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Electron Ionization-induced Fragmentation of Diphenylphosphino- and Diphenylphosphinoyl-substituted Ferrocene Derivatives

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Electron ionization mass spectra of several diphenylphosphino- and diphenylphosphinoyl-substituted ferrocenes of the general formula $[(\eta^5\text{-}C_5H_4X)Fe(\eta^5\text{-}C_5H_4Y)]$, $[X/Y = PPh_2/H$ (1), $P(O)Ph_2/H$ (2), PPh_2/CO_2H (3), $P(O)Ph_2/CO_2H$ (4), PPh_2/CO_2CH_3 (5) and $P(O)Ph_2/CO_2CH_3$ (6)] and of their deuterated analogues $[X/Y = PPh_2/CO_2D$ (3a), PPh_2/CO_2CD_3 (5a)] are reported. Fragmentation pathways for all compounds studied are presented. The proposed fragmentation schemes are based on accurate mass measurements, observations of metastable ion decompositions and the study of collisionally activated dissociations of important ions. A key role of the ferrocenyl metal centre in the transfer of oxygen-containing groups was confirmed. However, the introduction of another oxophilic group, i.e. trivalent phosphorus of the diphenylphosphino group in the present case, leads to a competition between the two different oxygen acceptors now present in the molecule. If the oxophilicity of the phosphorus atom is saturated by *P*-oxide formation, the fragmentation pathways change markedly in comparison with those of the parent phosphine. The structure of selected isobaric ions common to the spectra of various compounds is discussed as some of these exhibit different behaviour when originating from fragmentation of different parent molecules. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: electron ionization mass spectrometry; ferrocenes; metastable ions; collisionally activated dissociations; fragmentation

INTRODUCTION

A variety of ferrocene derivatives have attracted the attention of chemists since their first syntheses in the early 1950s. The ferrocene frame exhibits peculiar properties such as redox activity, capability of conjugation and strongly electron-donating character. Ferrocenes have been used to design excellent enantioselective catalysts and compounds with large non-linear optical properties which are of interest in material science.[1] Thanks to their sufficient volatility and thermostability as well as the usually highly abundant molecular ions present in the mass spectra, electron ionization mass spectrometry (EI/MS) has widely been employed to characterize the numerous ferrocene derivatives synthesized.[2–6] Owing to the aromatic character of the ferrocene moiety, some fragmentation reactions are very similar to those of analogous arenes. There are, however, additional fragmentation patterns typical for ferrocenes, in which the metal centre plays a key role. In addition to a simple cyclopentadienyl ring–Fe bond scission, the transfer of a functional group or its part to the iron atom,[2,7–13] and the transfer of a functional group or part of it from one cyclopentadienyl ring to the second[13,14] are of considerable importance.

We have observed similar behaviour in the case of phosphino carboxylates derived from the heteroannulary substituted ferrocene frame. However, further fragmentation processes involving phosphino substituents on one of the cyclopentadienyl rings have been detected in the EI mass spectra of these compounds. Since no systematic study of carboxy- or methoxycarbonyl-substituted ferrocenyl phosphines and corresponding phosphine oxides is available in the literature, we report here a study of EI-induced fragmentations of some phosphorus-substituted ferrocene derivatives (**1**–**7**). Although compounds **1** and **2** have been known for a long time, the mass spectrum of **1** has been reported only incompletely[15] and that of **2** has not likely been reported at all. The remaining compounds

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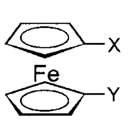
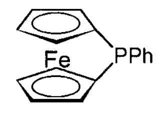


	X	Y
1	H	PPh2
2	H	P(O)Ph2
3	CO2H	PPh2
3a	CO2D	PPh2
4	CO2H	P(O)Ph2
5	CO2CH3	PPh2
5a	CO2CD3	PPh2
6	CO2CH3	P(O)Ph2



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were either prepared fairly recently (**3**–**5**) or newly synthetized (**6** and all deuterium-labelled compounds) in order to prove the proposed fragmentation pathways.

The fragmentation patterns were derived mainly from high-resolution EI/MS, metastable ion (MI) decompositions and collisionally activated dissociation (CAD) of important ionic species.

EXPERIMENTAL

Synthesis

Compounds **1**,[16] **3**–**5**[17] and **7**[18] were prepared by the literature procedures. Phosphine oxides **2** and **6** were synthesized by the standard hydrogen peroxide oxidation[19] of the parent phosphines **1** and **5**, respectively.

[*carboxy*-d_1]-1′-(Diphenylphosphino)ferrocenecarboxylic acid (**3a**) was obtained by crystallization of the non-deuterated acid **3** from a solution in $CH_3COOD–D_2O$ (50%, v/v; prepared by hydrolysis of $(CH_3CO)_2O$ in D_2O in a sealed tube at 80–90 °C). The crystals of **3a** were filtered off, dried under reduced pressure (1 kPa) and stored under an argon atmosphere (yield not determined; deuteration degree ~60% according to the mass spectra).

[*methyl*-d_3]-Methyl 1′-(diphenylphosphino)ferrocenecarboxylate (**5a**) was obtained as follows. Under an argon atmosphere, solid **5** (14.4 mg, 34 μmol) was added to a solution of sodium metal (~2 mg) in CD_3OD (1.4 ml) and the resulting clear solution was refluxed for 2.5 h. The mixture was diluted with water (20 ml) and neutralized with glacial acetic acid. Extraction with diethyl ether, drying ($MgSO_4$) and evaporation *in vacuo* afforded **5a** with a deuteration degree of 97% according to the mass spectra; the chemical yield was not determined.

Mass spectrometry

Standard EI mass spectra were recorded on a VG-7070E double-focusing mass spectrometer of EB geometry at electron energy 80 eV, trap current 100 μA, accelerating voltage 6 kV and ion source temperature 200 °C. Samples were introduced using a direct insertion probe. Accurate mass measurements were performed by the peak matching technique using perfluorokerosene or perfluorotributylamine as the internal mass scale standards (resolving power 8000, precision better than 5 ppm). MI decompositions in the first field-free region (FFR) were examined using daughter (B/E = const) and parent (B^2/E = constant) ion scans. To establish the structural identity of some isobaric ions resulting from the fragmentation of various precursors, CAD spectra in the first FFR were measured. Helium was introduced as the collision gas and its pressure was increased until the intensity of the primary ion beam was reduced to 50%.

EI mass spectra of **3a** and **5a** were measured on a Jeol JMS-D100 spectrometer (EB geometry) at ionization energy 80 eV, trap current 300 μA, acceleration voltage 3 kV and ion source temperature 200 °C. Before the spectra of deuterated acid **3a** were recorded, the ion source was conditioned with D_2O (99%, partial pressure ~2 mPa) for 1 h. Owing to the lower accelerating voltage used, i.e. extra time spent by ions in the ion source during which they can fragment, the spectra recorded on the Jeol spectrometer exhibit a higher abundance of fragment ions when compared with the spectra obtained on the VG-7070E spectrometer. To evaluate deuterium labelling effects, the spectra of **3** and **5** were re-measured under the same conditions.

Mass spectra of carboxy phosphine oxide **4** could not be obtained using the above procedure owing to its thermal lability. Notwithstanding, they were obtained when a small amount of finely pulverized sample was placed on the probe tip. The rapid temperature increase caused by the contact with the ionization chamber enabled to acquire reproducible mass spectra for several seconds at a sufficient intensity and without the presence of peaks due to decomposition products.

Chemical ionization (CI) mass spectra of **7** were recorded on the VG-7070E instrument using methane as the reagent gas (electron energy 100 eV, emission current 0.2 mA, source temperature 150 °C, methane pressure 5 mPa). For **7**: m/z (relative abundance, %) 293 (74; $[M + H]^+$), 292 ($M^{+\bullet}$; 100), 226 (6), 216 (3), 215 (25), 186 (2), 170 (3), 56 (7). For a comparison, see EI mass spectral data: m/z 292 (100; $M^{+\bullet}$), 291 (51), 233 (4), 226 (34), 213 (2), 202 (3), 170 (17), 157 (7), 146 (6; M^{2+}), 133 (4) 121 ($[C_5H_5Fe]^+$; 4), 115 (4), 107 (3), 94 (2), 81 (3), 56 ($Fe^{+\bullet}$; 17).

