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Comparison of electrospray mass spectrometry with other soft ionization techniques for the characterisation of cationic π-hydrocarbon organometallic complexes

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Abstract

Electrospray (ES) mass spectrometry provides a convenient method for the characterisation of a wide range of π-hydrocarbon complex salts of the general types $[FeCp(\eta\text{-arene})]BF_4$, $[M(CO)_3(\eta\text{-}C_7H_7)BF_4$ (M = Cr, Mo, W), $[Fe(CO)_2L\ (\eta^5\text{-dienyl})]BF_4$ (L = CO or PPh_3; dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9), $[CpFe(CO)_3]PF_6$ and $[CpFe(CO)_2(\eta\text{-}C_2H_4)]BF_4$. At low skimmer voltages (20 V), principal (molecular) ions are generally the only observed species. For the arene complexes, $[FeCp(\eta\text{-arene})]BF_4$, high skimmer voltages (80–135 V) are required before fragmentation is observed. However, for the carbonyl containing cations, moderate skimmer voltages (40–55 V) also give rise to $[M\text{-}CO]^+$, $[M\text{-}2CO]^+$ and $[M\text{-}3CO]^+$ ions. Very similar behaviour is observed with phosphonium and imidazolium adducts of the type $[Fe(CO)_3(\eta^4\text{-diene.Nuc})]^+$ (diene = C_6H_7 or C_7H_9; Nuc = PPh_3 or Im) and $[CpFe(CO)_2(\eta^1\text{-}C_2H_4.\ PPh_3)]^+$. Comparison with fast atom bombardment (FAB) and field desorption (FD) mass spectra for the same complex salts indicates that fragmentation decreases along the series FAB > ES > FD, and that ES mass spectrometry is the most convenient and informative of the three soft ionization techniques.

Keywords: π-Hydrocarbon complexes; Iron; Chromium; Molybdenum; Tungsten; Electrospray mass spectrometry

1. Introduction

The involatility of coordination and organometallic salts has generally precluded their characterisation by conventional electron impact (EI) and chemical ionization (CI) mass spectrometry. Some time ago, one of us [1–4] and others [5–8] demonstrated that such compounds could be successfully characterised by the soft ionization technique of field desorption (FD) mass spectrometry. In most cases the FD mass spectra were simple, being dominated by molecular $[M]^{+\bullet}$ and $[M+1]^+$ ions for the cationic part of their structure. However, technical difficulties, including poor reproducibility and the difficulty of producing effective emitter wires, has limited the use of this technique. More recently, another soft ionization method, fast atom bombardment (FAB) mass spectrometry has been utilised to provide mass spectra for coordination and organometallic salts that in many cases exhibit peaks for the molecular ions [9–11].

A potentially powerful new technique for characterising involatile coordination and organometallic salts is electrospray mass spectrometry (ESMS). This novel technique, developed for organic analysis by Fenn et al. [12,13], following the pioneering work of Dole [14], has recently found extensive application in the structural analysis of large biopolymers, especially proteins [15,16]. In marked contrast, only a few papers have appeared describing the ES mass spectrometry of coordination [17–23] and organometallic [24–27] complexes. These studies show ESMS spectra typically dominated by the principal (or molecular) ion known to be present in the solution. Further, it is known that the extent of fragmentation observed in ESMS spectra can be controlled by varying the conditions in the ion source. In sources in which skimmers are used to isolate the high pressure region, the voltage applied to the first source skimmer determines the degree of collisional activation of ions accelerated through the

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intermediate pressure region (1–2 mbar). Higher skimmer potentials therefore generate ions with increased internal energy and so there is more fragmentation (vide infra). Thus the combination of the ability to generate molecular species from organometallic compounds and the capacity to induce fragmentation indicates that ESMS has considerable promise for rapidly characterising such species. However, the range of organometallic cations examined to date has been quite small, being confined largely to alkyl- [26,27] and CO-containing complexes [24], and the only π-hydrocarbon complex reported is the ferrocenium ion $[\mathrm{Fe\ Cp_2}]^+$ [23].

