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Assigning the ESI mass spectra of organometallic and coordination compounds

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Abstract

Electrospray ionization mass spectrometry (ESI-MS) is a useful technique for solving organometallic and coordination chemistry characterization problems that are difficult to address using traditional methods. However, assigning the ESI mass spectra of such compounds can be challenging, and the considerations involved in doing so are quite different from assigning the mass spectra of purely organic samples. This is a tutorial article for organometallic/coordination chemists using ESI-MS to analyze pure compounds or reaction mixtures. The fundamentals of assigning ESI mass spectra are discussed within the context of organometallic and coordination systems. The types of ions commonly observed by ESI-MS are categorized and described. Finally, a step-by-step guide for the assignment of organometallic and coordination chemistry ESI mass spectra is provided along with two case studies.

KEYWORDS

coordination chemistry, electrospray ionization, methodology, organometallic chemistry, reaction monitoring, transition metals, tutorial

1 | INTRODUCTION

Electrospray ionization mass spectrometry (ESI-MS) is a valuable tool for the identification of organometallic and coordination complexes in solution and in complex reaction mixtures,[1,2] but analyzing the resulting ESI mass spectra can sometimes be a daunting task. In proteomics or metabolomics, spectral libraries are used to assign observed peaks but for organometallic and coordination complexes no such comprehensive database exists. Even if it did, it would be difficult to apply since depending on the exact ESI conditions used, metal complexes may lose or gain labile ligands, become oxidized or reduced, or react with oxygen or moisture.

Here, we briefly summarize the techniques that are commonly used to assign any ESI-MS spectrum, and the various types of ions one is likely to observe by ESI-MS. Then, we suggest a step-by-step plan of attack specifically for the analysis of organometallic and coordination systems. Finally, we provide two case studies.

2 | THE FUNDAMENTALS OF ASSIGNING ESI-MS SPECTRA

Any textbook on the fundamentals of MS will provide a detailed discussion on assigning ESI mass spectra.[3-5] Here, the focus is on a user-friendly guide tailored to organometallic and coordination chemists.

In order to assign any signal in a mass spectrum, an analyst checks for agreement between four key characteristics of the signal: the mass-to-charge ratio, the isotope pattern, the accurate mass, and the fragmentation pattern. All four characteristics must be in agreement to assign a peak.

2.1 | The mass-to-charge ratio (*m/z*)

The first, and simplest, characteristic to check is the mass-to-charge ratio (*m/z*) of a peak. Note that the *m/z* ratio is infrequently referred

to in units of thomson (Th).[6] The predicted *m/z* ratio for any ion can be calculated as molecular weight (in atomic mass units, u, or Dalton, Da) of the ion divided by the elementary charge of the ion (z).

$$m/z = \text{molecular weight of the ion}/\text{charge of the ion.}$$

From this definition, it is obvious that if the charge of the ion is one, then the signal for that ion will appear at the molecular weight of the ion. A 2+ ion will appear at half the mass of the ion. MS visualization software will, by default display the experimentally observed *m/z* ratio over major peaks in a spectrum. Simply compare your calculated *m/z* ratio with the experimentally observed value. As an initial check, look for a match that is within *m/z* 0.5 of the expected value.

If a signal of interest has more than one major peak because of the presence of an isotope pattern (see next section), do not attempt to calculate the *m/z* ratio using the average molecular mass or the nominal molecular mass of the ion. Instead, use an isotope distribution calculator to generate the expected isotope pattern.

2.2 | The isotope pattern

Many organometallic ions have a diagnostically useful isotope pattern, and even numbered elements in particular (because of nuclear stability) often have rich and characteristic distributions (Figure 1).

For example, iron has three isotopes (^{54}Fe, ^{56}Fe, and ^{57}Fe), so a signal from an ion containing a single iron atom will have the characteristic pattern shown in Figure 2A. The intensity of each isotopic peak is characteristic of the relative abundance of that isotope in the sample being measured. Figure 2B through E shows an example of the redox-active ferrocene oligomer **1** in various charge states studied by ESI-MS.[7]

The observed isotope pattern in the MS spectrum of **1** predominately originates from the various isotopes of iron and silicon (carbon also contributes to the overall isotope pattern). When the charge of the ion is greater than one and there is more than one peak in the isotope pattern, it is often immediately obvious in the spectrum. A signal from a + 1 ion will have isotopic peaks separated by the difference in the molecular weight of each isotope (Figure 2B) while a signal from a + 2 ion will have peaks separated by half as much (Figure 2C), and so forth (Figures 2D,E). This leads to a narrower peak width and reduced resolution as the charge state increases.

