

Reactions of organotin(IV) compounds with platinum complexes Part II. Oxidative addition of $\text{SnR}_x\text{Cl}_{4-x}$ to $[\text{Pt}(\text{COD})_2]$ and subsequent reactions with tertiary phosphines[☆]

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Abstract

Organotin(IV) compounds $\text{SnR}_x\text{Cl}_{4-x}$ ($\text{R} = \text{Me}, \text{Ph}; x = 4-0$) add oxidatively to $[\text{Pt}(\text{COD})_2]$ ($\text{COD} = \text{cycloocta-1,5-diene}$) to yield platinum(II) complexes in which Pt has inserted into the Sn–Cl or Sn–R bonds, displacing one COD entity. The new complexes react with tertiary phosphines, e.g. PEt_3 , PPh_3 , $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (DPPE) at or below room temperature with displacement of the remaining COD. Some of the resulting platinum–phosphine complexes, e.g. *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$, *cis*- or *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ cannot be prepared by the direct reaction between $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ or $[\text{Pt}(\text{PPh}_3)_3]$ and SnMe_4 or SnMe_3Cl , respectively, showing the advantage of this method. Both the COD complexes and their corresponding phosphine complexes were characterised by physical and spectroscopic methods. The thermodynamic stabilities of the complex $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$, its corresponding phosphine complex, *cis*- and *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$, and the complex *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ were studied. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organotin complexes; Platinum complexes; Cyclooctadiene complexes; Phosphine complexes

1. Introduction

In a previous paper [1], the oxidative addition of $\text{SnR}_x\text{Cl}_{4-x}$ compounds to $\text{Pt}(0)$ –phosphine complexes was surveyed. $\text{Pt}(0)$ complexes other than those containing phosphines, e.g. $[\text{Pt}(\text{COD})_2]$ ($\text{COD} = \text{cycloocta-1,5-diene}$) were first studied by Stone and co-workers [2], in which RX compounds ($\text{R} = \text{organic species}, \text{X} = \text{Cl or Br}$) add oxidatively to $[\text{Pt}(\text{COD})_2]$ to give $[\text{PtRX}(\text{COD})]$ complexes. The remaining COD can be replaced by other neutral ligands, e.g. tertiary phosphines and this was reported by Eaborn et al. [3]. The available literature provides no examples of the oxidative addition of organotin(IV) compounds to $[\text{Pt}(\text{COD})_2]$. The present paper describes the products obtained from the reaction of $\text{SnR}_x\text{Cl}_{4-x}$ ($\text{R} = \text{Me or Ph and } x = 4-0$) with $[\text{Pt}(\text{COD})_2]$, and their subsequent reactions with

tertiary phosphines. It also describes the thermodynamic stability of the complex obtained by reacting SnMe_3Cl and $[\text{Pt}(\text{COD})_2]$, its corresponding phosphine complex and the complex *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ at various temperatures.

2. Results and discussion

2.1. Reaction of $\text{SnR}_x\text{Cl}_{4-x}$ with $[\text{Pt}(\text{COD})_2]$

The reaction of organotin(IV) compounds $\text{SnR}_x\text{Cl}_{4-x}$ with $[\text{Pt}(\text{COD})_2]$ leads to complexes containing Pt–Sn bonds as summarised in Scheme 1.

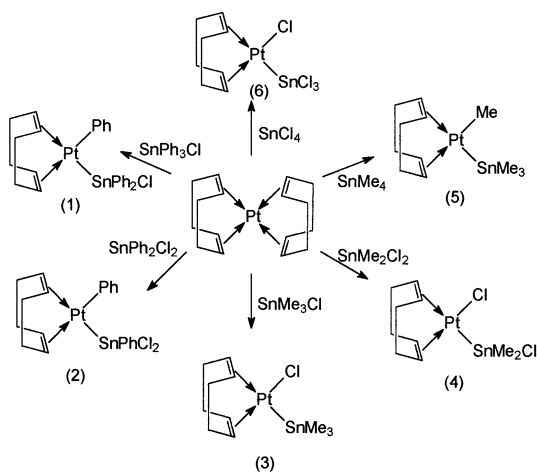
The complexes thus obtained were characterised physicochemically and spectroscopically in order to confirm their structures. Their physical properties are listed in Table 1.

It seems likely that the reaction of SnPh_3Cl and SnPh_2Cl_2 with $[\text{Pt}(\text{COD})_2]$ leads to insertion of Pt into Sn–Ph bonds to give complexes **1** and **2**, respectively (Scheme 1), as is usual for reactions of organotin

[☆] For Part I of this work, see Ref. [1].

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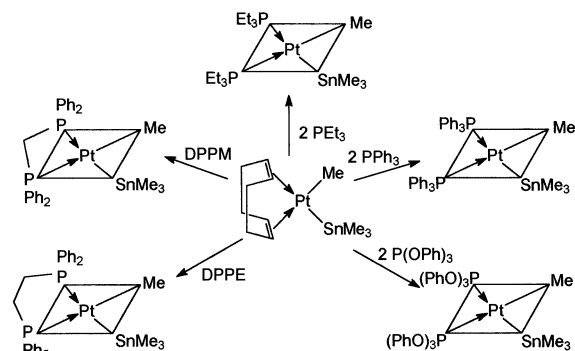
Scheme 1. The products (1–6) formed from the reaction of $[\text{Pt}(\text{COD})_2]$ and various tin compounds.

compounds with $\text{Pt}(0)$ complexes [4]. Confirmation is provided by the complete disappearance of $\nu(\text{Pt}–\text{Cl})$ in the IR spectra, as well as the ^{31}P -NMR spectral data of their corresponding *cis*-phosphine complexes (vide infra), which showed no $\text{P}–\text{Pt}–\text{Cl}$ species; the $^{195}\text{Pt}–^{31}\text{P}$ coupling constant is assigned to P in a *trans* relationship to Ph, rather than to Cl [5].

By contrast, SnMe_3Cl and SnMe_2Cl_2 react with $[\text{Pt}(\text{COD})_2]$ by insertion of Pt into Sn–Cl bonds to give complexes 3 and 4. This result was confirmed by the presence of an IR band at ca. 330 cm^{-1} in the products attributed to $\nu(\text{Pt}–\text{Cl})$ [6,7]. It is not surprising for the reaction of SnMe_2Cl_2 with $\text{Pt}(0)$ complexes to give complexes of an insertion of Pt into Sn–Cl bonds [4], but the unusual phenomenon is that for SnMe_3Cl in which all reported literature, prior to this work, stated that reactions of SnMe_3Cl with $\text{Pt}(0)$ complexes led always to complexes of an insertion of Pt into Sn–Me bonds [4].

