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REVIEW

Applications of fast atom bombardment mass spectrometry (FAB MS) to organometallic and coordination chemistry

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This article describes the technique of fast atom bombardment mass spectrometry (FAB MS) and its applications to the analysis of organometallic and coordination complexes. Sections on ion generation and matrices are followed by a Periodic Group-based review of FAB MS results obtained from Transition Metal and Main Group compounds, organometallic cluster carbonyls and their derivatives, and salts of poly-oxo-anions. The literature has been surveyed from 1981 to approximately mid-1986.

Keywords: FAB MS review, organometallic, coordination, ion generation, matrices

CONTENTS

ABBREVIATIONS

Mass spectrometry

CAD	Collision activated dissociation
CI	Chemical ionisation
DCI	Desorption chemical ionisation
DEI	Desorption electron impact
EI	Electron impact
FAB	Fast atom bombardment
FD	Field desorption
FI	Field ionisation
LC	Liquid chromatography
LIMS	Liquid ionisation mass spectrometry
MIKES	Mass-analysed ion kinetic energy spectrometry
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
SIMS	Secondary ion mass spectrometry
TAFAB	Thermally assisted fast atom bombardment
TLC	Thin layer chromatography

Ligands

bpma	bis(2-pyridylmethyl)amine
bpy	2,2′-bipyridyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
diars	benzene-1,2-bis(dimethylarsine)

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dien	diethylenetriamine
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Fc	ferrocenyl
Me-dien	methyldiethylenetriamine
Me_2-bpy	4,4′-dimethyl-2,2′-bipyridyl
PFK	perfluorokerosine
ppn	bis(triphenylphosphine)iminium
py	pyridine
tmpo	2,2,6,6-tetramethylpiperidinyl-1-oxo
tmtu	tetramethylthiourea
tpy	2; 2′,6′; 6″-terpyridyl

INTRODUCTION

In 1981 there appeared a brief communication describing a new method for the formation of ions from molecules which did not give mass spectra by conventional electron-impact (EI) methods.[1] The method was termed 'fast-atom-bombardment' (FAB), and among the materials which successfully afforded spectra were included vitamin B_{12} and its coenzyme, platinum ammine complexes, and covalent or ionic compounds containing $Au(PPh_3)$ groups. Later that year, the use of the new technique to obtain spectra of molecules such as $Rh(cod)\{\eta\text{-}C_5H_4(CH_2)_3Si(OMe)_3\}$, chlorophylls, and high molecular weight, thermally sensitive organic compounds was reported,[2] and its later application to a range of polar organic molecules, including quaternary phosphonium salts and nucleoside phosphates, for example, in both positive and negative ion modes, was described.[3] It was obvious that this new method would enable a significant extension of the mass spectrometric analysis of organometallic compounds to be achieved.

While conventional EI mass spectrometry has been long used in the analysis and characterisation of organometallic and inorganic molecules,[4–18] severe limitations to its application to ionic materials, high molecular weight metal cluster complexes and polymers were evident. Even where so-called 'softer' methods of ionisation, such as field ionisation (FI)[19] or chemical ionisation[20,21] were used, the requirement for the sample to be in the vapour state still exists, albeit at 10^{-5} to 10^{-6} torr vapour pressure.

Investigations into the production of ions from solid samples, using such methods as field or laser-induced desorption, or desorption chemical ionisation, have revealed that these techniques are frequently complementary to FAB MS.[22–27] In FAB mass spectrometry, the technique of sputtering ions from a solid or a solution is especially suited to the production of negative or positive ions which can be analysed by conventional mass spectrometric techniques. This review describes the technique briefly and surveys the applications to the analysis and characterisation of organometallic and coordination compounds. There has been the usual explosive upsurge of published results which follows the introduction of a new analytical technique, and for that reason, this account will not be comprehensive. However, we hope that by attention to the more practical aspects of the subject, this account will prove to be of use to others working in the field. There have been two earlier reviews,[28,29] but this account covers the literature from 1981 to mid-1986.

ION GENERATION

There have been many detailed descriptions of the processes involved in generating ions by bombarding a liquid sample with fast ('hot') atoms, and the interested reader is referred to these for technical details or theoretical discussion.[30–32] The phenomenon of sputtering was first observed over a century ago, and several scientists who have achieved eminence elsewhere have contributed to the subsequent literature. The mass spectrometric possibilities were first demonstrated by Benninghoven[33] and by Macfarlane,[34] at a time when the performance of the mass spectrometers used limited the range of applications, and it was Barber and coworkers who designed and developed a source suitable for contemporary high voltage, high mass range, double focussing instruments.[1]

Essentially, a focussed high intensity beam of ions (Ar^+ or Xe^+) of known kinetic energy undergo efficient resonant gas phase charge exchange with similar rare gas atoms: little loss of forward momentum occurs, resulting in the production of a beam of fast rare gas atoms. This impinges on the sample which is contained in a solvent (or 'matrix') of low volatility; the ions (positive and negative) which are produced can then be accelerated and analysed in a mass spectrometer of conventional geometry. The ideal solvent will achieve formation of a monolayer, so that solvent ions should not be observed under these conditions; however, the ideal situation may take a considerable amount of experimentation to achieve, and practically, spectra with a background of matrix ions are usually obtained. These matrix peaks may be removed on a spectrometer equipped with a computerised data system by digital subtraction. Figure 1 illustrates schematically the geometry of the commercial mass spectrometer which we have installed at Adelaide, while Fig. 2 shows details of the FAB source employed. Extension of the FAB process by chemical or electron ionisation of the abundant neutral species also sputtered from the matrix has been found to enhance the ion abundances by ion-molecule reactions. Selective enhancement of components of a mixture can be achieved by suitable choice of reagent gases.[35]

The precise details of ion generation are beyond the scope of this review, and indeed there is still controversy about some aspects of the sputtering process. However it is reasonable to

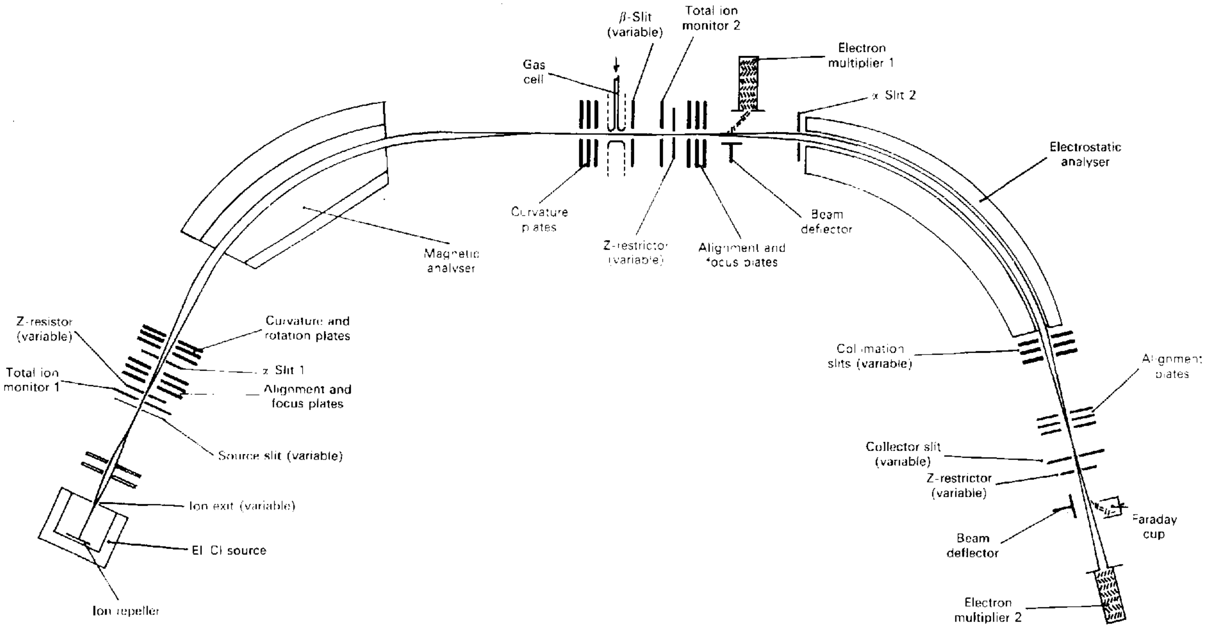

Figure 1 Schematic diagram of VG ZAB 2HF mass spectrometer [Reproduced with permission of VG Analytical Ltd].

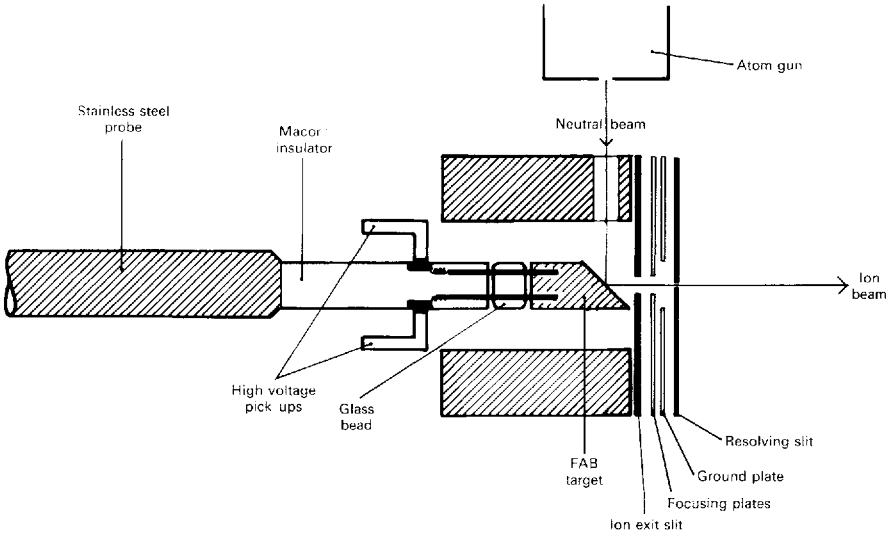

Figure 2 Schematic diagram of FAB ion source [Reproduced with permission from M A Baldwin, D M Carter and K J Welham, *Org. Mass Spectrom.*, 1983, 18: 176. © 1983 John Wiley and Sons Ltd].

suppose that considerable damage occurs to the surface of the sample, extending to several molecular thicknesses, by the impinging beam. This damaging effect can be seen clearly in the use of FAB as a depth-profiling technique, where an 8 Å min^{-1} etching in glass was found.[36] Ion formation probably occurs at a site considerably removed (several molecular diameters) from the impact area, with the fast atom transferring about 50 eV energy.[37–39] In a liquid matrix, continual renewal of this surface region is possible by convection, allowing spectral lifetimes of up to 20–30 minutes. Calculations suggest that clusters of between 15–1000 solvent molecules may be removed from the bulk matrix surface, inevitably entraining several solute molecules or ions. Evaporation of solvent allows both mono- and polynuclear ionic aggregates to escape into the mass spectrometer.

In a suggested gas phase collision model of the ionisation process, ion-molecule reactions such as recombination can occur in the high temperature, high density gas formed by the fast atom impact. The desorption temperature in this gas is likely to be around 2000 K. Once desorbed, it is the gas phase basicity (proton affinity) of the ions which determines whether $[M^+]$ or $[M+H]^+$ ions are observed.[40,41]

Ions produced by FAB of the sample held in the matrix are separated and analysed in the mass spectrometer by conventional magnetic and electrostatic analysers. In positive ion spectra, the highest ion observed for organic compounds is generally $[M+H]^+$ unless $[M+\text{matrix}]^+$ ions or ionic aggregates are present (see below); similarly $[M-H]^-$ is found in the negative ion spectrum. Both allow molecular weight information to be obtained. The $[M+H]^+$ ions are probably formed by proton transfer during bombardment or by direct protonation, while the $[M-H]^-$ ions are formed by proton abstraction by OR^- formed from glycerol, for example, in the proton transfer reaction. Similarly, alkali metal salts form stable adducts, e.g. $[M+K]^+$, as found for the potassium salt of a penicillin: in this case ions $[RCO_2K_2]^+$ and $[RCO_2]^-$ were observed.[30] However, covalent metal-containing complexes give $[M]^+$ ions, sometimes being accompanied by $[M+H]^+$ ions in the positive ion mode and $[M-H]^-$ ions in the negative ion mode.

Formation of $[M+H]^+$ ions from inorganic and organometallic compounds in FAB MS is considered to be a reductive process, resulting in a lowering of the oxidation state on protonation of an ion.[42] However, we note that if the proton is attached to the metal atom, a formal oxidative addition has resulted. Some workers have suggested that the best results are obtained from a weakly oxidising matrix to stabilise $[M]^+$ if this ion contains a reduced metal.[43]

Fragmentation involves processes already familiar to the mass spectrometrist and it is not our intention to provide a detailed discussion of these herein; the ions arise from the usual unimolecular decompositions in the gas phase, but not from thermal decomposition in the source. This feature gives a significant advantage over those methods which require organometallic compounds, which are often thermally sensitive, to be heated in order to introduce them into the vapour phase.

In general, salts $[A^+][B^-]$ will give $[A]^+$ and derived ions in the positive ion spectra, and $[B]^-$ and charged fragments thereof in the negative ion spectrum. Multicharged ions are relatively rare; in the gas phase, such ions have a high heat of formation, and in cases such as $[X^{2+}][Y^-]_2$, it is common to find the ionic aggregate $[X+Y]^+$ as the highest monopositive ion. However, we have observed a continuum of multiply-charged ions in certain triruthenium cluster carbonyl derivatives. Generally, in transition metal complexes, monodentate ligands can be lost from $[M]^+$, but bidentate and polydentate ligands are only lost from fragment ions. The formation of fragment ions occurs by simple ligand loss (with no change in oxidation state), or by formal reductive elimination of a neutral fragment. Thus we find successive loss of CO groups from metal carbonyl complexes, but where a ligand is prone to fragmentation, e.g. PPh_3, fragment ions can be formed by loss of radicals such as $Ph^\cdot$, or molecules, such as Ph_2. A study of several complexes of metals in different oxidation states suggested that a redox process is found if there is a 'redox-accessible zero oxidation state'.[26]

Low abundance ions occur at most masses up to and occasionally beyond $[M+H]^+$ or $[M-H]^-$, allowing ready assignment of nominal masses to the stronger peaks arising from the sample. Less useful is the rapid increase in background intensity on going to lower mass numbers; unless they are unusually strong, we find that sample peaks with $m/z < 100$–150 may be difficult to distinguish from the matrix background.

FAB MS is a natural outgrowth of the secondary ion mass spectrum (SIMS) technique, in which a sample is bombarded with ions. Here, short sample lifetimes and surface charging effects, together with a concern that only conducting samples were appropriate, have prevented its widespread application. Recently there has been interest in liquid SIMS, the close relation of FAB MS, where an ion beam, typically Cs^+, is used to sputter the sample which is dissolved in a matrix.* The great potential of FAB MS has encouraged the development of mass spectrometers with adequate resolving power and mass ranges, the present limitations being instrumental in nature. At present instruments such as the VG ZAB SE, Jeol HFX 110 and Kratos MS 50 RF are capable of working up to 10000–15000 Dalton at full accelerating potential. Indeed, one reason for the rapid adoption of the FAB technique has been the ready adaptation of existing ion sources and mass spectrometers.[44–46]

INSTRUMENTAL CONSIDERATIONS

(a) The FAB gun

Optimisation of beam parameters has been discussed by Biemann and coworkers.[47] Increasing the gas flow until the maximum permissible current (1–1.5 mA) is achieved at 7.5 keV gives the largest signal with the ZAB 2HF instrument. Raising the energy does not increase the sensitivity greatly. The gun should produce a stable discharge within minutes of firing. A large degree of instability (arcing) is typical of a leak in the gas inlet line. The usual fast atoms are argon or xenon with 6–10 keV kinetic energy; the use of mercury atoms has been claimed to result in extra sensitivity compared with argon.[48] Our experience has been that sensitivity is highly dependent on the interaction of the fast atom beam with the target, and that substitution of the more expensive xenon for argon results only in up to 5-fold increase in sensitivity if the probe geometry is carefully optimised. A study of the relative intensities of the base peak (*m*/*z* 1329) of cobalamin in spectra obtained by FAB with neon, argon and xenon gave values of 0.11:0.27:1, approximately the same as the relative masses of the rare gas atoms (0.15:0.30:1).[49] In general, compounds that were readily protonated in glycerol gave $[M+H]^+$ with intensities roughly proportional to the mass of the bombarding atoms, whereas for other species which are not readily protonated, this relationship did not hold.

Although not strictly a 'fast atom' gun, the results obtained using a focussed Xe^+ gun are comparable with the former, while the intensities are 5–10 times greater.[38] Use of an ion beam requires only modification of existing SIMS technology and when combined with the use of a liquid sample support has been termed 'liquid SIMS'. As the Cs^+ gun requires no gas leak, a considerably improved vacuum can be maintained in the source when it is used.[50] This is critical in obtaining spectra of high mass CsI clusters where a source pressure above 5×10^{-7} mTorr results in poor spectra being recorded. Changes in primary beam energy and accelerating voltage also have a marked effect in high mass work.[51] In a SIMS study of aniline using alkali metal ions, highest yields of secondary ions were obtained with Cs^+, the ion with the greatest 'nuclear stopping power'.[52]

Many variants of existing ion sources have been proposed: incorporation of a fast atom gun in an EI/CI quadrupole source allows a rapid switch-over between EI/CI and FAB modes,[53] and alternate or simultaneous FAB/EI spectra allow for calibration.[54]

(b) Probe design

A modified direct insertion probe is used for the introduction of samples into the FAB ion source. There are several variants of the commercially available probes. VG supply a 'wobble-probe' which presents alternating targets to the fast atom beam for use in peak-matching during accurate mass measurements. A 'rotatable probe' which fulfils the same function has also been described.[55] An integral probe, which incorporates a FAB gun mounted in a fixed position with respect to the target, is manufactured by Vacumetrics. The standard VG FAB probe is provided with a heatable target to aid volatilisation, although no improvement in sensitivity has been noted with organometallic compounds. This con-

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*Many practitioners argue that FAB MS is a straightforward extension of the SIMS method, the use of atoms rather than ions being more convenient for the instrumentation used for the development of the method. The essential difference is not atoms *vs* ions, but the use of the liquid matrix. A recent publication ['Desorption Mass Spectrometry: Are SIMS and FAB the Same?', (ACS Symposium Series No. 291), ed. P A Lyon, American Chemical Society, Washington, DC, 1985] makes interesting reading, but does not answer the question fully. Perhaps one's views reflect more the background of the user than any significant differences in the methods.

trasts with organic chemistry where the technique TAFAB (thermally assisted FAB) has proved successful in obtaining spectra that show background peaks with significantly lower intensity.[56] Here programmed heating of the target on which rests a saturated solution of the compound, for example fructose, gave an optimal temperature of desorption as the saturated matrix became liquid. Cooling of the probe tip, on the other hand, leads to improved spectra when using the more volatile matrices.[57] A recent development is the continuous flow probe which allows a continuous stream of solvent (containing a small amount of matrix) to enter the source. The sample is injected into the flow and evaporation results in the sample being presented to the atom beam in concentrated form, resulting in improved sensitivity.[58]

A unique probe inlet design that allows the loading of air-sensitive solids on to the target has been described.[59] The solid is transferred under vacuum to a pre-coated target by using a glass Schlenk tube connected to a modified ball-valve assembly.

