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FAST ATOM BOMBARDMENT MASS SPECTROMETRY AS A TECHNIQUE FOR STUDYING SOLUTION REACTIONS OF ALLYL-MOLYBDENUM AND -TUNGSTEN DERIVATIVES

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Summary

The fast atom bombardment (FAB) positive ion mass spectra of preformed complexes of the types $[MCl(CO)_2(\eta^3\text{-allyl})L_2]$ and $[M(CO)_2(\eta^3\text{-allyl})L_3]AX_n$ (M = Mo or W, $AX_n^- = BF_4^-$ or PF_6^-) exhibit the same metal ion fragmentation patterns as spectra produced from a glycerol matrix of $[MCl(CO)_2(\eta^3\text{-allyl})(NCMe)_2]$ doped with the appropriate ligands. In the absence of added ligands, these nitrile complexes yield $[(CO)_2(\eta^3\text{-allyl})(\text{glycerol})]^+$ as the strongest metal ion species with no evidence of metal–MeCN or metal–chloro containing ions. Thus mass spectral measurements on these organometallics reflect closely the known solution behaviour of the molybdenum complexes in hydroxylic solvents, and indicate that this technique may provide a valuable aid in studying certain solution reactions, particularly where only small quantities of reactants are available.

Introduction

Since the first description of the FAB technique for obtaining spectral data from polar and thermally labile molecules [1], several publications have been devoted to the application of this new technique to organometallic compounds [2]. Compared to the electron impact method of ionisation, FAB provides a relatively soft method of ionisation, but unlike other soft ionisation techniques, it often gives both molecular ion and fragmentation data. In order to obtain stable spectra from non-volatile samples, glycerol is frequently used as a matrix liquid on the probe-tip, although for hydrolytically unstable organometallics a non-hydroxylic material is preferred. To date FAB mass spectrometry has been used almost exclusively to characterise preformed ionic and covalent organometallics. However, in this paper we demonstrate that reactions in the liquid matrix can be followed by this technique and used to demonstrate some of the characteristic chemical properties of certain organometallic derivatives. Thus in suitable systems, information on bulk solution species can

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be deduced by this simple and quick technique which can be applied to exceedingly small quantities of material.

Results and discussion

In recent investigations, it has been shown that the solution behaviour of complexes of the type $[MX(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (M = Mo or W; X = halide and R = H or Me) is metal, halide, and solvent dependent [3]. In non-polar aprotic solvents, dissolution of the molybdenum complex (R = H, X = Cl) yields the salt $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_3]^+ [Mo_2(CO)_4(\eta^3\text{-}C_3H_5)_2Cl_3]^-$ which has been isolated and characterised crystallographically [4].

In methanol or water there is strong spectroscopic evidence that the same starting material yields solvated cationic molybdenum species which still contain the $Mo(CO)_2(\eta^3\text{-}C_3H_5)$ moiety [5], and as these solutions are catalytically active [6], we were interested in any technique which might allow us to further probe the nature and reactivity of alcoholic solutions of these and related materials.

On mixing $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (R = H (I) or Me (II)) with glycerol, yellow moderately air stable mulls were formed which yielded very stable positive ion spectra. Several molybdenum containing species were apparent from the metal isotope pattern, the most abundant ion corresponding to $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)\text{glycerol}]^+$ (Table 1 and Fig. 1). Weaker peaks caused by loss of one and two carbonyl groups from this ion were also observed, together with traces of $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(\text{glycerol})_x]^+$, where $x = 2$–4. No nitrile- or halogen-containing species could be detected in the spectrum of either complex. Traces of Mo_2 containing species were identified as $[Mo_2(CO)_4(C_3H_4R)_2(\text{glycerol-H})]^+$ and $[Mo_2(CO)_4(C_3H_4R)_2(2\text{glycerol-H})]^+$ by computer simulation of isotopic patterns. Pretreatment of the glycerol mull with methanol or benzyl alcohol tended to reduce but not eliminate peaks due to these binuclear species, but caused no other significant changes in the spectra.

