

## 177. The Reaction of $\text{SnCl}_2$ with the Complexes *cis*- $\text{PtCl}_2$ (phosphorus ligand) $_2$ as Studied by $^{31}\text{P}$ and $^{195}\text{Pt}$ NMR.

by Paul S. Pregosin and Siu Ning Sze

Laboratorium für Anorganische Chemie, ETH-Zentrum,  
CH-8092 Zürich, Switzerland

(31.III.78)

### Summary

The reactions of  $\text{SnCl}_2$  with the complexes *cis*- $\text{PtCl}_2\text{P}_2$ , P = trialkyl and triaryl phosphines and phosphites, in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  have been studied using  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR. methods. For equimolar amounts of Sn and Pt, products of the type  $\text{PtCl}(\text{SnCl}_3)\text{P}_2$  are formed with the complex geometry depending on the nature of P. For P =  $\text{PEt}_3$  and  $\text{P}(\text{OPh})_3$ , further addition of  $\text{SnCl}_2$  produces *trans*- $\text{Pt}(\text{SnCl}_3)_2\text{P}_2$  complexes. The syntheses of *trans*- $\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2$  and *trans*- $\text{Pt}(\text{SnCl}_3)_2(\text{OPh})_3$  are described.

**Introduction.** - The interaction between platinum salts and  $\text{SnCl}_2$  has long been of interest [1]. In particular *bis*-phosphine complexes of platinum of type *cis*- $\text{PtCl}_2(\text{phosphine})_2$  have recently been shown to be useful catalysts for the hydrogenation and hydroformylation of primary olefins in the presence of excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  [2]. Despite the useful characteristics displayed by this type of system, the complexes which form when  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  interacts with platinum salts are not well characterized. Thus although there is an early report [3] of the synthesis of yellow *cis*- $\text{PtCl}_2(\text{SnCl}_3)_2^{2-}$  and red *trans*- $\text{PtCl}_2(\text{SnCl}_3)_2^{2-}$  salts, the existence of the latter has been questioned in a *Mossbauer* study reporting that this red complex has the same spectrum [4] as the red pentakis anion  $\text{Pt}(\text{SnCl}_3)_5^{3-}$ , for which an X-ray structure exists [5]. The cluster complexes  $\text{Pt}_3\text{Sn}_2\text{Cl}_6(\text{C}_8\text{H}_{12})_3$  and  $(\text{Et}_4\text{N})_2[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]$  [6] as well as the monomeric *cis*- and *trans*- $\text{Pt}(\text{SnCl}_3)_2(\text{PPh}_3)_2$  complexes [7] have also been reported.

$^{31}\text{P}$  { $^1\text{H}$ }-NMR. measurements of platinum complexes containing tin and phosphorus should provide a sensitive probe for complex structures. This stems from the simplicity of these spectra (e.g. each type of phosphorus appears as a sharp, well defined signal) and the marked dependence of  $^1J(^{31}\text{P}, ^{195}\text{Pt})$  ( $^{195}\text{Pt}$ ,  $I = \frac{1}{2}$ , natural abundance = 33.7%) on the nature of the ligand *trans* to phosphorus [8]. Additionally, the two NMR. active isotopes of tin ( $^{117}\text{Sn}$ ,  $I = \frac{1}{2}$ , natural abundance = 7.7% and  $^{119}\text{Sn}$ ,  $I = \frac{1}{2}$ , natural abundance = 8.7%) can couple with phosphorus through the metal. The magnitude of this type of 2-bond interaction, e.g.  $^2J(\text{Sn}, \text{P})$ , has been shown to depend strongly on whether the 2 nuclei are *cis* (150–200 Hz)

or *trans* (2100–2400 Hz) for complexes of the type  $\text{PtR}(\text{PPh}_3)_2(\text{SnClR}_2)$  [9], thus providing an additional probe for the geometric relationship of the tin and phosphorus atoms. For the case where more than one tin is coordinated to the metal the relative *intensities* of the phosphorus signals can be of value. For a single tin where the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites overlap (e.g. the difference between  $^2J(^{117}\text{Sn}, \text{P})$  and  $^2J(^{119}\text{Sn}, \text{P})$  is not resolved) the phosphorus signals will appear as approximately 1:10:1 triplets. If the tin couplings are sufficiently different this ratio will be approximately 1:21:1, with ratios between 10 and 20 observed when the satellite lines are broad or poorly resolved. For 2 coordinated tin atoms the probability that *one* of the two tin atoms will be NMR. active is  $\sim 27\%$  (the likelihood that both are active is  $\sim 2.7\%$ ). The  $^{31}\text{P}$  resonance for such a complex will appear as either a 1:5.5:1 triplet or a 1:11:1 triplet depending on the size of the tin-phosphorus coupling, thus clearly distinguishing this type of complex from one containing only a single tin atom.

