

## 77. $^{31}\text{P}$ -, $^{119}\text{Sn}$ - and $^{195}\text{Pt}$ -NMR. Studies of Trichlorostannate Complexes of Pt (II) and Pd (II). $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ -Values

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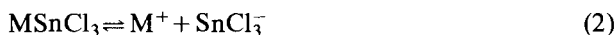
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### Summary

The synthesis and solution structures of new four- and five-coordinate phosphine and arsine complexes of Pt and Pd containing the trichlorostannate ligand are described. Complexes containing two and three  $\text{SnCl}_3^-$ -ligands have been identified from their  $^{31}\text{P}$ -,  $^{119}\text{Sn}$ - and  $^{195}\text{Pt}$ -NMR. spectra. The complexes *trans*- $[\text{M}(\text{SnCl}_3)_2\text{L}_2]$  ( $\text{M} = \text{Pt}$ ,  $\text{L} = \text{PEt}_3$ ,  $\text{PPr}_3$ ,  $\text{AsEt}_3$ ;  $\text{M} = \text{Pd}$ ,  $\text{L} = \text{AsEt}_3$ ) show unexpectedly large  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ -values (34,674–37,164 Hz) with the *trans*-orientation of these spins playing an important role. The heteronuclear coupling constant  $^2J(^{119}\text{Sn}, ^{31}\text{P})$  in the five-coordinate cationic complexes  $[\text{Pt}(\text{SnCl}_3)(\text{P}(o\text{-AsPh}_2\text{-C}_6\text{H}_4)_3)]^+$  and  $[\text{Pt}(\text{SnCl}_3)(\text{As}(o\text{-PPh}_2\text{-C}_6\text{H}_4)_3)]^+$  also shows a geometric dependence. New five-coordinate anionic complexes of type  $[\text{M}(\text{SnCl}_3)_3\text{L}_2]^-$  ( $\text{M} = \text{Pd}$ ,  $\text{Pt}$ ;  $\text{L} = \text{PEt}_3$ ,  $\text{AsEt}_3$ ) may be prepared *via* addition of three mol-equiv. of  $\text{SnCl}_2$  and one mol-equiv. of  $(\text{PPN})\text{Cl}$  to  $[\text{MCl}_2\text{L}_2]$  in acetone.

**Introduction.** – Trichlorostannate complexes of Pt and Pd have recently attracted increasing attention due to their ability to function as homogeneous hydrogenation catalysts [1]. Although solid state structures for a number of these complexes are known [2–5], the identification of the  $\text{MSnCl}_3$ -unit in solution is complicated by the equilibria given in *Equations 1* and *2* [6] [7]



Further, in the presence of excess  $\text{SnCl}_2$  poly- $\text{SnCl}_3^-$ -complexes can also be formed [8–10]. In previous studies we have noted that  $^1\text{H}$ -[11],  $^{31}\text{P}$ -[8] and  $^{195}\text{Pt}$ -[12] NMR. methods are useful in assigning solution structures of these complexes. To increase our understanding in this field and find additional physical methods which will allow the facile characterization of such complexes we have made  $^{119}\text{Sn}$ -, and additional  $^{31}\text{P}$ - and  $^{195}\text{Pt}$ -NMR. measurements on both new and previously characterized

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Pt- and Pd-trichlorostannate complexes. The  $^{119}\text{Sn}$ - and  $^{31}\text{P}$ -NMR. studies are especially relevant in Pd(II) chemistry since there are recent reports concerning the Pd,  $\text{SnCl}_3$  interaction in catalytically active complexes [1a] [13] [14].

We begin by considering mono-trichlorostannate derivatives; however, since more than one  $\text{SnCl}_3^-$ -ligand may be involved in the homogeneous hydrogenation catalyst [1] we concentrate, in this report, on the NMR. characteristics associated with complexes containing two and three  $\text{SnCl}_3^-$ -groups, and specifically, the spin-spin coupling between the Sn-atoms.

**Experimental.** – *General remarks.* – IR. spectra were measured as nujol mulls or CsBr-pellets using a Beckmann 4250 spectrophotometer over the range  $4000\text{--}200\text{ cm}^{-1}$ . – NMR. spectra were measured on a Bruker WM-250 at 101.27, 93.27 and 53.77 MHz for  $^{31}\text{P}$ ,  $^{119}\text{Sn}$  and  $^{195}\text{Pt}$ , respectively, as solutions in 10 or 15 mm tubes.  $^{31}\text{P}$ - and  $^{195}\text{Pt}$ -NMR. spectra were measured under conditions of broad-band  $^1\text{H}$ -decoupling. This was not necessary for the  $^{119}\text{Sn}$ -NMR. spectra. The spin-lattice relaxation times for  $^{119}\text{Sn}$  and  $^{195}\text{Pt}$  are relatively short and thus free-induction decay acquisition times of  $<0.2\text{ s}$  with  $50\text{--}70^\circ$  flip angles were routinely employed. For  $^{31}\text{P}$ , the acquisition time and flip angle were 0.7 s and  $35^\circ$ , respectively. The sample temperature was controlled by passing a stream of cooled  $\text{N}_2$  over the sample tube and is estimated to be accurate to  $\pm 1^\circ$ . Chemical shifts are in ppm relative to the following external standards: neat  $\text{H}_3\text{PO}_4$ , 10%  $(\text{CH}_3)_4\text{Sn}$   $\text{CDCl}_3$ -solution and  $\text{Na}_2\text{PtCl}_6$  (aq.), all at RT. Coupling constants ( $J$ ) are in Hz; with the accuracy of  $\pm 2$  for  $^{31}\text{P}$ -measurements,  $\pm 6$  for  $^{195}\text{Pt}$ - and  $^{119}\text{Sn}$ -measurements. A positive sign indicates a shift to lower field, higher frequency. The divisor for the  $\delta(^{195}\text{Pt})$ -calculations was chosen as 53.77. The synthesis of the trichlorostannate complexes was carried out under a  $\text{N}_2$ -atmosphere, although the  $[\text{PtCl}(\text{SnCl}_3)_2]$  and anionic  $[\text{Pt}(\text{SnCl}_3)_3\text{L}_2]^-$ -compounds proved not to be  $\text{O}_2$ -sensitive. The following are representative syntheses for the various types of Sn-complexes and the appropriate microanalytical results are given in Table 1.

*Preparation of trans-[PdCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] and trans-[PdCl(SnCl<sub>3</sub>)(PPr<sub>3</sub>)<sub>2</sub>].* Solid anh.  $\text{SnCl}_2$  (19 mg, 0.10 mmol) was added to a solution of 0.10 mmol of *trans*- $[\text{PdCl}_2(\text{PR}_3)_2]$  (R = Et, Pr) in 5 ml  $\text{CH}_2\text{Cl}_2$ . Following the slow dissolution of  $\text{SnCl}_2$  the solvent was removed, and recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane gave 51 mg (84%) of complex for R =  $\text{PEt}_3$ , and 59 mg (80%) for R =  $\text{PPr}_3$ . In the synthesis of the  $\text{PPh}_3$ - and  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ -complexes toluene was used as solvent.

