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Applications of HPLC–MS to carbonyl clusters of the iron triad. The behaviour of dinuclear "flyover-bridged" iron compounds

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Abstract

High-performance liquid chromatography coupled with mass spectrometry detection was used to separate and characterize some dinuclear iron derivatives of general formula $[Fe_2(CO)_5(Ph_2PXEPh_2\text{-}p)(Et_2C_2(CO)C_2Et_2)]$ ($X = CH_2$ or CH_2CH_2, $E = P$ or As). Reversed-phase conditions and a particle-beam (PB) interface were used. The chromatographic behaviour of these compounds depends strongly on the substituents in the ligands. The fragmentation pathways both in electron impact and in chemical ionization mode mass spectrometry were studied.

Key words: Iron; Carbonyls; High-performance liquid chromatography; Mass spectrometry

1. Introduction

The use of high-performance liquid chromatography (HPLC) for preparative and analytical separations of mono- and poly-nuclear organometallic compounds is now a well consolidated technique. It offers superior efficiency, high speed, and light and dioxygen exclusion compared with traditional column and thin-layer chromatography [1]. Recent papers in this field have described the behaviour of neutral and cationic dinuclear and cluster compounds [2] and the separation of a number of enantiomeric complexes with metal chiral centres [3].

The variable-wavelength spectrophotometric detector is the most widely used for organometallic compounds, owing to the high absorbance electronic bands of these systems. Nevertheless, the need for more sensitive and specific detectors has generated considerable interest in on-line liquid chromatography–mass spectrometry (LC–MS) which allows the simultaneous separation and identification of non-volatile compounds and provides structural information for each component, even of complex mixtures. Although LC–MS has been widely applied to the analysis of biomolecules and drugs, it has been rarely applied in the field of organometallic chemistry.

There has been significant recent progress towards interfacing the two techniques. The possibility of obtaining electron impact (EI) mass spectra, rich in structurally significant fragmentations, has been provided by the MAGIC [4] (Monodisperse Aerosol Generation for Introduction of liquid Chromatographic effluents) and PB [5] (Particle Beam) interfaces; chemical ionization (CI) mass spectra are also available for these interface devices.

In a systematic study on the influence of the structure of polynuclear organometallic compounds on their chromatographic behaviour, we have applied PB HPLC–MS to a small group of iron–carbonyl dinuclear complexes, with the aim of assessing the capabilities of this combined technique. The compounds were obtained while studying the reactivity of alkynes towards metal carbonyls: in the presence of Me_3NO, the "fer-

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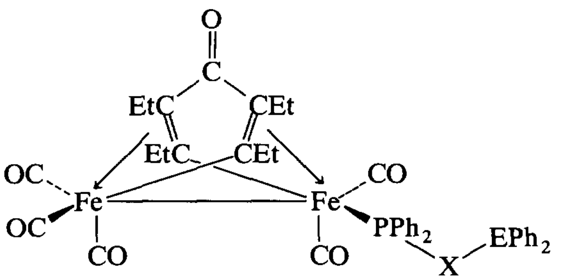

X = CH_2, E = P (**I**)
X = CH_2CH_2, E = P (**II**)
X = CH_2CH_2, E = As (**III**)

Scheme 1.

role" complex $[Fe_2(CO)_6(C_2Et_2)_2]$ reacts with Ph_2PXEPh_2 (E = P, X = CH_2, dppm; E = P, X = CH_2CH_2, dppe; E = As, X = CH_2CH_2, dppae), affording as major products the "flyover-bridged" derivatives $[Fe_2(CO)_5(Ph_2PXEPh_2\text{-}p)\{Et_2C_2(CO)C_2Et_2\}]$ (see Scheme 1), apparently produced by CO insertion into the central C–C single bond of the original butadiendiyl [6].

This paper deals with the separation and the mass spectral characterization of these dinuclear iron derivatives by on-line reversed-phase HPLC mass spectrometry. Mass spectra of the eluates were obtained using both EI and CI sources. In a preceding paper [7] we have described the HPLC behaviour and the fragmentation patterns of trinuclear alkyne(carbonyl)ruthenium derivatives.