A powerful complement to  $^{31}\text{P}$ -NMR. is  $^{195}\text{Pt}$ -NMR. spectroscopy [10]. The chemical shift range for this nucleus is  $> 10.000$  ppm and any change in molecular structure is generally accompanied by a change in  $\delta^{195}\text{Pt}$  of several hundred ppm. Further, inspection of the multiplet pattern stemming from the coupling with phosphorus will often provide directly the number and type of phosphorus atoms bound to the metal.

Given the sensitivity of these NMR. methods we have begun a  $^{31}\text{P}$  and  $^{195}\text{Pt}$ -NMR. study of the complexes which arise in solution when  $\text{SnCl}_2$  reacts with bis-phosphorus complexes of platinum and report here some of our results.

**Experimental Part.** -  $^{31}\text{P}$  and  $^{195}\text{Pt}$ -NMR. spectra were measured as solutions in 10 mm tubes using a Bruker HX-90 spectrometer operating at 36.43 and 19.34 MHz respectively.  $^{31}\text{P}$  and  $^{195}\text{Pt}$  chemical shifts are referred to external  $\text{H}_3\text{PO}_4$  ( $\pm 0.1$  ppm) and external  $\text{Na}_2\text{PtCl}_6$  ( $\pm 1$  ppm) at RT. with a positive sign indicating a shift to higher frequency (lower field) relative to the reference. Coupling constants are  $\pm 2$  Hz.

All preparative operations were carried out under  $\text{N}_2$ . Solvents were dried and degassed.  $\text{K}_2\text{PtCl}_4$  was obtained from Johnson-Matthey,  $\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$  from Eastman-Kodak and  $\text{P}(p\text{-ClC}_6\text{H}_4)_3$  from Fluka. *cis*- $\text{PtCl}_2(\text{DIOP})$  was a gift from Dr. G. Consiglio of the Technical Chemistry Institute, ETH Zürich. The starting materials *cis*- $\text{PtCl}_2\text{P}_2$  were obtained using literature methods [11].

*Trans*-[ $\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2$ ]. A solution of 0.05 g (0.1 mmol) *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$  and 0.19 g (0.1 mmol) anhydrous  $\text{SnCl}_2$  in  $\text{CH}_2\text{Cl}_2$  was stirred for 1 h after which the solvent was removed and the yellow residue recrystallized from hexane by cooling to  $-9^\circ$ . Yield: 0.042 g (60%).

*Cis*-[ $\text{PtCl}(\text{SnCl}_3)(\text{DIOP})$ ]. 0.039 g (0.05 mmol) *cis*-[ $\text{PtCl}_2(\text{DIOP})$ ] and 0.10 g (0.05 mmol) anhydrous  $\text{SnCl}_2$  were stirred in 8 ml  $\text{CH}_2\text{Cl}_2$  for 10 min. The resulting bright yellow solution was concentrated to 2 ml and 4 ml of hexane added. Filtration followed by cooling at  $-9^\circ$  for 3 h afforded colorless crystals. These were filtered, washed with hexane, and pumped dry. Yield: 0.044 g (90%).

*Cis*-[ $\text{PtCl}(\text{SnCl}_3)(\text{PPh}_3)_2$ ]. To a stirred solution of 0.113 g (0.14 mmol) *cis*-[ $\text{PtCl}_2(\text{PPh}_3)_2$ ] in 3.5 ml  $\text{CH}_2\text{Cl}_2$  was added a solution of 0.140 g (0.70 mmol) anhydrous  $\text{SnCl}_2$  in 7 ml acetone. The reaction mixture gradually became turbid. The suspension which resulted was stirred for 0.5 h at RT. and then filtered. The colorless solid product was washed with  $3 \times 1$  ml acetone, then  $2 \times 1$  ml  $\text{CH}_2\text{Cl}_2$ , and pumped dry under high vacuum for 6 h. Yield: 0.10 g (70%).

*Trans*-[ $\text{Pt}(\text{SnCl}_3)_2(\text{P}(\text{OPh})_3)_2$ ]. A solution of 0.112 g (0.13 mmol) *cis*-[ $\text{PtCl}_2(\text{P}(\text{OPh})_3)_2$ ] and 0.037 g (1.90 mmol) anhydrous  $\text{SnCl}_2$  in 5 ml  $\text{CHCl}_3$  was stirred for 3 h, filtered, and allowed to stand at  $-30^\circ$  for 3 days. The resulting colorless crystals were washed with 1 ml of  $\text{CHCl}_3$  and pumped dry. Yield: 0.04 g (29%).

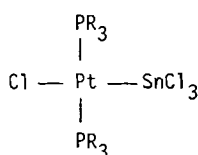
Analytical data for these complexes are shown in Table 1.

