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Normal-phase and reversed-phase high-performance liquid chromatographic behaviour and particle beam mass spectrometric characterization of alkyne-substituted iron–carbonyl clusters

M. Careri[a], P. Manini[a,*], G. Predieri[a], E. Sappa[b]

[a]Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale delle Scienze, 43100 Parma, Italy
[b]Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

Abstract

The chromatographic behaviour of seven iron–carbonyl compounds substituted with alkynes R_2C_2 was studied both in normal-phase and reversed-phase chromatography. Several kinds of stationary phases were considered, including silica, CN, C_{18} and phenyl columns. Positive-ion and negative-ion chemical ionization mass spectra of the compounds obtained with a particle beam MS system in flow injection analysis are reported. LC–MS experiments were performed for confirmation purposes and in order to check the integrity of the analytes after the LC separation. © 1997 Elsevier Science B.V.

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1. Introduction

Metal carbonyl clusters of the iron group metals react with alkynes R_2C_2 giving, in the first step, stable substitution derivatives of the type $[Fe_3(CO)_9(R_2C_2)]$, where the alkyne triple bond is disposed above the plane of the three metal atoms, parallel or perpendicular to one of the M–M bonds [1]. These species are also intermediates for the synthesis of more complex organometallic clusters [2,3], moreover they may also represent models for the chemisorption and reactivity of small molecules on metal surfaces [4]. Furthermore, these clusters can act as stoichiometric reactants or catalysts or catalysts precursors in the oligomerization or co-oligomerization of alkynes to form arenes, heterocy-cles or other functionalized organic derivatives [5]. These reactions often lead to complex mixtures containing different metal clusters, whose separation is not an easy task. However recent investigations have shown that high-performance liquid chromatography (HPLC) can be successfully employed in organometallic chemistry, offering superior efficiency, high speed and light and oxygen exclusion compared with traditional column and thin-layer chromatography (TLC) [6]. Moreover, the use of on-line coupled liquid chromatography–mass spectrometry (LC–MS) allows the simultaneous separation and identification of non-volatile and thermolabile compounds such as the alkyne–carbonyl clusters. Therefore, we have undertaken systematic investigations on the chromatographic and MS behaviour of organo–transition metal clusters and this paper deals with the results obtained with some

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*Corresponding author.

Table 1
Formulas and molecular masses of the triironcarbonyl compounds studied

Compound No.	Formula	M_r
1	$Fe_3(CO)_9(C_2Et_2)$	501.78
2	$Fe_3(CO)_9(C_2EtMe)$	487.75
3	$Fe_3(CO)_9(C_2MePh)$	535.80
4	$Fe_3(CO)_9(C_2Ph_2)$	597.87
5	$Fe_3(CO)_8(C_2Ph_2)_2$	748.09
6	$Fe_3(CO)_8(PPh_3)(C_2Et_2)$	736.06
7	$Fe_3(CO)_7(C_2Ph_2)(dppm)$	926.24

distinctive alkyne–carbonyl iron derivatives (Table 1).

2. Experimental

2.1. Synthesis

Compounds 1–6 were synthesized as reported in the literature [2,7–9]. Compound 7 is a new compound [10].

2.2. Liquid chromatography

Separations were obtained using a Hewlett-Packard Model HP 1050 liquid chromatograph (Palo Alto, CA, USA) equipped with a Rheodyne 7125 injection valve (Cotati, CA, USA) and with a variable-wavelength UV detector Hewlett-Packard HP 1050 series. Different kinds of stationary phases were used in order to separate the triironcarbonyl compounds listed in Table 1.

A column filled with 10 μm LiChrosorb Si-60, 250 mm×4.6 mm I.D. (Merck, Darmstadt, Germany) was used under normal-phase chromatography conditions, with a mobile phase composed of a variable percentage of dichloromethane (0–25%) in heptane. A gradient elution was employed in order to improve the separation of the organometallic compounds (4% CH_2Cl_2, 5 min; from 4% to 20% CH_2Cl_2 in 5 min with linear gradient; 20% CH_2Cl_2 held for 3 min). In normal-phase chromatography the use of a bonded-cyano stationary phase with 100% heptane as the eluent was also examined.