Table 1. Microanalytical results for the complexes

Complex	% C		% H		% Cl	
	Calc.	Found	Calc.	Found	Calc.	Found
<i>trans</i> - $[\text{PdCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$	23.89	24.36	5.01	5.12		
<i>trans</i> - $[\text{PdCl}(\text{SnCl}_3)(\text{PPr}_3)_2]$	31.45	31.77	6.12	6.33		
<i>trans</i> - $[\text{PdCl}(\text{SnCl}_3)(\text{AsEt}_3)_2]$	20.86	21.26	4.38	4.42		
<i>trans</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{AsMe}_3)_2]$	10.36	10.47	2.61	2.46	20.39	20.64
<i>trans</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{AsEt}_3)_2]$	18.48	18.68	3.88	3.90	18.19	18.04
<i>trans</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$	20.83	21.04	4.37	4.35	20.50	20.44
<i>cis</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{PPh}_2\text{Bz})_2]$	45.27	45.02	3.40	3.29	14.07	14.38
<i>cis</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$	44.11	43.97	3.08	3.27	14.47	14.65
<i>cis</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{P}(p\text{-Cl-C}_6\text{H}_4)_3)_2]$	36.43	36.13	2.04	2.04	29.87	30.44
<i>cis</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{P}(p\text{-OCH}_3\text{-C}_6\text{H}_4)_3)_2]$	43.48	43.33	3.65	3.60	12.22	12.40
$[(\text{Ph}_3\text{P})_2\text{N}][\text{Pt}(\text{SnCl}_3)_3(\text{AsMe}_3)_2]$	30.59	30.44	2.93	2.96	19.35	19.35
$[\text{Ph}_4\text{As}][\text{Pt}(\text{SnCl}_3)_3(\text{AsEt}_3)_2]$	27.41	27.34	3.19	3.14	20.22	20.07
$[(\text{Ph}_3\text{P})_2\text{N}][\text{Pt}(\text{SnCl}_3)_3(\text{PEt}_3)_2]$	35.04	35.24	3.68	3.57	19.40	19.90
$[(\text{Ph}_3\text{P})_2\text{N}][\text{Pt}(\text{SnCl}_3)_3(\text{PMe}_2\text{Ph})_2]$	37.06	36.91	3.11	3.12	18.93	18.99
$[(\text{Ph}_3\text{P})_2\text{N}][\text{Pt}(\text{SnCl}_3)_3(\text{P}(\text{OEt})_3)_2]$	33.11	32.53	3.47	3.38	18.33	19.17

*Preparation of trans-[PdCl(SnCl<sub>3</sub>)(AsEt<sub>3</sub>)<sub>2</sub>].* *trans*-[PdCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (50 mg; 0.10 mmol) and SnCl<sub>2</sub> (19 mg; 0.10 mmol) were dissolved in 5 ml acetone and allowed to stand for 15 min. Removal of the solvent gave a glass which after drying *in vacuo* overnight afforded a yellow powder in essentially quantitative yield. This complex may also be obtained *via* the method described for *trans*-[PdCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>].

*Preparation of cis-[PtCl(SnCl<sub>3</sub>)(P(p-X-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]-complexes (X=H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl).* Solid anh. SnCl<sub>2</sub> (19 mg, 0.10 mmol) was added to a solution of 0.10 mmol *cis*-[PtCl<sub>2</sub>(P(p-X-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>] in 3 ml of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 2 h at RT. the yellow-orange solution was filtered, and 20 ml petroleum ether (30–60°) was carefully added to the clear filtrate so that two separate layers were formed. Storage at –20° for a week led to precipitation of the less soluble *cis*-isomer. *Yields:* *cis*-[PtCl(SnCl<sub>3</sub>)-(PPh<sub>3</sub>)<sub>2</sub>]: 65 mg (66%); *cis*-[PtCl(SnCl<sub>3</sub>)(P(p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]: 84 mg (79%); *cis*-[PtCl(SnCl<sub>3</sub>)-(P(p-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]: 55 mg (47%); *cis*-[PtCl(SnCl<sub>3</sub>)(P(p-Cl-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]: 110 mg (93%).

*Preparation of the solutions containing [M(SnCl<sub>3</sub>)<sub>2</sub>L<sub>2</sub>].* All of the bis(trichlorostannate)-complexes were prepared as follows: the complex (0.2 mmol) and tin(II) chloride (0.4 mmol) were suspended in 6 ml CH<sub>2</sub>Cl<sub>2</sub> and the mixture stirred for 2 h. The reaction mixture was then filtered to remove undissolved tin(II) chloride and 1.5 ml of CD<sub>2</sub>Cl<sub>2</sub> was added. The solution was transferred to an NMR. tube and measured directly. The measurements indicate the presence of a mixture of *trans*-[M(SnCl<sub>3</sub>)<sub>2</sub>L<sub>2</sub>] and *trans*-[MCl(SnCl<sub>3</sub>)L<sub>2</sub>]. We find that there is more bis-complex, a) for M = Pt than for M = Pd, b) for L = AsEt<sub>3</sub> than for L = PEt<sub>3</sub>.

*Preparation of the anionic complexes of type [M(SnCl<sub>3</sub>)<sub>3</sub>L<sub>2</sub>]<sup>-</sup>.* All the anionic complexes were generated *in situ* by the addition of D<sub>6</sub>-acetone to a solid-mixture of three mol-equiv. of anh. SnCl<sub>2</sub> and one mol-equiv. of [MCl<sub>2</sub>L<sub>2</sub>]. NMR. spectra of the resulting orange-red solutions were measured immediately after preparation.

*Preparation of (Ph<sub>4</sub>As)[Pt(SnCl<sub>3</sub>)<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>].* To a solution of *cis*-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (59 mg, 0.10 mmol) and SnCl<sub>2</sub> (57 mg, 0.30 mmol) in 3 ml acetone was added a solution of Ph<sub>4</sub>AsCl (42 mg, 0.10 mmol) in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. Addition of ether is accompanied by the precipitation of product as orange crystals (140 mg, 88%).

*Preparation of ((Ph<sub>3</sub>P)<sub>2</sub>N)[Pt(SnCl<sub>3</sub>)<sub>3</sub>L<sub>2</sub>] (L = AsMe<sub>3</sub>, AsEt<sub>3</sub>, PEt<sub>3</sub>, PMe<sub>2</sub>Ph, P(OEt)<sub>3</sub>).* *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (0.10 mmol) and SnCl<sub>2</sub> (57 mg, 0.30 mmol) were dissolved in 2 ml acetone. The resulting orange solution was then treated with [(Ph<sub>3</sub>P)<sub>2</sub>N]Cl (57.5 mg, 0.10 mmol) dissolved in 1 ml CH<sub>2</sub>Cl<sub>2</sub>. Evaporation of the solvent gives an oil. After adding 3 ml CH<sub>2</sub>Cl<sub>2</sub>, the solution was filtered and then treated with 15 ml petroleum ether (30–60°) so that the two phases remain immiscible. Storage at –20° for a week led to the slow precipitation of the product as orange crystals which were filtered off and dried. *Yields:* for L = AsMe<sub>3</sub>: 142 mg (86%), for L = AsEt<sub>3</sub>: 160 mg (92%), for L = PEt<sub>3</sub>: 145 mg (88%), for L = PMe<sub>2</sub>Ph: 165 mg (98%), for L = P(OEt)<sub>3</sub>: 155 mg (89%).

