Inorganica Chimica Acta, 134 (1987) 123–129

The Mass Spectrometric Behavior of *trans*-[$PtHCl(PPh_3)_2$] and its Gas-phase, Ion–Molecule Reaction with $SnCl_2$

R. BERTANI and P. TRALDI

C.N.R. Centro di Chimica Metallorganica e Area della Ricerca, Padua, Italy

(Received March 2, 1987)

Abstract

Electron impact (EI) mass spectrometric behavior of *trans*-[$PtHCl(PPh_3)_2$] (1) and *trans*-[$PtH(SnCl_3)(PPh_3)_2$] (2) are described and discussed in detail with the aid of linked scans, accurate mass measurements and collisional experiments. Reactions of **1** with $SnCl_2$ and of **2** with C_2H_4 and CO, performed within the ion source of a mass spectrometer, were studied.

Introduction

Pt complexes in combination with Group IVA metal halides catalyze the homogeneous hydroformilation of olefins to aldehydes [1] under mild conditions and with high selectivity, while normally platinum complexes do not catalyze this reaction. Recently, a study on the reactivity of the system *trans*-[$PtHCl(PPh_3)_2$]/$SnCl_2$ with ethylene showed that *trans*-[$PtH(SnCl_3)(PPh_3)_2$] rapidly inserts ethylene at −80 °C to yield *cis*-[$PtEt(SnCl_3)(PPh_3)_2$] [1] which is the first intermediate of the hydroformilation reaction.

The availability of a mass spectrometer suitable for both the study of gas phase reactions and the characterization of reaction products and of intermediates [2, 3] prompted us to study the gas phase reaction of *trans*-[$PtHCl(PPh_3)_2$] with $SnCl_2$ and of *trans*-[$PtH(SnCl_3)(PPh_3)_2$] with C_2H_4 and CO in order to investigate the intimate mechanisms.

Experimental

Materials, Instrumentation and General Procedures

The working technique for air- and moisture-sensitive compounds was used for complex synthesis and sample preparation [4]. Solvents were dried according to literature methods and kept under nitrogen atmosphere [5]. Analytical grade $SnCl_2 \cdot 2H_2O$ was dehydrated before use [6].

trans-[$PtHCl(PPh_3)_2$] (1) and *trans*-[$PtH(SnCl_3)(PPh_3)_2$] (2) were prepared according to literature procedures and identified by comparison of ^1H and ^{31}P NMR spectra with reported data [7, 8].

trans-[$PtDCl(PPh_3)_2$] (**1a**) was prepared by reacting at −20 °C a solution of [$Pt(CH_2{=}CH_2)(PPh_3)_2$] [9] (0.300 g; 0.40 mmol) in C_6H_6 (10 ml) and EtOD (1 ml) with an equivalent amount of $(CH_3)CC(O)Cl$ (0.05 ml; 0.40 mmol) freshly distilled. A whitish solid separated from the solution by adding Et_2O. It was filtered off, recrystallized from 1,2 dichloroethane/Et_2O and dried at reduced pressure (0.245 g, 81% yield). Melting point (m.p.) 298 °C dec. IR ν(Pt–D) 1585 cm^{-1} (Nujol mull). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 14.31 ppm (J(Pt–P) = 3672.1 Hz). *Anal.* Found: C, 57.0; H, 3.9; Cl, 4.7. Calc. for $PtC_{36}H_{30}DP_2Cl$: C, 57.11; H, 3.99; Cl, 4.68%.

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer as Nujol mulls using CsI windows; spectra were calibrated with reference to polystyrene absorption at 1601 cm^{-1}. The ^1H NMR spectra were recorded on a Varian FT80A instrument in $CDCl_3$ solution. The ^{31}P NMR spectra were recorded on the same instrument operating at 32.204 MHz.