In the case of reversed-phase chromatography, the performance of a 250 mm×4.6 mm I.D., 5 μm, LiChrosorb RP-18 (Merck) column was checked; the elution of the compounds was obtained with mixtures made up of methanol and acetonitrile in variable ratios, the percentage of acetonitrile ranging from 20% to 100%. Moreover, in the reversed-phase mode, the use of a Hypersil Phenyl (HPLC technology, Cheshire, UK), 150 mm×4.6 mm I.D., 3 μm, was considered, the mobile phase containing acetonitrile and water in a percentage varying from 5% to 20%.

In all cases, the flow-rate was set at 1.0 ml/min. UV detection of the analytes was performed at 254 nm. Fresh dichloromethane solutions of the purified compounds (at μg/μl concentration level) were injected in the LC system, first separately and then in proper mixtures (injection volume, 10 μl). The solutions were prepared daily and stored in the dark at 4°C.

2.3. Mass spectrometry

The mass spectra of all the compounds examined were obtained by using a particle beam (PB) LC–MS system. The mass spectrometer was a Hewlett-Packard 5989A equipped with a dual electron impact (EI)/chemical ionization (CI) ion source, a hyperbolic quadrupole mass analyzer and with a Hewlett-Packard Model 59980A PB interface. The spectra were obtained under CI conditions, monitoring the signal of both positive- and negative-ions. High purity methane was used as the reagent gas at ca. 1.2 Torr (1 Torr=133.322 Pa). The operative temperature values were: 45°C for the desolvation chamber of the interface; 250°C and 100°C for the ion source and for the quadrupole analyzer of the mass spectrometer, respectively. The pressure of the nebulizing gas used in the interface (helium) was 45 p.s.i. (1 p.s.i.=6894.76 Pa). The electron energy was set at 230 eV and the electron multiplier at 2350 V. The mass spectra were acquired in the 105–980 u mass range. For the acquisition a HP MS 59940A Chem Station (HP-UX Series) was used. The mass spectra were obtained in the flow injection analysis (FIA) mode without LC column by injecting few micrograms of each compound dissolved in dichloromethane. In order to check the integrity of the analytes after the chromatographic separation, the column was connected to the PB-MS system to perform

LC–MS experiments. The chromatographic conditions, i.e., column and gradient elution program, were the same employed in normal-phase chromatography with UV detection.

3. Results and discussion

From the chromatographic point of view, the separation of the iron–carbonyl complexes listed in Table 1 is not a easily solvable problem, especially in the case of the mono-substituted derivatives 1–4, each of them differing from the others for the R and R′ substituents bonded on the acetylenic moiety C_2RR'. The separation of this first group of four compounds (1–4) from the other three (5–7) appears to be less complex; in fact, the substitution of one (5) or two (6, 7) carbonyl ligands with a second acetilyde C_2Ph_2 (5), or with a triphenylphosphine PPh_3 (6) or with the diphosphine $PPh_2CH_2PPh_2$ (7) makes these compounds very different in terms of polarity and steric features. Metal carbonyl compounds substituted with phosphines are known to be more retained both in normal-phase and in reversed-phase chromatography [11]. In order to solve the problem of the separation of the $Fe_3(CO)_9(C_2R_2)$ 1–4, several kinds of commercially available stationary phases were considered.

3.1. Normal-phase chromatography: silica column

Stationary phases for normal-phase chromatography based on silica are sensitive to small differences in polarity like the ones determined by the different substitution on the C_2RR' ligand, which characterizes the considered series of compounds. A 10 μm LiChrosorb Si-60 column was the first choice for this kind of separation, considering the results reported in the literature and our experience in the field of HPLC of metal carbonyl compounds [11–14]. Retention was studied as a function of the variation of dichloromethane percentage in heptane. The capacity factors obtained by varying the mobile phase composition are summarized in Fig. 1. The use of heptane 100% as the eluent was tried for the less polar compounds, but it immediately appeared to be not suitable because, even though shortly retained, chromatographic peaks were broad and showed a big
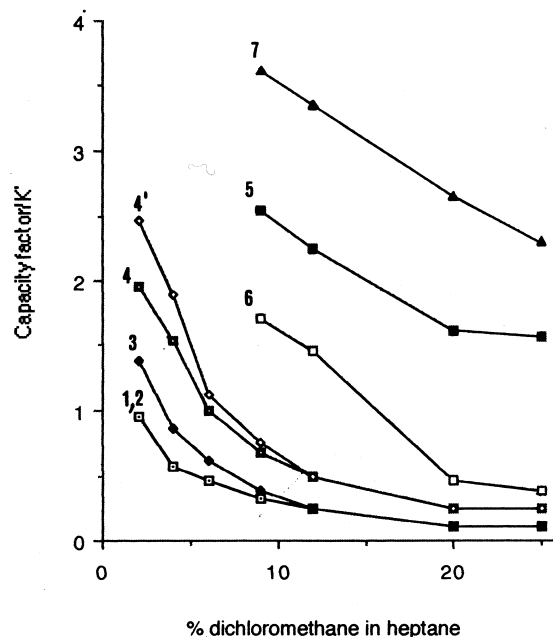