Isotope patterns are useful, first, as a way to triage all of the signals in a spectrum and identify, by inspection, the ones that contain a certain metal atom. Second, a positive match between the expected isotope pattern for a given complex and the experimentally observed signal, as shown in Figure 3, provides a strong piece of evidence for peak assignment. To determine the expected isotope pattern for an ion, use an isotope pattern calculator such as *ChemCalc* (a free online resource).[8] Be aware that the resolution of your mass spectrum will change the appearance of the experimental isotope pattern. The *ChemCalc* software and other proprietary MS software allow you to select the resolution of the predicted spectrum so that you can demonstrate a good match. For a good match, the experimental data must contain all of the peaks present in the calculated signal, and the intensity of each peak in the signal should be similar to that observed in the calculated signal. The lower the intensity of your experimental signal, the more difficult it will be to obtain a good match. Try averaging many scans (50-200) to improve the quality of the experimental data. Overlapping peaks in the experimental data from other ions may also interfere with obtaining a good match. Check for nonsymmetrical peak shape and run your sample on a higher resolution mass spectrometer if possible.

To display an isotope match graphically, the convention is to overlay the experimentally obtained signal (line) over the calculated isotope pattern (solid bars) as in the example below (Figure 3). If baseline resolution is not achieved between isotopic peaks, a better visual match may be obtained if the experimental resolution is accounted for in the calculated spectrum using an isotope pattern calculator. Then, both the experimental and resolution-corrected calculated isotope patterns are best displayed using lines.

Python-based tools for generating such plots have been recently presented,[9] and these can accommodate cases where multiple

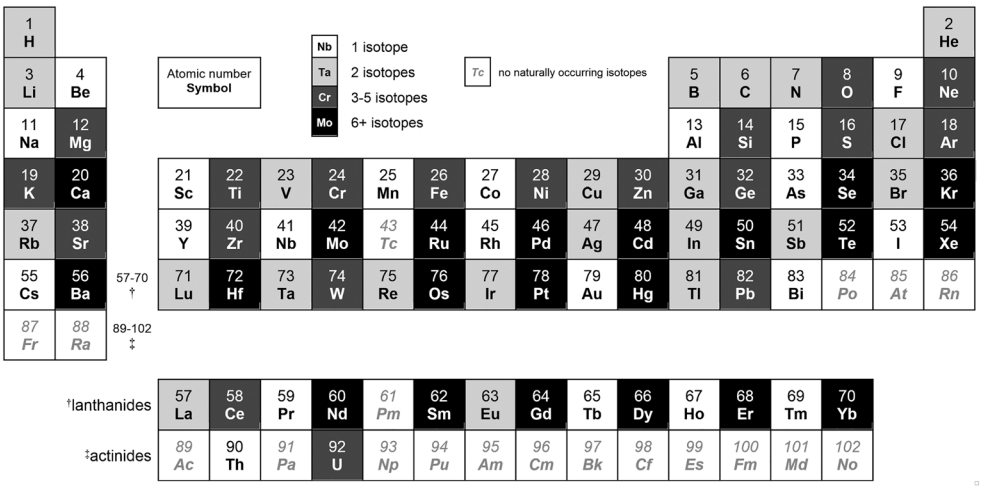


FIGURE 1 Periodic table (up to no, Z = 102) shaded by number of isotopes (more = darker)