(c) Target design

The fast atom beam is incident on a metal strip in the probe tip called the target. This is usually manufactured from stainless steel, molybdenum, silver or copper and presents the sample in the matrix at a fixed angle with respect to the atom beam. In some instances, copper has been found to react with the sample.[60] The efficiency of the sputtering process is greatly affected by small changes in this angle, which ideally should be near the grazing incidence angle. Our current targets have an angle of 45° (Fig. 3a). As the incident beam also affects the ion exit angle there may be deviations from the normal SIMS angle of incidence (60°) in different instruments.[61] The geometry of the probe tip has been explored.[62] For routine studies we favour the simple wedge design, final positioning after entry to the source being adjusted for maximum sample ion current.

Organometallic species have been found to imbed into the surface of the standard VG target (Fig. 3c), and it has been necessary to prepare the surface by wrapping a layer of aluminium foil around the target.[63] In the case of the solid stainless steel target, this can be avoided by polishing the surface with fine emery paper. Another procedure which has been successfully employed is the immersion of the target in 2 mol dm^{-3} sodium hydroxide solution followed by repeated rinsing in distilled water and methanol.[64] This also enables the surface to be completely wetted, although it is unlikely to remove imbedded species. A needle target (Fig. 3d) has been used to enable smaller amounts of sample to be analysed. However, the sensitivity is reduced as a result of the divergence of the atom beam, which in the VG ZAB source is at least 1 cm^2 in diameter by the time it impinges on the target.[65]

A number of approaches to the problem of using external mass standards with FAB MS have been explored. The problem relates to the separation of the reference compound from the sample. The 'wobble-probe' previously mentioned has been used; a target developed for this probe is shown in Fig. 3b. The reference target geometry has a close relation to that of the sample target, so that the tuning and peak shape are affected as little as possible. Figure 3e shows a split target used with the rotatable probe which separates the reference and sample in a similar manner.

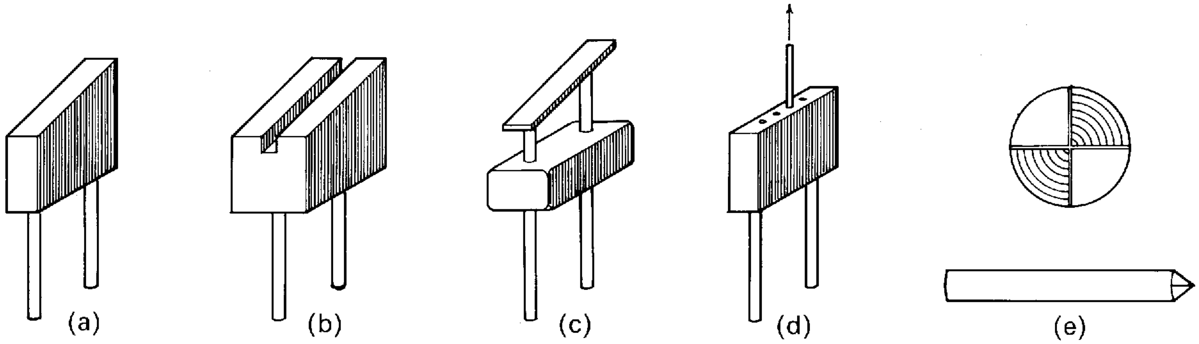


Figure 3 Some FAB targets (a) wedge target, normal; (b) wedge target, split; (c) standard VG target; (d) needle target; (e) split target for rotatable probe.

(d) Sample preparation

Dissolution of the sample in the matrix is generally important to the success of the FAB method. A notable exception is the surface precipitation technique where the sample (in a co-solvent) is deposited and concentrated on the surface of the matrix directly on the target.[66] Surface migration results in the maintenance of a steady ion current with this technique, spectra lasting for up to 30 minutes. Impurities can suppress ionisation (particularly in the case of organic compounds which have been in contact with buffers, enzymes or derivatisation reagents). Methods for the removal of such impurities have been described,[47] but such measures are not often necessary for organometallics. In rare cases, liquid samples do not need a matrix. Ideally, the compound to be analysed will be soluble in the matrix. If this is the case, a small amount (ca 1 μL) of the matrix is applied to the target which is pre-coated with the compound. Very small quantities of compound can be analysed in this manner, 100 pmol being a useful response limit.[30] Alternatively, if careful control is required, then the use of a stereomicroscope has been successful; accurate amounts of sample were transferred by syringe to the target which was then blown to dryness.[64] By this means 1 ng (ca 1 pmol) quantities of angiotensin have been analysed.

More frequently, organometallic compounds must be dissolved in a co-solvent before introduction into the matrix. Typically, 1 mg sample is dissolved in ca 0.01 cm^3 co-solvent, e.g. CH_2Cl_2, which is then added to the matrix (ca 0.01 cm^3) in a Petri dish. The mixture is stirred to achieve homogeneity and the co-solvent blown off in a stream of nitrogen until essentially only the matrix remains. By this method, clear solutions (often supersaturated) of sample in the matrix are obtained. Alternatively, 3 μL matrix may be applied as a thin film to the target using a glass rod. A 3 μL sample of compound (ca 75 μmol) in co-solvent is then combined with the matrix.[67] If the matrix is not particularly viscous it may well form into a drop on the target. If this occurs after the probe is placed in the source, a spectrum will appear and then vanish as the drop rolls out of the target area. Addition of very fine, non-reactive particulate matter to the matrix/sample mixture on the target prevents this effect. Typically, graphite dust, silica (400 mesh, for TLC) or alumina can be used for this purpose.

The introduction of the matrix into the source results in an increase in source pressure. If this becomes severe, extensive (ca 30 minutes) pumping should result in restoration of a usable vacuum. The FAB source does not show any memory effects. After prolonged use, however, a thorough baking is necessary to remove matrix completely from the system.

The formation of ions at the surface of the matrix is aided by the introduction of a pre-ionising agent, e.g. acid, base, NH_4Cl, and these materials have been frequently used in conjunction with organic materials. Their utility with regard to organometallic compounds has also been established.[67] Addition of $AgNO_3$ to the matrix has also been used to form $[M+Ag]^+$ ions from organic compounds where $[M+H]^+$ is not formed.[68] This is preferable to the addition of LiCl or NaCl, which may generate many (matrix +metal halide) ion clusters, thereby complicating the spectra. A recent report suggests that the addition of counter-ions such as $[NBu_4]^+$ (as hydroxide) to the matrix serves to concentrate oppositely-charged species at the surface of the matrix.[69] The addition of a surfactant with opposite charge to that of the ion mode being observed and with appropriate R groups to attract sample molecules results in a greatly reduced matrix background. The surface is effectively covered with surfactant with a concentration gradient of sample beneath it. So far this technique has been applied only to organic compounds.[70]

A method for the analysis of fractions separated by thin layer chromatography (TLC) has been described.[71] After location of the TLC spot, the FAB target, which has been covered with a piece of double-sided sticky tape, is pressed on to the spot. The surface layer of TLC adsorbent will stick to the target, and after addition of 1–2 μL suitable co-solvent and 2–5 μL matrix, the spectrum is run in the normal way. A belt transfer mechanism has been developed for sampling of LC eluates, the method being termed LC/FAB MS.[72]

(e) Mass calibration

Although most spectrometers are equipped with built-in Hall-effect mass markers, these must be calibrated to provide a precise mass scale. The ready suppression of FAB spectra by impurities in the sample or matrix has meant that the usual methods of calibration by incorporation of a suitable reference, such as perfluorokerosene (PFK) or *sym*-(perfluoroalkyl)triazines, are inappropriate. PFK has been used as an external standard for computer calibration of the mass scale; the target is cooled in liquid nitrogen.[73] The ready production of high mass ions under FAB conditions has necessitated the development of new mass markers.[73–77] One such is the amphoteric surfactant Zonyl FSB. This may be added to a glycerol matrix (ca 0.2%); under FAB conditions, a series of peaks between 280–780 amu are found, with major peaks at *m/z* 307, 352, 407, 452, 510, 552, 610, 652 and 710.[55] Other electronic methods of mass measurement, based on comparative scans of sample and reference,[78] or on scanning the accelerating voltage (ESCAN) at constant magnetic field,[79] have been described.

The assignment of accurate mass numbers in FAB MS has been examined by several groups.[55,78–82] Internal referencing appears to give more reliable results, but when high molecular weights are analysed, it becomes difficult to find suitable reference compounds that will not suppress the sample spectrum entirely. Extrapolation of low-mass calibration (using a Hall probe mass marker) into the high-mass regions (>1000 amu) causes considerable errors, even at low resolution, e.g. 4000 ± 5 amu. This means that care must be taken when calibrating a spectrum as all regions of the mass range must be checked. We have found that most instrumental parameters, e.g. ion repeller, ion energy, focussing, will influence the positions of the Hall probe marker when using FAB on the VG instrument. Nothing must be changed between experimental runs to ensure that the calibration remains correct.

Many workers have described the use of salt ion clusters generated from alkali metal halides, which can be used for calibration of FAB mass spectra.[51,83,84] These can be produced in both positive and negative ion modes, and have the general formulations $[M(MX)_n]^+$ and $[(MX)_nX]^-$, respectively. Of most use are the ions formed by CsI, and cluster ions up to *m/z* 25854 ($[Cs(CsI)_{99}]^+$ and 22730 ($[(CsI)_{87}I]^-$) have been observed.[85,86] Unresolved peaks and valleys have been reported up to *m/z* 90000.[87] Within the spectra, unusually strong ions, with $n=13$ or 22, or with $n=6$, 9, 12, 15, etc., for example, are found. These are formed by unicluster decompositions of unstable aggregates in times of $>100\,\mu$s, and are thought to have stable cubic or stacked hexagonal ring structures. Table 1 lists the masses and relative intensities of the positive and negative ions in the CsI FAB spectrum up to $n=47$, while closer spaced peaks have been obtained using equimolar mixtures of NaI, RbI and CsI.[88]

At present we use CsI as an internal reference for low resolution calibration (± 0.5 amu). A concentrated CsI/glycerol mixture is dissolved in the matrix (1/2 v/v); this is then mixed with the matrix containing the compound on the target. The CsI ions are usually easily suppressed. The CsI calibration ensures that the true position of the Hall probe marker is known, and the major peaks of the sample are also observed. As CsI and glycerol result in extra ions, it is necessary to run a spectrum without calibrant. For high resolution mass matching, the 'wobble-probe' mentioned earlier provides reliable results if care is taken with the measurements and suitable reference compounds with appropriate peaks are available.

The ability of FAB MS to provide an accurate isotopic envelope for the identification of $[M]^+$ was examined for the complex $[RuCl(CO)(bpy)_2]^+$, overall agreement being within 10% of the calculated pattern of intensities.[63] Experimentally, computer averaging of 16 scans was required to accommodate variations in sample ion currents and isotopic relative intensities. A careful comparison of experimental and theoretical isotope patterns for $[Ru(CH_2Ph)(CO)(bpy)_2]^+$ indicated an absolute error of 0.4%, well within the random experimental error resulting from variations in the FAB secondary ion current.[89]

MATRICES

Although initial experiments with solid samples (molecular beam solid analysis, MBSA) afforded usable spectra, lifetimes are short as a result of damage to the sample caused by the atom beam.[31] This disadvantage is removed entirely by use of a liquid matrix in which the sample is dissolved. This key feature sets FAB MS apart from the other 'soft' ionisation techniques and allowed its acceptance as a routine analytical technique.

Choice of matrix and co-solvent basically depends on polarity. The co-solvent must dissolve the compound readily and be reasonably volatile to achieve a high concentration of solute in the matrix. Common co-solvents include dichloromethane, acetone, diethyl ether, acetonitrile, tetrahydrofuran, dimethylformamide, water, etc. The choice of matrix is more difficult, although a first step is to select from matrices used previously for

Table 1 Accurate masses and compositions of ions in FAB mass spectrum of cesium iodide to *m/z* 12340: (a) positive ions; (b) negative ions

(*a*) Positive Ions					
Cs	132.90543	$Cs_{17}I_{16}$	4289.8640	$Cs_{33}I_{32}$	8446.8226
Cs_2I	392.71534	$Cs_{18}I_{17}$	4549.6739	$Cs_{34}I_{33}$	8706.6325
Cs_3I_2	652.52525	$Cs_{19}I_{18}$	4809.4838	$Cs_{35}I_{34}$	8966.4424
Cs_4I_3	912.33516	$Cs_{20}I_{19}$	5069.2937	$Cs_{36}I_{35}$	9226.2523
Cs_5I_4	1172.1451	$Cs_{21}I_{20}$	5329.1036	$Cs_{37}I_{36}$	9486.0622
Cs_6I_5	1431.9550	$Cs_{22}I_{21}$	5588.9135	$Cs_{38}I_{37}$	9745.8721
Cs_7I_6	1691.7649	$Cs_{23}I_{22}$	5848.7235	$Cs_{39}I_{38}$	10005.682
Cs_8I_7	1951.5748	$Cs_{24}I_{23}$	6108.5334	$Cs_{40}I_{39}$	10265.492
Cs_9I_8	2211.3847	$Cs_{25}I_{24}$	6368.3433	$Cs_{41}I_{40}$	10525.302
$Cs_{10}I_9$	2471.1946	$Cs_{26}I_{25}$	6628.1532	$Cs_{42}I_{41}$	10785.112
$Cs_{11}I_{10}$	2731.0045	$Cs_{27}I_{26}$	6887.9631	$Cs_{43}I_{42}$	11044.922
$Cs_{12}I_{11}$	2990.8144	$Cs_{28}I_{27}$	7147.7730	$Cs_{44}I_{43}$	11304.732
$Cs_{13}I_{12}$	3250.6244	$Cs_{29}I_{28}$	7407.5829	$Cs_{45}I_{44}$	11564.541
$Cs_{14}I_{13}$	3510.4343	$Cs_{30}I_{29}$	7667.3928	$Cs_{46}I_{45}$	11824.351
$Cs_{15}I_{14}$	3770.2442	$Cs_{31}I_{30}$	7927.2027	$Cs_{47}I_{46}$	12084.161
$Cs_{16}I_{15}$	4030.0541	$Cs_{32}I_{31}$	8187.0126	$Cs_{48}I_{47}$	12343.971
(*b*) Negative Ions					
I	126.90448	$Cs_{16}I_{17}$	4283.8630	$Cs_{32}I_{33}$	8440.8216
CsI_2	386.71439	$Cs_{17}I_{18}$	4543.6730	$Cs_{33}I_{34}$	8700.6315
Cs_2I_3	646.52430	$Cs_{18}I_{19}$	4803.4829	$Cs_{34}I_{35}$	8960.4414
Cs_3I_4	906.33421	$Cs_{19}I_{20}$	5063.2928	$Cs_{35}I_{36}$	9220.2513
Cs_4I_5	1166.1441	$Cs_{20}I_{21}$	5323.1027	$Cs_{36}I_{37}$	9480.0612
Cs_5I_6	1425.9540	$Cs_{21}I_{22}$	5582.9126	$Cs_{37}I_{38}$	9739.8712
Cs_6I_7	1685.7639	$Cs_{22}I_{23}$	5842.7225	$Cs_{38}I_{39}$	9999.6811
Cs_7I_8	1945.5739	$Cs_{23}I_{24}$	6102.5324	$Cs_{39}I_{40}$	10259.491
Cs_8I_9	2205.3838	$Cs_{24}I_{25}$	6362.3423	$Cs_{40}I_{41}$	10519.301
Cs_9I_{10}	2465.1937	$Cs_{25}I_{26}$	6622.1522	$Cs_{41}I_{42}$	10779.111
$Cs_{10}I_{11}$	2725.0036	$Cs_{26}I_{27}$	6881.9621	$Cs_{42}I_{43}$	11038.921
$Cs_{11}I_{12}$	2984.8135	$Cs_{27}I_{28}$	7141.7721	$Cs_{43}I_{44}$	11298.731
$Cs_{12}I_{13}$	3244.6234	$Cs_{28}I_{29}$	7401.5820	$Cs_{44}I_{45}$	11558.541
$Cs_{13}I_{14}$	3504.4333	$Cs_{29}I_{30}$	7661.3919	$Cs_{45}I_{46}$	11818.350
$Cs_{14}I_{15}$	3764.2432	$Cs_{30}I_{31}$	7921.2018	$Cs_{46}I_{47}$	12078.160
$Cs_{15}I_{16}$	4024.0531	$Cs_{31}I_{32}$	8181.0117	$Cs_{47}I_{48}$	12337.970

similar compounds, if known. The ideal matrix is a viscous liquid of low volatility with reasonable solvent power. Table 2 lists some commonly-used matrices which we and others have employed for organometallic compounds. In addition, Gower has reviewed FAB matrices for other applications.[90] The following comments on individual matrices incorporate observations from a number of groups.

