Inorganica Chimica Acta, *86* (1984) 55–60

^{119}Sn and ^{195}Pt NMR Spectroscopy of $SnCl_3^-$ Complexes of Platinum and Palladium. Some Chemistry of the Complexes $(Ph_4P)_2[PtCl_4]$ and $[Pt(\mu\text{-}Cl)Cl(PEt_3)]_2$ with $SnCl_2$

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Received September 24, 1983

^{119}Sn and ^{195}Pt NMR solution data for the complex anions cis-*$[PdCl_2(SnCl_3)_2]^{2-}$, $[Pd(SnCl_3)_5]^{3-}$, $[PtCl(SnCl_3)_3]^{2-}$, $[Pt(SnCl_3)_4]^{2-}$, $[PtH(SnCl_3)_4]^{3-}$ and $[PtH(SnCl_3)_2(PEt_3)_2]^-$ are reported and compared with those for known related complexes. An increasing number of $SnCl_3^-$-ligands per metal results in deshielding of the ^{119}Sn, but a shielding of the ^{195}Pt nuclei. The values $^1J(^{195}Pt, ^{119}Sn)$ and $^2J(^{119}Sn, ^{117}Sn)$ are found to be especially useful probes for molecular structure in this chemistry. Reaction of the complexes* sym-trans-*$[PtCl(\mu\text{-}Cl)L]_2$, L = PEt_3, $PTol_3$, $AsEt_3$, with one and two equivalents of $SnCl_2$ leads to $[PtClL(\mu\text{-}Cl)_2Pt(SnCl_3)L]$ and* sym-trans-*$[Pt(\mu\text{-}Cl)(SnCl_3)L]_2$ respectively, and these compounds have been characterized by ^{119}Sn, ^{195}Pt and ^{31}P NMR spectroscopy.*

Introduction

Mixtures of platinum or palladium salts with excess tin(II) chloride are recognized as being homogeneous hydrogenation catalysts [1, 2]. Such mixtures contain trichlorostannate complexes and several studies have shown that the anions *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ are stable, isolatable [3–7] and, in some cases [8, 9] useful catalyst precursors. As part of our continuing interest in the chemistry of the $SnCl_3^-$ ligand [10–14] we have measured ^{119}Sn and, where appropriate, ^{195}Pt NMR spectra of solutions containing varying $[MCl_4]^{2-}/SnCl_2$ ratios, M = Pd, Pt, and have identified several new $SnCl_3^-$ complexes. Additionally, we have studied the reactions of the dimeric complexes *sym-trans*-$[Pt(\mu\text{-}Cl)ClL]_2$, L = PEt_3, $PTol_3$, Tol = $p\text{-}CH_3C_6H_4$, and $AsEt_3$ with $SnCl_2$ in the hope of gaining insight into how and where the $SnCl_2$ attacks the transition metal. We report here on our multinuclear NMR studies in both of these areas.

Results and Discussion

Reactions of $(Ph_4P)_2[PtCl_4]$, with $SnCl_2$

The chemistry of $SnCl_2$ with $[PtCl_4]^{2-}$ can be described qualitatively by the following equations:

$$[PtCl_4]^{2-} + SnCl_2 \xrightarrow[\substack{CH_2Cl_2\\CDCl_3}]{} [PtCl_3(SnCl_3)]^{2-}, (I) \tag{1}$$

$$[PtCl_3(SnCl_3)]^{2-} + SnCl_2 \xrightarrow[\substack{CH_2Cl_2\\CDCl_3}]{} cis\text{-}[PtCl_2(SnCl_3)_2]^{2-}, (II) \tag{2}$$

$$cis\text{-}[PtCl_2(SnCl_3)_2]^{2-} + SnCl_2 \xrightarrow[\substack{CH_2Cl_2\\CDCl_3}]{} [PtCl(SnCl_3)_3]^{2-}, (III) \tag{3}$$

$$[PtCl(SnCl_3)_3]^{2-} + SnCl_2 \xrightarrow[\substack{CH_2Cl_2\\CDCl_3}]{} [Pt(SnCl_3)_4]^{2-}, (IV) \tag{4}$$