2. Experimental section

The three dinuclear substituted "flyover-bridged" complexes were obtained by the method described in ref. 6 for the dppm derivative **I**. A derivative similar to compound **II** was obtained by photochemical substitution of one CO by dppe in the diphenylacetylene-flyover complex [8]. Compounds **II** (dppe) and **III** (dppae) are new compounds (yields 25% and 30% respectively); they gave satisfactory elemental (C, H) analyses and were inferred to have the same structural framework of **I** on the basis of spectroscopic evidence. Compound **II**: IR (heptane), ν(CO, carbonyl) 2048vs, 1996vs, 1986vs, 1946s cm^{-1}, ν(CO, ketonic) 1650s cm^{-1}; ^{13}C NMR (chloroform-d_1, TMS), in the carbonyl region, δ 201.1s (ketonic), 208.1s, 211.2s, 211.9s, 211.4d, 212.9d ppm; ^{31}P NMR (choroform-d_1, H_3PO_4), δ 48.5d, −13.4d ppm (J(P, P) 26 Hz). Found: C, 62.2; H, 5.4. $C_{44}H_{44}Fe_2O_6P_2$ requires: C, 62.7; H, 5.3%. Compound **III**: IR (heptane), ν(CO, carbonyl) 2050vs, 1997vs, 1988vs, 1946s cm^{-1}, ν(CO, ketonic) 1642s cm^{-1}; ^{13}C NMR (chloroform-d_1, TMS), in the carbonyl region, δ 201.5s (ketonic), 208.0s, 210.2s, 211.7s, 211.1d, 212.5d ppm; ^{31}P NMR (chloroform-d_1, H_3PO_4), δ 50.1s ppm (P coordination). Found: C, 59.3; H, 4.9; $C_{44}H_{44}AsFe_2O_6P$ requires: C, 59.6; H 5.0%.

For the chromatographic separations a Hewlett-Packard Model HP1090 chromatograph equipped with a Rheodyne 7125 injector was used. A stainless steel column (25 cm × 0.4 cm i.d.) filled with 5 μm LiChrosorb RP-18 (Merck) was used. In the case of HPLC–UV, a Perkin Elmer LC-75 variable-wavelength UV–visible detector was used, monitoring the eluates at 300 nm; dichloromethane or acetonitrile solutions of the compounds (20 μl) were injected. An acetonitrile–methanol (80/20) mixture was used for the isocratic elution of the dinuclear iron compounds. The flow rates were 0.8 and 1 ml min^{-1} for the LC–MS and LC–UV, respectively. The solvents used were HPLC grade (C. Erba).

The interface was a Hewlett-Packard model HP 59980A particle beam LC/MS device. As nebulizing gas, high purity helium at 50 psi (1 psi = 6894.76 Pa) was used, the desolvation chamber temperature being maintained at 55°C.

The mass spectrometer was a Hewlett Packard Model HP5989A; the HP MS apparatus was equipped with dual electron impact (EI)/chemical ionization (CI) ion source, a hyperbolic quadrupole mass analyzer, a continuous dynode electron multiplier detector and a differentially pumped vacuum system with diffusion pumps. An HP MS 59940A ChemStation (HP-UX series) was used as analytical workstation. Both EI and CI sources were utilized; source temperature was held at 260°C, the optimum value. Using the electron impact source, mass spectra were obtained under these conditions: electron energy 30 eV, electron multiplier voltage 2300 V. When operating under CI conditions, a CH_4-NH_3 95/5 mixture was used as the reagent gas: the ionization energy was 230 eV and the voltage applied to the electron multiplier was 2100 V. In this case, both positive and negative ions were monitored. The quadrupole temperature was maintained at 100°C; for scan acquisition, the system was scanned from 150 to 900 amu.

3. Results and discussion

The three dinuclear "flyover-bridged" iron complexes were separated under reversed-phase conditions with an acetonitrile–methanol (80/20) mixture. The flow rate used was higher (0.8 ml min^{-1}) than those normally adopted (0.4–0.5 ml min^{-1}) for the PB interface nebulizer, because at this flow-rate an efficient