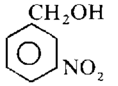
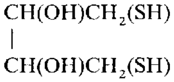
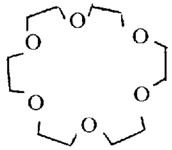
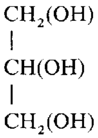
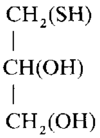
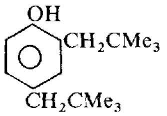
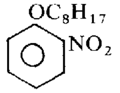
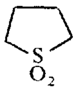
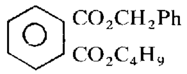
(a) Glycerol (glyc)

This is the original matrix and probably still the most widely used. It has the advantage that it is miscible with many polar solvents, including water, alcohols, dimethylformamide and dimethyl sulphoxide. Where addition of acid or base is required to improve sensitivity, the use of glycerol is an advantage. With organic compounds, protonated molecular ions $[M+H]^+$ are formed in positive ion spectra, while $[M-H]^-$ are formed in negative ion spectra. Ionic aggregates incorporating the matrix are formed; from glycerol itself, positive ions are found at *m/z* $[93+92n]^+$ (where *n* may be up to 15), while negative ions occur at *m/z* $[91+92n]^-$. Ions $[M+glyc+H]^+$ or $[2M+glyc+H]^+$ have been shown to be precursors of $[M+H]^+$ by metastable scanning; the ionisation mechanism is thus not a simple one.[91]

(b) Thioglycerol

This material is becoming preferred over glycerol, particularly for more ionic compounds. The un-

Table 2 Common matrices for, FAB MS

Matrix	Formula	Matrix abbreviation	Molecular weight	M.pt (°C) (B.pt, °C/mm)
3-Nitrobenzyl alcohol		NOBA	153	30–32
Dithiothreitol/ Dithioerythritol (6/1)	 $\mathrm{CH(OH)CH_2(SH)-CH(OH)CH_2(SH)}$ (isomers)	DTT/DTE	154	ca. 15
18-Crown-6/Tetraglyme (9/1)	 $CH_3(OCH_2CH_2)_4OCH_3$	18-C-6/TETRA	264 222	ca. 15
Glycerol	 $\mathrm{CH_2(OH)-CH(OH)-CH_2(OH)}$	GLYC	92	20 (182/20)
Thioglycerol	 $\mathrm{CH_2(SH)-CH(OH)-CH_2(OH)}$	TGLYC	108	(118/5)
2,4-Di-*t*-pentyl phenol		DAP	235	24–26
2-Nitrophenyl octyl ether		NPOE	251	(197–198/760)
Sulfolane		SULF	120	27 (285/760)
Triethanolamine	$N(CH_2CH_2OH)_3$	TEA	149	18 21 (190/5)
Butyl benzyl phthalate		BBP	312	(370/760)
Polyethyleneglycols	$H(OCH_2CH_2)_nOH$	PEG 200 CARBOWAX 200	190–210	−20 to −15
Polyoxyethylene ethers	$(CH_2CH_2O)_n$	TRITON X100	647	63–69[a]
Hydrochloric acid (dilute)	HCl	HCl	36	—
Phosphoric acid (85%)/ Sulphuric acid (98%) 2/1	H_3PO_4 H_2SO_4	H_3PO_4/H_2SO_4	98	—

[a] Turbid point

pleasant odour associated with this compound is tolerable if an efficient fume hood is used.

(c) Triton X100

Triton X100 is an alkylphenyl-polyethyleneglycol and has been used (ca 1%) to improve solubility of samples in glycerol; it has been employed particularly with chlorophylls and porphyrins. Occasionally samples have been run using the neat matrix.

(d) Polyethyleneglycols (PEGs)

The use of high molecular weight polyethyleneglycols has been well documented.[92,93] The most useful fractions are those with molecular weights around 200, 400 and 600. In cases where glycerol forms molecular complexes, such as with boronic acids, FAB mass spectra have been successfully obtained from a polyethyleneglycol matrix.[62]

(e) Triethanolamine (TEA)

Reported uses of this matrix have included the production of improved spectra (over glycerol) for vitamin B_{12}. For other compounds, mixtures with 1,1,3,3-tetramethylurea have been recommended; for acids, dissolving the sample in a saturated aqueous solution of TRIS buffer has been suggested.

(f) 2,2′-Thiodiethanol (thiodiglycol)

This matrix has been used for selected rhodium and osmium complexes where glycerol was unsuitable.[94]

(g) 2,4-Di-*t*-alkylphenols (alkyl = butyl, DBP; pentyl, DAP)

These liquids have superior dissolving power to glycerol and polyethyleneglycols, and are particularly suitable for less polar compounds.

(h) 18-Crown-6

Tetraglyme (10% w/w) is often added to this matrix to depress the melting point below room temperature. It is a useful matrix for non-polar compounds, although spectra are complicated by matrix aggregate ions such as $[2(18\text{-C-6})-\text{H}]^+$, $[3(18\text{-C-6})-3\text{H}]^+$. We have found that mixed 18-crown-6/3-nitrobenzyl alcohol has the greatest dissolving power for organometallic compounds and metal salts.[95]

(i) 2-Nitrophenyl octyl ether (NPOE)

This is a useful matrix for metal-containing corrin and porphyrin compounds. The aprotic nature of this matrix has proved successful in suppressing hydrogenation reactions that occur in matrices such as glycerol.

(j) 3-Nitrobenzyl alcohol (NOBA)

The use of this weakly oxidising matrix has been found to be necessary for the correct analysis of cobyrinic acid derivatives, corrins and porphyrins, as this compound prevents chemical degradation during the run.[43,96,97] In our laboratory this material has become the standard matrix for all compounds that will dissolve in co-solvents such as dichloromethane. Spectra generally show a clear $[\text{M}]^+$ ion, although others have reported $[\text{M}+\text{H}]^+$ as the typical pseudo-molecular ion for peptides, for example.[43,96,97] Fragments due to the matrix are observed below *m/z* 153 and we have so far observed only two instances of ions $[\text{M}+\text{matrix}]^+$. However, in the molecular ion region there are frequently small peaks which appear to correspond to $[\text{M}+\text{N}]^+$, $[\text{M}+\text{O}]^+$, $[\text{M}+\text{NH}_3]^+$, $[\text{M}+\text{N}_2]^+$, $[\text{M}+\text{O}_2]^+$ or $[\text{M}+\text{NO}_2]^+$ species. These ions are typically an order of magnitude smaller than $[\text{M}]^+$. Similar adducts may also be found for high intensity fragment ions. In several comparisons that we have made with DDT/DTE (below) or 18-crown-6/tetraglyme, NOBA gives a clearer fragmentation pattern and, given variations in solubilities, a stronger $[\text{M}]^+$.

(k) Dithiothreitol/dithioerythritol (6/1) (DTT/DTE)

The liquid mixture of these two diastereomers has proved to be a suitable matrix for organometallic and coordination complexes, and we have found it especially useful for a range of mono- and poly-nuclear ruthenium compounds. The molecular ion $[\text{M}]^+$ is most frequently observed, but is often accompanied by $[\text{M}+\text{matrix}]^+$. As with thioglycerol, the odour problem is best avoided by working in an efficient fume hood.

(l) Butyl benzyl phthalate

Phthalate esters are well established as suitable matrix compounds in organic chemistry, the particular example cited having been used for a range of coordination complexes and phthalocyanines.

(m) Sulpholane

This is a useful matrix for organic derivatives of Group 4B elements.

Generally, our approach has been to use 3-nitrobenzyl alcohol, 18-crown-6 or the dithiothreitol/dithioerythritol mixture initially, followed by the increasingly polar materials such as glycerol. While it is useful to have suitable precedents for the complexes under study, the choice of a suitable matrix is by no means straightforward, and success often depends on chemical intuition and luck as much as on logic.

APPLICATIONS TO SOLUTION STUDIES

The requirement of FAB MS for a liquid matrix support gives the method a unique advantage over other methods of ion production, that of the ability to follow chemical reactions as the ionisation process is occurring. Problems associated with the quantitative determination of molecules in solution have been studied, and the application of FAB MS to the determination of apparent pK_a values has been reviewed.[98] In the context of this review, measurements of binding constants of crown ether ligands to alkali metal cations have been determined by measuring relative abundances of $[\text{ligand}+M]^+$ ($M=Na$, K, Cs). Additionally, the selectivity of complex formation between alkali metal cations and glycerol/water or macrocylic ligands was also studied.[99,100]

FAB MS STUDIES OF ORGANOMETALLIC AND COORDINATION COMPOUNDS

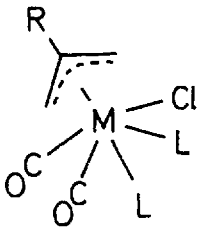
This summary is intended to be illustrative of the applications of the technique of FAB MS to the study of organometallic compounds rather than a comprehensive account of the results obtained. In the following discussion, we have used the convention ($[\text{fragment}]^{+\text{or}-}$, m/z, % relative intensity) where appropriate; the symbol $[M]^+$ is used for the molecular ion. When individual spectra are considered, we have generally listed all peaks with relative intensities of >5% of the metal-containing base peak, although one of the features of FAB mass spectra is that there is generally to be found at least a small peak at every mass number up to, and sometimes beyond, the molecular ion. For the purposes of this discussion, only representative spectra will be presented in detail.

The coverage of complexes has been ordered according to Periodic Group; our major interest has centred on the Transition Metals, so that we have more information concerning these complexes, which are dealt with first. While complexes could also be divided according to charge, we note that ions of both polarities can be frequently obtained, that is, although salts of the type $[ML_n][Y]$ might be expected to give positive ions derived from $[ML_n]^+$, and a negative ion spectrum derived from $[Y]^-$, this is not always the case. For example, the spectrum of the complex $[Os_4H_3(CO)_{12}\text{-}(NCMe)_2][PF_6]$ contains positive ions such as $[M]^+$ and $[M-2MeCN]^+$, while the negative ion spectrum also shows $[M-2MeCN]^-$.[101]

(a) Chromium, molybdenum and tungsten

Brisdon and Floyd[102] have reported the FAB mass spectra of various neutral molybdenum and tungsten allyl complexes of the type $MCl(CO)_2(L)_2(\eta^3\text{-}C_3H_4X)$ (I; M = Mo, W; L = NCMe, py; X = H, Me). These exhibit ligand exchange in a glycerol matrix to give ions where L_2 = glycerol, the strongest peak being $[M(CO)_2(L)_2(C_3H_4X)]^+$. Similar spectra were obtained when mixtures of $MCl(CO)_2(L)_2(\eta^3\text{-}C_3H_4X)$ and dien or bpma (bis(2-pyridylmethyl)amine) were compared with the related, preformed complexes such as $[Mo(CO)_2(\text{dien})(\eta^3\text{-}C_3H_5)]^+$, indicating that FAB MS can be used to monitor bulk solution chemistry. In the spectrum of the cation, both $[M]^+$ and $[M+\text{glyc}]^+$ were present.

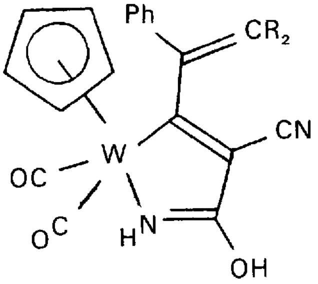
We have characterised the complexes $W(L)(CO)_2(\eta\text{-}C_5H_5)$ (II) [$L=NH{=}C(OH)C(CN){=}CCPh{=}CR_2$, R = CN or CF_3] which contain five-membered metallocyclic systems. Neither complex gives an EI spectrum, but $[M]^+$ ions are found in the FAB MS at m/z 552 (33%) and 637 (90%), respectively. The



I

M=Mo, W
L=NCMe, py
R=H, Me

fragmentation patterns indicate stepwise loss of CO, OH and C_5H_5 groups. In conjunction with other spectroscopic and analytical data the illustrated structures were postulated, and confirmed in one case by an X-ray crystal structure.



II

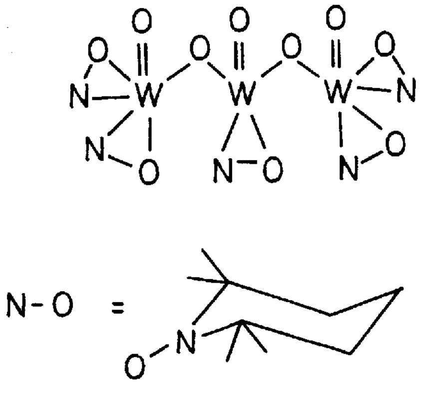
R=CN, CF_3

A variety of substituted molybdenum carbonyl complexes have been investigated by Connor and coworkers,[103–105] who found that both positive and negative ion FAB mass spectra could be obtained, while EI mass spectra presented difficulties. The comparison was made for the complexes *cis* and *trans* $Mo(CO)_2(L)_2(bpy)$ [$L = PBu_3$, $P(OMe)_3$]. In the FAB mode, ions were formed by H loss, such as $[M-H]^+$ and $[M-L-H]^+$, whereas the EI spectra contained $[M]^+$ and $[M-L]^+$ ions.[103] Molecular ions, at *m/z* 551 and 679, respectively, were reported for *trans*-$[Mo(CO)_2(bpy)_2]^+$ and $[Mo(CO)_2(bpy)_2(NCMe)]^+$.[105] Both positive and negative ion spectra of *cis*-$M(CO)_4(4,4'$-X_2-bpy) ($M = Mo$, W; $X = H$, Me, Bu^t, Cl) gave informative fragmentation patterns. Ions $[M]^+$, $[M+H]^+$ and $[M-CO]^+$ were observed in the positive ion spectra, as well as adduct ions such as $[M+glyc+DMF+H]^+$ formed with the glycerol/DMF matrix. In the negative ion mode, adduct ions were not generally observed. The ion $[M]^-$ fragmented by successive loss of CO groups in a fashion similar to that found for $[M]^+$.

The neutral Mo(VI) complex *cis*-$Mo(O)_2(S_2CNEt_2)_2$ was studied by Bursey and coworkers;[26] the highest ions observed were $[M-O]^+$ (FAB) and $[M]^+$ (FD). However, the FAB spectrum provided a structurally informative fragmentation pattern, whereas the FD technique gave only the molecular ion. The loss of oxygen found in the FAB spectrum is interesting as the cation contains a thermally labile oxo group. Other fragments observed included $[M-S_2CNEt_2]^+$ and $[M-O-NEt_2]^+$, the latter being formed by a ligand fragmentation process.

FAB MS proved to be less successful than LIMS (liquid ionisation mass spectrometry) for analysis of molybdenum(V) (2-ethylhexyl)dithiocarbamate complexes. The $[M+H]^+$ peak was of lower intensity and the fragmentation pattern less easily interpreted in the FAB spectrum.[106]

An open chain trimeric tungsten complex $W_3(\mu$-$O)_2(O)_3(tmpo)_5$ (III) (tmpo = 2,2,6,6-tetramethylpiperidinyl-1-oxo) was characterised with the aid of FAB MS.[107] A high resolution study and simulation of the $[M]^+$ ion at *m/z* 1410 was used to identify the compound along with characteristic fragmentation by successive loss of O followed by elimination of WO_2 groups.



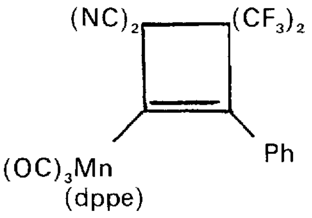
III

(b) Manganese, technetium and rhenium

In the spectrum of the cyclobutenyl complex

$\mathrm{Mn\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_3(dppe)}$ (IV)

(Fig. 4a), $[M^+]$ is observed together with ions formed by the usual CO loss and breakdown of the cyclobutenyl ring. In this case, loss of the olefin $(CF_3)_2C{=}C(CN)_2$ from the $[M-3CO]^+$ ion is characteristic of the four-membered ring; in the case of the ring-opened butadienyl derivative, this mode of fragmentation is not observed. Addition of NOBA to the molecular ion is an unusual feature of this spectrum, as this matrix does not often coordinate under FAB conditions. Observation of fluorine loss is complemented by the formation of $[MnF(dppe)]^+$ as the base peak, further underscoring the importance of formation of metal fluoride species by transition metal fluorocarbon complexes in the mass spectrometer.[108] This type of process has often been observed in EI MS, but the intensities of ions formed by loss of metal fluoride, or of metal fluoride ions, are generally much lower.



IV

The complex $[ppn][Mn(CO)_5]$ gives a negative ion spectrum showing $[Mn(CO)_5]^-$ at m/z 195, and a positive ion spectrum with $[ppn]^+$ at m/z 538, together with appropriate fragment ions in each case.

Davis et al.[101] have looked at some substituted rhenium complexes using a mixed DAP/glycerol matrix. The complexes $ReX(CO)_3\{P(C_6H_4R\text{-}4)_3\}_2$ (R = F, Me; X = Cl or ONO_2) showed $[M+H-X]^-$ as the highest ion, although there is no evidence for loss of X in solutions of these complexes. Similar behaviour has been noted for $M(ONO_2)(CO)_5$ (M = Mn, Re).[109,110]

In a study of coordination complexes, Bursey et al.[26] compared the complexes $[ReCl_2(bpy)(PMe_2Ph)_2][PF_6]$ and $[Re(CO_3)(bpy)(PMe_2Ph)_2][PF_6]$. In the first example $[M]^+$ fragments by loss of Cl and PMe_2Ph. The loss of phosphine demonstrates a parallel with known solution substitution chemistry. Dissociation of Cl was shown to occur by homolytic bond cleavage and was related to the solution electrochemistry where a facile reductive process from Re(III) to Re(II) occurs. In the second complex another redox process was observed where reduction of Re(III) to Re(I) was accompanied by a change in coordination, the ion $[Re(bpy)(PMe_2Ph)_2]^+$ being formally four-coordinate. Different metal-ligand fragmentation processes were observed with the Re(I) compounds *cis,trans*-$[Re(CO)_2(bpy)(PMe_2Ph)_2]^+$ and *fac*-$ReCl(CO)_3(bpy)$. In the former, loss of phosphine was found to occur in preference to CO; this was related to the weaker π-donor ligand being lost preferentially. The second example gave a base peak $[M-Cl]^+$; $[M]^+$ was not found. This process (loss of chloride) also resembles the solution substitution chemistry of these complexes in polar solvents, where *fac*-$[Re(L)(bpy)(CO)_3]^+$ complexes (L = entering ligand) are formed.

The cationic complexes $[ReH_3(PPh_3)_2(\eta^5\text{-}C_6H_4R_3)]^+$ (R = H, Me) gave spectra showing $[M-2H]^+$ ions at m/z 791 and 833, respectively. Loss of 2H was also found in the EI spectra of related neutral complexes and would therefore appear to be typical of this system.[111] For complexes of the type $[ReH_2(PPh_3)_2(\eta^6\text{-}C_6H_{6-n}X_n)]^+$ (X = H, Me; $X_2 = Me_2$; $X_3 = Me_3$), molecular ions were found.[112]

A detailed study of some technetium and iron complexes, such as $[TcCl(dppe)_2]^+$ and $[FeCl_2(dmpe)_2]^+$, by FAB MS/MS and FAB MIKES techniques was carried out by Unger.[113] These powerful methods enabled structural elucidation of the various fragments and indicated that the two factors determining complex ion stability for these systems are the nature of the transition metal centre and the size of the substituent (alkyl or aryl) attached to the equatorial chelating ligand.