*Preparation of the five-coordinate cationic complexes [Pt(SnCl<sub>3</sub>)(P(o-AsPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sup>+</sup>, [Pt(SnCl<sub>3</sub>)(As(o-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sup>+</sup> and [Pd(SnCl<sub>3</sub>)(P(o-AsPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sup>+</sup>.* They were prepared by addition of 1.1 mol-equiv. of solid anh. SnCl<sub>2</sub> to solutions of the corresponding chlorides as their BPh<sub>4</sub><sup>-</sup>-salts in CH<sub>2</sub>Cl<sub>2</sub> (provided by L. M. Venanzi, ETH-Zürich). The suspensions were stirred for 0.5 h and then filtered. The <sup>31</sup>P-NMR. spectra showed Sn-satellites at RT. and little, or no unreacted starting material. The remaining SnCl<sub>3</sub><sup>-</sup>-complexes were prepared as described previously [8].

**Results and Discussion.** – 1. *Mono-trichlorostannate complexes.* Reaction of one mol-equiv. of SnCl<sub>2</sub> with either *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] or *trans*-[PdCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] leads to mono-trichlorostannate complexes of composition [MCl(SnCl<sub>3</sub>)(PR<sub>3</sub>)<sub>2</sub>] (M = Pd, Pt). We have reported our studies on the four-coordinate Pt-complexes previously [8], and consequently, begin with a description of the four-coordinate Pd-compounds. The PEt<sub>3</sub>-, PPr<sub>3</sub>-, PPh<sub>3</sub>- and PTol<sub>3</sub>- (Tol = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) derivatives are all yellow air-stable solids. In solution, the alkylphosphines have the *trans*-geometry, whereas the aryl-phosphines exist as a mixture of *cis*- and *trans*-isomers, the *cis*-component predominating. For [PdCl(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] <sup>31</sup>P-NMR. spectroscopy reveals 55% *cis*- and 40% *trans*-isomers, whereas for [PdCl(SnCl<sub>3</sub>)(PTol<sub>3</sub>)<sub>2</sub>] we find 68% *cis*- and 23% *trans*-isomers with the remaining few percent attributable to the starting dichloride. The assignment of geometry is made using <sup>119</sup>Sn- and <sup>31</sup>P {<sup>1</sup>H}-NMR. spectroscopy.

copy and is based on the values  ${}^2J({}^{119}\text{Sn}, {}^{31}\text{P})$ , as well as the *AB*-spectrum arising from the non-equivalent phosphine P-atoms in the  ${}^{31}\text{P}$ -NMR. spectra for the *cis*-isomers. The arsine complex *trans*-[PdCl(SnCl<sub>3</sub>)(AsEt<sub>3</sub>)<sub>2</sub>] was identified *via* IR. and  ${}^{119}\text{Sn}$ -NMR. spectroscopies and microanalysis.

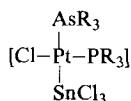
It is interesting that several reports [1a] [13] [14] assign the *trans*-geometry to [PdCl(SnCl<sub>3</sub>)(PPH<sub>3</sub>)<sub>2</sub>] whereas we find the *cis*-isomer to predominate, at least in chlorinated hydrocarbons.

Our Pd-phosphine complexes are dynamic on the NMR. time-scale; moreover the arylphosphine derivatives require lower temperatures than the alkyl analogs before sharp signals are observed. The analogous Pt(II) molecules behave in a similar fashion [8], however, there are important quantitative differences. The alkylphosphine complexes of Pt(II) with SnCl<sub>3</sub> appear not to be dynamic at RT., whereas the arylphosphine complexes give static spectra at  $\approx -40^\circ$ . Interestingly, an equimolar mixture of [PtCl(SnCl<sub>3</sub>)(P(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>] and [PtCl(SnCl<sub>3</sub>)(As(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>] in CDCl<sub>3</sub> prepared at RT. shows a  ${}^{119}\text{Sn}$ -NMR. spectrum at  $-25^\circ$  consistent with a statistical scrambling of the tertiary phosphine and arsine ligands. In addition to the starting materials, the complex [PtCl(SnCl<sub>3</sub>)(P(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)(As(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>))] is readily observable. Based on the  ${}^1J({}^{195}\text{Pt}, {}^{31}\text{P})$ -,  ${}^1J({}^{195}\text{Pt}, {}^{119}\text{Sn})$ - and  ${}^2J({}^{119}\text{Sn}, {}^{31}\text{P})$ -values, we assign structure **I** to this complex and the  ${}^{195}\text{Pt}$ -NMR. spectrum supports this proposal. On the other hand the same experiment with *trans*-[PtCl(SnCl<sub>3</sub>)(PET<sub>3</sub>)<sub>2</sub>] and *trans*-[PtCl(SnCl<sub>3</sub>)(AsEt<sub>3</sub>)<sub>2</sub>] does *not* lead to the exchange and the expected mixed phosphine-arsine complex. These observations may be relevant when discussing differences in the catalytic activity of aryl- and alkylphosphine complexes.

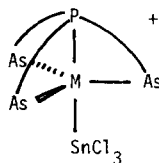
Given *Equations 1* and *2*, and the dynamic character of the *cis*-[MCl(SnCl<sub>3</sub>)L<sub>2</sub>]-complexes, it was conceivable that the *trans*-arrangement of phosphine- and SnCl<sub>3</sub><sup>-</sup>-ligands was unfavorable thereby resulting in the dissociation of SnCl<sub>3</sub><sup>-</sup>; however, equally likely was a step involving the cleavage of the (metal, phosphorus)-bond. To gain further insight into this field we have synthesized the five-coordinate complexes **II–IV**, which contain the tetradentate ligands P(*o*-AsPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> and As(*o*-PPH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. These chelating ligands have the structures shown in [15] and provide models for molecules containing P- or As-atoms *trans* to Sn. The nature of these ligands makes it unlikely that the central P- or As-atom will dissociate from the metal, whereas the trichlorostannate suffers no such restriction.

For **II–IV** we find *no* dynamic behaviour on the NMR. time-scale in CH<sub>2</sub>Cl<sub>2</sub>-solution. The  ${}^{31}\text{P}$ -,  ${}^{119}\text{Sn}$ - and, where applicable,  ${}^{195}\text{Pt}$ -NMR. spectra, all afford sharp signals at sample temperature ( $\approx 30^\circ$ ). For example: the  ${}^{119}\text{Sn}$ -NMR. spectrum of **II** consists of a doublet derived from the ( ${}^{119}\text{Sn}, {}^{31}\text{P}$ )<sub>*trans*</sub>-coupling, accompanied by  ${}^{195}\text{Pt}$ -satellites. The  ${}^{195}\text{Pt}$ -NMR. spectrum shows the expected doublet multiplicity arising from the ( ${}^{195}\text{Pt}, {}^{31}\text{P}$ )-coupling, flanked by  ${}^{117}\text{Sn}$ - and  ${}^{119}\text{Sn}$ -satellites. The *trans*-orientation of the P- and Sn-spins is proven by the magnitude of  ${}^2J({}^{119}\text{Sn}, {}^{31}\text{P})$  (see below).

Although the solution behaviour of these five-coordinate molecules does not prove the phosphine dissociation in the square planar complexes, at least there is one environment containing P or As *trans* to SnCl<sub>3</sub><sup>-</sup> where the Pt, Sn-bond is intact.



