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The gas-phase ion-molecule reaction of η^3-allyl-PtP$(C_6H_5)_3$Cl with $SnCl_2^{+\cdot}$

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Abstract

The electron impact (EI) mass spectral behaviour of η^3-$C_3H_5PtP(C_6H_5)_3Cl$ (**1**) and η^3-$C_3H_5PtP(C_6H_5)_3SnCl_3$ (**2**) is described. The collisional spectra of **2** are compared with that of addition product obtained by the gas-phase ion-molecule reaction of **1** with $SnCl_2^{+\cdot}$. The fragmentation pathway observed for both **2** and (**1** + $SnCl_2$) suggests the existence of the pentacoordinate intermediate η^3-$C_3H_5PtP(C_6H_5)_3SnCl_2Cl$.

Introduction

Insertion of $SnCl_2$ ligand into transition metal–chlorine bond produces complexes containing the labile $SnCl_3$ entity [1–4]. This type of complexes, particularly of platinum(II) species, have been extensively investigated owing to their importance in catalysis [5–10].

When we investigated the nature of the metal–tin ligand interaction in complexes of type η^3-allyl-PtSnCl$_3$L (L = alkyl, aryl phosphines), we observed in solution a pairwise exchange of the allyl *syn* and *anti* protons which was consistent with the dissociation of tin species [4]. For the process we proposed either (i) dissociation of $SnCl_3^-$, or (ii) formation of "five-coordinate" complex of the type η^3-allyl-PtSnCl$_2$ClL and subsequent loss of $SnCl_2$.

Modern mass spectrometry has proved to be a powerful technique for observing and characterizing intermediates not detectable by other techniques. In particular,

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in the study of gas-phase ion-molecule substitution reactions of Pt complexes, the formation of pentacoordinate Pt complexes was observed [11]. Their successful structural characterization was due to the very narrow time window of a mass spectrometric experiment (10^{-7}–10^{-6} s), and the same gas-phase ion-molecule reaction performed in an ICR cell (with a residence time of 10^{-3} s) gave the substitution product only, with no evidence for the pentacoordinate intermediate [12].

More recently [13] we studied the reactivity of *trans*-$PtHCl[P(C_6H_5)_3]_2$ with respect to $SnCl_2$. The collisional spectra of condensed-phase reaction products was compared with that of addition product obtained by the gas-phase ion-molecule reaction within the ion source of the mass spectrometer.

$$trans\text{-}PtdHCl[P(C_6H_5)_3]_2 + SnCl_2^{+\cdot} \rightarrow \{PtHSnCl_3[P(C_6H_5)_3]_2\}^{+\cdot}$$

The clear differences in daugther ion spectra proved that while the species generated in the ion chamber have a pentacoordinate Pt structure, the molecular ion of the condensed phase reaction product largely maintains the original structure.

In this context we thought it of interest to undertake a study of the reactivity of η^3-allyl-Pt complexes with $SnCl_2$, in particular the reaction:

$$\underset{(\mathbf{1})}{C_3H_5PtP(C_6H_5)_3Cl} + SnCl_2^{+\cdot} \rightarrow \underset{(\mathbf{2})}{[C_3H_5PtP(C_6H_5)_3SnCl_3]^{+\cdot}}$$