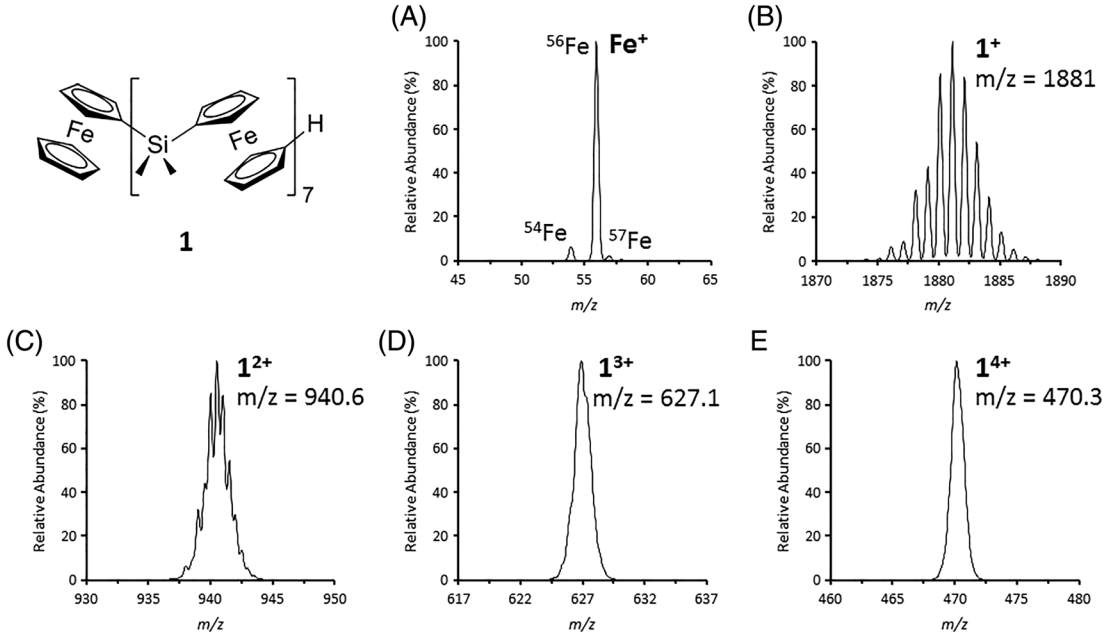


FIGURE 2 Simulated spectra of Fe^+ and **1** in various oxidation states

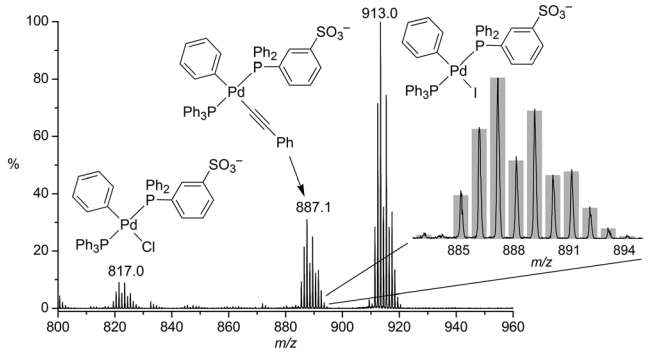


FIGURE 3 Displaying an isotope pattern match. Negative-ion electrospray ionization mass spectrometry of a palladium catalyzed copper-free Sonogashira reaction mixture showing various observed intermediates.[10] The inset shows the isotope pattern match for [Pd($PPh_2(C_6H_4SO_3)(PPh_3)(Ph)(C_2Ph)$)]$^-$ (*m/z* 887.1) using the line (experimental) and bar (calculated) convention. Adapted from the study of Vikse et al[10]

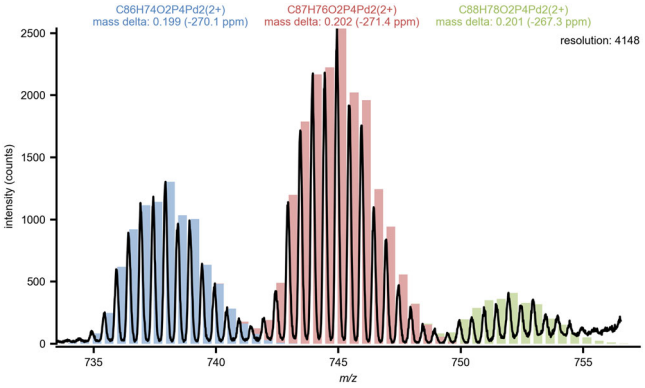


FIGURE 4 Isotope pattern matching for three related dipalladium dications [Colour figure can be viewed at wileyonlinelibrary.com]

isotope patterns are present and even when they are overlapping (Figure 4).