As the behaviour of I or II in glycerol, as revealed by mass spectrometry, appears to closely parallel the solution behaviour of these complexes in methanol [5], it seemed worth exploring the possibility of investigating some of the chemical reactions of these substrates in the matrix. To this end we have recorded the FAB mass spectra of several neutral and cationic $Mo(CO)_2(\eta^3\text{-}C_3H_4R)$ containing complexes and where possible have compared their spectra with those from the glycerol matrix doped with $[MoCl(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ and the appropriate reactant needed to generate the complex under normal reaction conditions in hydroxylic solvents [5]. Without exception we have found that very similar spectra are produced whether the preformed complex, or intimate mixture of the reactants in glycerol are used to generate the spectra. Thus $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)L_2]$ (L_2 = 2py (III) or bipy (IV)) yield not only $(M - Cl)^+$ and related fragments, but also ions due to replacement of the nitrogen bases and chloride ligands by glycerol (Table 1). The same metal-containing ions were obtained from a mixture of I and the appropriate ligand in glycerol. Similarly, a mixture of diethylenetriamine (dien) or bis(2-pyridylmethyl)amine (bpma) with I in glycerol reproduced the metal ion spectral features of the preformed cationic species $[Mo(CO)_2(\eta^3\text{-}C_3H_5)L_3]^+$ (where L_3 = dien (VII) or bmpa (VIII)) (Fig. 1). No replacement of the tridentate ligand with glycerol was apparent in these cases.

TABLE 1

FAB POSITIVE ION MASS SPECTRA OF ALLYL-MOLYBDENUM AND -TUNGSTEN DERIVATIVES [a] (GLYCEROL MATRIX)

Complex		m/z relative abundance and assignment [b]
$MoCl(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2$	(I)	569, 4.3, (A_2 + 2glycerol − H); 477, 3.0, (A_2 + glycerol-H); 379, 8.9, (A + 2glycerol); 287, 100, (A + glycerol); 259, 11.1 (A + glycerol − CO); 231, 16.9 (A + glycerol − 2CO).
$MoCl(CO)_2(\eta^3\text{-}C_3H_4Me)(NCMe)_2$	(II)	597, 4.3, (A_2 + 2glycerol − H); 577, 1.0, (A + 4glycerol); 505, 5.6, (A_2 + glycerol − H); 485, 3.5, (A + 3glycerol); 393, 20.1, (A + 2glycerol); 301, 100, (A + glycerol); 273, 12.0, (A + glycerol − CO); 245, 21.0, (A + glycerol − 2CO).
$MoCl(CO)_2(\eta^3\text{-}C_3H_5)py_2$	(III)	379, 24.2, (A + 2glycerol); 366, 2.9, (M + glycerol − Cl); 353, 2.1, (M − Cl); 287, 60.6, (A + glycerol); 274, 1.4, (M − Cl − py); 259, 5.0, (A + glycerol − CO); 231, 5.3, (A + glycerol − 2CO).
$MoCl(CO)_2(\eta^3\text{-}C_3H_5)$bipy	(IV)	535, 0.7, (M + 2glycerol − Cl); 443, 2.8, (M + glycerol − Cl); 351, 11.5, (M − Cl); 323, 3.3, (M − Cl − CO); 295, 4.5, (M − Cl − 2CO).
$[Mo(CO)_2(\eta^3\text{-}C_3H_5)$(bipy)py]$BF_4$	(V)	44.3, 38.6, (M + glycerol − py); 351, 100, (M − py); 295, 59.8, (M − py − 2CO).
$[Mo(CO)_2(\eta^3\text{-}C_3H_5)$(bipy)$P(OMe)_3]BF_4$	(VI)	527, 15.7, (M + glycerol − C_3H_4); 495, 16.3, (M + glycerol − C_3H_4 − CH_3OH); 475, 71.5, (M); 447, 100, (M − CO); 435, 61.8, (M − C_3H_4); 403, 20.5; (M − C_3H_4 − CH_3OH); 351, 29.2, (M − $P(OMe)_3$); 295, 50.0, (M − $P(OMe)_3$ − 2CO).
$[Mo(CO)_2(\eta^3\text{-}C_3H_5)$dien]$PF_6$	(VII)	390, 6.7, (M + glycerol); 298, 100, (M); 270, 17.3, (M − CO); 242, 10.6, (M − 2CO).
$[Mo(CO)_2(\eta^3\text{-}C_3H_5)$bpma]$PF_6$	(VIII)	492, 10.7, (M + glycerol); 394, 100, (M); 366, 10.0 (M − CO); 338, 13.0, (M − 2CO); 296, 14.7, (M − 2CO − C_3H_6).
$WCl(CO)_2(\eta^3\text{-}C_3H_4Me)(NCMe)_2$	(IX)	663, 2.9, (A + 4glycerol); 571, 6.4, (A + 3glycerol); 479, 33.9, (A + 2glycerol); 387, 100, (A + glycerol); 359, 17.3, (A + glycerol − CO); 331, 15.1, (A + glycerol − 2CO).
$[W(CO)_2(\eta^3\text{-}C_3H_4Me)$dien]$BF_4$	(X)	582, 5.4, (M + 2glycerol); 490, 16.1, (M + glycerol); 398, 100, (M); 342, 18.0, (M + glycerol − 2CO).
$[W(CO)_2(\eta^3\text{-}C_3H_4Me)$bpma]$BF_4$	(XI)	494, 5.7, (M); 438, 1.7, (M − 2CO).