Mass Spectrometric Procedures

All mass spectrometric measurements were performed on a VG ZAB2F instrument [10] operating in electron impact (EI) mode (70 eV, 200 μA). Compounds **1**, **1a** and **2** were introduced under direct electron impact (DEI) [11] conditions, with a source temperature of 200 °C. Collisionally activated decomposition mass-analyzed ion kinetic energy (CAD MIKE) [2] spectra were obtained by 8 keV ions colliding with air in the second field free region. The pressure in the collisional chamber was such as to reduce main beam intensity to 40% of its value. Metastable transitions were detected by B/E linked scan experiments which are indicated in the Schemes by asterisks. Accurate mass measurements were performed by peak matching techniques at 10 000 resolving power (10% valley definition). Kinetic energy release values ($T_{1/2}$) were calculated from the usual formula [12]. Charge-exchange experiments were obtained using NH_3 as acidic species. For ion–

0020-1693/87/$3.50

molecule reactions, the reacting species were admitted to the source through different introduction ports, in order to guarantee the reaction occurrence in the gas phase. Sample vapour pressures were monitored by means of a Pirani head directly mounted on one of the insertion ports of the ion source [13]. The typical pressure range for ion–molecule reaction occurrence was 0.1–1 torr. C_2H_4 was introduced under pressure conditions so as to exclude the production of $C_2H_5^+$ ions. Negative ion mass spectra were obtained in electron attachment conditions using methane as a slow electron producer.

Results and Discussion

The 70 eV EI mass spectrum of compound **1** is reported in Fig. 1 and the related fragmentation pattern, as obtained by B/E linked scans and accurate mass measurements is shown in Scheme 1. Well

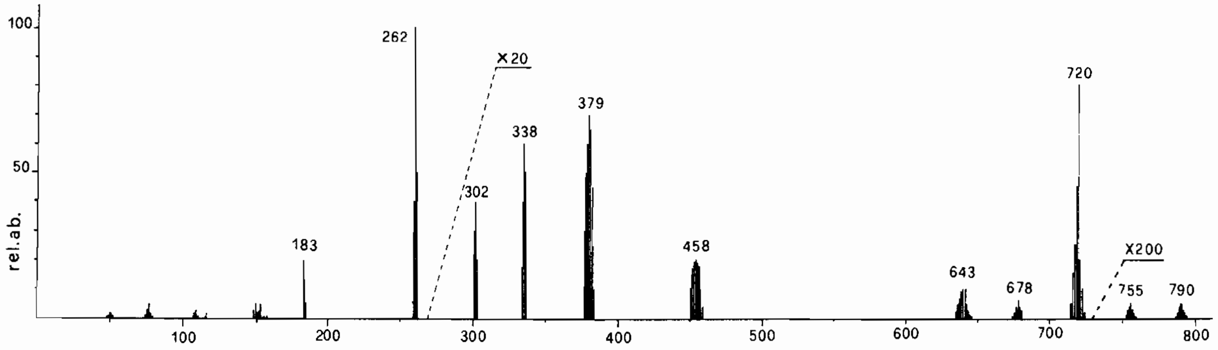
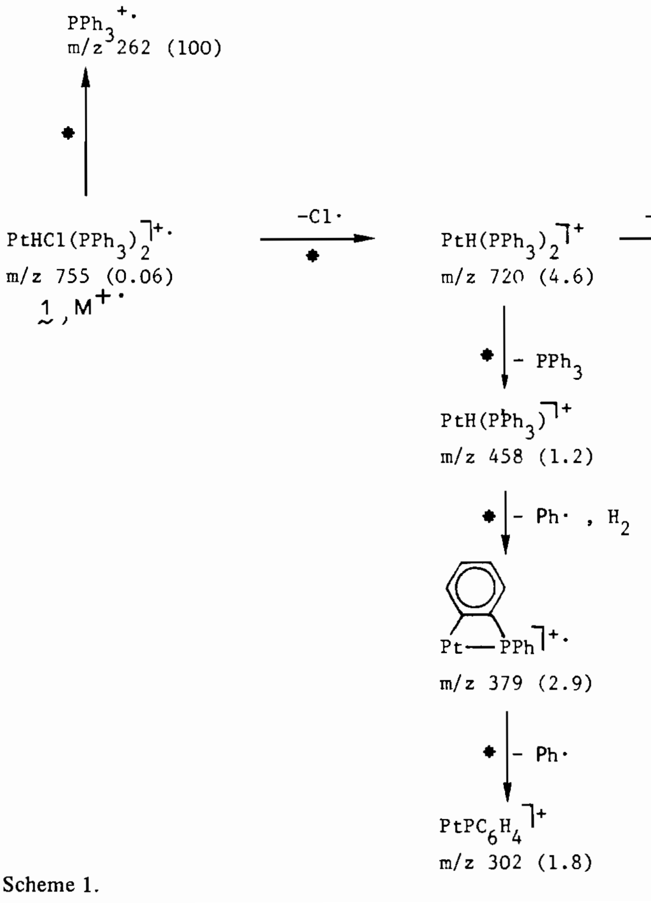


Fig. 1. EI mass spectrum of **1**.