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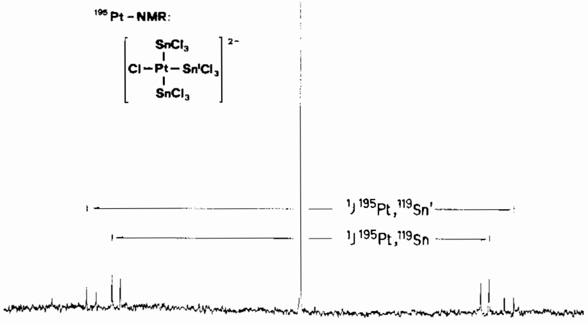
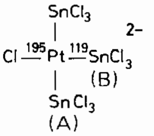


Fig. 1. ^{195}Pt NMR spectrum of the $[PtCl(SnCl_3)_3]^{2-}$ anion. There are two $^1J(^{195}Pt, ^{119}Sn)$ values as well as two $^1J(^{195}Pt, ^{117}Sn)$ values. $\delta^{195}Pt = -4829$.

$$[Pt(SnCl_3)_4]^{2-} + SnCl_2 \xrightarrow[HCl]{acetone} [Pt(SnCl_3)_5]^{3-}, (V) \qquad (5)$$

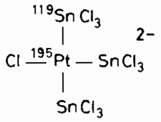
In reaction (5) the fifth $SnCl_3^-$ ligand can be generated either by direct addition of a suitable salt, *e.g.* $(Ph_4P)SnCl_3$, or by addition of excess $SnCl_2$. Complexes (I), (II) and (V) have been described previously [3–5, 15]; (III) and (IV) are new and warrant further discussion.

Compound (III) is the major component* of the reaction of $(Ph_4P)_2[PtCl_4]$ with three equivalents of $SnCl_2$ and its ^{195}Pt NMR spectrum is shown in Fig. 1. The different $^1J(^{195}Pt, ^{119}Sn)$ couplings, 21448 Hz and 24236 Hz, arising from the isotopomers (VI)–(VIII) are clearly visible, as are the appropriate ^{117}Sn splittings (^{119}Sn and ^{117}Sn have I = ½, with 8.6% and 7.6% natural abundance, respectively). The differences in intensity between the satellite lines are accounted for by statistical arguments, *i.e., both* (VII) and (VIII) contribute to $^1J(^{195}Pt, ^{119}Sn(A))$, but only (VI) to $^1J(^{195}Pt, ^{119}Sn(B))$. The ^{119}Sn NMR spectrum of (III) shows signals centered at $\delta = -78$ for Sn(A), with the observed value of 21448 Hz in agreement with that found for $^1J(^{195}Pt, ^{119}Sn)$ in the ^{195}Pt spectrum. The smaller signals from the *three* types of $^2J(^{119}Sn, ^{117,119}Sn)$, arising from (IX)–(XI), could also be observed.



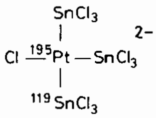
$$\left[\begin{array}{c} SnCl_3 \\ | \\ Cl\overset{195}{-}Pt\overset{119}{-}SnCl_3 \\ |\;(B) \\ SnCl_3 \\ (A) \end{array}\right]^{2-}$$

(VI)



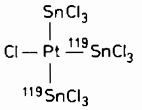
$$\left[\begin{array}{c} ^{119}SnCl_3 \\ | \\ Cl\overset{195}{-}Pt-SnCl_3 \\ | \\ SnCl_3 \end{array}\right]^{2-}$$

(VII)



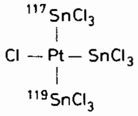
$$\left[\begin{array}{c} SnCl_3 \\ | \\ Cl\overset{195}{-}Pt-SnCl_3 \\ | \\ ^{119}SnCl_3 \end{array}\right]^{2-}$$

(VIII)



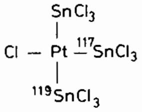
$$\begin{array}{c} SnCl_3 \\ | \\ Cl-Pt\overset{119}{-}SnCl_3 \\ | \\ ^{119}SnCl_3 \end{array}$$

