N(SiMe_3)_2\}_2NO_2)(PBu_3)_2]$ **(4)** were prepared analogously.

$[PtCl(Sn\{N(SiMe_3)_2\}_2Cl)(DPPE)]$ **(5):** The stannylene $Sn\{N(SiMe_3)_2\}_2$ (0.11 g, 0.25 mmol) was added to a suspension of $[PtCl_2(DPPE)]$ (0.15 g, 0.22 mmol) in toluene (10 ml). The mixture was stirred for *ca* 2 h, then filtered through Celite. The filtrate was concentrated to *ca* 1 ml and *n*-hexane was added to the point of turbidity. Pale yellow crystals separated out after 12h at –10 °C, and these were washed with *n*-hexane and dried *in vacuo* for several hours.

The complexes $[MCl(Sn\{N(SiMe_3)_2\}_2Cl)(DPPE)]$ were prepared similarly as yellow–orange crystals (M = Pd) **(6)** or a red powder (M = Ni) **(7)**.

cis-$[PtCl(Sn\{N(SiMe_3)_2\}_2Cl)(PPh_3)(PEt_3)]$ **(8):** A solution of *trans*-$[\{Pt(\mu\text{-}Cl)(Sn\{N(SiMe_3)_2\}_2Cl)(PEt_3)\}_2]$ (0.11g, 0.067 mmol) in CD_2Cl_2 (0.6 ml) was placed in an 8 mm NMR tube and PPh_3 (0.04 g, 0.076 mmol) was added. The ^{31}P NMR spectrum was recorded after *ca* 10 min. The mixture was filtered through Celite; the filtrate concentrated, and *n*-hexane added. The solution was kept at –10 °C for *ca* 12 h to yield fine orange crystals, which were washed with *n*-hexane and dried *in vacuo* for several hours.

The reaction between *trans*-$[\{Pt(\mu Cl)(Sn\{N(SiMe_3)_2\}_2Cl)(PEt_3)\}_2]$ (0.1 g, 0.061 mmol) and a slight excess of pyridine in dichloromethane (0.6 ml) was carried out similarly. The main product *cis*-$[PtCl(Sn\{N(SiMe_3)_2\}Cl)(Py)(PEt_3)]$ **(9)**, was isolated from a mixture containing both the *cis*- and *trans*- isomers by using their differential solubility in CH_2Cl_2/ *n*-hexane.

---

*To receive any correspondence. E-mail:talal_al_allaf@hotmail.com

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

The same procedure for the reaction between *trans*-[{Pt(μ-Cl)(Sn{N(SiMe$_3$)$_2$}$_2$Cl) (PEt$_3$)}$_2$] (0.065 g, 0.040 mmol) and AsPh$_3$ (0.025 g, 0.082 mmol) in dichloromethane (0.6 ml) yielded *cis*-[PtCl(Sn{N(SiMe$_3$)$_2$}$_2$Cl)(AsPh$_3$)(PEt$_3$)] **(10)** from a mixture containing both isomers.

trans-[{Pt(μ-Cl)(Sn{N(SiMe$_3$)$_2$}$_2$Cl)(PEt$_3$)}$_2$] **(11):** This was prepared using a method similar to that published previously:[4]

The stannylene Sn{N(SiMe$_3$)$_2$}$_2$ (0.3 g, 0.68 mmol) was added to a suspension of [{Pt(μ-Cl) Cl(PEt$_3$)}$_2$] (0.2g, 0.26 mmol) in *n*-hexane (20 ml). The mixture was stirred for *ca* 30 min, by which time almost all the starting materials had dissolved. The mixture was filtered through Celite and the yellow filtrate was reduced in volume to *ca* 4 ml and kept at – 25 C° to give yellow crystals. Recrystallisation from toluene/*n*-hexane gave yellow cubic crystals, which were washed with *n*-hexane and dried *in vacuo* for several hours. The yellow, crystalline complex *trans*-[{Pt(μ-Cl)(Sn{CH(SiMe$_3$)$_2$}Cl) (PEt$_3$)}$_2$] **(12)** was prepared in a similar way to that used for the Sn{N(SiMe$_3$)$_2$}$_2$ analogue.

