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Decomposition pathways of platinum(II) complexes containing alkyl and halide ligands investigated by electrospray mass spectrometry. The X-ray crystal structure of *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$].

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Abstract—The platinum(II) alkyl-halide complexes *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$], *cis*-[PtCl{$CH_2C(O)CH_3$}$(PPh_3)_2$], *trans*-[PtI(Me)$(PPh_3)_2$], [Pt{$EtSCH_2C(O)CH_2$}Br(PPh_3)] and [Pt{$MeSCH_2C(O)CH_2$}I(PPh_3)] have been investigated by electrospray mass spectrometry (ESMS). For all complexes, loss of halide ion provides the initial ionization pathway and the resulting ions may contain coordinated ligands from the solvent (acetonitrile, ammonia and added pyridine). At high cone voltages, all complexes undergo cyclometallation of one of the triphenylphosphine ligands. However, for the chloroacetonyl complex *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$], fragmentation to the ion $[PtCl(PPh_3)_2]^+$ preceeds cyclometallation. It is proposed that this complex fragments *via* initial oxidative addition of the C—Cl bond, forming an unstable platina (IV)cyclobutan-3-one (oxodimethylenemethane) complex, which undergoes reductive elimination of cyclopropanone. The X-ray crystal structure of *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$] is also reported. © 1997 Elsevier Science Ltd

Keywords: platinum; alkyl; halide; electrospray; crystal structure.

We have previously reported the synthesis of the chloroacetonyl platinum complex *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$] (**1**), formed by oxidative addition of 1,3-dichloroacetone to the zero-valent platinum complex [Pt{*trans*-PhCH=CHPh}$(PPh_3)_2$] [1,2]. The synthesis of this complex has also been independently reported by other workers [3]. Compound **1** has been found to be a versatile precursor for the synthesis of a number of organometallic platinum complexes. Dechlorination of **1** by means of sodium amalgam afforded the platinum(II) oxodimethylenemethane (platinacyclobutan-3-one) complex **2** [1], which has also been synthesized by a number of other routes. [4] Reaction of **1** with Na_2S results in cyclization to afford the cyclic thiolate complex **3** [2] and we have investigated the coordination chemistry of this complex towards other metal centres [5].

We have now undertaken a study of complex **1**, together with a number of other platinum(II) halide complexes by electrospray mass spectrometry (ESMS) [6]. ESMS is a relatively recent mass spectrometric ionization method, which is receiving ever-increasing attention for inorganic complexes [7]. To date, the technique has been applied to a number of different types of coordination [7,8] and organometallic complexes. The latter include metal-alkyls of tin [9], mercury, [10] gold [11], indium [11] and thallium [11], cyclopentadienyl compounds [12], π-alkene and arene compounds [13], and metal carbonyl complexes [14].

In a previous report, we described that ESMS can be used to identify platinum(II) complexes containing orthometallated triphenylphosphine ligands, the orthometallated complexes being formed in the mass

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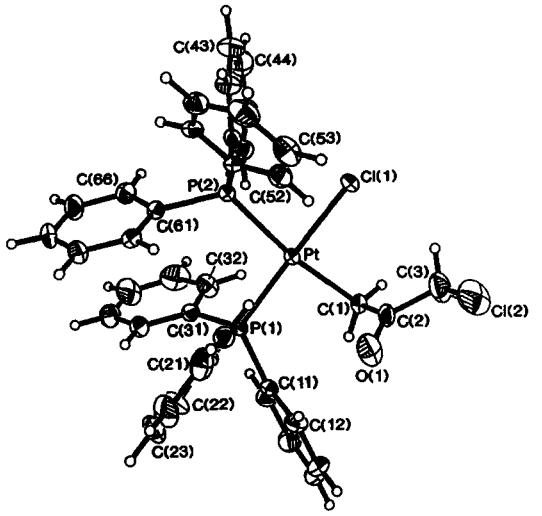


Fig. 1. Molecular structure of *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$] (**1**), showing the atom numbering scheme.

spectrometer by the use of high skimmer cone voltages [15]. We subsequently reasoned that ESMS provides a useful means of probing decomposition pathways of organometallic complexes, rapidly, and using only very small quantities of material. Mass spectrometric studies may then provide an impetus for synthetic studies. In this paper we describe mass spectrometric studies on **1** and some other platinum complexes containing alkyl and halide ligands. The results of a single-crystal X-ray diffraction study on the complex **1** are also reported.

RESULTS AND DISCUSSION

The chloroacetonyl complex *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$] (**1**) was synthesized by the literature method [2], involving oxidative addition of one of the C—Cl bonds of 1,3-dichloroacetone to the zerovalent platinum complex [Pt(*trans*-PhCH=CHPh)$(PPh_3)_2$]. It is noteworthy that this synthetic route furnishes a highly pure product and purification is unnecessary. These observations indicate that at room temperature the C—Cl bond of **1** is unreactive towards either intra- or intermolecular oxidative addition reactions. Additionally, **1** is unreactive towards oxidative addition of 1,3-dichloroacetone (since an excess is used in the synthetic procedure). In this case, the steric bulk of the complex may restrict the nucleophilic attack of a second platinum centre. Other systems show different behaviour, for example, the platinum(II) chloroacetylide complex [PtCl(C=CCl)$(PEt_3)_2$], which undergoes oxidative addition of the C—Cl bond to a second platinum(0) centre, giving a dinuclear complex [16].