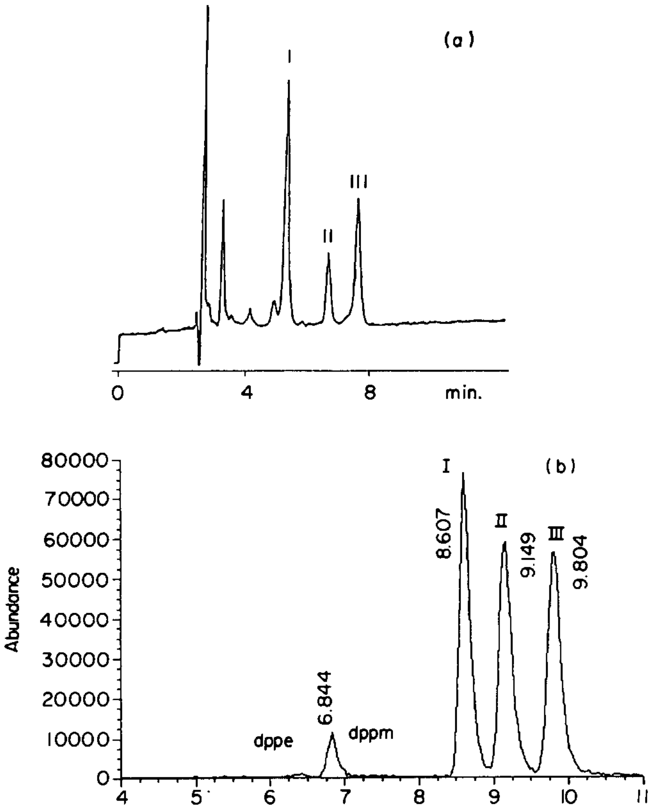

Fig. 1. Reversed-phase HPLC separation of compounds I–III, under the conditions described in the Experimental section: (a) UV detection (λ = 300 nm); (b) MS detection (EI, total ion signal).

TABLE 1. Main fragments observed in the electron impact (EI) mass spectra of the examined dinuclear "flyover" compounds

m/z	Ion	I [a]	II [a]	III [a]
183	$[PPh_2\text{-}2H]^+$	18	100	100
185	$[PPh_2]^+$	5	49	49
192	$[(C_2Et_2)_2CO]^+$	5	9	9
199	$[PPh_2CH_2]^+$	25	2	–
262	$[PPh_3]^+$	100	42	85
276	$[Fe_2(C_2Et_2)_2]^+$	1	28	7
289	$[PPh_3CH_2CH]^+$	–	65	69
307	$[dppm\text{-}Ph]^+$	1	–	–
321	$[dppe\text{-}Ph]^+$	–	3	–
365	$[dppae\text{-}Ph]^+$	–	–	5
343	$[Fe_2(PPh_2CH_2PH)]^+$	5	–	–
370	$[PPh_2]_2^+$	–	37	–
414	$[Ph_2PAsPh_2]^+$	–	–	14
384	$[dppm]^+$	24	–	–
398	$[dppe]^+$	–	45	–
442	$[dppae]^+$	–	–	67
440	$[Fe(dppm)]^+$	1	–	–
454	$[Fe(dppe)]^+$	–	3	–
498	$[Fe(dppae)]^+$	–	–	1

[a] Percentage in compounds I, II, and III.

separation was obtained and only a slight reduction in sensitivity was observed.

Figure 1 compares the chromatograms obtained with UV detection at 300 nm (Fig. 1(a)) with the total-ion signals from LC–MS (Fig. 1(b)), which shows excellent chromatographic fidelity. The total ion chromatogram was obtained by using the electron-impact source and monitoring positive ion signals of the compounds. As expected, upon monitoring an abundant single ion ($m/z = 262$, $[PPh_3]^+$) present in the fragmentation patterns of all the compounds, the peaks due to the free diphosphines dppm and dppe (present in unpurified samples of the complexes) were considerably enhanced.

The chromatographic behaviour of the three dinuclear compounds apparently depends on two factors: the length of the alkyl chain and the nature of the donor atoms. Compound **II** is eluted after **I** because the alkyl chains are different, whereas **III** is more strongly adsorbed than **II** because of the presence of the less electronegative uncoordinated arsenic atom. These effects previously observed for ruthenium carbonyl clusters [9] are particularly marked in this case, probably because the alkyl chain and one donor atom are dangling and able to interact more strongly with the stationary phase. However, these two factors do not operate in the same way for the free donors, as dppe is eluted before dppm, as shown in Fig. 1(b).

Tables 1–3 report the most significant ionic fragments found in the EI, PICI and NICI mass spectra of the three compounds respectively, while Figs. 2–4 show the mass spectra of compound **III** obtained in the three modes: EI (Fig. 2), PICI (Fig. 3) and NICI (Fig. 4). The