The corresponding complexes of the stannylene Sn{N(SiMe$_3$)$_2$}$_2$ with PBu$_3$ **(13)**, PMe$_2$Ph **(14)** or PPh$_3$ **(15)** in place of PEt$_3$ were prepared similarly.

trans-[{Pt(μ-Cl)(SnCl$_3$)(PEt$_3$)}$_2$] **(16):** An excess of SnCl$_2$ (0.25 g, 1.3 mmol) was added to a solution of [{Pt(μ-Cl) Cl(PEt$_3$)}$_2$] (0.20 g, 0.26 mmol) in dichloromethane (10 ml) and the mixture was stirred for *ca* 6 h then filtered through Celite. The yellow filtrate was concentrated to *ca* 2 ml and *n*-hexane was added to the point of turbidity. After *ca* 12 h at –10 ºC, yellow crystals of the product had separated, and these were washed with *n*-hexane and dried in vacuo for several hours.

Results and discussion

Reactions of R$_2$Sn compounds {R = N(SiMe$_3$)$_2$ or CH(SiMe$_3$)$_2$}: 1. With platinum(II) complexes: The reactions of a slight excess of Sn{N(SiMe$_3$)$_2$}$_2$ with *cis*-[PtX$_2$L$_2$] (X= Cl, L= PEt$_3$; X = N$_3$ or NO$_2$ and L = PBu$_3$) in hexane or toluene resulted in insertion of the stannylene into the Pt–X bonds as shown by the ^{31}P NMR spectra of the products. Similarly, the reactions of Sn{N(SiMe$_3$)$_2$}$_2$ with the complexes [MCl$_2$(DPPE)] (M = Ni, Pd, Pt) led to complexes containing M–Sn bonds via insertion of the stannylene into M-Cl bonds.

In contrast, the reaction of Sn{CH(SiMe$_3$)$_2$}$_2$ with *cis*-[PtCl$_2$(PEt$_3$)$_2$] in 1:1 molar ratio in toluene-d$_8$ yielded a mixture of three complexes: *cis*-[PtCl(Sn- {CH(SiMe$_3$)$_2$}$_2$Cl)-(PEt$_3$)$_2$] **(2)** (61%), *trans*-[PtCl(Sn{CH(SiMe$_3$)$_2$}$_2$Cl)(PEt$_3$)$_2$] (20%) and the *trans*-[PtCl$_2$(PEt$_3$)$_2$] (19%). The ^{31}P NMR parameters of each of these complexes are listed in Table 1 and the physical properties of some selected complexes are listed in Table 2.

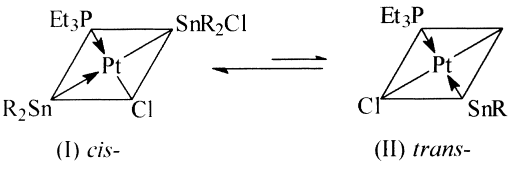
The reactions of Sn{N(SiMe$_3$)$_2$}$_2$ with [{Pt(μ-Cl)Cl(L)}$_2$] (L = PEt$_3$, PBu$_3$, PMe$_2$Ph or PPh$_3$) were studied. With L = PEt$_3$, the reaction was carried out with 1:2 or 1:4 molar ratios of [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] and Sn{N(SiMe$_3$)$_2$}$_2$ in hexane at room temperature for *ca* 30 min. After removal of the solvent, the residual solid was dissolved in benzene-d$_6$ or toluene-d$_8$ and the ^{31}P NMR spectrum recorded. This revealed the presence of *cis*-[{Pt(μ-Cl)(Sn{N(SiMe$_3$)$_2$}$_2$Cl)(PEt$_3$}$_2$] **(11)** and its *trans*-isomer in 70:30 ratio and both resonances had associated with tin satellites (Table 1).This complex was previously prepared[4] and it is mentioned here for two reasons, first to study its ^{31}P and Sn^{119} NMR and to use it as a precursor for bridge cleavage by neutral ligands. When the mixture was kept for a longer time or was heated, the ^{31}P NMR spectrum showed that only the *trans*-isomer was present. This was crystallised from toluene/hexane to give yellow cubic crystals. The crystal structure was determined.[5]