The availability of single crystals of **1** furnished the opportunity of a single-crystal X-ray diffraction study, in order to try and rationalize the reactivity of the complex in terms of its structural features. The molecular structure of **1** is shown in Fig. 1, together with the atom-numbering scheme, while selected bond lengths and angles are given in Table 1. To the best of our knowledge, only one previous structural determination of a related acetonyl complex has been reported, that of the analogous tetrafluoro analogue *cis*-[PtCl{$CF_2C(O)CF_2Cl$}$(PPh_3)_2$] (**4**) [17].

Complex **1** has the expected approximately square-planar geometry about the platinum atom, with this atom deviating by only 0.010 Å from the least-squares plane defined by the atoms P(1), P(2), Cl(1) and C(1). Overall, the complex **1** bears a strong resemblance to that of the fluorinated analogue **4**, with similar effects caused by the presence of two ligands (alkyl and chloride) having differing *trans*-influences. In both **1** and **4**, the Pt—P bond *trans* to the alkyl moiety is sig-

Table 1. Selected intramolecular bond lengths (Å) and angles (°) for **1** with estimated standard deviations in parentheses

Pt—P(1)	2.238(2)	Pt—P(2)	2.334(2)
Pt—Cl(1)	2.361(2)	Pt—C(1)	2.116(8)
C(1)—C(2)	1.475(13)	C(2)—C(3)	1.49(2)
C(2)—O(1)	1.226(12)	C(3)—Cl(2)	1.734(13)
P(1)—Pt—C(1)	91.6(2)	P(1)—Pt—P(2)	97.89(8)
C(1)—Pt—Cl(1)	85.9(2)	P(2)—Pt—Cl(1)	84.88(8)
Pt—C(1)—C(2)	107.1(6)	C(1)—C(2)—C(3)	117.1(9)
C(1)—C(2)—O(1)	122.8(9)	C(3)—C(2)—O(1)	120.0(11)
C(2)—C(3)—Cl(2)	116.0(9)		
Triphenylphosphine ligands			
P(1)—C(11)	1.851(9)	P(2)—C(41)	1.821(9)
P(1)—C(21)	1.823(10)	P(2)—C(51)	1.838(9)
P(1)—C(31)	1.818(9)	P(2)—C(61)	1.847(8)
C(11)—P(1)—C(21)	99.5(4)	C(41)—P(2)—C(51)	105.4(4)
C(11)—P(1)—C(31)	102.6(4)	C(41)—P(2)—C(61)	103.8(4)
C(21)—P(1)—C(31)	109.3(4)	C(51)—P(2)—C(61)	100.7(4)

nificantly longer than the Pt—P bond *trans* to the chloride ligand. In **1**, these values are 2.334(2) and 2.238(2) Å, respectively. The chloroacetonyl ligand of **1** appears to have a lower *trans*-influence than the corresponding tetrafluorinated analogue, as evidenced by the shorter *trans* P—Pt bond in **1** [2.334(2) Å] when compared with that of **4** [2.362(5) Å]. The Pt—Cl bonds of **1** and **4** are 2.361(2) and 2.349(6) Å, respectively. Pt—Cl bonds *trans* to phosphine ligands typically lie within the range 2.36–2.39 Å. The C—Cl bonds of **1** and **4** appear to be comparable, within experimental error. There appear to be no unusual features regarding the structure of **1**.

Electrospray mass spectrometry (ESMS)

Complex **1**, together with a number of other related platinum(II) complexes containing alkyl and halide ligands were investigated by ESMS, using a MeCN–H_2O mobile phase. The related complex *cis*-$[PtCl\{CH_2C(O)CH_3\}(PPh_3)_2]$ (**5**) together with *trans*-$[PtI(CH_3)(PPh_3)_2]$ and *cis*-$[PtCl_2(PPh_3)_2]$ were also studied to provide comparative data for species without reactive alkyl halide groups. ESMS data are summarized in Table 2. Identification of species was aided by comparison of observed and calculated isotope distribution patterns, the latter being calculated using the *Isotope* program [18]. Platinum has a number of isotopes, and in combination with one or more chlorine atoms, provides distinctive isotope patterns which aid assignment.

trans-$[PtI(CH_3)(PPh_3)_2]$. The behaviour of this complex in positive-ion ESMS is typical of that displayed by platinum-phosphine-halide complexes [15,19]. Loss of one halide ligand is the predominant ionization mechanism, leaving a positively charged platinum centre. Additional coordination of an MeCN solvent molecule also occurs, but the relative amounts of solvated and non-solvated species is highly dependent on the cone voltage. Similar results have been observed for the analysis of the anticancer drug Cisplatin, *cis*-$[PtCl_2(NH_3)_2]$ in acetonitrile–water–acetic acid solutions [20].