(c) Iron, ruthenium and osmium

It is often more convenient to obtain EI mass spectra for low molecular weight compounds, as they are often more volatile, and matrix ions complicate the low mass regions of FAB mass spectra. An example is ferrocene, where $[M]^+$ is difficult to obtain by the FAB method. These difficulties may be related to the relatively non-polar nature of these metallocenes. However, ionic complexes are best examined by the FAB

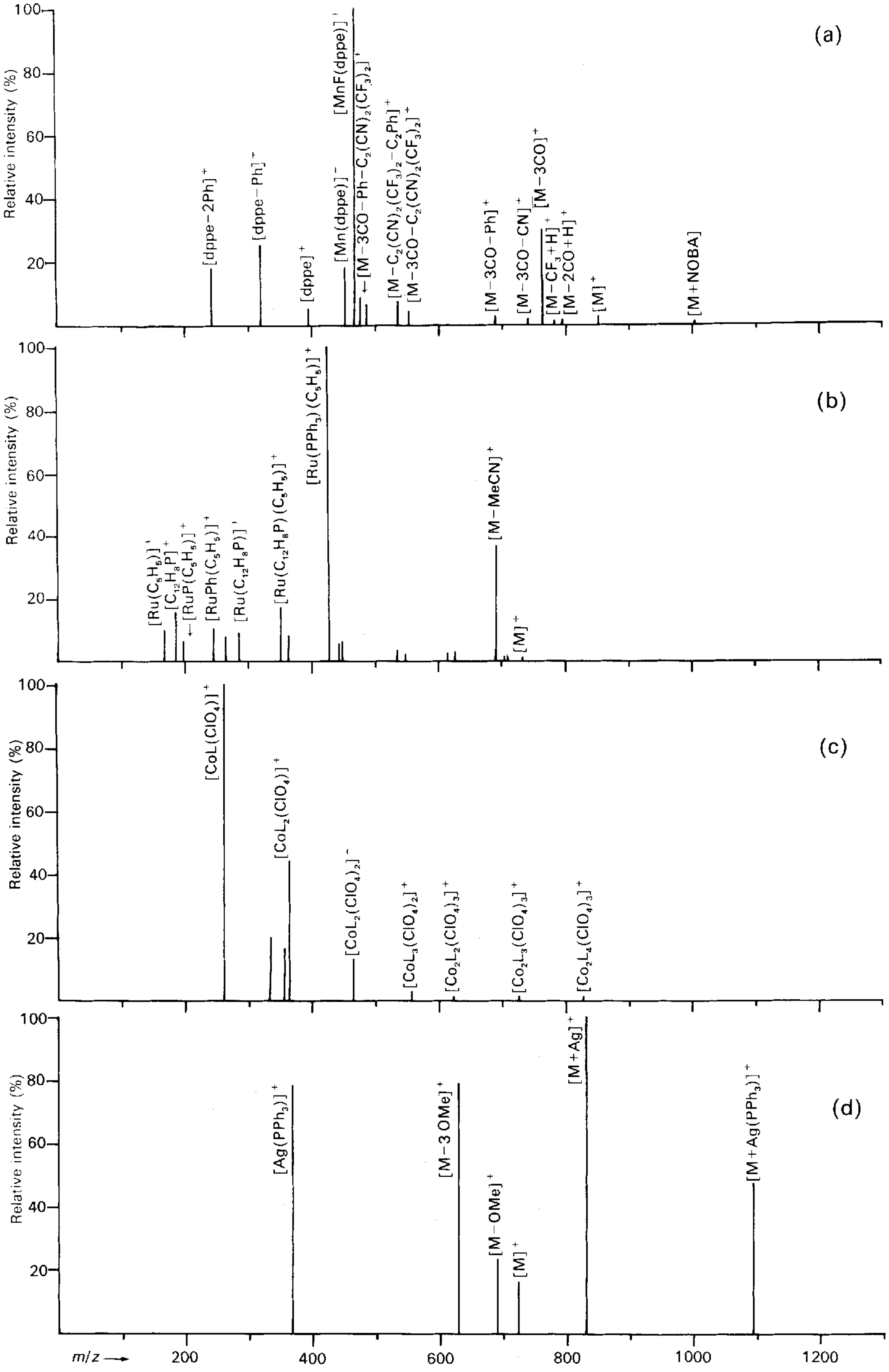


Figure 4 · FAB mass spectra of selected transition metal complexes:

(a) $\mathrm{Mn}\{\overline{\mathrm{C{=}CPhC(CF_3)_2C}}\mathrm{(CN)_2}\}\mathrm{(CO)_3(dppe)}$ (IV);

(b) $\mathrm{[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]}$;

(c) $\mathrm{[Co(dien)_2][ClO_4]_3}$ (L = dien);

(d) $\mathrm{Ag(PPh_3)\{C_5(CO_2Me)_5\}}$.

In Figures 4–8, normalised monoisotopic spectra are shown for those compounds containing multi-isotopic elements (based on ^{12}C, ^{56}Fe, ^{102}Ru, ^{107}Ag, ^{197}Au).

method. A range of cationic complexes of the type $[\mathrm{Fe}\{\mathrm{C(O)Me}\}(\mathrm{CO})_2(\mathrm{L})(\mathrm{diars})]^+$ $[\mathrm{L}=\mathrm{PR}_3$ or $\mathrm{P(OR)}_3]$ have been studied by Jablonski et al.[114] Evidence for a rearrangement fragmentation analogous to the well-known decarbonylation of acyl-metal complexes (Eqn 1)

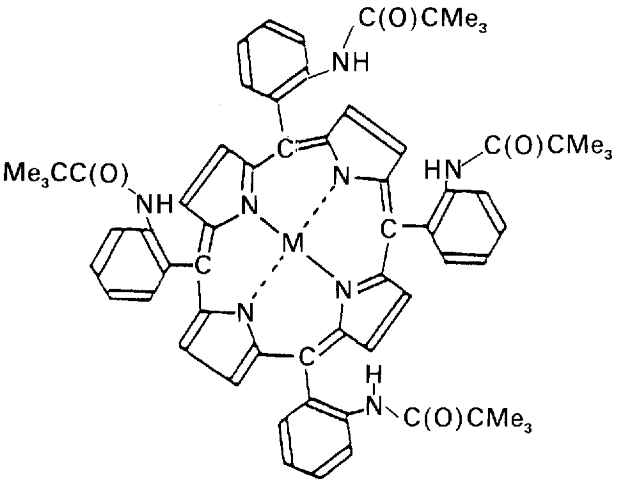
$$[\mathrm{Fe}\{\mathrm{C(O)Me}\}]^+ \rightarrow [\mathrm{FeMe}]^+ + \mathrm{CO} \qquad [1]$$

was presented along with $[\mathrm{M}]^+$ information for these complexes.

The 1,3-cyclobutenylidene complex $[\{\mathrm{Fe}(\mathrm{CO})(\mathrm{PPh}_3)(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\}_2(\mu\text{-}\mathrm{C}_4\mathrm{H}_3)][\mathrm{PF}_6]$ was obtained by intermolecular attack of an ethynyl complex on the analogous vinylidene cation; the FAB spectrum confirmed the binuclear formulation.[115] Smith et al.[116] found that the spectrum of $\mathrm{Fe}_2(\mathrm{CO})_7(\mathrm{dppm})$ gave the expected $[\mathrm{M}]^+$ at m/z 692, while the mononuclear $\mathrm{Fe}(\mathrm{CO})_4(\eta^1\text{-}\mathrm{dppm})$ formed in the same reaction showed $[\mathrm{M}]^+$ and $[\mathrm{M}-n\mathrm{CO}]^+$ $(n=2-4)$. Similarly, the complex $\mathrm{Fe}\{\mathrm{C}_5(\mathrm{CO}_2\mathrm{Me})_5\}$ gave an easily interpreted fragmentation pattern derived from a strong $[\mathrm{M}]^+$ at m/z 766 (86%) followed by loss of $\mathrm{CO}_2\mathrm{Me}$ groups.

Campana and Freas have recorded the FAB mass spectra of iron complexes containing phthalocyanine or tetrakis(cumylphenoxy)-phthalocyanine ligands.[117] In both cases, $[\mathrm{M}]^+$ and $[\mathrm{M}+\mathrm{H}]^+$ ions were observed, but little structural information could be obtained. A series of iron(III) porphyrin complexes afforded both molecular weight and structural information from the fragmentation patterns, especially for complexes containing the picket-fence *meso*-tetra (α, α, α, α-2-pivalaminophenyl)porphyrin (V).[118] In a comparison with DEI and DCI ionisation methods, FAB was found to be the only technique capable of providing $[\mathrm{M}]^+$ information for all the derivatives of deuteroprophyrin-IX investigated. FAB spectra contained strong molecular adduct ions in several cases, attributed to an in situ coordination of iron-containing porphyrins with sulphur-containing matrix molecules.

FAB MS has been recommended as a preliminary screening technique for potentially novel siderophores, which are low molecular weight chelating agents with an affinity for iron, secreted by microorganisms. The spectra of some hydroxamate-iron siderophore complexes were analysed.[119] In early FAB MS accounts, their use in characterising bleomycins A_2 and B_2 and their metal complexes was described. The FeSO_4 complex of bleomycin A_2 gives a high mass ion at m/z 1566, assigned to $[\mathrm{A}_2-\mathrm{H}+\mathrm{FeSO}_4]^+$.[120] FAB analysis of two metallocene bis(crown ether) complexes (VI; M = Fe, Ru) demonstrated that the cavity formed between two cofacial amidobenzo-15-crown-5 units provides high selectivity for K^+ over Na^+ and Cs^+ in competition experiments.[121]



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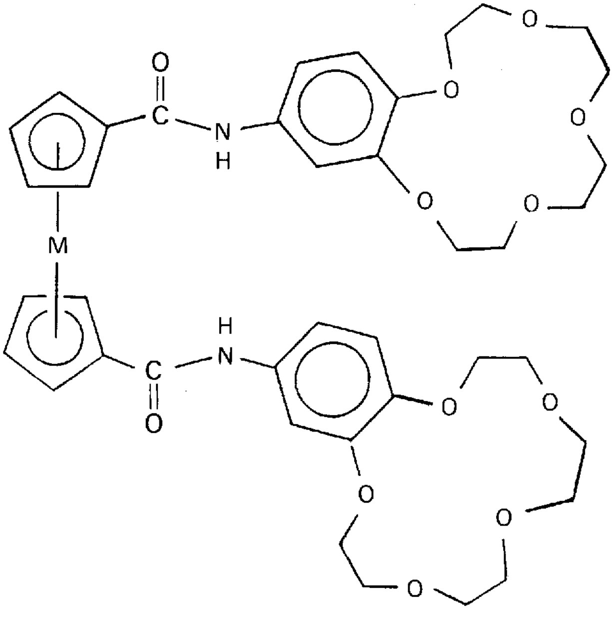
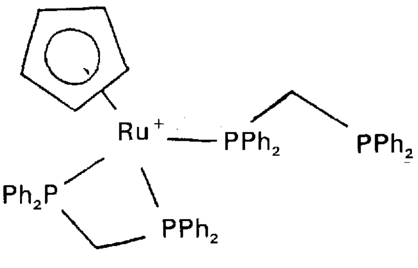


VI

M=Fe, Ru

A wide variety of ruthenium complexes have been studied with our instrument. Comparison of FAB mass spectra with EI spectra shows that similar fragmentation patterns are frequently found. In the FAB spectra, $[M]^+$ is more frequently found. Table 3 includes the FAB spectra of three complexes, $[Ru(NCMe)(PR_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (R = Ph, OMe) and $[Ru(dppm)_2(\eta\text{-}C_5H_5)][BF_4]$. The difference in relative intensities of several fragment ions gives an indication of the relative stability of these species, and can also be related to the solution chemistry of the complexes. Structural information can also be gleaned from these spectra: in the dppm complex, that one dppm is η^1-bonded ('dangling') is suggested by the ready loss of this ligand to give $[Ru(dppm)(C_5H_5)]^+$. An X-ray structural study of the cation (VII) confirmed this feature.[122]



VII

In complexes of the type $RuX(L)_2(\eta\text{-}C_5H_5)$, the formation of ions $[M]^+$ or $[M-X]^+$ may be affected by changing the polarity of the matrix (Table 4). For example, the molecular ion of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ is not observed in a DTT/DTE matrix, whereas in NOBA, this ion has 25% relative intensity. In DTT/DTE, the highest ion is $[Ru(PPh_3)_2(C_5H_5)+\text{matrix}]^+$. An analogy can be drawn with the known solution chemistry of complexes $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$, where dissolution in a polar solvent allows exchange of halide for L (L = solvent or neutral ligand, such as RCN, PR_3) to give complexes such as $[Ru(L)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$.[123] In general the ion $[Ru(PPh_3)_2(C_5H_5)]^+$ is more abundant in

Table 3 FAB mass spectra of some η-cyclopentadienyl-ruthenium complexes

			Ions (*m/z*, relative intensity)		
Complex	Matrix	Cosolvent	$[M]^+$		Principal fragments
$[RuNCMe)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][PF_6]$	NOBA	CH_2Cl_2	456(68)	$[M-CH_3CN]^+$ 415(100)	$[Ru\{P(OMe)_3\}(C_5H_5)]^+$ 291(24)
$[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$	NOBA	CH_2Cl_2	732(0.2)	$[M-CH_3CN]^+$ 691(36)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)
$[Ru(dppm)_2(\eta\text{-}C_5H_5)][BF_4]$	DTT/DTE	CH_2Cl_2	935(16)	$[Ru(dppm)(C_5H_5)]^+$ 551(100)	$[Ru(PPh)_2(C_5H_5)]^+$ 352(24)
$RuH\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	416(100)	$[M-OMe]^+$ 385(35)	$[M-P(OMe)_3-H]^+$ 291(31)
$RuH(PPh_3)_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	692(39)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)	$[RuPPh_2)(C_5H_5)]^+$ 352(20)
$Ru\{C(CO_2Me){=}CH(CO_2Me)\}$- $(PPh_3)_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	834(1)	$[M-PPh_3]^+$ 572(100)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(96)
$Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	516(100)	$[M-C_2Ph]$ 415(26)	$[M-Me-P(OMe)_3]^+$ 377(26)
$Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	792(11)	$[M-C_2Ph]$ 691(27)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)
$Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$	NOBA	CH_2Cl_2	730(4)	$[M-C_2Me]$ 691(21)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)
$Ru\{C{=}CPhC(CF_3)_2C(CN)_2\}$- $(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (VIII)	NOBA	CH_2Cl_2	772(84)	$[M-(CN)_2C_2(CF_3)_2]^+$ 558(11)	$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)
$Ru\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}$- $(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (IX)	NOBA	CH_2Cl_2	772(14)		$[Ru(PPh_3)(C_5H_5)]^+$ 429(100)
$Ru\{C{=}PhC(CF_3)_2C(CN)_2\}$- (dppe) $(\eta\text{-}C_5H_5)$	DTT/DTE	$CHCl_3$	880(71)	$[M-Ph]^+$ 803(21)	$[M-(CN)_2C_2(CF_3)_2]^+$ 666(100)
$Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}$	DTT/DTE	CH_2Cl_2	522(48)	$[M-OMe]^+$ 491(100)	$[Ru(C_5H_5)]^+$ 167(38)

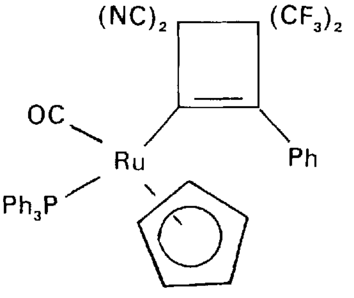
Table 4 Some common ions in FAB mass spectra of complexes $RuX(L)_2(\eta\text{-}C_5H_5)$

X	L	Matrix (cosolvent)	Ions (m/z, relative intensity)^a			
			$[M]^+$	$[M-X]^+$	$[M-L]^+$	$[M-X-L]^+$
Cl	$P(OMe)_3$	$NOBA(CH_2Cl_2)$	450(100)	415(50)	326(76)	291(31)
Cl	PPh_3	$NOBA(CH_2Cl_2)$	726(25)	691(30)	464(43)	429(100)
		$DTT/DTE(CH_2Cl_2)$	—	691(30)	—	429(100)
Br	PPh_3	$NOBA(CH_2Cl_2)$	770(2)	691(27)	508(5)	429(100)
I	PPh_3	$NOBA(CH_2Cl_2)$	818(15)	691(17)	556(42)	429(100)

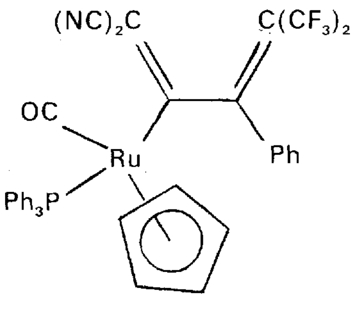
^{a}Based on ^{35}Cl, ^{79}Br, ^{102}Ru

the FAB spectra than in the EI spectra, although with both techniques, $[Ru(PPh_3)(C_5H_5)]^+$ is often the base peak. This observation may relate to the thermal stability of the species, the first PPh_3 ligand being easily displaced at elevated temperature. The related complexes $RuX\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ give spectra which show that both the phosphite and halide ligands are firmly bound to the metal as found in their chemistry.[122] For X = Cl, the FAB spectrum contains a high mass peak corresponding to $[\{Ru\{P(OMe)_3\}_2(C_5H_5)\}_2Cl]^+$ at m/z 865, a clear indication that ion-molecule aggregation reactions may be occurring in the ion source. It is interesting to note that similar species have been obtained in vitro by halogenation of $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2$.[124]

Both EI and FAB spectra of the cyclobutenyl (VIII) and butadienyl (IX) isomers of $Ru\{C_2Ph\text{-}C(CN)_2C(CF_3)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ shows $[M]^+$ followed by loss of CO and Ph. In the cyclic complex, loss of the olefin is also observed, thus reversing the cycloaddition reaction by which this complex is formed. Loss of PPh_3 from $[M]^+$ is only found in the EI mass spectrum and suggests that this may be a thermally induced dissociation. The strong $[PPh_3]^+$ (m/z 262) and associated fragment ions found in the EI spectrum support this view.



VIII



IX

The utility of FAB MS for obtaining structural information about cationic complexes is very well illustrated by the spectrum of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (Fig. 4b). Low amplification is required to observe a fully resolved $[M]^+$, although this is relatively weak compared with the base peak $[Ru(PPh_3)(C_5H_5)]^+$ (m/z 429). The fragmentation pathway is similar to that found for related neutral complexes, and involves loss of neutral molecules (MeCN, PPh_3), neutral fragments (Ph), and molecules formed by transfer of H to radicals (C_6H_6). As mentioned previously, addition of oxygen to fragment ions is frequently seen, for example at m/z 707, which is formulated as $[Ru(PPh_3)_2(C_5H_5)+O]^+$.

The advent of FAB MS proved to be very useful for our studies of a series of cationic vinylidene complexes of the iron triad metals.[125–127] All such complexes that we have examined show $[M]^+$ and a readily assignable fragmentation pattern based on competitive loss of the vinylidene substituents. This contrasts with EI studies, where the complex spectra that are obtained suggest, not surprisingly, that pyrolysis of these complexes occurs in the source.