However, the complex *trans*-[{Pt(μ-Cl)(Sn{N(SiMe$_3$)$_2$}$_2$Cl) (PEt$_3$)}$_2$] **(11)** showed a large tin–platinum coupling constant of 28, 760 Hz. The complex [{Pt(μ-Cl)(SnCl$_3$)(PEt$_3$)}$_2$] **(16)** was prepared by treating [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] with an excess of SnCl$_2$ in dichloromethane, to give a mixture of *cis*-(25%) and *trans*-(47.5%) [{Pt(μ-Cl)(SnCl$_3$)(PEt$_3$)}$_2$] together with unreacted platinum starting material (27.5%). When the mixture was kept for a further 6 h, the ^{31}P NMR spectrum showed the presence of the *trans*-isomer only. This was isolated as yellow crystals. The ^{119}Sn NMR spectrum in CD$_2$Cl$_2$ showed $J(^{119}\text{Sn}–^{195}\text{Pt})$ to be 35,388 Hz, *c.f.*, 35,034 Hz in [{Pt(μ-Cl)Cl(SnCl$_3$)}$_2$].[20]

The reaction of Sn{CH(SiMe$_3$)$_2$}$_2$ with [{Pt(μ-Cl)-Cl(PEt$_3$)}$_2$] took a different course from that involving Sn{N(SiMe$_3$)$_2$}$_2$. Starting from a 4:1 molar ratio of Sn to Pt, after *ca* 30 min, the ^{31}P NMR spectrum of the product in benzene-d$_6$ revealed the presence of only one phosphorus-containing species. The coupling J(PtP) 4500 Hz can be clearly assigned to P *trans*- to the more electronegative group, *i.e.*, Cl. The two sets of tin satellites; ^2J(SnPtP) 129.4 and 34.2 Hz obviously come from tin in *cis*-relationship to P. Thus the suggested structure is *cis*-[PtCl(SnR$_2$Cl)(η^2-SnR$_2$)(PEt$_3$)], {R = CH(SiMe$_3$)$_2$}**(17)**, and the two SnPtP couplings arise from the presence of two different tin ligands, *i.e.*, SnR$_2$ and SnR$_2$Cl, with coupling constants much lower than those expected. Similar results were obtained with *cis*-[PtCl(SnR$_2$Cl)(PEt$_3$)$_2$], (R = CH(SiMe$_3$)$_2$) **(2)** for which ^2J(SnPtP) is 76 Hz (Table 1); this is probably due to the lower electronegative of CH(SiMe$_3$)$_2$ than of N(SiMe$_3$)$_2$. We believe that the larger coupling constant (129.4 Hz) is associated with SnR$_2$, in which the electron density on Sn is higher than that in SnR$_2$Cl (34.2 Hz). In a separate experiment on a larger scale of the reactants [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] and Sn{CH(SiMe$_3$)$_2$)} the ^{31}P NMR spectrum revealed, in addition to the main product, *cis*-[PtCl(SnR$_2$Cl)(η^2-SnR$_2$)(PEt$_3$)] **(17)** (55%), the presence of a resonance (45%) with the parameters δ 20.5 ppm and J(PtP) 2490 Hz (in benzene) and a signal-to-noise ratio too low for observation of tin satellites. The possibility that this resonance was due to *trans*-[PtCl$_2$(PEt$_3$)$_2$] {δ 12.0 ppm; *J*(PtP) 2400 Hz}[21] or *trans*-[PtCl(SnR$_2$Cl)(PEt$_3$)] {δ 11.8 ppm; J(PtP) 2300 Hz (Table 1)} was excluded. We believe that this secondary complex is (II), formed by isomerization of the main product (Eqn 1).

The *trans*-isomer was first observed by Lappert *et al.*[2,3] and identified from its elemental analysis and IR, ^{1}H NMR and Mössbauer spectra only.

When a 2:1 molar ratio of Sn{CH(SiMe$_3$)$_2$}$_2$ and [{Pt(μ-Cl)Cl(PEt$_3$)}$_2$] was used the ^{31}P NMR spectrum indicated the presence of three complexes, judged to be *trans*-[{Pt(μ-Cl)(Sn{CH(SiMe$_3$)$_2$}$_2$Cl)(PEt$_3$)}$_2$] **(12)** (28.5%), *cis*-[PtCl(Sn{CH(SiMe$_3$)$_2$}$_2$Cl)(η^2-Sn{CH(SiMe$_3$)$_2$}$_2$)(PEt$_3$)] **(17)** (43%) and *trans*-[PtCl$_2$(PEt$_3$)$_2$] (28.5% proportion) (for the parameters, see Table 1). It is possible that Sn{CH(SiMe$_3$)$_2$}$_2$ was first inserted into Pt–Cl bonds to give the bridged complex (I) with the latter then undergoing bridge opening and migration of Cl to give complex(II) (Eqn 2) and this probably explains why earlier workers obtained a reduced yield of complex(I) when they used 2:1 molar ratio of R$_2$Sn and the starting bridged complex.[4]