SnMe_4 is inert towards reactions with $\text{Pt}(0)$, apart from one statement by Steele and co-workers [8], who reported that SnMe_4 reacts with $[\text{Pt}(\text{PET}_3)_4]$ in benzene under reflux to give *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PET}_3)_2]$. We believe this result was incorrect (vide infra). However, we discovered that SnMe_4 does react with $[\text{Pt}(\text{COD})_2]$ under certain conditions to give $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ (5) as an unstable oil at ambient temperature. This complex serves as a good precursor for many corresponding phosphine- or nitrogen-containing ligand–platinum complexes that cannot be prepared by other routes (vide infra).

The reaction of SnCl_4 with $[\text{Pt}(\text{COD})_2]$ gives complex 6, i.e. $[\text{PtCl}(\text{SnCl}_3)(\text{COD})]$, which can also be prepared by treating SnCl_2 with an equimolar quantity of $[\text{PtCl}_2(\text{COD})]$ [9]. The ^{119}Sn -NMR spectrum of complex 6 showed a rather large $^{195}\text{Pt}–^{119}\text{Sn}$ coupling constant, i.e. 26 208 Hz (Seddon et al. observed a lower value:



Scheme 2. The products formed from the reaction of $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ with various tertiary phosphines.

24 300 Hz and Pregosin et al. observed an even higher value: 28 954 Hz, for similar complexes [10,9]). This result was due to the fact that both the Pt and Sn atoms are attached to a more electronegative group (Cl), which in turn allows a large coupling, cf. $J(^{195}\text{Pt}–^{119}\text{Sn})$ of complex 3, i.e. $[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{COD})]$ (13 135 Hz) almost half of that of complex 6.

Many attempts were made to react SnPh_4 with $[\text{Pt}(\text{COD})_2]$ in order to obtain a complex containing Pt–Sn bonds. All were unsuccessful.

It is noteworthy that SnPh_4 , in contrast to SnMe_4 , reacts readily with other $\text{Pt}(0)$ complexes, e.g. $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ [4], $[\text{Pt}(\text{PET}_3)_n]$ ($n = 3$ or 4) [1], to give complexes containing Pt–Sn bonds.

Complexes 1–6 (Scheme 1) can serve as very good starting materials for the preparation of many complexes containing Pt–Sn bonds, which could not be easily made by direct methods.

2.2. Displacement of COD by tertiary phosphine

The complexes 1–6 (Scheme 1) were treated separately with the tertiary phosphines PET_3 , PPh_3 , $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (DPPM), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (DPPE), the tertiary phosphite $\text{P}(\text{OPh})_3$ and bipyridine, in chlorinated or non-chlorinated solvents. The structure of the complexes varied according to the reaction conditions.

The complex $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ reacts readily with various tertiary phosphines in toluene at ca. -40°C to give the corresponding phosphine complexes (Scheme 2).

All the complexes prepared showed ^{31}P -NMR patterns within the expected parameters for *cis* complexes together with the platinum-195 and tin-119/117 satellites, and the data are listed in Table 2. For example, the ^{31}P -NMR spectrum of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ in dichloromethane at ca. -40°C consists of two principal doublets, relating to the non-equivalent phosphorus atoms, both having platinum and tin satellites in a *cis*

Table 1
Characterisation data for complexes containing Pt–Sn bonds with COD ligand

Seq.	Complex	Colour	m.p. (°C)	Analysis (Found (Calc.) (%))			IR ^a data (cm ^{−1})		¹ H-NMR ^b data (δ ppm and <i>J</i> Hz)			¹¹⁹ Sn-NMR data (δ ppm and <i>J</i> Hz)	
				C	H	Cl	ν(Pt–Cl)	ν(Sn–Cl)	δ Me	³ <i>J</i> (PtCH)	² <i>J</i> (SnCH)	δ Sn	<i>J</i> (SnPt)
1	[PtPh(SnPh ₂ C l)(COD)]	Off white	120–124 dec.	46.0 (45.5)	4.0 (4.0)	5.4 (5.2)		295–262 s					
2	[PtPh(SnPhCl ₂)(COD)]	Yellow –orange	82–86 dec.	36.8 (37.1)	3.5 (3.4)	11.0 (11.0)		310, 265 s					
3	[PtCl(SnMe ₃) (COD)]	Yellow	87–88	26.4 (26.3)	4.1 (4.2)		330 m		0.45	9.5	48		
4	[PtCl(SnMe ₂ C l)(COD)]	Yellow	79–80	22.7 (22.9)	3.6 (3.5)		335 m	280 s	1.0	5.0	48	−98.7	13 125
5	[PtMe(SnMe ₃) (COD)]	Yellow	Oil	–	–		–	–	0.5 ^d	13 ^d	42 ^d		
6	[PtCl(SnCl ₃) (COD)]	Yellow –orange	152–154 dec.	17.2 (17.0)	2.2 (2.2)		325 ^c s	325 ^c s				−126.8	26 208

^a Spectra recorded, using KBr disc, m, medium and s, strong bands.

^b Spectra recorded in C₆D₆, using C₆H₆ as a reference at δ 7.2 ppm.

^c Not well-resolved broad peak.

^d Data for the methyl group attached to platinum, δ (Me) 1.47 ppm, ²*J*(PtCH) 64 Hz.