For fragment ions in the EI (80 eV) mass spectra of **1**–**6**: m/z (relative abundance, %; elemental composition by exact mass determination), **1**, 370 (100, $C_{22}H_{19}FeP$, $M^{+\bullet}$) 305 (2), 293 (34, $C_{16}H_{14}FeP$), 262 (8, $C_{16}H_{14}Fe$), 226 (7, $C_{11}H_7FeP$), 185 (6, M^{2+}), 183 (4), 171 (12, $C_{11}H_8P$), 170 (10, $C_{11}H_7P$), 141 (3), 133 (4), 121 (12), 56 (14); **2**, 386 (100, $C_{22}H_{19}FeOP$, $M^{+\bullet}$), 321 (48, $C_{17}H_{14}FeOP$), 243 (4), 215 (3), 197 (13, $C_{11}H_9Fe$), 193 (5, M^{2+}), 183 (3), 179 (3), 170 (4, $C_{11}H_7P$), 141 (16, $C_{11}H_9$), 133 (5), 121 (8), 115 (7), 56 (14); **3**, 414 (100, $C_{23}H_{19}FeO_2P$, $M^{+\bullet}$), 386 (4, $C_{22}H_{19}FeOP$), 370 (25, $C_{22}H_{19}FeP$), 321 (13, $C_{17}H_{14}FeOP$), 304 (6), 302 (7, $C_{17}H_{11}FeP$), 293 (13, $C_{16}H_{14}FeP$), 244 (13, $C_{11}H_9FeOP$), 226 (23, $C_{11}H_7FeP$), 197 (17, $C_{11}H_7Fe$), 183 (10), 171 (19, $C_{11}H_8P$), 170 (21, $C_{11}H_7P$), 167 (11), 141 (8), 133 (6), 121 (8), 115 (8), 92 (5), 73 (10), 56 (19); **4**, 430 (72, $C_{23}H_{19}FeO_3P$, $M^{+\bullet}$), 386 (11, $C_{22}H_{19}FeOP$), 338 (100, $C_{17}H_{15}FeO_2P$), 321 (9), 320 (8), 319 (20, $C_{17}H_{12}FeOP$), 302 (10, $C_{17}H_{11}FeP$), 273 (7, $C_{17}H_{13}Fe$), 243 (11, $C_{11}H_8FeOP$), 217 (4), 216 (5), 215 (5, $C_{17}H_{11}$), 206 (4, $[M - H_2O]^{2+}$), 197 (6), 170 (5), 141 (12), 133 (7), 119 (6), 115 (7), 92 (6), 73 (3), 56 (12); **5**, 428 (100,

$C_{24}H_{21}FeO_2P$, $M^{+\cdot}$), 413 (4, $C_{23}H_{18}FeO_2P$), 397 (3), 370 (3, $C_{22}H_{19}FeP$), 351 (5, $C_{18}H_{16}FeO_2P$), 321 (21, $C_{17}H_{14}FeOP$), 306 (17, $C_{17}H_{15}FeP$), 305 (13, $C_{17}H_{14}FeP$), 228 (26, $C_{11}H_9FeP$), 226 (34, $C_{11}H_7FeP$), 214 (4, M^{2+}), 197 (5, $C_{11}H_7Fe$), 183 (8), 171 (12, $C_{11}H_8P$), 170 (14, $C_{11}H_7P$), 151 (6), 141 (4), 133 (6), 121 (13), 115 (4), 56 (19); **6**, 444 (85, $C_{24}H_{21}FeO_3P$, $M^{+\cdot}$), 413 (3), 352 (10, $C_{18}H_{17}FeO_2P$), 322 (100, $C_{17}H_{15}FeOP$), 275 (3), 273 (3), 245 (11), 244 (16, $C_{11}H_9FeOP$), 226 (7, $C_{11}H_7FeP$), 206 (6, $[M - CH_3OH]^{2+}$), 198 (18, $C_{11}H_{10}Fe$), 197 (19, $C_{11}H_9Fe$), 196 (8), 180 (8), 142 (7), 141 (11), 133 (11), 121 (19), 115 (5), 56 (17).

RESULTS AND DISCUSSION

The EI mass spectral data for diphenylphosphino (Ph_2P^{III})- and diphenylphosphinoyl [$Ph_2P^V(O)$]-substituted ferrocenes **1**–**6** are summarized in the Experimental Section. The elemental composition of the ions observed is given only when confirmed by exact mass determination. EI-induced fragmentation pathways of the **1**–**6** are presented in Schemes 1–6. They were derived from EI and MI mass spectra and mass spectra of the deuterated derivatives **3a** and **5a**. CAD spectra were used to compare the fragmentation and structures of some important isobaric ions originating from ionization and/or fragmentation of different precursors. In the schemes, an asterisk indicates a fragmentation reaction which was confirmed by observations of the corresponding MI transitions.

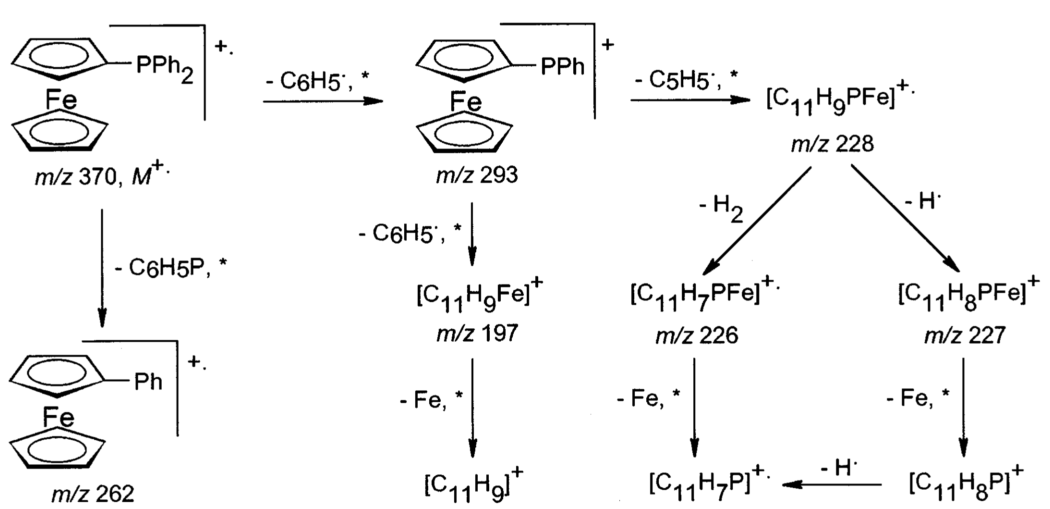
Phosphine 1 and phosphine oxide 2

The most abundant ions in the spectrum of phosphine **1**, *m*/*z* 293 (Scheme 1), correspond to the loss of the phenyl group from the molecular ion. The product ions most likely arise through a σ-cleavage of the P—C(phenyl) bond as kinetically simple processes are favoured for internal energy-rich ions. A displacement mechanism of that step resulting in the formation of ions with a ferrocenophane-like structure is ruled out since the fragmentations of ions at *m*/*z* 293 originating from **1** and those prepared by CI of ferrocenophane, $[M + H]^+$ of **7**, are completely different. Protonated molecules of ferrocenophane **7** decompose almost exclusively by the elimination of the benzene molecule (→*m*/*z* 215). In the EI mass spectra, the molecular ions of **7** dissociate by loss of a cyclopentadiene molecule or by losing a hydrogen radical to give product ions which in turn eliminate cyclopentadienyl ($C_5H_5^\cdot$) radical ($M^{+\cdot} - C_5H_6 \rightarrow$ *m*/*z* 226; for CI and EI data of **7**, see Experimental section). In contrast, the ions at *m*/*z* 293 arising from **1** eliminate the cyclopentadienyl radical or combinations of H, H_2 and Fe species, as shown in Scheme 1. A further fragmentation route of ions at *m*/*z* 293 involves the elimination of a cyclopentadienyl radical followed by the loss of an iron atom to afford species of *m*/*z* 197 and 141, respectively. The ions at *m*/*z* 305 resulting from the direct loss of the $C_5H_5^\cdot$ radical from $M^{+\cdot}$ of **1** are ~20 times less abundant than ions at *m*/*z* 293.

