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MS of organometallics (for Volume 6 of EMS)

Correct choice of ionization technique in the analysis of organometallic compounds is crucial to the success of the experiment. Organometallic compounds display a huge range of properties: from volatile compounds of low mass such as ferrocene, nickel carbonyl and tetraethyllead, to thermally sensitive, highly charged and involatile clusters containing hundreds of metal atoms. No single technique can be relied on to successfully characterize all organometallic compounds, but the lessons from organic and biological applications of mass spectrometry have been well-learned and adapted successfully to the organometallic field.[1] As important as the ionization technique is sampling handling; unlike most samples submitted for mass spectrometric analysis, organometallic compounds are frequently air- and moisture sensitive and thermally labile to the point that routine handling of the sample is liable to cause at least partial and often catastrophic decomposition. This added complication means that this tutorial will also concern itself with sample introduction methodologies, and make mention of the precautionary measures required in handling the sample.

Electron ionization

Electron ionization (EI; see this volume, chapter 3: *Electron Ionization*) involves accelerating electrons to 70 eV and passing them through a chamber containing the vaporized sample M, generating radical cations $[M]^{\bullet+}$. The ionization process is sufficiently energetic that extensive fragmentation occurs, generating a spectrum that provides a characteristic fingerprint for the compound in question (in organic chemistry, the intensities and *m/z* values of the most prominent ions can be automatically indexed and matched against an electronic library for the purposes of identification). Loss of a single electron is often well tolerated by electropositive metals and so molecular ions are frequently appreciably abundant. Because ionization efficiencies are low in EI, multiple charging is unusual for organic molecules. As a result, spectra generally show only singly charged ions, i.e. all ions appear at their mass values (*m/z* where $z = 1$). The probability of observing doubly charged ions is much higher with metal-containing compounds, because they tend to be more electropositive than organic compounds.

For organometallic compounds, the fragmentation process is frequently quite predictable. In compounds ML_n where M is a metal and L atoms or groups of atoms bonded to M, nearly all the ions in the spectrum will contain M:

i.e. $\mathbf{[ML_n]^{+\bullet}} \rightarrow \mathbf{[ML_{n-1}]^{+}} + L^{\bullet}$

not $\mathbf{[ML_n]^{+\bullet}} \rightarrow ML_{n-1}^{\bullet} + \mathbf{[L]^{+}}$

The metal retains the positive charge and the ligand departs as a neutral radical (not detected). This phenomenon occurs essentially because M-containing species are more electropositive and generally have lower ionisation potentials than the ligands. This phenomenon is obvious in cases where the metal is polyisotopic; the isotope pattern characteristic of the metal will be repeated in all the fragment ions of the spectrum. The other common fragmentation pathway involves elimination of L as a chemically stable entity:

i.e. $\mathbf{ML_n^{+\bullet}} \rightarrow \mathbf{ML_{n-1}^{+\bullet}} + L$

Loss of L is common for complexes in which the ligands are neutral molecules such as CO, PR_3, alkene, etc. Neutral ligands that occupy multiple coordination sites such as arenes and chelating diphosphines tend to be considerably more tenacious, and clean cleavage of such ligands is rare. Ligands that carry a formal negative charge such as cyclopentadienyls and halides are eliminated with difficulty as radicals. Ligands with a formal charge but that can be eliminated as a stable neutral molecule can be removed comparatively easily. For example, the nitrosyl ligand is formally regarded sometimes as NO^+, sometimes as NO^-, but is usually eliminated as neutral nitric oxide, NO. If the ligand ions have the largest peak intensity in the spectrum, thermal decomposition of the sample should always be suspected.

A reasonable rule of thumb is that if the compound can be (vacuum) distilled or sublimed it is well-suited to EI analysis. Any compound that can survive passage through a gas chromatograph can certainly be analyzed with ease, and this fact is taken full advantage of in the powerful hyphenated technique of GC-MS (see volume 8, chapter 2: *GC-MS principles, ionization and instrumentation*). Any compound that has a mass of less than about 1000 *m/z* and is thermally stable is potentially fair game for EI. This includes many of the organometallic compounds of groups 13, 14 and 15, but also

covers some transition metal organometallic complexes as well. Neutral metal carbonyls [2] and ferrocene derivatives (Figure 1) often provide good EI mass spectra.[3]

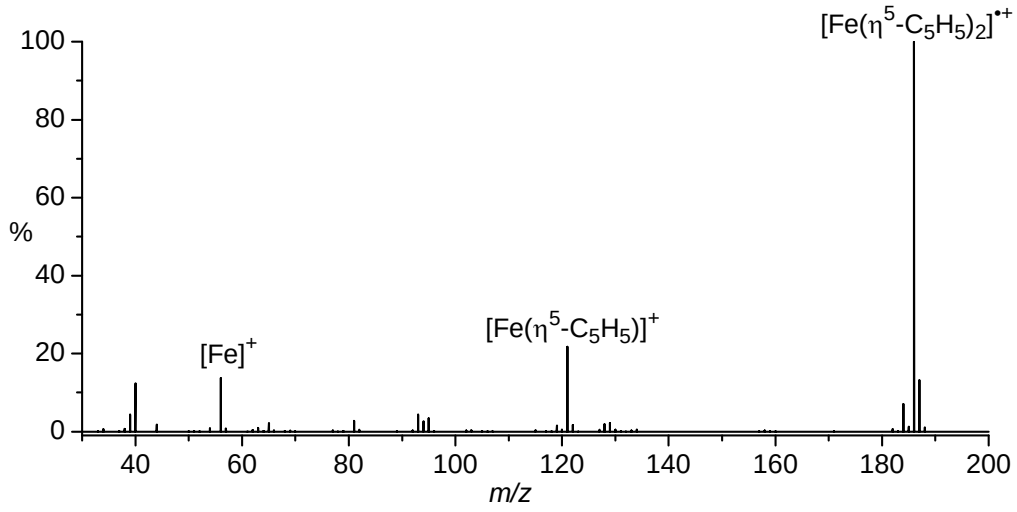

Figure 1. EI mass spectrum of ferrocene. Unusually, the molecular ion is the base peak. Adapted with permission from reference 1.