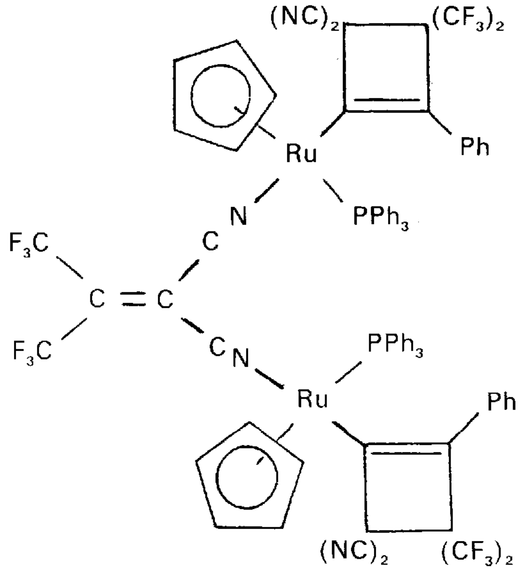
Complexes containing two $Ru(PPh_3)(\eta\text{-}C_5H_5)$ moieties have been studied, including

$$\{Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C(CN)_2{=}C(CF_3)_2\} \qquad (X)$$

and

$$\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4) \qquad (XI)$$

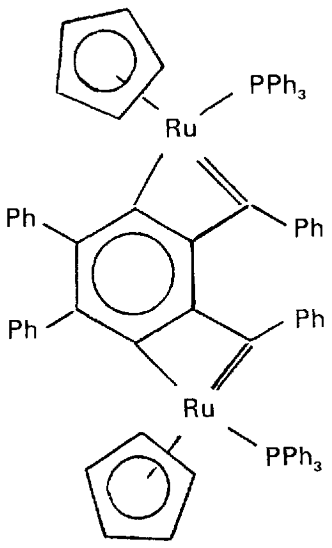
The first complex gives a molecular ion at m/z 1702 (0.6%), together with $[M+O]^+$ (1.5%). Fragmentation by loss of the cyclobutenyl ring and loss of a ruthenium-cyclobutenyl moiety indicate the stability of the bridging unit. In the second example, $[M^+]$ was found at m/z 1262 (65%) with principal fragmentation pathways involving loss of PPh_3 and Ph groups.



X

Some phosphine-rich complexes do not give satisfactory EI mass spectra as a result of thermal decomposition in the spectrometer. An example is $RuCl_2(PPh_3)_3$, for which satisfactory FAB mass spectra have been obtained, providing structural information.[101] The highest ion observed was $[M-PPh_3+H]^+$, which loses 2Cl stepwise and a second PPh_3 ligand. The facile loss of PPh_3 is again related to known solution chemistry.

We have looked at the FAB spectra of $OsBr_2(PPh_3)_3$. Interestingly, although no $[M]^+$ was found, a pseudo-molecular ion is found at m/z 1087, corresponding to $[OsBr(NO)(PPh_3)_3]^+$, apparently formed by exchange of Br for NO from the matrix (NOBA). Fragmentation of this ion occurs by loss of Br, PPh_3, NO and Ph: the base peak is $[OsBr(NO)(PPh_3)_2]^+$.



XI

Bursey et al.[26] have studied the neutral complex *mer*-$OsCl_3(PMe_2Ph)_3$. The highest ion is $[M-Cl]^+$ (m/z 676). This observation also can be related to the solution chemistry in which the dominant reaction is loss of Cl^- rather than of the tertiary phosphine. For the cations $[Os(tpy)_2]^{2+}$ and *cis*-$[OsO_2(bpy)_2]^{2+}$, positive ions were derived from a molecular ion which had been reduced, rather than the doubly-charged cation, $[M]^{2+}$. FDMS has been shown to effect a similar reduction for these complexes.

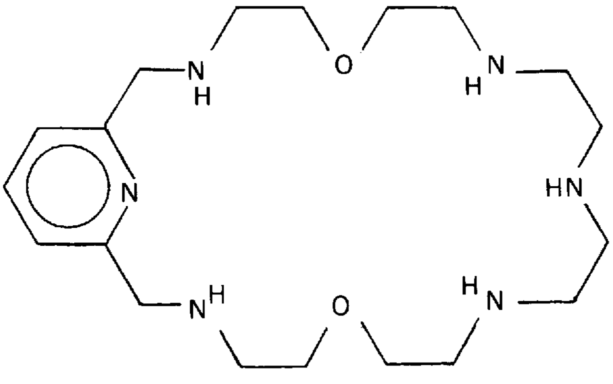
These authors also studied a series of osmium complexes containing π-bound ligands $[OsCl(L)(bpy)_2]^+$ $[L=C_2H_4$, $PhCH{=}CH_2$, C_2Et_2, PhC_2Me, $C_2(CO_2Me)_2]$.[63] FD methods provided only $[M]^+$ for these complexes whereas FAB gave $[M]^+$, $[M-L]^+$ and $[M-L-HCl]^+$ ions. The loss of the π-bound ligand gave the base peak in all cases except $L=C_2(CO_2Me)_2$. In the same paper the spectra of $RuCl(bpy)(\eta\text{-}C_5H_5)$ and $[RuCl(bpy)(\eta\text{-}C_6H_6)]^+$ were discussed. The former gave $[M-Cl]^+$ as the highest and most intense peak whereas the latter gave $[M]^+$ as well as $[M-Cl]^+$. The bimetallic complex $[RuCl(bpy)_2(PPh_2Fc)]^+$ produced ions $[M]^+$, $[M-PPh_2Fc]^+$ and $[M-PPh_2Fc-Cl]^+$, together with $[PPh_2Fc]^+$ and $[PPhFc]^+$, which clearly illustrates the use of FAB MS for the determination of the molecular constituents of complex systems. The complexes $[MX(CO)(bpy)_2]^+$ (M = Ru, Os; X = Cl, OC(O)H, $OC(O)CF_3$) and $[MR(CO)(bpy)_2]^+$ (M = Ru, Os; R = H, C_5H_{11}, CH_2Ph) gave intense $[M]^+$ ions as well as $[M-X \text{ (or R)} - CO]^+$.

(d) Cobalt, rhodium and iridium

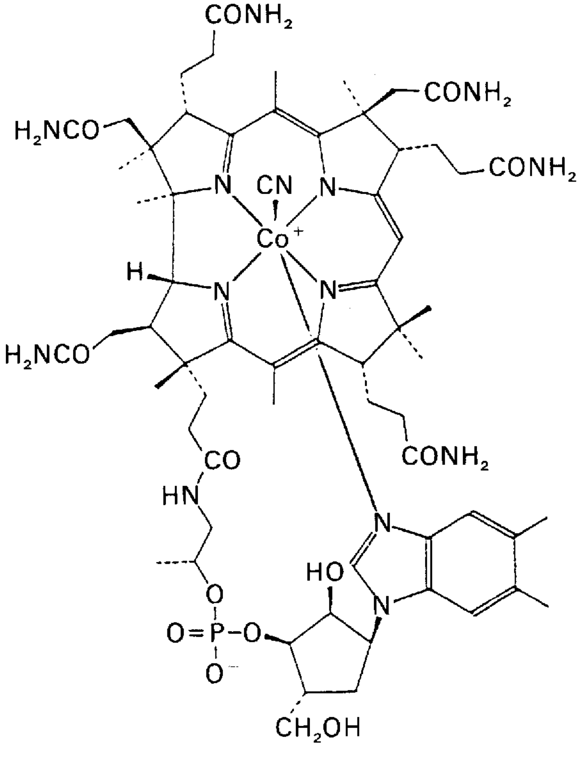
The compounds *mer*-$[Co(dien)_2][ClO_4]_3$ and *s-fac*-$[Co(Me\text{-}dien)_2][ClO_4]_3$ gave FAB mass spectra which contained significant peaks corresponding to ion-molecule aggregates. These are clearly seen in the former (Fig. 4c). No ion $[CoL_2]^{3+}$ (L = dien or Me-dien) was observed although the complex ion $[CoL_2(ClO_4)_2]^+$ was found. The higher molecular weight species suggest that the observed ions correspond to an aggregate of ions around $[M]^+$ in solution and that these aggregate ions are present to a greater or lesser extent in the spectrometer depending on the stabilities of the ion clusters. At this stage it is not clear if these or other mechanisms are at work; MIKES spectra should help in establishing which are the major ions formed initially.

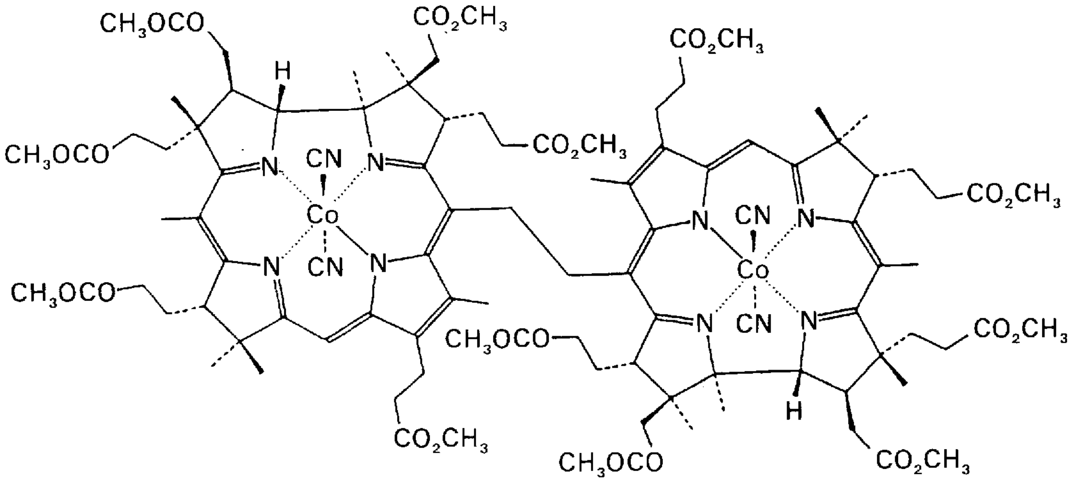
The compound $Co\{C_5(CO_2Me)_5\}_2$ (glycerol matrix) afforded a complex spectrum which at high mass contained the ions $[M+Co+glyc]^+$ (*m/z* 920, 21%), $[M+glyc]^+$ (861, 11%), and $[M+Co]^+$ (828, 18%) as well as $[M]^+$ (769, 16%) and $[M+H]^+$ (770, 17%). Such complexities make the assignment of molecular weights difficult and indicate that a considerable degree of aggregation occurs at the surface of the matrix.

FAB MS proved useful in determining the degree of complexation of cobalt with a ditopic macrocycle, pyridine[24]-N_6O_2 (XII); formation of a 1/1 complex was confirmed by the appearance of $[M]^+$ at *m/z* 440.[128]


XII

Cobalt derivatives of phthalocyanine and tetrakis(cumylphenoxy)phthalocyanine have been examined by Freas and Campana,[117] principally to obtain molecular weight information. Grotjahn and Ernst[129] looked at the monomeric corrinoids, vitamin B_{12} (XIII) and dicyanocobyrinic acid *a,c*-diamide pentamethyl ester, which gave informative positive and negative ion spectra. Pseudo-molecular ions $[M+H]^+$ and $[M-H]^-$ were obtained, together with higher mass peaks corresponding to oxygen adducts; the latter were confirmed by high resolution studies. A dimeric corrinoid of composition $Co_2C_{102}H_{132}N_{12}O_{24}$ (XIV) was also examined; as with the monomeric complexes, negative ion FAB MS provided more reliable molecular weight information. Loss of CN ligands was observed; in one instance, loss of HCN was also found. In a glycerol matrix, successive addition of glycerol molecules was found, whereas in NPOE, exchange of the two CN groups for NO was found. In several cases the observed spectrum changed after short periods of bombardment. A proper knowledge of the processes involved in similar systems is there-


XIII



XIV

fore required to obtain correct information from FAB MS of corrinoids.

This conclusion contrasts with the results of Schwarz et al.[130,131] who suggested that FAB MS provided unequivocal and rapid molecular weight information on corrins with two axial CN groups. In this study of a series of dicyanocobyrinic acid heptamethyl ester derivatives, no $[M]^+$ or $[M+H]^+$ ions were observed in the positive ion mode, but ready loss of 2CN groups with reduction of Co(III) to Co(I) occurred, as in the EI spectra. The negative ion spectra contained very strong $[M-H]^-$ peaks (20–100%) along with fragment ions formed by consecutive loss of the axial ligands.

Studies of suitable matrices for cobalamins mention that information about one or both axial ligands can be obtained readily from the FAB spectra. For cobyrinic acids, triethyl or tributyl citrates (TEC or TBC), benzyl benzoate, and 2-nitrophenol octyl ether (NPOE) were found to give good spectra.[43] Meili and Seibl also demonstrated the need for correct choice of matrix for dioxosecocorrin.[97] In a glycerol matrix, $[M]^+$ was not found, the base peak corresponding to the hydrogenation product $[M-2CN+2H]^+$. In NPOE however, $[M]^+$ is observed, followed by successive loss of CN groups. The latter matrix was therefore recommended as a useful aprotic matrix for the analysis of corrin and porphyrin complexes. Molecular radical cations are formed typically and hydrogenation reactions are suppressed.

Cobalamins are characterised by a strong peak at *m/z* 1329, formed by loss of one axial ligand.[132] In coenzyme B_{12}, $[M+H]^+$ at *m/z* 1579 decomposes in this way, with loss of deoxyadenosine. Similar losses of Me, CN or OH groups were observed for the appropriately substituted cobalamines. Most other fragments are formed by breakdown of the second axial ligand, dimethylbenzimidazole, and cleavage of the sugar and phosphate links. The negative ion spectra are complementary, appearing 2 amu below the positive ions, and are derived from $[M-H]^-$.[133] Tandem mass spectrometry (MS/MS) has been used to identify spurious peaks in the spectra of vitamin B_{12}.[134] A peak at *m/z* 1388 which grows at the expense of $[M+H]^+$ (*m/z* 1355) was shown by collisionally activated dissociation (CAD) to be formed by intermolecular transfer of a cobalt atom from one molecule to the phosphate group of a second molecule. In contrast, high resolution positive ion FAB studies of cobalamin (vitamin B_{12}) established the loss of a 59 amu fragment from $[M+H-CN]^+$ corresponds to the loss of acetamide and not the central cobalt atom.[135] A comparison of FAB and FD techniques applied to cobalamin derivatives showed that the former gave impact-ionisation related fragments, whereas FD produced ions characteristic of thermal degradation.[136] A didehydrocorrinoid derivative, 'pyrocobester', is oxygenated in the presence of light to give '5,6-dioxosecopyrocobester'. This compound was analysed by FAB MS. In the positive ion mode, the base peak at *m/z* 994 was found to be $[M+H-2CN]^+$, while in the negative ion mode, the base peak is *m/z* 1046, corresponding to $[M]^-$.[137]

A comprehensive review of the potential of 10 different ionisation methods for the mass spectrometric investigation of corrins and vitamin B_{12} derivatives has recently been published.[138] Of the soft ionisation techniques that were considered, FD MS appears to give the most conclusive information, especially when backed up by FAB MS which provides a constant ion current suitable for fragment elucidation techniques such as CAD, MIKES, linked scan and MS/MS.

In a comparison of FAB and FD methods applied to the complexes $[Rh(L)(cod)]^+$ (L = bpy, phen), ions $[M]^+$ and $[M-cod]^+$ were found in the former spectra, whereas FD spectra contained only $[M]^+$.[26] The positive FAB mass spectrum of $Rh(cod)\{\eta\text{-}C_5H_4(CH_2)_3Si(OMe)_3\}$ was described in detail in the first full paper on the FAB MS technique.[30] This complex is a viscous liquid and spectra could be obtained without the use of a matrix. The highest ion is $[M]^+$, which fragments by loss of cod, $HSi(OMe)_3$ and $Si(CH{=}CH_2)(OMe)_3$.

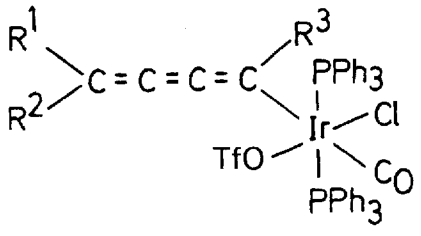
Several groups have examined Wilkinson's complex, $RhCl(PPh_3)_3$. Geoffroy et al.[95] found that use of an 18-crown-6/tetraglyme matrix enabled the observation of $[M]^+$ and $[M-Cl]^+$, whereas Davis et al.,[101] using a DAP matrix, observed $[M+H]^+$ as well as $[M]^+$. The fragmentation pattern is generally independent of the matrix, although use of DAP also produced protonated ions. Major peaks include $[M-Cl]^+$, $[M-PPh_3]^+$, $[M-Cl-PPh_3]^+$, $[M-Cl-PPh_3-Ph]^+$ and $[M-2PPh_3]^+$, with only weak $[M]^+$ (1% in DAP). Stang et al.[139] also used a mixed 18-crown-6/tetraglyme matrix, but found only the fragmentation pattern derived from $[M-Cl]^+$. These discrepant observations illustrate the importance both of finding a suitable matrix and of optimising operating conditions. The related $RhBr(PPh_3)_3$ afforded $[M]^+$ and $[M+H]^+$, with a fragmentation pattern resembling that of the chloro complex.[101]

A series of cationic rhodium(III) and iridium(III) complexes containing bidentate N-donor ligands $[MCl_2(L)_2]^+$ (L = bipyridyls, bipyrimidyl, biquinolyl, phenylazopyridine) have been studied by FAB MS.[140] With thioglycerol, $[M]^+$ were obtained for all examples, loss of Cl being the major fragmentation pathway. The rhodium complexes exhibited transient $[M]^+$ and associated fragment peaks which were replaced by ions formed by attack of thioglycerol radical, $HOCH_2CH_2S^{\bullet}$ (= SR), such as $[Rh(SR)(L)_2]^+$, $[Rh(SR)_2(L)_2]^+$ or $[RhCl(SR)(L)_2]^+$. In glycerol, these effects were not observed. The iridium complexes were stable in both matrices, as well as in tetraglyme, and gave similar ions and relative intensities to the rhodium complexes. Attachment of hydrogen to give $[M+4H]^+$ was found for both the rhodium and iridium phenylazopyridine complexes, and deuterium labelling established that addition had occurred to the ligand. In the spectrum of the iridium complex

$$\overline{IrHCl(C_6H_4N{=}N}C_6H_3NMe_2\text{-}4)(PPh_3)_2,$$

the molecular ion fragments by loss of Cl, PPh_3 and the azo ligand, azb ($[M]^+$ 10%, $[M-Cl]^+$ 58%, $[M-PPh_3]^+$ 15%, $[M-Cl-PPh_3]^+$ 100%, $[M-azb]^+$ 15%).[141]

The two carbonyl chloro complexes $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) afford $[M]^+$, $[M-Cl]^+$ and $[M-CO]^+$ ions, and loss of PPh_3 is also a major fragmentation pathway.[139] The iridium complex has $[M]^+$ as base peak whereas for the rhodium derivative this ion has only 16% relative intensity, illustrating the stability gained for this type of cation in descending a group. A series of rhodium and iridium cumulene complexes afforded useful spectra, in which loss of ligands could be related to the donor capability of the group, anionic groups being lost most readily, followed by unsaturated organic ligands, then π-acid ligands.[47] The σ-bonded complexes of the type $IrCl(OTf)(CR_1{=}C{=}C{=}CR_2R_3)(CO)(PPh_3)_2$ (XV; OTf = OSO_2CF_3; R = H, Me, Ph, C_9H_{14}) gave $[M]^+$ followed by loss of triflate, CO and Cl. Loss of the organic group occurs in a single step; the bond between the metal and organic groups is stronger than found in a series of related π complexes. The influence of differing instrumentation was also evaluated, using VG ZAB, Kratos MS950 and Varian-MAT 731 spectrometers; similar results were obtained using either argon or xenon, and with or without data systems.