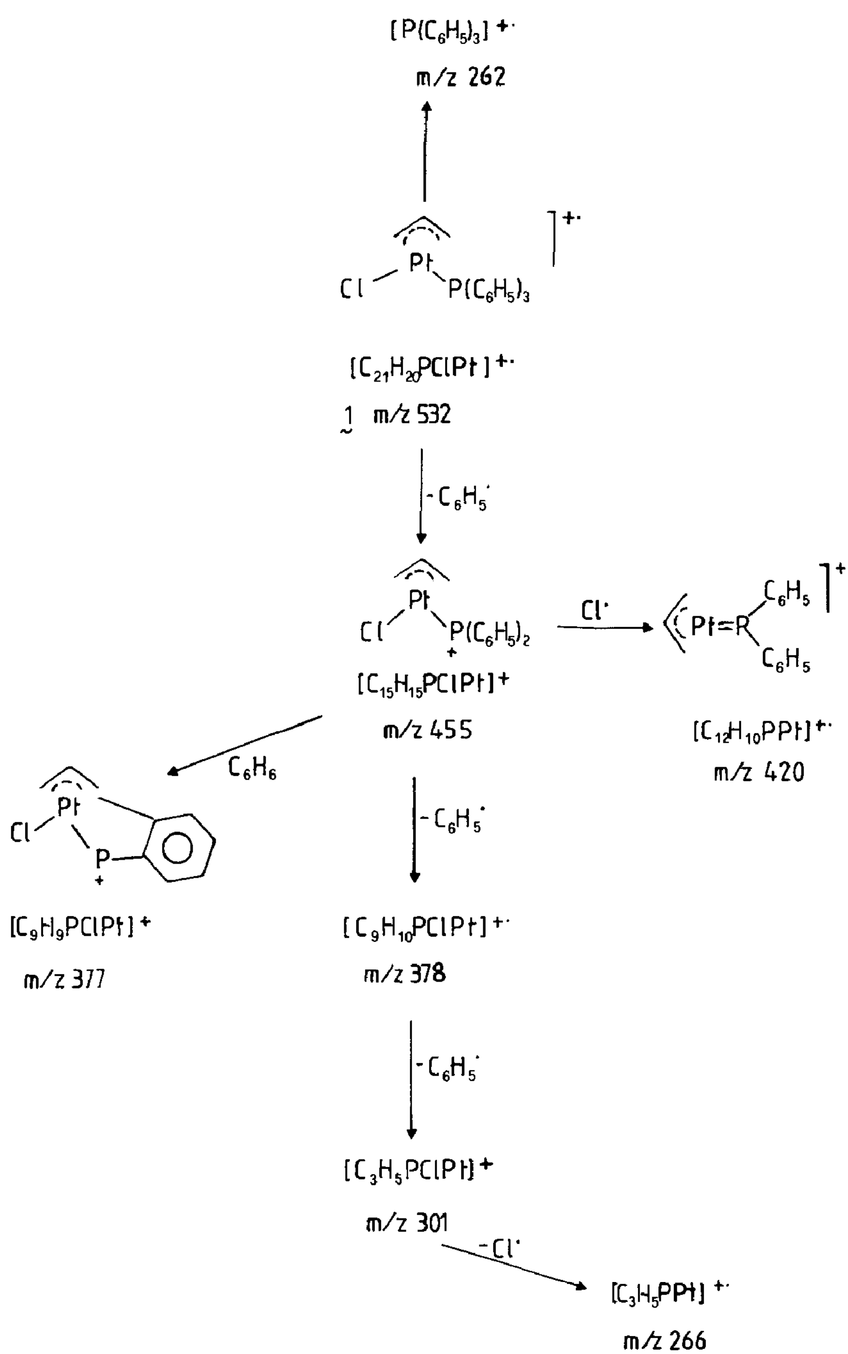
Experimental

All mass spectrometric measurements were obtained by a VG ZAB2F instrument operating in EI conditions (70 eV, 200 μA). Metastable transitions were detected by B/E linked scans [14]. The gas-phase, ion-molecule reactions were performed by introducing compound **1** and $SnCl_2$ via two different insertion ports of the ion source operating in CI mode (100 eV, 2 mA), with a $SnCl_2$ vapour pressure of 0.5 torr, as measured by a Pirani head directly mounted on the ionization chamber [15]. Collisionally activated decomposition mass analyzed ion kinetic energy (CAD MIKE) spectra [16] were obtained by 8 keV ions colliding with air in the second field-free region. The pressure in the collision cell was such to reduce the main beam intensity to 60% of its usual value. Compound **1** was an analytically pure sample synthesized and purified according to literature [17], as well as compound **2** [4]. $SnCl_2$ was purchased by Carlo Erba (Italy).