Chemical ionization

CI involves generation of highly reactive gas-phase species such as CH_5^+ (by using CH_4 as a reagent gas; see this volume, chapter 8: *Chemical Ionization*), which upon encountering a molecule M will transfer a proton to generate a pseudomolecular ion $[M + H]^+$. CI is most commonly used when a compound does not provide a detectable molecular ion under EI conditions. Because organometallic compounds generally provide relatively intense molecular ions in EI – loss of a single electron is often well tolerated by electropositive metals and does not in general cause extensive fragmentation – CI has few advantages over EI. However, atmospheric pressure CI (APCI, see this volume, chapter 9: *Atmospheric Pressure Chemical Ionization*) is a promising method for studying species soluble only in non-polar solvents such as toluene or hexane, where ESI is essentially ineffectual. For example, silsesquioxanes may be characterized from hexane solution as $[M + H]^+$ ions using APCI-MS (Figure 2).[4] Care must be taken in these experiments as the combination of a corona discharge and a flammable solvent poses an ignition risk, but using nitrogen as a desolvation gas and purging the source in advance cures this problem.

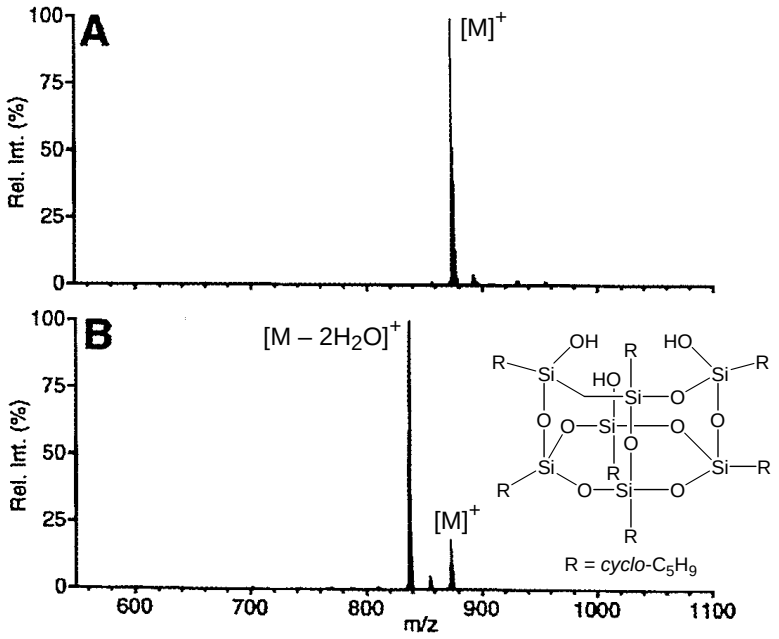

Figure 2. APCI-MS for (a) heptacyclopentyl-T_7-silsequioxane (*m/z* 875) and (b) CID spectrum yielding a base peak at *m/z* 857 corresponding to loss of $2H_2O$. Adapted from reference 4 with permission.

Field ionization / Field desorption

A molecule encountering a sufficiently high potential gradient (such as at the tip of a very sharp electrode) can have its molecular orbitals distorted to the point that quantum tunneling of an electron to an anode can occur, and a positive ion formed. This process is called field ionization when the molecule is in the gas phase; if the sample is adsorbed on the surface of the anode ("emitter"), it is called field desorption (FD, see this volume, chapter 19: *Ionization in Strong Electric Field*). Both are relatively "soft" ionization techniques and an abundant $[M]^{\bullet+}$ ion is generated, which is not prone to fragmentation. In both cases, careful preparation of the emitter – a tedious process requiring separate apparatus – is crucial to the success of the experiment. It is this limitation that renders FI/FD a specialist technique in the face of more recently developed, convenient means of ionization (especially ESI).

FI offers the organometallic chemist few advantages over EI, as appreciable molecular ion intensity is rarely a problem. However, FD has the ability to analyze compounds that are less volatile and/or thermally robust than required for EI, and a wider range of compounds is therefore accessible. FD is also capable of obtaining molecular weight information from neutral complexes for which FAB obtains only fragment ions.[5] The general inconvenience of the technique has meant it has been under-utilized,

but the development of liquid injection field desorption ionization (LIFDI; see volume 8, chapter 3), in which sample is supplied to the emitter in solution from a sealed vial *via* a capillary, has enhanced the utility of the technique for organometallic chemists.[6] Figure 3 shows the spectrum of the hydrido ruthenium cluster $H_4Ru_4(CO)_{12}$; note the absence of fragmentation and high signal-to-noise ratio.