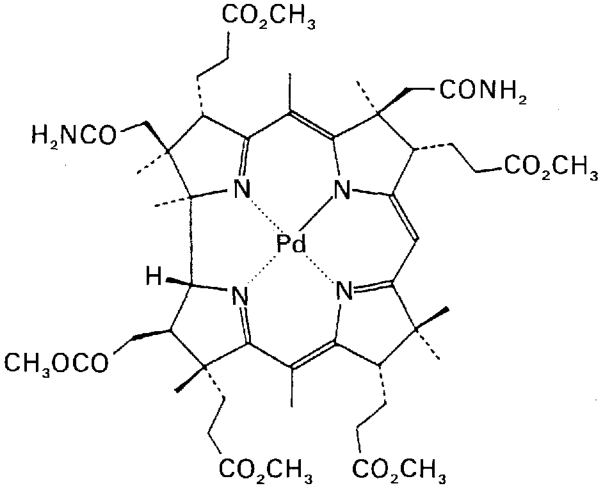


XV

The FAB mass spectrum of $Rh_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(cod)_2$ (18-crown-6/tetraglyme) shows both $[M]^+$ and $[M+H]^+$, which fragment by loss of Cl, Ph and cod groups.[95]

(e) Nickel, palladium and platinum

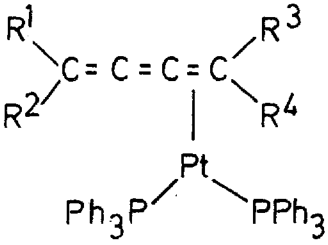
Nickel complexes of phthalocyanine and the tetrakis(cumylphenoxy) derivative have been studied by Campana and Freas.[117] From a strongly acid matrix (85% H_3PO_4/H_2SO_4), ions $[M+H+O]^+$, $[M+O_2]^+$, $[M+H+O_2]^+$ and $[M+OH_2]^+$ were found in addition to the expected $[M]^+$ and $[M+H]^+$. The palladium and platinum phthalocyanines did not give any molecular weight information; however, in solution these compounds are known to form oligomeric aggregates, which apparently cannot be sputtered from the matrix. A palladium-containing corrinoid, methoxypalladibyrinic acid *a,c*-diamide pentamethyl ester (XVI), showed $[M+H]^+$ which by high resolution was shown to overlap with $[M-MeOH+2O]^+$.[129]



XVI

The FAB and FD spectra of cationic η^3-allyl complexes of nickel and palladium have been compared, the former technique giving weak $[M]^+$ and fragment ions, while the latter gave strong $[M]^+$ with little fragmentation.[27] These spectra were obtained for $[Ni(PPh_3)_2(\eta^3\text{-crotyl})]^+$, $[Pd(PR_3)_2(\eta^3\text{-}C_4H_7)]^+$ (R = Ph, Cy, Bu, OPH) and $[Pd(L_2)(\eta^3\text{-}C_4H_7)]^+$ (L_2 = dppe, tmtu). For the dppe complex, $[M^+]$ is the base peak with the principal fragment ions being $[Pd(dppe)]^+$, $[Pd(PPh_2)]^+$ and $[M-C_4H_7Ph]^+$. For complexes containing two ligands, the main fragments are $[M-C_4H_7]^+$ and $[M-PR_3]^+$. Ligand exchange was observed when the PBu_3 and tmtu complexes were mixed, with ions such as $[Pd(tmtu)(PBu_3)(C_4H_7)]^+$ and $[Pd(tmtu)(PBu_3)]^+$ being found.

Some platinum cumulene π-complexes, $Pt(\eta^2\text{-}CR^1R^2{=}C{=}C{=}CR^3R^4)(PPh_3)_2$ (XVII); R = H, C_2Me_4,Ph, $SiEt_3$, $GeEt_3$) were studied by Stang et al.[139] In all cases, the allene was readily lost to give $[Pt(PPh_3)_2]^+$ as the base peak; $[M]^+$ varied in intensity from 8–34%. The complex $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$ loses ethene readily in its solution chemistry; in the FAB mass spectrum, the base peak is $[Pt(PPh_3)_2]^+$ formed by the same process, other ions including $[M]^+$ and $[M-PPh_3]^+$.



XVII

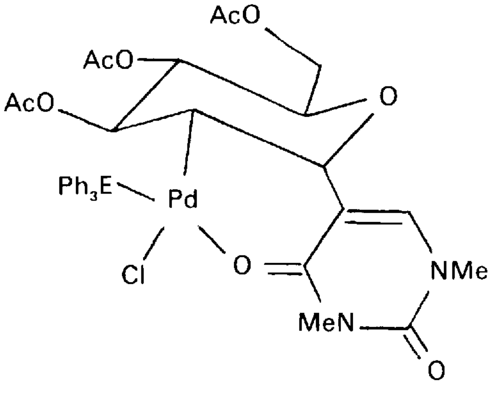
FAB mass spectra of $M(PPh_3)_4$ (M = Pd, Pt) have been obtained.[101] In neither case was $[M]^+$ observed, the highest mononuclear fragment ion being $[M-PPh_3]^+$, thus paralleling the solution chemistry. However, in the spectrum of the platinum complex, the binuclear species $[Pt_2(PPh_3)_n]^+$ (n = 2–4) were also found.

Studies of the dicationic complex $[Pt_2(\mu\text{-}dppm)_2(\mu\text{-}CH_2)(PMe_2Ph)_2][PF_6]_2$ showed that doubly-charged ions were not formed, with the highest ion being a cation-anion aggregate $[M+PF_6]^+$.[142] Of course, the precise structure of ions of this type is unknown, but it is worth recalling that the PF_6 anion is one of the more weakly coordinating ligands. The related complex $Pt_2(\mu\text{-}dppm)_2(\mu\text{-}CH_2)Cl_2$ shows a strong $[M]^+$ (*m/z* 1240) which readily loses Cl. For the related mononuclear complexes, $Pt(dppm)_2$ gave $[M+H]^+$ at *m/z* 960, whereas $PtMe_2(dppm)$ gave a weak $[M+H]^+$ which lost methane to give a strong $[M-Me]^+$ at *m/z* 593. We have obtained a weak molecular ion for the complex

$PtB_{10}H_{12}(PEt_3)_2$ at *m*/*z* 553 (0.8%) relative to a base peak at *m*/*z* 226 assigned to $[PtB_3H_n]^+$.

The FAB spectrum of $Pd(OAc)_2$ was reported in glycerol/acetic acid and triethanolamine. In the former matrix the reduced species $[Pd]^+$, $[Pd+glyc]^+$ and $[Pd+2glyc]^+$ were observed, while in the amino alcohol, the aggregates $[Pd+TEA]^+$, $[Pd+TEA+DEA-H]^+$ and $[Pd+2TEA-H]^+$ were found (DEA = diethanolamine, present in the TEA).[67]

Parker has shown the utility of FAB MS in demonstrating the formation of a 1/1 coordination complex between nickel perchlorate and the macrocycle pyridine[24]-N_6O_2 (XII), whereas 1/2 complexes were obtained with $PdCl_2(NCMe)_2$ and $PtCl_2(NCBu^t)_2$.[128] The latter are dicationic with Cl^- counter-ions; the observed pseudo-molecular ion was $[M+Cl]^+$ which initially fragmented by loss of Cl. Spectra of two stable glucopyranosylpalladium chloro complexes $PdCl(gl)(EPh_3)$ (XVIII; E = P, As) derived from 1,3-dimethyl-5-(3,4,6,tri-O-acetyl-2-deoxy-α-D-arabinohexopyranosyl)-2,4(1H,3H)-pyrimidinedione (glH) exhibited $[M-Cl]^+$ at highest mass, confirming the composition. In both complexes, an ion $[Pd(gl)]^+$ was observed; Group 15 ligand migration gave $[Pd(EPh_3)_2]^+$ and $[Pd(E_2Ph_5)]^+$, while metal-free ions included $[EPh_4]^+$, $[EPh_3(OH)]^+$, and for E = As, $[(gl)]^+$ and $[gl-HOAc]^+$.[143]

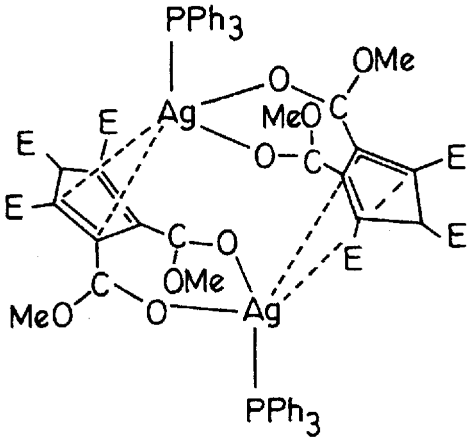


XVIII

The spectra of complexes of *cis*-$PtCl_2(NH_3)_2$ (*cis*-platin) with guanosine have been studied.[133,144] The 1/2 complex does not give $[M]^+$, the highest fragments being $[M-Cl]^+$ and $[M-Cl-HCl]^+$, together with the glycerol adducts of these species. Enantiomerically pure amino acid complexes $K[PtCl_2\{NH_2CHRCO_2\}]$ (R = H, Ph, C_6H_4OH) and related dipeptide complexes $PtCl_2$(met-OMe) and $PtCl_2$(leu-met-R) (R = OMe, NH_2) have been studied by FAB MS.[145] For the ionic compounds intense spectra were recorded in the negative ion mode, the most abundant ions generally being the $[M-K]^-$ cluster. The $[M-H]^-$ cluster was also observed, as were $[M+H_2O-H]^-$ and $[M+glyc-K]^-$. The neutral complexes showed only positive ions from the dipeptide ligand with no platinum-chlorine containing peaks. The negative ion spectrum contained a series of Pt/Cl clusters up to *m*/*z* 2000. Molecular weight information could be obtained for all samples by FD, although the spectra were not easy to obtain.

(f) Copper, silver and gold

Very little data have been reported for compounds of the Group 1B metals. We have obtained a spectrum of $Cu\{C_5(CO_2Me)_5\}_2$ showing $[M]^+$ (*m*/*z* 773, 25%) which fragments by loss of OMe and Me groups from the cyclic ligands. The organic ligand also affords $[HC_5(CO_2Me)_5]^+$. A related compound $Cu\{C_5(CO_2Me)_5\}(PPh_3)_2$ does not show $[M]^+$, but a fragmentation pattern derived from the ion $[M-PPh_3]^+$, involving loss of OMe groups from the cyclic ligand, followed by loss of Ph and finally cleavage of the remaining C_5 group was found. Bimetallic species such as $[Cu_2(PPh_3)\{C_5(CO_2Me)_5\}]^+$ were also present. This associative behaviour is even more pronounced for the silver analogue $[Ag(PPh_3)\{C_5(CO_2Me)_5\}]_2$ (XIX) where



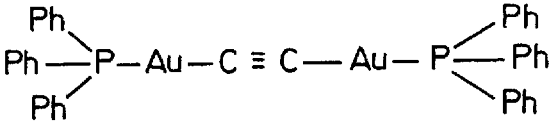
XIX E = CO_2Me

$[M+Ag(PPh_3)]^+$ (47%) and $[M+Ag]^+$ (100%) have a greater intensity than $[M]^+$ (16%) (Fig. 4d). Again, loss of OMe groups and of the C_5 ring were found. A more complex pattern was found for $Au(PPh_3)\{C_5(CO_2Me)_5\}$. The base peak is $[M-3OMe]^+$, which is also strong in the Cu and Ag derivatives, but $[M]^+$ has only 0.07% relative intensity. In this case also, higher mass aggregates are found with low intensity. The highest ion observed corresponds to $[2M-7OMe]^+$ (*m/z* 1411, 0.13%).

Phthalocyanine complexes of copper were studied by Freas and Campana.[117] A strong molecular envelope of ions $[M+H]^+$, $[M+O]^+$, $[M+OH]^+$, $[M+H_2O]^+$, $[M+O_2]^+$ and $[M+H_2O_2]^+$ was observed for the parent compound in a concentrated acid (H_3PO_4/H_2SO_4) matrix. In benzyl butyl phthalate, copper tetrakis(cumylphenoxy)phthalocyanine gave weak peaks for $[M]^+$ and $[M+H]^+$. Cupribalamin (the copper analogue of vitamin B_{12}) has also been studied: cluster formation in the molecular ion region was observed in the FAB spectrum.[135] In the positive ion spectrum an intense $[M+H]^+$ was found together with higher mass copper-containing clusters corresponding to successive addition of copper atoms to the molecular ion. The negative ion spectra also show this feature together with peaks corresponding to $[M]^-$ and $[M-H]^-$. Observation of the latter was suggested to be the result of reduction of copper(II) to copper(I). A non-polar surfactant (nonoxynol) was used as the matrix for copper tetraphenylporphyrin.[66] Using the surface precipitation technique, $[M+H]^+$ was clearly observed, fragmenting via loss of Ph.

Comparison of the FD and FAB mass spectra of $[Ag(bpy)_2][ClO_4]$ show major differences in ion intensities, suggesting more energy is imparted to the cation during the latter process, resulting in a greater degree of fragmentation.[26] Major ions are $[Ag(bpy)_n]^+$ ($n=1,2$); the matrix aggregate ions $[Ag(bpy)+glyc]^+$ and $[Ag+n(glyc)]^+$ ($n=1,2$) were found in the FAB spectrum, while the FD spectrum contained weak $[Ag_2(ClO_4)]^+$.

Unusual spectra were obtained from the binuclear complexes $(R_3P)AuC_2Au(PR_3)$ (XX; R = Ph, 3-tolyl), which in the solid state consist of discrete binuclear molecules with no intermolecular interactions.[122] In the example shown (Fig. 5), the fragments observed are similar (in ascending mass) to those found for the PPh_3 complex until the $[M_2]Au$ core is reached.



XX

Strong peaks in the spectra of both complexes are $[Au(PR_3)]^+$, $[Au(PR_3)_2]^+$, $[M+H]^+$, $[M+Au]^+$, $[M+Au(PR_3)]^+$, $[M_2+Au]^+$ and $[M_2+(Au_2C_2)+Au(PR_3)]^+$. In both cases also, the ion $[M+Au(PR_3)]^+$ is of note as this is of 66% relative intensity for the PPh_3 complex and 34% for the $P(C_6H_4Me\text{-}3)_3$ compound. Considerable attention has been drawn to the isolobal analogy between H^+ and $[Au(PR_3)]^+$ in synthetic strategies where stabilisation of an anion is required.[146] In this instance we observe a pseudo-molecular ion $[M+Au(PR_3)]^+$ which is more stable than $[M+H]^+$. Also of interest is the observation of weak ions which appear to correspond to the cations $[AuC_2(PR_3)_n]^+$ ($n=1, 2$).

(g) Zinc, cadmium and mercury

Campana and coworkers[118] studied several porphyrins by FAB, DCI and DEI MS. In all cases, $[M+H]^+$ ions were obtained, with higher mass peaks being recorded for some examples. Both Me and K ion attachment were supposed to give rise to these higher mass ions. For zinc deuteroporphyrin-IX carboxylic acid, fragmentation by α and β cleavage at both propionic acid side chains occurred. The methyl ester derivative fragmented chiefly by β-cleavage. The FAB spectrum was similar to that of the free porphyrin. For the *meso*-tetra(2-aminophenyl) derivative, benzylic cleavage of the anilino groups affords some of the fragment ions. Comparison of the techniques showed FAB to be generally superior in providing molecular weight and structural information. In a related study of zinc phthalocyanines, $[M+H]^+$ ions were found for both complexes examined.[117]

Complex FAB spectra were shown by the complexes $Me\{C_5(CO_2Me)_5\}_2$ (Me = Zn, Cd, Hg) obtained from a glycerol matrix. Only the Cd and Hg compounds showed $[M]^+$ ions, but in all cases ions $[Me\{C_5(CO_2Me)_5\}]^+$ were found. Higher mass peaks were found for the Zn and Hg compounds, the highest observed being

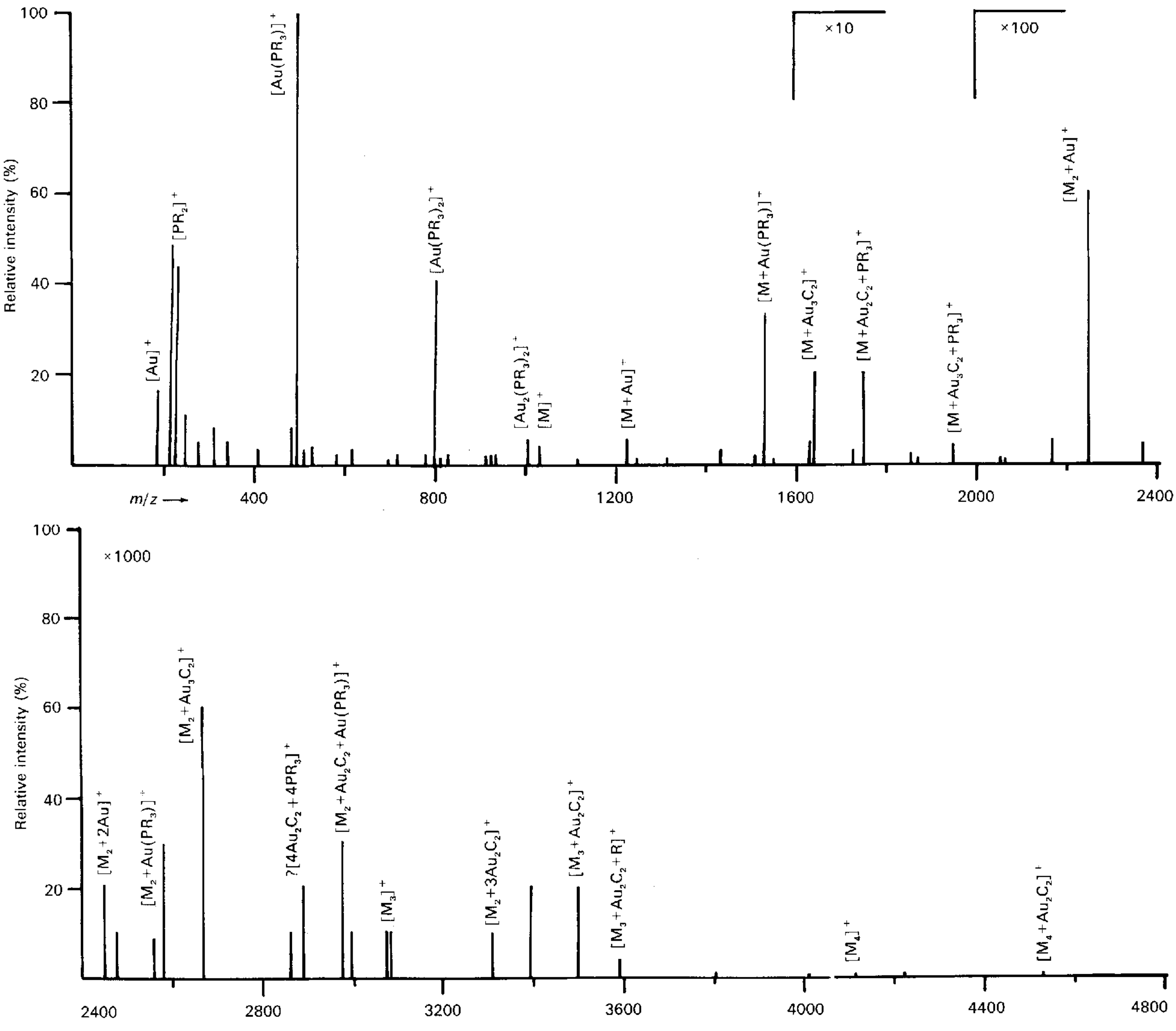


Figure 5 FAB mass spectrum of $C_2\{Au[P(C_6H_4Me\text{-}3)_3]\}_2$ ($R=C_6H_4Me\text{-}3$).