Scheme 1.

detectable $M^{+\cdot}$ is present at *m/z* 755 (corresponding to ^{195}Pt isotope). The most significant primary pathway consists in a $Cl^{\cdot}$ loss giving rise to the abundant ionic species at *m/z* 720. This indicates either that the hydrogen has a strong *trans* influence in labilizing the ligand opposite to itself [14] or that $Cl^{\cdot}$ is, as usual, a good leaving group. In order to investigate the intimate mechanism of this $Cl^{\cdot}$ loss, spectra were recorded at different ion source temperatures (in the range 150–250 °C). On increasing the temperature the $[M]^{+\cdot}/[M - Cl]^{+}$ ratio remained unchanged, proving that the $Cl^{\cdot}$ loss is, in our conditions, not a thermal process but an EI induced one. Furthermore, also working in charge-exchange conditions, the $[M]^{+\cdot}/[M - Cl]^{+}$ ratio did not vary showing that the $Cl^{\cdot}$ loss is a fragmentation process requiring a small internal energy content in $M^{+\cdot}$.

The maintenance of the hydrogen atom should be emphasized. It was previously reported that for phosphine containing hydrido complexes no $[M - H]^{+}$ ions were found, while in carbonyl hydride complexes competitive loss between hydrogen and CO was observed [15]. However, we did not observe, also in B/E and MIKE conditions, $[M - HCl]^{+\cdot}$ ions. This fragmentation process detected in the mass spectrometry of $[PtHCl(PEt_3)_2]$, was probably due to the implication of H atoms of the PEt_3 moiety [15].

Further PPh_3 and $Ph^{\cdot}$ losses from the ions at *m/z* 720 are observed as usually described in mass spectrometry of phosphino-Pt derivatives [16–18]. From the ions at *m/z* 458 ionic species at *m/z* 379 are obtained through contemporary losses of $Ph^{\cdot}$ and H_2. For the quite high kinetic energy release [12] associated with this decomposition pathway, we propose for the ions at *m/z* 379 an orthometallated structure such as that reported in Scheme 1. The comparison with the deuteride derivative (**1a**) fully supports the above findings. B/E linked scans of deuterated molecular ions (*m/z* 756) show the formation of ions at *m/z* 721 as a primary decomposition product proving the maintenance of the D atom in this moiety. Analogously ionic species at *m/z* 643 and 458 for **1** are shifted in **1a** to *m/z* 644 and 459 respectively (see Table I).

Negative ion mass spectrometry of compound **1** shows only the molecular anion $M^{-\cdot}$; the complete absence of Cl^{-} proves that the only chlorine species present in the ion source are $Cl^{\cdot}$ arising from the decomposition pathways described above.

The presence of abundant ionic species at *m/z* 790 in positive ion mass spectra of **1** formally corresponding to $[M + Cl]^{+}$ ions requires further comments. This adduct could in principle originate through the following reaction mechanisms:

$$M_S + Cl^{\cdot} \xrightarrow{\Delta} [M + Cl]^{\cdot} \xrightarrow{EI} [M + Cl]^{+} \qquad \text{(i)}$$

$$M_g + Cl^{\cdot} \xrightarrow{\Delta} [M + Cl]^{\cdot} \xrightarrow{EI} [M + Cl]^{+} \qquad \text{(ii)}$$

$$M^{+\cdot} + Cl^{\cdot} \longrightarrow [M + Cl]^{+} \qquad \text{(iii)}$$

$$M^{+\cdot} + M \longrightarrow [M + Cl]^{+} + [M - Cl]^{\cdot} \qquad \text{(iv)}$$

We are inclined towards mechanisms (ii) and (iii) for the strong dependence of the $[M + Cl]^{+}/[M]^{+\cdot}$ ratio on the sample vapour pressure. Furthermore, mechanism (i) must be excluded from the above findings, *i.e.* the primary $Cl^{\cdot}$ loss is not a thermal process and consequently cannot be operative in the solid state. The $Cl^{\cdot}$ originating from the primary decomposition pathway of M_I can easily react with either neutral or ionized molecules leading to $[M + Cl]^{+}$ species.