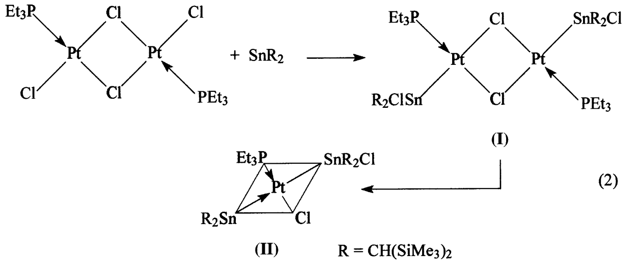
(1)

Complex (**I**) was isolated as yellow crystals from the mixture by making use of its low solubility in hexane; its elemental analysis is satisfactory (Table 2). When we attempted to isolate complex (**II**) from the mixture by keeping the solution for a long time to allow build up of crystals, an X-ray diffraction study revealed that complex (**II**) was unstable in solution and had broken down to give (SnR$_2$Cl)$_2$.[5]

Table 1 $^{31}P\text{-}\{^1H\}$ NMR data δ (ppm) and *J*(Hz) for complexes containing R_2Sn species, R = $N(SiMe_3)$ or $CH(SiMe_3)_2$

Seq	Complex	R	Proportion /%[c]	δ $P^{(A)}$ trans- to Sn	$^1J(PtP^A)$	$^2J(SnP^A)$ ^{119}Sn	$^2J(SnP^A)$ ^{117}Sn	δ $P^{(B)}$ cis- to Sn	$^1J(PtP^B)$	$^2J(SnP^B)$ $^{119}Sn/^{117}Sn$	$^2J(P^AP^B)$
(1)	*cis*-$[PtCl(SnR_2Cl)(PEt_3)_2]^a$	$N(SiMe_3)_2$	100	18.0	2258	3728	3550	3.7	3777	187	15
(2)	*cis*-$[PtCl(SnR_2Cl)(PEt_3)_2]^a$	$CH(SiMe_3)_2$	61	16.8	1946	2530	2419	3.7	4133	76	12
	trans-$[PtCl(SnR_2Cl)(PEt_3)_2]^a$	$CH(SiMe_3)_2$	20					11.8	2300	–	
(3)	*cis*-$[PtN_3(SnR_2N_3)(PBu_3)_2]^a$	$N(SiMe_3)_2$	90	14.0	2251	3618	3432	–7.4	3413	233	15
(4)	*cis*-$[Pt(NO_2)\{SnR_2(NO_2)\}(PBu_3)_2]^a$	$N(SiMe_3)_2$	100	10.5	2451	2911	2790	–19.3	2937	239	17
(5)	$[PtCl(SnR_2Cl)(DPPE)]^a$	$N(SiMe_3)_2$	100	50.7	2293	3767	3601	37.7	3794	151	5
(6)	$[PdCl(SnR_2Cl)(DPPE)]^a$	$N(SiMe_3)_2$	100	49.1	–	4334	4140	53.5	–	144	29
(7)	$[NiCl(SnR_2Cl)(DPPE)]^a$	$N(SiMe_3)_2$	100	49.2	–	3123	2979	52.5	–	701	9
(8)	*cis*-$[PtCl(SnR_2Cl)(PPh_3)(PEt_3)]^b$	$N(SiMe_3)_2$	100	28.5	2315	3867	3682	5.0	3735	147	15
(9)	*cis*-$[PtCl(SnR_2Cl)(py)(PEt_3)]^b$	$N(SiMe_3)_2$	55					–0.7	3359	206	
	trans-$[PtCl(SnR_2Cl)(py)(PEt_3)]^b$	$N(SiMe_3)_2$	26					–4.1	3252	–	
(10)	*cis*-$[PtCl(SnR_2Cl)(AsPh_3)(PEt_3)]^b$	$N(SiMe_3)_2$	58					6.2	3748	154	
	trans-$[PtCl(SnR_2Cl)(AsPh_3)(PEt_3)]^b$	$N(SiMe_3)_2$	26					5.5	3359	–	
(11)	*cis*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]^a$	$N(SiMe_3)_2$	70					8.0	4109	186	
	trans-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]^a$	$N(SiMe_3)_2$	30					6.8	3960	170	
(12)	*trans*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]^a$	$CH(SiMe_3)_2$	100					7.0	4304	80	
(13)	*trans*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PBu_3)\}_2]^a$	$N(SiMe_3)_2$	100					1.0	3962	169	
(14)	*cis*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PMe_2Ph)\}_2]^a$	$N(SiMe_3)_2$	35					–19.8	4092	177	
	trans-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PMe_2Ph)\}_2]^a$	$N(SiMe_3)_2$	65					–24.2	4241	185	
(15)	*cis*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PPh_3)\}_2]^a$	$N(SiMe_3)_2$	35					10.2	4151	–	
	trans-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PPh_3)\}_2]^a$	$N(SiMe_3)_2$	65					14.1	4417	170	
(16)	*cis*-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]^b$	Cl	25					11.9	3796	–	
	trans-$[\{Pt(\mu\text{-}Cl)(SnR_2Cl)(PEt_3)\}_2]^b$	Cl	48					13.0	3467	235	
(17)	*cis*-$[PtCl(SnR_2Cl)(\eta^2\text{-}SnR_2)(PEt_3)]^a$	$CH(SiMe_3)_2$	55					12.9	4497	129(SnR_2) 34(SnR_2Cl)	
	trans-$[PtCl(SnR_2Cl)(\eta^2\text{-}SnR_2)(PEt_3)]^a$	$CH(SiMe_3)_2$	45					15.5	2490	–	