(IX)



$$\begin{array}{c} ^{117}SnCl_3 \\ | \\ Cl-Pt-SnCl_3 \\ | \\ ^{119}SnCl_3 \end{array}$$

(X)



$$\begin{array}{c} SnCl_3 \\ | \\ Cl-Pt\overset{117}{-}SnCl_3 \\ | \\ ^{119}SnCl_3 \end{array}$$

(XI)

Fortunately, these various isotopomers can be identified as there is now a substantial literature concerning $^2J(^{119}Sn, ^{117}Sn)_{cis}$ and $^2J(^{119}Sn, ^{117}Sn)_{trans}$ in square planar complexes [11–13, 16].

As expected [13], the resonance at $\delta = -78$ shows a very large $^2J(^{119}Sn, ^{117}Sn)_{trans}$ value of 43689 Hz stemming from (X) and a much smaller $^2J(^{119}Sn, ^{117}Sn)_{cis}$ coupling of 2039 Hz, arising from (XI).

The >40 KHz two-bond coupling for two *trans* $SnCl_3^-$ ligands is no longer surprising, especially since the value found in the *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ anion is larger at 46582 Hz [16]. There is a ^{119}Sn signal at $\delta = -228$ which we tentatively assign to Sn(B)**.

Complex (IV) is obtained by reacting the $[PtCl_4]^{2-}$ anion with four equivalents of $SnCl_2$ in $CH_2Cl_2/CDCl_3$. Its ^{195}Pt spectrum is centered at $\delta = -5615$ and one-bond couplings to both ^{119}Sn and ^{117}Sn are clearly observable, *e.g.* $^1J(^{195}Pt, ^{119}Sn) = 19421$ Hz. The relative intensities of the tin satellites [17] are consistent with a formulation having four equivalent $SnCl_3^-$ ligands. The ^{119}Sn signals for (IV) are centered at $\delta = -20$, and the relative intensities of the ^{117}Sn satellites as well as the presence of both $^2J(^{119}Sn, ^{117}Sn)_{cis} = 1835$ Hz, and $^2J(^{119}Sn, ^{117}Sn)_{trans} = 29882$ Hz further support the structure assigned to this complex.

There are relatively few tetrakis $SnCl_3^-$–platinum complexes and those which have been characterized are usually five-coordinate, *e.g.*, $[Pt(SnCl_3)_4(PEt_3)]^{2-}$ which we recently prepared [16], and $[PtH(SnCl_3)_4]^{3-}$ prepared earlier [18] for which we give new NMR data in Table I. Since $[Pt(SnCl_3)_5]^{3-}$ is a hydrogenation catalyst [9], and assuming that a coordinatively unsaturated species activates the hydrogen, perhaps affording $[PtH(SnCl_3)_4]^{3-}$ or some related platinum hydride, (IV) may be a catalyst precursor resulting fron $SnCl_3^-$ dissociation from the pentakis complex. The recognition of

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*The reaction mixture also contains the *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and the $[Pt(SnCl_3)_5]^{3-}$ ions as well as the $[Pt(SnCl_3)_4]^{2-}$ ion.

**Although the value of $^1J(^{195}Pt, ^{119}Sn(B))$ observed in the ^{119}Sn spectrum agrees with that found in the ^{195}Pt spectrum, the intensity of the signal at $\delta = -228$ is ≅ *one sixth,* and not one half of that found at $\delta = -78$. We have no explanation for this observation.

TABLE I. NMR Data[a] for the $SnCl_3^-$ Complexes.