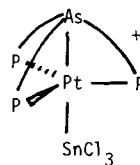
I R = *p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>



II M = Pt  
 $^2J(^{119}\text{Sn}, ^{31}\text{P}) = 3044 \text{ Hz}$

III M = Pd  
 $^2J(^{119}\text{Sn}, ^{31}\text{P}) = 3649 \text{ Hz}$

P(*o*-AsPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>



IV As(*o*-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>  
 $^2J(^{119}\text{Sn}, ^{31}\text{P}) = 271 \text{ Hz}$

2. *Bis(trichlorostannate) complexes.* The reaction of two mol-equiv. of anh. SnCl<sub>2</sub> with *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> results, first, in the formation of *trans*-[PtCl(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] [8] and then of *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]. This bis(trichlorostannate) complex has been reported [10] as an orange solid. The presence of at least two coordinated SnCl<sub>3</sub><sup>-</sup>-ligands is implied by the intensities of the Sn-satellites relative to the main bands in the <sup>195</sup>Pt {<sup>1</sup>H}-spectrum (<sup>117</sup>Sn and <sup>119</sup>Sn have natural abundances of 7.6 and 8.6%, respectively) and is confirmed by the observation of a (<sup>119</sup>Sn, <sup>117</sup>Sn)-coupling in the <sup>119</sup>Sn-NMR. spectrum.

The suggestion that this molecule is a bis(trichlorostannate) complex and not a tris(trichlorostannate) is based on the statistical distribution of Sn-isotopes in the <sup>119</sup>Sn-NMR. spectrum. Bis-complex will give <sup>117</sup>Sn-satellites with a relative intensity of 4.1%, whereas for tris-complexes this value would be 8.2% [16]. It is important that the spectral signal-to-noise ratio be adequate and the phasing correct to avoid ambiguous results [17]. The assignment of the *trans*-geometry proceeds once again from the (<sup>119</sup>Sn, <sup>31</sup>P)-coupling. Pt-complexes containing two trialkyl-tin ligands have been reported previously [18] [19] and these often have a *trans*-geometry (e.g. *trans*-[Pt(SnPh<sub>3</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] and *trans*-[Pt(SnPh<sub>3</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] [8] [19] as well as *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(P(OPh)<sub>3</sub>)<sub>2</sub>]), although the yellow PtCl<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub><sup>2-</sup>-anion has the *cis*-geometry [9].

For the complex *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>], both the <sup>119</sup>Sn- (see Fig. 1) and <sup>195</sup>Pt-NMR. spectra support the bis(trichlorostannate) formulation and the value <sup>1</sup>J(<sup>195</sup>Pt, <sup>119</sup>Sn) is consistent with a *trans*-geometry. The assignment of the *trans*-orientation in [Pd(SnCl<sub>3</sub>)<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] was made by analogy. In all of the spectra of our bis-complexes we find signals which are attributable to the presence of mono- and tris-complexes and we have, thus far, been unable to isolate a sample of analytically pure bis-complex. Complexes of the type [Pt(SnCl<sub>3</sub>)<sub>2</sub>L<sub>2</sub>] may have some synthetic utility since we observe that two mol-equiv. of SnCl<sub>2</sub>-combine with *cis*-[PtCl<sub>2</sub>(P(*p*-X-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>] (X = Cl, F, H, CH<sub>3</sub>, OCH<sub>3</sub>), in the presence of molecular hydrogen to give the hydride *trans*-[PtHCl(P(*p*-X-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>] in good yields [20]. As the yield can not be increased by adding more SnCl<sub>2</sub>, perhaps bis(trichlorostannate) complexes are worthy of further study in connection with the activation of gaseous hydrogen.

3. *Tris(trichlorostannate) complexes.* The limited solubility of SnCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> precludes the preparation of sufficiently concentrated solutions containing (Sn/Pt)-

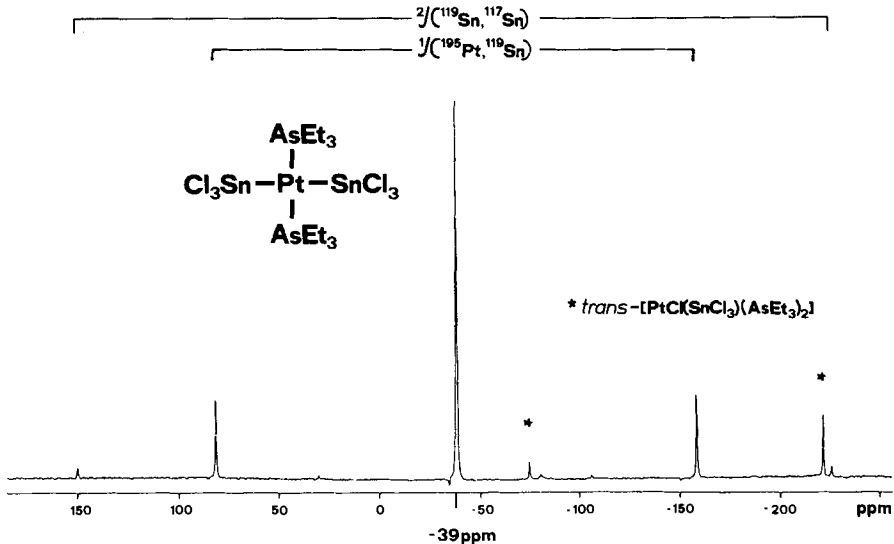


Fig. 1.  $^{119}\text{Sn}$ -NMR. spectrum of *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] in CDCl<sub>2</sub> at -75° (The signal at higher field comes from *trans*-[PtCl(SnCl<sub>3</sub>)(AsEt<sub>3</sub>)<sub>2</sub>]. The ratio of the main signal to  $^{117}\text{Sn}$ -satellite is about 30:1)

ratios of greater than two; however, satisfactory solutions containing three mol-equiv. of Sn per Pt (or Pd) were easily prepared using either acetone or methanol as solvent. Figures 2 and 3 show the  $^{195}\text{Pt}$ - and  $^{119}\text{Sn}$ -NMR. spectra for the [Pt(SnCl<sub>3</sub>)<sub>3</sub>(P(OEt)<sub>3</sub>)<sub>2</sub>]<sup>-</sup> anion. This new type of five-coordinate complex is identified by, a) the  $^{119}\text{Sn}$ - and  $^{117}\text{Sn}$ -satellite intensities, b) the multiplicity due to the P-spins, c) conductivity measurements, and d) microanalytical data.