Fig. 1. Effect of the percentage of dichloromethane in the mobile phase on the capacity factors (k') of the compounds 1–7 under normal-phase conditions.

shoulder; in some cases peaks appeared double. This phenomenon can be explained by invoking a decomposition process, which could occur on the silica surface in the chromatographic column when the mobile phase is completely apolar. A small percentage of dichloromethane (2%) was found to be enough to obtain sharp peaks and to avoid the presence of the shoulder.

As can be noticed from the capacity factors plotted in Fig. 1, the separation of compounds 1 and 2 was impossible, even with only the 2% of dichloromethane; the difference in polarity between a methyl and an ethyl group (i.e., the R substituent in the acetylide ligand C_2EtR) is too small to allow the separation of the two compounds. The presence of one polarizable and hindered aryl group, Ph, bonded on the acetylenic ligand leads to a difference both in polarity and in steric features, which generates a different chromatographic behaviour for compound 3. When the number of the Ph substituents increases, the retention of the compounds increases as well: compounds 4 is more retained by the stationary phase and it exists in two geometric isomers (proba-

bly due to the different disposition of the alkyne molecule on the surface of the trinuclear clusters) which can be easily separated by the silica. Silica stationary phases are known to be efficient in separating organometallic compounds which are geometric isomers [13]. The hypothesis that the two peaks obtained by injecting compound 4 are due to isomers and not to degradation products of the clusters formed after the interaction with the stationary phase was confirmed by means of the on-line MS detection: the LC column was connected to the PB-MS system in order to check and to evaluate the mass spectra obtained for the chromatographic eluates. The two identical negative-ion CI (NCI) mass spectra showing a $m/z = 430$ main peak attributable to the ion $[M-6CO]^-$ demonstrated that no degradation occurred in the LC column and that the two compounds are eluted without decomposition and therefore they are two isomers.

Because of the difference in polarity existing between the first group of compounds (1–4) and the second one (5–7), their chromatographic behaviour was studied separately and different mobile phases were used for the elution. The separation of the triironnonacarbonyl clusters 1–4 was obtained isocratically with heptane–dichloromethane (96:4, v/v), whereas for the separation of a mixture of the compounds 5–7 the elution required the 25% of dichloromethane in heptane. To separate the mixture containing all the seven compounds a gradient elution program was necessary (see Section 2.2); the chromatogram is shown in Fig. 2.

3.2. Normal-phase chromatography: cyano-bonded stationary phase

All the chromatograms, obtained with a cyano-bonded column when dichloromethane solutions of the examined compounds were injected showed a similar appearance, characterized by the presence of a large number of peaks, probably due to the cluster demolition. In fact, it seems that the cyano group interacts with the iron complex and provocates the substitution of the ligands. A similar phenomenon can be observed when the carbonyl compounds are dissolved in acetonitrile.
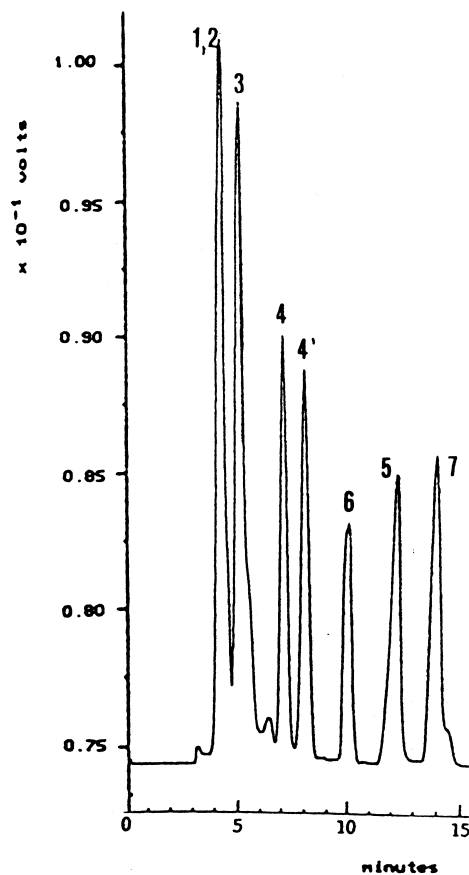