Table 2

³¹P{¹H}-NMR data δ (ppm) and J (Hz) for complexes containing Pt–Sn bonds ^a

Complex	$-\delta$ P ^(A) <i>trans</i> to Sn	¹ J (PtP ^A)	² J (SnP ^A)		$-\delta$ P ^(B) <i>cis</i> to Sn	¹ J (PtP ^B)	² J (SnP ^B)		² J (P ^A P ^B)
			¹¹⁹ Sn	¹¹⁷ Sn			¹¹⁹ Sn	¹¹⁷ Sn	
<i>cis</i> -[PtCl(SnMe ₃)(PPh ₃) ₂] ^b	105.7	1946	1683	1610	117.6	4516	84.3 ^f		12.4
<i>trans</i> -[PtCl(SnMe ₃)(PPh ₃) ₂] ^b	110.6	2959					115 ^f		
<i>trans</i> -[PtCl(SnMe ₃)(PPh ₃) ₂] ^c	132.4	2529.3					139	120	
[PtCl(SnMe ₃)(DPPE)] ^d	91.0	1785	1902	1719	96.0	4070	95 ^f		
<i>cis</i> -[PtMe(SnMe ₃)(PEt ₃) ₂] ^b	125.2	2063	1995	1914	127.5	2102	183	149	17.0
<i>cis</i> -[PtMe(SnMe ₃)(PPh ₃) ₂] ^b	108.4	2061	1846	1765	114.1	2227	154 ^f		14.7
<i>cis</i> -[PtMe(SnMe ₃){P(OPh) ₃ } ₂] ^{b,c}	89	3076.2	2426.8	2336.4	80.6	3654.7	215	161	27.0
[PtMe(SnMe ₃)(DPPM)] ^b	179.7	1440.4	1280	1168	161.2	1536	124.5 ^f		24.4
[PtMe(SnMe ₃)(DPPE)] ^b	88.7	1920		1842 ^f	86.1	1883	138 ^f		
[PtCl(SnMe ₂ Cl)(DPPE)] ^d	89.3	2102	2317	2219	97.0	3839	92 ^f		3.7
[PtMe(SnMe ₂ Cl)(DPPE)] ^{d,e}	86.8	2358	2316	2227	88.3	1826	105 ^f		5.0
[PtPh(SnPhCl ₂)(DPPE)] ^d	91.6	2932	2877	2754	90.8	1835	148 ^f		4.9
[Pt(SnMe ₃) ₂ (DPPE)] ^d	81.9	2190	1553	1474.6			153.9	129.4	
<i>trans</i> -[PtPh(SnPhCl ₂)(PPh ₃) ₂] ^c	119.5	2839					197.8 ^f		
[PtPh(SnPh ₂ Cl)(DPPE)] ^{d,e}	91.1	2507	2365	2262	90.5	1866	123.6	116	3.6
[PtPh(SnPh ₃)(DPPE)] ^{d,e}	91.3	2193	1942	1852	92.0	1792	130 ^f		3.7
[Pt(C≡CPh)(SnMe ₃)(DPPE)] ^{d,e}	94.7	1747	1658	1589	86.6	2590	106	95	6.0

^a Data obtained using CH₂Cl₂ as a solvent. External references, TMP for r.t. and TMPO for low temperature.^b Complex prepared and spectrum recorded at -70°C .^c Complex prepared and spectrum recorded in toluene at -40°C .^d Complex prepared and spectrum recorded at r.t.^e Complex prepared by method other than displacement of COD (see text).^f Not well resolved Sn(119) and Sn(117) satellites.

and *trans* relationship to phosphorus. The parameters were in agreement with those expected for such a complex (Table 2). The $^1\text{H-NMR}$ spectrum of this complex in CD_2Cl_2 at ca. -20°C showed a resonance at $\delta -0.35$ ppm for the SnMe_3 group protons, associated with platinum and tin satellites, and a resonance for the Pt-Me protons, split into four lines by the two non-equivalent phosphorus atoms, the four lines being accompanied by weak platinum satellites. The complex was isolated from cold solution as a yellow powder. It is stable at room temperature (r.t.), and analysed to give the correct analytical figures (Table 3). All the complexes listed in Scheme 2 represent novel platinum complexes that could not be prepared by the direct reaction of SnMe_4 and Pt(0) complexes containing phosphine ligands. The statement by Steele and co-workers is an exception [8]. In their work, SnMe_4 reacts with $[\text{Pt}(\text{PEt}_3)_4]$ in benzene under reflux for ca. 5 h to give *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PEt}_3)_2]$ but no tin satellites were observed and the complex was not isolated. In the absence of full characterisation, there is some doubt, therefore, that this complex would in fact be formed under their conditions [8]. We therefore, decided to prepare the complex *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PEt}_3)_2]$ by reacting $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ with PEt_3 in CH_2Cl_2 at ca. -40°C (Scheme 2) and to record the $^{31}\text{P-NMR}$ spectrum. This revealed very clearly the presence of the correct complex (Table 2). We found that this complex is unstable in solution at ambient temperature and hence Steele and co-workers [8] had been wrong in their assignments.

Treatment of complex **3** (Scheme 1), $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$, with PPh_3 , PBU_3 , and DPPE in CH_2Cl_2 at ca. -70°C gave the corresponding phosphine complexes, i.e. *cis*- and *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$, *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PBU}_3)_2]$ and $[\text{PtCl}(\text{SnMe}_3)(\text{DPPE})]$, respectively. The $^{31}\text{P-NMR}$ spectral data of these complexes (Table 2) were commensurate with the expected structures [5]. Earlier workers suggested that *cis*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ could be obtained from SnMe_3Cl and $[\text{Pt}(\text{PPh}_3)_3]$ (see Ref. [1]), however Eaborn and co-workers [4] found that this was incorrect. After treating SnMe_3Cl with the more convenient Pt(0) complex, i.e. $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$, they found that *cis*- $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{PPh}_3)_2]$ was formed. We have previously suggested that the reaction of SnMe_3Cl with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ leads initially to *cis*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$, which then converts into the thermodynamically more stable *cis*- $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{PPh}_3)_2]$ via the formation of a Pt(IV) intermediate [11]. Details about this mechanism will be published in a future article. However the complex *cis*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ was isolated at -70°C as a yellow crystalline product, and characterised by its elemental analysis and IR spectrum (Table 3). This complex is prepared for the first time and cannot be

Table 3
Characterisation data for complexes containing Pt–Sn bonds

Complex	Colour	m.p. ($^\circ\text{C}$)	Analysis (Found (Calc.) (%))	IR ^a data (cm^{-1})		$^1\text{H-NMR}$ ^b data (δ ppm and J Hz)			
				ν (Pt–Cl)	ν (Sn–Cl)	δ (SnMe)	3J (PtCH)	2J (SnCH)	
<i>cis</i> - $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$	Yellow	116–118	51.0 (51.0)	320 w		^c			
<i>cis</i> - $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$	Yellow	80–83	53.5 (53.5)			-0.35^{d}	8	37	
$[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{bipy})]^{\text{f}}$	Yellow	170–184 dec.	25.6 (25.2)	340 m	280–265 s	^e			
$[\text{PtCl}(\text{SnMe}_3)(\text{DPPE})]$	Yellow	162–167	44.0 (43.9)	300 m		-0.3	6.5	44	
$[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{DPPE})]$	Yellow	152–156 dec.	40.7 (41.3)	295 s	275 s	0.3	^e	41	
$[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{DPPE})]$	White	190–196 dec.	53.5 (54.0)		292–277 sh				
$[\text{PtPh}(\text{SnPhCl}_2)(\text{DPPE})]$	Pale yellow	206–210	48.5 (48.7)		310–297 s				

^a Spectra recorded, using KBr disc, w, weak; m, medium; s, strong; and sh, shoulder bands.