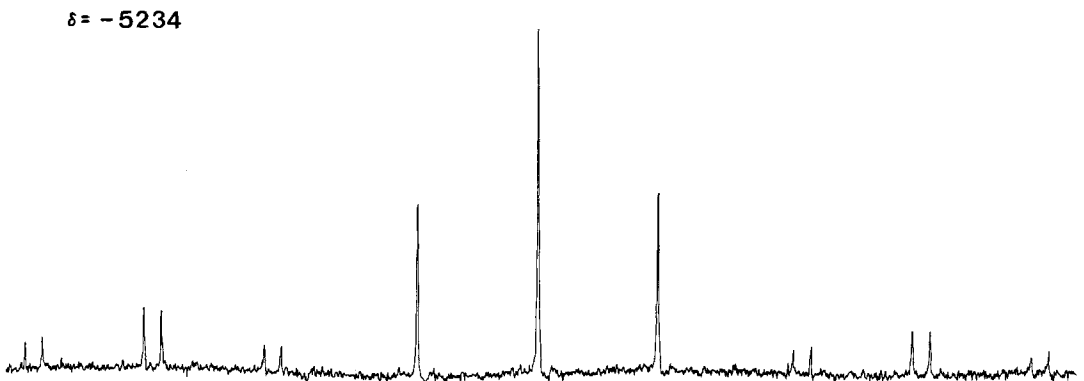


Fig. 2.  $^{195}\text{Pt}$ -NMR. spectrum of [Pt(SnCl<sub>3</sub>)<sub>3</sub>(P(OEt)<sub>3</sub>)<sub>2</sub>]<sup>-</sup> (The intense triplet in the center of the spectrum stems from the two equivalent  $^1J(^{195}\text{Pt}, ^{31}\text{P})$ -values. The smaller, symmetrically placed signals result from the coupling constants  $^1J(^{195}\text{Pt}, ^{119}\text{Sn})$  and  $^1J(^{195}\text{Pt}, ^{117}\text{Sn})$ )

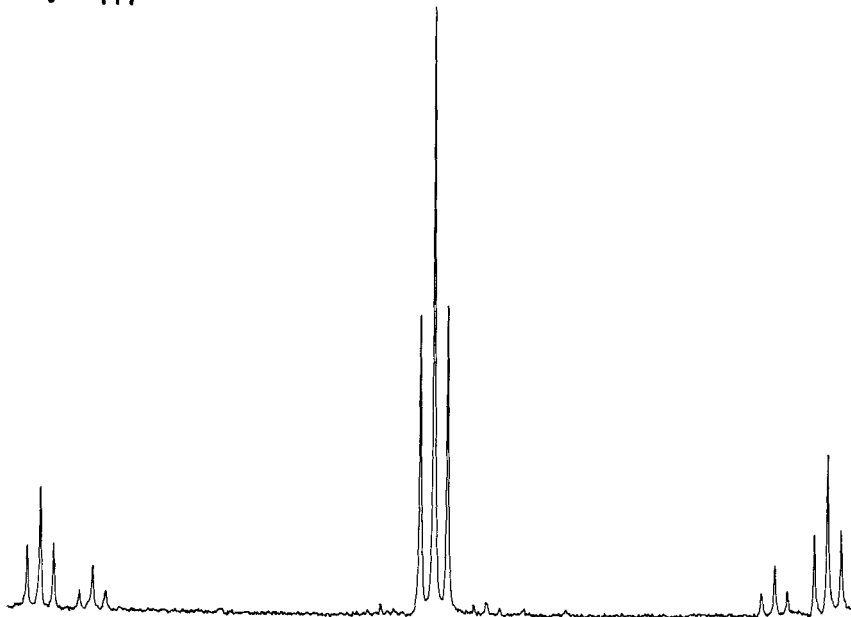
$\delta = -117$ 

Fig. 3.  $^{119}\text{Sn}$ -NMR. spectrum of  $[\text{Pt}(\text{SnCl}_3)_3(\text{P}(\text{OEt}_3)_2)]^-$  (The triplet in the center of the spectrum results from the coupling of the two equivalent P-atoms, whereas the two sets of satellites represent the spin-spin coupling to  $^{195}\text{Pt}$  (more intense, with the larger coupling constant) and  $^{117}\text{Sn}$ )

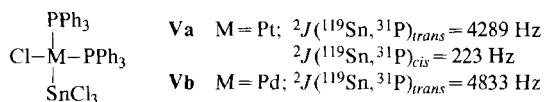
For  $[\text{Pt}(\text{SnCl}_3)_3(\text{PEt}_3)_2]^-$  the NMR. parameters using methanol as solvent are very similar to those for acetone solutions. Interestingly, the data for acetone as solvent reported by Koch *et al.* [10] for the presumed  $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$  are in good agreement with our results for the tris-complex, *i.e.*, we find for  $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$   $\delta(^{31}\text{P}) = 8.3$ ,  $^1J(^{195}\text{Pt}, ^{31}\text{P}) = 1865$  Hz; for  $[\text{Pt}(\text{SnCl}_3)_3(\text{PEt}_3)_2]^-$   $\delta(^{31}\text{P}) = -7.4$ ,  $^1J(^{195}\text{Pt}, ^{31}\text{P}) = 1453$  Hz. Koch *et al.* reported for  $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$   $\delta(^{31}\text{P}) = -7.4$ ,  $^1J(^{195}\text{Pt}, ^{31}\text{P}) = 1453$  Hz. Given the sizable differences in  $^1J(^{195}\text{Pt}, ^{31}\text{P})$  and  $\delta(^{31}\text{P})$  of these two types of poly-tin complex, we feel that this earlier report may be between error. Consequently, *trans*- $[\text{Pt}(\text{SnCl}_3)_2(\text{P}(\text{OPh})_3)_2]$  remains as the only well characterized complex containing two trichlorostannate and two tertiary P-ligands [8].

We will not comment further on the structure of our tris(trichlorostannate) complexes<sup>2)</sup> except to state that they are dynamic on the NMR. time-scale at RT. Moreover, the sharp signals observed between  $-50^\circ$  and  $-90^\circ$  for our compounds may indicate a slow ligand-exchange, but do not exclude a fast *Berry*-type rearrangement. We note that Moreto & Maitlis [21] have recently reported on the complex anions of the type  $[\text{Pt}(\text{C}_4\text{R}_4)(\text{SnCl}_3)_3]^-$  ( $\text{R} = \text{Me}, \text{Et}$ ), and therefore that tris(trichlorostannate) complex anions may be more readily available than expected.

<sup>2)</sup> X-Ray studies for the  $[\text{Pt}(\text{SnCl}_3)_3(\text{AsMe}_3)_2]$ -anion indicate a trigonal bipyramidal structure with three equatorial Sn-ligands (A. Albinati & P. S. Pregosin, unpublished results).

As the  $[M(\text{SnCl}_3)_3\text{L}_2]^-$ -complexes are obtained from  $[M\text{Cl}_2\text{L}_2]$  plus 3 mol-equiv.  $\text{SnCl}_2$ , the presence of one additional Cl-atom must be rationalized. The first two  $\text{SnCl}_2$ -molecules can sequentially attack  $[M\text{Cl}_2\text{L}_2]$ ; however, another source of  $\text{Cl}^-$  is required to react with the third mol-equiv. of Sn. The most plausible explanation involves the attack of  $\text{SnCl}_2$  on either  $[M\text{Cl}_2\text{L}_2]$  or  $[M\text{Cl}(\text{SnCl}_3)\text{L}_2]$  to produce  $\text{SnCl}_3^-$  and solvated cationic complexes, e.g.  $[M(\text{SnCl}_3)(\text{solvent})\text{L}_2]^+$ . This implies that there will be a mixture of complexes in solution. Indeed, both we and Koch *et al.* [10] observe signals in the  $^{31}\text{P}$ -NMR. spectrum of  $[\text{Pt}(\text{SnCl}_3)_3(\text{PEt}_3)_2]^-$  centered at  $\delta = 14.8$  which have similar  $^{31}\text{P}$ -NMR. characteristics to  $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$  but with a very different  $^{119}\text{Sn}$ -chemical shift ( $\delta(^{119}\text{Sn})$  for *trans*- $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2] = -199$  ( $\text{CDCl}_3$ ),  $\delta$  for the unknown =  $-270$  (acetone)). If the solutions are prepared using three  $\text{SnCl}_2$  per Pt, plus a Cl-source, e.g.  $\text{Ph}_4\text{AsCl}$  or  $(\text{PPN})\text{Cl}$ , the conversion to the tris-complex is essentially quantitative and these may then be isolated in good yield. Further studies concerning solvent complexes are in progress.