The second prominent fragmentation pathway observed for $M^{+\cdot}$ of **1** is the elimination of a C_6H_5P species leading to the formation of ionic species at *m*/*z* 262. The phenylferrocene structure was proposed for the latter, as an C_6H_5P extrusion has to be accompanied by the migration of one of the phenyl groups from phosphorus to the cyclopentadienyl ring.

The fragmentation routes of $M^{+\cdot}$ of phosphine **1** and phosphine oxide **2** differ markedly. Molecular ions of **2** decompose mainly by detachment of the cyclopentadienyl ligand yielding ions at *m*/*z* 321 ($M^{+\cdot} \rightarrow C_5H_5^\cdot + m/z$ 321; Scheme 2), whereas the abundance of ions due to the loss of the phenyl group from $M^{+\cdot}$ of **2** is negligible. Ions at *m*/*z* 321 further eliminate a benzene molecule or a C_6H_5PO fragment to give ions at *m*/*z* 243 and 197, respectively.

Such differences in fragmentation can be ascribed to a higher electron-withdrawing character of the



Scheme 1. Fragmentation scheme for phosphine **1**.

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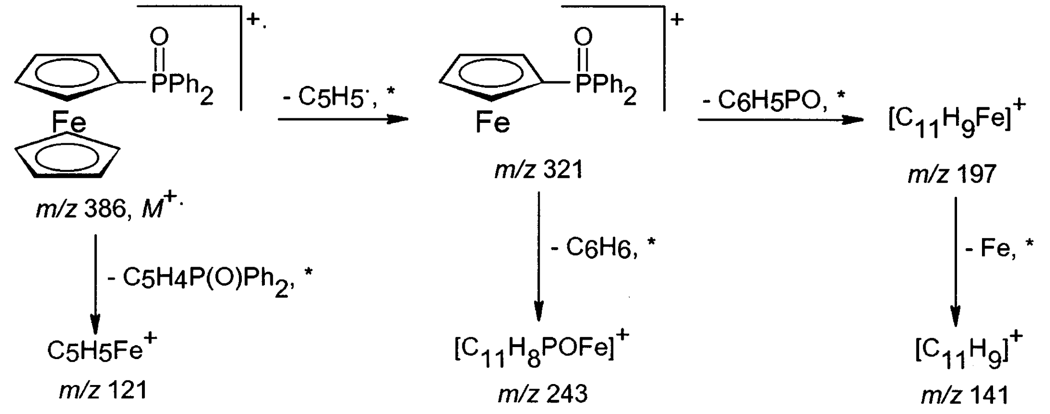
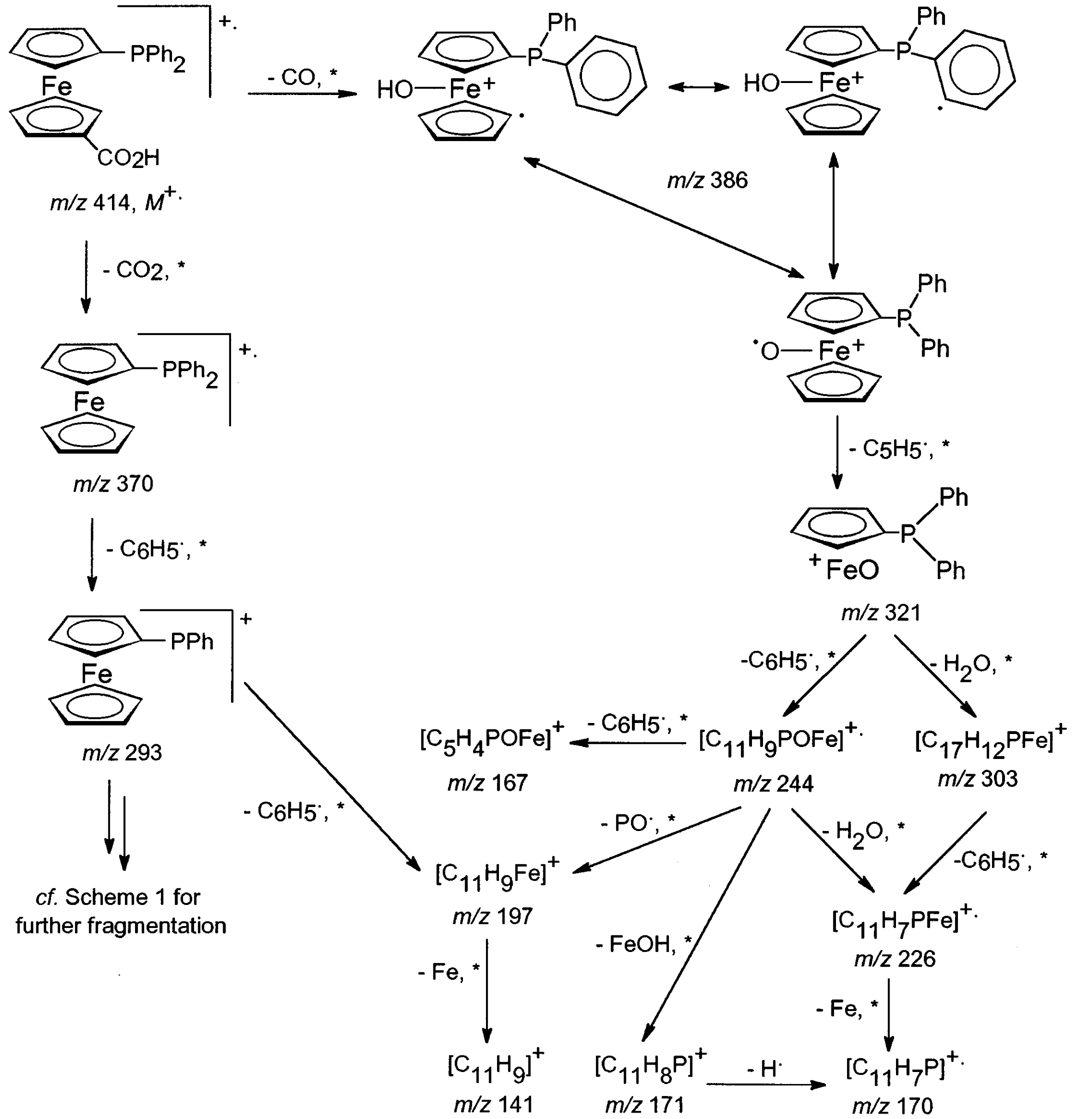


Scheme 2. Fragmentation scheme for phosphine oxide **2**.

diphenylphosphinoyl group in comparison with that of the diphenylphosphino group, resulting in a weakening of the iron–cyclopentadienyl ring bonds and, hence, to a higher abundance of ions due to the loss of $C_5H_5^{\bullet}$ radical from $M^{+\bullet}$ of **2**. Furthermore, in the case of phosphine **1**, one of the phosphorus lone pair electrons can be removed easily to yield ions of the $R_3P^{+\bullet}$ type. The resulting ion-radical centre localized at the phosphorus



Scheme 3. Fragmentation pathways for carboxy phosphine **3** showing the structure of the ions at *m/z* 321.

atom, at least partially, induces a σ-bond splitting of the P—Ph bond.[20] Since the ionization energy values of organic phosphine oxides are markedly higher than those of the corresponding phosphines,[21] the ion radical site in $M^{+\bullet}$ of **2** is most likely localized at the iron atom, at which the most abundant fragmentation reactions observed are initiated.