Results and discussion

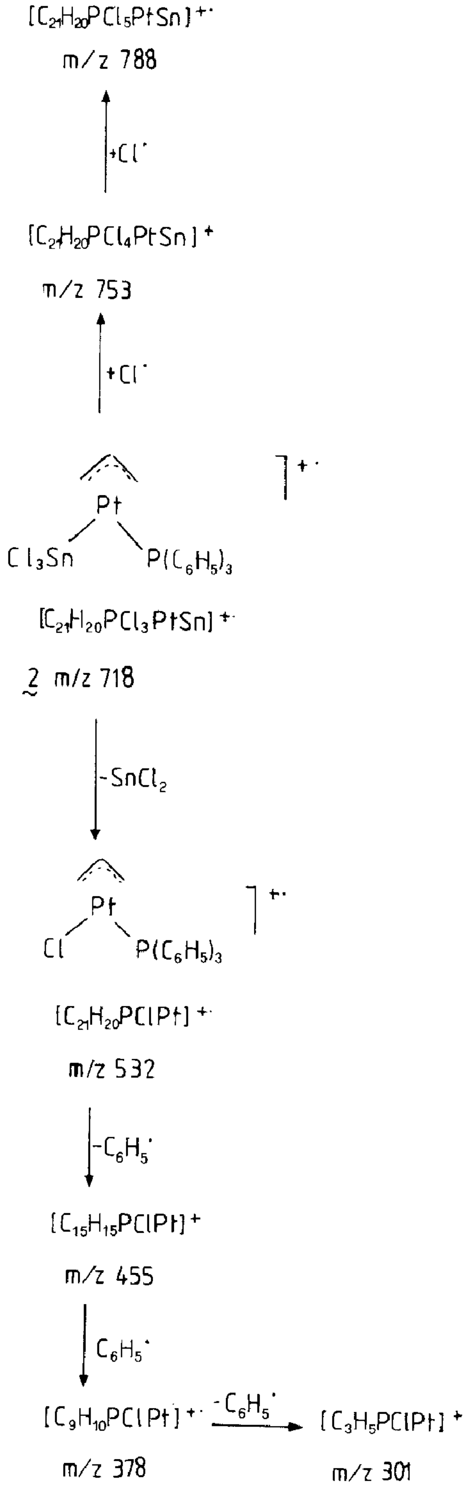
The 70 eV EI mass spectra of compounds **1** and **2** are available from the authors as supplementary material.

The decomposition pattern of compound **1**, as obtained by B/E linked scans, is shown in Scheme 1. The first point to be noted is the complete absence of the ion $[M - P(C_6H_5)_3]^{+\cdot}$ that is usually observed for phosphine-containing organometallic compounds. The only primary metastable supported decomposition process is that due to phenyl loss, leading to the ionic species at m/z 455 (all the m/z values discussed in this paper refer to the following isotopes: ^{12}C, ^{1}H, ^{31}P, ^{35}Cl, ^{116}Sn and



Scheme 1

^{194}Pt). Further sequential $C_6H_5^{\cdot}$ losses lead to the abundant ionic species at *m/z* 378 and 301. The loss of benzene from the ions at *m/z* 455 is noteworthy, and probably leads to *ortho*-metallated species like those shown in Scheme 1. Finally we note the complete preservation of the allyl–Pt bond, which is consistent with the chemical behaviour of the neutral moiety as well as with the previously described mass spectrometric behaviour of allyl complexes [18].

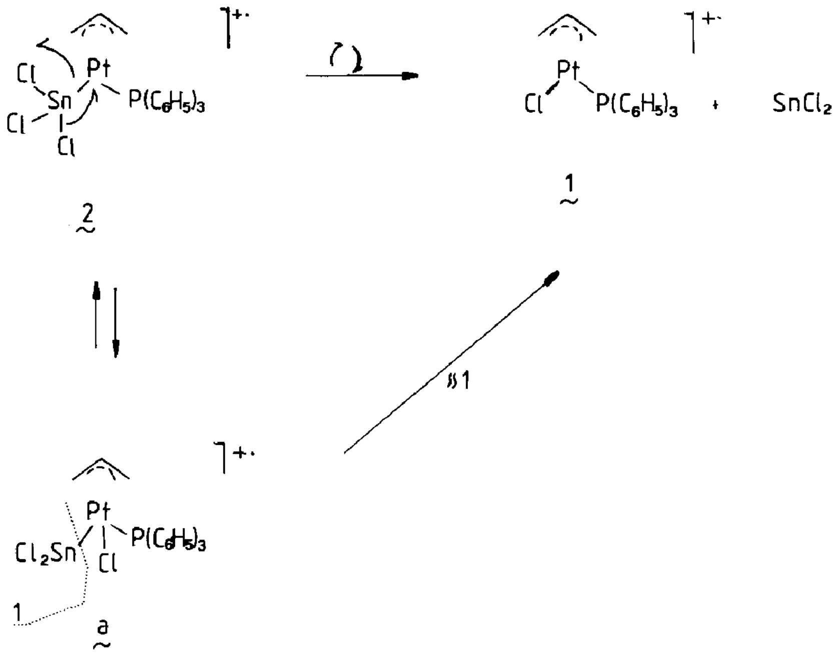

[C21H20PCl5PtSn]+·
m/z 788
+Cl·
[C21H20PCl4PtSn]+
m/z 753
+Cl·
Pt
Cl3Sn
P(C6H5)3
+·
[C21H20PCl3PtSn]+·
2 m/z 718
-SnCl2
Pt
Cl
P(C6H5)3
+·
[C21H20PClPt]+·
m/z 532
-C6H5·
[C15H15PClPt]+
m/z 455
C6H5·
[C9H10PClPt]+·
-C6H5·
[C3H5PClPt]+
m/z 378
m/z 301