The accessibility of high-resolution instruments continues to improve, especially with the advent of Orbitrap instruments. These instruments have resolutions of greater than 100 000 and are capable of resolving the individual combinations of ions that make up each nominal mass. For example, the ion $[PtCl_3]^-$ has a rich isotope pattern thanks to contributions from ^{190}Pt, ^{191}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt, ^{35}Cl, and ^{37}Cl. The lowest mass combination ($^{190}Pt^{35}Cl_3$) is unique, but higher mass peaks have contributions from different combinations, eg, *m/z* 301 has contributions from $^{190}Pt^{37}Cl_3$ (*m/z* 300.858), $^{194}Pt^{35}Cl_2{}^{37}Cl$ (*m/z* 300.866), and $^{194}Pt^{35}Cl_3$ (*m/z* 300.872). These individual contributions can be resolved by an Orbitrap (or FTICR) instrument, and so it is important to know which combination is being measured when examining the pattern. Note the apparent differences in the isotope pattern of $[PtCl_3]^-$ when calculated at resolutions of 1000 (Figure 5, left) and 100,000 (Figure 5, right).

2.3 | The accurate mass

Ions with the same nominal mass can be distinguished from each other using the measured accurate mass. The measured accurate mass can be determined by collecting *m/z* data in the full MS mode. Many scientific journals do not have specific author guidelines on the required accuracy of accurate mass measurements; however, the *Journal of Organic Chemistry* specifies a found value within 0.003 *m/z* units for compounds with molecular masses below 1000 amu (ie, .003/100*1 000 000 = 30 ppm for an ion of 100 amu or .003/500*1 000 000 = 6 ppm for an ion of 500 amu).[11] A conservative (and

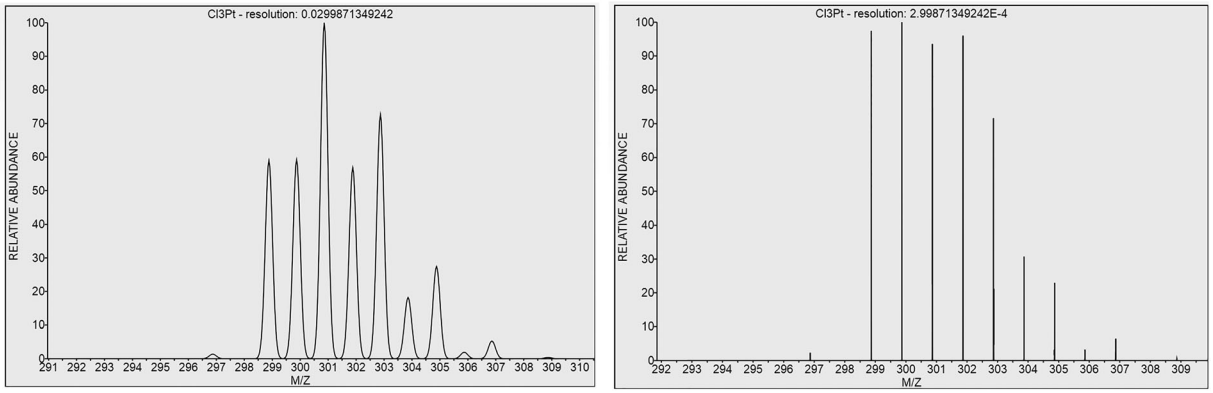


FIGURE 5 Isotope patterns calculated at different resolutions for $[PtCl_3]^-$: 1000 (left) and 100 000 (right)

recommended) rule of thumb for positive identification of a small molecule is a found *m/z* value within 5 ppm of the calculated value. The *ACS Style Guide* provides a standard format for reporting accurate mass data.[12] For example, a high resolution spectrum taken by ESI-MS of the compound featured in Figure 3 above would be reported as follows: HRMS–ESI/Q-TOF (*m/z*): $[M]^-$ calcd for $C_{50}H_{39}O_3SP_2{}^{106}Pd$, 887.11300; found 887.112.