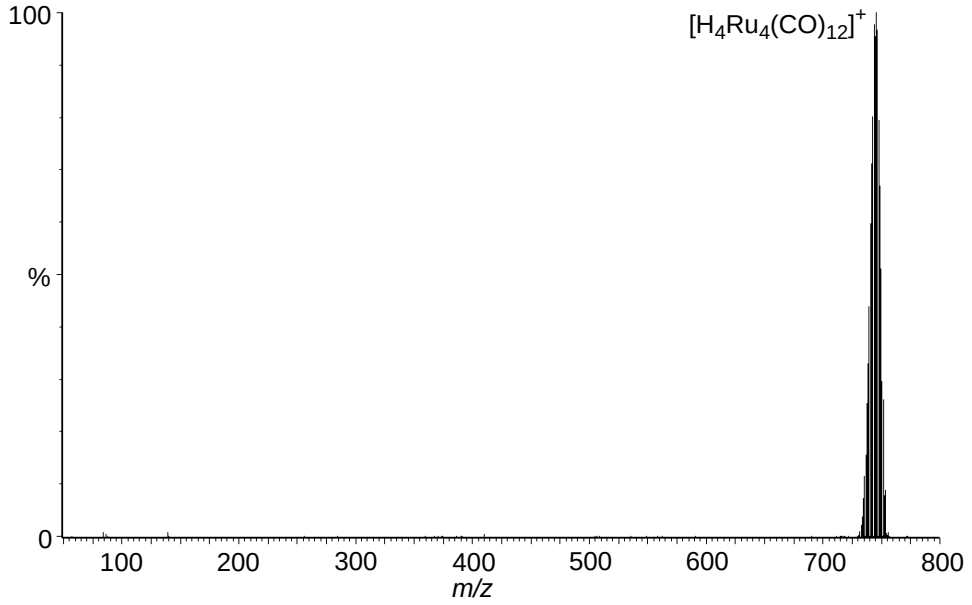

Figure 3. LIFDI spectrum of $H_4Ru_4(CO)_{12}$. Spectrum provided by H. B. Linden.

Plasma desorption

Plasma desorption mass spectrometry (PDMS, see this volume, chapter 14: *Cf-252 Plasma Desorption*) uses radioactive ^{252}Cf as a source of bombarding particles. ^{252}Cf decomposes into two particles, each about half the nuclear mass and traveling with very high kinetic energies. One fission fragment passes through a thin film of sample, causing the sample to desorb directly as ions. The other particle is used to trigger a time-of-flight (TOF) mass analyzer. Because of the low fission fragment flux, it is very slow to collect spectra (sometimes hours). PDMS was the first particle bombardment technique, but has been superseded by the more convenient FAB/LSIMS and MALDI techniques.

The molecular weight of compounds such as ferrocenyl-plumbanes [7] or $[n\text{-}Bu_4N]_4[Cu_8(S_2CC(CN)_2)]$ [8] can be routinely determined; Figure 4 shows the spectrum collected for the latter. Extensive fragmentation and/or aggregation is frequently observed in the spectra of large transition metal carbonyl cluster anions.[9]

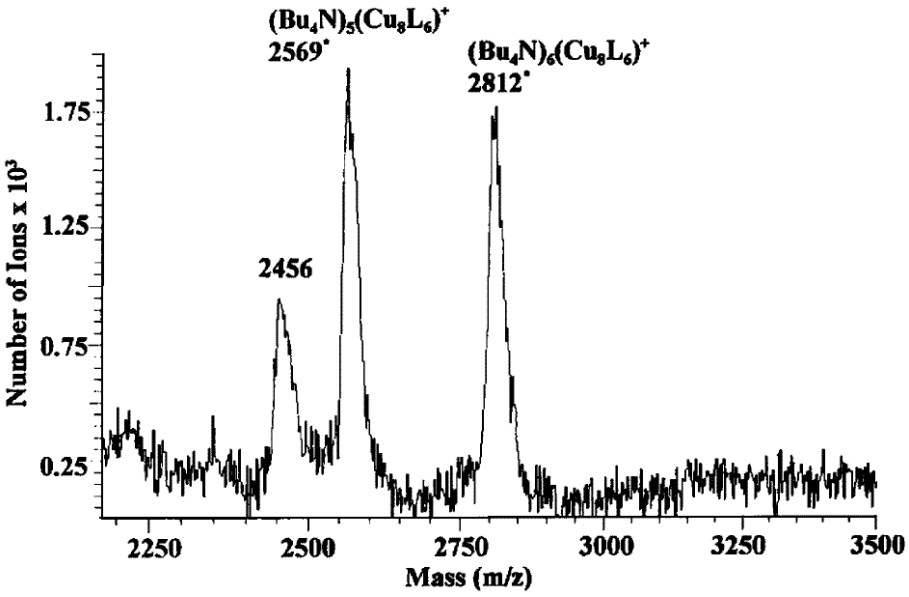

Figure 4. The positive ion ^{252}Cf-PD mass spectrum of [*n*-$Bu_4N]_4[Cu_8(S_2CC(CN)_2)]$ adsorbed on Hybond N+. Adapted with permission from reference 8.