[a] Data obtained with benzene or toluene as solvent and H_3PO_4 as external reference.
[b] Data obtained with dichloromethane as solvent and H_3PO_4 as external reference.
[c] Proportions of complexes were inferred directly from the relative peak areas in the $^{31}P\text{-}\{^1H\}$NMR spectra.



It is clear that the reaction of R_2Sn, R = $N(SiMe_3)_2$ or $CH(SiMe_3)_2$, with the complexes $[PtCl_2L_2]$ and $[\{Pt(\mu\text{-}Cl)Cl(L)\}_2]$ involves direct insertion of R_2Sn into Pt–Cl bonds. This is in contrast to our previous conclusion that the stannylenes R_2Sn, released from the cyclic tin compounds $(R_2Sn)_n$, (R = Me or Ph, *n* = 6; R = Et, *n* = 9) upon exposure to light react with platinum complexes in a different manner[22]. The reactions of *trans*-$[\{Pt(\mu\text{-}Cl)(Sn\{N(SiMe_3)_2\}_2Cl)(PEt_3)\}_2]$ with the neutral species PPh_3, pyridine and $AsPh_3$ were carried out in dichloromethane to allow determination of the ^{31}P NMR spectra of the products.

The results showed that bridge cleavage was involved in all of these reactions to give in almost all cases a mixture of *cis*- and *trans*- isomers of $[PtCl(Sn\{N(SiMe_3)_2\}_2Cl)(PEt_3)L]$ (L = PPh_3, py, $AsPh_3$), *i.e.*, complexes **(8)**,**(9)** and **(10)**, respectively. When L was PPh_3 only the *cis*-isomer was present in the solution. Its ^{31}P NMR parameters showed signals from two different phosphorus nuclei, with parameters of δ 28.0 ppm, *J*(PtP) 2315.3Hz and δ 5.0 ppm, *J*(PtP) 3735.3 Hz, respectively. The upfield resonance (δ 28.0 ppm) is due to PPh_3 *trans*- to Sn, while the downfield resonance (δ 5.0 ppm) is due to PEt_3 *trans*- to Cl {as can be seen from the large J(PtP) coupling; 3735 Hz}. Both resonances were associated with tin satellites and were clearly resolved.

The other complexes with L = pyridine and $AsPh_3$ were similarly identified by ^{31}P NMR spectroscopy (Table 1).