In this paper we report the electrospray (ES) mass spectra of a wide range of π-hydrocarbon complexes of the general types $[\mathrm{FeCp}(\eta\text{-arene})]\mathrm{BF_4}$, $[\mathrm{M(CO)_3}(\eta\text{-}\mathrm{C_7H_7})]\mathrm{BF_4}$ (M = Cr, Mo, W), $[\mathrm{Fe(CO)_2L}(\eta^5\text{-dienyl})]\mathrm{BF_4}$ (L = CO or $\mathrm{PPh_3}$;dienyl = $\mathrm{C_6H_7}$, 2-$\mathrm{MeOC_6H_6}$, or $\mathrm{C_7H_9}$), $[\mathrm{CpFe(CO)_3}]\mathrm{PF_6}$, and $[\mathrm{CpFe(CO)_2}(\eta\text{-}\mathrm{C_2H_4})]\mathrm{BF_4}$, together with cationic phosphonium and imidazolium adducts formed with electrophilic cations of the type $[\mathrm{Fe(CO)_3}(\eta^5\text{-dienyl})]^+$ and $[\mathrm{CpFe(CO)_2}(\eta\text{-}\mathrm{C_2H_4})]^+$. In all cases strong principal (molecular) ions are observed for the intact cationic portion of these complexes. Fragmentation with loss of CO ligands is observed at relatively low skimmer voltages, while very high voltages are required for loss of π-hydrocarbon ligands. These electrospray (ES) data are compared with FAB and FD mass spectral data for similar compounds, showing ESMS to be the most convenient and informative of these soft ionization techniques.

2. Experimental

The electrospray mass spectra were obtained with a Fisons/VG Biotech Quattro (Altrincham, UK) mass spectrometer. This is a tandem mass spectrometer with quadrupoles for MS1 and MS2, each with a mass range of 4000 u for singly-charged ions, a hexapole collision cell, and photo-multiplier detectors. The salt to be studied was dissolved in acetonitrile (50–100 pmol $\mu\mathrm{l}^{-1}$). The solvent stream was 50% aqueous acetonitrile, delivered by an ISCO (Lincoln, NE, USA) SFC - 500 syringe pump at a flow rate of 5 μl min^{-1} and 10