FAB/LSIMS

Fast atom bombardment (FAB) and liquid secondary ion mass spectrometry (LSIMS) involve bombarding a sample (dissolved in a liquid matrix) with fast-moving atoms (e.g. Xe, FAB) or ions (e.g. Cs^+, LSIMS) (see this volume, chapter 13: *SIMS and Fast Atom Bombardment*). A wide variety of liquids have been tried as matrices. Desirable properties for the matrix include low volatility, chemical inertness, low viscosity, ability to dissolve the sample and to assist ionization. Popular choices include glycerol, 3-nitrobenzyl alcohol (3-NBA) or 2-nitrophenyloctylether (NPOE; for non-polar samples). Continual bombardment of the matrix leads to fragmentation and rearrangement and this manifests itself as a relatively strong chemical background over a wide *m/z* range (known as "grass"). FAB can be complicated by redox, fragmentation and clustering processes in the study of metal complexes,[10] but is nonetheless a widely applicable method for mass spectrometric analysis of organometallic and coordination compounds, whether charged or neutral.[11]

Ions in FAB/LSIMS generally result from charge exchange between the incident particles and sample to produce $[M]^{\bullet+/-}$, or frequently protonation or cationization to provide pseudomolecular ions $[M + H]^+$, $[M + Na]^+$, etc. Singly charged ions are usually transferred to the gas phase fairly efficiently; doubly charged ions often undergo reduction or oxidation to the ±1 state, or may associate with a singly charged counterion to provide a singly charged ion. Acidic compounds may provide an $[M - H]^-$ ion.

FAB/LSIMS are relatively soft ionization techniques, though harder than either ESI or FD insofar as a fragment ion is often the base peak.[12] Common fragment ions are due to loss of a neutral monodentate donor ligand such as CO or PR_3. Figure 5 shows the LSIMS spectrum of [Ru(bipyridine)$_3$]Cl_2, which shows numerous typical features: chemical noise at low *m/z*, loss of neutral ligands, charge reduction, and association with a counterion.

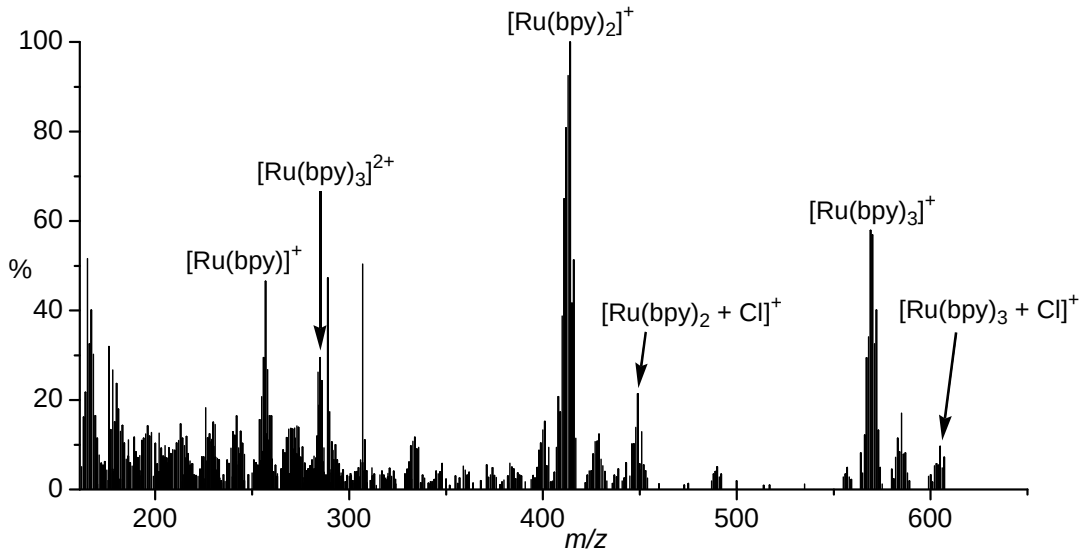

Figure 5. Positive-ion LSIMS of [Ru(bipyridine)$_3$]Cl_2 in a 3-nitrobenzyl alcohol matrix. Adapted with permission from reference 1.

ESI

Electrospray ionization mass spectrometry (ESI-MS) involves spraying an ion-containing solution from a highly charged capillary, generating a fine mist of droplets that are desolvated by a warm bath gas (see this volume, chapter 12: *Electrospray Ionization*). The fact that ESI can be used to probe solution speciation coupled with the fact that it is a very soft ionization technique means that it has proven popular with organometallic chemists. Common solvents used as the mobile phase include water, methanol, acetonitrile and dichloromethane. For air- and moisture-sensitive compounds, the solvent must be thoroughly dried and the instrument itself must be as free as possible from moisture. This requirement is often difficult to fulfill on an open-access instrument, as water is a popular mobile phase for organic compounds and biomolecules. Sample preparation usually involves serial dilution of the

sample to much less than 1 mg mL^{-1}; a useful rule of thumb, given that many organometallic compounds are coloured, is that a solution that is anything more than extremely pale in colour is likely to be far too concentrated. Solids only sparingly soluble in a the solvent of choice may be dissolved in a drop of a good solvent for that compound then diluted with the electrospray solvent.