For best accurate mass results from scanning instruments (eg, ion traps or quadrupoles, but not time-of-flight instruments), it helps to collect a spectrum over a small *m/z* range just around the peak of interest. By decreasing the *m/z* window and leaving the scan time unchanged, the instrument can average more data around the signal of interest and thus produce a more reliable reading. Some MS software has a special mode for this (eg, "zoom scan"), but it can also be done manually. It is important to avoid collecting accurate mass measurements in MS^n mode since the ions are energetically energized before detection and this can give slightly inaccurate *m/z* readings in some instruments. In cases where the standard instrument calibration does not provide acceptable results, a standard of known mass can be added to the sample as secondary calibration, and the *m/z* value of the signal of interest may be reported with respect to the standard. The best type of standard should give a naturally strong MS signal and have a *m/z* value as close as possible (without overlap) to that of the ion of interest.

2.4 | The fragmentation pattern (MS^n)

Ions with the same nominal mass can also be distinguished from each other based on how they fragment. Fragmentation experiments involve accelerating a precursor ion of interest, colliding it with neutral, gaseous helium, nitrogen, or argon and observing the resulting product ions. These types of fragmentation or collision experiments can be done in a dedicated collision chamber (called MS/MS or MS^n where n is the number of sequential fragmentation steps performed) within the mass spectrometer or in the ESI source of a mass spectrometer (called in-source fragmentation).

Relatively low collision energies yield predictable fragmentation patterns for organometallic species: at low collision energies, the loss of labile L-type ligands or solvent adducts is frequently observed (and in fact, the most labile ligands, such as monodentate alkene ligands, are hard to observe intact at all because of in-source fragmentation). At moderate collision energies, the inherent reactivity of the complex of interest can be probed since the observed gas-phase reactivity often mimics the solution-phase reactivity.[13,14] However, it is important to bear in mind the conditions of gas-phase MS/MS experiments when making comparisons between the gas and solution phases. In the gas phase,

1) The medium is nonpolar (a vacuum);
2) There are no solvent effects;
3) There are no counterions;
4) Processes involving the separation of opposite charges are highly unfavored.
5) Fragmentation (ie, the reaction being studied) must occur to an appreciable extent within milliseconds to be observed. This time scale can be extended to seconds in an ion trap instrument.
6) Unimolecular reactions are strongly favored (occasionally reactions with background H_2O or O_2 present in the mass spectrometer may be observed).
7) The effective thermal energy of ions isolated within the MS can vary dramatically. In ion trap mass spectrometers, trapped ions have been shown to exist at approximately room temperature and they are considered "thermalized" with their surroundings.[15,16] However, the same has not been proven for other types of mass analyzers.

With these caveats in mind, it is clear that unimolecular processes that involve nonpolar transition states and that release neutral products (eg, reductive elimination, beta-hydride elimination, and so on) are easiest to study by MS/MS and can provide insights that are relevant to the analogous solution-phase processes. For example, the MS/MS spectra of two copper complexes shown below (Figure 6) at *m/z* 477 and *m/z* 525 include fragmentation pathways for loss of an L-type ligand (*m/z* 341, the charged phosphine) and decarboxylation at the metal center (loss of 44 Da) - a reaction known to occur in solution

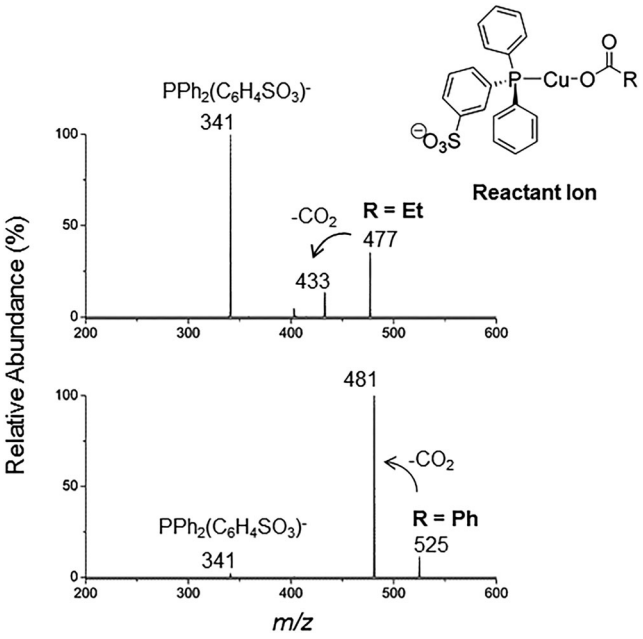


FIGURE 6 MS/MS spectra of [Cu ($PPh_2(C_6H_4SO_3)$)(CO_2R)]$^-$ where *R* = Et (top, *m/z* 477) and *R* = Ph (bottom, *m/z* = 525). Adapted from the study of Vikse et al[17]

for these types of complexes.[17] Furthermore, the favored fragmentation pathway is dependent on the *R* group of the ligand, and the trend observed in the gas-phase mimics the common trend in solution that decarboxylation from sp^2 hybridized carbon centers (*R* = Ph in this case) is favored over decarboxylation from sp^3 hybridized carbon centers (*R* = Et).