Thus, at a relatively low cone voltage (20 V), the predominant species was $[PtMe(MeCN)(PPh_3)_2]^+$ (*m/z* 775), while at moderate cone voltages, $[PtMe(PPh_3)_2]^+$ predominated. At yet higher cone voltages (> *ca* 40 V), cyclometallation of one of the triphenylphosphine ligands occured, presumably with concomitant loss of methane, yielding the orthometallated species **6**, at *m/z* 718. Further increasing the cone voltage effects loss of the remaining triphenylphosphine ligand from **6**. We have observed cyclometallated triphenyl-phosphine and -phosphites previously, when high cone voltage conditions are used [15]. Platinum complexes containing cyclometallated ligands are quite well known, including a number of structurally characterized examples [21]. The ability to access reactions such as orthometallations by ESMS suggested that complex **1**, containing an additional alkyl halide moiety, might also undergo interesting decomposition pathways. ESMS has been used to directly probe these pathways.

cis-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ *and* cis-$[PtCl\{CH_2C(O)CH_3\}(PPh_3)_2]$. The ES spectra of **1** at a cone voltage of 20 V have a resemblance to that of *trans*-$[PtI(Me)(PPh_3)_2]$, in that the major species is formed by replacement of Cl^- by MeCN, *viz.* $[Pt\{CH_2C(O)CH_2Cl\}(MeCN)(PPh_3)_2]^+$ and $[Pt\{CH_2C(O)CH_3\}(MeCN)(PPh_3)_2]^+$. The complex $[Pt\{CH_2C(O)CH_2Cl\}(NH_3)(PPh_3)_2]^+$ was observed as a minor peak, with the source of the ammonia being the acetonitrile mobile phase; we have observed such behaviour previously [15]. Further increasing the cone voltage causes the expected loss of the neutral MeCN or NH_3 ligands, as with the *trans*-$[PtI(Me)(PPh_3)_2]$ complex, and thus at a cone voltage of 30 V, $[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ dominated the ES spectrum. It is possible that the C=O group may be involved in intramolecular coordination to the positively charged platinum centre, in the absence of the solvent ligands.

For the acetonyl complex *cis*-$[PtCl\{CH_2C(O)CH_3\}(PPh_3)_2]$ it is noteworthy that a weak ion at *m/z* 810 is consistent with the presence of a small quantity of a product derived from either 1,1- or 1,3-dichloroacetone. This is readily understandable, since the commercial monochloroacetone used contains small quantities of 1,1-dichloroacetone (typically 2.6%) and 1,3-dichloroacetone (typically 0.2%), in addition to mesityl oxide [22]. Oxidative addition of 1,1-dichloroacetone to $[Pt(trans\text{-}PhCH{=}CHPh)(PPh_3)_2]$ would furnish a small amount of the complex *cis*-$[PtCl\{ClCHC(O)CH_3\}(PPh_3)_2]$, which would be indistinguishable from $[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ by ESMS.

Upon further increasing the cone voltage, different behaviour is observed for the two complexes **1** and **5**. At a cone voltage of 50 V $[PtCl(PPh_3)_2]^+$ was the major ion observed for **1** at *m/z* 755, together with $[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (*ca* 70% relative intensity), as illustrated in Fig. 2. Excellent agreement was observed between observed and calculated isotope patterns of the $[PtCl(PPh_3)_2]^+$ ion. At 50 V there was only a small peak (*ca* 10%) due to the cyclometallated species **6**. Upon increasing the cone voltage to 60 V, $[PtCl(PPh_3)_2]^+$ remained the base peak, with the intensity of **6** increasing to around 28%. When the ES spectrum of **1** is recorded at yet higher cone voltages (e.g. 80 V), the orthometallated triphenylphosphine species **6** is the major ion observed. As a comparison, when the compound *cis*-$[PtCl_2(PPh_3)_2]$ is investigated at high cone voltages, cation **6** is also observed. Scheme 1 shows a proposed mechanism which accounts for the observation of the ion $[PtCl(PPh_3)_2]^+$. The initial ion $[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (**7**) undergoes oxidative addition of the γ-C—Cl bond, generating the intermediate platina(IV)cyclobutan-3-one complex **8**. (This may be alternatively formulated as an η^3-oxodimethylene-

Table 2. Electrospray mass spectrometric data (positive ion mode) for various platinum-alkyl-halide complexes, recorded in MeCN–H_2O solution