Table 1
Electrospray (ES) mass spectral data for organometallic salts

Compound	Skimmer voltage (V)	Major ions in ESMS (m/z)
$[\mathrm{CpFe}(\eta\text{-}\mathrm{C_6H_6})]\mathrm{BF_4}$	20–50	$[\mathrm{M}]^+$ (199, 100%)
$[\mathrm{CpFe}(\eta\text{-}\mathrm{MeC_6H_5})]\mathrm{BF_4}$	20–50	$[\mathrm{M}]^+$ (213, 100%)
$[\mathrm{CpFe}(\eta\text{-}\mathrm{Me_3C_6H_3})]\mathrm{BF_4}$	20–50	$[\mathrm{M}]^+$ (241, 100%)
$[\mathrm{CpRh}(\eta^5\text{-}\mathrm{MeC_5H_4})]\mathrm{BF_4}$	50	$[\mathrm{M}]^+$ (246, 100%)
$[\mathrm{Cr(CO)_3}(\eta\text{-}\mathrm{C_7H_7})]\mathrm{BF_4}$	20	$[\mathrm{M}]^+$ (227, 100%), $[\mathrm{M{-}CO}]^+$ (199, 2%)
	45	$[\mathrm{M}]^+$ (227, 21%), $[\mathrm{M{-}CO}]^+$ (199, 100%), $[\mathrm{M{-}2CO}]^+$ (171, 91%), $[\mathrm{M{-}3CO}]^+$(143, 10%)
$[\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_7H_7})]\mathrm{BF_4}$ [a]	20	$[\mathrm{M}]^+$ (273, 100%), $[\mathrm{M{-}CO}]^+$ (245, 5%)
	45	$[\mathrm{M}]^+$ (273, 28%), $[\mathrm{M{-}CO}]^+$(245, 100%), $[\mathrm{M{-}2CO}]^+$ (217, 10%)
$[\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_7H_7})]\mathrm{BF_4}$ [a]	20	$[\mathrm{M}]^+$ (359, 100%).
	55	$[\mathrm{M}]^+$ (359, 26%), $[\mathrm{M{-}CO}]^+$(331, 100%), $[\mathrm{M{-}2CO}]^+$ (303, 12%)
$[\mathrm{CpFe(CO)_3}]\mathrm{PF_6}$	20	$[\mathrm{M}]^+$ (205, 100%).
	50	$[\mathrm{M}]^+$ (205, 25%), $[\mathrm{M{-}CO}]^+$(177, 100%), $[\mathrm{M{-}2CO}]^+$ (149, 46%), $[\mathrm{M{-}3CO}]^+$ (121, 5%)
$[\mathrm{CpFe(CO)_2}(\eta\text{-}\mathrm{C_2H_4})\mathrm{BF_4}]$	20	$[\mathrm{M}]^+$ (205, 100%)
	45	$[\mathrm{M}]^+$ (205, 10%), $[\mathrm{M{-}CO}]^+$ (177, 100%), $[\mathrm{M{-}2CO}]^+$ (149, 21%), $[\mathrm{M{-}2CO{-}C_2H_4}]^+$ (121, 1%)
$[\mathrm{Fe(CO)_3}(\eta^5\text{-}\mathrm{C_6H_7})]\mathrm{BF_4}$	18	$[\mathrm{M}]^+$ (219, 100%)
	40	$[\mathrm{M}]^+$ (219, 65%), $[\mathrm{M{-}CO}]^+$ (191, 100%), $[\mathrm{M{-}2CO}]^+$ (163, 50%), $[\mathrm{M{-}3CO}]^+$ (135, 45%)
$[\mathrm{Fe(CO)_3}(\eta^5\text{-2-}\mathrm{MeOC_6H_6})]\mathrm{PF_6}$	20	$[\mathrm{M}]^+$ (249, 100%), $[\mathrm{M{-}CO}]^+$ (221, 1%)
	50	$[\mathrm{M}]^+$ (249, 12%), $[\mathrm{M{-}CO}]^+$ (221, 100%), $[\mathrm{M{-}2CO}]^+$ (193, 93%), $[\mathrm{M{-}3CO}]^+$ (165, 77%)
$[\mathrm{Fe(CO)_3}(\eta^5\text{-}\mathrm{C_7H_9})]\mathrm{BF_4}$	20	$[\mathrm{M}]^+$ (233, 100%)
	50	$[\mathrm{M}]^+$ (233, 40%), $[\mathrm{M{-}CO}]^+$ (205, 100%), $[\mathrm{M{-}2CO}]^+$ (177, 55%)
$[\mathrm{Fe(CO)_2(PPh_3)}(\eta^5\text{-}\mathrm{C_6H_7})]\mathrm{BF_4}$	20	$[\mathrm{M}]^+$ (453, 100%)
	53	$[\mathrm{M}]^+$ (453, 22%), $[\mathrm{M{-}CO}]^+$ (425, 100%), $[\mathrm{M{-}2CO}]^+$ (397, 8%), $[\mathrm{O{=}PPh_3H}]^+$ (279, 3%)
$[\mathrm{Fe(CO)_2(PPh_3)}(\eta^5\text{-2-}\mathrm{MeOC_6H_6})]\mathrm{BF_4}$	20	$[\mathrm{M}]^+$ (483, 100%)
	53	$[\mathrm{M}]^+$ (483, 100%), $[\mathrm{M{-}CO}]^+$ (455, 38%), $[\mathrm{M{-}2CO}]^+$ (427, 2%), $[\mathrm{O{=}PPh_3H}]^+$ (279, 7%)

[a] Only the most abundant isotope listed. Intensities for the other metal isotopes were in agreement with natural abundance.

