

FIELD DESORPTION MASS SPECTRA OF $[M(\text{CO})_3(\eta\text{-ARENE})]\text{X}$ ($M = \text{Mn}$, Re ; $\text{X} = \text{BF}_4$, PF_6) SALTS

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Summary

Field desorption mass spectra are reported for a range of $[M(\text{CO})_3(\eta\text{-arene})]\text{X}$ ($M = \text{Mn}$ or Re , $\text{X} = \text{BF}_4$ or PF_6) salts. In most cases the spectra are simple, being dominated by molecular, $[M]^+$, $[M + 1]^+$, and $[M - \text{CO}]^+$ ions for the cationic part of their structure. However, with the π -chloroarene complexes $[\text{Mn}(\text{CO})_3(\eta\text{-ClC}_6\text{H}_5)]\text{PF}_6$ and $[\text{Mn}(\text{CO})_3(\eta\text{-1-Cl, 4-MeC}_6\text{H}_4)]\text{PF}_6$, facile loss of the chloro substituent and further fragmentation leads to unusually complex spectra, which include strong peaks arising from recombination of fragment species. Cluster ions are also noted in several cases, allowing identification of the anion.

Introduction

In recent studies we [1–4] and others [5,6] have established the utility of field desorption (f.d.) mass spectrometry in characterising cationic π -hydrocarbon organometallic complexes. These involatile salts are unsuitable for conventional electron impact (e.i.) mass spectrometry. The f.d. mass spectra of $[M(\text{CO})_3(\pi\text{-hydrocarbon})]\text{BF}_4$ species were noteworthy for their absence of major fragmentation, being generally dominated by molecular $[M]^+$, $[M + 1]^+$, and $[M - \text{CO}]^+$ ions for the cationic portion of their structure. As an extension of these studies, we report here f.d. mass spectra for a range of $[M(\text{CO})_3(\eta\text{-arene})]\text{X}$ ($M = \text{Mn}$ or Re ; $\text{X} = \text{BF}_4$ or PF_6) complexes. Of particular interest are the chloroarene compounds, which reveal for the first time extensive fragmentation of the π -hydrocarbon ligand.

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Experimental

The $[\text{Mn}(\text{CO})_3(\eta\text{-arene})]\text{BF}_4$ (or PF_6) salts were prepared and purified using published procedures [7,8]. The related rhenium complexes were synthesized by a recently reported improved route [9]. Solutions of the complexes in acetone were loaded onto benzonitrile-activated tungsten emitters using a 5 μl syringe. The time between sample loading and insertion of the f.d. probe into the mass spectrometer was minimized (ca. 30 sec) for the rhenium species to avoid nucleophilic displacement [9] of the π -arene by acetone. F.d. mass spectra were recorded using a combined f.d. — f.i. — e.i. source on a Varian CH5D mass spectrometer linked to a Varian SS100 data system. The source temperature was 80°C, and emitter currents of up to 23 mA were employed to desorb each of the cations. Spectra were recorded over a mass range up to 1200, with a resolution (10% valley) of approximately 1,000.

Results and discussion

Typical f.d. mass spectra for the various π -hydrocarbon organometallic salts are summarised in Table 1. As with other $[\text{M}(\text{CO})_3(\pi\text{-hydrocarbon})]\text{BF}_4$ species investigated to date [1–4,6], the spectra of the benzene and alkyl-substituted benzene complexes are dominated by molecular, $[\text{M}]^{++}$, $[\text{M} + 1]^+$, and $[\text{M} - \text{CO}]^+$ ions for the cationic part of their structure. The base peaks usually correspond to the molecular $[\text{M}]^{++}$ ions, although with $[\text{Mn}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]\text{BF}_4$ the most abundant ion is that due to the $[\text{M} - \text{CO}]^+$ species.