**<sup>31</sup>P-NMR. Results.** - The <sup>31</sup>P spectra of solutions which contain *cis*-PtCl<sub>2</sub>P<sub>2</sub> complexes P = a phosphorus ligand, and anhydrous SnCl<sub>2</sub> in equimolar amounts are markedly different from the solutions in the absence of SnCl<sub>2</sub>, indicating the formation of new species. Starting from *cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>, the <sup>31</sup>P{<sup>1</sup>H} spectrum at -50° reveals a sharp singlet at δ 13.6 ppm (14.3 ppm at RT.) symmetrically flanked by <sup>195</sup>Pt and <sup>117,119</sup>Sn satellites, in addition to the signals of starting material (<5%). Eventual work-up of the CH<sub>2</sub>Cl<sub>2</sub> solution afforded a yellow solid whose analysis (Table 1) is consistent with the formulation *trans*-PtCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>, **1a** (see Scheme). Further support for the *trans* geometry comes from a) the observed value of <sup>1</sup>J(Pt,P) (2042 Hz) consistent with 2 phosphorus atoms *trans* to one another [12], b) the <sup>1</sup>H-NMR. spectrum showing a pseudo quintet at δ 1.14 for the CH<sub>3</sub> resonance [13] and c) the values <sup>2</sup>J(<sup>117,119</sup>Sn,P) (227 Hz, 237 Hz) consistent with a structure in which Sn is *cis* to P [9]. The <sup>31</sup>P{<sup>1</sup>H}-NMR. spectrum of this

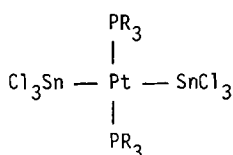
Table 1. Microanalytical Data for the Complexes

Compound	Empirical Formula	M.P. (°C)	Analysis (%)					
			Found			Calc.		
			C	H	Cl	C	H	Cl
<i>trans</i> -PtCl(SnCl <sub>3</sub> )(PEt <sub>3</sub> ) <sub>2</sub>	C <sub>12</sub> H <sub>30</sub> Cl <sub>4</sub> P <sub>2</sub> PtSn	92	21.02	4.35	20.26	20.83	4.37	20.47
<i>trans</i> -Pt(SnCl <sub>3</sub> ) <sub>2</sub> (P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	C <sub>36</sub> H <sub>30</sub> Cl <sub>4</sub> O <sub>6</sub> SnPt	233	34.24	2.36	16.69	34.15	2.39	16.79
<i>cis</i> -PtCl <sub>2</sub> (P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	C <sub>36</sub> H <sub>24</sub> Cl <sub>6</sub> P <sub>2</sub> Pt	284	43.83	2.80	27.37	43.36	2.43	28.44
<i>cis</i> -PtCl <sub>2</sub> (P( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	C <sub>42</sub> H <sub>42</sub> Cl <sub>2</sub> O <sub>6</sub> P <sub>2</sub> Pt	290	52.03	4.34	7.17	51.96	4.36	7.31
<i>cis</i> -PtCl(SnCl <sub>3</sub> )(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	C <sub>36</sub> H <sub>30</sub> Cl <sub>4</sub> P <sub>2</sub> PtSn	288	43.66	3.10	14.75	44.12	3.09	14.43
<i>cis</i> -PtCl(SnCl <sub>3</sub> )(DIOP)	C <sub>31</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> PtSn	270	39.77	3.62	15.18	38.69	3.35	14.71

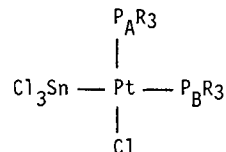
## Scheme



**1a** = Et  
**b** = Pr<sup>n</sup>



**2a** = Et  
**b** = nPr  
**c** = OEt  
**d** = OPh  
**e** = *p*-ClC<sub>6</sub>H<sub>4</sub>  
**f** = *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>



**3a** = OEt  
**b** = OPh  
**c** = *p*-ClC<sub>6</sub>H<sub>4</sub>  
**d** = Ph  
**e** = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
**f** = *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