Carboxyphosphine 3 and carboxyphosphine oxide 4

There were two major pathways found in the fragmentation of ions $M^{+\bullet}$ of **3**. The initial step of the first one (Scheme 3) is the elimination of a CO_2 molecule generating ions at *m*/*z* 370. Taking into account the subsequent decomposition of the ions at *m*/*z* 370, mainly the loss of the phenyl group, these were proposed to be structurally identical with (diphenylphosphino)ferrocene ion radical, $M^{+\bullet}$ of **1**. This is further supported by the close similarity of the corresponding CAD spectra. Similarly to the fragmentation of **1**, an elimination of the phenyl radical from ions at *m*/*z* 370 upon P—C(phenyl) bond cleavage led to the formation of ionic species at *m*/*z* 293. The ions at *m*/*z* 293 observed for **1** and **3** fragment identically and are of the same structure, as evidenced by their CAD spectra.

The second fragmentation pathway of $M^{+\bullet}$ of **3** starting by an elimination of the CO molecule ($\rightarrow$ *m*/*z* 306) continues through the loss of the $C_5H_5^\bullet$ radical generating ions at *m*/*z* 321. The ions at *m*/*z* 321 decompose further as shown in Scheme 3. Common product ions at *m*/*z* 226, 197, 171 and 170 merge both fragmentation channels mentioned above.

Comparing the CAD and MI spectra of the isobaric ions at *m*/*z* 321 originating from $M^{+\bullet}$ of **2** and **3** (Fig. 1), a structural difference between these is obvious

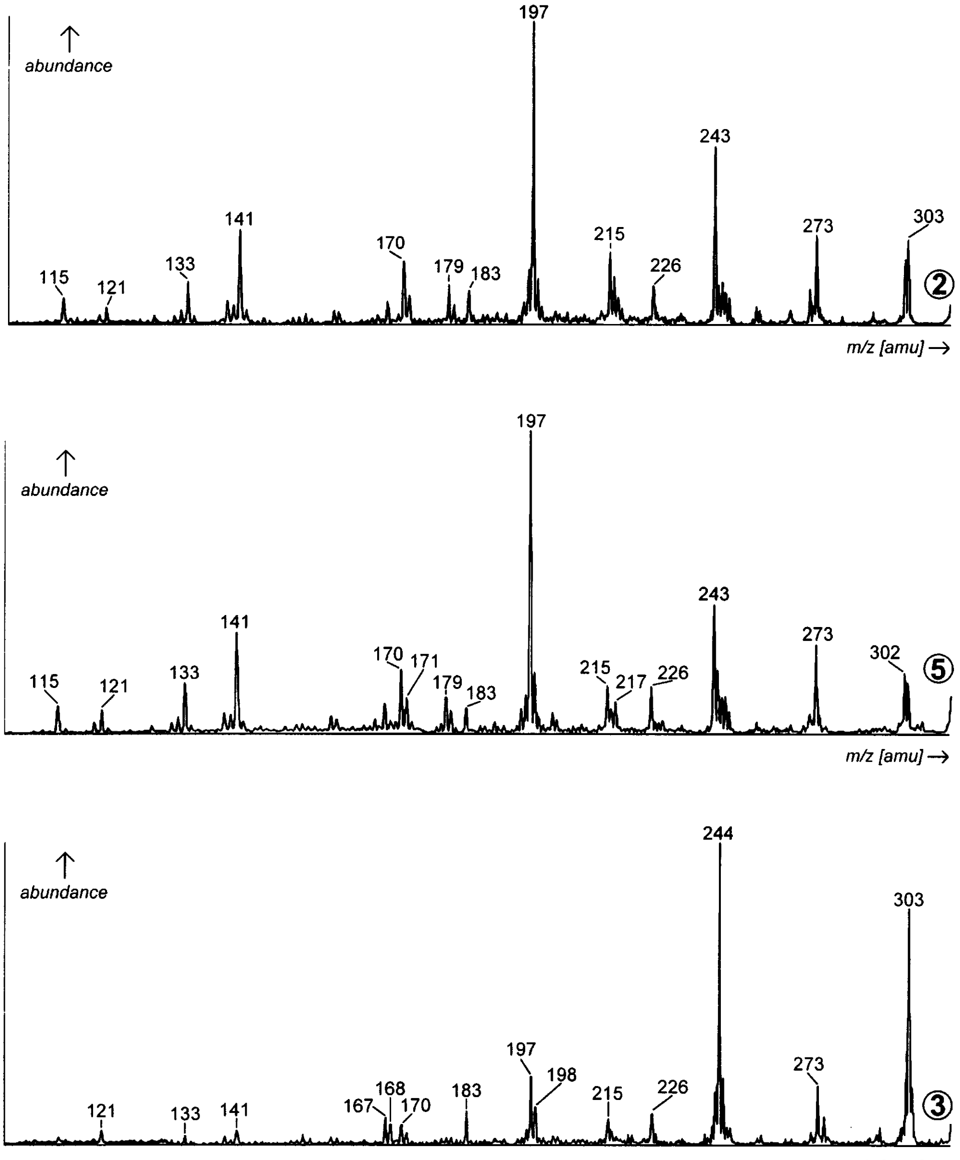


Figure 1. CAD mass spectra of the ions at *m*/*z* 321 originating from **2** (top), **5** (middle) and **3** (bottom).