^b Spectra recorded in CD_2Cl_2 using CH_2Cl_2 as a reference at δ 5.32 ppm.

^c Complex not soluble enough to give a good $^1\text{H-NMR}$ spectrum.

^d Data for the methyl group attached to platinum, δ (Me) 0.52 ppm, 2J (PtCH) 74 Hz.

^e Platinum satellites obscured by the principal lines.

^f Found: Cl, 12.6; N, 4.8%; Calc.: Cl, 12.5; N, 4.9%.

obtained by the direct reaction of SnMe_3Cl and $[\text{Pt}(\text{PPh}_3)_n]$ ($n = 3, 4$) or $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$, due to its unstability in solution at temperatures close to r.t.

The complex $[\text{PtCl}(\text{SnMe}_3)(\text{DPPE})]$ was first suggested by Clemmit and Glockling [12] to be obtained from the reaction of SnMe_3H and $[\text{PtCl}_2(\text{DPPE})]$ as a white powder. We decided to prepare this complex by treating $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ with DPPE in dichloromethane at low temperature. The ^{31}P -NMR spectrum of the product revealed the presence of one *cis* complex having the parameters shown in Table 2. In order to compare the properties of our product with those previously reported, we isolated the complex $[\text{PtCl}(\text{SnMe}_3)(\text{DPPE})]$ from the mixture as a yellow crystalline product (Table 3). As the two sets of data were different, we [13] repeated the procedure of the earlier workers and the product obtained was examined by ^{31}P -NMR. It seems possible therefore that Clemmit and Glockling [12] may have obtained the complex $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{DPPE})]$ (Table 2), which of course, has the same elemental composition as the complex $[\text{PtCl}(\text{SnMe}_3)(\text{DPPE})]$.

The complex $[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{COD})]$ reacts with tertiary phosphines, e.g. PPh_3 , PEt_3 , PBU_3 to yield known complexes. Treatment with DPPE or bipy in dichloromethane at ambient temperature leads to formation of the new complexes $[\text{PtCl}(\text{SnMe}_2\text{Cl})\{\text{(DPPE)} \text{ or } (\text{bipy})\}]$, which could not be prepared by other routes, e.g. from Me_2SnCl_2 and $[\text{Pt}(\text{DPPE})_2]$ or from $[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{PPh}_3)_2]$ and DPPE. However, the complexes were isolated and fully characterised (Table 3).

The reaction of $[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{COD})]$ with PPh_3 at or below r.t. yields the known complex *cis*- $[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{PPh}_3)_2]$ [8]. Using DPPE in CH_2Cl_2 at r.t., the reaction gave a complex with ^{31}P -NMR parameters (Table 2) identical to those of $[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{DPPE})]$. This complex was isolated and characterised (Table 3). The reaction of $[\text{PtPh}(\text{SnPhCl}_2)(\text{COD})]$ with PPh_3 in CH_2Cl_2 , at -70°C or at r.t., gave the known complex *cis*- $[\text{PtPh}(\text{SnPhCl}_2)(\text{PPh}_3)_2]$ [4]. An in situ reaction between $[\text{Pt}(\text{COD})_2]$ and SnPh_2Cl_2 in toluene at ca. -40°C for ca. 60 min was carried out in the hope of obtaining $[\text{PtCl}(\text{SnPh}_2\text{Cl})(\text{COD})]$, the toluene then being evaporated off while the temperature was maintained below -40 to -10°C . The residue was dissolved in CH_2Cl_2 at -40°C and PPh_3 added and the ^{31}P -NMR spectrum was recorded at -40°C , which revealed the presence of *cis*- (53%) and *trans*- (47%) $[\text{PtPh}(\text{SnPhCl}_2)(\text{PPh}_3)_2]$. The complex *cis*- $[\text{PtCl}(\text{SnPh}_2\text{Cl})(\text{PPh}_3)_2]$ could not be detected. It seems that the *trans*- $[\text{PtPh}(\text{SnPhCl}_2)(\text{PPh}_3)_2]$, which it observed for the first time (Table 2), is stable in solution only at low temperature, for when the solution containing this complex was allowed to warm up, the proportion of the *trans* complex gradually fell and it was completely converted into the *cis* isomer at r.t.

Furthermore, treatment of $[\text{PtPh}(\text{SnPhCl}_2)(\text{COD})]$ with DPPE in CH_2Cl_2 at r.t. leads to formation of the new complex $[\text{PtPh}(\text{SnPhCl}_2)(\text{DPPE})]$, which again could not be prepared by other routes, i.e. SnPh_2Cl_2 and $[\text{Pt}(\text{DPPE})_2]$ or $[\text{PtPh}(\text{SnPhCl}_2)(\text{PPh}_3)_2]$ and DPPE. It was isolated and fully characterised (Tables 2 and 3).

The reaction of $[\text{PtCl}(\text{SnCl}_3)(\text{COD})]$ with tertiary phosphines leads to known complexes that can be prepared from the direct reaction of SnCl_4 and $\text{Pt}(0)$ complexes.