Also in keeping with previous studies of related organometallic salts is the

TABLE 1
FIELD DESORPTION MASS SPECTRA OF $[(\pi\text{-HYDROCARBON})\text{M}(\text{CO})_3]\text{BF}_4$ (OR PF_6) SALTS

No.	Complex	<i>M</i>	<i>m/z</i> (% rel. int.)
I	$[(\eta\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]\text{BF}_4$	217	522(28), 521(100), 520(25), 218(12), 217(40), 189(14), 79(10)
II	$[(\eta\text{-MeC}_6\text{H}_5)\text{Mn}(\text{CO})_3]\text{BF}_4$	231	549(1), 548(0.5), 233(5), 232(35), 231(100), 204(0.5)
III	$[(\eta\text{-1,4-Me}_2\text{C}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{BF}_4$	245	247(6), 246(16), 245(100), 231(5), 217(8)
IV	$[(\eta\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)\text{Mn}(\text{CO})_3]\text{BF}_4$	259	260(5), 259(7), 233(5), 232(13), 231(100), 203(9), 190(4), 121(8), 120(41)
V	$[(\eta\text{-ClC}_6\text{H}_5)\text{Mn}(\text{CO})_3]\text{PF}_6$	251	293(3), 254(8), 253(56), 252(9), 251(100), 218(8), 217(64), 112(2)
VI	$[(\eta\text{-1-Cl,4-MeC}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{PF}_6$	265	359(3), 358(7), 357(33), 356(20), 355(100), 329(1), 327(2), 326(2), 325(12), 323(2), 322(10), 321(49), 316(1), 315(5), 313(5), 268(3), 267(28), 266(7), 265(64), 232(2), 231(14), 139(2)
VII	$[(\eta\text{-MeC}_6\text{H}_5)\text{Re}(\text{CO})_3]\text{PF}_6$	362	365(6), 364(45), 363(100), 362(36), 361(92)
VIII	$[(\eta\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)\text{Re}(\text{CO})_3]\text{PF}_6$	391	393(3), 392(8), 391(100), 390(8), 389(50), 379(1), 378(5), 377(19), 376(2), 375(18), 120(16)
IX	$[(1\text{-}\eta\text{-C}_6\text{H}_7)\text{Os}(\text{CO})_3]\text{BF}_4$	355	356(37), 355(100), 354(23), 353(50), 352(53), 351(20), 323(10)

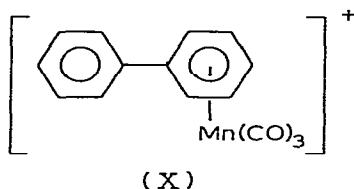
absence of major fragmentation. Loss of only one CO ligand is generally observed for the manganese complexes, and no CO loss is noted at all in the corresponding rhenium species. Interestingly, the weak peak at m/z 203 in the spectrum of $[\text{Mn}(\text{CO})_3(\eta\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]\text{PF}_6$ represents the first observation of a $[M - 2\text{CO}]^+$ ion in the f.d. mass spectra of tricarbonyl (π -hydrocarbon) metal salts.

The source of the weak peak in this spectrum at m/z 190 is unknown, although it may possibly be associated with a $[M - 2\text{CO} - \text{Me} + 1]^+$ species. Fragmentational loss of a methyl substituent is also suggested in the related $[\text{Mn}(\text{CO})_3(\eta\text{-}1,4\text{-Me}_2\text{C}_6\text{H}_4)]\text{BF}_4$ salt, where a weak peak corresponding to $[M - \text{Me}]^+$ was observed at m/z 231. The group of peaks between m/z 375 and 379 in the spectrum of $[\text{Re}(\text{CO})_3(\eta\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]\text{PF}_6$ may also be ascribed to $[M - \text{Me}]^+$ and $[M - \text{Me} + 1]^+$ ions. However, in view of the low abundance of these apparent methyl-fragmentation ions, it is possible that they arise from small amounts of arene impurities.

With the $[\text{M}(\text{CO})_3(\eta\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]\text{PF}_6$ ($M = \text{Mn}, \text{Re}$) complexes, loss of the π -hydrocarbon ligand was also noted, moderately abundant peaks appearing at m/z 120 corresponding to the [mesitylene] $^+$ ion. Similarly, a weak peak at m/z 79 in the spectrum of $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]\text{BF}_4$ is attributed to the [benzene + 1] $^+$ ion.

