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# Electron impact mass spectrometric behaviour of bis(substituted benzoato)complexes of bis($\eta$-cyclopentadienyl)titanium(IV)

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## Abstract

The electron impact mass spectrometric behaviour of bis(cyclopentadienyl)-bis(benzoato)titanium(IV) and related phenyl substituted complexes containing a halogen atom ($Cp_2TiL_2$, with Cp = $\eta$-$C_5H_5$; L = $C_6H_5COO$, $C_6{}^2H_5COO$, $FC_6H_4COO$ or $ClC_6H_4COO$) is investigated with the aid of metastable ion analysis, deuterium labelling and determination of monoisotopic ion masses. Evidence is presented for the occurrence of intramolecular fluorine migrations, gas phase ion–molecule and ion–radical reactions and *ortho* effects.

## Introduction

In a previous study we have found electron impact (EI) mass spectrometry to be a useful tool for the structural characterization of titanium(IV) complexes of the type ($\eta$-Cp)$_2$TiL$_2$, where Cp is a cyclopentadienyl group, $C_5H_5$; L is a benzoic acid ligand, $C_6H_5COO$, or a benzoic acid ligand substituted with a halogen atom, $XC_6H_4COO$ [1]. Although no molecular ions are observed, structurally informative ions are formed, e.g. $Cp_2TiL^+$, $CpTiL_2{}^+$, $CpTiL^{+\cdot}$ and $CpTiX^{+\cdot}$, amongst other Ti-containing fragment ions. Furthermore, ions characteristic of the ligands L are present, including the molecular ion of HL.

In this work we study the EI mass spectrometric behaviour of these titanium(IV) complexes with the aid of metastable ion analysis, deuterium labelling and determination of monoisotopic ion masses. In particular, we direct the attention to possible hydrogen transfer reactions giving rise to the $HL^{+\cdot}$ ions, halide migration reactions, gas phase ion–molecule and ion–radical reactions, and *ortho* effects. EI mass spectral characteristics of structurally related ($\eta$-Cp)$_2$Ti complexes have been documented in the literature [2–7].

## Experimental

### *Materials*

The complexes were synthesized by reaction of ($\eta$-$C_5H_5$)$_2$TiCl$_2$ with the sodium salt of the appropriately substituted benzoic acid in benzene, purified by crystallization from benzene and characterized from elemental analyses and various spectra as described by Dang *et al.* [1] and Razunaev *et al.* [8].

### *Mass spectrometric procedures*

All mass spectrometric measurements were performed on a VG70SEQ instrument operating in the electron impact (EI) mode (70 eV). The complexes were introduced using the direct probe inlet with a source temperature of 200 °C unless otherwise stated. The direct probe was programmed from 20–320 °C at a rate of 50 °C min$^{-1}$. The mass spectra reported were obtained by averaging five spectra taken at the maximum of the evaporation profile. The $Cp_2Ti(XC_6H_4COO)_2$ complexes started to evaporate after 5 min. The amount of complex analyzed was 1 $\mu$g unless otherwise stated. Determination of monoisotopic ion masses was performed at 10 000 resolution using perfluorokerosene as reference. Parent–daughter ion relationship were determined by performing parent or daughter ion scanning. Daughter ion spectra were obtained by manual selection of the precursor ion of interest and scanning the quadrupole mass analyzer. Parent ion spectra were obtained by transmitting the daughter ion under investigation through the quadrupole analyzer and scanning the magnetic field. In both types of experiments, spontaneous metastable decompositions were monitored, because no gas was introduced into the quadrupole collision cell. Parent and daughter ion spectra were obtained in the continuum mode of acquisition and by accumulating five scans.