TABLE 2. Main fragments observed in the positive-ion chemical-ionization (PICI) mass spectra of the examined dinuclear "flyover" compounds

m/z	Ion	I [a]	II [a]	III [a]
187	$[PPh_2H_2]^+$	4	3	3
193	$[H+(C_2Et_2)_2CO]^+$	100	100	100
201	$[HPPh_2CH_3]^+$	4	1	1
210	$[PPh_2CCH]^+$	13	14	6
229	$[AsPh_2]^+$	–	–	19
322	$[OAsPh_3]^+$	–	–	7
333	$[H+Fe_2\{(C_2Et_2)_2CO\}(CO)]^+$	11	7	27
385	$[H+dppm]^+$	95	–	–
399	$[H+dppe]^+$	–	96	–
443	$[H+dppae]^+$	–	–	94
401	$[H+O+dppm]^+$	6	–	–
415	$[H+O+dppe]^+$	–	11	–
459	$[H+O+dppae]^+$	–	–	11
440	$[Fe(dppm)]^+$	1	–	–
454	$[Fe(dppe)]^+$	–	1	–
747	$[H+Fe_2\{(C_2Et_2)_2(CO)\}(dppae)]^+$	–	–	1
803	$[H+Fe_2\{(C_2Et_2)_2(CO)\}(CO)_2(dppae)]^+$	–	–	1

[a] Percentage in compounds I, II, and III.

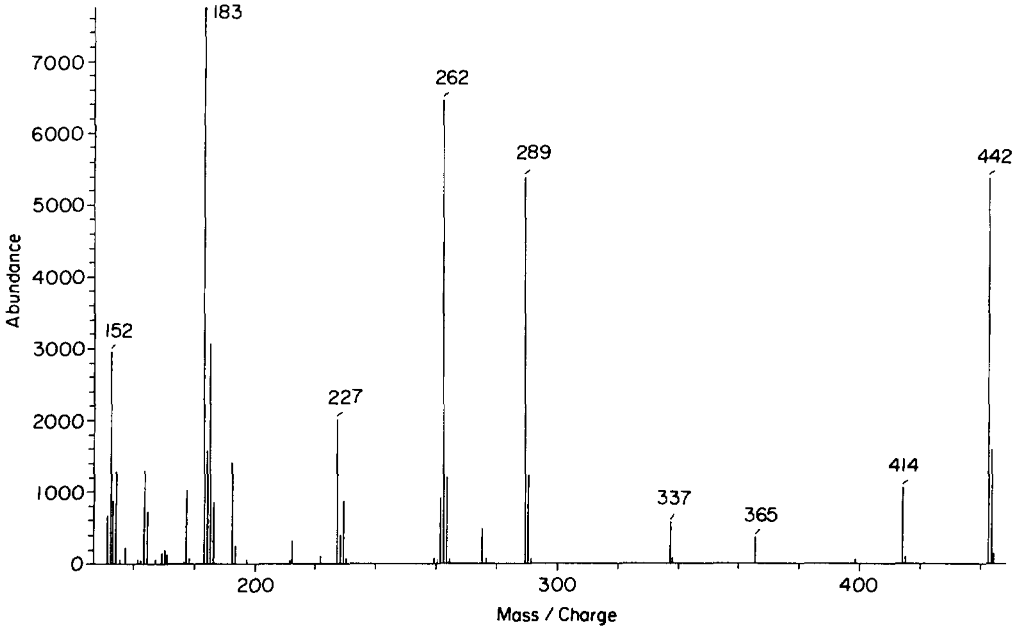

Fig. 2. Electron-impact (EI) LC–PB–MS mass spectrum of compound **III**.

EI fragmentation patterns of all the compounds are dominated by the fragments derived from the Group-15 donors, those with $m/z = 183$ ($[PPh_2 - 2H]^+$), 262 ($[PPh_3]^+$) and 289 ($[PPh_3CH_2CH_2]^+$, only for **II** and **III**) being the most abundant (Table 1). The signals due to the intact diphosphines or phosphino-arsine (67% in **III**) are also rather intense, whereas the most abundant iron-containing peak is due to the fragment $[Fe_2(C_2Et_2)_2]^+$ (28% in **II**, 7% in **III**), which has been also found (38.5%) in the spectrum of the unsubstituted "flyover" compound [10].