Fig. 2. NP chromatogram of a mixture of the seven iron–carbonyl compounds obtained in gradient elution mode. Chromatographic conditions: column, LiChrosorb Si-60, 250×4.6 mm I.D., 10 μm; mobile phase, heptane–dichloromethane in gradient elution mode; flow-rate, 1.0 ml/min. UV detection at 254 nm. For gradient program, see Section 2.2.

3.3. Reversed-phase chromatography: C_{18} stationary phase

The separation of this class of carbonyl compounds was not achieved by reversed-phase chromatography using a RP-18 stationary phase (LiChrosorb 5 μm). Different mobile phases containing methanol and acetonitrile were employed in order to study the retention of the analytes but only one compound, 6, showed a chromatographic behaviour significantly different from the others. The interaction of the triphenylphosphine derivatives with the C_{18} alkyl chains is easily understandable and well known [11].

Small differences in the retention are shown by compounds 1, 3 and 4, the more retained compound being 1, the less retained being 4. The retention in reversed-phase mode is opposite to that observed in normal-phase chromatography and the reason is in both cases the polarizability of the phenyl group, whereas the alkyl group is not polarizable at all. The separation of 1 and 2 was impossible in reversed-phase mode as well.

3.4. Reversed-phase chromatography: phenyl-bonded stationary phase

The presence of a variable number of phenyl groups as the substituents on the alkyne moiety lead us to try a stationary phase with phenyl groups bonded on the silica particles, with the aim to obtain a greater solubility of the analytes in the stationary phase. As expected, the retention of the compounds was found to be strongly dependent on the number of phenyl groups present in the molecule: as the number of the Ph groups increases, the compounds are more retained by the stationary phase. On the other hand, the column was not able to separate compounds 1

and 2, which do not contain any aryl substituent. Fig. 3 shows a chromatogram of a mixture of the iron–carbonyl complexes 1–6, obtained with an acetonitrile–water (80:20, v/v) mobile phase. Under these chromatographic conditions, compound 3, which contains only one Ph group, was not completely separated from 1; the two compounds can be baseline resolved by means of an higher percentage of water in the mobile phase (33%). Like in the case of normal-phase chromatography (silica), it was possible to separate the two isomers of 4, a complex containing two phenyl substituents and therefore more retained than 1 and 3. Compound 5 elutes after 4, because of the double substitution of two carbonyl ligands with C_2Ph_2 (in total four Ph groups), but before 6, the compound which shows a PPh_3 as a ligand.

3.5. Mass spectrometry

All the NCI mass spectra of the examined compounds show the decarbonylation pathway typical of this class of organometallic derivatives [11–14]. As reported in Table 2, there is no evidence of the
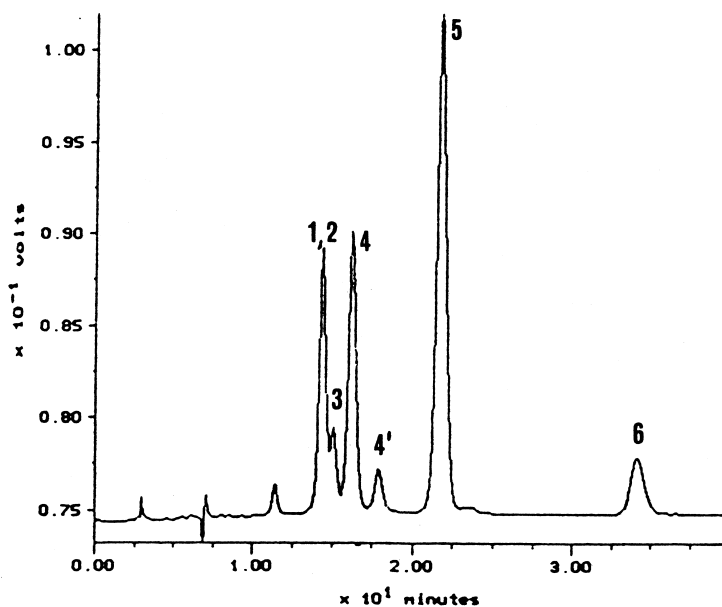