μl of the solution were injected for each analysis. Dry nitrogen gas at atmospheric pressure was employed to assist evaporation of the electrospray droplets. The electrospray probe tip potential was 3.5 kV, with 0.5 kV on the chicane counter electrode.

Skimmer voltages between 20 and 50 V were generally used, although higher voltages were employed (up to 130 V) to explore ligand fragmentation. The resolution was set to 1 u (width at half-heights), and a photomultiplier voltage of 650 V was employed. The mass spectrum was typically scanned at a rate of 1 s per 100 u. Data from 3–5 scans were summed to obtain representative spectra. FAB mass spectra were obtained with a VG 12-12 quadrupole mass analyser with a mass range of 1200 u for singly-charged ions and fitted with an Ion Tech fast atom gun. Xe was used for the fast atom beam (7 keV), and 1:1 dithioerithritol dithiothreitol for the matrix. The various organometallic complexes were prepared and purified by published procedures [28–34].

3. Results and discussion

3.1. ES mass spectra

The ES mass spectra obtained for each of the π-hydrocarbon metal complex salts are summarised in Table 1. At relatively low skimmer voltages (20–50 V), the only ions observed for the [CpFe(η-arene)]BF_4 and [CpRh(η^5-MeC_5H_4)]BF_4 salts are base $[M]^+$ peaks due to the intact principal (molecular) ions of the cationic components (e.g. Fig. 1(a)). This behaviour parallels that previously reported by Colton and Traeger [23] for the ferrocenium cation $[Cp_2Fe]^+$. The high thermodynamic stability of the M–Cp and M–arene bonds in these complexes is reflected in the fact that high skimmer voltages of between 80 and 135 V are required before fragmentation of the π-hydrocarbon complexes is noted (Fig. 1(b)).

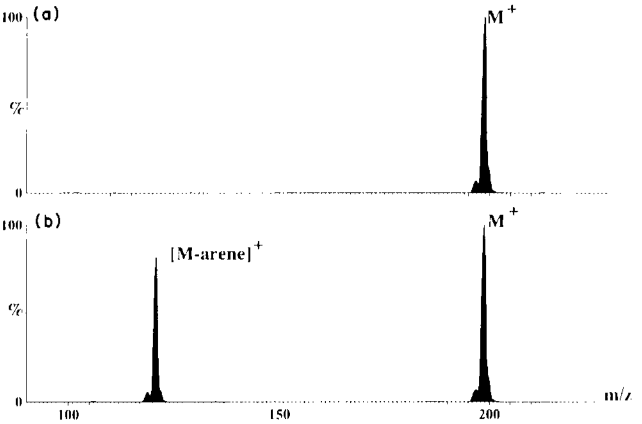

Fig. 1. Electrospray (ES) mass spectrum of [CpFe(η-C_6H_6)]BF_4 at a skimmer voltage of (a) 50 V; (b) 120 V.

Principal (molecular) ions are also the only observed ions at low skimmer voltage (20 V) for the other [(π-hydrocarbon)M$(CO)_2$L]$^+$ (L = CO, C_2H_4) cations examined here, namely [M$(CO)_3$(η-C_7H_7)]BF_4 (M = Cr, Mo, W), [CpFe$(CO)_2$L]BF_4 (L = CO,C_2H_4), and [Fe$(CO)_2$L(η^5-dienyl)]X (L = CO or PPh_3; dienyl = C_6H_7, 2-MeOC_6H_6, or C_7H_9; X = BF_4 or PF_6) (e.g. Fig. 2(a)). In a few cases, very weak (1–5% intensity) peaks are also observed for $[M-CO]^+$ ions. However, at moderate skimmer voltages (40–55 V), for each of these complexes the base peak corresponds to the $[M-CO]^+$ ion, indicating relatively facile loss of a CO

Table 2

Electrospray (ES) mass spectra of phosphonium and imidazolium adducts of organometallic cations