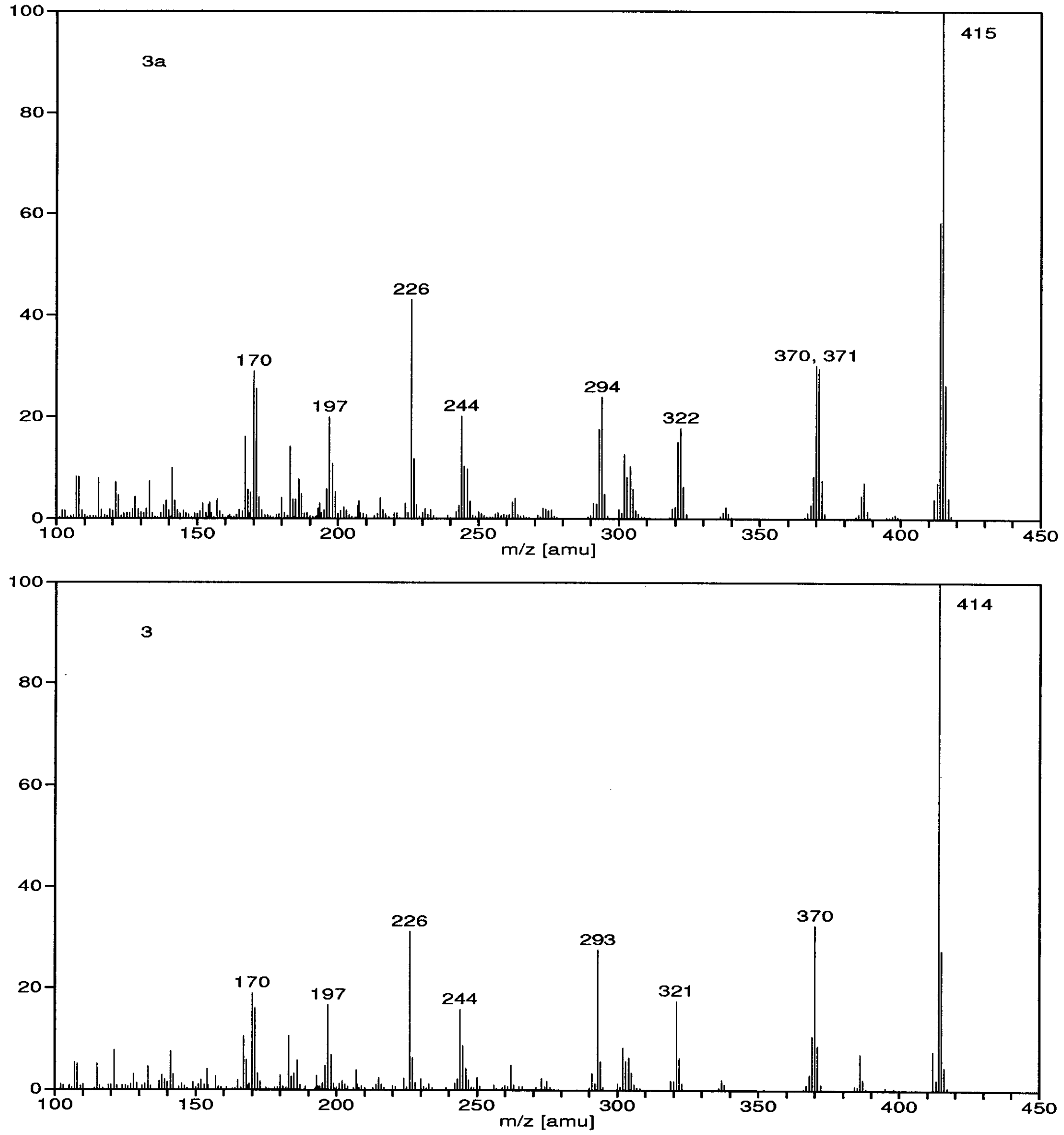


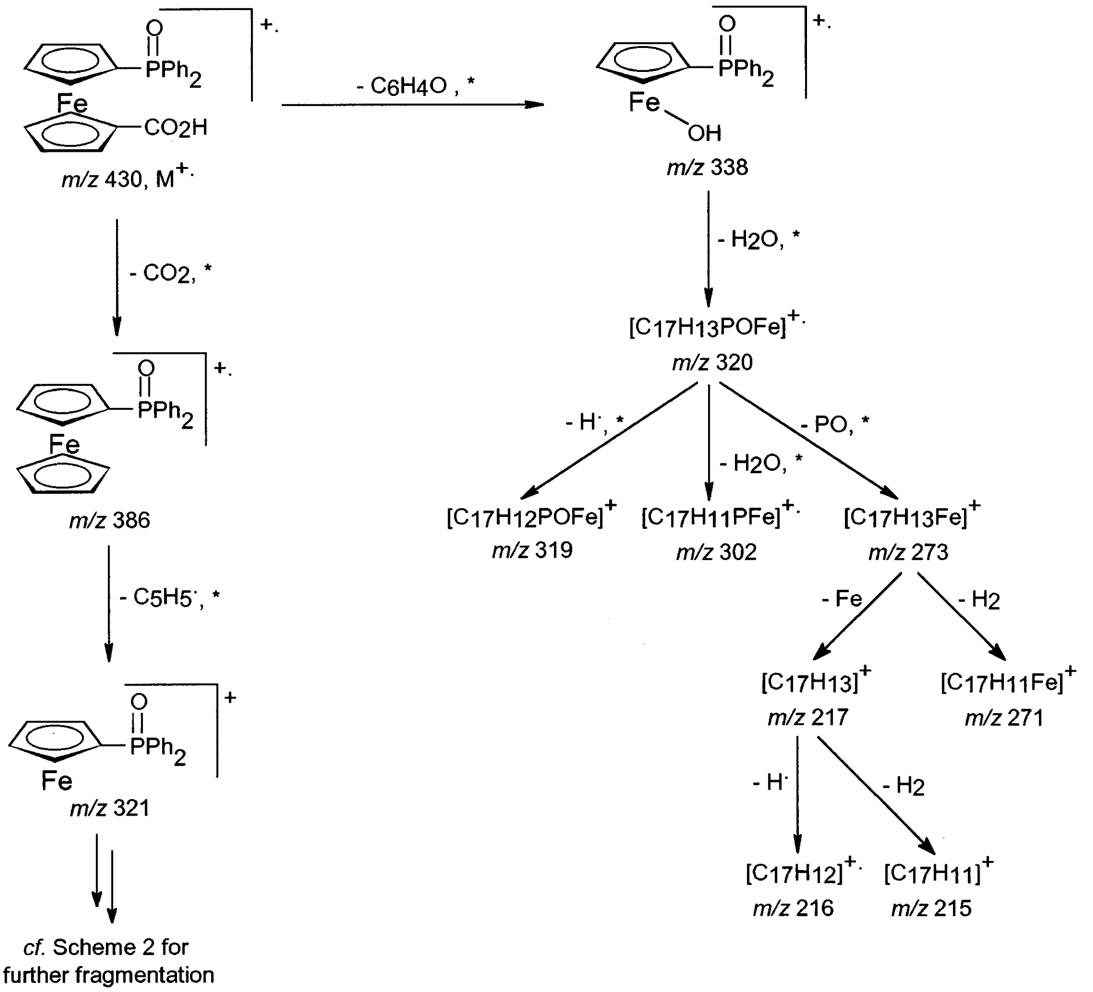
Figure 2. EI (80 eV) mass spectra of carboxyphosphine **3** and its deuterated analogue **3a**. The deuteration degree of only ~60% was reached due to a fast H/D exchange of active hydrogen atoms.

(compare Schemes 2 and 3). A low abundance of the ions at *m/z* 386 in the EI mass spectra of **3** prevents them from obtaining their CAD spectra of sufficient quality and thus any comparison with the CAD spectra of $M^{+\bullet}$ of **2**.

The deuterium labelling experiment (compound **3a**, deuteration degree ~60%) revealed an extensive H/D scrambling of the hydrogens on the carboxylated cyclopentadienyl ring, the hydroxyl proton and the phenyl hydrogens, as might be documented by only partial loss of the deuterium content during the course of initial fragmentation processes (Fig. 2).

The determination of the mass spectrometric fragmentation of $M^{+\bullet}$ of **4** was difficult as the phosphine oxide is thermally unstable and decomposes rapidly upon attempted evaporation in the direct inlet probe. Nevertheless, a fragmentation map describing the main decomposition pathways was constructed (Scheme 4) from conventional mass spectra, metastable ion transitions in the second FFR and high-resolution MS (HRMS) measurements. Similarly to ferrocenecarboxylic acid ($FcCO_2H$, Fc = ferrocenyl),[22] the most abundant fragment ions in the mass spectra of **4** are ions at *m/z* 338 due to the loss of a C_6H_4O species from $M^{+\bullet}$. Subsequent decomposition by the elimination of a water molecule provides weakly abundant ions at *m/z* 320. They are further stabilized by the instant elimination of a hydrogen radical. In addition, the ions at *m/z* 320 decompose by the elimination of a water molecule or a PO fragment. The ions at *m/z* 273 formed by the elimination of the PO species further fragment by the loss of an iron atom. This step is followed by an elimination of a hydrogen radical or a dihydrogen molecule.

The second fragmentation channel observed in the case of the carboxyphosphine oxide **4** is initiated through decarboxylation. Similarly to the fragmentation of $M^{+\bullet}$ of **2**, the ions at *m/z* 386 formed by the loss of carbon dioxide disintegrate by the loss of the $C_5H_5^{\bullet}$ radical and the resulting product ions further eliminate



Scheme 4. Fragmentation pathways for carboxy phosphine oxide **4**.

either a benzene molecule or release a C_6H_5PO fragment and iron atom (see Scheme 2). Hence the ions at *m/z* 386 are most likely of the same structure as the molecular ions of **2**.