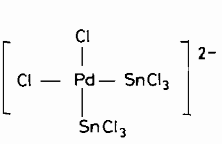
	$\delta\,^{119}Sn$[b]	$\delta\,^{195}Pt$[c]	$^1J(^{195}Pt, ^{119}Sn)$	$^2J(^{119}Sn, ^{117}Sn)$
$[PtCl_3(SnCl_3)]^{2-}$	−596	−2748	33165	
cis-$[PtCl_2(SnCl_3)_2]^{2-}$	−383	−4202	27966	2564
$[PtCl(SnCl_3)_3]^{2-}$	−228 (B)	−4829	24236	2039
	−78 (A)		21448	43689
$[Pt(SnCl_3)_4]^{2-}$	−20	−5615	19421	1835
				29882
$[Pt(SnCl_3)_5]^{3-}$	−128	−5894	16015	6226
$[PtH(SnCl_3)_4]^{3-}$[d]	−114	−5824	18737	7178
$[PtH(SnCl_3)_2(PEt_3)_2]^{3-}$[e]	−122	−5396	4488	2356
cis-$[PdCl_2(SnCl_3)_2]^{2-}$	−242			1575
$[Pd(SnCl_3)_5]^{3-}$	+68			7460

[a] Chemical shifts in ppm, coupling constants in Hz. [b] Relative to ext. $(CH_3)_4Sn$. [c] Relative to ext. $Na_2[PtCl_6]$. [d] $\delta\,^1H = -15.3$, $^1J(^{195}Pt, ^1H) = 692$, $^2J(^{119}Sn, ^1H) = 367$; room temp. in acetone. [e] $\delta\,^1H = -12.6$, $^1J(^{195}Pt, ^1H) = 1326$, $^2J(^{119}Sn, ^1H) = 787$; CD_2Cl_2, 173 K.

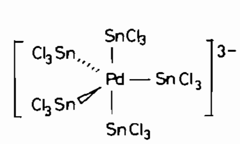
(III) and (IV) in solution shows that polytrichlorostannate complexes with between one and five coordinated $SnCl_3^-$ ligands are all relatively stable materials.

Reactions of $[PdCl_4]^{2-}$ with $SnCl_2$

The identification of the products resulting from reactions of $[PdCl_4]^{2-}$ with $SnCl_2$ is more difficult as we do not have the spin I = ½ metal to assist us; nevertheless, based on $\delta\,^{119}Sn$, the magnitude of $^2J(^{119}Sn, ^{117}Sn)$ and the relative ^{117}Sn satellite intensities, we have identified complexes (XII) and (XIII). Compound (XII) is observed in ~95% NMR yield* at $\delta = -242$ when the tetrachloropalladate dianion reacts with two equivalents of tin(II) chloride ($CH_2Cl_2/CDCl_3$). The assignment of the *cis* isomer for (XII) follows from the modest value of 1575 Hz observed for $^2J(^{119}Sn, ^{117}Sn)$. The *trans* coupling would be in excess of 20000 Hz [13]. The relative intensities of the ^{117}Sn satellite lines confirm that there are only two coordinated $SnCl_3^-$ ligands.



(XII)



(XIII)

The five-coordinate (XIII) oils out of a $CH_2Cl_2/CDCl_3$ solution when $(Bu_4{}^nN)_2[PdCl_4]$ is treated with five equivalents of tin(II) chloride and one equivalent of $(Bu_4{}^nN)Cl$, but redissolves upon addition of a few drops of acetone. Its ^{119}Sn NMR spectrum shows the expected series of lines centered at $\delta = +68$, with an average $^2J(^{119}Sn, ^{117}Sn)$ of 7460 Hz. Interestingly, for (XIII) we observe a broad ^{119}Sn signal at room temperature which sharpens to the expected group of lines at −20 °C. Since we observe chemically equivalent $SnCl_3^-$ ligands at this low temperature, the intramolecular scrambling is still rapid. Consequently, we attribute the broad line at room temperature to $SnCl_3^-$ exchange. This contrasts with the findings of Nelson and co-workers [5] for the $[Pt(SnCl_3)_5]^{3-}$, species, which shows sharp ^{119}Sn resonances at ambient probe temperature.