Adduct	Skimmer voltage (V)	Major ions in ESMS (m/z)
[Fe$(CO)_3$(η^4-C_6H_7.PPh_3)]BF_4	20	$[M]^+$ (481, 100%), $[PPh_3H]^+$ (263, 1%) $[M-PPh_3]^+$ (219, 1%)
	40	$[M]^+$ (481, 91%), $[M-PPh_3]^+$ (219, 100%), $[M-PPh_3-CO]^+$ (191, 2%) {weak peaks also at 341(C_6H_7.PPh_3^+), 279 (O=PPh_3H^+), and 263 (PPh_3H^+)}
[Fe$(CO)_3$(η^4-C_7H_9.PPh_3)]BF_4	20	$[M]^+$ (495, 100%)
	40	$[M]^+$ (495, 100%), $[M-CO]^+$ (467, 2%), $[M-PPh_3]^+$ (233, 70%), $[M-PPh_3-CO]^+$ (205, 1%), {weak peaks also at 355 (C_7H_9.PPh_3^+), 279(O=PPh_3H^+), and 263 (PPh_3H^+)}
[CpFe$(CO)_2$(η^1-C_2H_4.PPh_3)]BF_4	20	$[M]^+$ (467, 10%), $[M-PPh_3]^+$ (205, 100%)
	40	$[M]^+$ (467, 8%), $[M-PPh_3]^+$ (205, 40%), $[M-PPh_3-CO]^+$ (177, 100%), $[M-PPh_3-2CO]^+$ (149, 4%)
[Fe$(CO)_3$(η^4-C_6H_7.Im)]PF_6	20	$[M]^+$(287, 100%), $[M-Im]^+$ (219, 85%)
[Fe$(CO)_3$(η^4-C_6H_7.N-MeIm)]BF_4	20	$[M]^+$ (301, 100%), $[M-MeIm]^+$ (219, 80%), $[MeIm + H]^+$ (83, 73%)
[Fe$(CO)_3$(η^4-C_6H_7.2-MeIm)]BF_4	20	$[M]^+$ (301, 100%), $[M-MeIm]^+$ (219, 18%).
[Fe$(CO)_3$(η^4-2-MeOC_6H_6.Im)]PF_6	15	$[M]^+$ (331, 62%), $[M-Im]^+$ (249, 100%
[Fe$(CO)_3$(η^4-C_7H_9.Im)]BF_4	20	$[M]^+$ (301, 100%), [M–Im] (233, 92%), $[Im + H]^+$ (69, 11%)

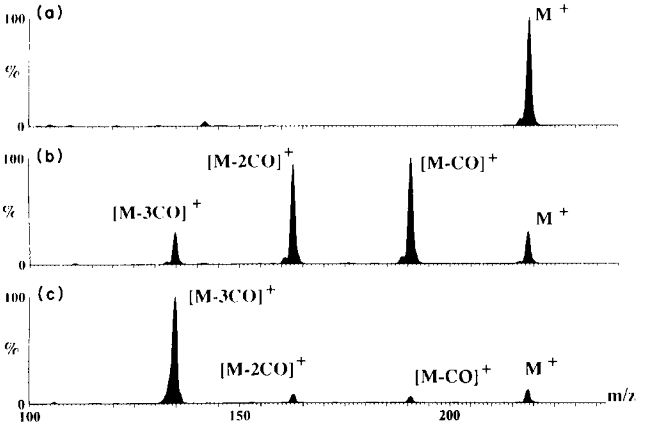

Fig. 2. Electrospray (ES) mass spectrum of $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]BF_4$ at a skimmer voltage of (a) 18 V; (b) 50 V; (c) 100 V.

ligand via collisional activation in the ion source. Progressively less intense ions are also noted for the corresponding $[M\text{–}2CO]^+$ and $[M\text{–}3CO]^+$ ions (Fig. 2(b)). Similar loss of CO ligands from organometallic complexes has been previously reported [23] in the ESMS of the cation trans-$[Cr(CO)_2(dpe)_2]^+$.