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## Results and discussion

Figure 1(a) shows the EI mass spectrum obtained for $Cp_2Ti(C_6H_5COO)_2$. The high resolution data recorded for the most abundant fragment ions are listed in Table 1. The EI induced fragmentation is relatively simple and is partially rationalized in Scheme 1. The pathways indicated with an asterisk were all supported by establishing parent–daughter relationships, determined by recording either daughter ion spectra or parent ion spectra (see 'Supplementary material'). The presence of Ti having five isotopes ($^{46}Ti$, RA = 10.8%; $^{47}Ti$, 9.9%; $^{48}Ti$, 100%; $^{49}Ti$, 7.5%; $^{50}Ti$, 7.3%), in the fragment ions at *m/z* 355, 299, 234, 190, 141 and 129 is also evident from the appearance of clusters, clearly revealing ions containing $^{46}Ti$, $^{47}Ti$ and $^{48}Ti$. It is interesting to note that the valency of Ti changes upon fragmentation; the fragment ions $CpTiL^{+\bullet}$ and $CpTiC_6H_5{}^+$ at *m/z* 234 and 190, respectively, contain Ti(III) instead of Ti(IV). Furthermore, it is also worth mentioning that loss of Cp in the case of the fragmentation of $Cp_2TiL^+$ ions violates the even-electron

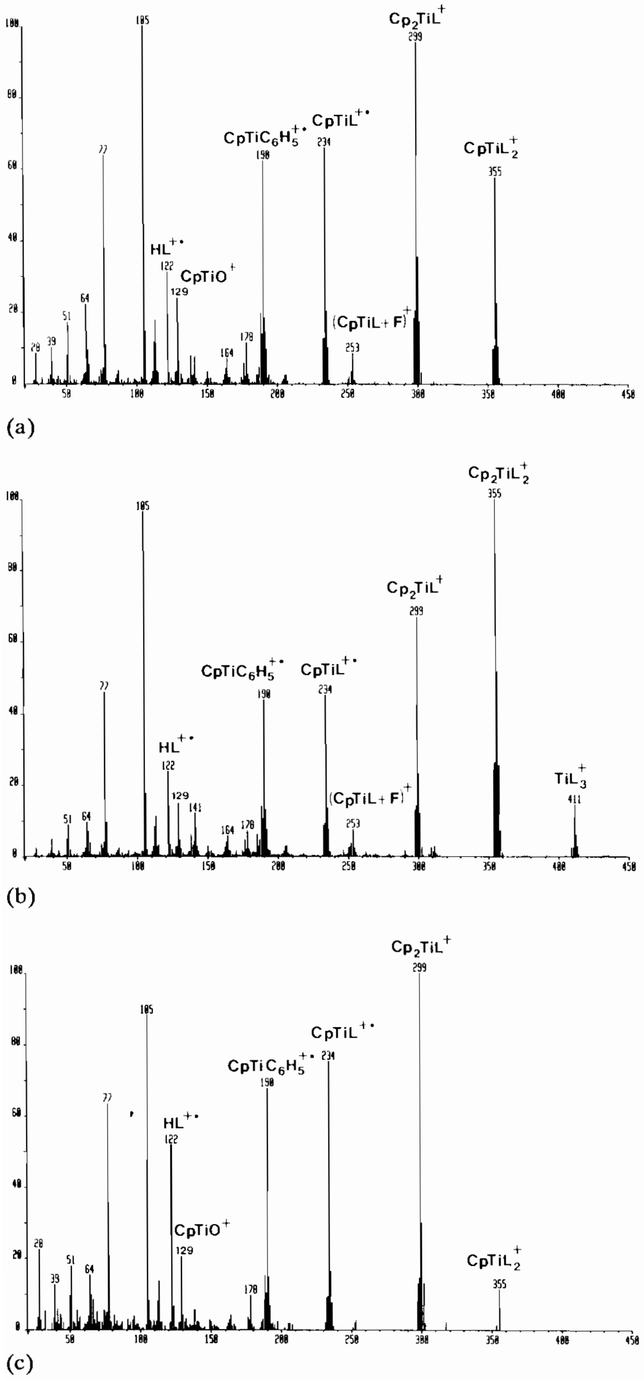
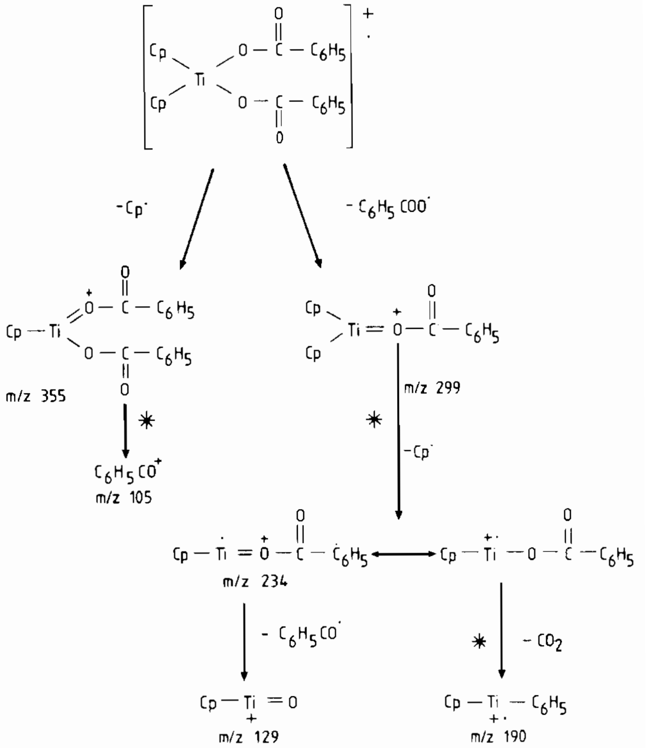