Scheme 2

For compound **2**, the primary loss is due to the retrosynthetic process, leading to ionic species at *m/z* 532 (Scheme 2). This behaviour parallels that observed in the case of *trans*-$PtHCl[P(C_6H_5)_3]_2$ [13]. This $SnCl_2$ loss could in principle be either thermally or EI induced. The absence of a relation between the ion source temperature and the $[M]^{+\cdot}/[M - SnCl_2]^{+\cdot}$ ratio excludes the first hypothesis, and demonstrates that $SnCl_2$ loss is a genuine EI induced fragmentation process. For solutions, no evidence was obtained for the presence of species in which the allyl acts as a η'-ligand [4]. If similar behaviour is assumed for this decomposition in the gas phase two possible mechanisms can be proposed (Scheme 3). The first is a concerted process involving a Cl migration to Pt and simultaneous loss of $SnCl_2$. The second involves formation of a molecular pentacoordinate Pt species (structure **a** of Scheme 3), which readily decomposes by cleavage 1 to give the molecular ion of **1**.

The CAD MIKE spectrum of the molecular species of **2** is shown in Fig. 1a. The most abundant peaks are due to phenyl, $SnCl_2$, ($SnCl_2$, C_6H_5), ($SnCl_2$, $C_{12}H_{10}$) and ($SnCl_5$, $C_{18}H_{15}$) losses. The observation of an initial highly favoured loss of $SnCl_2$ strongly suggests that this moiety is present in the molecular ion structure. In contrast, only minor $SnCl_3$ and SnCl losses are observed. Hence these results are in agreement with a structure for the $M^{+\cdot}$ species of **2** different from that of the neutral moiety, i.e. a pentacoordinate Pt-complex structure bearing a $SnCl_2$ group. The results may mean that: (i) the most stable structure of the molecular ion of **2** is **a**, independent of the internal energy content of $M^{+\cdot}$; (ii) the isomerization process $M_2^{+\cdot} \rightarrow M_a^{+\cdot}$ is endothermic, involving a discrete enthalpy change.

In order to clarify this aspects we carried out charge exchange experiments on **2**, using $Xe^{+\cdot}$ as the acidic species. The CAD MIKE spectrum of $M_2^{+\cdot}$ obtained under these condition is shown in Fig. 1b. It will be seen that the molecular species of **2**