Fig. 3. RP chromatogram of a mixture of the complexes 1–6. Chromatographic conditions: column, Hypersil Phenyl, 150×4.6 mm I.D., 3 μm; mobile phase, acetonitrile–water (80:20, v/v), flow-rate, 1.0 ml/min. UV detection at 254 nm.

Table 2
NCI mass spectra of the iron–carbonyl compounds 1–7

Ion	1	2	3	4	5	6	7
$[M-CO]^-$	474 (3)	460 (7)	508 (3)	–	720 (<1)	–	–
$[M-2CO]^-$	446 (100)	432 (100)	480 (100)	542 (1)	692 (<1)	–	–
$[M-3CO]^-$	418 (3)	404 (1)	452 (2)	514 (<1)	664 (<1)	652 (<1)	842 (<1)
$[M-4CO]^-$	390 (2)	376 (<1)	424 (1)	486 (<1)	636 (<1)	624 (<1)	814 (1)
$[M-5CO]^-$	362 (1)	348 (<1)	396 (2)	458 (<1)	608 (1)	596 (<1)	786 (12)
$[M-6CO]^-$	334 (9)	320 (6)	368 (9)	430 (100)	580 (<1)	568 (2)	758 (15)
$[M-7CO]^-$	306 (2)	292 (1)	340 (1)	402 (2)	552 (1)	540 (6)	730 (8)
$[M-8CO]^-$	278 (3)	264 (<1)	312 (<1)	374 (1)	524 (1)	512 (25)	–
$[M-9CO]^-$	250 (3)	236 (<1)	284 (<1)	346 (1)	–	–	–
$[Fe_2(CO)_5]^-$	252 (17)	252 (6)	252 (<1)	252 (1)	–	252 (46)	–
$[Fe(CO)_4]^-$	168 (99)	168 (<1)	168 (1)	168 (1)	–	168 (100)	168 (13)
$[Fe(CO)_3]^-$	140 (2)	140 (1)	140 (1)	140 (1)	–	140 (1)	–
$[Fe(CO)_3(C_2R_2)]^-$	222 (6)	208 (1)	256 (1)	318 (1)	–	–	–
$[Fe(CO)_2(C_2R_2)]^-$	194 (2)	180 (2)	228 (2)	290 (2)	–	–	–
$[Fe_3(CO)_3(C_2H_2)(C_2Ph_2)]^-$	–	–	–	–	456 (1)	–	–
$[Fe_3(CO)_2(C_2H_2)(C_2Ph_2)]^-$	–	–	–	–	428 (3)	–	–
$[Fe_3(CO)(C_2H_2)(C_2Ph_2)]^-$	–	–	–	–	400 (22)	–	–
$[Fe_3(CO)_6(C_2H_2)C_2]^-$	–	–	–	–	386 (83)	–	–
$[Fe_3(CO)_8(C_2)_2]^-$	–	–	–	–	440 (1)	–	–
$[Fe_3(CO)_7(C_2)_2]^-$	–	–	–	–	412 (2)	–	–
$[Fe_3(CO)_6(C_2)_2]^-$	–	–	–	–	384 (100)	–	–
$[Fe_3(CO)_8(C_2Et)]^-$	–	–	–	–	–	445 (13)	–
$[Fe_3(CO)_8(C_2)]^-$	–	–	–	–	–	416 (28)	–
$[Fe_2(CO)_5(C_2Et_2)]^-$	–	–	–	–	–	334 (29)	–
$[Fe_2(CO)_4(C_2Et_2)]^-$	–	–	–	–	–	306 (5)	–
$[Fe_2(CO)_3(C_2Et_2)]^-$	–	–	–	–	–	278 (1)	–
$[Fe_2(CO)_4]^-$	–	–	–	–	–	224 (6)	–
$[Fe_2(C_2Et_2)]^-$	–	–	–	–	–	194 (18)	–
$[Fe_3(CO)_2(dppm)]^-$	–	–	–	–	–	–	608 (18)
$[Fe_2(CO)(dppm)]^-$	–	–	–	–	–	–	524 (22)
$[Fe_2(dppm)]^-$	–	–	–	–	–	–	496 (56)
$[Fe(CO)(dppm)]^-$	–	–	–	–	–	–	468 (13)
$[Fe(dppm)]^-$	–	–	–	–	–	–	440 (41)
$[Fe_3(CO)_3(C_2Ph_2)]^-$	–	–	–	–	–	–	430 (100)
$[Fe_2(CO)(PPh_2CH_2)]^-$	–	–	–	–	–	–	339 (32)