Another excellent recent example is the study of reductive elimination at iron (III) complexes by ESI-MS.[18]

On the other hand, dissociation of an X-type ligand from a positively charged ion would require charge separation and solvent stabilization and will therefore not occur during MS/MS (in the negative ion mode dissociation of an X-type ligand is possible (eg, $[PtCl_4]^{2-} \rightarrow [PtCl_3]^- + Cl^-$). The absence of solvent interactions also makes C-H activation processes such as orthometallation common in the gas phase[19] and makes dissociation of chelating ligands highly unlikely. In general, processes involving highly polarized transition states will be disfavored. This can sometimes be useful. For example, a recent report demonstrates that the simple screening of chelated beryllium species in solution is possible by ESI-MS because of the stability of those chelated species with respect to the ESI-MS process.[20]

At higher collision energies, the observed fragments become harder to predict and the gas-phase fragmentation patterns no longer mimic typical solution-phase processes (as the effective temperature is much higher than can be achieved in solution). Fragmentation of ligand backbones while the ligand is still bound to the metal often occurs.

In summary, when all four of the above characteristics (the mass-to-charge ratio, the isotope pattern, the accurate mass, and the fragmentation pattern) are in agreement, one may confidently assign the peak; however, it is important to note that structural (eg, *cis/trans*) isomers cannot be resolved by classical MS methods.[21] In such cases, a complementary technique should be used to refine the assignment.

3 | TYPES OF IONS OBSERVED IN THE ESI MASS SPECTRA OF ORGANOMETALLIC COMPOUNDS

The types of organometallic ions that may be observed by ESI-MS can be divided into two groups: even-electron ions and odd-electron ions. In the following discussion, generic cations will be represented as C, anions as A, and neutral compounds as N. A note about the negative ion mode. Most of the discussion below focuses on the positive ion mode. Spectra collected in the negative ion mode are often less intense but simpler because of the fact that there are fewer available common ionization pathways. In some cases, this is advantageous.

3.1 | Even-electron ions

Even-electron ions are the most commonly observed ions. In a simple case, a cation, $[C]^+$, or a protonated neutral molecule, $[N + H]^+$, can be observed directly in the positive ion mode as the major signal (the analogous anionic signals, $[A]^-$ and $[N - H]^-$, can be observed in the negative ion mode). However, assignment is often not that straightforward. Multiply charged ions ($[C]^{n+}$) or cationized species $[N + C]^+$ may be observed, and other permutations of the simple ion may exist as well depending on the experimental conditions used during analysis. Below, the most common scenarios are described.

3.1.1 | Inherently, singly charged species

Even-electron species that are inherently charged may be observed directly by ESI-MS as their molecular ion. For example, a cation, C^+, with a mass of 459 Da and a charge of +1 may give a peak at *m/z* 459 (Figure 7, black). But do not be discouraged if this is not the only signal in your spectrum! There are a number of other ways this species may manifest.

1) The ion may appear as an aggregate ion with one or more associated counterion. For example $[C_2A]^+$ or $[C_3A_2]^+$ (Figure 7, green, where A is iodide).
2) If desolvation in the ESI process is incomplete (often because of low cone voltages, low source temperatures or low desolvation gas flow), an inherently charged species may be observed with solvent adducts $[C\ (solv)_n]^+$ (Figure 7, blue, where the solvent is methanol). Solvent adducts are most likely to be seen if the solvent has good coordinating ability. For example, acetonitrile is often used as a solvent and is a good ligand in its own right.