Fig. 1. EI mass spectra of $(\eta\text{-}C_5H_5)_2Ti(C_6H_5COO)_2$ obtained under different experimental conditions. (a) Source temperature 200 °C, amount sample 1 μg; (b) source temperature 200 °C, amount sample 10 μg; (c) source temperature 250 °C, amount sample 1 μg.

TABLE 1. High resolution data obtained for $Cp_2TiL_2$, where $Cp = \eta\text{-}C_5H_5$ and $L = C_6H_5COO$

| *m/z* | Assignment | Mass measured | Mass calculated |
|---|---|---|---|
| 355 | $CpTiL_2{}^+$ | 355.0464 | 355.0449 |
| 299 | $Cp_2TiL^+$ | 299.0555 | 299.0551 |
| 234 | $CpTiL^{+\bullet}$ | 234.0155 | 234.0120 |
| 190 | $CpTiC_6H_5{}^{+\bullet}$ | 190.0251 | 190.0261 |
| 129 | $CpTiO^+$ | 128.9823 | 128.9819 |
| 122 | $C_6H_5COOH^{+\bullet}$ | 122.0370 | 122.0367 |



Scheme 1.

rule. This fragmentation behaviour may be rationalized by the unusual stability of the delocalized cyclopentadienyl radical and the apparently facile reduction of Ti(IV) to Ti(III). The ion at *m/z* 178 corresponds to the $Cp_2Ti^+$ ion (no high resolution data available) and was shown to be a daughter ion of the $Cp_2TiL^+$ ion at *m/z* 299. During the course of the high resolution measurements, a significant increase was observed in the relative abundance of the ion at *m/z* 253, corresponding to an elemental composition of $C_{12}H_{10}O_2TiF$. This observation indicates that a $(CpTiL+F)^+$ ion has been formed, in which the fluorine atom originates from the reference compound, perfluorokerosene. The $(CpTiL+F)^+$ ion is likely a product ion of the $CpTiL^{+\cdot}$ ion undergoing an ion–molecule reaction and a consequence of the high stability of the metal–fluorine bond [9]. The ion at *m/z* 253 has a relatively low abundance (RA = 8%; Fig. 1(a)) in the low resolution EI spectrum and is probably due to a halogen 'memory' effect. Halogen 'memory' effects were reported for a variety of complexes whereby prior introduction of a halogen-containing compound leaves enough halogen atoms in the source to react with organometallic compounds [9]. As a consequence, interpretation of small peaks in the EI spectra of these types of titanocene complexes should be performed with some caution.