4. *Two-bond coupling constants.* – a)  $^2J(^{119}\text{Sn}, ^{31}\text{P})$ . The observed value for  $^2J(^{119}\text{Sn}, ^{31}\text{P})_{\text{trans}}$  in *cis*- $[\text{PdCl}(\text{SnCl}_3)(\text{P}(p\text{-CH}_3\text{-C}_6\text{H}_4)_3)_2]$  is 4848 Hz, which is much larger than that found for  $^2J(^{119}\text{Sn}, ^{31}\text{P})_{\text{cis}}$  which is typically 180–240 Hz. This difference of more than a factor of twenty has also been found in the analogous Pt-complexes [8], e.g., **V**, as well as in a few compounds containing alkyl-Sn ligands [22]. Although this is a very large algebraic difference, a factor of 10–20 is not unusual for the geometric dependence of a two-bond coupling, with  $^2J(^{31}\text{P}, ^1\text{H})$  [23a] and  $^2J(^{31}\text{P}, ^{31}\text{P})$  [23b] representing well studied cases. The coupling constants  $^2J(^{119}\text{Sn}, ^{31}\text{P})$  for **II–IV** also show the expected dependence, but both **II** and **III** have considerably reduced  $^2J(^{119}\text{Sn}, ^{31}\text{P})_{\text{trans}}$ -values relative to a four-coordinate such as **V**. The source of this geometric dependence is not immediately obvious; however, this does not prevent us from using this empiricism to assign structure, e.g.  $^2J(^{119}\text{Sn}, ^{31}\text{P})$  for the bis-complexes  $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$  and  $[\text{Pt}(\text{SnCl}_3)_2(\text{PPr}_3)_2]$  are 244 and 247 Hz, respectively, thereby supporting a *trans*-geometry (*cis*-orientation of the two spins).



Similarly,  $^2J(^{119}\text{Sn}, ^{31}\text{P})_{\text{trans}} = 4833$  Hz for *cis*- $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$  clearly marks the geometry of these two spins, whereas *trans*- $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$  has  $^2J(^{119}\text{Sn}, ^{31}\text{P}) = 179$  Hz. Interestingly, we have not been able to observe the *cis* two-bond coupling in **Vb**.

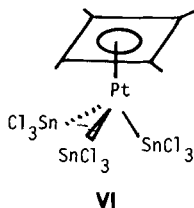
Some values for two-bond coupling constants involving Sn are: 96.9 Hz for  $^2J(^{119}\text{Sn}, ^1\text{H})$  in  $\text{CH}_3\text{SnCl}_3$  [24], 249.5 Hz for  $^2J(^{119}\text{Sn}, ^{19}\text{F})$  in  $(\text{CH}_3)_3\text{SnCF}_2\text{CF}_2\text{H}$  [25], 1,650 Hz for  $^2J(^{119}\text{Sn}, ^{31}\text{P})$  in  $[(\text{CH}_3)_3\text{Sn}-\text{Pt}(\text{C}\equiv\text{CPh})(\text{PMePh}_2)_2]$  [26] and 450 Hz for  $^2J(^{119}\text{Sn}, ^{119}\text{Sn})$  in  $(\text{Et}_3\text{Sn})_2\text{Sn}(i\text{-Bu})_2$  [27].

b)  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ . The separation of the  $^{117}\text{Sn}$ -satellites in the  $^{119}\text{Sn}$ -NMR. spectrum directly affords the two-bond Sn, Sn-coupling. For *trans*- $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$   $^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 34,674$  Hz and this value is increased to 37,164 Hz when



$\text{AsEt}_3$  is substituted for  $\text{PEt}_3$ . These are certainly remarkably large, and indeed, exceed most known one-bond coupling constants. Although we have not been able to isolate these bis(trichlorostannate) molecules there seems little doubt that their structures are correct. One-bond Sn, Sn-coupling constants are  $< 6000$  Hz [27] and one-bond Sn, P-values  $< 3000$  Hz [28–33] so that we can exclude these as possible sources of the splitting.  $^1J(^{195}\text{Pt}, ^{119}\text{Sn})$  can be  $> 20,000$  Hz [12]; however, both the  $^{195}\text{Pt}$ - and  $^{117}\text{Sn}$ -satellites are present in our  $^{119}\text{Sn}$ -spectrum (see *Fig. 1*) and these are readily assignable on the relative-intensity basis ( $^{195}\text{Pt}$  has natural abundance = 33.7%). The two-bond Sn, Sn-coupling constants in the five-coordinate anions are also quite large (16,504–20,990 Hz) and help to confirm that  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  values of  $> 16,000$  Hz are not unusual.

It is tempting to think of these values in the  $[\text{M}(\text{SnCl}_3)_3\text{L}_2]^-$ -anions as resulting from an average of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})_{\text{trans}}$  and  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})_{\text{cis}}$ . For the complex anion  $[\text{Pt}(\text{C}_4\text{Me}_4)(\text{SnCl}_3)_3]^-$ , originally prepared by *Moreto & Maitlis* [21],  $^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 2,392$  Hz. Since it seems reasonable to assume that this anion has a pseudo ‘piano-stool’ structure **VI** perhaps we are observing the differences in the two-bond Sn, Sn-coupling as a function of the angle between the Sn-ligands. For the complexes of type *trans*- $[\text{M}(\text{SnCl}_3)_2\text{L}_2]$  this angle would be  $180^\circ$ , in the  $[\text{M}(\text{SnCl}_3)_3\text{L}_2]^-$ -complexes with three equatorial Sn-ligands,  $120^\circ$ , and somewhat smaller yet for the cyclobutadiene complex. The complex anion *cis*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$  has  $^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 2,485$  Hz [9]. Lacking definitive structural information for all these complexes, this proposal must remain in the realm of speculation. Additional coupling constants and  $^{31}\text{P}$ -,  $^{119}\text{Sn}$ - and  $^{195}\text{Pt}$ -chemical shifts are shown in *Table 2*.



To better evaluate the factors which can affect  $^2J(\text{A}, \text{B})$  we assume that *Equation 3* is appropriate to describe our two-bond coupling [34]. The  $\gamma$ 's are

$$^2J(\text{A}, \text{B}) = \alpha \gamma_{\text{A}} \gamma_{\text{B}} |\psi(\text{O})|_{\text{ns}}^2 |\psi_{\text{B}}(\text{O})|_{\text{ns}}^2 \pi_{\text{A}, \text{B}} \quad (3a)$$

$$\pi_{\text{A}, \text{B}} = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\varepsilon_j - \varepsilon_i)^{-1} C_{\text{is}_\text{A}} C_{\text{js}_\text{A}} C_{\text{is}_\text{B}} C_{\text{js}_\text{B}} \quad (3b)$$

the magnetogyric ratios; the  $|\psi(\text{O})|_{\text{ns}}^2$ -expressions, the valence shell s-electron expectation values, and the  $\pi$ -term, the polarizability. *Equation 3b* contains the s-coefficients of the atomic orbitals used in the linear combinations which make up the occupied and unoccupied molecular orbitals with energies  $\varepsilon_i$  and  $\varepsilon_j$ , respectively.