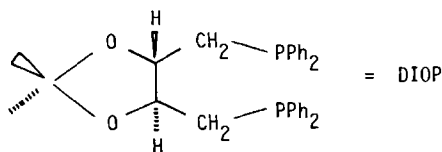


Table 2. NMR. Data<sup>a)</sup> for the Pt-Sn complexes

	<sup>1</sup> J(Pt,P)	<sup>2</sup> J(Sn,P)	δP	δPt <sup>b)</sup>	<sup>2</sup> J(P,P)
<b>1a</b> <i>trans</i> -PtCl(SnCl <sub>3</sub> )(PEt <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	2042	227, 237	13.6	-4790	
<b>2</b> <i>trans</i> -Pt(SnCl <sub>3</sub> ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	1873	234, 246	8.4	-5093	
<i>cis</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> <sup>d)</sup> e)	3518		9.3	-4475	
<i>trans</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> <sup>d)</sup> e)	2397		12.2	-3916	
<b>1b</b> <i>trans</i> -PtCl(SnCl <sub>3</sub> )(PnPr <sub>3</sub> ) <sub>2</sub>	2028	226, 238	3.7		
<b>2b</b> <i>trans</i> -Pt(SnCl <sub>3</sub> ) <sub>2</sub> (PnPr <sub>3</sub> ) <sub>2</sub> <sup>f)</sup>	1844	235, 247	0.3		
<i>cis</i> -PtCl <sub>2</sub> (PnPr <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	3486		0.0		
<i>trans</i> -PtCl <sub>2</sub> (PnPr <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	2347		3.8		
<b>3a</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P(OEt) <sub>3</sub> ) <sub>2</sub>	4761	Sn <i>trans</i> to P	85.2		<sup>2</sup> J(P,P) = 23.8
	5431	Sn <i>trans</i> to Cl	80.2		
<b>2c</b> <i>trans</i> -Pt(SnCl <sub>3</sub> ) <sub>2</sub> (P(OEt) <sub>3</sub> ) <sub>2</sub>	3623 <sup>d)</sup>	256 <sup>d)</sup> , 268 <sup>d)</sup>	104.0 <sup>d)</sup>	-5302 <sup>g)</sup>	
<i>cis</i> -PtCl <sub>2</sub> (P(OEt) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup>	5697		68.1	-4363 <sup>g)</sup>	
<b>3b</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P(OPh) <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	4695		74.8		<sup>2</sup> J(P,P) = 26.8
	5642		73.5		
<b>2d</b> <i>trans</i> -Pt(SnCl <sub>3</sub> ) <sub>2</sub> (P(OPh) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup>	3930	244, 256	97.0		
<i>cis</i> -PtCl <sub>2</sub> (P(OPh) <sub>3</sub> ) <sub>2</sub>	5796 <sup>c)</sup> e)		59.2 <sup>c)</sup> e)	-4298 <sup>d)</sup>	
<b>3c</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup>	2956	Sn <i>trans</i> to P	27.6		<sup>2</sup> J(P,P) = 14.7
	3664	Sn <i>trans</i> to Cl	10.5		
<b>2e</b> <i>trans</i> -PtCl(SnCl <sub>3</sub> )(P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup>	2334	215, 225	18.0	-4812	
<i>cis</i> -PtCl <sub>2</sub> (P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	3652 <sup>c)</sup>		13.2 <sup>c)</sup>	-4428 <sup>d)</sup> e)	
<b>3d</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	3083	Sn <i>trans</i> to P	27.9		<sup>2</sup> J(P,P) = 14.7
	3637	Sn <i>trans</i> to Cl	10.5		
<i>cis</i> -PtCl <sub>2</sub> (P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>c)</sup>	3678		13.8		
<b>3e</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	3135	Sn <i>trans</i> to P	26.8		<sup>2</sup> J(P,P) = 14.9
	3623	Sn <i>trans</i> to Cl	7.8		
<i>cis</i> -PtCl <sub>2</sub> (P( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	3691		12.1		
<b>3f</b> <i>cis</i> -PtCl(SnCl <sub>3</sub> )(P( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup>	3127	Sn <i>trans</i> to P	4093, 4283	25.8	-4742
	3622	Sn <i>trans</i> to Cl	207 <sup>h)</sup>	6.6	<sup>2</sup> J(P,P) = 14.7
<i>trans</i> -PtCl(SnCl <sub>3</sub> )(P( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub>	2249		219, 229	14.8	
<i>cis</i> -PtCl <sub>2</sub> (P( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub> <sup>d)</sup> e)	3706		10.8	-4407	
<i>cis</i> -PtCl(SnCl <sub>3</sub> )(DIOP) <sup>c)</sup>	2852	4082, 4278	8.9		<sup>2</sup> J(P,P) = 17.9
	3510	214 <sup>h)</sup>	-0.8		
<i>cis</i> -PtCl <sub>2</sub> (DIOP) <sup>c)</sup>	3517		-1.4		

<sup>a)</sup> Coupling constants are in Hz and are correct to ± 3. Chemical shifts are in ppm referred to external H<sub>3</sub>PO<sub>4</sub> at RT. and are correct to ± 0.1 ppm.

<sup>b)</sup> Upfield from external Na<sub>2</sub>PtCl<sub>6</sub>. Data at -50°. A negative sign indicates a shift to higher field.

<sup>c)</sup> In CH<sub>2</sub>Cl<sub>2</sub> at -50°.

<sup>d)</sup> In CHCl<sub>3</sub> at -50°.

<sup>e)</sup> Measured at RT.

<sup>f)</sup> At -80° as a mixture with **1b**.