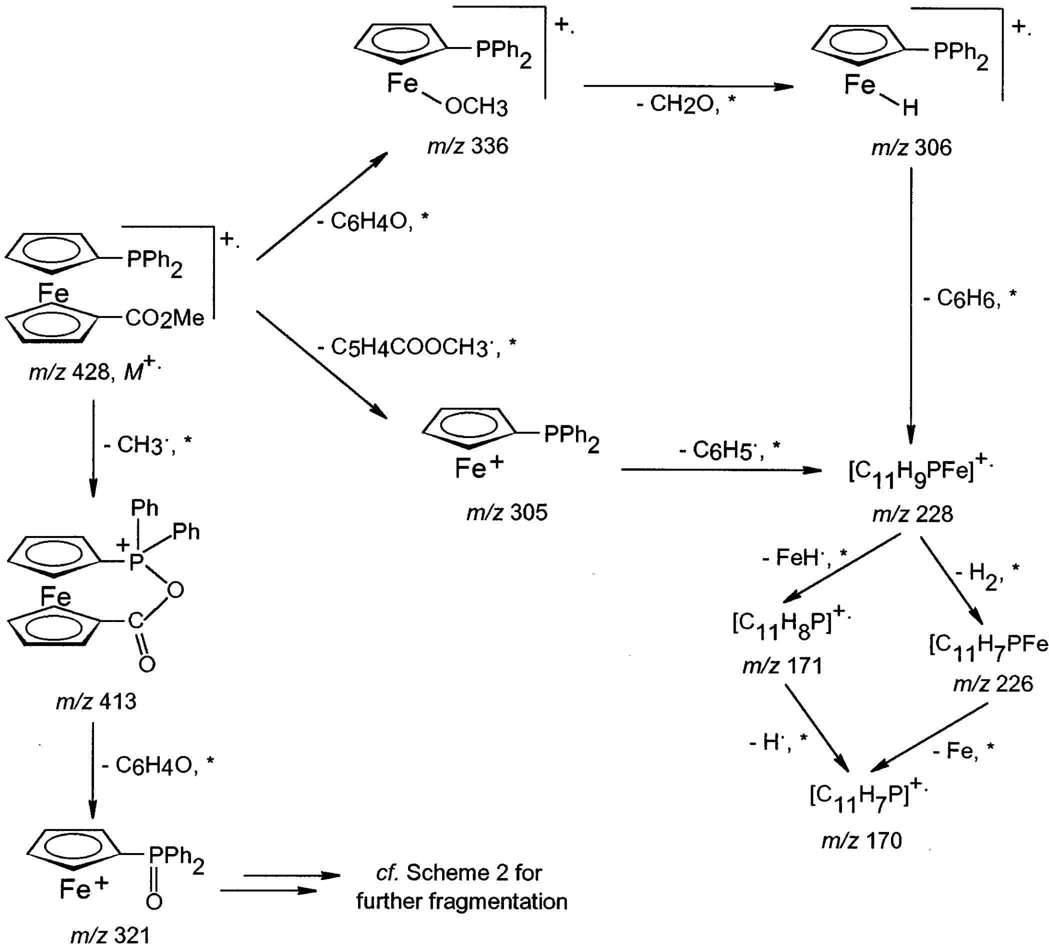
Carboxyphosphine methyl ester 5 and carboxyphosphine oxide methyl ester 6

The most interesting feature in the EI-induced fragmentation of carboxyphosphine methyl ester **5** is the loss of the ester methyl group. Probably, such an unusual splitting of the C—O bond is the result of phosphorus-assisted methyl group extrusion yielding ions at *m/z* 413, which might possess the structure of positively charged phospha-oxa-[3]ferrocenophane (Scheme 5).

The [3]ferrocenophane structure was proposed regarding the known oxophilicity of trivalent phosphorus, and it is further evidenced by the subsequent loss of a neutral fragment C_6H_4O, leading to the formation of ions at *m/z* 321. Fragmentation of the latter is identical with the fragmentation of the ions at *m/z* 321 observed in the spectra of non-carboxylated phosphine oxide **2** as documented by the CAD spectra (Fig. 1). Therefore, the structures of the ions at *m/z* 321 originating by fragmentation of **5** and **2** are assumed to be identical. Deuterium labelling (**5a**) has shown partial deuterium retention during the elimination of the methyl group from the molecular ion. The loss of the ester methyl group (CD_3) from $M^{+\cdot}$ of **5a** proceeds as the loss of the CD_3, CD_2H and CDH_2 species in the relative ratio of 72:27:1 (Fig. 3). No deuterium is present, however, after the subsequent loss of the carboxylated cyclopentadienyl ring ($\rightarrow$*m/z* 321; $[413 - C_6H_4O]^+$). This points to a partial exchange of the methyl deuterium atoms with the hydrogens of the cyclopentadienyl ring.

Direct elimination of a C_6H_4O fragment from $M^{+\cdot}$ of **5** is connected with the transfer of a methoxy group from the methoxycarbonyl group to the iron atom. This step is followed by the elimination of a formaldehyde molecule providing ions at *m/z* 306. Similar fragmentation has already been observed for other ferrocene derivatives bearing the alkoxycarbonyl group. For $FcCOOCD_3$, it has been found[23] that all deuterium atoms are retained after the methoxy group transfer to the iron atom, while a mixture of deuterium containing formaldehyde molecules is eliminated (i.e. CH_2O, CHDO and CD_2O). For **5**, we observed no significant H/D randomization, the formaldehyde molecule being eliminated almost exclusively as CD_2O (Fig. 3). The fragment ions at *m/z* 306 subsequently decompose through combinations of Fe, H and H_2 losses.

The molecular ions of **5** further decompose losing the whole methoxycarbonyl-substituted cyclopentadienyl



Scheme 5. Major fragmentation paths for carboxy phosphine methyl ester **5**.

ring to give ions at m/z 305. The loss of one hydrogen atom from ions at m/z 306 merge the fragmentation channels including ions at m/z 306 and 305, the contribution of the $M^{+\cdot} \rightarrow 305$ reaction being very low according to the spectra of **5a**. The loss of a phenyl group from ions at m/z 305 and the elimination of a benzene molecule from ions at m/z 306, afford ions at m/z 228. Deuterium labelling (**5a**) showed extensive H/D randomization of all hydrogen atoms after elimination of the formaldehyde molecule as manifested by a very high deuterium retention in the ions arising from a loss of hydrogen (→m/z 305), whereas ~75% of the ions at m/z 228 originating from the loss of the phenyl group or benzene molecule from ions at m/z 306 and 305, respectively, contain no deuterium (Fig. 3). In addition to these major fragmentation pathways, we found other but significantly less populated fragmentation channels among the fragmentation pathways of $M^{+\cdot}$ of **5**: a direct loss of phenyl or methoxy groups from $M^{+\cdot}$ (→m/z 351 and 397, respectively), and the elimination of a formaldehyde molecule instantly followed by the elimination of carbon monoxide yielding ions at m/z 370, which probably possess the structure of $M^{+\cdot}$ of **1**.

The consecutive loss of a neutral C_6H_4O fragment and a formaldehyde molecule, relatively weakly populated in the spectra of **5**, is the main fragmentation reaction of $M^{+\cdot}$ of **6** (Scheme 6). The resulting ions at m/z 322 split off either a PO species, a benzene molecule or a phenyl radical. Ions at m/z 244 formed by the elimination of benzene molecule and the ions at m/z 245 formed by the loss of a phenyl radical decompose further by the elimination of a PO fragment to give ions at m/z 197 and 198, respectively. The subsequent loss of the iron atom provides ions at m/z 141 and 142, respectively. These facts and an observed loss of a water molecule from ions at m/z 244 imply that the structures of these ions observed in the spectra of **3** and **6** are similar.