Relative abundances in parentheses.

molecular ion $[M]^-$ for anyone of the clusters; this behaviour is characteristic of the iron–carbonyl clusters as already observed elsewhere [12]. For the monosubstituted compounds 1–3, the main peak of the spectrum corresponds to the fragment ion $[M-2CO]^-$ or, in the case of compound 4, to $[M-6CO]^-$. The di or trisubstituted iron–carbonyl complexes 5–7 are characterized by different base peaks, not simply derived by loss of several carbonyl ligands: $[Fe_3(CO)_6(C_2)_2]^-$ at $m/z=384$, 5, $[Fe(CO)_4]^-$ at $m/z=168$, 6, and $[Fe_3(CO)_3(C_2Ph_2)]^-$ at $m/z=430$, 7. A signal attributable to $[Fe(CO)_2(C_2R_2)]^-$ is visible in the spectra of 1–4 with an abundance of 2% and in any case this is the low-mass fragment ion detectable in those spectra. By contrast, the mass spectra of the three other compounds appear complicated by the existence of several parallel fragmentation pathways.

For instance, in the case of compound 6, decarbonylation can occur starting from $[M]^-$, $[Fe_2(CO)_5]^-$, $[Fe(CO)_4]^-$ or from $[Fe_2(CO)_5(C_2Et_2)]^-$; for 7 the main decarbonylation pathway starts from $[Fe_2(CO)_5(dppm)]^-$. As an example, Fig. 4b shows the NCI mass spectrum of 3; while Fig. 4a shows the corresponding positive-ion CI (PCI) spectrum.

The PCI mass spectra (Table 3) of 1, 2 and 3 are characterized by the presence of a small signal ($<1\%$) attributable to the protonated molecule $[M+H]^+$. A series of peaks at a 28 u distance is due to the ion $[M+H-nCO]^+$, with $n=1-9$. All these decarbonylation fragment ions have abundances lower than 10%. In the case of compound 4, the $[M+H-nCO]^+$ ions are visible starting from $n=5$; the polysubstituted compounds 5–7 do not show any of those fragments due to the release of the carbonyl ligands. The main peak in the spectra of the mono-substituted compounds 1–4 is in any case the one attributable to the loss and the protonation of the C_2RR' ligand, that means $[C_2RR'+H]^+$. Compound 7 shows the ion $[C_2Ph_2+H]^+$ at $m/z=179$ (100% abundance) as well. PCI spectra of metal–carbonyl compounds substituted with phosphines usually show only the signals arising from the protonated phosphine itself and by its fragmentation. For this reason, the spectrum of 6 provides poor structural information: the only ions detectable are the ones at $m/z=263$ and 185, $[PPh_3+H]^+$ and $[PPh_2+H]^+$, respectively. Similarly, the spectrum of compound 7 shows the signals at $m/z=385$, $[dppm+H]^+$ and at $m/z=109$ $[PPh+H]^+$.