In the case of $[CpFe(CO)_2(\eta\text{-}C_2H_4)]BF_4$ at a skimmer voltage of 45 V, a very weak (1%) peak is also observed at m/z 121, corresponding to the $[M\text{–}2CO\text{–}C_2H_4]^+$ ion. Loss of the π-ethene ligand in this complex, in contrast to the fragmentational stability of the π-Cp, π-arene, π-C_7H_7 and π-dienyl ligands in the other complexes, is consistent with the reported [31] susceptibility of this cation towards ethene ligand substitution in solution.

Particularly interesting are the ES mass spectra shown in Table 2 for representative phosphonium and imidazolium ion adducts of the electrophilic cations $[Fe(CO)_3(\eta^5\text{-dienyl})]^+$ (dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9) and $[CpFe(CO)_2(\eta\text{-}C_2H_4)]^+$. At low skimmer voltages (20 V), each of the adduct species $[Fe(CO)_3(\eta^4\text{-diene.PPh}_3)]^+$ and $[Fe(CO)_3(\eta^4\text{-diene.Im})]^+$ generally exhibits a base (or very intense) peak for the intact principal (molecular) ion. For the various imidazole adducts, a further moderate-to-intense peak

Table 3
Fast atom bombardment (FAB) mass spectra for representative organometallic salts in Table 1

Compound	Major ions in FAB MS (+ve ion) (m/z)
$[CpFe(\eta\text{-}C_6H_6)]BF_4$ [a]	$[M+H]^+$ (200, 3%), $[M]^+$ (199, 30%)
$[CpFe(\eta\text{-}MeC_6H_5)]BF_4$	$[M+H]^+$ (214, 10%), $[M]^+$ (213, 100%)
$[CpFe(\eta\text{-}Me_3C_6H_3)]BF_4$	$[M+H]^+$ (242, 13%), $[M]^+$ (241, 89%)
$[Cr(CO)_3(\eta\text{-}C_7H_7)]BF_4$ [a]	$[M+H]^+$ (228, 8%), $[M]^+$ (227, 47%), $[M+H\text{–}CO]^+$ (200, 12%), $[M\text{–}CO]^+$ (199, 56%), $[M+H\text{-}2CO]^+$ (172, 10%), $[M\text{–}2CO]^+$ (171, 33%), $[M+H\text{–}3CO]^+$ (144, 9%), $[M\text{–}3CO]^+$ (143, 30%)
$[Mo(CO)_3(\eta\text{-}C_7H_7)]BF_4$ [a,b]	$[M]^+$ (273, 10%), $[M\text{–}CO]^+$ (245, 8%), $[M\text{–}2CO]^+$ (217, 3%)
$[W(CO)_3(\eta\text{-}C_7H_7)]BF_4$ [a,b]	$[M]^+$ (359, 16%), $[M\text{–}CO]^+$ (331, 8%), $[M\text{–}2CO]^+$ (303, 5%), $[M\text{–}3CO]^+$ (275, 2%)
$[CpFe(CO)_2(\eta\text{-}C_2H_4)]BF_4$	$[M]^+$ (205, 40%), $[M\text{–}CO]^+$ (177, 100%), $[M\text{–}2CO]^+$ (149, 28%), $[M\text{–}2CO\text{–}C_2H_4]^+$ (121, 67%)
$[Fe(CO)_3(\eta^5\text{-}C_6H_7)]BF_4$	$[M]^+$ (219, 28%), $[M\text{–}CO]^+$ (191, 43%), $[M\text{–}2CO]^+$ (163, 45%), $[M\text{–}3CO]^+$ (135, 80%)
$[Fe(CO)_3(\eta^5\text{-}2\text{-}MeOC_6H_6)]BF_4$	$[M]^+$ (249, 53%), $[M\text{–}CO]^+$ (221, 52%), $[M\text{–}2CO]^+$ (193, 47%), $[M\text{–}3CO]^+$ (165, 100%)
$[Fe(CO)_3(\eta^5\text{-}C_7H_9)]BF_4$ [a]	$[M]^+$ (233, 12%), $[M\text{–}CO]^+$ (205, 13%), $[M\text{–}2CO]^+$ (177, 16%)
$[Fe(CO)_3(\eta^4\text{-}C_6H_7.PPh_3)]BF_4$	$[M]^+$ (481, 2%), $[M\text{–}PPh_3]^+$ (219, 100%), $[M\text{–}PPh_3\text{–}CO]^+$ (191, 70%), $[M\text{–}PPh_3\text{–}2CO]^+$ (163, 82%), $[M\text{–}PPh_3\text{–}3CO]^+$ (135, 50%) {peaks also at m/z 279 ($O{=}PPh_3H^+$) and 263 (PPh_3H^+)}
$[Fe(CO)_3(\eta^4\text{-}C_7H_9.PPh_3)]BF_4$	$[M]^+$ (495, 2%), $[M\text{–}PPh_3]^+$ (233, 86%), $[M\text{–}PPh_3\text{–}CO]^+$ (205, 76%), $[M\text{–}PPh_3\text{–} 2CO]^+$ (177, 100%), $[M\text{–}PPh_3\text{–}3CO]^+$ (149, 27%) {weak peaks also at m/z 355 ($C_7H_9.PPh_3^+$), 279 ($O{=}PPh_3H^+$) and 263 (PPh_3H^+)}
$[CpFe(CO)_2(\eta^1\text{-}C_2H_4.PPh_3)]BF_4$	$[M\text{–}PPh_3]^+$ (205, 95%), $[M\text{–}PPh_3\text{–}CO]^+$ (177, 100%), $[M\text{–}PPh_3\text{–}2CO]^+$ (149, 49%)
$[Fe(CO)_3(\eta^4\text{-}C_6H_7.N\text{-}MeIm)]BF_4$	$[M\text{–}MeIm]^+$ (219, 100%), $[M\text{–}MeIm\text{–}CO]^+$ (191, 68%), $[M\text{–}MeIm\text{–}2CO]^+$ (163, 55%), $[Me\text{–}MeIm\text{–}3CO]^+$ (135, 67%)
$[Fe(CO)_3(\eta^4\text{-}C_7H_9.Im)]BF_4$	$[M\text{–}Im]^+$ (233, 100%), $[M\text{–}Im\text{–}CO]^+$ (205, 51%), $[M\text{–}Im\text{–}2CO]^+$ (177, 52%), $[M\text{–}Im\text{–}3CO]^+$ (149, 8%)