Table 2. NMR. Parameters<sup>a)</sup> for the complexes

M=	L=	$^2J(^{119}\text{Sn}, ^{117}\text{Sn})$	$^2J(^{119}\text{Sn}, ^{31}\text{P})$	$^1J(^{195}\text{Pt}, ^{119}\text{Sn})$	$^1J(^{195}\text{Pt}, ^{31}\text{P})$	$\delta(^{31}\text{P})$	$\delta(^{119}\text{Sn})$	$\delta(^{195}\text{Pt})$
<i>[M(SnCl<sub>3</sub>)<sub>3</sub>L<sub>2</sub>]<sup>-</sup></i>								
Pd	PEt <sub>3</sub> <sup>b)</sup>	20,990	314			26.1	13	
Pt	PEt <sub>3</sub> { acetone methanol <sup>d)</sup> }	18,182	277 <sup>c)</sup>	20,410	1460		-83	-5152
			17,810	274	20,239	1466	-10.3	-77
Pt	PPr <sub>3</sub> <sup>d)</sup>	17,834	274	20,422	1457	-18.2	-73	-5120
Pt	P(OEt) <sub>3</sub> <sup>e)</sup>	16,504	317	19,049	2883	77.0	-117	-5234
Pt	AsEt <sub>3</sub> <sup>f)</sup>	18,115		19,788			-79	-5400
Pt	AsMe <sub>3</sub> <sup>g)</sup>	17,504		19,031			-67	-5363
<i>trans-[M(SnCl<sub>3</sub>)<sub>2</sub>L<sub>2</sub>]</i>								
Pd	AsEt <sub>3</sub> <sup>h)</sup>	37,164					11	
Pt	AsEt <sub>3</sub> <sup>h)</sup>	35,090		22,364			-39	-5305
Pt	PEt <sub>3</sub> <sup>h)</sup>	34,674	244	23,517	1865	8.3	-41	-5082
Pt	PPr <sub>3</sub> <sup>h)</sup>	34,790	247	23,682	1850	0.4	-40	-5061
<i>trans-[MCl(SnCl<sub>3</sub>)L<sub>2</sub>]</i>								
Pd	PEt <sub>3</sub> <sup>i)</sup>		231			23.2	-75	
Pd	PPr <sub>3</sub> <sup>i)</sup>		235			13.2		
Pd	PTol <sub>3</sub> <sup>g)</sup>		188			25.2	-113	
Pd	AsEt <sub>3</sub> <sup>h)</sup>						-70	
Pt	PEt <sub>3</sub>		235 <sup>j)</sup>	29,077 <sup>h)</sup>	2056 <sup>j)</sup>	13.8 <sup>j)</sup>	-199 <sup>h)</sup>	-4779 <sup>h)</sup>
Pt	PPr <sub>3</sub>		237 <sup>j)</sup>	29,272 <sup>h)</sup>	2027 <sup>j)</sup>	3.6 <sup>j)</sup>	-201 <sup>h)</sup>	-4746 <sup>h)</sup>
Pt	AsEt <sub>3</sub> <sup>h)</sup>			27,536			-221	-4857
Pt	P( <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> <sup>g)</sup>		226	28,052	2327	17.5	-222	
Pt	AsTol <sub>3</sub> <sup>k)</sup>			27,222			-250	-4835
<i>cis-[MCl(SnCl<sub>3</sub>)L<sub>2</sub>]</i>								
Pd	PTol <sub>3</sub> <sup>g)</sup>	P <i>trans</i> to Sn	4848			38.8		
		P <i>cis</i> to Sn	not observed			32.8	-131	
Pt	PTol <sub>3</sub> <sup>k)</sup>	P <i>trans</i> to Sn	4298		3107	26.2		
		P <i>cis</i> to Sn	216	16,321	3634	7.9	-59	-4718
Pt	P( <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> <sup>g)</sup>	P <i>trans</i> to Sn	4296		2972	26.6		
		P <i>cis</i> to Sn	219	16,931	3662	9.2	-72	
Pt	AsTol <sub>3</sub> <sup>k)</sup>			20,043			-136	-4785
PtCl(SnCl <sub>3</sub> )(AsTol <sub>3</sub> )- (PTol <sub>3</sub> ) <sup>k)</sup>		As <i>trans</i> to Sn	207	22,314	3528		-131	-4722
II <sup>l)</sup>			3044	13,745	2014	119.3	-205	-5480
III <sup>l)</sup>			3649			141.5	15	
IV <sup>l)</sup>			271	16,913	2436	33.3	-232	-5300
[Pt(C <sub>4</sub> Me <sub>4</sub> )(SnCl <sub>3</sub> ) <sub>3</sub> ] <sup>-j,m)</sup>		2,392		21,692			-143	

<sup>a)</sup> Chemical shifts in ppm, coupling constants in Hz. Shifts to lower field, higher frequency are denoted by a positive sign. Unless other stated *J* values are for <sup>119</sup>Sn. <sup>b)</sup> Acetone, 183°K. <sup>c)</sup> Average of <sup>119</sup>Sn- and <sup>117</sup>Sn-coupling constants. <sup>d)</sup> Methanol, 193 K. <sup>e)</sup> Acetone, 243 K. <sup>f)</sup> Acetone, 203 K. <sup>g)</sup> CDCl<sub>3</sub>, 233 K, measured as a mixture of *cis*- and *trans*-isomers. <sup>h)</sup> CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub>, 198 K. <sup>i)</sup> CDCl<sub>3</sub>, 273 K for PEt<sub>3</sub>, room temperature for PPr<sub>3</sub>. <sup>j)</sup> CDCl<sub>3</sub>, 233 K. <sup>k)</sup> CDCl<sub>3</sub>, 248 K, measured as a mixture of *cis*- and *trans*-isomers. <sup>l)</sup> CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> at room temperature. <sup>m)</sup> (PPh<sub>3</sub>)N<sup>+</sup> salt.

The magnetogyric ratio for Sn is relatively large, but not dissimilar to that of <sup>31</sup>P (which we take as a model in view of the extensive literature on <sup>2</sup>*J*(<sup>31</sup>P, <sup>31</sup>P) [23b]). The  $|\psi(\text{O})|^2$ -expression for Sn will be approximately a factor of 2–3 larger

than for P [35], due to its position in the Periodic Table. Assuming a value of approximately 500 Hz [23b] for  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$  in a Pd(II)-*trans*-bis(phosphine) complex, the  $|\psi(\text{O})|^2$  is insufficient to explain the 30–40 fold difference in magnitude between  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  and  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$ . Consequently, perhaps something is affecting  $\pi_{\text{A,B}}$ .