TABLE I. Mass Spectra (*m/z*) (relative abundance)

Compound **1a**	261(10.5), 262(100), 263(55.7), 302(0.4), 303(0.5), 304(0.4), 305(0.2), 334(0.7), 335(0.5), 336(0.02), 337(0.01), 376(0.3), 377(0.3), 378(0.3), 457(0.2), 458(0.3), 459(0.5), 460(0.4), 461(0.4), 642(0.1), 643(0.1), 644(0.2), 645(0.1), 646(0.1), 676(0.1), 677(0.1), 678(0.2), 679(0.3), 680(0.1), 718(0.3), 719(0.3), 720(0.6), 721(0.7), 722(0.4), 723(0.2), 755(0.3), 755(0.04), 756(0.04), 757(0.03), 789(0.02), 790(0.03), 791(0.04), 792(0.03), 793(0.01)
Compound **2**	261(10.6), 262(100.0), 263(62.5), 298(0.6), 299(0.6), 300(0.8), 301(1.0), 302(1.2), 303(0.9), 454(0.2), 455(0.6), 456(0.9), 457(0.8), 458(0.3), 459(0.3), 495(0.1), 496(0.1), 497(0.3), 498(0.5), 499(0.4), 500(0.4), 501(0.2), 502(0.1), 529(0.2), 530(0.6), 531(0.5), 532(0.5), 533(0.7), 534(0.6), 535(0.6), 536(0.2), 537(0.1), 538(0.1), 640(0.2), 641(0.3), 642(0.8), 643(1.2), 644(0.8), 645(0.7), 646(0.2), 675(0.7), 676(0.9), 677(1.7), 678(2.0), 679(1.1), 680(0.6), 681(1.5), 682(3.1), 683(3.0), 684(3.2), 685(1.8), 686(1.7), 687(0.8), 688(0.3), 689(0.1), 690(0.1), 717(0.8), 718(2.0), 719(8.1), 720(10.0), 721(7.0), 722(3.6), 723(1.5), 752(1.0), 753(4.5), 754(4.7), 755(8.0), 756(7.8), 757(1.2), 758(1.6), 788(2.3), 798(5.5), 790(7.2), 791(5.0), 792(4.3), 793(1.0), 794(1.0), 836(0.2), 837(0.3), 838(1.0), 839(0.8), 840(0.9), 841(0.6), 842(0.2), 843(0.1), 873(0.3), 874(1.4), 875(1.6), 876(2.0), 877(1.8), 878(1.7), 879(1.2), 880(1.0), 881(0.5), 907(0.6), 908(1.0), 909(2.0), 910(2.5), 911(3.0), 912(2.8), 913(2.9), 914(2.5), 915(2.3), 916(2.0), 917(1.5), 918(0.2), 942(0.6), 943(0.8), 944(1.3), 945(1.5), 946(1.5), 947(1.0), 948(0.9), 949(0.5), 950(0.4), 974(0.2), 975(0.6), 977(0.9), 978(1.8), 979(2.0), 980(2.4), 981(2.5), 982(2.2), 983(2.1), 984(1.5), 985(0.9), 986(0.7), 987(0.3), 988(0.1)

In the case of charge-exchange experiments the $[M + Cl]^+/[M]^{+\cdot}$ ratio dramatically drops, due to the quencher effect of the reacting gas, giving evidence that the $Cl^\cdot$ addition occurs in the gas phase. Also increasing the $Cl^\cdot$ amount (introducing for example $CHCl_3$ into the ion source) causes an increase of the $[M + Cl]^+/[M]^{+\cdot}$ ratio, so excluding mechanism (iv) and further supporting (ii) and (iii). A distinction between (ii) and (iii) is quite difficult. The low abundance of $M^{+\cdot}$ could suggest that it cannot be one of the reacting species: consequently (ii) should be the most reasonable mechanism; on the other hand, the scarce abundance of $M^{+\cdot}$ could, in principle, be due to its high reactivity towards $Cl^\cdot$.

The synthesis in mass spectrometric conditions of five-coordinate platinum complexes has been already described [19]: also if in that case an anionic mechanism was operative leading to five-coordinate Pt anion, the present findings indicate the quite high stability of cationic five-coordinate Pt complexes in the gas phase, too.