We also experienced that is is difficult to record EI spectra free from chemical ionization-like artifacts. In particular, the $Cp_2TiL^+$ and $CpTiL_2{}^+$ ions at *m/z* 299 and 355, respectively, readily show corresponding hydrogenated $Cp_2TiLH^{+\cdot}$ and $CpTiL_2H^{+\cdot}$ ions, resulting in increased abundances of the ions at *m/z* 300 and 356, respectively (Fig. 1(b)). These hydrogenated species may be formed either by reaction of the $Cp_2TiL^+$ and $Cp_2TiL_2{}^+$ ions with a hydrogen atom or by reaction of the corresponding neutral radicals with a proton. Therefore, the amount of sample introduced into the EI source was kept to a minimum ($\leqslant 1$ $\mu$g). Moreover, under the conditions where chemical ionization-like effects were apparent, a ligand exchange reaction was noted giving rise to $TiL_3{}^+$ ions, probably due to an ion–molecule reaction. In addition, it can also be noted that the relative abundances of the major ions, $Cp_2TiL^+$ and $CpTiL_2{}^+$, at *m/z* 299 and 355, respectively, have changed considerably.

The ion at *m/z* 122, corresponding to $C_6H_5COOH^{+\cdot}$, has shifted to *m/z* 127 in the spectrum of the $^2$H-labelled isotopomer $Cp_2Ti(C_6{}^2H_5COO)_2$ (not shown). All the other peaks in the EI spectrum of $Cp_2Ti(C_6{}^2H_5COO)_2$ showed the expected mass increments, which are consistent with the assignments for the unlabelled product given in Table 1 and Scheme 1. EI mass spectra of organic esters, R′COOR, often show free acid $R'COOH^{+\cdot}$ ions, formed by transfer of a hydrogen from the R group to the R′COO moiety [10–13]. The mass increment of 5 u found for $C_6H_5COOH^{+\cdot}$ in the mass spectrum of $Cp_2Ti(C_6{}^2H_5COO)_2$ suggests that the hydrogen atom involved originates from the cyclopentadienyl moiety, which implies that there is an interaction between the cyclopentadienyl and benzoyl ligands. However, it was not possible to determine whether this interaction occurs intramolecularly, because no precursor ions could be found for the $C_6H_5COOH^{+\cdot}$ ion by performing a parent ion scan. The formation of $C_6H_5COOH^{+\cdot}$ can also be very well explained by thermal degradation of the $Cp_2Ti(C_6H_5COO)_2$ complex giving rise to $C_6H_5COOH$ and subsequent electron ionization. The presence of a relation between the ion source temperature and the relative abundance of the $C_6H_5COOH^{+\bullet}$ ion demonstrates that the formation of this ion is thermally induced (Fig. 1(c)).

Table 2 lists the mass spectral data obtained for phenyl substituted complexes of bis(cyclopentadienyl)-bis(benzoato)titanium(IV), $(\eta\text{-}C_5H_5)_2Ti(XC_6H_4COO)_2$, where X is F or Cl. The spectra of the fluorobenzoato derivatives all show, besides the $CpTiL^{+\cdot}$ ion at *m/z* 252 (L includes one fluorine atom), an ion at *m/z* 271 containing a second fluorine atom, as confirmed by determination of its monoisotopic mass (Fig. 2). In an effort to determine the origin of the latter $(CpTiL+F)^+$ ion, parent ion scanning was performed which indicated that the $CpTiL_2{}^+$ and $Cp_2TiL^+$ ions are both precursor ions for the $(CpTiL+F)^+$ ion. The formation of the $(CpTiL+F)^+$ ion from the $CpTiL_2{}^+$ ion can be explained by an intramolecular fluorine migration (*vide infra*), whereas the formation of the $(CpTiL+F)^+$ ion from the $Cp_2TiL^+$ ion can be rationalized by an exchange reaction in which a Cp radical is substituted by a F radical, generated during the primary decompositions (Scheme 2). It has been well documented that gas phase ion–radical reactions do occur for the platinum complex *trans*-[PtHCl(PPh$_3$)$_2$] during electron ionization conditions [14].

$$Cp_2TiL^+ + F^\cdot \longrightarrow (CpTiL + F)^+ + Cp^\cdot$$

Scheme 2.