Another interesting feature is cluster ion formation in the spectra of $[\text{Mn}(\text{CO})_3(\eta\text{-arene})]\text{BF}_4$ (arene = C_6H_6 and MeC_6H_5). For example, the base peak at m/z 521 in the spectrum of the benzene salt corresponds to the cluster ion, $[\text{M}_2\text{BF}_4]^+$. The f.d. mass spectrum of $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]\text{BF}_4$ has been previously reported by Bursey et al. [6]. However, they observed only a molecular, $[M]^+$, ion for this salt.

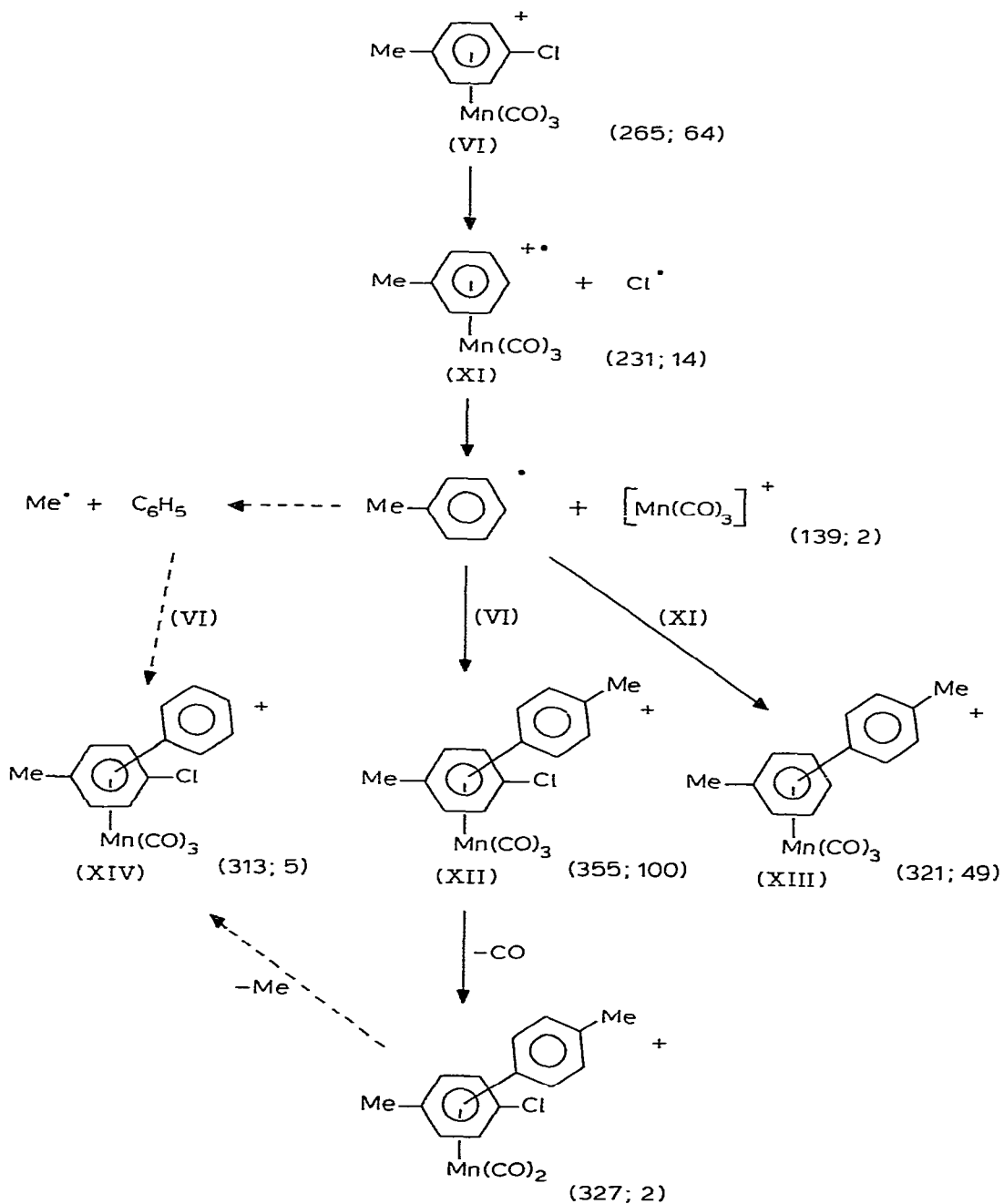
In contrast to the above results and our previous experience with other organometallic salts, the f.d. mass spectra for the chloro-arene tricarbonyl manganese complexes (V) and (VI) reveal extensive fragmentation of the hydrocarbon ligand. With the chlorobenzene complex, the base peak at m/z 251 corresponds to the molecular, $[M]^+$ ion for the cationic part of the molecule. However, an intense peak is also observed at m/z 217 associated with loss of the chloro substituent. Interestingly, a weak peak is also found at m/z 293, which may be attributed to the species X formed via combination of fragmentation products. No ions associated with CO ligand loss are observed for the chlorobenzene salt. However, a small amount of π -hydrocarbon loss is confirmed by the presence of a weak peak at m/z 112.