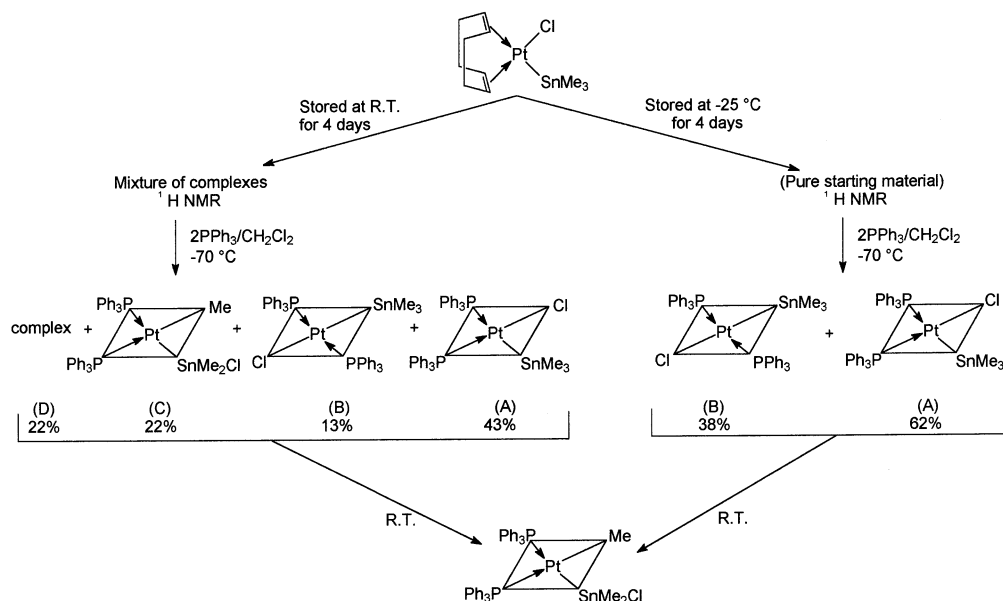
2.3. Decomposition of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ and its *PPh*₃ analogue

It is evident that the complex $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ is thermally unstable at r.t., and its decomposition products were studied carefully by using ^{31}P -NMR spectroscopy after adding phosphine.

Two samples of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ (0.1 g, 0.2 mmol) were kept for 4 days, one at -25°C and the other at r.t. Each was then dissolved in CH_2Cl_2 , the solution cooled to -70°C , a pre-cooled solution to -70°C of PPh_3 (0.1 g, 0.4 mmol) in CH_2Cl_2 added, and the ^{31}P -NMR spectrum recorded. The spectrum (at -70°C) from the sample kept at -25°C , revealed the presence of *cis*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ (**A**) (62%) and *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ (**B**) (38%) (Scheme 3). The spectrum (at -70°C) of the sample kept at r.t. revealed the presence of three known complexes: **A**, **B**, *cis*- $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{PPh}_3)_2]$ (**C**) (43, 13 and 22%, respectively), and an unknown complex (**D**) (22%) (Scheme 3) having the parameters: $\delta -105.2$ ppm, $J(\text{PtP})$ 2075.2 Hz (*P cis* to Sn); $\delta -114.1$ ppm, $J(\text{PtP})$ 2131.3 Hz (*P trans* to Sn); $^2J(\text{P-Pt-P})$ 10 Hz. Both signals were associated with tin satellites; those in *cis* relationship to phosphorus, $^2J(\text{SnP})$ 103 Hz, and those in a *trans* relationship to phosphorus being obscured by the other lines. Product **D** was found to be thermally very unstable, for when the mixture was warmed to -60°C , the proportion of it decreased by ca. 50% and it had totally disappeared at -50°C . When both samples were warmed to r.t., only complex **C** (the thermodynamically stable species) was observed (Scheme 3).

A sample of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ was prepared and stored at r.t. under argon for 1 week then dissolved in CH_2Cl_2 . The solution was cooled to -70°C and PPh_3 was added (as above). This again gave a mixture of the three known complexes: **A**, **B** and **C** (22, 6, and 45%, respectively) and complex **D** (27%).

A sample of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ was prepared and stored at r.t. under argon for 5 weeks, then dissolved in CH_2Cl_2 . The solution was cooled to -70°C and treated with PPh_3 (as above). The ^{31}P -NMR spectrum revealed the presence of a mixture of complex **C** (47.5%), a complex (16%) having the parameters δ



Scheme 3. Products formed from the reaction of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ (stored at -25°C once and at r.t. for another 4 days) with PPh_3 at -70°C , and at r.t.

–112.5 ppm, $J(\text{PtP})$ 1919 Hz, identified as *cis*- $[\text{PtMe}_2(\text{PPh}_3)_2]$ [14], a complex (10%) having the parameters δ –109.2 ppm, $J(\text{PtP})$ 3120 Hz, identified as *trans*- $[\text{PtMeCl}(\text{PPh}_3)_2]$ [15], and complex **D** (26%) (Scheme 3); no *cis*- or *trans*- $[\text{PtCl}(\text{SnMe}_3)(\text{PPh}_3)_2]$ was detected in the mixture.

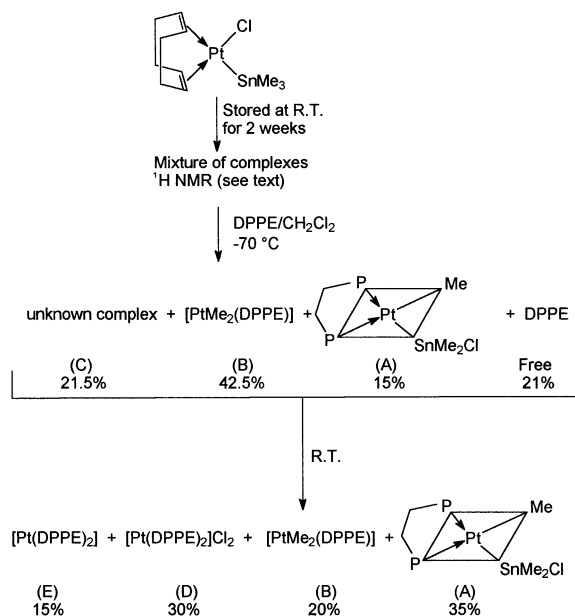
In order to study the decomposition products of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$, without having the *trans* complexes, DPPE was used instead of PPh_3 . A sample of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ was stored at r.t. for ca. 2 weeks, then dissolved in CH_2Cl_2 , and the solution was cooled to -70°C and treated with DPPE (as above). The ^{31}P -NMR spectrum recorded at -70°C revealed (in addition to the unreacted DPPE), the presence of three complexes (Scheme 4). Complex **A** (15%) identified as $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{DPPE})]$ (Table 2), complex **B** (42.5%) having the parameters δ –92.8 ppm, $J(\text{PtP})$ 1814 Hz, identified as $[\text{PtMe}_2(\text{DPPE})]$ [16], and an unknown complex **C** (21.5%) having the parameters δ –73.0 ppm, $J(\text{PtP})$ 2329 Hz, δ –80.8 ppm, $J(\text{PtP})$ 2977 Hz, accompanied by tin satellites, those in a *cis* relationship to phosphorus having $^2J(\text{Sn-P})$ 90 Hz and those in a *trans* relationship being obscured by the signals of other complexes. The PP coupling was very small and could not be resolved. Again, when the mixture was warmed to r.t., complex **C** (Scheme 4) completely disappeared and the complexes **D** and **E** appeared.