2. *With platinum(0) complexes:* When the reaction of a slight excess of $Sn\{N(SiMe_3)_2\}_2$ with the Pt(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ in toluene at room temperature was carried out, the ^{31}P NMR spectrum showed broad lines mainly from one product along with signals from some unchanged platinum starting material. When a similar reaction was carried out at –70°C and the ^{31}P NMR spectrum recorded at – 50°C, the broad line was sharper. The parameters, δ –86 ppm and *J*(PtP) 4958 Hz are attributed to a platinum–phosphine cluster, and no resonances associated with tin satellites were observed, although signal to noise ratio was high enough for such observation.

In contrast, the more convenient platinum(0) starting material, $[Pt(COD)_2]$ reacts with an excess of R_2Sn, (R = $N(SiMe_3)_2$) in toluene to give pale orange crystals identified by X-Ray diffraction study as $[Pt(SnR_2)_3]$.[5]

Later studies of the corresponding reactions of $M'\{N(SiMe_3)_2\}_2$, (M′ = Ge or Sn) with platinum and palladium complexes showed that the homoleptic complexes $[M(M'\{N(SiMe_3)_2\}_2)_3]$, M = Pt or Pd were formed.[23]

An unsuccessful attempt was made to prepare the homoleptic complex $[Pt\{Pb(NR_2)_2\}_3]$, (R = $SiMe_3$), from the reaction of $Pb(NR_2)_2$ with $[Pt(COD)_2]$ in toluene at 25°C; the reaction gave a brown solution with a black solid. In a separate experiment the reaction mixture was shaken vigorously while the temperature was maintained between –70 and –50°C for few minutes, then kept at –50°C for *ca* 2h to give yellow crystals. These were very unstable and underwent rapid decomposition to a white solid above –30°C. No further studies on this complex were carried out.

No resonance from a complex containing Pt–Pb bonds was revealed by ^{31}P NMR spectroscopy when a mixture of $Pb(NR_2)_2$, (R = $SiMe_3$), and either *cis*-$[PtCl_2(PEt_3)_2]$ or *cis*-$[Pt(N_3)_2(PBu_3)_2]$ in toluene was kept for *ca* 2 days. A previous study showed that a complex containing Pt-Pb bonds could be obtained from the reaction of $Pb(NR_2)_2$ with the bridged complex $[\{Pt(\mu\text{-}Cl)Cl(PEt_3)\}_2]$ in hexane.[24]

Table 2 Characterisation data for selected complexes containing R$_2$Sn species, R = N(SiMe$_3$)$_2$ or CH(SiMe$_3$)$_2$

Seq.	Complex	R	Colour	m.p. /°C	Analysis: Found (calc.)%			IR data/cm^{-1}			^{119}Sn NMR data (δ/ppm, *J*/Hz)		
					C	H	N	$\nu_{(Sn-Cl)}$	$\nu_{(Sn-N)}$	$\nu_{(Pt-Cl)}$	δSn	*J*(SnPt)	^{2}*J*(SnPtP)
(1)	*cis*-[PtCl(SnR$_2$Cl)(PEt$_3$)$_2$]	N(SiMe$_3$)$_2$	white	156–158	30.70 (30.60)	6.90 (7.00)	3.00 (3.00)	282	360	390			
(3)	*cis*-[PtN$_3$(SnR$_2$N$_3$)(PBu$_3$)$_2$]^a	N(SiMe$_3$)$_2$	Colourless	126–140	38.90 (38.50)	7.90 (8.00)	9.90 (10.00)	–	365				
(5)	[PtCl(SnR$_2$Cl)(DPPE)]	N(SiMe$_3$)$_2$	pale yellow	88	41.30 (41.35)	5.15 (5.40)	2.50 (2.54)	285	360	310			
(6)	[PdCl(SnR$_2$Cl)(DPPE)]	N(SiMe$_3$)$_2$	yellow-orange	130–138	45.00 (45.00)	5.80 (5.90)	2.60 (2.75)	280	360	–			
(11)	*trans*-[{Pt(μ-Cl)(SnR$_2$Cl)(PEt$_3$)}$_2$]^b	N(SiMe$_3$)$_2$	yellow	154–156	26.20 (26.20)	6.00 (6.20)	3.60 (3.40)	285	360	–	–395	28,760^b	171
(12)	*trans*-[{Pt(μ-Cl)(SnR$_2$Cl)(PEt$_3$)}$_2$]	CH(SiMe$_3$)$_2$	pale yellow	152	29.55 (29.25)	6.40 (6.45)		290					
(13)	*trans*-[{Pt(μ-Cl)(SnR$_2$Cl)(PBu$_3$)}$_2$]	N(SiMe$_3$)$_2$	yellow	158–160	31.90 (31.80)	7.00 (6.95)	2.95 (3.10)	295	360	–			
(15)	*trans*-[{Pt(μ-Cl)(SnR$_2$Cl)(PPh$_3$)}$_2$]	N(SiMe$_3$)$_2$	yellow-brown	136	37.30 (37.20)	5.30 (5.40)	2.90 (2.80)	304	360	–			
(16)	*trans*-[{Pt(μ-Cl)(SnR$_2$Cl)(PEt$_3$)}$_2$]	Cl	yellow	170–172	13.00 (12.90)	2.70 (2.70)		327, 350, 330			–384	35, 388^c	244