In the EI spectra of the halogen substituted $(\eta\text{-}C_5H_5)_2Ti(XC_6H_4COO)_2$ complexes, where X is F or Cl, additional fragmentations of interest can be noted. The $CpTiXC_6H_4{}^{+\cdot}$ ion at *m/z* 208 or 224 fragments further by loss of HX or $C_2H_2$, whereby the elimination of $C_2H_2$ is typical for the cyclopentadienyl group (Fig. 3). It is worth noting that the *ortho* isomers show the highest ratio for $[CpTiXC_6H_4{}^{+\cdot}]/[CpTiL^{+\cdot}]$ (Table 3). The increased loss of $CO_2$ from the $CpTiL^{+\cdot}$ ion in the *ortho* isomers compared to the *meta* and *para* isomers can be rationalized by steric effects, which are known to be important in *ortho* isomers [15, 16]. This *ortho*

TABLE 2. Mass spectra of $Cp_2TiL_2$ complexes ($L=XC_6H_4COO$ and X = substituent); *m/z* values (> 100) with relative abundances (RA > 5%) are given in parentheses. The $Cp_2TiL^+$ peak has been used for normalization

| X | Base peak | $CpTiL_2^+$ | $Cp_2TiL^+$ | $(CpTiL+X)^+$ | $CpTiL^{+\cdot}$ | $(CpTiL-CO_2)^{+\cdot}$ $CpTiXC_6H_4^{+\cdot}$ | $Cp_2TiX^+$ | $(CpTiXC_6H_4-HX)^{+\cdot}$ |
|---|---|---|---|---|---|---|---|---|
| H | 105 | 355(61) | 299(100) | 253(9) | 234(70) | 190(66) | –[a] | 188(21) |
| 2-F | 123 | 391(45) | 317(100) | 271(14) | 252(33) | 208(60) | 197(7) | 188(17) |
| 3-F | 123 | 391(77) | 317(100) | 271(19) | 252(69) | 208(33) | – | – |
| 4-F | 123 | 391(61) | 317(100) | 271(13) | 252(76) | 208(48) | | |
| 2-Cl | 333 | 423(12) | 333(100) | – | 268(11) | 224(42) | – | 188(35) |
| 3-Cl | 333 | 423(17) | 333(100) | – | 268(60) | 224(7) | – | 188(7) |
| 4-Cl | 333 | 423(37) | 333(100) | – | 268(69) | 224(35) | – | – |

| X | $(CpTiXC_6H_4-C_2H_2)^{+\cdot}$ | $Cp_2Ti^{+\cdot}$ | $XC_6H_4COOH^{+\cdot}$ | $CpTiX^{+\cdot}$ | $CpTiO^+$ | $XC_6H_4CO^+$ | Other ions |
|---|---|---|---|---|---|---|---|
| H | 164(8) | 178(12) | 122(33) | 114(18) | 129(26) | 105(105) | |
| 2-F | 182(7) | 178(7) | 140(47) | 132(36) | 129(17) | 123(102) | 204(16); 113(6) |
| 3-F | 182(33) | 178(11) | 140(38) | 132(37) | 129(27) | 123(116) | 113(11) |
| 4-F | 182(15) | 178(7) | 140(48) | 132(27) | 129(23) | 123(122) | 113(9) |
| 2-Cl | – | 178(12) | 156(40) | 148(25) | 129(19) | 139(78) | 232(12); 204(24); 111(42) |
| 3-Cl | 198(46) | 178(15) | 156(54) | 148(30) | 129(28) | 139(74) | 111(59) |
| 4-Cl | 198(10) | 178(11) | 156(42) | 148(37) | 129(30) | 139(97) | 111(64) |

[a] RA < 5%.