Except for very easily oxidized or reduced compounds, ESI simply transfers charged species from solution to the gas phase (the "ionization" part of the ESI name therefore is somewhat misleading). As a result, formally charged compounds provide the most intense spectra but excellent results can also be obtained from neutral compounds where these readily associate with a charged species. Most commonly, this involves protonation to provide $[M + H]^+$ pseudomolecular ions, but cationization with NH_4^+, Na^+ and K^+ is also common. In these cases, the molecule M must have somewhere on the periphery (i.e. not coordinated to the metal) a moderately basic site, most often nitrogen or oxygen lone pairs. Acidic compounds frequently provide $[M - H]^-$ ions. Addition of chloride ions may also result in anionization to provide $[M + Cl]^-$ in cases where the analyte is H-bonding. A number of derivatization agents have been introduced to broaden the applicability of ESI-MS, for example the use of alkoxide ions, RO^-, to provide $[M + OR]^-$ ions from metal carbonyl complexes,[13] or Ag^+ to provide $[M + Ag]^+$ ions from compounds with M-M bonds or with extensive π-systems (polyalkynyl groups, aromatic rings).[14] Metal complexes with halide ligands often lose halide ions to produce $[M - X]^+$ ions; the vacant coordination site is often filled by a solvent molecule hence $[M - X + solvent]^+$ ions are also frequently observed.[15] Ligands may also be deliberately employed because of their amenability towards electrospray analysis, for example the use of the commercially available $P(p\text{-}C_6H_4OMe)_3$ or $P(p\text{-}C_6H_4NMe_2)_3$ in the place of the ubiquitous PPh_3 allows ready cationization.[16]

Most organometallic compounds are at least reasonably soluble in solvents suitable for ESI-MS, and the most useful solvents are probably dichloromethane and acetonitrile. Frequently, spectra can be collected under conditions very much milder than that required for samples of biological origin, which usually involve water as a component of the mobile phase. As such, spectra should be run under extremely mild conditions in the first instance: low temperature (even sub-ambient; see this volume, chapter 12: *Cold-spray ionization*) and desolvation gas flow rates, and especially very gentle settings for collision-induced dissociation (CID; sometimes CAD, see volume 1, chapter ?: MS code 76). For example, ESI-MS of the rhodium clusters $[Rh_6H_n(PR_3)_6]^{2+}$ (n = 12 or 16; R = isopropyl or cyclohexyl) in dichloromethane may be collected with the source and desolvation gas at ambient temperature (Figure 6).[17]

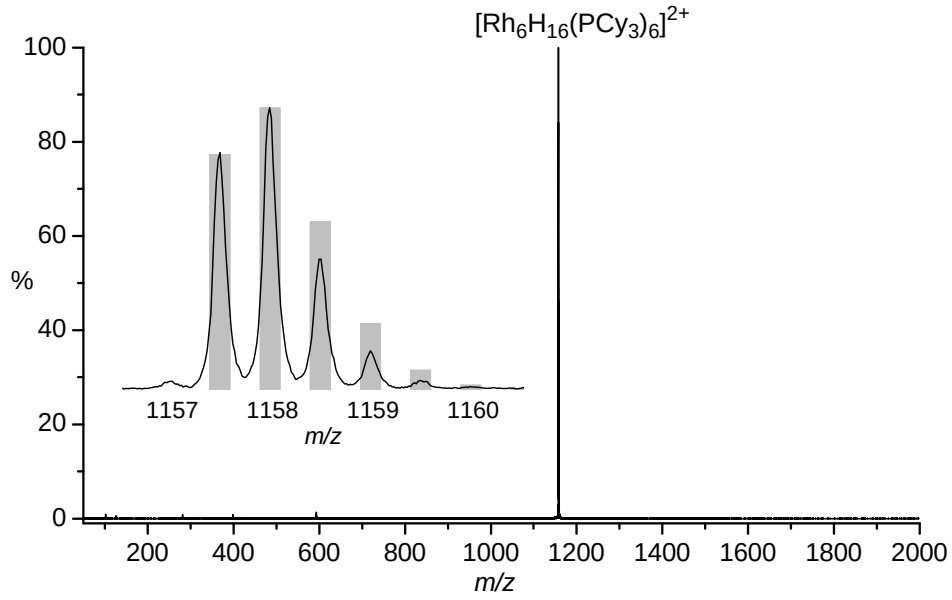

Figure 6. Positive-ion ESI-MS of $[Rh_6H_{16}(PCy_3)_6]^{2+}$ in dichloromethane. The inset shows calculated and experimental isotope patterns. Note the lack of fragmentation. Used with permission from reference 17.

Structural information can be gained from ESI-MS using CID (see this volume, chapter 11: *Energy Dependent ESI*). ESI-MS is also an important tool for studying reactivity in the gas phase, especially involving catalytic reactions.[18]

MALDI

Matrix-assisted laser desorption ionization (MALDI, see this volume, chapter 18: *Matrix-Assisted Laser Desorption*) involves using a pulsed UV laser to ablate material from a surface consisting of sample co-crystallized with a matrix, usually an aromatic acid. The popularity of MALDI is disproportionately low in the organometallic community, more so perhaps than any other ionization technique. The lack of success is probably largely due to a lack of suitable matrices; many of the studies of organometallic complexes have used no matrix at all. Neutral matrices such as dithranol are usually favored in the analysis of organometallic compounds. MALDI of air- and moisture-sensitive compounds can be difficult due to exposure of the target slide to the atmosphere prior to analysis.