$[M_3-2OMe]^+$. In the case of the mercury derivative, the ion $[M+Hg]^+$ was found together with further aggregates up to $[Hg_2\{C_5(CO_2Me)_5\}_4]^+$.

In a pioneering study of the use of FAB MS to study reactions of organometallics in solution, Kalinoski et al.[67] followed the palladium-mediated reactions of organomercury compounds. When equimolar amounts of ArHg(OAc) (Ar = heteroaryl), a chiral pyranoid or furanoid glycal, and $Pd(OAc)_2$ were added to a glycerol matrix together with PPh_3, the transmetallation process was observed directly: (Eqn 2)

$$ArHg(OAc)+Pd(OAc)_2 \rightleftharpoons ArPd(OAc) + Hg(OAc)_2 \qquad [2]$$

Species such as $[PdAr]^+$ and $[PdAr(NCMe)]^+$ were also found. The observation of these ions suggested the formation of unstable arylpalladium-glycal complexes. They concluded that FAB MS could be used to analyse the solution dynamics of complex organometallic reactions.

Several organomercury compounds were also examined. Compounds Hg(OAc)R (R = dimethylpyrimidinedionyl, 2- or 4-methoxynaphthyl) afforded ions $[HgR+TEA]^+$ in triethanolamine, and $[HgR+glyc]$ and $[HgR_2+H]^+$ in glycerol/acetic acid.[67] The formation of the last ion indicates some disproportionation is occurring in this matrix although the other component, $Hg(OAc)_2$, was not observed. Ions corresponding to

$[Hg+glyc]^+$, $[Hg+2glyc-H]^+$ and $[Hg+3glyc-H]^+$ were formed from $Hg(OAc)_2$ in glycerol.

Rose et al.[147] discovered metal exchange occurred on running FAB mass spectra of $Hg_2(\mu\text{-}I)_2I_2(PPr_3)_2$ on a copper probe tip, when they found formation of ions of the type $[Cu_xI_{x-1}(PPr_3)_y]^+$ ($x=1$–4, $y=2,3$).

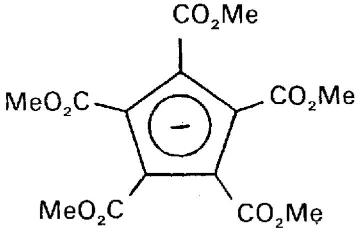
(h) Main group organometallics

Quinuclidine and BF_3 react in a glycerol matrix to give ions $[BF_2L_2]^+$ and $[BF_2L]^+$ (L= quinuclidine).[29]

The analysis of octadecyldimethylchlorosilane supported on silica by static FAB MS allowed the measurement of organic secondary ion intensities as a function of monolayer coverage by the silane. The intensity ratio $[SiOH]^+/[SiO]^+$ decreases with increasing coverage confirming the removal of silanol groups by the silane, which correlates with results obtained from other methods of surface analysis.[148]

FAB and FAB-MIKES techniques were used to investigate the nature of organolithium compounds LiMe, Li_2CH_2 and CLi_4.[59] Molecular ions were not observed for these species, the major peaks being $[Li]^+$ and $[Li_2]^+$; other ions of interest were $[Li_3]^+$ found for LiMe, and $[CLi_n]^+$ ($n=1,2$) found for Li_2CH_2.

We have recorded FAB mass spectra for a series of alkali metal salts of $HC_5(CO_2Me)_5$.[141] These are of the type $M\{C_5(CO_2Me)_5\}$ (M = Li, Na, K, Rb, Cs). Figure 6 illustrates the major features of these spectra as found for the potassium salt. All complexes are ionic and behave as 1/1 electrolytes in solution, the $[C_5(CO_2Me)_5]^-$ anion (XXI) being very stable. In the spectra, ionic aggregates that form are probably the result of concentration of the ions at the surface of the matrix, or in the relatively high pressure region directly above the surface. In contrast, the compound $Tl\{C_5(CO_2Me)_5\}$ shows only $[Tl]^+$ in the positive ion spectrum, and $[C_5(CO_2Me)_5]^-$ in the negative ion spectrum.


XXI

The largest aggregates identified so far are $[M_6\{C_5(CO_2Me)_3\}-OMe]^+$ (M = Na, K). The ions $[M_2\{C_5(CO_2Me)_5\}]^+$ lose OMe, O_2Me and CO_2Me groups. The addition of further metal atoms to each of the main aggregates $[M_2L]^+$, $[M_3L_2]^+$ and $[M_4L_3]^+$ [$L=C_5(CO_2Me)_5$] and loss of specific groups from the organic ligands are also common features of these systems. As the atomic mass increases the observation of the higher mass aggregates becomes progressively more difficult and for Rb and Cs only the $[M_3L_2]^+$ series can be observed. In no case is the molecular ion observed. It appears that the presence of a high alkali metal concentration prevents the formation of $[M+H]^+$ even in glycerol (which is a strongly protic matrix). In this instance, therefore, the ion $[M_2L]^+$ can be

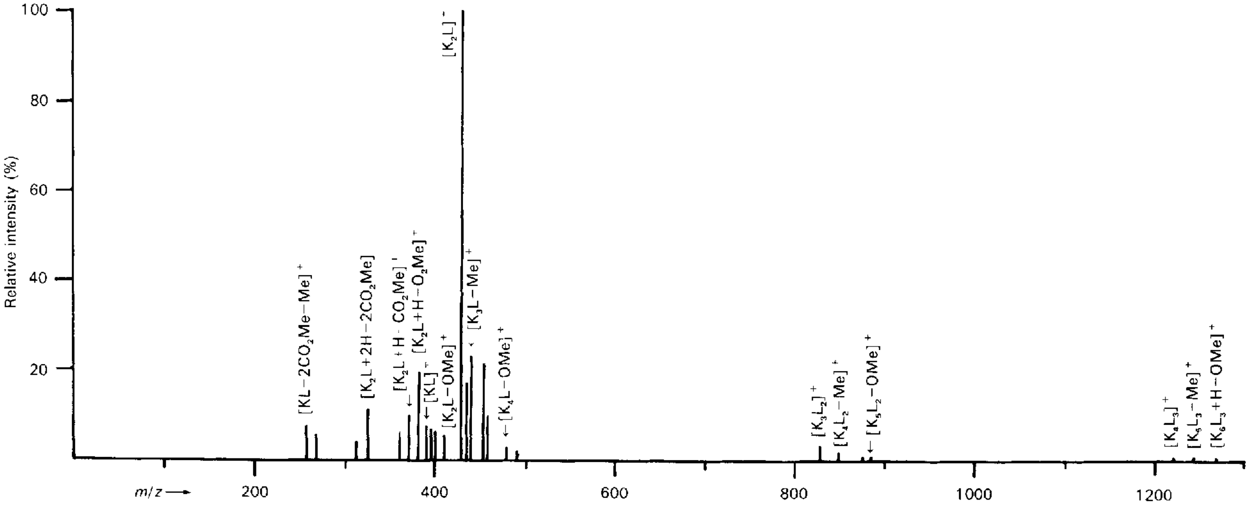


Figure 6 FAB mass spectrum of $KC_5(CO_2Me)_5$ ($L=C_5(CO_2Me)_5$).

regarded as a pseudo-molecular ion. Small abundances of such ions are frequently encountered in organic FAB MS and special precautions have to be taken to exclude them. The deliberate sodium ion 'cationisation' of organic complexes has been mentioned elsewhere.[149]

No molecular ion was found for Mg $\{C_5(CO_2Me)_5\}_2$, but again the ion $[M+Mg]^+$ may be regarded as the pseudo-molecular ion. Loss of Me, OMe and CO_2Me groups is found, the principal fragment ions being $[MgL-H^+]$ and $[M-OMe]^+$. Higher mass aggregates are found corresponding to $[Mg_2L_3]^+$, $[Mg_4L_4-OMe]^+$, $[Mg_4L_5-Me]^+$, $[Mg_5L_6-OMe]^+$ and $[Mg_7L_7-2OMe]^+$.

Many metal ions were found to form crown ether/cation complexes when mixtures were examined by FAB MS.[99] Salts of the form $M^{n+}X_n^-$ (X = Cl, I, NO_3, OAc) when dissolved in glycerol with the crown ether (C) afford ions corresponding to $[MX_{n-1}+C]^+$. Complex formation between alkali metal cations and the macrocyclic ligands 15-crown-5, 18-crown-6, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8 and crypt-222 have also been observed by FAB MS.[100] In competition experiments the variation in abundance of ions corresponding to metal-ligand cations closely parallels the expected concentrations calculated from known stability constants. Similar studies of divalent metal ions with the macrocycle 1, 4, 8, 11-tetrathiacylclotetradecane (L) showed that only ions corresponding to $[ML]^+$ (M = Ag, Cu, Hg) were observed. From these results it was suggested that FAB MS can be used routinely to examine complex formation between metal cations and macrocyclic ligands in solution.

The FAB mass spectra of a series of organo-Group 4B halides, $MClPh_3$ (M = Ge, Sn, Pb), $PbXPh_3$ (X = Cl, Br, I) and $SnCl_{4-n}Ph_n$ (n = 1–4) have been compared with the corresponding EI spectra.[150] The effects of various matrices were also compared in this study. No molecular ions were observed using either technique. Primary FAB ionisation was suggested to occur in the condensed phase. More recently, results of comparative FAB and EI studies of the HMPA adducts of the tin and lead compounds, $MXPh_3.HMPA$ and $MX_2Ph_2.2HMPA$ (M = Sn, Pb; X = Cl, Br, I) have been published.[151] The main difference in the FAB spectra is the preferred loss of halide compared with phenyl, the reverse of the situation in the EI spectra. Molecular ions were not detected by either technique; several metal-containing ions with added HMPA were present in the FAB spectra. An early study of organo-Group 4B compounds compared the EI and FAB spectra of $SnPh_3(EC_6F_5)$ (E = O, S); similar fragmentation was found, but weak $[M]^+$ ions in the EI spectra were not found in the FAB spectra. Attachment of the matrix (glycerol) to give weak ions $[M+2glyc-2H]^+$ and $[Sn+glyc-H]^+$ was found in these cases.[29] The use of linked scan techniques has shown that glycerol adduct ions of inorganic compounds which are formed in the spectrometer, such as $[SnCl_3+2glyc]^+$, behave as though the matrix molecules are covalently bound, loss of HCl rather than of glycerol occurring.[131]

Organoarsenicals, particularly arsenobetaine, $Me_3As^+CH_2CO_2^-$, have been studied in biological systems, especially seafoods. The FAB spectrum of the pure compound contained $[AsMe_4]^+$ as the base peak, formed by decarboxylation and protonation, whereas in marine extracts, high resolution analysis was used to establish the presence of $[M+H]^+$ in low abundance.[152]

(i) Polynuclear compounds

A major disadvantage of EI MS has been the limited applications to the study of metal cluster compounds occasioned by the relatively low volatility of these complexes. The advent of FAB MS has allowed their characterisation, and many reports have listed molecular weight information of new cluster compounds, often into the thousands. We have found that where satisfactory results can be obtained using EI MS, such as with the cluster carbonyl $Ru_3(CO)_{12}$, then the FAB MS technique does not give strong spectra or additional structural information. Presumably this is because these molecules are approximately spherical, non-polar compounds, although solubility effects are probably important as well. Conversely, substituted cluster carbonyls are often not volatile enough to obtain EI MS before thermal decomposition occurs in the source, but afford well-resolved FAB mass spectra. In the example of $Ru_3(CO)_{12}$, which we have studied extensively, great difficulty was found in finding a suitable solvent/matrix combination, although 18-crown-6/tetraglyme proved successful. Figure 7 compares the EI and FAB mass spectra of this molecule and the advantages of the former are readily apparent. In both cases, the typical stepwise loss of CO is shown, although the relative

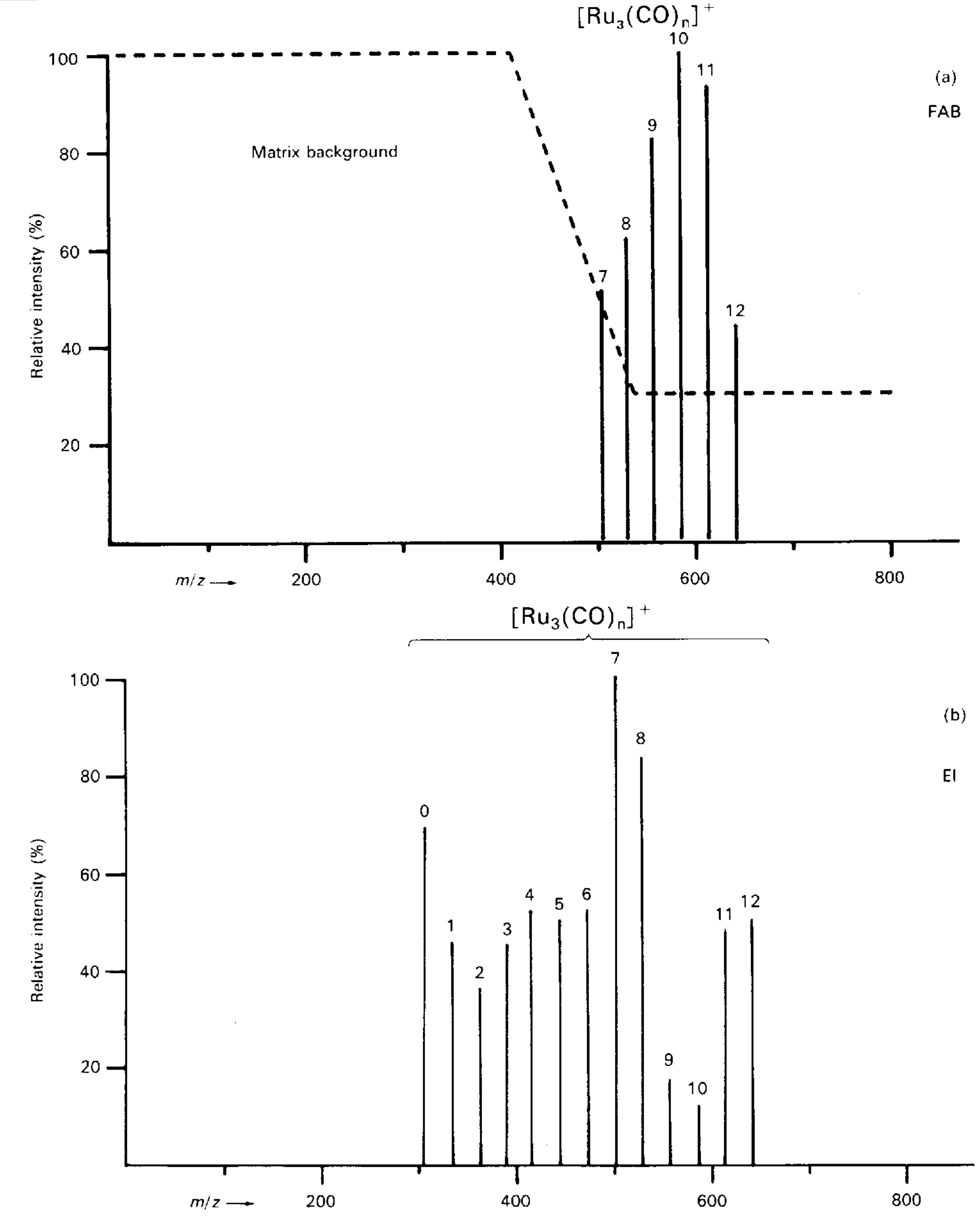


Figure 7 Mass spectra of $Ru_3(CO)_{12}$: (a) FAB; (b) EI.

intensities of individual ions vary, suggesting different interactions in the ionisation or fragmentation process.

The advantages of FAB MS are illustrated by a study of substituted derivatives $Ru_3(CO)_{12-n}(L)_n$ ($L = PPh_3$, $n = 1$–3). These compounds are not amenable to study by EI MS, whereas with the FAB technique, both molecular weight and fragmentation data are readily available. Even tetrasubstituded ruthenium carbonyl clusters are amenable to study, as shown in Table 5. Generally, stepwise loss of CO groups occurs, accompanied by fragmentation of the tertiary phosphine ligand. The utility of the method is demonstrated by the spectrum of $\{Ru_3(CO)_{11}\}_2$ (μ-dppa), which shows a weak $[M]^+$ at m/z 1620 (0.01%), together with ions formed by loss of up to 12 CO groups and a Ph radical.