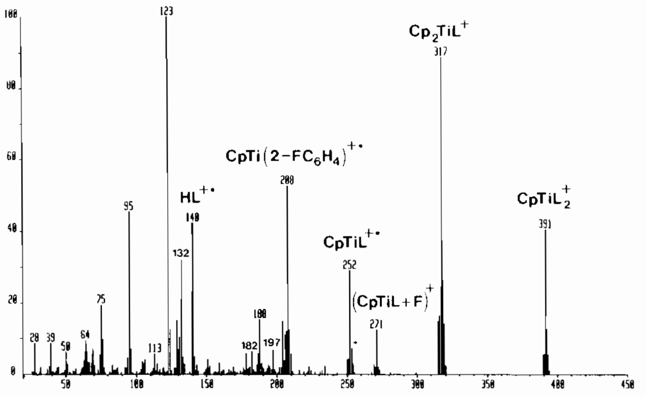


Fig. 2. EI mass spectrum of $(\eta\text{-}C_5H_5)_2Ti(2\text{-}FC_6H_4COO)_2$. Source temperature 200 °C, amount sample: 1 μg.

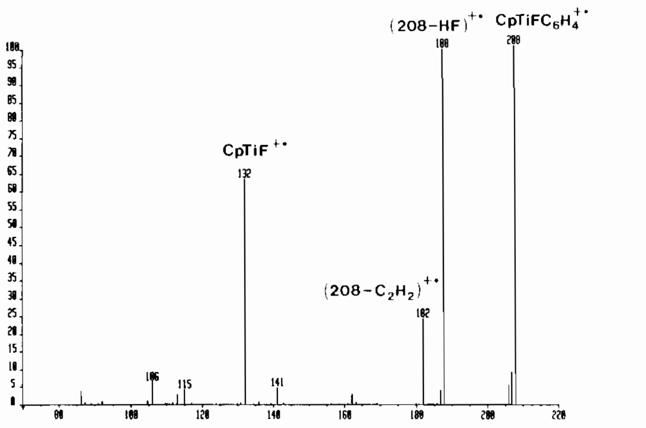


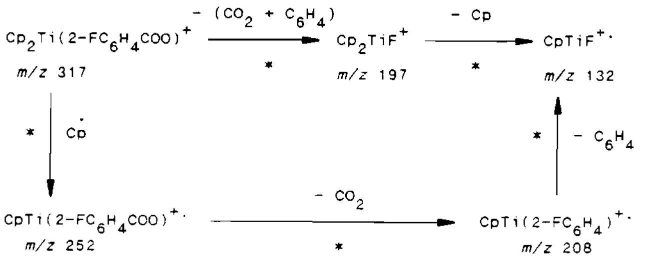
Fig. 3. Daughter ion spectrum obtained for the $CpTi(2\text{-}FC_6H_4)^{+\cdot}$ ion at *m/z* 208.

TABLE 3. Abundance ratios $[CpTiL^{+\cdot}-CO_2]/[CpTiL^{+\cdot}]$ as a function (*ortho*, *meta* and *para*) of a substituent X on the phenyl ring in L ($=XC_6H_4COO$)

| X | $[CpTiL^{+\cdot}-CO_2]/[CpTiL^{+\cdot}]$ |
|---|---|
| H | 3.7 |
| 2-F | 1.8 |
| 3-F | 0.5 |
| 4-F | 0.6 |
| 2-Cl | 3.8 |
| 3-Cl | 0.1 |
| 4-Cl | 0.5 |

effect is more pronounced for the 2-Cl isomer than for the 2-F isomer, probably because the chlorine substituent forms a stabilizing bridge with the Ti atom in the product ion. Furthermore, the $CpTiXC_6H_4^{+\cdot}$ ion shows an enhanced elimination of HX in the case of the *ortho* isomers, yielding an ion at *m/z* 188. This enhanced loss of HX can be explained by the close proximity of the halogen atom and a hydrogen atom of the cyclopentadienyl moiety. In addition, it can be observed that the ion at *m/z* 182 or 198, formed by fragmentation of the $CpTiXC_6H_4^{+\cdot}$ ion through $C_2H_2$ loss in the cyclopentadienyl moiety, has the highest abundance in the *meta* isomers. However, a straightforward explanation for this *meta* effect could not be found.