NMR Trends

There are several NMR features worth noting:

1. Increasing the number of coordinated $SnCl_3^-$ ligands shifts $\delta\,^{195}Pt$ to successively *higher* field.
2. Increasing the number of coordinated $SnCl_3^-$ ligands shifts $\delta\,^{119}Sn$ to successively *lower* field.
3. There is a *cis* effect of $SnCl_3^-$ on $^1J(^{195}Pt, ^{119}Sn)$ such that substitution of $SnCl_3^-$ for Cl^-, *cis* to a second $SnCl_3^-$, decreases this coupling constant.
4. $^2J(^{119}Sn, ^{117}Sn)_{trans}$ is always $>{}^2J(^{119}Sn, ^{117}Sn)_{cis}$.
5. The values for $^2J(^{119}Sn, ^{117}Sn)$ are larger in the five-coordinate complexes than in the four-coordinate *cis* complexes. This is understandable if we assume that there is an averaging of $^2J_{trans}$ and $^2J_{cis}$ in the five-coordinate compounds due to intramolecular exchange. This relatively large ^2J observed

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*There are two small resonances at $\delta\,^{119}Sn = -207$ and -227, each ≅2 - 3%.

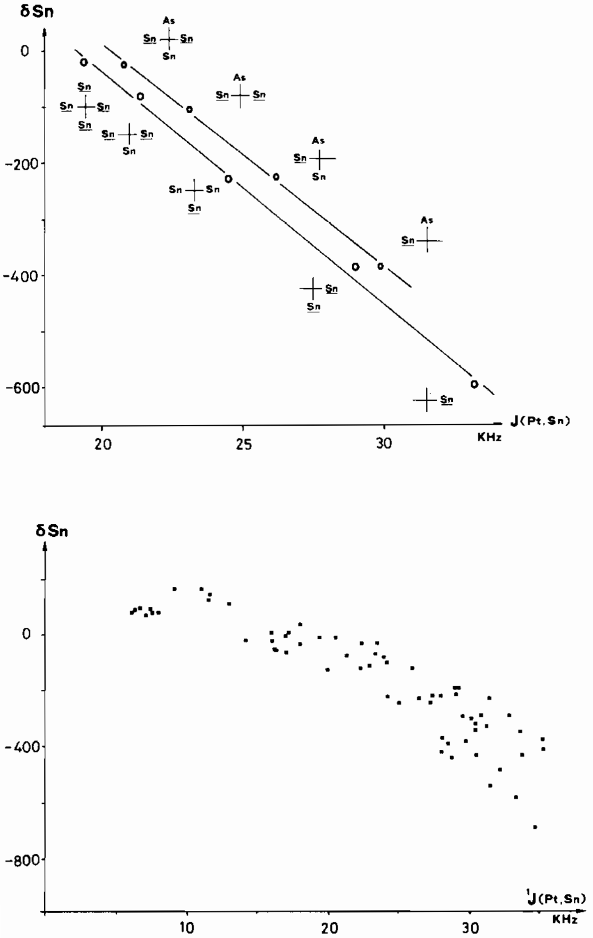


Fig. 2. Plots of δ^{119}Sn *vs.* $^1J(^{195}Pt, ^{119}Sn)$ for (top) the complexes $[PtCl_n(SnCl_3)_{(4-n)}]^{2-}$, n = 0–3, $[PtCl_n(SnCl_3)_{(3-n)}(AsMe_3)]^-$, n = 0–3, and (bottom) a variety of trichlorostannate complexes from references 10–14 and 16.

in the five-coordinates might be helpful in distinguishing a square planar from a trigonal bipyramidal compound. Observations 2 and 3 are illustrated graphically in Fig. 2, together with some additional data from earlier studies [16].

Clearly, the *combined cis and trans* effects are resulting in an approximately linear relationship between δ^{119}Sn and $^1J(^{195}Pt, ^{119}Sn)$ for these two series of molecules. Attempts to expand this correlation *via* the use of our full data base [10–14, 16] leads to significant deviations from linearity (see Fig. 2, bottom) although a general trend is still observable. We consider curves such as that shown in the figure to be useful empirical aids in assigning the structure of unknown trichlorostannate complexes.