[a] Based on the most intense peak of the M_n containing fragment i.e. 98 for Mo; 192 for Mo_2 and 184 for W. [b] A represents the $M(CO)_2$(allyl) moiety whereas M corresponds to m/z of the cation or of the neutral molecule.

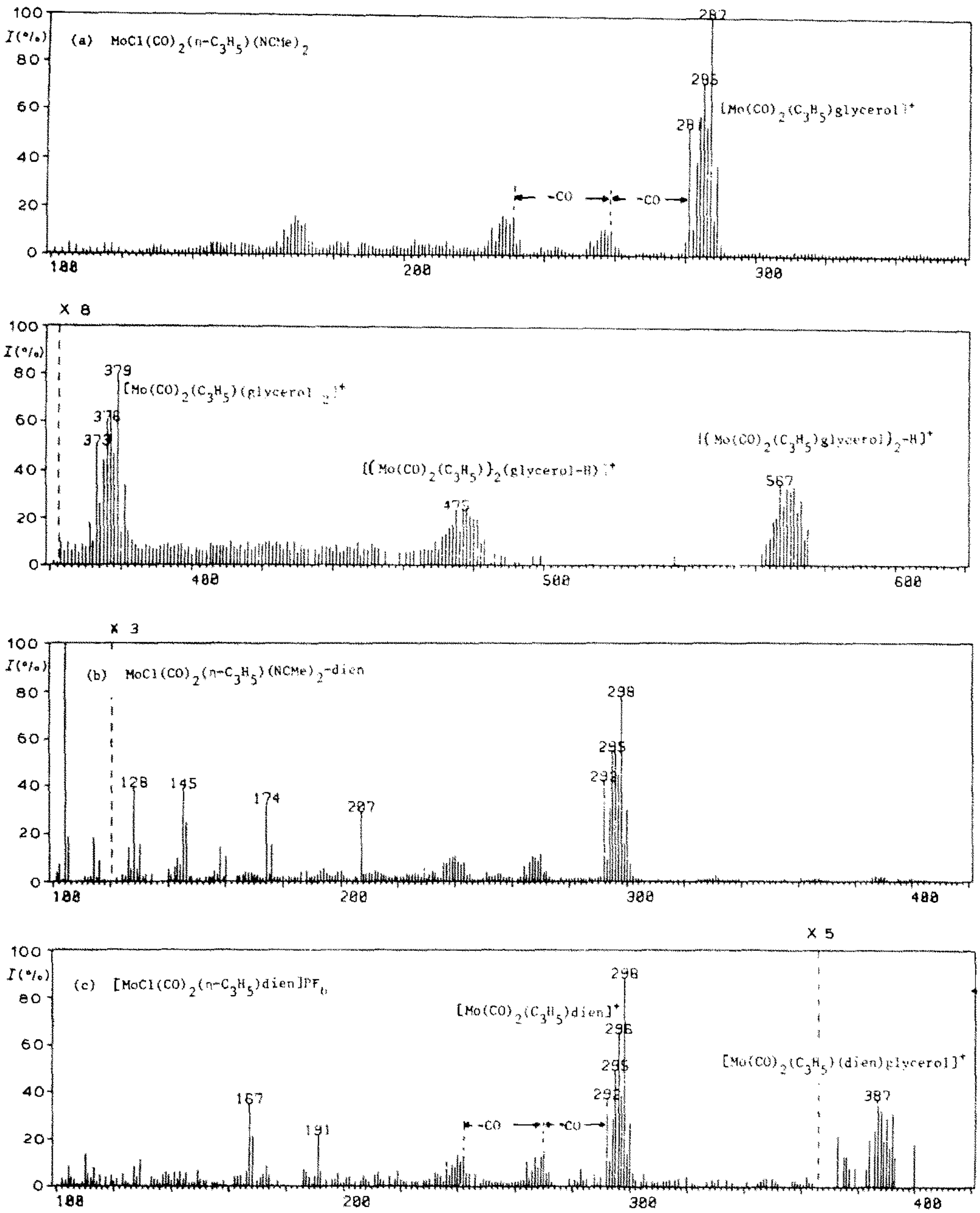

Fig. 1. FAB mass spectra of selected molybdenum complexes.