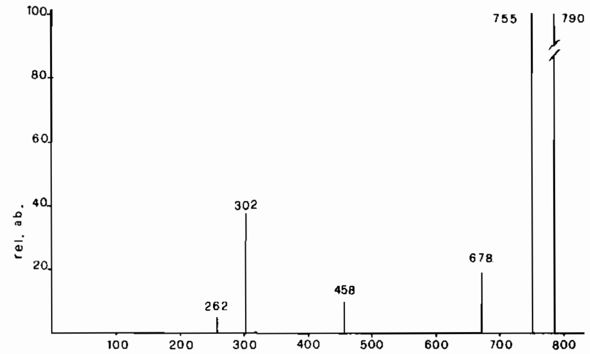


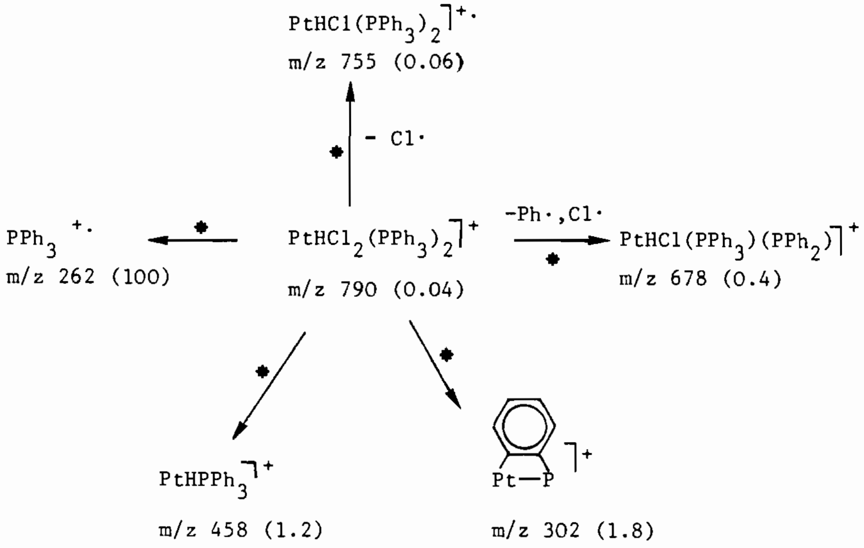
Fig. 2. B/E linked scan of ionic species at *m/z* 790.

The five-coordinate $[M + Cl]^+$ species give rise to the fragmentation pattern reported in Scheme 2. The related B/E spectrum, shown in Fig. 2, shows losses of $Cl^\cdot$ (formally the retrosynthetic process) and $Ph^\cdot$ + $Cl^\cdot$ together with the formation of phosphine molecular ions and ionic species at *m/z* 458 and 302 (see Scheme 2). The $Ph^\cdot + Cl^\cdot$ loss could originate, in principle, either by a first, fast $Cl^\cdot$ loss followed by the $Ph^\cdot$ loss or by a concerted mechanism; we are inclined for the first due to the abundance of the ionic species at *m/z* 755 in the B/E spectrum of *m/z* 790.