4. Conclusions

This work demonstrates the capability of the

Table 3
PCI mass spectra of the iron–carbonyl compounds 1–7

| Ion	1	2	3	4	5	6	7
$[M+H]^+$	503 (<1)	489 (<1)	537 (<1)	–	–	–	–
$[M+H-CO]^+$	475 (<1)	461 (<1)	509 (<1)	–	–	–	–
$[M+H-2CO]^+$	447 (<1)	433 (1)	481 (<1)	–	–	–	–
$[M+H-3CO]^+$	419 (1)	405 (1)	453 (<1)	515 (<1)	–	–	–
$[M+H-4CO]^+$	391 (<1)	377 (<1)	425 (<1)	487 (<1)	–	–	–
$[M+H-5CO]^+$	363 (2)	349 (5)	397 (1)	459 (5)	–	–	–
$[M+H-6CO]^+$	335 (5)	321 (1)	369 (4)	431 (3)	–	–	–
$[M+H-7CO]^+$	307 (1)	293 (1)	341 (1)	403 (2)	–	–	–
$[M+H-8CO]^+$	279 (2)	265 (<1)	313 (3)	375 (3)	–	–	–
$[M+H-9CO]^+$	251 (2)	237 (7)	285 (2)	347 (2)	–	–	–
$[C_2R_2+H]^+$	87 (100)	73 (100)	117 (100)	179 (100)	179 (100)	–	179 (100)
$[Fe(CO)_2(C_2R_2)+H]^+$	195 (5)	181 (32)	229 (4)	291 (12)	–	–	–
$[Fe(CO)(C_2R_2)+H]^+$	167 (8)	153 (35)	201 (7)	263 (<1)	–	–	–
$[Fe(C_2R_2)+H]^+$	139 (15)	125 (60)	173 (13)	235 (6)	–	–	–
$[Fe_3(CO)_3(C_2H_2)(C_2Ph_2)+H]^+$	–	–	–	–	457 (1)	–	–
$[Fe_3(CO)_2(C_2H_2)(C_2Ph_2)+H]^+$	–	–	–	–	429 (1)	–	–
$[Fe_3(CO)(C_2H_2)(C_2Ph_2)+H]^+$	–	–	–	–	401 (4)	–	–
$[Fe_3(CO)_7(C_2)_2+H]^+$	–	–	–	–	413 (16)	–	–
$[Fe_3(CO)_6(C_2)_2+H]^+$	–	–	–	–	385 (100)	–	–
$[Fe_3(CO)_5(C_2)_2+H]^+$	–	–	–	–	357 (5)	–	–
$[PPh_3+H]^+$	–	–	–	–	–	263 (28)	263 (20)
$[PPh_2+H]^+$	–	–	–	–	–	185 (100)	185 (73)
$[PPh+H]^+$	–	–	–	–	–	–	109 (76)
$[dppm+H]^+$	–	–	–	–	–	–	385 (35)

Relative abundances in parentheses.
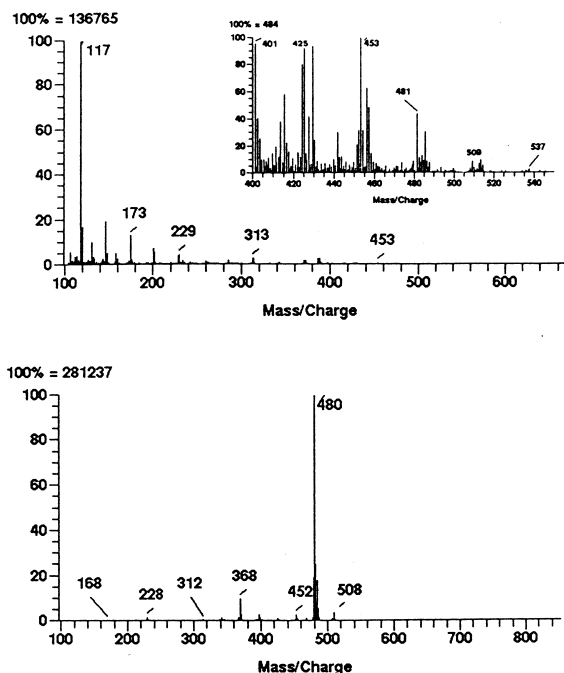
Fig. 4. (a) PCI and (b) NCI particle beam mass spectra of compound 3. Reagent gas: methane; acquisition range: 105–980 u.

coupled HPLC–MS technique in metal carbonyl chemistry for the separation and the structural elucidation of organometallic compounds. Concerning the chromatographic behaviour of the alkyne-substituted iron–carbonyl clusters, normal-phase on silica column and reversed-phase on phenyl column gave the best results.

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