The two cationic molybdenum complexes [Mo(CO)$_2$(η^3-C$_3$H$_5$)(bipy)L]BF$_4$ (where L = py (V) or P(OMe)$_3$ (VI)) produced completely different fragmentation patterns. Major fragments for complex V corresponded to loss of pyridine and CO, whereas for complex VI loss of C$_3$H$_4$, presumably from the allyl group, proved to be a facile alternative to CO loss. This latter process was insignificant for the other seven allyl-molybdenum complexes examined.

It was noticeable that stronger FAB spectra were obtained for the cationic species than for the neutral species. This does not seem to be dependent a priori on the ligand combination but is related to the solubility of the complex in the glycerol matrix. Thus $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)L']^+$ ($L' = py$ (V) or $P(OMe)_3$ (VI)) which were glycerol soluble produced very much stronger spectra than the neutral complexes III or IV which are much less soluble, and no significant metal ion containing species were observed in the FAB spectrum of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)]$ which has a very low solubility in alcohols.

To date, no data has been published on the ionisation of $[WCl(CO)_2(\eta^3\text{-}C_3H_4Me)(NCMe)_2]$ (IX) in hydroxylic solvents, but the FAB spectrum of IX in glycerol was very similar to the spectrum of the molybdenum analogue II. Thus a strong $[W(CO)_2(\eta^3\text{-}C_3H_4Me)glycerol]^+$ peak together with weaker signals caused by loss of one or two CO ligands from this ion were observed, but although $[W(CO)_2(\eta^3\text{-}C_3H_4R)(glycerol)_x]^+$ ($x = 2$–4) ions were weakly present in the spectrum, binuclear species were almost entirely absent unless the sample was pretreated with methanol, when $[W_2(CO)_4(C_3H_4Me)_2(glycerol\text{-}H)]^+$ became noticeable. Again mixtures of IX and dien or bmpa gave the same metal ion species in their mass spectra as the preformed complexes $[W(CO)_2(\eta^3\text{-}C_3H_4Me)dien]BF_4$ (X) and $[W(CO)_2(\eta^3\text{-}C_3H_4Me)bmpa]BF_4$ (XI).

Attempts to obtain metal-containing negative ion spectra from I, II or IX in glycerol matrices were completely unsuccessful, confirming our beliefs, based on NMR evidence for I and II, that in neutral hydroxylic solvents, metal–cation rather than –anion formation is strongly favoured for these substrates.

Conclusions

It is well known that SIMS spectra incorporate features caused by ion-neutral association reactions occurring in selvedge (the region of relatively high pressure just above the surface), as well as direct sputtering of charged species [7]. Thus some of the cationised molybdenum molecules observed in our FAB spectra are likely to result from reactions in this region. Nevertheless, these metal ions appear to be simply related to, and diagnostic of, the bulk solution species, and FAB mass spectrometry should therefore provide a valuable aid in studying solution reactions in a suitable liquid matrix.

Experimental

Starting materials. The neutral (η^3-allyl)dicarbonylmolybdenum and -tungsten(II) complexes were prepared by standard literature procedures [8–10], as were the cationic complexes $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)py]BF_4$ [11], $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)L_3]PF_6$ ($R = H$ or Me; $L_3 =$ dien or bpma) [5], and $[W(CO)_2(\eta^3\text{-}C_3H_4Me)dien]BF_4$ [12].

Physical measurements. The FAB mass spectra were recorded on a V.G. 70-70E mass spectrometer and DS 2025 data system, using Xenon as the fast atom beam.

Preparation of $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)P(OMe)_3]BF_4$ (VI)

Silver tetrafluoroborate (0.21 g, 1.0 mmol) was stirred at room temperature under an atmosphere of N_2 gas with a suspension of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)bipy]$ (0.38 g, 1.0 mmol) in acetone (25 cm^3). After 0.5 h the mixture was filtered and the stirred filtrate treated dropwise with $P(OMe)_3$ (0.12 g, 1.0 mmol). The clear solution was evaporated to low bulk, cooled to 0°C and the complex precipitated by the dropwise addition of diethyl ether. Yield 0.38 g, 70%. Complex VI. Found: C, 38.9; H, 4.1; N, 4.9. $MoC_{18}H_{22}N_2O_5PBF_4$ calcd.: C, 38.5; H, 3.9; N, 5.0%.

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