Compound	Cone voltage (V)	Ions (m/z, %)[a]
trans-[PtI(Me)(PPh_3)$_2$]	20	$[PtMe(PPh_3)_2]^+$ (734, 70), $[PtMe(PPh_3)_2(MeCN)]^+$ (775, 100)
	40	$[Pt(o\text{-}C_6H_4PPh_2)]^+$ (456, 8), $[Pt(o\text{-}C_6H_4PPh_2)(MeCN)]^+$ (497, 19), $[PtMe(PPh_3)_2]^+$ (734, 100)
	60	$[Pt(o\text{-}C_6H_4PPh_2)]^+$ (456, 13), $[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$, **6** (718, 100), $[PtMe(PPh_3)_2]^+$ (734, 13)
cis-[PtCl{$CH_2C(O)CH_2Cl$}(PPh_3)$_2$] (**1**)	15	$[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (811, 90), $[Pt\{CH_2C(O)CH_2Cl\}(NH_3)(PPh_3)_2]^+$ (828, 100), $[Pt\{CH_2C(O)CH_2Cl\}(MeCN)(PPh_3)_2]^+$ (852, 39)
	30	$[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (811, 100), $[Pt\{CH_2C(O)CH_2Cl\}(NH_3)(PPh_3)_2]^+$ (828, 18)
	50	$[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$, **6** (718, 11), $[PtCl(PPh_3)_2]^+$ (755, 100), $[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (811, 68)
	80	$[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$ (718, 100), $[PtCl(PPh_3)_2]^+$ (755, 22)
cis-[PtCl{$CH_2C(O)CH_3$}(PPh_3)$_2$] (**5**)	20	$[Pt\{CH_2C(O)CH_3\}(PPh_3)_2]^+$ (776, 100), $[Pt\{CH_2C(O)CH_3\}(NH_3)(PPh_3)_2]^+$ (793, 42), $[Pt\{CHClC(O)CH_3\}(PPh_3)_2]^+$/$[Pt\{CH_2C(O)CH_2Cl\}(PPh_3)_2]^+$ (811, 8),
	60	$[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$, **6** (718, 100), $[Pt\{CH_2C(O)CH_3\}(PPh_3)_2]^+$ (776, 68)
	100	$[Pt(o\text{-}C_6H_4PPh_2)]^+$ (455, 74), $[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$, **6** (718, 100)
cis-[PtCl{$CH_2C(O)CH_3$}(PPh_3)$_2$] + py	15	$[Pt\{CH_2C(O)CH_3\}(PPh_3)_2]^+$ (776, 10), $[Pt\{CH_2C(O)CH_3\}(py)(PPh_3)_2]^+$ (855, 100)
[Pt{$EtSCH_2C(O)CH_2$}Br(PPh_3)]	15	$[Pt\{EtSCH_2C(O)CH_2\}(MeCN)(PPh_3)]^+$ (615, 100), $[Pt\{EtSCH_2C(O)CH_2\}(PPh_3)_2]^+$ (836, 3)
	50	$[Pt\{EtSCH_2C(O)CH_2\}(PPh_3)]^+$ (574, 100), $[Pt\{EtSCH_2C(O)CH_2\}(PPh_3)_2]^+$ (836, 8)
[Pt{$EtSCH_2C(O)CH_2$}Br(PPh_3)] + py	15	$[Pt\{EtSCH_2C(O)CH_2\}py(PPh_3)]^+$ (653, 100)
[Pt{$MeSCH_2C(O)CH_2$}I(PPh_3)]	15	$[Pt\{MeSCH_2C(O)CH_2\}(MeCN)(PPh_3)]^+$ (601, 100), $[Pt\{MeSCH_2C(O)CH_2\}(PPh_3)_2]^+$ (822, 3)
	50	$[Pt\{MeSCH_2C(O)CH_2\}(PPh_3)]^+$ (558, 100), $[Pt\{EtSCH_2C(O)CH_2\}(PPh_3)_2]^+$ (822, 4)
	70	$[Pt(o\text{-}C_6H_4PPh_2)]^+$ (456, 100), $[Pt\{MeSCH_2C(O)CH_2\}(PPh_3)]^+$ (558, 70), $[Pt\{EtSCH_2C(O)CH_2\}(PPh_3)_2]^+$ (822, 7)
[Pt{$MeSCH_2C(O)CH_2$}I(PPh_3)] + py	15	$[Pt\{MeSCH_2C(O)CH_2\}py(PPh_3)]^+$ (639, 100)

[a]Species are identified by the peak of highest intensity in the isotope distribution pattern. py = pyridine.