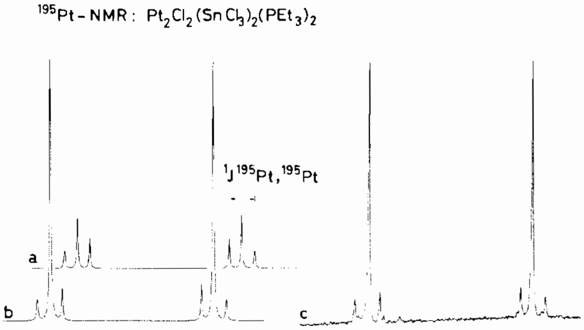
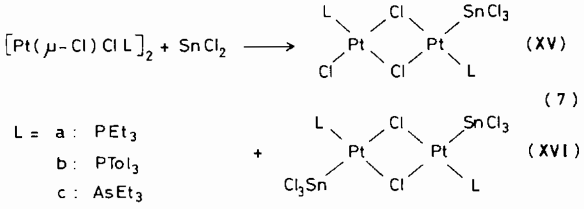


Fig. 3. Experimental ^{195}Pt NMR spectrum of $[Pt(\mu\text{-}Cl)(SnCl_3)(PEt_3)_2]$, *c*, with simulations for the spectrum with two ^{195}Pt atoms, *a*, and for the composite of all the isotopomers involving platinum, *b*. $\delta^{195}Pt = -4320$.

Reactions of Dimeric Complexes

Although $SnCl_2$ reacts with many transition metal halogen bonds to give trichlorostannate complexes [5–7, 10–14], there is no accepted mechanism for this reaction. To obtain some qualitative insight into this area we have studied the reactions of $SnCl_2$ with the dimers *sym-trans*-$[Pt(\mu\text{-}Cl)ClL]_2$, (XIV), as shown in (7). Reaction with one equivalent of $SnCl_2$ in $CH_2Cl_2/CDCl_3$ leads to a mixture of (XV) and (XVI) plus some unreacted starting material. The mono $SnCl_3^-$ complex (XVa) is readily identified from its ^{195}Pt NMR spectrum. There are two distinct ^{195}Pt absorptions of equal integral at $\delta = -3419$ and -4270 which are coupled to one another, $^2J(^{195}Pt, ^{195}Pt) = 238$ Hz. The higher field signal has a $^1J(^{195}Pt, ^{119}Sn)$ value of 33642 Hz; however, there is no observable tin coupling to the lower field platinum. The ^{31}P spectrum provides complementary data in that there are two ^{31}P resonances of equal integral with $^4J(^{31}P, ^{31}P) = 3$ Hz, and only one of these shows an observable coupling to tin. A summary of all of these data is given in Table II.



Addition of a second equivalent of $SnCl_2$ affords primarily (XVI). The dimeric nature of (XVIa) is supported by the observation of a $^2J(^{195}Pt, ^{195}Pt)$ coupling, 531 Hz (see Fig. 3), and the remaining NMR parameters are consistent with this formulation*. (XVIb) and (XVIc) were assigned by analogy.

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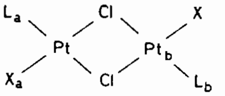
*Please for footnote see overleaf.

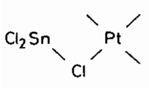
TABLE II. NMR Data* for the Dimeric Complexes.



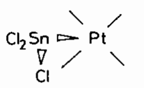
L	X_a	X_b	δPt_a	δPt_b	δSn	δP_a	δP_b	$^1J(Pt,Sn)$	$^1J(Pt,P)$	$^2J(Pt,Pt)$	$^2J(Sn,P)$
PEt_3	Cl	Cl	−3409			10.3			3850		
	Cl	$SnCl_3$	−3419	−4270	−355	11.2	12.5	33642	3814 3490	238	238
	$SnCl_3$	$SnCl_3$	−4320		−383	12.2		35309	3480	531	238
$PTol_3$	Cl	Cl	−3353			3.3			4065		
	Cl	$SnCl_3$	−3293	−4157	−385	1.5	5.6	33890	4004 3660		224
	$SnCl_3$	$SnCl_3$	−4178		−425	5.0		35278	3721		215
$AsEt_3$	Cl	Cl	−3069								
	Cl	$SnCl_3$	−3045	−4170	−412			32519			
	$SnCl_3$	$SnCl_3$	−4231		−440			33691			

* ^{195}Pt, ^{119}Sn and ^{31}P chemical shifts are relative to external $Na_2[PtCl_6]$, $(CH_3)_4Sn$ and H_3PO_4, respectively.