As a conclusion, it seems that the complex $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ decomposes in the solid state at r.t. to give $[\text{PtMe}(\text{SnMe}_2\text{Cl})(\text{COD})]$ via an unknown intermediate, the extent of decomposition increases with time, and the longer the complex is stored the

greater the number of decomposition products. Further studies concerning the mechanisms of such reaction will be published later.

2.4. Decomposition of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$

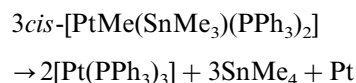
Two samples of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ were prepared by treating $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ with two molar equivalents of PPh_3 in CH_2Cl_2 at -70°C . The first was



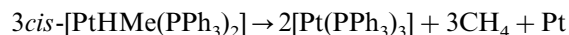
Scheme 4. Products formed from the reaction of $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$ (stored at r.t. for 2 weeks) with DPPE at -70°C , and at r.t.

allowed to warm gradually and the ^{31}P -NMR spectrum was recorded at 10°C intervals. No change occurred over the range -70 to -10°C , but the spectrum at 0°C comprised resonances from the original complex (70%) and from a new complex (15%) $\{\delta - 90.5$ ppm, $J(\text{PtP})$ 4465 Hz $\}$ identified as $[\text{Pt}(\text{PPh}_3)_3]$ [17,18], in addition to *cis*- $[\text{PtMe}_2(\text{PPh}_3)_2]$ [14], which was present in the spectrum from the start (above). When the sample was warmed to r.t., the solution turned brown and the proportion of $[\text{Pt}(\text{PPh}_3)_3]$ grew to 60%, while that for the original compound was reduced to 25%. When the sample was allowed to stand at r.t. for a further ca. 30 min, the spectrum showed that the original complex had completely disappeared. The second sample was warmed rapidly to r.t., and the ^{31}P -NMR spectrum recorded during 20 min showed only the presence of $[\text{Pt}(\text{PPh}_3)_3]$. For this sample, the ^1H -NMR was recorded to show a resonance at 0.07 ppm, associated with tin satellites, $^2J(\text{SnCH})$ 51 Hz; this was attributed to SnMe_4 , and the assignment was confirmed by addition of SnMe_4 , which caused an increase in the height of the signal.

It is concluded that *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ is unstable in solution at temperatures somewhat below 0°C , and decomposes:



Similarly, Abis et al. [19] observed the formation of $[\text{Pt}(\text{PPh}_3)_3]$ when a solution of *cis*- $[\text{PtHMe}(\text{PPh}_3)_2]$ prepared at -80°C , was warmed to -25°C :



A sample of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ (93.5%) was prepared in situ from $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ and exactly two molar equivalents of PPh_3 in CH_2Cl_2 at -70° . The remaining 6.5% was *cis*- $[\text{PtMe}_2(\text{PPh}_3)_2]$ and no free PPh_3 was observed in the spectrum. An excess of PPh_3 (1.5 molar equivalents) was added to the solution at -60°C and the ^{31}P -NMR showed no change even on warming the solution to $+10^\circ\text{C}$. At r.t., the spectrum was recorded during ca. 30 min and showed the presence of PPh_3 , traces of the original complex and two new complexes in an almost 1:1 molar ratio. These have the parameters (a) $\delta - 109.6$ ppm, $J(\text{PtP})$ 3342 Hz and (b) $\delta - 110.2$ ppm, $J(\text{PtP})$ 3320 Hz; neither resonance was associated with tin satellites. The parameters do not correspond to any of *cis*- $[\text{PtMe}_2(\text{PPh}_3)_2]$ [14], *trans*- $[\text{PtXY}(\text{PPh}_3)_2]$ X = Me, Y = Cl [15]; X = H, Y = Cl [20]; X = CH_2Cl , Y = Cl [21] or *cis*- or *trans*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ [22]. One of the complexes may be the *trans*- $[\text{PtMe}_2(\text{PPh}_3)_2]$ (parameters not available in the literature). No further investigations were carried out on these complexes.

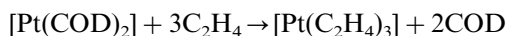
It appears therefore, that decomposition of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ in the presence of PPh_3 does not give $[\text{Pt}(\text{PPh}_3)_3]$ as was observed from the decomposition in the absence of PPh_3 .

Another sample of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ prepared, as above, in toluene at -70°C was saturated with ethylene. The ^{31}P -NMR showed no change had occurred at -70°C , or up to -30°C , but when the ethylene was slowly bubbled into solution while the temperature was allowed to rise to r.t., the solution turned brown. The spectrum recorded at -50°C revealed the presence of two complexes: $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ (73%) $\delta - 106.6$ ppm, $J(\text{PtP})$ 3711 Hz and $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$ (27%), $\delta - 116.3$ ppm, $J(\text{PtP})$ 3388.7 Hz; [15] $\delta - 116.0$ ppm, $J(\text{PtP})$ 3425 Hz.

The formation of the first complex can be understood as a result of the initial decomposition of *cis*- $[\text{PtMe}(\text{SnMe}_3)(\text{PPh}_3)_2]$ to $[\text{Pt}(\text{PPh}_3)_2]$ followed by combination with ethylene to give $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$. The formation of the second complex can possibly be understood as a result of the initial decomposition of $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$ that was left unreacted with a sufficient quantity of PPh_3 ; when this decomposes in the presence of ethylene it gives $[\text{Pt}(\text{C}_2\text{H}_4)_3]$, and this has been shown to react with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ in the presence of ethylene to give $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$.