CONCLUSION

Generally, many common features were found in the spectra of the phosphino- and phosphinoylferrocenes bearing carboxy or methoxycarbonyl groups on the opposite cyclopentadienyl ring and of their unsubstituted analogues. Mainly ions representing an advanced fragmentation frequently appear as common ionic species in the spectra of different parent molecules and thus merge separate fragmentation paths of one compound. These include, for instance, ions at m/z 226 (**1**, **3**, **5** and **6**), 170 (**1**–**5**) and 197 (**2**–**6**), daughter ions of the latter ions at m/z 141 and 140 and the ions which are indicative of the ferrocene frame (m/z 121 and 56). Furthermore, it is worth noting that the loss of CO_2 from molecular ions of **4** results in the formation of ions at m/z 386, which are probably of the same structure as molecular ions of phosphine oxide **2**. Similarly, the elimination of a CO_2 molecule from $M^{+\cdot}$ of **3** leads to the generation of the same ions as these

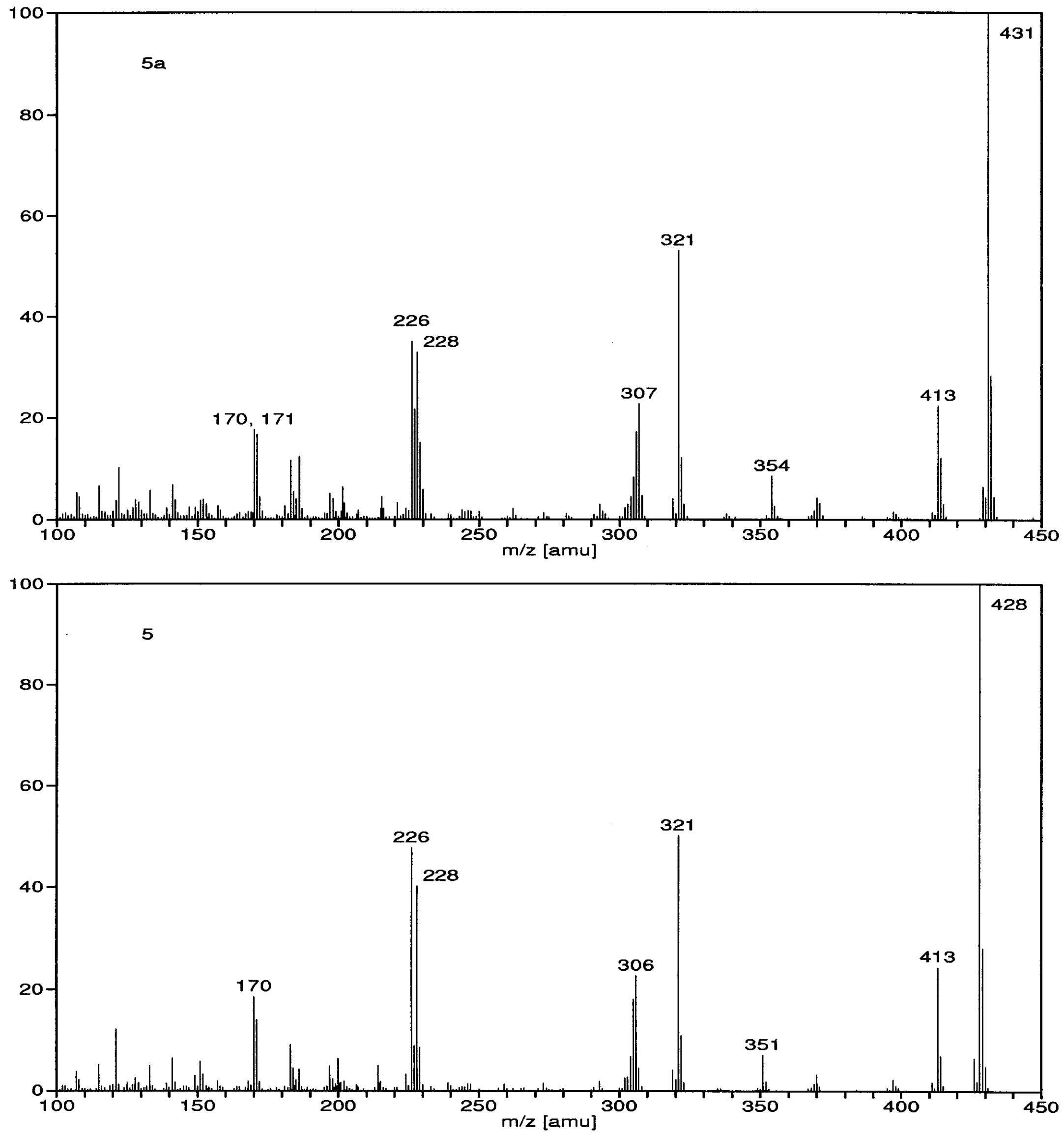


Figure 3. EI (80 eV) mass spectra of carboxyphosphine methyl ester **5** (bottom) and its d_3-isotopomer **5a** (top).

are formed by the ionization of phosphine **1**. Similarly, ions at *m/z* 293, $[FcPPh]^+$, were observed in the spectra of phosphines **1** and **3** and also as a weakly populated species in the spectra of **5**.

The loss of the unsubstituted cyclopentadienyl ring in as the $C_5H_5^{\bullet}$ radical from the molecular ions of the phosphine oxide $FcP(O)Ph_2$ (**2**) leads to the formation of ions at *m/z* 321. The latter further originate by fragmentation of methoxycarbonyl derivative (**5**). The CAD and/or MI spectra indicate the structural identity of these ions (type A). The ions of type A most likely possess the *P*-oxide structure $[(\eta^5\text{-}C_5H_4P(O)Ph_2)Fe]^+$. However, the ions at *m/z* 321 formed by fragmentation of carboxyphosphine (**4**) are clearly of a different structure and were proposed to be ions of the $[(\eta^5\text{-}C_5H_4PPh_2)FeO]^+$ structure (type B). Such a difference in fragmentation upon changing the hydroxy (**4** → type B) and methoxy groups (**5** → type A) can be ascribed to the higher thermodynamic stability of the methyl radical ($\Delta H_f^\circ = 146$ kJ mol^{-1}) in comparison with that of the hydrogen radical ($\Delta H_f^\circ = 217$ kJ mol^{-1}).[21] The elimination of the $CH_3^{\bullet}$ radical from $M^{+\bullet}$ of **5** leads to the formation of the [3]ferrocenophane structure, which is followed by subsequent fragmentation yielding ions at *m/z* 321 of type A. The transfer of the carboxylic hydroxy group to the iron atom and the elimination of the CO molecule from $M^{+\bullet}$ of **4** lead to the formation of ion-radicals at *m/z* 386, which further fragment through the loss of $C_5H_5^{\bullet}$ radical, generating ions at *m/z* 321 with the hydroxyl oxygen atom being attached to the metal centre or strongly interacting with it (type B). The CAD spectra were used to distinguish the two isomeric ionic species.

On the other hand, the fragmentation of methoxycarbonylphosphine oxide (**6**) leads to the formation of species at *m/z* 322 which were proposed to be of $[(\eta^5\text{-}C_5H_4P(O)Ph_2)FeH]^+$ structure. In addition, further related ions at *m/z* 320 were found in the spectra of carboxyphosphine oxide (**4**).

The results reported here have fully confirmed the significant role of the metal centre in the fragmentation of ferrocene derivatives, mainly in the transfer of oxygen-containing groups. The results, however, demonstrate the possibility of further reactions due to a