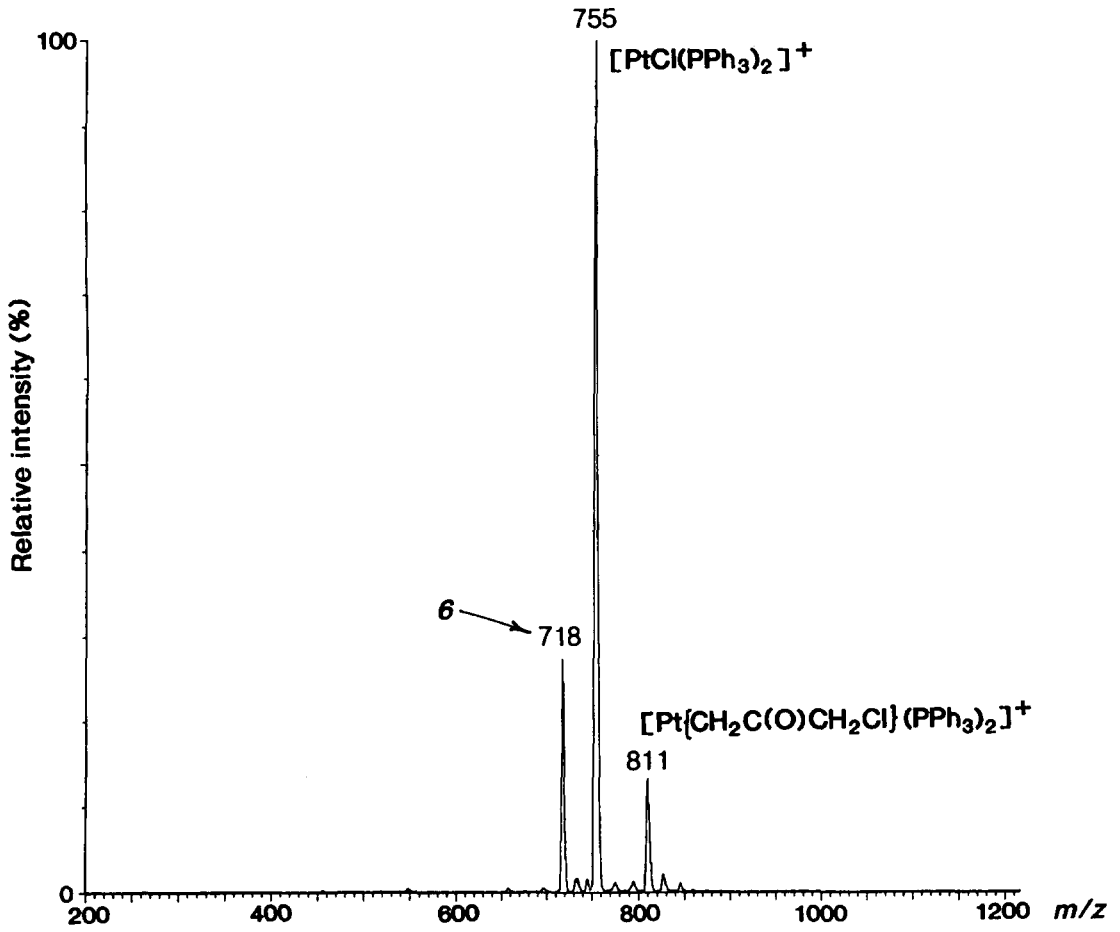
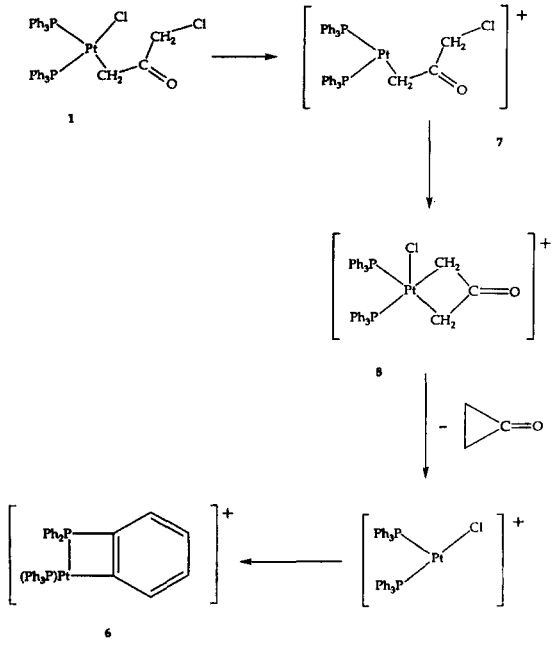


Fig. 2. Positive-ion electrospray mass spectrum (cone voltage 60 V) of *cis*-[PtCl{$CH_2C(O)CH_2Cl$}$(PPh_3)_2$] (**1**), recorded in MeCN : H_2O (1 : 1), showing assignments of the major ions.

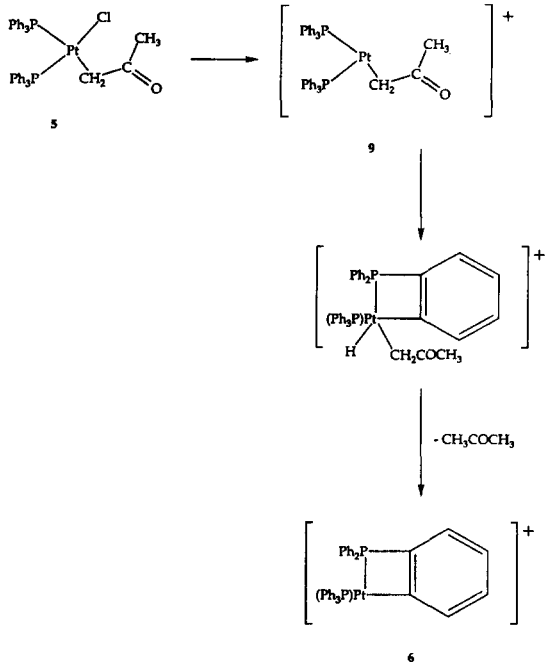
methane complex, analogous to **2**.) This species is most probably unstable and undergoes reductive elimination of cyclopropanone, yielding the observed ion $[PtCl(PPh_3)_2]^+$. It must be noted, however, that the species **7** and **8** are isobaric and cannot be distinguished by ESMS. However, there have been several unsuccessful attempts at the synthesis of platina(IV)cyclobutane and platina(IV) cyclobutanone tertiary phosphine complexes by oxidative addition reactions to the parent platinum(II) complexes. In these cases, the organic fragment is lost from the metal centre, presumably by a reductive elimination process. Reductive elimination appears to be promoted by the presence of phosphine ligands, since platina(IV)cyclobutanes containing ancillary nitrogen donor ligands have been isolated [23].