This was confirmed by the two following experiments: (a) ethylene was bubbled into a toluene solution of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ for several minutes at r.t., and the ^{31}P -NMR spectrum indicated that no change had occurred. (b) When a mixture of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ and a slight excess of $[\text{Pt}(\text{COD})_2]$ was dissolved in toluene, the ^{31}P -NMR spectrum gave no indication of change, although the solution had turned brown. When ethylene was bubbled into this solution (or into a similar mixture freshly prepared), for ca. 2 min, the solution turned dark brown, and the spectrum revealed the presence of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$ only.

These results are consistent with the following equations:



This represents a superior method for the preparation of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$ in comparison with that reported earlier [23]. It should be noted that the preparation should be carried out at low temperatures to avoid decomposition.

3. Experimental

3.1. General

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 proton-decoupled FT ^{31}P -NMR spectra were recorded at 40.48 MHz on a Jeol PFT-100 spectrometer using trimethylphosphine (TMP) or trimethylphosphate (TMPO) as external references. The proton-decoupled FT ^{119}Sn -NMR spectra were recorded at 33.34 MHz on a Jeol FX-90Q spectrometer using SnMe_4 as external reference. The tin spectra were performed by Dr W. McFarlane and Dr B.V. Cheesman at the City of London Polytechnic in early 1980.

The IR spectra were recorded as Nujol mull smears between CsI discs on a Perkin–Elmer 457 or 597 grating infrared spectrometer. Elemental analyses were carried out at the microanalytical laboratory at the School of Molecular Sciences, Sussex University, Brighton, UK.

3.2. Starting materials

K_2PtCl_4 , PtCl_2 , cycloocta-1,5-diene (COD) and cycloocta-1,3,5,7-tetraene (COT) were commercial products. COD and COT were distilled under nitrogen before use. The tertiary phosphines PEt_3 , PPh_3 , P(OPh)_3 , $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (DPPM), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (DPPE), ... etc. and other neutral ligands were either obtained commercially or prepared by standard methods. The organotin(IV) compounds $\text{SnR}_x\text{Cl}_{4-x}$, $\text{R} = \text{Me}$, Ph and $x = 4-0$, were either commercial products or prepared by standard methods. The platinum complexes used in this study were prepared by standard methods: $[\text{PtCl}_2(\text{COD})]$ [24], $[\text{Pt}(\text{COD})_2]$ [25] and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ [26].

3.3. Preparation of complexes

3.3.1. $[\text{PtCl}(\text{SnMe}_3)(\text{COD})]$

To a solution of SnMe_3Cl (0.220 g, 1.1 mmol) in toluene (2 ml), a solution of $[\text{Pt}(\text{COD})_2]$ (0.411 g, 1.0 mmol) in toluene (10 ml) was added at r.t. The mixture was stirred for ca. 30 min, and the yellow solution was filtered through Celite and reduced in volume to 0.5 ml. *n*-Hexane (3 ml) was added at 0°C and the solution was decanted from the crystalline product, which was washed with hexane (3×3 ml), and dried under vacuum to give pale yellow fine crystals of the product (0.379 g, 75%). This complex is unstable in the solid state at r.t., but can be safely kept at -25°C for several months without decomposition.

3.3.2. $[\text{PtCl}(\text{SnMe}_2\text{Cl})(\text{COD})]$

A solution of SnMe_2Cl_2 (0.1 g, 0.46 mmol) in toluene (2 ml) was treated with a solution of $[\text{Pt}(\text{COD})_2]$ (0.2 g,

0.49 mmol) in toluene (8 ml) at r.t. The mixture was stirred for ca. 30 min then filtered through Celite, and the filtrate was reduced in volume to ca. 0.5 ml. *n*-Hexane (3 ml) was added, and the solution was decanted from the yellow crystals, which were washed with hexane (3×3 ml), and dried under vacuum (yield, 0.2 g, 80%).

3.3.3. $[\text{PtMe}(\text{SnMe}_3)(\text{COD})]$

An excess of SnMe_4 was added to a solution of $[\text{Pt}(\text{COD})_2]$ (0.2 g, 0.49 mmol) in toluene (5 ml) under argon. The mixture was kept for ca. 16 h at r.t., during which it turned yellow–brown. It was filtered through Celite and the filtrate was taken to dryness and kept under vacuum for ca. 2 h. The product was obtained as yellow oil, and many unsuccessful attempts were made to crystallise it. The complex was found to decompose readily at r.t. to metallic platinum, but it is wholly satisfactory for immediate use. It can also be stored safely at ca. -25°C for a long time.

3.3.4. $[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{COD})]$

A solution of $[\text{Pt}(\text{COD})_2]$ (0.100 g, 0.24 mmol) in benzene (4 ml), was added dropwise under nitrogen to a solution of SnPh_2Cl (0.094 g, 0.24 mmol) in benzene (6 ml) at r.t.; the mixture turned yellow soon after the first few drops were added. The mixture was stirred for ca. 15 min, then reduced in volume to ca. 2 ml, and *n*-hexane was added dropwise to precipitate the unidentified brown material (possibly decomposition products). The solution was filtered through Celite and the clear yellow filtrate was reduced in volume to ca. 0.5 ml. *n*-Hexane (3 ml) was added and the solution was cooled to ca. -10°C , then the liquid was decanted from the off-white crystals, which were washed with hexane (3×2 ml) then dried in vacuo for ca. 1 h (yield, 0.100 g, 60%).

The complex $[\text{PtPh}(\text{SnPhCl}_2)(\text{COD})]$ was prepared similarly from equimolar quantities of $[\text{Pt}(\text{COD})_2]$ and SnPh_2Cl_2 in benzene.

3.3.5. $[\text{PtCl}(\text{SnCl}_3)(\text{COD})]$

This was prepared by two methods: (a) a solution of $[\text{Pt}(\text{COD})_2]$ (0.20 g, 0.49 mmol) in toluene (8 ml) was added gently to a solution of SnCl_4 (0.15 g, 0.58 mmol) in toluene (2 ml) under nitrogen. An immediate precipitate separated; this was filtered off, washed with *n*-hexane and dried in vacuo to give yellow–orange crystals of the product (0.20 g, 73%).

(b) A mixture of $[\text{PtCl}_2(\text{COD})]$ (0.20 g, 0.53 mmol) and anhydrous SnCl_2 (0.10 g, 0.53 mmol) was suspended in dichloromethane (15 ml) and the mixture was stirred for ca. 2 h at r.t. The suspension was reduced in volume to ca. 5 ml, then the solid was separated by filtration, washed with hexane, and dried in vacuo, to give a yellow–orange product (0.26 g, 95%).