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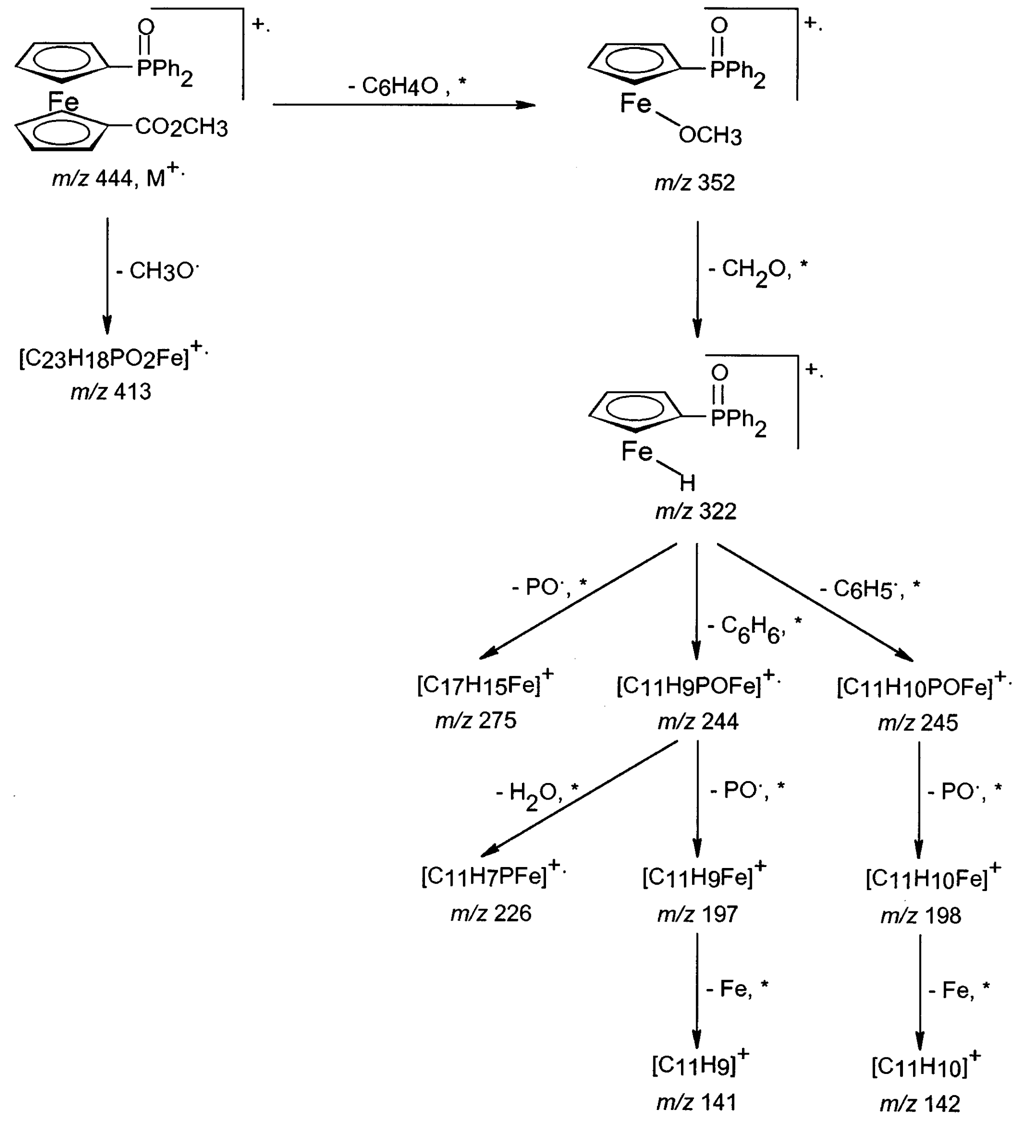

Scheme 6. Fragmentation scheme for carboxy phosphine oxide methyl ester **6**.

transfer of the oxygen-containing group to another oxophylic group present in the molecule due to a competition between proximate groups, e.g. the formation of a species containing pentavalent phosphorus from phosphino-substituted ferrocenes upon an oxygen atom transfer, which has already been mentioned here. The features in the mass spectra correspond to the sequence of bond dissociation energies $Fe^+—O \approx Fe^+—C_5H_5 > Fe^+—OH > Fe^+—CH_3 > Fe^+—H > Fe^+—H_2O$ ($Fe^+—O$ 376 ± 58 kJ mol^{-1}; $Fe^+—C_5H_5$ 369 ± 29 kJ mol^{-1}; $Fe^+—OH$ 305 ± 13, 322 ± 25 kJ mol^{-1}; $Fe^+—CH_3$ 289 ± 21, 272 ± 21 kJ mol^{-1}; $Fe^+—H$ 243 ± 8 kJ mol^{-1}; $Fe^+—H_2O$ 137, 120 kJ mol^{-1}; at 298 K for all values reported here[24]). Considering also the P—C[25] and P=O (in $O=PCl_3$)[26] bond energies of 513.4 ± 0.8 and 510 ± 21 kJ mol^{-1}, respectively, P=O bond formation is the driving force of the transfer of an oxygen atom to the phosphorus.

The reported gas-phase reactions accompanied by the migration of group(s) across a wide part(s) of energy-rich charged molecules leading to interconversions among related molecular species or merging fragmentation pathways of these should be taken into account when interpreting the mass spectra of such compounds.

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REFERENCES

1. For a recent review, see, e.g., A. Togni and T. Hayashi (Eds), *Ferrocenes*. VCH, Weinheim (1995).
2. M. Cais and M. S. Lupin in *Advances in Organometallic Chemistry*, edited by F. G. A. Stone and R. West, pp. 211–333. Academic Press, New York (1970), and references cited therein.
3. F. G. N. Cloke, J. P. Day, A. M. Greenway, K. R. Seddon, A. A. Shimran and A. C. Swain, *J. Organomet. Chem.* **372**, 231 (1989).
4. S. Barfuss, K.-H. Emrich, W. Hirschwald, P. A. Dowben and

© 1998 John Wiley & Sons, Ltd.

N. M. Boag, *J. Organomet. Chem.* **391**, 209 (1990).
5. P. Zanello, G. Opromolla, G. Giorgi, G. Sasso and A. Togni, *J. Organomet. Chem.* **506**, 61 (1996).
6. J. Podlaha, P. Štěpnička, R. Gyepes, V. Mareček, A. Lhotský, M. Polášek, J. Kubišta and M. Nejezchleba, *Collect. Czech. Chem. Commun.* **62**, 185 (1997).
7. M. I. Bruce, *Org. Mass Spectrom.* **2**, 997 (1969).
8. K. Yamakawa and M. Hisatome, *Org. Mass Spectrom.* **6**, 167 (1972).
9. K. H. Pannell and L. J. (Russwinkle) Bittman, *Org. Mass Spectrom.* **10**, 550 (1975).
10. S. R. Patil, U. N. Kantak and D. N. Sen, *Org. Mass Spectrom.* **18**, 138 (1983).
11. G. Innorta, F. Scagnolari, A. Modelli, S. Torroni, A. Foffani and S. Sorrison, *J. Organomet. Chem.* **241**, 375 (1983).
12. V. Rapic and N. Filipovic-Marinic, *Org. Mass Spectrom.* **20**, 104 (1985).
13. (a) Y. S. Nekrasov and D. V. Zagorevskij, *Org. Mass Spectrom.* **26**, 733 (1991); (b) D. V. Zagorevskij, T. V. Volkova, S. O. Yakushin, B. G. Antipov and Y. S. Nekrasov, *Org. Mass Spectrom.* **26**, 748 (1991).
14. C. F. Sheley and D. L. Fishel, *Org. Spectrom.* **6**, 1131 (1972).
15. I. R. Butler and W. R. Culen, *Organometallics* **5**, 2537 (1986).
16. (a) G. P. Sollot, H. E. Mertwoy, S. Portnoy and J. L. Snead, *J. Org. Chem.* **28**, 1090 (1963); (b) J. C. Kotz and C. L. Nivert, *J. Organomet. Chem.* **52**, 387 (1973).
17. J. Podlaha, P. Štěpnička, J. Ludvík and I. Císařová, *Organometallics* **15**, 543 (1996).
18. D. Seyferth and H. P. Withers, Jr, *Organometallics* **1**, 1275 (1982).
19. T. Hayashi, T. Mise, M. Fukusuma, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.* **53**, 1138 (1980).
20. F. W. McLafferty and F. Tureček, *Interpretation of Mass Spectral Data*, 4th edn. University Science Books, Mill Valley, CA (1993).
21. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1 (1988).
22. A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, 3847 (1964).
23. D. T. Roberts, Jr, W. F. Little and M. M. Bursey, *J. Am. Chem. Soc.* **89**, 6156 (1967).
24. B. S. Freiser (Ed.), *Organometallic Ion Chemistry*, pp. 283–332. Kluwer, Dordrecht (1995).
25. S. Smoes, C. E. Myers and J. Dowart, *Chem. Phys. Lett.* **8**, 10 (1971).
26. J. A. Kerr, *Chem. Rev.* **66**, 465 (1966).

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