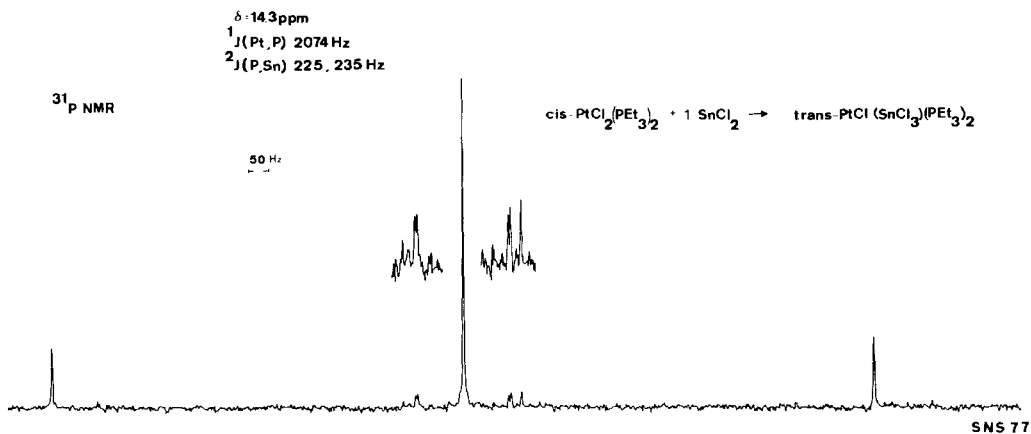
<sup>g)</sup> Measured in acetone.

<sup>h)</sup> Average of <sup>117</sup>Sn and <sup>119</sup>Sn couplings.

<sup>i)</sup> As a mixture with **3a** at -50°.

complex is shown in *Figure 1*. Further addition of  $\text{SnCl}_2$  to this solution leads to a mixture of **1a** and a second complex showing a single  $^{31}\text{P}$  signal at  $\delta$  8.4 surrounded by both  $^{195}\text{Pt}$  and  $^{117,119}\text{Sn}$  satellites. We assign to this complex the structure *trans*- $\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2$  based on a) the relative intensity of the main band to the Sn satellites, b) the values  $^2J(^{117,119}\text{Sn},\text{P})$  and c) the value of  $^1J(\text{Pt},\text{P})$  (1873 Hz) which, although somewhat small in comparison with other *trans*-Pt(II) phosphine complexes, is consistent with *trans* phosphorus atoms. Fully analogous results are obtained beginning with *cis*- $\text{PtCl}_2(\text{PPr}_3)_2$  (see *Table 2*), and for both phosphines identical results are obtained whether one begins with the *trans* or the *cis* bis-phosphine platinumous chloride.

The aryl phosphine compounds *cis*- $\text{PtCl}_2(\text{DIOP})$  and *cis*- $\text{PtCl}_2(\text{P}(p\text{-XC}_6\text{H}_4)_3)_2$ ,  $\text{X}=\text{OCH}_3, \text{CH}_3, \text{H}, \text{Cl}$ , react with an equimolar amount of  $\text{SnCl}_2$  to afford solutions whose  $^{31}\text{P}$ -NMR. spectra at  $-50^\circ$  show new resonances corresponding to either AX (or AB) type spin systems (see *Fig. 2*). For the DIOP complex this was the only detectable product whereas for the monodentate systems these signals are accompanied by 2 sharp singlets, one due to an additional complex and the other to starting material (<10%). At RT. the spectra are broader and sometimes featureless. The signals due to the 2 phosphorus atoms of the AX system are flanked by  $^{195}\text{Pt}$  satellites whose separations suggest that one phosphorus is *trans* to chloride whereas the other is opposite to a ligand of stronger *trans* influence. In some cases the spectral signal-to-noise was sufficient to measure the  $^{117,119}\text{Sn}$  couplings to phosphorus and these confirmed, *via* their grossly different values, that one phosphine was *cis* to Sn while the other was *trans* thus suggesting products of the form *cis*- $\text{PtCl}(\text{SnCl}_3)(\text{P}(p\text{-XC}_6\text{H}_4)_3)_2$ . The second complex has  $^1J(\text{Pt},\text{P})$  and, where measurable,  $^2J(\text{Sn},\text{P})$  values consistent with *trans* phosphines and we are tentatively considering these as the isomeric *trans* complexes. The magnitude of the values  $^2J(\text{Sn},\text{P})_{\text{trans}}$  in our trichloro stannane complexes deserves further comment. This



*Fig. 1.* The  $^{31}\text{P}\{^1\text{H}\}$ -NMR. spectrum of *trans*- $\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2$  formed by mixing approximately equimolar amounts of  $\text{SnCl}_2$  and *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$ . The small signal ( $\sim 2\%$ ) to the right of the high field Sn satellites is starting material