It has been noted that fluorine migrations take place in organotitanium compounds bearing perfluorocarbon ligands and that the presence of an atom and/or group such as –S– and –OCO– between titanium and the perfluoro ligand does not prevent the migrations [5, 9,



Scheme 3.

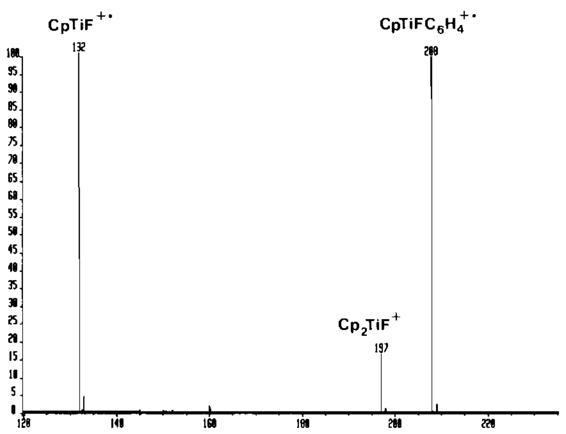


Fig. 4. Parent ion spectrum obtained for the $CpTiF^{+\bullet}$ ion at *m/z* 132.

17]. The facile migration of fluorine (hard acid), not chlorine, to titanium (soft base), can be rationalized by the hard–soft base theory [18, 19]. The $CpTiF^{+\bullet}$ and $Cp_2TiF^+$ ions at *m/z* 132 and 197, respectively, can be considered as ions formed through intramolecular fluorine migrations. The fragmentation pathways leading to the formation of $CpTiF^{+\bullet}$ and $Cp_2TiF^+$ ions in the case of $Cp_2Ti(2\text{-}FC_6H_4COO)_2$ are summarized in Scheme 3 and were supported by recording parent as well as daughter ion spectra. It is worth noting that loss of $Cp^\bullet$ is observed from $Cp_2Ti(2\text{-}FC_6H_4COO)^+$ and $Cp_2TiF^+$ ions. This unusual fragmentation behaviour violates the even-electron rule and has already been discussed in the case of the fragmentation of $Cp_2Ti(C_6H_5COO)^+$ ions (*vide supra*). Figure 3 illustrates the daughter ion spectrum obtained for the $CpTi(2\text{-}FC_6H_4)^{+\bullet}$ ion at *m/z* 208, showing daughter ions at *m/z* 188, 182 and 132. Figure 4 gives the parent ion spectrum obtained for the $CpTiF^{+\bullet}$ ion at *m/z* 132, indicating precursor ions at *m/z* 197 and 208. See also, 'Supplementary material'.

## Conclusions

The EI mass spectral data obtained on the formation of the $HL^{+\bullet}$ ion do not allow us to draw conclusions about the occurrence of an intramolecular hydrogen transfer reaction and indicate that the thermal degradation resulting in the formation of the free acid HL and subsequent electron impact ionization should be considered. With regard to the EI behaviour of the substituted titanium(IV) complexes, $Cp_2TiL_2$, where $L = XC_6H_4COO$ and X = halogen, a number of characteristic effects need to be reported. First, the complexes were shown to undergo bimolecular (ion-neutral) reactions leading to the formation of unusual ions such as the $(CpTiL+F)^+$ ion. Second, intramolecular halide migrations were observed and supported by metastable ion analysis. Third, two different *ortho* effects were found with respect to the loss of $CO_2$ from the $CpTi(XC_6H_4COO)^{+\bullet}$ ion and the loss of HX from the $CpTiXC_6H_4^{+\bullet}$ ion.

## Supplementary material

Other relevant parent and daughter ion spectra are available from the authors on request.

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