Before pursuing the discussion further we would like to draw a parallel between  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  and  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$ . For square planar and octahedral complexes of the second and third transition series,  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})_{\text{trans}} \gg {}^2J({}^{31}\text{P}, {}^{31}\text{P})_{\text{cis}}$ , with observed differences in magnitude of at least a factor of 5, and sometimes even 20 (e.g.  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$  in *cis*- and *trans*-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] are –18.9 and +510 Hz, respectively [36]). Assuming that  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})_{\text{trans}} \approx 35,000$  Hz and  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})_{\text{cis}} \approx 2,500$  Hz [9], we have the same geometric dependence as observed previously for the two-bond coupling constant  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$ . We have already mentioned the similar geometric dependence of  ${}^2J({}^{119}\text{Sn}, {}^{31}\text{P})$ . After inspecting these data it seems reasonable that a similar mechanism is operating to affect changes in all three, i.e., the P, P-, P, Sn- and Sn, Sn-coupling constants. Several authors have attempted to explain differences in  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$  using a model which invokes the  $(\epsilon_i - \epsilon_j)$  expression [23] [37]. *Verkade* [23b] has offered an explanation for the signs of  ${}^2J_{\text{trans}}$  (usually positive) and  ${}^2J_{\text{cis}}$  (usually negative), whereas in a more relevant study *Bright et al.* [38] found that the sequence for  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$  in [MX<sub>2</sub>P<sub>2</sub>]-complexes (M=Ni, Pd, Pt), correlates inversely with the energy separation between the nd and (n+1)p atomic orbitals for these metals. The net result is  ${}^2J({}^{31}\text{P}, {}^{31}\text{P})_{\text{Pd}} > {}^2J({}^{31}\text{P}, {}^{31}\text{P})_{\text{Pt}}$ .

Returning to our complexes we find the same trend:

$${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})_{\text{Pd}} > {}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})_{\text{Pt}} \text{ and } {}^2J({}^{119}\text{Sn}, {}^{31}\text{P})_{\text{Pd}} > {}^2J({}^{119}\text{Sn}, {}^{31}\text{P})_{\text{Pt}}$$

Taken together, these arguments suggest that changes in the  $\pi$ -term may be responsible for the differences in  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$ , although the issue remains open<sup>3)</sup>. Indeed, contributions other than those from the *Fermi*-term may also be involved<sup>4)</sup>. Whatever the source, only one SnCl<sub>3</sub><sup>-</sup>-ligand is required to produce unusually large  ${}^1J(\text{Sn}, \text{X})$ -values. The values of about 1700 Hz for  ${}^2J({}^{119}\text{Sn}, {}^1\text{H})$  in the complexes of type *trans*-[PtH(SnCl<sub>3</sub>)(PR<sub>3</sub>)<sub>2</sub>] represent the largest two-bond couplings to a proton ever to be observed [11].

5. *One-bond Pt, Sn-coupling constants.* The one-bond Pt, Sn-coupling constants vary from 13,745 to 29,272 Hz. We have already noted that the one-bond Pt, Sn-coupling constant decreases to 9,067 Hz for *trans*-[PtH(SnCl<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] and is only slightly larger (11,512 Hz) for *trans*-[PtH(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] [12]. Taken together, our results span a range > 20,000 Hz. Qualitatively, these changes follow a classical *trans*-influence series in which the coupling constant increases when the *trans*-ligand is a poorer donor, i.e. Cl > SnCl<sub>3</sub> > As > P > H. In addition, we observe that  ${}^1J({}^{195}\text{Pt}, {}^{119}\text{Sn})$  is generally somewhat smaller in the five-coordinate than in the

<sup>3)</sup> *Parish*, using *Mössbauer* spectroscopy, has suggested that  $|\psi(\text{O})_{\text{5s}}|^2$ -term for Sn in related complexes need not be constant [39].

<sup>4)</sup> Non-*Fermi* contact term contributions are recognized for  ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$  [40].

four-coordinate complexes. Presumably, for complexes with the  $\text{SnCl}_3^-$ -ligand *trans* to an oxygen-ligand the values will be larger.

Where coupling constants are concerned, very large values often attract attention; however, it is also informative to know which ligand combinations result in smaller magnitudes. With  $\text{SnCl}_3^-$  as ligand, we find for *trans*-[Pt( $\text{C}_6\text{H}_5$ )( $\text{SnCl}_3^-$ )( $\text{PEt}_3$ )<sub>2</sub>] a much smaller  $^1J(^{195}\text{Pt}, ^{119}\text{Sn})$  of 6,414 Hz, thus affording a total change in this one-bond coupling of approximately a factor of 5. This is somewhat larger than normally observed for an NMR.-active-ligand coordinated to Pt(II), e.g., the total change for both  $^1J(^{195}\text{Pt}, ^{31}\text{P})$  and  $^1J(^{195}\text{Pt}, ^{15}\text{N})$  [41] [42] is about a factor of 4. Using  $\text{SnBr}_3^-$ , generated from the appropriate bromide complex *via* addition of  $\text{SnBr}_2$ , decreases  $^1J(^{195}\text{Pt}, ^{119}\text{Sn})$  further to 5,780 Hz, presumably in part, due to the electronegativity difference between these halogens. A more detailed study on this one-bond interaction will appear separately.

6.  $^{119}\text{Sn}$ -Chemical shifts. There is not much known on  $^{119}\text{Sn}$ -chemical shifts in transition metal complexes. *Harris et al.* [43] have shown that the 'M-SnMe<sub>3</sub>' moiety can afford  $^{119}\text{Sn}$ -values which stretch over more than 500 ppm, depending on the transition metal. We confirm this point and note that, in our Pt-complexes, all of which have the Pt-SnCl<sub>3</sub> fragment, the range of  $\delta$ -values approaches 400 ppm. Given that *trans*-[PtH(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] has  $\delta(^{119}\text{Sn}) = +130$  ppm, the total range exceeds 500 ppm even though the number and type of atoms coordinated to Sn remain formally unchanged. Two points of interest are: a) where analogous Pd(II)- and Pt(II)-compounds are available, the  $\delta(^{119}\text{Sn})$  of the former frequently appears at lower field. This point seems generally valid when the complex contains *trans*-PR<sub>3</sub>- or AsR<sub>3</sub>-ligands, and b) there is a moderate dependence of  $\delta(^{119}\text{Sn})$  on L in the complexes of type *trans*-[PtCl(SnCl<sub>3</sub>)L<sub>2</sub>]. We take these observations as evidence that the  $\text{SnCl}_3^-$ -ligand can have an electronic structure which varies markedly with the remaining ligands on Pt and plan further measurements in this area.

**Concluding remarks.** – We have shown here that  $\text{SnCl}_2$  reacts with Pt- and Pd-phosphine complexes to produce molecules containing one-, two- or three-coordinated  $\text{SnCl}_3^-$ -ligands, the latter being five-coordinate. Using tetradentate ligands it is possible to obtain kinetically robust five-coordinate trichlorostannate complexes which contrasts with the more labile monodentate phosphine complexes. The combination of  $^{195}\text{Pt}$ -,  $^{119}\text{Sn}$ - and  $^{31}\text{P}$ -NMR. methods is most informative in this field, and has allowed us to empirically establish trends in the coupling constants  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ ,  $^2J(^{119}\text{Sn}, ^{31}\text{P})$  and  $^1J(^{195}\text{Pt}, ^{119}\text{Sn})$ . With these tools it is much easier to recognize and characterize the various intermediates which are likely to be present in a catalytically active mixture.

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