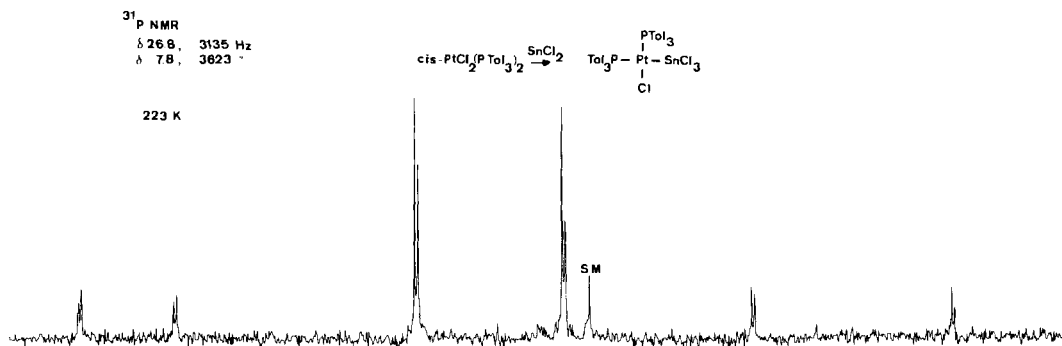


Fig. 2. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR. spectrum of  $\text{cis-PtCl}(\text{SnCl}_3)(\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3)_2$  formed by mixing approximately equimolar amounts of  $\text{SnCl}_2$  and  $\text{cis-PtCl}_2(\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3)_2$ . The signal labelled S.M. is starting material

type of coupling has been mentioned for the complexes  $\text{cis-PtPh}(\text{PPh}_3)_2(\text{SnMe}_n\text{Ph}_{(3-n)}\text{Cl})$  [9] and has an approximate value of 2200–2400 Hz. This is nearly one order of magnitude larger than  $^2J(\text{P}, \text{Sn})_{\text{cis}}$ . For the complexes  $\text{cis-PtCl}(\text{SnCl}_3)(\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3)_2$  and  $\text{cis-PtCl}(\text{SnCl}_3)(\text{DIOP})$  (see *Scheme* for structures) we find  $^2J(\text{Sn}, \text{P})_{\text{trans}} > 4000$  Hz, making this 2-bond coupling one of the largest ever reported. The increase from  $\sim 2000$  to  $\sim 4000$  Hz is probably related to the electron withdrawing substituents on the tin which may increase the term  $\psi_{\text{Sn}}(\text{O})^2$  for tin and/or the term  $a_{\text{Sn}}^2$  in the *Fermi* contact expression [12]. In any case this coupling should serve as a sensitive probe for the geometric relation of phosphorus and tin in square planar complexes. For all of our complexes  $^2J(\text{P}, \text{Sn})_{\text{cis}}$  values fall in the range 207–262 Hz<sup>1)</sup>.

The *cis* and *trans* isomers for the complex  $\text{PtCl}(\text{SnCl}_3)(\text{PPh}_3)_2$  have been reported previously [7]. Our  $^{31}\text{P}$  data ( $-50^\circ$ ) shows that the analytically pure white solid, reported to be the *trans* isomer in the solid state, gives a colorless solution when dissolved in  $\text{CH}_2\text{Cl}_2$  containing primarily the *cis* isomer (*cis/trans* = 82/18) ( $\delta P_A$  10.5,  $^1J(\text{Pt}, \text{P}) = 3637$  Hz,  $\delta P_B = 27.9$ ,  $^1J(\text{Pt}, \text{P}) = 3083$  Hz). The solutions of the  $\text{P}(p\text{-ClC}_6\text{H}_4)_3$  and  $\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$  derivatives containing one  $\text{SnCl}_2$  at  $-50^\circ$  showed both *cis* and *trans* isomers with *cis/trans* ratios of  $\sim 1/9$  and  $2.5/1^2)$ , respectively. Thus the substituents on the phenyl rings significantly affect the isomer distribution in these phosphine complexes. In this connection we note that  $^1J(\text{PtB}_B) (3f) > ^1J(\text{Pt}, \text{P}_B) (3c)$ .

The  $^{31}\text{P}$  signals from the reaction of  $\text{SnCl}_2$  with the phosphite complexes  $\text{cis-PtCl}_2(\text{P}(\text{OR})_3)_2$ ,  $\text{R} = \text{Et}, \text{Ph}$  showed features similar to those of the aryl phosphines *e.g.* starting material, an AB system plus a second new complex showing a sharp singlet. Further addition of  $\text{SnCl}_2$  results in the complete disappearance of the bis-dichloride and increasing quantities of the second complex. From separation of the  $^{117,119}\text{Sn}$  satellites in this latter derivative, the phosphite is *cis* to tin

1) The average of the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  couplings.