3.3.6. *cis*-[PtCl(SnMe₃)(PPh₃)₂]

Freshly prepared [PtCl(SnMe₃)(COD)] (0.1 g, 0.20 mmol) was dissolved in dichloromethane (0.5 ml) and the solution was cooled to ca. –70°C in an acetone–dry ice bath. A solution of PPh₃ (0.1 g, 0.38 mmol) in dichloromethane (0.3 ml) was added at ca. –70°C and the mixture was shaken for ca. 60 s to ensure homogeneity. A few drops of *n*-hexane were added to the point of turbidity, and within ca. 30 min yellow crystals began to separate. After a further 30 min the supernatant liquid was decanted from the crystals, which was washed with *n*-hexane (3 × 1 ml) at ca. –70°C and dried in vacuo to give fine pale yellow crystals of the product.

The complex [PtCl(SnMe₃)(DPPE)] was prepared similarly, from [PtCl(SnMe₃)(COD)] (0.20 g, 0.40 mmol) and DPPE (0.14 g, 0.35 mmol) in toluene (3 ml) at ca. –20°C, as a yellow powdered product.

3.3.7. *cis*-[PtMe(SnMe₃)(PPh₃)₂]

A mixture of [Pt(COD)₂] (0.1 g, 0.24 mmol) and an excess of SnMe₄ in toluene (8 ml) was left aside at r.t. for ca. 16 h. The mixture was then filtered through Celite and the yellow filtrate was reduced in volume to ca. 2 ml, then cooled to ca. –50°C in an acetone–dry ice bath. A solution of PPh₃ (0.1 g, 0.38 mmol) in toluene (0.5 ml) was added at –50°C, and the mixture was shaken for ca. 60 s. *n*-Hexane was added to the point of turbidity, and a yellow solid separated. The supernatant liquid was decanted from the solid, which was washed with hexane (3 × 2 ml) at –50°C and dried in vacuo to give the final product as a yellow powder.

3.3.8. [PtPh(SnPh₂Cl)(DPPE)]

The [PtPh(SnPh₂Cl)(COD)] (0.14 g, 0.2 mmol) was dissolved in dichloromethane (2 ml) and a solution of DPPE (0.08 g, 0.2 mmol) in dichloromethane (1 ml) was added. The mixture was shaken for ca. 60 s and *n*-hexane was added to precipitate the product. The solid was crystallised from dichloromethane–hexane and dried under vacuum to give white crystals of the product.

The complexes [PtPh(SnPhCl₂)(DPPE)] and [PtCl(SnMe₂Cl)(DPPE)] were obtained analogously as pale yellow crystalline products.

3.3.9. [PtCl(SnMe₂Cl)(bipy)]

The [PtCl(SnMe₂Cl)(COD)] (0.10 g, 0.20 mmol) was dissolved in toluene (6 ml) and bipyridine (0.07 g, 0.45 mmol) was added at r.t. The mixture was stirred for ca. 30 min, during which a yellow crystalline complex separated. This was filtered off, washed with *n*-hexane (3 × 3 ml), and dried in vacuo for ca. 1 h to give a yellow crystalline product.

3.4. NMR tube in situ reactions

3.4.1. Tertiary phosphine with COD complexes

3.4.1.1. Low-temperature reaction. A typical reaction, between PPh₃ and [PtCl(SnMe₃)(COD)] is described. The latter (0.1 g, 0.20 mmol) was dissolved in dichloromethane (0.5 ml) under nitrogen and the solution placed in an 8 mm NMR tube flushed with nitrogen. The tube was then sealed with a rubber subaseal and cooled to ca. –70°C in an acetone–dry ice bath. The PPh₃ (0.1 g, 0.38 mmol) was dissolved in dichloromethane (0.3 ml) and the solution was carefully injected through the subaseal cap, so that drops of the liquid fell first on to the cold inside of the tube; in this way the two solutions were mixed at –70°C. The mixture was shaken carefully, then the ³¹P-NMR spectrum recorded at –70°C.

The reaction between [PtCl(SnMe₃)(COD)] and PBu₃ or PEt₃ was carried out analogously, but by using toluene at ca. –40°C.

A similar procedure was carried out for the reactions between [PtMe(SnMe₃)(COD)] and PPh₃, PEt₃, DPPM, DPPE in dichloromethane at –70°C. With P(OPh)₃ the reaction was carried out in toluene at –40°C.

3.4.1.2. Room-temperature reactions. A typical reaction, between [PtCl(SnMe₂Cl)(COD)] and PPh₃ was carried out as follows. The [PtCl(SnMe₂Cl)(COD)] (0.1 g, 0.20 mmol) was dissolved in dichloromethane (0.5 ml) in an 8 mm NMR tube under nitrogen. A solution of PPh₃ (0.1 g, 0.38 mmol) in dichloromethane (0.3 ml) was introduced into the NMR tube under nitrogen and the mixture was shaken for ca. 30 s. The ³¹P-NMR spectrum was then recorded.

The reaction between [PtCl(SnMe₂Cl)(COD)] and DPPE was carried out in the same way. With PBu₃ and PEt₃, the reactions were carried out in toluene.

A similar procedure, with toluene as solvent, was used for the reactions between [PtCl(SnMe₃)(COD)] and DPPE, [PtPh(SnPh₂Cl)(COD)] or [PtPh(SnPhCl₂)(COD)] and PPh₃ or DPPE and {[PtCl(SnCl₃)(COD)] and PBu₃}.

3.4.2. Reaction between *cis*-[PtRR'(PPh₃)₂] and DPPE

The complex *cis*-[PtRR'(PPh₃)₂] (R = Ph, R' = SnPh₃, SnPh₂Cl; R = Me, R' = SnMe₂Cl) (0.2 mmol) (prepared as described in Ref. [4]) was dissolved in dichloromethane (5 ml) at r.t. and DPPE (0.2 mmol) was added. After ca. 5 min the solution was reduced in volume to ca. 1 ml and the ³¹P-NMR spectra recorded.

Attempts were made to obtain a similar complex from the reaction between *cis*-[PtPh(SnPhCl₂)(PPh₃)₂] and DPPE but were unsuccessful even at –30°C, as were those between *cis*- and *trans*-[PtCl(SnMe₂Cl)(PPh₃)₂] and DPPE, but at r.t.

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