[a] Base peak is from matrix.
[b] Only the most abundant isotope listed.

is observed at low skimmer voltages corresponding to the [M–Im]$^+$ ions, indicating relatively facile loss of the imidazole nucleophile from the diene ring (e.g. Fig. 3(a)). Similar behaviour is shown by each of the phosphonium adducts in Table 2.

At moderate skimmer voltages (40–50 V) the base peak for each of the phosphonium adducts is the associated [M–PPh$_3$]$^+$ ion arising from loss of PPh$_3$. Minor CO loss also occurs via collision activation in the source, as shown by the presence of weak (1–2%) [M–CO]$^+$ and [M–PPh$_3$–CO]$^+$ ions. Weak peaks corresponding to the free phosphonium ions (e.g.[C$_6$H$_7$.PPh$_3$]$^+$ at *m/z* 341) are also observed (Table 2) in the ESMS of the phosphonium adducts at low skimmer voltages, as well as minor peaks due to the protonated free phosphine and phosphine oxide (e.g. [PPh$_3$H]$^+$ and [O=PPh$_3$H]$^+$ at *m/z* 263 and 279, respectively). Formation of phosphine oxide from phosphine ligands has been previously reported [21] in the ESMS of some coordination complex cations, and was believed to occur within the ion source.

3.2. Dependence of ESMS on skimmer potential

Comparison of the ES mass spectra of representative π-hydrocarbon metal complexes over a range of skimmer voltages shows the expected increase in fragmentation with increasing potential. For example, while only the principal (molecular) ion is observed for the [CpFe(η-arene)]$^+$ cations at low or moderate skimmer voltages (20–80 V) (Fig. 1(a)), at higher voltages substantial loss of the π-arene ligands occurs. [M-arene]$^+$ ions dominate for voltages greater than 120 V (Fig. 1(b)).