Preliminary synthetic studies are also in agreement with the results of the ESMS study described above. Upon refluxing the chloroacetonyl complex **1** in xylene, a mixture of *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$ separated on cooling. Furthermore, the metathetical replacement of the chlorine groups of **1** by treatment with LiBr in acetone at room temperature gives only *cis*-$[PtBr_2(PPh_3)_2]$. Possibly, metathesis of the CH_2Cl group to a more reactive CH_2Br moiety results in rapid oxidative addition (at room temperature) with subsequent reductive elimination of cyclopropanone, as described above.

Under the same conditions at which **1** yields $[PtCl(PPh_3)_2]^+$ (cone voltage 60 V), the acetonyl complex **5** does not show this ion, but instead shows the orthometallated triphenylphosphine species **6** at *m/z* 718, as shown in Fig. 3. The oxidative addition of the relatively unreactive γ-CH bond of **5** is expected to be unfavourable when compared with that of on *ortho*-phenyl C—H bond, resulting in orthometallation being the preferred pathway, as summarized in Scheme 2. Presumably, an oxidative addition (analogous to the oxidative addition of C—Cl in Scheme 1) of a γ-CH bond would yield a platinum(IV) cyclobutanone hydride, which would then be expected to reductively eliminate cyclopropanone yielding $[PtH(PPh_3)_2]^+$; no such ion was observed. We note, however, that oxidative addition reactions of γ-C—H bonds have been described in the literature, such as in the conversion of the bis(neopentyl) complex $[Pt(CH_2CMe_3)_2(PEt_3)_2]$ to the platinacyclobutane complex $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$ [24]. However, in the case of complex **1**,



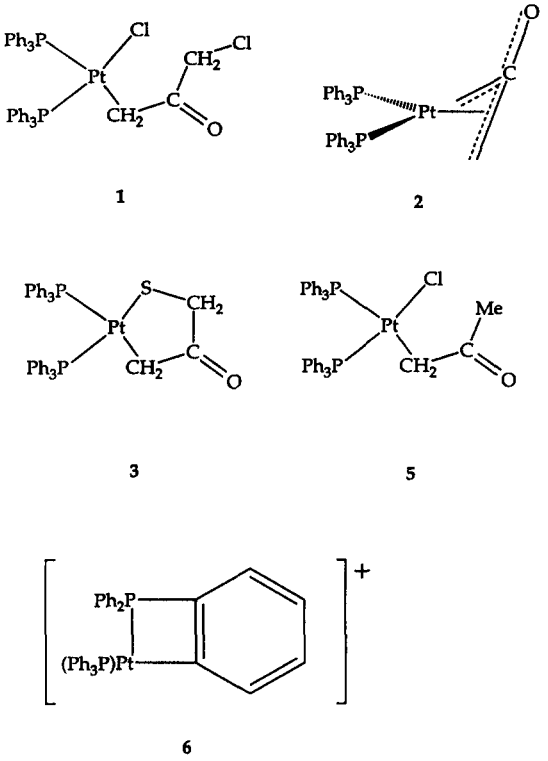
Scheme 1. Showing the proposed ESMS fragmentation pathway for the chloroacetonyl complex **1**. Solvation of complex **7** has been omitted for simplicity.



Scheme 2. Showing the proposed ESMS fragmentation pathway for the acetonyl complex **5** solvation of complex **9** has been omitted for simplicity.

oxidative addition of the more reactive alkyl chloride appears to provide the more facile route for fragmentation.

ESMS also allows ligand substitution reactions to



Scheme 3.

be investigated in a very simple manner. Thus, the acetonyl complex **5** shows the expected behaviour on addition of excess pyridine (py). The complex $[Pt\{CH_2C(O)CH_3\}(py)(PPh_3)_2]^+$ was observed as the base peak in the spectrum at a cone voltage of 15 V, with $[Pt\{CH_2C(O)CH_3\}(PPh_3)_2]^+$ also observed as a weak peak.