MALDI is most successful in the analysis of metal derivatives of compounds that are known to be amenable to MALDI themselves. Generally, these tend to be molecules of high molecular weight that are difficult to characterize by other means, and the ability of MALDI to provide a definitive molecular

weight is crucial. Complexes of biomolecules (peptides, sugars, proteins, oligonucleotides), polymers, dendrimers and supramolecular assemblies that provide good MALDI spectra in the uncomplexed form can often be successfully characterized when metal fragments are attached.[19] Compounds which themselves strongly absorb UV light often produce intense spectra under laser ablation even in the absence of added matrix (i.e. simple LDI). Notable examples include porphyrins [20] and fullerenes.[21] Transition metal carbonyl cluster compounds also provide strong spectra without matrices in both positive- and negative-ion modes, but the spectra contain only products attributable to fragmentation and/or aggregation, and the absence of molecular ions renders LDI-MS useless as a characterization tool (Figure 7).[22]

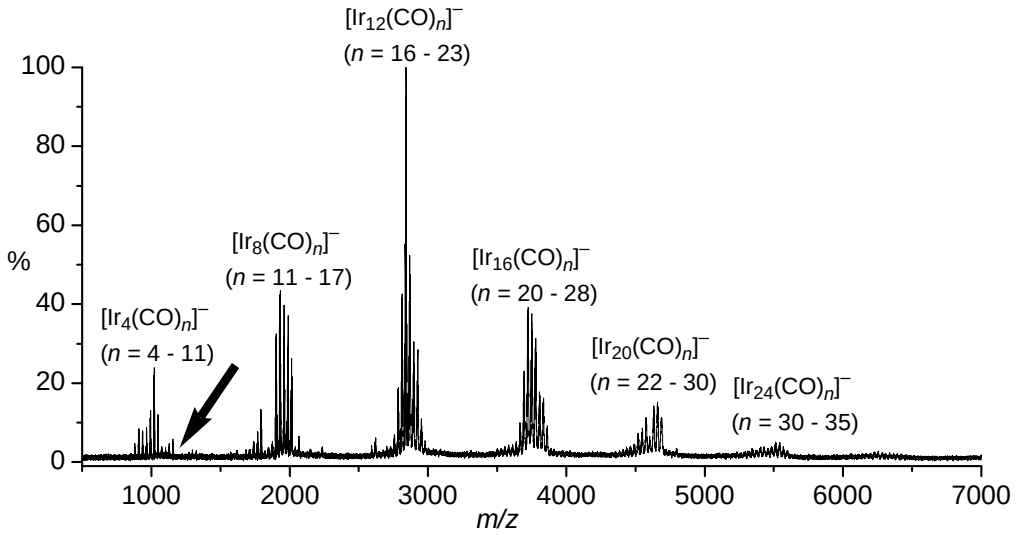

Figure 7. Laser desorption-ionization mass spectrum of $Ir_4(CO)_{12}$ in the negative-ion mode. Note the absence of a molecular ion (arrow) and the presence of extensive high mass aggregation products. Adapted with permission from reference 21.

ICP

Inductively coupled plasma mass spectrometry (ICP-MS) is essentially a form of elemental analysis, as it involves the conversion of all analytes to singly charged gas phase ions using a very high-temperature plasma and so provides no chemical information regarding the molecular form or oxidation state of the sample (see volume 5, chapter 1: *Plasma Ionization*). ICP-MS is a highly sensitive technique used to measure trace elements in a variety of solid and liquid materials, including measuring concentrations of important organometallic pollutants, especially of tin, mercury and lead.[23] For the purposes of molecular characterization, ICP-MS is best used to establish ratios of heavy

elements, especially in cluster chemistry. Published spectra are rare, with data usually simply tabulated, but an example of the raw data is shown in Figure 8 for a plutonium standard solution.[24] This figure shows how unit mass resolution is perfectly sufficient, and hints at a potential complication of the technique: overlap of isotopes (e.g. ^{104}Ru with ^{104}Pd). However, for most elements a suitable isotope can usually be selected for which overlap does not occur and this problem is not usually significant for samples of synthetic origin.

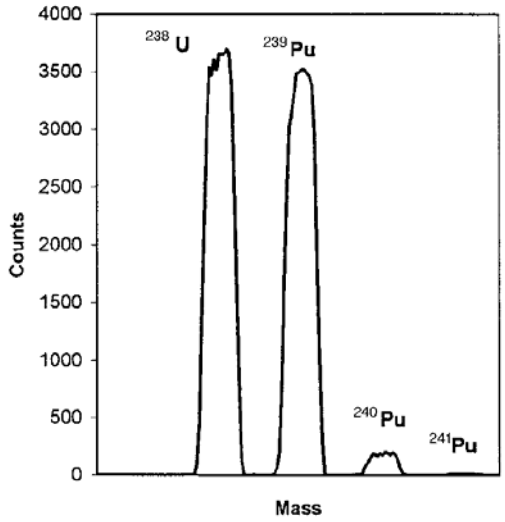

Figure 8. ICP-MS trace for a 10 pg ml^{-1} ^{239,240}Pu standard solution with a ^{240}Pu/^{239}Pu ratio of 0.054. Adapted with permission from reference 23.

Handling of air-sensitive samples

Precautions that should be taken for the analysis of air- and moisture-sensitive samples, depending on sample type and introduction method follow.