Fragmentational loss of CO ligands from [M(CO)$_2$L(π-hydrocarbon)]$^+$ cations is also much more significant at higher skimmer voltages (e.g. Figs. 2(b), 2(c) and Fig. 3(b)). Most striking in this respect is the facile loss of the phosphine and imidazole groups from the associated adducts at higher skimmer voltages (Fig. 3(b)). While the principal (molecular) ions for the intact adducts dominate at low potentials (20–40 V), at higher skimmer voltages (> 60 V) only ions associated with ligand fragmentation are observed.

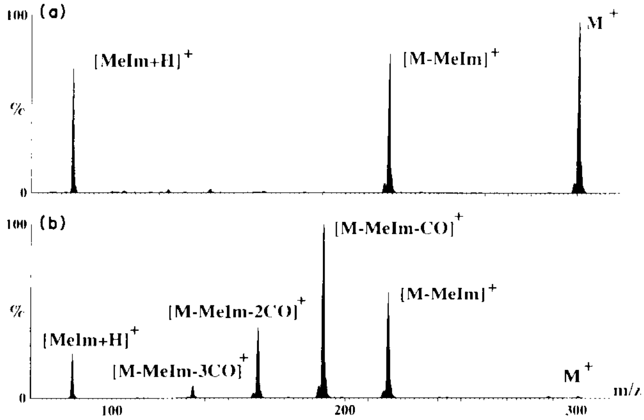

Fig. 3. Electrospray (ES) mass spectrum of [Fe(CO)$_3$(η^4-C$_6$H$_7$.N-Me Im)]BF$_4$ at a skimmer voltage of (a) 20 V; (b) 50 V.

3.3. Comparison of ESMS with FAB and FD mass spectra

In order to compare quantitatively the efficacy of ES and FAB mass spectrometry for such π-hydrocarbon organometallic salts, the FAB mass spectra of representative compounds were also recorded (Table 3) (in most cases we have also previously measured their FD mass spectra [1]).

Comparison of the results in Tables 1–3 shows considerable similarities between the ES and FAB mass spectra of these organometallic cations. For example, with the [CpFe(η-arene)]$^+$ species, the most intense peak using each technique arises from the intact [M]$^+$ ion. However, in the FAB-MS weak-to-moderate intensity peaks are also observed for associated [M + H]$^+$ ions.

Moderate intensity [M]$^+$ ions are again observed in FAB-MS of the [M(CO)$_2$L(π-hydrocarbon)]$^+$ complexes, together with substantial fragmentation arising from CO loss, which parallels the above ES mass spectral behaviour. However, the most striking difference between the ES and FAB mass spectra is observed for the phosphonium adducts [Fe(CO)$_3$(diene.PPh$_3$)]$^+$(diene = C$_6$H$_7$, C$_7$H$_9$); whereas, the ES mass spectra exhibit base peaks associated with the intact adducts (Table 2), only very weak molecular [M]$^+$ peaks (ca. 2% intensity) are observed in their FAB mass spectra. Much more extensive CO fragmentation is also apparent in the FAB-MS of these phosphonium adducts, as well as intense [M-PPh$_3$]$^+$ peaks.

The above results indicate that for π-hydrocarbon metal complex cations of the type examined here, electrospray (ES) mass spectrometry is a softer ionization technique than FAB-MS. Comparison with our earlier field desorption (FD) mass spectral studies [1] of the same salts indicates that fragmentation decreases along the series FAB > ES > FD. Overall, we consider electrospray (ES) to be the most convenient and informative of the three soft ionization techniques for such involatile salts. Not only is it generally possible to observe strong peaks associated with the principal (molecular ions), but also by employing increasingly higher skimmer voltages one can observe substantial fragmentation of value in structure elucidation.

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