$Pt\{EtSCH_2C(O)CH_2\}Br(PPh_3)_2]$ *and* $[Pt\{MeSCH_2C(O)CH_2\}I(PPh_3)]$. These complexes were prepared by the alkylation of the cyclic thiolate complex **3** with bromoethane and iodomethane, respectively, according to the procedure published previously [5]. The mass spectrometric behaviour of these complexes is analogous to that of *trans*-$[PtI(Me)(PPh_3)_2]$ described above. Thus, at low cone voltages, the principal observed ions are the acetonitrile-solvated cations $[Pt\{RSCH_2C(O)CH_2\}(MeCN)(PPh_3)]^+$ (R = Me or Et). The complexes $[Pt\{RSCH_2C(O)CH_2\}(PPh_3)_2]^+$ were observed as minor ions in these spectra, possibly as a result of a ligand redistribution reaction. When the spectrum of $[Pt\{MeSCH_2C(O)CH_2\}I(PPh_3)]$ is recorded at a high cone voltage (70 V), cyclometallation of the triphenylphosphine ligand occurs, giving the ion $[Pt(o\text{-}C_6H_4PPh_2)]^+$ at *m/z* 456. It is noteworthy that the ion $[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$ (**6**) was observed only as a very minor ion in this instance, presumably as a result of the starting complex having only *one* coordinated phosphine ligand.

Addition of a small quantity of CsBr to the solution of the complex $[Pt\{EtSCH_2C(O)CH_2\}Br(PPh_3)]$ gave

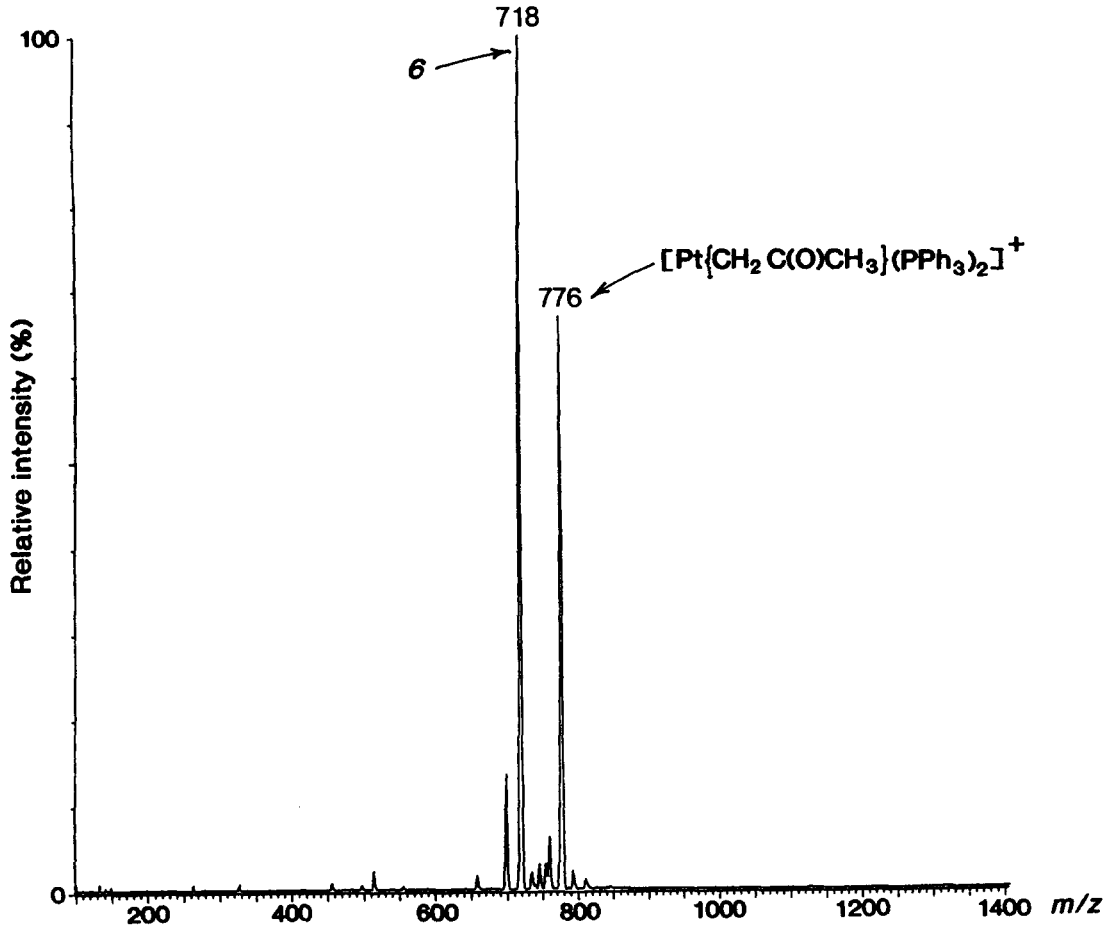


Fig. 3. Positive-ion electrospray mass spectrum (cone voltage 60 V) of *cis*-[PtCl{$CH_2C(O)CH_3$}$(PPh_3)_2$] (**4**), recorded in MeCN : H_2O (1 : 1), showing assignments of the major ions.

a small peak due to the complex [Pt{Et-$SCH_2C(O)CH_2$}$Br(PPh_3)+Cs]^+$ at *m/z* 787; in this case the spectrum was complicated by the appearance of a large number of caesium-bromide clusters of the type $[Cs_xBr_{x-1}]^+$. Addition of a more strongly coordinating ligand (py) to the solutions of [Pt{Et $SCH_2C(O)CH_2$}$Br(PPh_3)$] and [Pt{$MeSCH_2C(O)$ CH_2}$I(PPh_3)$] gave the ions [Pt{$RSCH_2C(O)$ CH_2}$py(PPh_3)]^+$ as the base peaks in the spectra.