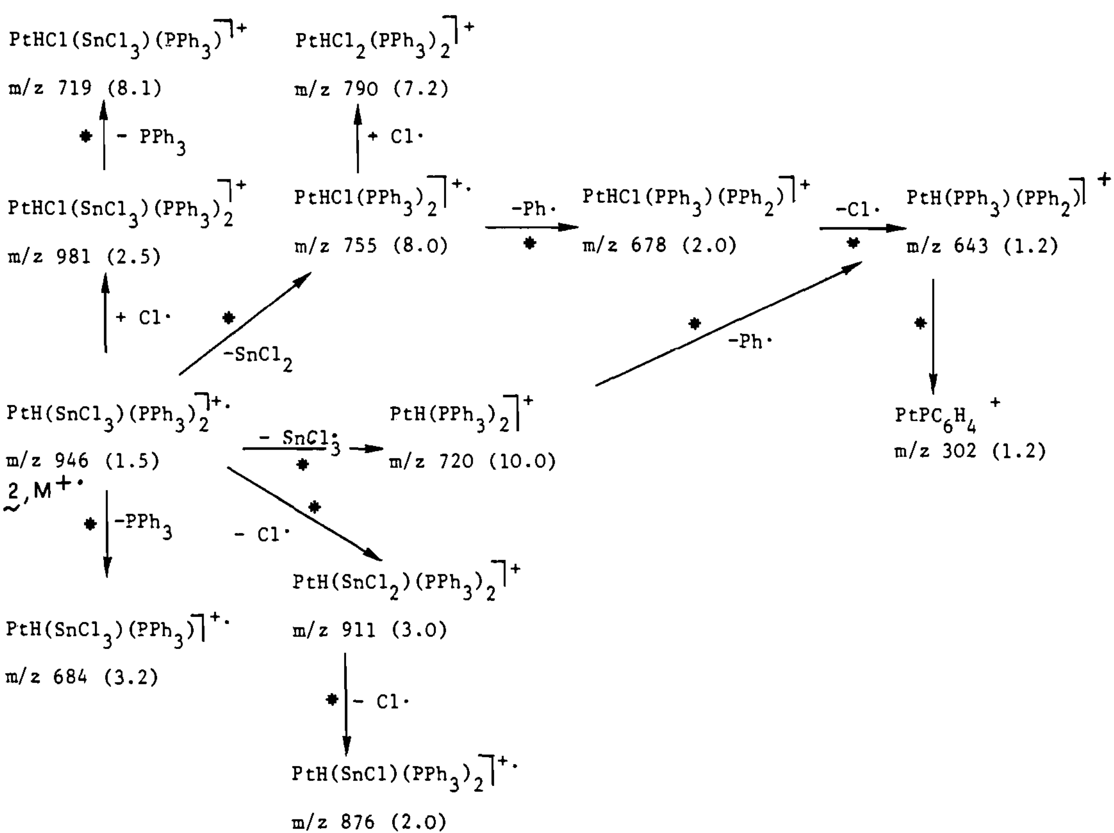
The ionic species at *m/z* 302 originates from both $M_1^{+\cdot}$ and $[M_1 + Cl]^+$ ions and the structure reported in Scheme 2 can be reasonably proposed. The only decomposition pathway of these ions is through a $C_5H_4P^\cdot$ loss, to which a high kinetic energy release is associated (456 meV) in agreement with the cleavage of a stressed, cyclic structure [12].

Gas Phase Ion–Molecule Reactions

(a) The complex *trans*-$[PtHCl(PPh_3)_2]$ (1) reacts in CH_2Cl_2 with $SnCl_2$ to yield *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (2) which has been shown to homogeneously catalyze hydroformilation reactions [20]. The mass spectrometric behavior of compound 2 is reported in Scheme 3: well detectable $M^{+\cdot}$ is present at *m/z* 946. Primary $Cl^\cdot$ and PPh_3 losses lead to ions at *m/z* 911 and 684 respectively; $SnCl_2$ release, the retrosynthetic process, leads to ionic species at *m/z* 755; $SnCl_3^\cdot$ loss leads to ionic species at *m/z* 720. Five-coordinate species originated from reactions with $Cl^\cdot$ are present, too, at *m/z* 981 and 790. Negative ion mass spectrometry shows, with a scarcely abundant $M^{-\cdot}$ ionic species (*ca.* 1%), $SnCl_3^-$ ions only.



Scheme 2.



Scheme 3.

We thought it of interest to study the occurrence of the reaction between 1 and $SnCl_2$ in the ion source of a mass spectrometer. Introducing through two different introduction ports $SnCl_2$ and 1 in a ratio such that $[M_{SnCl_2}]^{+\bullet}/[M_1]^{+\bullet}$ was about 100, not abundant but well detectable ionic species at *m/z* 946, formally corresponding to $[M_1 + SnCl_2]^{+\bullet}$, were evident. This indicates the occurrence of the gas phase ion–molecule reaction:

$$M_1 + SnCl_2^{+\bullet} \longrightarrow [M_1 + SnCl_2]^{+\bullet}$$

The difference between the B/E spectra of $M_2^{+\bullet}$ and $[M_1 + SnCl_2]^{+\bullet}$ indicates that these ionic species have different structures. In fact, for 2 primary losses of PPh_3, $SnCl_2$, $SnCl_3^\bullet$ and $Cl^\bullet$ are observed (Fig. 3A and Scheme 3). For the *in situ* produced species $[M_1 + SnCl_2]^{+\bullet}$ only $SnCl_2$ loss is present (Fig. 3B): this strongly suggests for this ionic species a five-coordinate structure with both chlorine and $SnCl_2$ bonded to the metal. These species arise from the gas phase ion–molecule reaction involving a $SnCl_2$ moiety with more pronounced electrophilic character, enhancing its reactivity *versus* the metallic centre. The detectability of the species must be ascribed to the very narrow time window of the mass spectrometric experiments (10^{-7} s).