Scheme 3

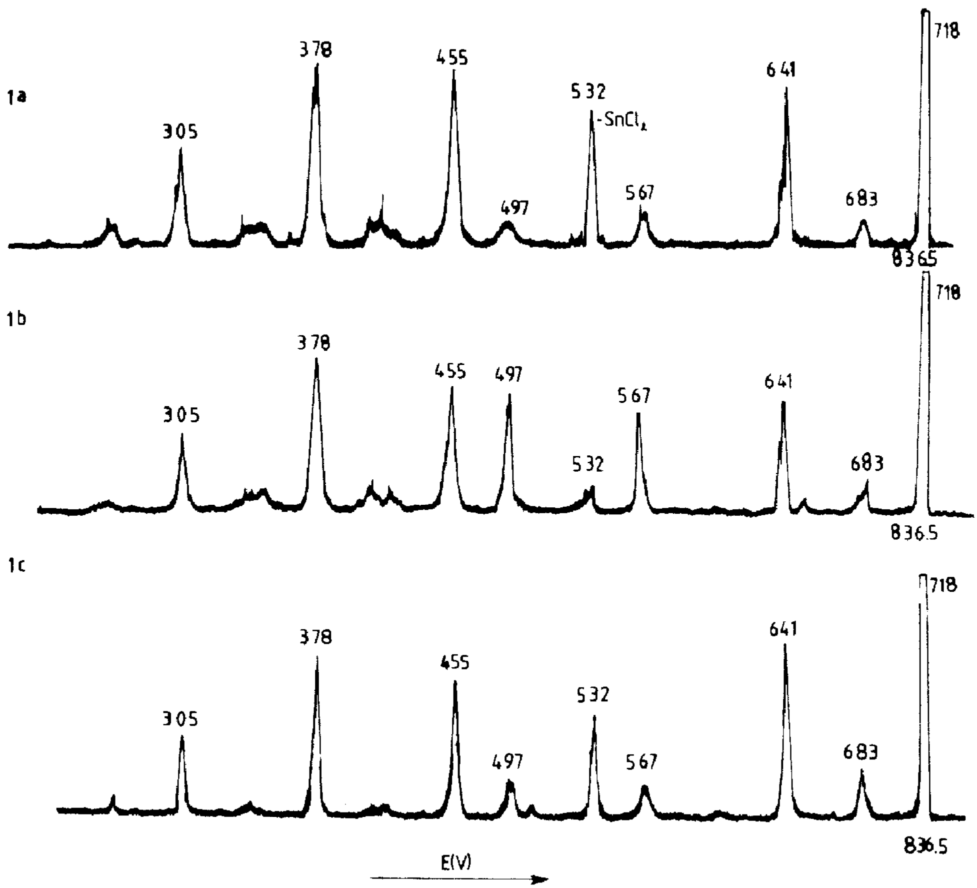


Fig. 1.

obtained under charge exchange conditions do not show any collisionally-induced SnCl_2 loss, which is strong evidence that in these conditions the internal energy content of $M_2^{+\cdot}$ is not sufficient to overcome the isomerization barrier.

After this initial study on the structure of $M^{+\cdot}$ of compound **2**, we examined the reaction of **1** with $\mathrm{SnCl}_2^{+\cdot}$ within the ion source of the mass spectrometer.

With the ionization chamber operating in CI mode the introduction through two separate insertion ports, of compound **1** and SnCl_2 in a ratio such that $[\mathrm{SnCl}_2]^{+\cdot}/[M_1]^{+\cdot} = 100$, led to generation of abundant ionic species at m/z 718, formally corresponding to the addition product. The reaction in the gas phase can be related to that in condensed phase, the only difference consisting in the presence of $\mathrm{SnCl}_2^{+\cdot}$ ions, whose nucleophilic character is partially reduced owing to its positive charge. The SnCl_2 is assumed to act as a carbene analogue and initially coordinate to the metal. The collisional spectrum of the ionic species at m/z 718 so obtained is practically superimposable on that of the $M^{+\cdot}$ species of **2** formed under EI conditions (see Fig. 1c), i.e. the product ion arising from the gas-phase ion-molecule reaction between $\mathrm{SnCl}_2^{+\cdot}$ and M_1 is a pentacoordinate species.

This behaviour is clearly different from that observed in the case of $\mathrm{PtHSnCl_3[P(C_6H_5)_3]_2}$ (see Introduction). Our results show that:

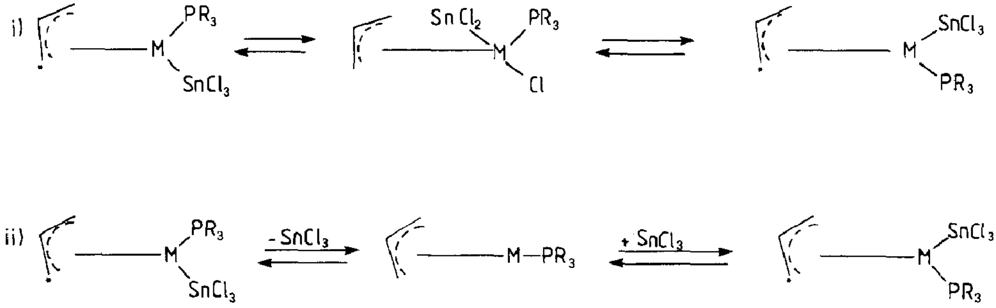
(i) Under EI conditions the molecular ion of **2** mainly has a pentacoordinate structure;

(ii) The isomerization between tetracoordinate and pentacoordinate species involves a quite high energy barrier and in charge-exchange experiments, the molecular ion of **2** mainly has the structure of the neutral initial species.

(iii) The gas-phase ion-molecule reaction between **1** and $SnCl_2^{+\cdot}$ also gives still the pentacoordinate species.

Concluding remarks

The dynamic behaviour observed in solution, i.e. the pairwise exchange of the allyl protons, is consistent with both of the proposed mechanisms reported in Scheme 4. Our results lead us to mechanisms i. The retroreaction clearly shows the presence of pentacoordinate species, both in the molecular ion of **2** obtained in EI conditions and in the product ions arising from the gas-phase ion-molecule reaction of **1** with $SnCl_2^{+\cdot}$



Scheme 4

The lack of evidence for a pentacoordinated intermediate in the case of $PtHSnCl_3[P(C_6H_5)_3]_2$ can be attributed to the presence of a weaker $Pt{-}SnCl_3$ bond as a result of the strong *trans* influence of the hydride.

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