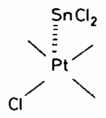
Furthermore, we have crystallized (XVIa) and confirmed its dimeric structure by X-ray diffraction [14]. It would seem that for molecules of type (XIV), $SnCl_2$ does *not* split the halogen bridges, in contrast to the behavior of nucleophilic nitrogen, phosphorus and arsenic ligands [19]. Conceivably, the $SnCl_2$ chooses to attack electrophilically at the relatively electron-rich terminal Cl^-, or alternatively a carbene-like insertion is possible. It may also be that the tin lone-pair coordinates to the platinum without bridge cleavage. All three of these possibilities are shown as (XVII)–(XIX). Although there is some support for a structure similar to (XVII) in the complexes *trans*-$[IrCl(SnCl_2)(CO)(P(p\text{-}XC_6H_4)_3)_2]$ [20], and $[Ag(SnCl_3)(PP)]$, PP = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene [21], the compounds $[MoCl(SnCl_2CH_3)(CO)_3(2,2\text{-bipyridyl})]$ [22], $[WCl(SnCl_2CH_3)(CO)_3(CH_3SCH_2CH_2SCH_3)]$ [23] contain structural units related to (XVIII). It may well develop that the choice between (XVII)–(XIX), and perhaps others, will be dictated by the metal and its ligand.



(XVII)



(XVIII)



(XIX)

Acknowledgements

We thank the E.T.H. Zürich for support and the Johnson Matthey Research Centre, England for the loan of platinum salts.

Experimental

The ^{195}Pt and ^{119}Sn NMR spectra were measured using a Bruker WM-250 spectrometer as described previously [11–13]. The solutions for the measurements were prepared as follows:

Preparation of the $[PtCl_{3-n}(SnCl_3)_n]^{2-}$ Ions

A solution of $(Ph_4P)_2[PtCl_4]$ (203 mg, 0.20 mmol) in 5 ml CH_2Cl_2 was treated with solid $SnCl_2$ (n X 38 mg, n X 0.2 mmol) and then stirred for *ca.* 24 h. The solvent was removed *i.v.* and the resulting solid dissolved in $CH_2Cl_2/CDCl_3$, 1:1, and the NMR spectra recorded. The five coordinate $[Pt(SnCl_3)_3)_5]^{3-}$ was prepared according to literature methods [9].

Preparation of the cis-*$[PdCl_2(SnCl_3)_2]^{2-}$ and $[Pd(SnCl_3)_5]^{3-}$ Anions*

$(Bu_4{}^nN)_2[PdCl_4]$ (73.3 mg, 0.10 mmol) was dissolved in 3 ml $CH_2Cl_2/CDCl_3$, 1:1, and then treated with solid $SnCl_2$ (38 mg, 0.20 mmol) at room temperature for 2 h. The resulting solution was employed directly for the NMR measurement. The

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*$SnCl_2$ does not insert between two platinum atoms. This would result in two large $^1J(^{195}Pt, ^{119}Sn)$ values. See Goodfellow and Herbert, *Inorg. Chim. Acta, 65,* L161 (1982).

$[Pd(SnCl_3)_5]^{3-}$ was prepared similarly except that a) solid $(Bu_4N)Cl$ was added directly after the 5 equivalents of $SnCl_2$, and b), the resulting oil was dissolved by the addition of a minimum amount of acetone.

Preparation of the Dimers (XV) and (XVI)

The complexes (XV) may be generated by adding solid $SnCl_2$ (19 mg, 0.10 mmol) to a solution containing 0.1 mmol of (XIVa-c) in 3 ml CH_2Cl_2/$CDCl_3$. Further addition of $SnCl_2$ (19 mg, 0.10 mmol) affords the symmetrical dimers (XVIa-c).

References

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