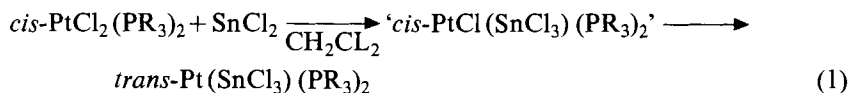
2)  $\sim 65\%$   $\text{cis-PtCl}(\text{SnCl}_3)(\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3)_2$ ,  $\sim 26\%$   $\text{trans-PtCl}(\text{SnCl}_3)(\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3)_2$  and  $\sim 9\%$   $\text{cis-PtCl}_2(\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3)_2$ .

whereas their intensities relative to the main signal suggest that this is a bis-tin complex. The  $^1J(\text{Pt}, \text{P})$  values of 3623 and 3924 Hz for the  $\text{P}(\text{OEt})_3$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$  compounds respectively are consistent with *trans* phosphorus atoms. As with the  $\text{PEt}_3$  and  $\text{P}^n\text{Pr}_3$  analogs we propose the formula *trans*- $\text{Pt}(\text{SnCl}_3)_2(\text{P}(\text{OR})_3)_2$  for these derivatives. For the triphenyl phosphite complex we have isolated a solid whose analysis is consistent with this composition. Analogous attempts with triethyl phosphite led to an oil.

The values of  $^2J(\text{P}, \text{P})_{\text{cis}}$  in the complexes of type 3 fall in the range 14–27 Hz and are consistent with the literature values for this type of *cis* coupling, further supporting the suggestion that these are all *cis*-phosphorus complexes.

**$^{195}\text{Pt}$ -NMR. Results.** -  $^{195}\text{Pt}$ -NMR. data for those complexes which were sufficiently soluble at  $-50^\circ$  are shown in Table 2. All of the  $^{195}\text{Pt}$  spectra can be satisfactorily analyzed as the X parts of  $\text{A}_2\text{X}$  or  $\text{ABX}$  spin systems thus demonstrating that 2 phosphorus atoms are bound to the metal. If one considers the chemical shift data for each of the stannane complexes relative to the appropriate *cis*-bis-phosphorus complex (e.g.  $\text{PtCl}(\text{SnCl}_3)(\text{PR}_3)_2$  relative to *cis*- $\text{PtCl}_2(\text{PR}_3)_2$ ), one finds that the introduction of the  $\text{SnCl}_3^-$  ligand is associated with an upfield shift of the  $^{195}\text{Pt}$  signal. For *trans*- $\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2$ , *trans*- $\text{PtCl}(\text{SnCl}_3)\text{P}(p\text{-ClC}_6\text{H}_4)_3$  and *cis*- $\text{PtCl}(\text{SnCl}_3)\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$  the changes are 315, 384 and 335 ppm, respectively. For *trans*- $\text{PtCl}(\text{GeH}_2\text{Cl})(\text{PEt}_3)_2$  and *trans*- $\text{PtCl}(\text{SiHCl}_2)(\text{PEt}_3)_2$  the corresponding values are 456 and 465 ppm [14]. Given that  $\text{Pt}(\text{IV})$  complexes often appear 500–2000 ppm *downfield* from an analogous  $\text{Pt}(\text{II})$  species [10] our  $^{195}\text{Pt}$ -NMR. data would appear consistent with the idea that our complexes have retained their initial oxidation state. The introduction of a second mole of  $\text{SnCl}_2$ , as in the  $\text{PEt}_3$  case produces a new complex whose  $^{195}\text{Pt}$  resonance has moved yet another 303 ppm higher. We have observed similar changes in the  $^{195}\text{Pt}$  spectrum of the analogous  $\text{P}(\text{OEt})_3$  complexes when dissolved in acetone; however, the  $^{31}\text{P}$  spectrum for this phosphite in  $\text{CDCl}_3$  and acetone differ significantly and further study is required.

**Conclusion.** - The  $^{31}\text{P}$ - and  $^{195}\text{Pt}$ -NMR. data for chlorohydrocarbon solutions at  $-50^\circ$  containing equimolar amounts of  $\text{SnCl}_2$  and  $\text{PtCl}_2\text{P}_2$ ,  $\text{P}$  = a phosphorus ligand, show that new products are formed in good yield. The NMR. data for the trialkylphosphine complexes containing one tin ligand are consistent with structures **1** and **1b**. Since the same product results from either *cis* or *trans* starting materials the insertion of  $\text{SnCl}_2$  into the platinum/chloride bond in *cis*- $\text{PtCl}_2(\text{PR}_3)_2$  is followed by rapid isomerization<sup>3)</sup> (eq. 1). Addition of a second mole of  $\text{SnCl}_2$  leads to a second insertion (eq. 2).



<sup>3)</sup> We do not exclude a 5-coordinate complex as a reaction intermediate in either step in eq. 1 but merely suggest, based on the phosphite and aryl phosphine data, that a *cis* planar precursor is likely to be formed.