(b) Complex 2 reacts with ethylene at –80 °C in CD_2Cl_2 to yield *cis*-$[PtEt(SnCl_3)(PPh_3)_2]$ through a five-coordinate species arising from the interaction of C_2H_4 with the complex 1 [1] stabilized by the $SnCl_3^-$ ligand [21]. Since some five-coordinate adducts are stable on the time scale of the mass spectrometric experiments, we tried to perform the reaction between 2 and C_2H_4 in the ion source. Surprisingly when introducing the reacting species in different ratios (2:C_2H_4 from 1:10 to 1:100) no addition products were detected. Looking at the mass spectrum of M_2 in $C_2H_4^{+\bullet}$ atmosphere, we observe (Fig. 4):

(i) The presence of $[M + H]^+$ ions which indicate the occurrence of an acid–base equilibrium

$$M_2 + C_2H_4^{+\bullet} \longrightarrow [M_2 + H]^+ + C_2H_3$$

(Dihydridoplatinum complexes are involved in equilibria between hydridoplatinum compounds and acids [22].)

(ii) A clear increase of the ratio $[M]^{+\bullet}/[M - SnCl_3]^+$ suggesting the occurrence of a charge-exchange reaction

$$M_2 + C_2H_4^{+\bullet} \rightleftarrows M_2^{+\bullet} + C_2H_4$$

Hence interactions between 2 and $C_2H_4^{+\bullet}$ are present but no addition products are detectable. This can be due to two different factors: (a) reactions (i) and (ii) are more energetically favoured with respect to the addition reaction; (b) the addition product is formed

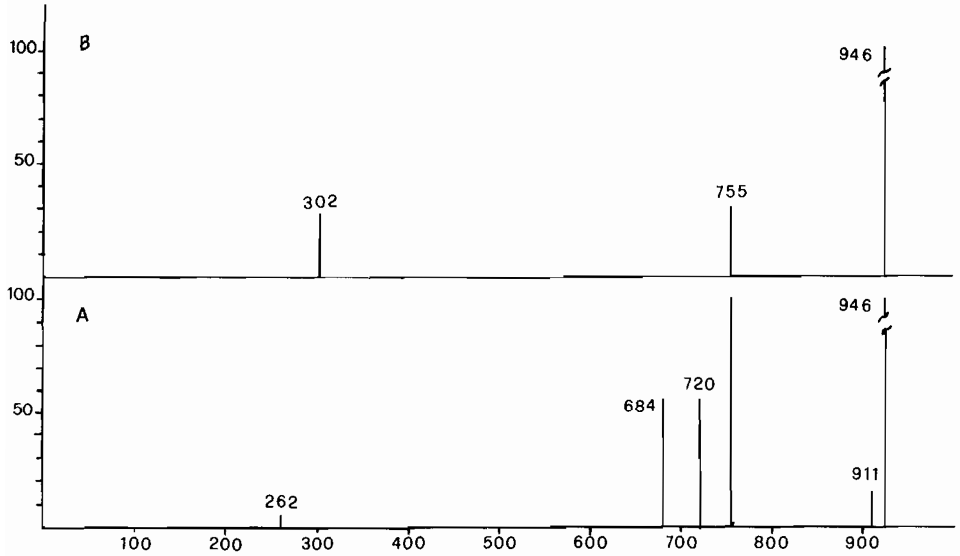


Fig. 3. A: B/E linked scan of the molecular ions of 2 (m/z 946); B: B/E linked scan of ionic species at m/z 946 arising from ion–molecule reaction between 2 and $SnCl_2^{+\bullet}$

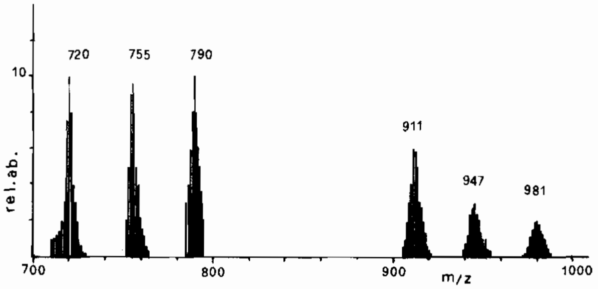
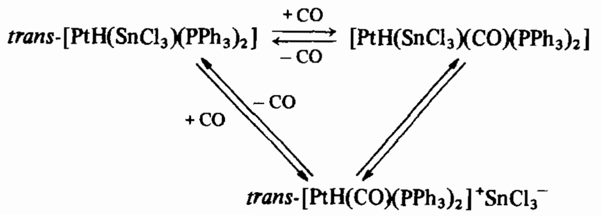


Fig. 4. EI mass spectrum of 2 in $C_2H_4^{+\bullet}$ atmosphere.

but it is so unstable that it immediately decomposes. In this regard it must be emphasized that the complex *cis*-[PtEt($SnCl_3$)($PPh_3)_2$] is unstable in the condensed phase too.