Solid samples are placed on a probe, which is introduced directly into the source of the mass spectrometer. This is the typical introduction method for EI except when the compounds are volatile enough to be introduced via a GC. The sample must be transferred from flask to probe, and without special apparatus this transfer must be done in air. Simply carrying out the transfer at speed may be enough. If not, a large clear plastic bag enveloping sample (typically in a Schlenk flask), probe and source may be purged several times with inert gas and the sample transferred inside the bag. Alternatively, a strong flow of nitrogen through a wide-bore flexible tube may be used to bathe the sample in the inert gas while the transfer is taking place.

Volatile liquids are best done by headspace analysis by gas-tight syringe from a sealed vial. Syringe contents can be delivered direct to mass spectrometer through suitable portal (including via GC/MS, if available, but care – if your sample is air sensitive, might it also react with the column?).

Involatile liquids or samples in **liquid matrices** require the same precautions as solid probe. Liquids can be very air-sensitive due to their inability to form a protective oxidized coating. The sample is best preloaded into a gas-tight syringe; because this is less fiddly than a spatula and flask, a relatively small nitrogen-filled plastic bag may do a good job as an atmospheric barrier.

When using a **solid matrix**, the sample and matrix must be co-crystallised in an inert atmosphere; because of the size of the sample trays, this usually dictates a glovebox. Transfer to the mass spectrometer will entail brief exposure to the air, and the same sort of precautions taken in solid probe analysis will be required. However, the matrix does provide a degree of protection to the sample and this effect can be enhanced by having an unusually high matrix : sample ratio and depositing especially thick layers on to the sample slide. Of course, all these precautions are useful only if the *matrix itself has been rigorously purified and dried*; once so treated, the matrix should be stored in a glovebox. The best solution is to have a glovebox interfaced directly to the mass spectrometer (Figure 9), but this requires a custom-built set-up.

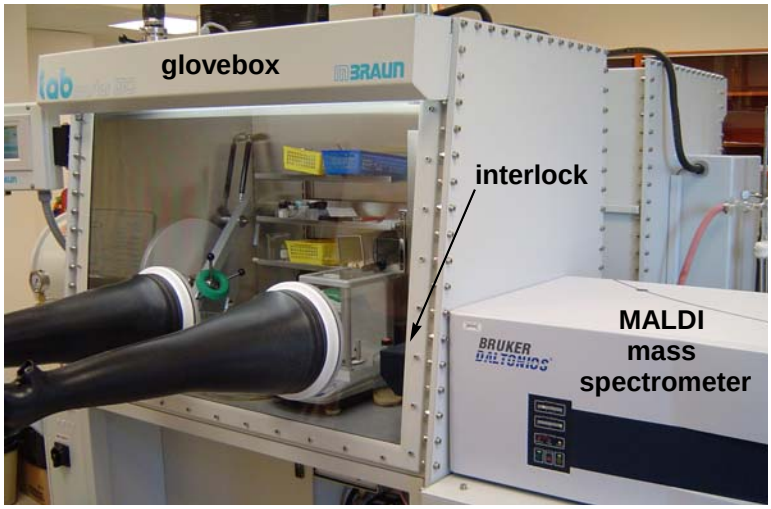

Figure 9. Mass spectrometer interfaced with an inert-atmosphere glovebox. Photo taken in the laboratory of Prof. D. Fogg, University of Ottawa.

Solutions are trivial to introduce anaerobically to a mass spectrometer, simply by means of a gas-tight syringe loaded from a Schlenk flask or in a glove box. However, all solution injection systems are prone to cross-contamination because all samples are introduced through the same capillary line. The first precaution to take is that each user of an instrument ought to have their own syringe, flexible tubing and connectors, leaving only the stainless-steel capillary to be shared by all users and passing the bulk of the responsibility for minimizing cross-contamination to the user. Solvents need to be rigorously dried, recalling that an ESI mass spectrometer is quite capable of detecting charged species at the low part-per-million range, the level to which most solvents can be dried. However, for very air-sensitive samples, residual water in the mass spectrometer can compromise analysis and lengthy flushing of the system with (preferably more than one) dry solvent prior to analysis may be required. A recommended protocol if water has been used as the mobile phase recently is to flush first with dry methanol before flushing with the intended solvent (typically acetonitrile or dichloromethane).

Ionization techniques for organometallic applications: a summary

Table 1 summarizes the information contained in the main text, and adds some extra data to enable some direct comparisons. It should be treated as a guide only; an experienced operator is often able to "push the envelope" in terms of mass range and sample type. The table does not take into account derivatisation methods; there are many available that make a sample more amenable to analysis by a given ionization technique, e.g. methylation to make samples more volatile for EI, addition of alkoxide ions to metal carbonyls for characterization by ESI.