For the triaryl phosphine derivatives the  $^{31}\text{P}$  data clearly show that the *cis*-complexes, **3**, are the primary products formed with an equimolar quantity of  $\text{SnCl}_2$ , although the corresponding *trans* isomer is often present and is the major component in the case of  $\text{P}(p\text{-ClC}_6\text{H}_4)_3$ . The reaction of chelate complex *cis*- $\text{PtCl}_2(\text{DIOP})$  with  $\text{SnCl}_2$  affords a product whose structure is analogous to **3**. The  $\text{P}(\text{OEt})_3$  and  $\text{P}(\text{OC}_6\text{H}_5)_3$  bis-complexes show similar results in that the first insertion produces *cis* complexes of type **3** which then react further with a second mole of  $\text{SnCl}_2$  to produce *trans* bis-trichlorostannane complexes of type **2**. The synthesis of a series of complexes of general structure **1** and **2** containing  $\text{Sn}(\text{OC}_6\text{H}_5)_3^-$  and  $\text{Sn}(\text{O}_2\text{CC}_6\text{H}_5)_3^-$  ligands has been recently reported [15] further supporting the credibility of our proposed structures.

The limited solubility of  $\text{SnCl}_2$  in chlorinated hydrocarbon solvents has prevented our studying the further reactions of  $\text{SnCl}_2$  with complexes such as **2**; however, the analogous NMR. studies in acetone, in which  $\text{SnCl}_2$  is reasonably soluble, have given different results and these will be the subject of a separate report.

In summary,  $\text{SnCl}_2$  reacts readily with an equimolar quantity  $\text{PtCl}_2\text{P}_2$  complexes at RT. to give both *cis* and *trans* mono trichlorostannane complexes whose relative ratios, lability in solution and ease of isolation markedly depend upon the nature of the phosphorus ligand. For phosphite and trialkyl phosphine ligands further addition of  $\text{SnCl}_2$  produces the *trans* complexes  $\text{Pt}(\text{SnCl}_3)_2\text{P}_2$ .

We wish to thank the Swiss National Science Foundation for support (S.N.S.).

#### REFERENCES

- [1] R. Pietropaolo, M. Graziani & U. Belluco, *Inorg. Chemistry* **8**, 1506 (1969); R. Pietropaolo, G. Dolcetti, M. Giustiniani & U. Belluco, *ibid.* **9**, 549 (1970).
- [2] H. Itatani & J.C. Bailor Jr., *Ind. Eng. chem. Prod. Res. Develop.* **11**, 146 (1972); G.C. Bond & M. Hellier, *J. Catalysis* **7**, 217 (1967); J.F. Knifton, *J. Org. Chem.* **41**, 793 (1976); J.F. Knifton, *J. Catalysis* **45**, 256 (1976); G. Consiglio & P. Pino, *Helv.* **59**, 642 (1976).
- [3] J.F. Young, R.D. Gillard & G. Wilkinson, *J. chem. Soc.* **1964**, 5176.
- [4] R.V. Parish & P.J. Rowbotham, *J. chem. Soc.* **1973**, 37.
- [5] R.D. Cramer, R.V. Lindsay, C.T. Prewitt & U.G. Stolberg, *J. Amer. chem. Soc.* **87**, 658 (1965).
- [6] R.V. Lindsay, G.W. Parshall & U.G. Stolberg, *Inorg. Chemistry* **5**, 109 (1966).
- [7] M.C. Baird, *J. Inorg. nucl. Chemistry* **29**, 367 (1967).
- [8] A. Pidcock, R.E. Richards & L.M. Venanzi, *J. chem. Soc. A* **1966**, 1707.
- [9] C. Eaborn, A. Pidcock & B.R. Steele, *J. chem. Soc. Dalton* **1975**, 809; *ibid.* **1976**, 767.
- [10] A. Pidcock, R.E. Richards & L.M. Venanzi, *J. chem. Soc. A* **1968**, 1970; J.D. Kennedy, W. McFarlane, R.J. Puddephatt & P.J. Thompson, *J. chem. Soc. Dalton* **1976**, 874; W. Freeman P.S. Pregosin, S.N. Sze & L.M. Venanzi, *J. Magn. Res.* **22**, 473 (1976).
- [11] J.C. Bailor, Jr. & H. Itatani, *Inorg. Chemistry* **4**, 1618 (1965).
- [12] J. Nixon & A. Pidcock, in: 'Ann. Rev. of NMR. Spectroscopy' (Ed. E.F. Mooney), Academic Press **1969**, Vol. 2, p. 345.
- [13] J.M. Jenkins & B.L. Shaw, *J. chem. Soc. A* **1966**, 770; H.C. Clark & C.S. Wong, *J. organomet. Chemistry* **92**, C31 (1975) and ref. therein.
- [14] D.W.W. Anderson, E.A.V. Ebsworth & D.W.H. Rankin, *J. chem. Soc. Dalton* **1973**, 2370.
- [15] D.R. Coulson & L.P. Seiwel, *Inorg. Chemistry* **15**, 2563 (1976).