The PICI spectra are rather uninformative as shown in Table 2 and in Fig. 3, for compound **III**. One of the strongest peaks is due to the protonated dppae at $m/z = 443$ (also **I** and **II** gave the corresponding peaks); it is accompanied by a signal due to the corresponding protonated mono-oxide (11%), which may be

TABLE 3. Main fragments observed in the negative-ion chemical-ionization (NICI) mass spectra of the examined dinuclear "flyover" compounds

m/z	Ion	I [a]	II [a]	III [a]
138	$[Fe(C_2Et_2)]^-$	2	1	2
192	$[(C_2Et_2)_2CO]^-$	15	22	11
218	$[Fe_2(C_2Et)_2]^-$	2	2	1
276	$[Fe_2(C_2Et_2)_2]^-$	3	3	2
304	$[Fe_2\{(C_2Et_2)_2CO\}]^-$	100	100	48
305	$[H + Fe_2\{(C_2Et_2)_2CO\}]^-$	34	23	12
339	$[Fe(CO)_3(PPh_2CH_2)]^-$	2	–	–
354	$[H + Fe(CO)_3(PPh_2CH_2CH_2)]^-$	–	2	2
416	$[Fe_2\{(C_2Et_2)_2CO\}(CO)_4]^-$	3	2	2
444	$[Fe_2\{(C_2Et_2)_2CO\}(CO)_5]^-$	89	98	100
496	$[Fe(CO)_2(dppm)]^-$	3	–	–
510	$[Fe(CO)_2(dppe)]^-$	–	51	–
554	$[Fe(CO)_2(dppae)]^-$	–	–	25
661	$[H + Fe_2(C_2Et_2)_2(dppm)]^-$	15	–	–
675	$[H + Fe_2(C_2Et_2)_2(dppe)]^-$	–	1	–
719	$[H + Fe_2(C_2Et_2)_2(dppae)]^-$	–	–	4
745	$[H + Fe_2\{(C_2Et_2)_2(CO)\}(CO)_2(dppm)]^-$	1	–	–
787	$[H + Fe_2\{(C_2Et_2)_2(CO)\}(CO)_3(dppe)]^-$	–	1	–
831	$[H + Fe_2\{(C_2Et_2)_2(CO)\}(CO)_3(dppae)]^-$	–	–	1

[a] Percentage in compounds **I**, **II**, and **III**.

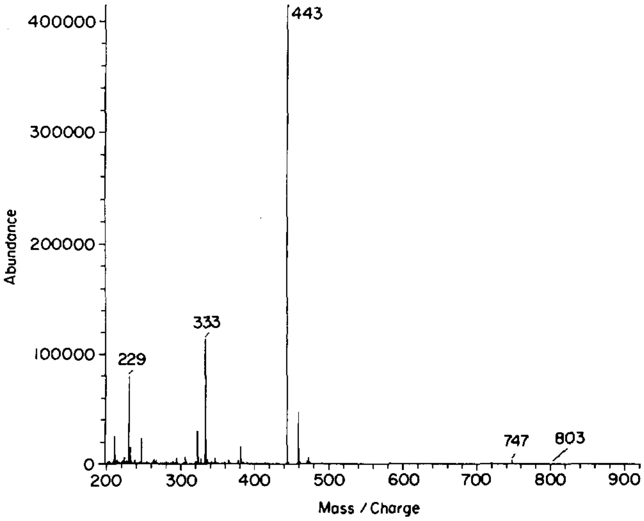

Fig. 3. Positive-ion chemical-ionization (PICI) LC–PB–MS mass spectrum of compound **III**.

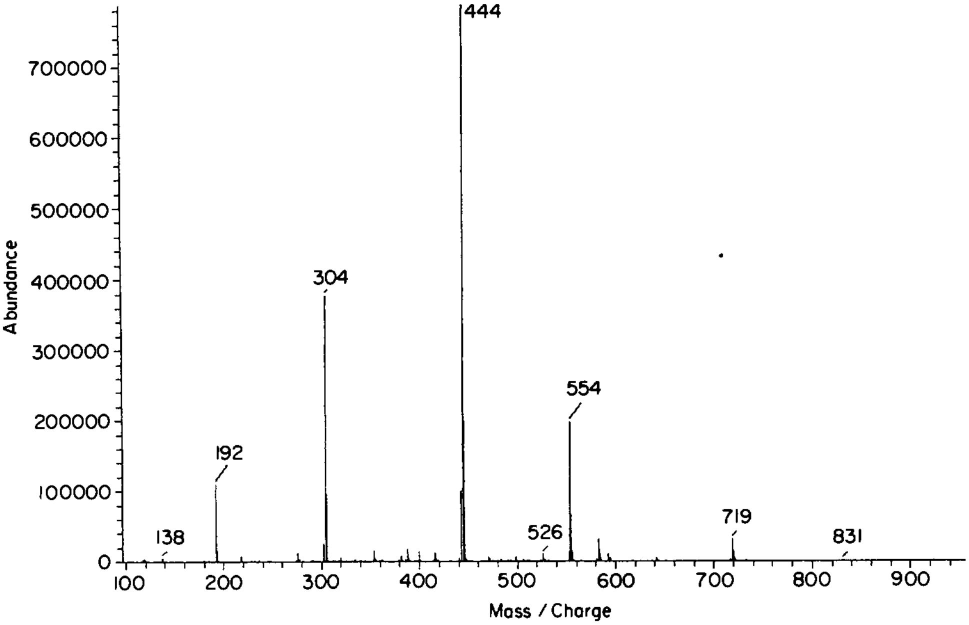

Fig. 4. Negative-ion chemical-ionization (NICI) LC-PB-MS mass spectrum of compound III.