Smith et al.[116] have given details of the spectra of some ligand-substituted ruthenium and osmium cluster carbonyls. Only molecular weight information was provided for the complexes $Ru_3(CO)_6(dppm)_3$, $Os_3(CO_{12-2n}(dppm)_n$ ($n = 1$, 2)

Table 5 FAB mass spectra of some substituted ruthenium cluster carbonyls

Complex	Matrix (cosolvent)	Principal ions (assignment, *m/z*, %)[a]
$Ru_3(CO)_{11}(PPh_3)$	NOBA (CH_2Cl_2)	$[M]^+$, 875(13); $[M-4CO]^+$, 763(18); $[M-5CO]^+$, 735(21); $[M-6CO]^+$, 707(24); $[M-7CO]^+$, 679(24); $[M-8CO]^+$, 651(21); $[M-9CO]^+$, 623(22); $[M-10CO]^+$, 595(20); $[M-11CO]^+$, 567(25); $[Ru_2(CO)_4(PPh_3)]^+$, 578(100)
$Ru_3(CO)_{10}(PPh_3)_2$	18-C-6/TETRA (CH_2Cl_2)	$[M]^+$, 1100(100); $[M-2CO]^+$, 1044(20)
$Ru_3(CO)_9(PPh_3)_3$	NOBA/18-C-6/TETRA (CH_2Cl_2)	$[M]^+$, 1343(25); $[M-CO]^+$, 1315(42); $[M-5CO]^+$, 1203(46); $[M-3CO-PPh_3]^+$, 997(100); $[M-4CO-PPh_3]^+$, 969(80)
$Ru_3(CO)_8\{P(OCH_2CF_3)_3\}_4$	NOBA (acetone)	$[M]^+$, 1842(4); $[M-CO]^+$, 1814(2); $[M-4CO-L]^+$, 1404(18); $[Ru_3(CO)_{11}(L)]^+$, 914(44); $[Ru_2(CO)_{18}(L)]^+$, 756(100)
$Ru_3(CO)_8\{P(OCH_2)_3CEt\}_4$	NOBA (CH_2Cl_2)	$[M]^+$, 1178(77); $[M-3CO]^+$, 1094(92); $[M-4CO]^+$, 1066(97); $[M-5CO]^+$, 1038(67); $[M-2CO-L']^+$, 960(100); $[M-3CO-L']^+$, 932(92); $[M-4CO-L']^+$, 904(60); $[M-5CO-L']^-$, 876(95)

[a] $L = P(OCH_2CF_3)_3$; $L' = P(OCH_2)_3CEt$

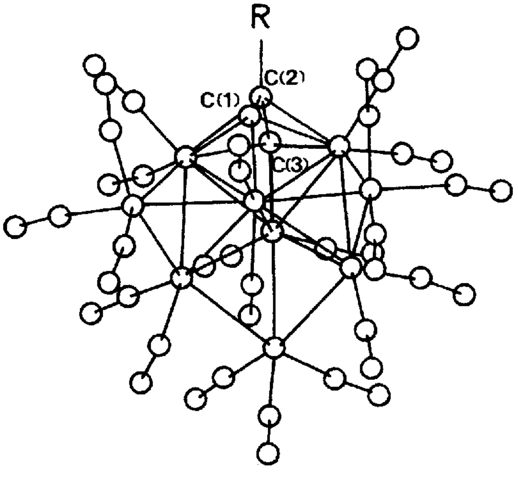
and $Os_3(CO)_9(dppm)(\eta^1\text{-dppm})$, which were run in di-*t*-butylphenol/glycerol.

An interesting result was obtained with the complex $Ru_3(\mu_3\text{-NPh})_2(CO)_9$, which shows in addition to the expected $[M]^+$ (*m/z* 739, 19%) and loss of CO groups, peaks corresponding to $[Ru_3(CO)_{11}(N_2)]^+$ and fragment ions down to $[Ru_3(CO)_7(N_2)]^+$, ions having the same nominal mass as $[Ru_3(CO)_n]^+$ ($n = 12$–8). FAB MS also proved successful in providing molecular weight information for the cluster $(Os_3(\mu\text{-H})_4(\mu_3\text{-NH})(CO)_8$ ($[M]^+$ at *m/z* 813) which was not amenable to study by EI MS.[153]

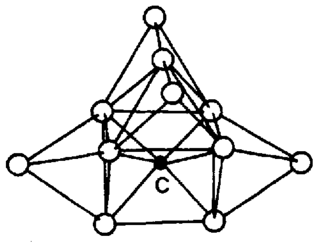
The phosphido-bridged cluster $Co_3(\mu\text{-PPh}_2)_3(CO)_6$ was studied by Geoffroy and Minard,[95] who found a prominent $[M]^+$ and stepwise loss of CO groups. Characterisation of $Fe_3\{\mu_3\text{-SbCH(SiMe}_3)_2\}_2(CO)_9$ was aided by the FAB mass spectrum, which showed $[M]^+$ and successive loss of nine CO groups.[154] Molecular weight in formation has been reported for the cluster $Os_{10}(\mu_4\text{-S})_2(CO)_{33}$, $[M]^+$ appearing at *m/z* 2682.[155]

The tetrameric clusters $[M_4H_4(\eta\text{-C}_5Me_5)_4]^{2+}$ (M = Rh, Ir) and $[Ru_4H_4(\eta^6\text{-p-cymene})_4]^+$ have been characterised with the aid of FAB MS. The rhodium and ruthenium complexes gave $[M]^+$ ions, while the highest ion for the iridium cluster was $[M-4H]^+$ at *m/z* 1312.[156]

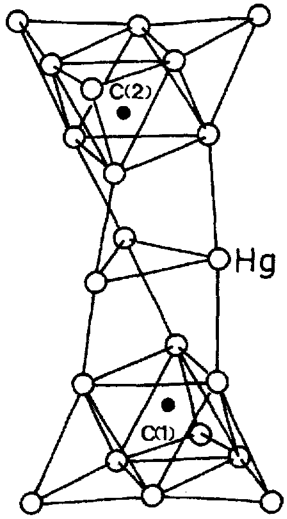
Several polynuclear anions have been examined. Molecular weight data for $[Os_9(\mu\text{-CHCRCH})(CO)_{21}]^-$(XXII; R = Me, Et) [157] and $[Os_{11}C(CO)_{27}]^{2-}$ (XXIII)[158] have been reported;



XXII R=Me, Et



XXIII $Os_{11}C$ core



XXIV $HgOs_{20}C_2$ core

in the last example, $[M+H]^-$ was observed at m/z 2880. The compound $[Os_{20}HgC_2(CO)_{48}]^{2-}$ (XXIV) clearly demonstrates the ability of FAB MS to characterise high molecular weight species.[159] A molecular ion was reported at m/z 5408, which appears to be the highest observed for an organometallic cluster so far (December 1986).

A variety of mixed clusters have been studied. Davis et al.[101] have recorded the FAB mass spectrum of $AuFe_4C(\mu\text{-}H)(CO)_{12}(PPh_3)$, which gives a positive ion spectrum with $[M+H]^+$ at m/z 1033 (60%) and a negative-ion spectrum with $[M+H]^-$ at m/z 1033 (8.2%). This observation contrasts with normal organic negative ion spectra which have $[M-H]^-$ as the quasi-molecular ions. Other gold-containing clusters include $AuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$, which gave $[M-H]^+$ at m/z 1048 (21%), $Au_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ which gave $[M]^+$ at m/z 1504 (100%), and $Au_3Ru_3(\mu_3\text{-}S)(C_{12}H_{15})(CO)_8(PPh_3)_3$, which showed $[M+2H]^+$ at m/z 2067 (88%). The latter addition of 2H appears to be unique amongst organometallics at present, and possibly arises by further protonation of the $[M+H]^+$ species. The identification was achieved by comparision of computed relative intensities of ion clusters with the observed highest ions.[160] There is, however, a precedent in organic FAB MS where the ions $[M+H]^+$, $[M+2H]^+$ and $[M+3H]^+$ have been established for guanosine by high resolution analysis;[89] multiple protonation appears to be occurring in solution.

Other examples which all afforded $[M]^+$ ions were $Fe_2Pt(CO)_8\{P(OPh)_3\}_2$ (CH_2Cl_2/NOBA), $Os_2Pt(CO)_8(PPh_3)_2$ (CH_2Cl_2/NOBA), $Fe_2Ir(\mu_3\text{-}C_2Ph)(CO)_8(PPh_3)$ (CH_2Cl_2/NOBA), $Cu_4Ir_2(C_2C_6H_4F\text{-}4)_8(PPh_3)_2$($H_2Cl_2$ /18-crown-6/tetraglyme), $Cu_4Ir_2(C_2C_6H_4Me\text{-}4)_8(PPh_3)_2$ (CH_2Cl_2/18-crown-6/tetraglyme). In the last two examples, a very simple fragmentation pattern is observed, with only one $C_2C_6H_4R$ (R = F or Me) fragment being lost from the $[M]^+$ ions, which are found at m/z 2114 and 2082, respectively. The carbonyl-containing clusters show CO and Ph loss as the typical patterns. The mixed metal cluster $Rh_2Ru_2(CO)_7(\eta\text{-}C_5Me_5)_2$ has been characterised using FAB to confirm the molecular weight.[161] Similarly, the spectra of $[R][Fe_2Mn(CO)_{11}(L)]$ ($R = NEt_4$, ppn; L = CO, $PMePh_2$) were easy to obtain and show fragments resulting from loss of the CO ligands (Fig. 8).

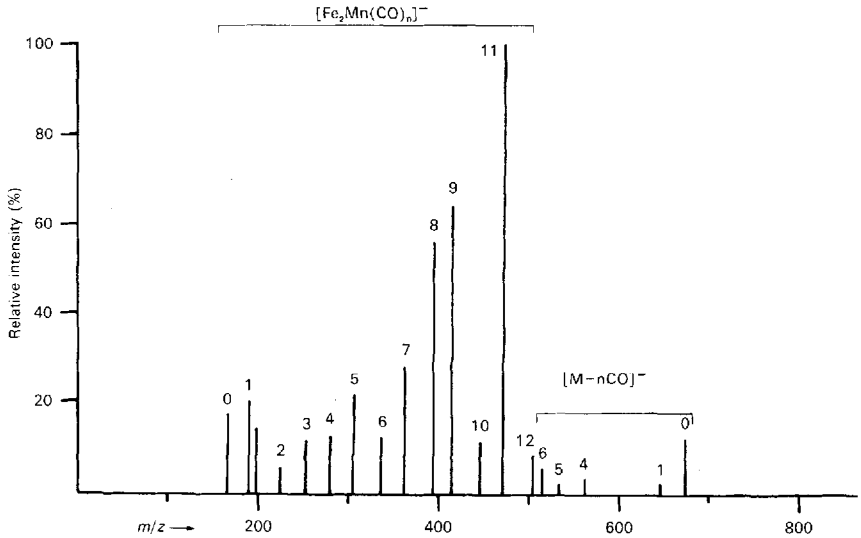


Figure 8 FAB mass spectrum of $[ppn][Fe_2Mn(CO)_{11}(PMePh_2)]$.

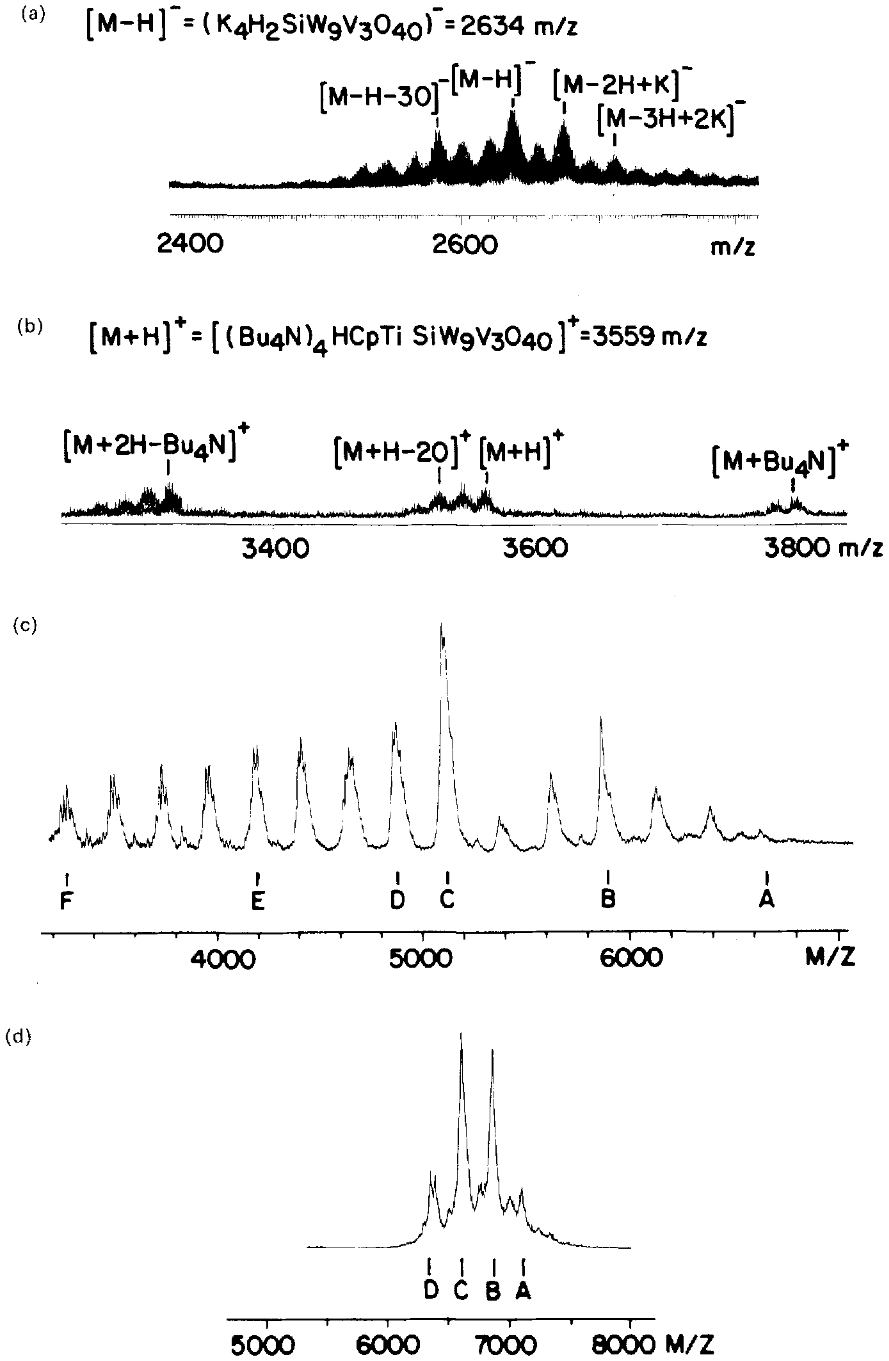


Figure 9 Some high mass ions in the spectra of poly-oxo-anion salts: (a) $K_4H_3SiW_9V_3O_{40}$, negative ion, molecular anion region (*m/z* 2400–2800); (b) $[NBu_4]_4[\eta\text{-}C_5H_5)TiSiW_9V_3O_{40}]$, positive ion, region *m/z* 3300–3800; (c) $[NBu_4]_6[H_2Si_2W_{18}Nb_6O_{77}]$, negative ion, region *m/z* 3200–7000 (labelled ion clusters are: A, $[M+H+6NBu_4]^-$; B, $[M+4H+3NBu_4-2O]^-$; C, $[M+7H-4O]^-$; D, $[M+7H-4O-WO_3[^-$; E, $[M+7H-4O-4WO_3]^-$; F, $[M+7H-4O-8WO_3]^-$, *where* $M=Si_2W_{18}Nb_6O_{77}$); (d) $[NBu_4]_6[H_2Si_2W_{18}Nb_6O_{77}]$, positive ion, region *m/z* 6000–7500 (labelled ions are: A, $[M+H+8NBu_4]^+$; B, $[M+2H+7NBu_4]^+$; C, $[M+3H+6NBu_4]^+$; D, $[M+4H+5NBu_4-O]^+$; M as in (c). [Reprinted with permission from R G Finke, M W Droege, J C Cook and K S Suslick, *J. Am. Chem. Soc.*, 1984, 106: 5750, and K S Suslick, J C Cook, B Rapko, M W Droege and R G Finke, *Inorg. Chem.*, 1986, 25: 241. © 1984, 1986 American Chemical Society].

(j) Poly-oxo-anions

FAB MS is a powerful technique for the characterisation of high molecular weight poly-oxo-anions. Organometallic derivatives of poly-oxo anions have been examined by Finke et al.[162–164] Some of the high mass ion clusters are shown in Fig. 9. For the complex $[NBu_4]_4[(\eta\text{-}C_5H_5)TiSiW_9V_3O_{40}]$ a pseudo-molecular ion $[M+H]^+$ was found at *m/z* 3559, together with ions formed by cation exchange and loss of oxygen $[M+NBu_4]^+$, $[M+H-2O]^+$ and $[M+2H-NBu_4]^+$. The remainder of the fragmentation pattern is dominated by multiple loss of O atoms and WO_3 groups. Only the $[SiW_9V_3O_{40}]^{7-}$ fragment of the complex $[(OC)_3ReSiW_9V_3O_{40}]^{6-}$ was found. Ionisation is suggested to occur at the metal of the organometallic group in this case. Alternatively addition of solvated electrons and/or H^+ to the poly-oxo anion weakens the organometallic-poly-oxo-anion bond and results in net loss of the organometallic. As $[(\eta\text{-}C_5H_5)TiSiW_9V_3O_{40}]^{4-}$ contains a non-ionisable d^0 metal, Ti(IV), it is considered that the ionisation process must occur on the poly-oxo anion thus giving useful spectra in both positive and negative ion modes. It is interesting to note that in these cases the counterion is generally observed coordinated to the complex; combination with elemental analysis is usually sufficient to enable a molecular formula to be established, as with $[NBu_4]_7[HSi_2W_{18}Zr_3O_{68}]$, for example. The largest anion that has been reported is that in the complex $[NBu_4]_6[H_2Si_2W_{18}Nb_6O_{77}]$ which contains the aggregate ions $[M+3H+6NBu_4]^+$ at *m/z* 6613 and $[M+H+8NBu_4]^+$ at *m/z* 7095. As the resolution and sensitivity of mass spectrometers improves, molecular weight information in the region 10000–20000 Dalton should become routinely available.

CONCLUSION

This survey has shown that inorganic and organometallic chemists should now be able to take advantage of the significant improvements in mass spectrometric analysis of their compounds now available as the result of the development of fast atom bombardment as a soft ionisation technique which is readily accessible to existing mass spectrometers. The method allows a considerable increase in the range of compounds which can be studied and analysed by mass spectrometry, including salts and poorly volatile materials, and developments in instrumentation now make the study of compounds of high molecular weight possible.

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