(c) *trans*-[PtH($SnCl_3$)($PPh_3)_2$] reacts with CO in CD_2Cl_2, at room temperature, to yield the five-coordinate complex [PtH($SnCl_3$)(CO)($PPh_3)_2$] involved in solution in equilibrium (1):



We performed the reaction between 2 and CO in the ion source. No addition products were detected, but looking at the mass spectrum of 2 in $CO^{+\bullet}$ atmosphere a general decrease of five-coordinate species is observed. $CO^{+\bullet}$ operates, in these experimental conditions, as a radical trapper as proved by the presence of abundant ions at m/z 98 corresponding to $COCl_2^{+\bullet}$.

Conclusions

In previous works [18, 23] the high potentialities of the modern mass spectrometric techniques were used in the study of ion–molecule reactions involving organometallic compounds and in the structural characterization of intermediates not detectable by other analytical techniques. These results were mainly due to the very narrow time window of the mass spectrometric experiments. In the present case, while the reaction with $SnCl_2$ led to interesting results, the reaction products with C_2H_4 and CO were undetectable, probably due to different kinetics incompatible with the time scale of the instrument.

References

1 A. Scrivanti, A. Berton, L. Toniolo and C. Botteghi, *J. Organomet. Chem., 314,* 369 (1986).
2 C. J. Porter, J. H. Bejnon and T. Ast, *Org. Mass Spectrom., 16,* 101 (1981).
3 A. P. Bruins, K. R. Jennings and S. Evans, *Int. J. Mass Spectrom., 26,* 395 (1978).

4 D. F. Shriver, 'The Manipulation of Air Sensitive Compounds', McGraw-Hill, New York, 1969.

5 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, U.K., 1966.

6 'Organikum Deutscher Verlag der Wissenschaften', Berlin 1969, p. 697.

7 P. S. Pregosin and H. Ruegger, *Inorg. Chim. Acta, 54,* L59 (1981).

8 C. Y. Hsu and M. Orchin, *J. Am. Chem. Soc., 97,* 3553 (1975).

9 U. Nagel, *Chem. Ber., 115,* 198 (1982).

10 R. P. Morgan, G. H. Beynon, R. H. Bateman and B. N. Green, *J. Mass Spectrom. Ion Phys., 28,* 171 (1979).

11 P. Traldi, U. Vettori and F. Dragoni, *Org. Mass Spectrom., 17,* 587 (1982).

12 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, in 'Metastable Ions', Elsevier, Amsterdam, 1973, Appendix IV.

13 B. Facchin, C. Pagura, S. Daolio and P. Traldi, *Org. Mass Spectrom., 19,* 347 (1984).

14 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).

15 B. F. Johnson and J. Lewis, *J. Chem. Soc. A,* 1684 (1970).

16 P. Haake and S. H. Mastin, *J. Am. Chem. Soc.,* 6823 (1971).

17 F. Glokling, T. McBride and R. J. I. Pollock, *Inorg. Chim. Acta, 8,* 81 (1974).

18 R. Bertani, A. M. Maccioni, P. Traldi and G. Carturan, *Inorg. Chim. Acta, 121,* 147, 155 (1986).

19 A. Turco, A. Morvillo, U. Vettori and P. Traldi, *Inorg. Chem., 24,* 1123 (1985).

20 J. Schwager and J. F. Knifton, *J. Catal., 45,* 256 (1976).

21 R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt and U. G. Stolberg, *J. Am. Chem. Soc., 87,* 658 (1965).

22 D. M. Roundhill, *Adv. Organomet. Chem., 13,* 273 (1975).

23 G. Cetini, P. Michelin Lausarot, L. Operti, G. A. Vaglio, M. Valle and P. Volpe, *Int. J. Mass Spectrom., 64,* 25 (1985).