In summary, we have demonstrated that ESMS is a convenient method for probing decomposition pathways for a selection of organoplatinum complexes and for rapidly investigating their coordination chemistry. This methodology should be equally applicable to a wide range of transition-metal complexes.

EXPERIMENTAL

General experimental techniques were as described in a previous paper [15]. Chloroacetone and 1,3-dichloroacetone were obtained from Aldrich and used as supplied. The complexes *cis*-[PtCl{$CH_2C(O)CH_2Cl$} $(PPh_3)_2$] (**1**) [2], *cis*-[PtCl{$CH_2C(O)CH_3$}$(PPh_3)_2$] (**5**) [3] and *trans*-[$PtI(CH_3)(PPh_3)_2$] [25] were prepared by the literature procedures. The complex *cis*-[$PtCl_2(PPh_3)_2$] was prepared *via* displacement (using 2 mol equiv. of triphenylphosphine in dichloromethane [26]) of the 1,5-cyclo-octadiene ligand from [$PtCl_2$(COD)] [27]. The purity of all phosphine complexes was checked by ^{31}P ^1H NMR spectroscopy.

Electrospray mass spectra were obtained in positive-ion mode on a VG Platform II mass spectrometer using a 1 : 1 v/v acetonitrile : water mobile phase. The compounds were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mM and spectra were recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 0.01 cm^3 sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60°C) at a flow rate of 0.01 cm^3 min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Cone voltages were typically varied from 10 to 80 V, in order to investigate the effect of higher voltages on fragmentation of parent ions. Confirmation of all species in this ESMS

study is aided by comparison of the observed and predicted isotope distribution patterns, the latter being calculated using the *Isotope* computer program [18].

Effect of heat on **1**

A solution of complex **1** (0.20 g, 0.21 mmol) in xylene (40 cm^3) was refluxed for 2 h and deposited, on cooling, yellow and white crystals which were identified as a mixture of (0.18 g, 95%) of *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$ (1 : 1) by ^{31}P NMR.

Reaction of **1** *with LiBr*

To a suspension of **1** (0.100 g, 0.118 mmol) in acetone (10 cm^3) was added LiBr (0.70 g, excess) and the mixture stirred at room temperature overnight. Evaporation to dryness under reduced pressure, followed by extraction of the product with dichloromethane (20 cm^3), filtration and evaporation of the filtrate yielded a pale yellow solid which was shown to be *cis*-$[PtBr_2(PPh_3)_2]$ by its ^{31}P ^1H NMR spectrum.

X-ray structure determination on **1**

Colourless crystals were obtained by slow recrystallization from a dichloromethane–light petroleum solution. Crystallographic data, together with details of the solution and refinement, are summarized in Table 3 and in the supplementary data.

Accurate unit-cell parameters were determined by least-squares refinement of 49 centred reflections with $4.6 < \theta < 12.5°$. Reflections were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on psi-scans was applied to the data with the maximum and minimum transmission factors being 0.96 and 0.403, respectively. All hydrogen atoms were included in calculated positions

Table 3. Summary of crystal data, intensity collection and structure refinement for **1**

Crystal data	
Empirical formula	$C_{39}H_{34}Cl_2O_1P_2Pt$
Formula weight	846.59
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	10.303(1)
b (Å)	17.272(4)
c (Å)	19.904(2)
V (Å^3)	3542(1)
Z	4
D_{calc} (g cm^{-3})	1.588
Data collection	
Diffractometer	Siemens P4
Radiation	Mo-K_α
Wavelength (Å)	0.71073
Temperature (K)	293(2)
Crystal size (mm)	$0.75 \times 0.39 \times 0.10$
Data collection mode	ω-scans
θ range for data collection (°)	2.52–29.99
Index ranges	$-1 \leqslant h \leqslant 14$ $-1 \leqslant k \leqslant 24$ $-1 \leqslant l \leqslant 28$
Reflections collected	6879
Independent reflections	6630 ($R_{int} = 0.0329$)
Absorption coefficient (mm^{-1})	4.232
$F(000)$	1672
Structure analysis and refinement	
Solution by	Patterson method
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	6629/0/406
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.0997$
R indices (all data)	$R_1 = 0.0660$, $wR_2 = 0.1092$
Largest difference peak and hole (e Å^{-3})	1.547 and −1.644
Programs used	SHELXTL-PC [28] and SHELXL93 [29]

Lists of final atomic coordinates, thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

(C—H = 0.96 Å) with a single fixed thermal parameter (0.08 Å).

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