Table 1. Ionization Techniques: A Summary

	Strengths	Weaknesses	Mass range	Mass analysis	Popularity
APCI	• can handle less polar samples and solvents than can ESI • coupling to HPLC	• high flow rates required are less suitable for one-off analyses • hot desolvation	• Moderate – generally gives singly charged ions up to 1500 Da	• most commonly triple quads, ion traps, hybrids	• Low
CI	• softer than EI, less fragmentation • more likely to get molecular weight information	• volatile compounds only • results depend strongly on conditions (reagent gas, P, nature of sample)	• low – typically less than 1000 Da	• Any	• Low
EI	• non-polar compounds • reproducible spectra, many fragments allow library searching	• volatile compounds only • molecular ion may be absent	• low – typically less than 1000 Da, best below 500 Da	• Any – usually quadrupole or ion trap when used in GC/MS	• Medium – used mostly for ligand characterization
ESI	• good for charged and polar samples • very soft ionization • low background • excellent detection limits • good for MS/MS • coupling to HPLC	• poor for non-polar compounds • sensitive to contaminants	• High – multiple charging allows access to molecules of very high molecular weight, though most are analyzed below 2000 *m/z*	• any, but infrequently sectors; most commonly triple quads, ion traps, hybrid Q/TOFs, FTICR	• High – many applications in solution-phase organometallic chemistry
FAB/LSIMS	• simple, low T • reasonably soft • good for wide variety of samples	• high chemical background • low *m/z* range dominated by matrix ions	• Moderate – most effective from 200-2000 Da, up to 5000 Da possible	• Usually sector	• Medium; a routinely used technique but popularity suffered with the introduction of ESI and MALDI
FI/FD	• soft, abundant $[M]^{\bullet+}$ • little chemical background	• emitter preparation tedious • sensitive to sample overloading • slow	• moderate – less than 3000 Da for FD (FI requires volatile samples)	• TOF, FTICR, sector	• Low; superseded first by FAB/LSIMS then ESI and MALDI
ICP	• trace element analysis • any sort of sample	• no structural information	• *n/a* – creates singly charged elemental ions (only need mass range up to ~ 250 Da)	• usually quadrupole	• Low, but high in the field of analytical inorganic chemistry
MALDI	• soft ionization • good for high molecular weight samples	• MS/MS difficult • aggregation processes can complicate spectra • few matrices suitable for organometallics	• Very high – beyond 50,000 Da	• nearly always TOF, but others may be used for the analysis of low molecular weight ions (FTICR, ion trap)	• Low, perhaps due to lack of suitable matrices
PD	• soft, little fragmentation	• requires radioactive source • very slow	• Very high – beyond 50,000 Da	• TOF	• Very low; essentially obsolete

Selecting an ionization technique

The following flowchart (Figure 10) may assist in the selection of an ionization technique, based on the known properties of a sample. EI and ESI together provide good coverage of most samples likely to be encountered, with the exception of high-molecular weight, non-polar samples. FAB/LSIMS and FD are also both reasonably versatile, though the latter considerably less convenient.

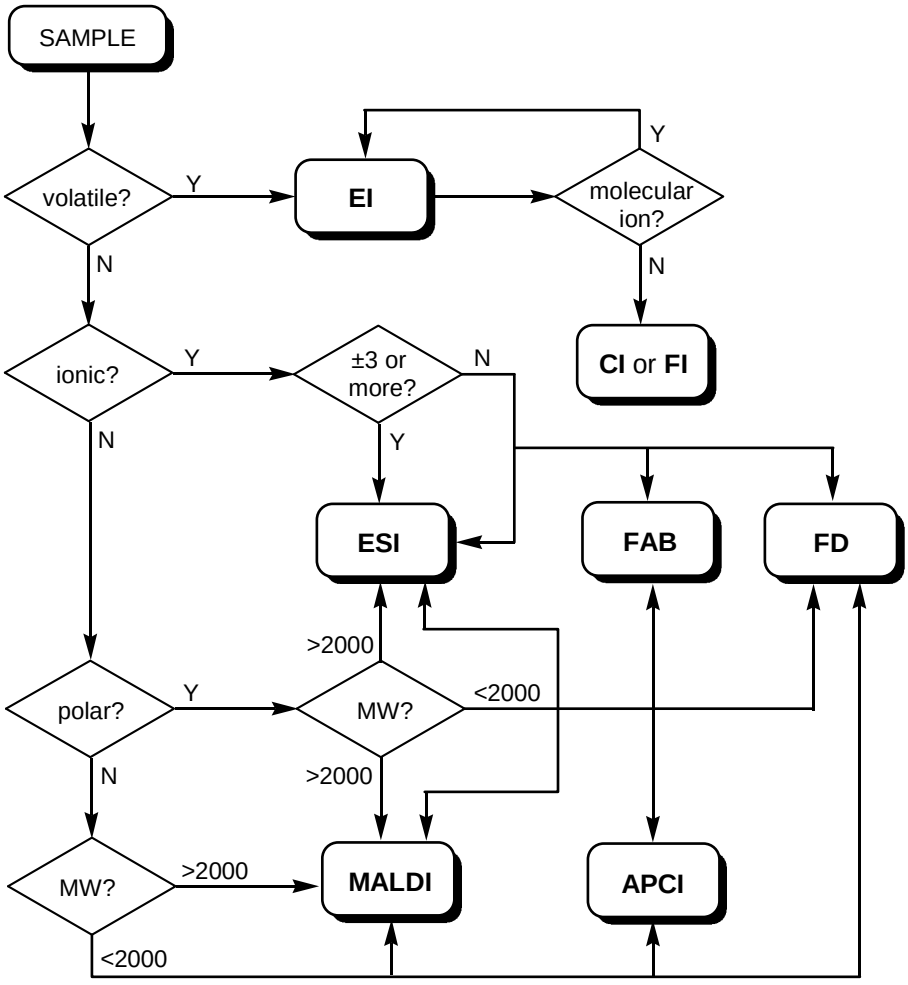

Figure 10. Flowchart for choosing an ionization technique based on the properties of the sample. LSIMS is treated as synonymous with FAB. PDMS is rare so does not appear; it can handle similar types of samples as does MALDI. ICP-MS can handle all sample types, but provides no molecular weight information and so is not included.

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