produced by the reaction of the dppae with residual oxygen or water in the source. The most intense iron-containing signal is due to the protonated dinuclear fragment $[H + Fe_2\{(C_2Et_2)_2CO\}(CO)]^+$ ($m/z = 333$). The partially decarbonylated, protonated ions $[H + Fe_2\{(C_2Et_2)_2CO\}(dppae)]^+$, *i.e.* $[M - 5CO]^+$, $m/z = 747$, and $[H + Fe_2\{(C_2Et_2)_2CO\}(CO)_2(dppae)]^+$, $[M - 3CO]^+$, $m/z = 803$, were also detected (1%).

The NICI spectra are richer in metal-containing fragments, as shown in Table 3. In particular, in all the three spectra the most intense peak is due to the loss of the bidentate ligand at $m/z = 444$, corresponding to the fragment $[Fe_2\{(C_2Et_2)_2CO\}(CO)_5]^+$. By loss of five carbonyls, it gives the second most abundant peak at $m/z = 304$, followed by further degradation. The main fragmentation path which is illustrated in Fig. 5 along with two other minor pathways is also evident in the corresponding spectra of I and II.

An interesting family of peaks is that of the fragments at $m/z = 661$, 675 and 719 of Table 3. They correspond to the central fragmentation pathway of Fig. 5 in the case of compound III. These peaks are attributable to the ions $[H + Fe_2(C_2Et_2)_2(Ph_2PXEPh_2)]^-$ which should have the structure of the totally decarbonylated, substituted "ferrole" complex, from which the three "flyover" derivatives were prepared.

Finally, the last fragmentation path of Fig. 5 is based on the formation of the mononuclear fragment $[Fe(CO)_2(dppae)]^-$ i.e. an unsaturated substitution derivative of iron pentacarbonyl, probably stabilized by the bidentate chelating ligand; the corresponding fragments, containing dppm and dppe, respectively, were detected in the mass spectra of I and II (Table 3). The greater ability of dppe and dppae (compared to dppm) to chelate explains the fact that this fragment is abundant (51% and 25%) in the case of dppe and dppae and rather scarce (3%) in the case of dppm.

In conclusion, this and preceding work [7] demonstrate the applicability of the combined techniques HPLC and MS in metal carbonyl and cluster chemistry. High efficiency separations, even of complex mixtures, and unambiguous recognition of compounds can be simultaneously performed with this powerful combina-

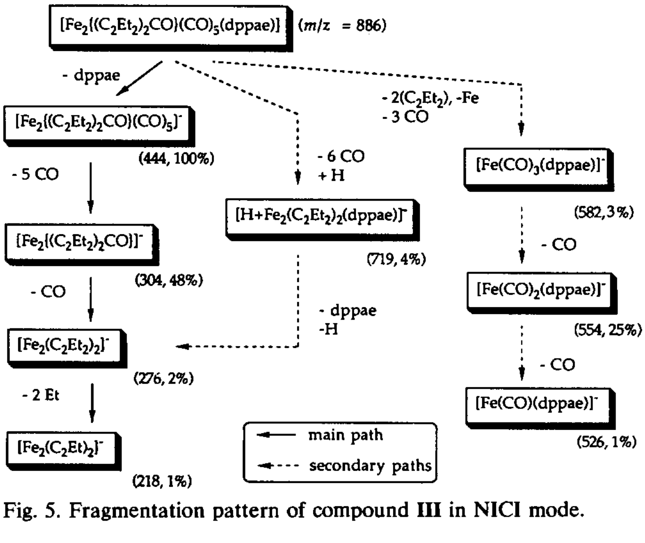

Fig. 5. Fragmentation pattern of compound III in NICI mode.

tion of analytical techniques. Furthermore, valuable structural information for the identification of unknown species can be obtained, particularly from the NICI spectra, which give rise to a richer fragmentation pattern, including a greater number of metal-containing fragments.

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