The f.d. mass spectrum of $[\text{Mn}(\text{CO})_3(\eta\text{-}1\text{-Cl},4\text{-MeC}_6\text{H}_4)]\text{PF}_6$ (VI) is quite complex, indicating even more extensive fragmentation of the π -hydrocarbon ligand. A strong molecular, $[M]^+$, ion for the cationic part of the molecule is observed at m/z 265. However, the base peak is at m/z 355. We assign this to

the species (XII; ^{35}Cl) produced via reaction of the molecular $[M]^{+\bullet}$ ion with a toluene radical fragment formed as shown in Scheme 1. Initial loss of the chloro substituent from $[\text{Mn}(\text{CO})_3(\eta\text{-1-Cl, 4-MeC}_6\text{H}_4)]\text{PF}_6$ to produce (XI) is

SCHEME 1
(values in brackets are m/z and % rel. int.)



confirmed by the presence of a weak peak at m/z 231. Support for subsequent fragmentation of a toluene radical from XI comes from the weak peak at m/z 139 attributable to $[\text{Mn}(\text{CO})_3]^+$. A further moderate intensity peak at m/z 321 may be similarly assigned to the ion XIII formed by recombination of XI with a toluene radical (see Scheme 1).

No ions associated with CO ligand loss from the molecular ion are observed in the spectrum of VI. However, CO fragmentation from the base peak ion XII is noted as evidence by the weak peak at m/z 327. Another minor fragmentation path involves loss of a methyl substituent, the weak peak at m/z 313 being attributable to the species XIV. Some possible fragmentation routes to this latter ion are outlined in Scheme 1.

Other significant peaks observed in the spectrum of VI are those associated with $[\text{C} + 1]^+$ and $[\text{C} + 2]^+$ ions (where C is a molecular or fragment ion), and species containing the ^{37}Cl isotope. Spectra varied somewhat with the emitter current employed. Interestingly, in one case a series of weak peaks were seen between m/z 675 and 677, arising from the cluster ion $[2\text{M.PF}_6]^+$.

Finally, the f.d. mass spectrum of $[\text{Os}(\text{CO})_3(1-5-\eta\text{-C}_6\text{H}_7)]\text{BF}_4$ (IX) in Table 1 shows features similar to those previously observed [1] for a range of related tricarbonyl (1-5- η -dienyl) iron cations. The base peak at m/z 355 corresponds to the molecular, $[\text{M}]^+$, ion for the cationic portion of the molecule. The other moderate intensity peaks grouped between m/z 351 and 356 arise from the various osmium isotopes and from $[\text{M} + 1]^+$ ions. A relatively weak peak (m/z 323) is also observed for the $[\text{M} - \text{CO}]^+$ species.

The above results, taken together with earlier observations, confirm that $[\text{M}(\text{CO})_3(\pi\text{-hydrocarbon})]\text{BF}_4$ (or PF_6) salts generally yield simple f.d. mass spectra in which $[\text{M}]^+$, $[\text{M} + 1]^+$, and $[\text{M} - \text{CO}]^+$ ions generally predominate. Little other fragmentation is usually observed, making this technique useful for rapid salt identification. However, in the case of chloroarene π -complexes facile loss of the chloro-substituent and further fragmentation can lead to quite complex spectra in which the base peaks can arise from recombination of fragment species.

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