^{a}IR The signals from ν (Sn–N$_3$) and ν (Pt–N$_3$) are 320 and 390 cm^{-1}, respectively.
^{b}Data obtained with toluene-d$_8$ as solvent, melting point and elemental analysis of the complex are closely similar to those reported^4.
^{c}Data obtained with CD$_2$Cl$_2$ as solvent.

This work was carried out in the School of Molecular Sciences, Sussex University in association with Professor Michael F. Lappert . The author is very grateful to him for his kind help and valuable advice during the work.

Received 15 April 2002; accepted 20 July 2002
Paper 02/1324

References

1 M.F. Lappert and P.P. Power, *Adv. Chem. Ser. Am. Chem. Soc. Washington*, 1976 , **157**, 70.
2 (a) P.T. Davidson, D.H. Harris and M.F. Lappert, *J. Chem. Soc., Dalton Trans.* 1976, 2268; (b) J. D. Cotton, P. J. Davidson and M.F. Lappert, *J.Chem.Soc. Dalton Trans*., 1976, 2275.
3 J.D. Cotton, P.J. Davidson, M.F. Lappert, J.D. Donaldson and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1976, 2286.
4 M.F. Lappert and P.P. Power, *J. Chem. Soc. Dalton Trans.*, 1985, 51.
5 T.A.K. Al-Allaf, C. Eaborn, P.B. Hitchcock, M.F. Lappert and A. Pidcock, *J.Chem.Soc., Chem. Commun.*, 1985, 548.
6 P.B. Hitchcock, M.F. Lappert and M.C. Misra, *J.Chem.Soc., Chem.Commun.*, 1985, 863.
7 G.K. Campbell, P.B. Hitchcock, M.F. Lappert and M.C. Misra, *J. Organomet. Chem.*, 1985, **289**, C1.
8 M.F. Lappert and R.S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267.
9 T.A.K. Al-Allaf, *Asian J. Chem.*,1999, **11**, 348, and refs therein.
10 T.A.K. Al-Allaf, *J.Organomet. Chem.*, 1999, **590**, 25, and refs therein.
11 B.G. Segal, M. Kaplan and G.K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191
12 G.A. Bowmaker, P.D.W. Boyd, G.K. Campbell, J.M. Hope and R.L. Martin, *Inorg. Chem*.,1982, **21**, 1152.
13 A.C. Smithies, M. Rycheck and M. Orchin, *J.Organomet. Chem.*, 1968, **12**,199.
14 J. Chatt and G.A. Rowe, *Nature*, 1961, **191**, 1191.
15 K.A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **299**, 225.
16 L. Malatesta and C. Cariello, *J. Chem. Soc*., 1958, 2323.
17 J.X. Mc Dermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
18 C.D. Cook and G.S. Jouhal, *J. Am. Chem. Soc*., 1968, **90**, 1464.
19 J.L. Spencer, *Inorg. Synth*.,1979, **19**, 213.
20 P.S. Pregosin, *International Conference on the Chemistry of Platinum Group Metals*; 19-24 July, 1981, Bristol, UK.
21 S.O. Grim, R.L. Keiter and W. McFarlane, *Inorg. Chem*., 1967, **6**, 1133.
22 T.A.K. Al-Allaf, *J. Organomet. Chem*., 2002, **654**, 21.
23 M.C. Misra, PhD thesis, Sussex University, 1986.
24 P.P. Power, PhD thesis, Sussex University, 1977.