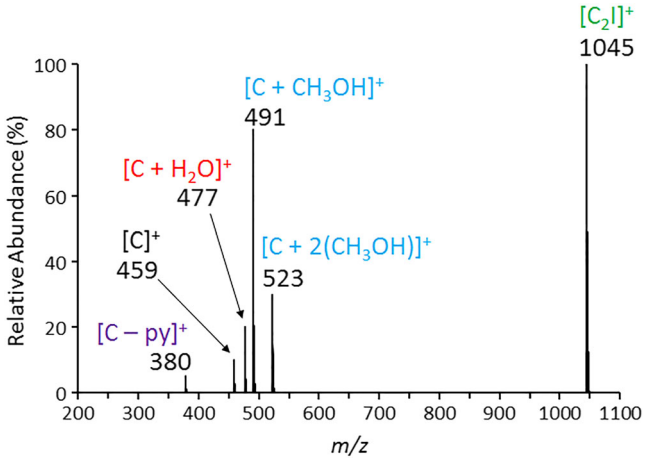


FIGURE 7 Simulated spectrum showing commonly observed signals for a generic cation, C^+: The bare ion (459 Da, black), solvated ions (blue), a cluster ion (green), an adventitious adduct (red), and a neutral loss (purple, py = pyridine). Peak intensities are hypothetical and may vary dramatically

3) Formation of adducts with adventitious neutral molecules present in the instrument is also possible—and especially likely when ion trap analyzers are used (Figure 7, red, where the neutral molecule is water). Water is by far the most common example but if a previous user was spraying a high boiling point solvent like DMF or DMSO, these molecules may also be observed as adducts.
4) For complexes with loosely bound ligands, it is common to see loss of a neutral ligand, $[C - L]^+$, and this process will be more prevalent when harsher source conditions are employed (Figure 7, purple, where the ligand is pyridine).

Adjusting the ESI source parameters (desolvation gas, temperature, and source voltages) can significantly change the relative intensities of these various incarnations of the parent ion with harsh conditions favoring fragmentation and fewer adducts or clusters. Adjusting the sample concentration can also influence the amount of clustering observed.

3.1.2 | Inherently, multiply charged species

Multiply charged species (eg, $[C]^{2+}$) may be observed for larger metal complexes; while small multiply charged species will tend to undergo charge reduction if possible. The key limiting factor is charge density. Complexes with high charge density are disfavored in the gas phase. Because of this, most organometallic complexes will be observed as 1+ or 2+ ions (rarely 3+ or higher). To minimize charge density, multiply charged species often form complexes with counterions (eg, $C^{2+} + A^- \rightarrow [CA]^+$) or remain more solvated than the analogous singly charged ions. Easily reduced/oxidized metal centers may be directly reduced or oxidized by the electrospray process itself (eg, Cu (II) → Cu(I)).

As mentioned above, multiply charged peaks with significant isotope patterns are often easily identifiable by the distance between peaks in the isotope pattern. Multiply charged ions without significant isotope patterns such as complexes containing gold may be more difficult to spot. In cases like these, fragment patterns are useful in identifying multiply charged species. The fragmentation patterns of multiply charged species have two unique characteristics: (a) some of the product peaks are observed at *m/z* ratios higher than that of the originally isolated precursor ion, and (b) pairs of product ions will be observed. For example, a 2+ ion will fragment into two observable 1+ ions equidistant from the precursor peak. Figure 8 below shows an example of a 3- ion (*m/z* 347.7) fragmenting into a 1- (*m/z* 553.1) and 2- ion (*m/z* 245.0).[22] Note that the singly charged product ion is twice as far removed from the precursor ion as the doubly charged product ion.

3.1.3 | Protonated/deprotonated species

When the compound of interest is not inherently charged but has a basic site, it is common to observe the compound in its protonated form, $[N + H]^+$. In fact, the first investigation of a catalytic reaction by ESI-MS took advantage of this possibility (Figure 9).[23]

The most common sites for protonation are nitrogen and oxygen groups on ligands. If the $[N + H]^+$ signal is not observed or if it has low intensity and if the analyte is tolerant to acid, the sample solution may be acidified by adding a drop of dilute (approximately 0.1 M) formic acid just before analysis. Dimerization, $[2\ N + H]^+$ is also possible.

Multiple protonation $[N + nH]^{n+}$ is possible for complexes with multiple basic sites; however, single protonation will likely be favored unless there is a large excess of acid in the solution or unless the species of interest is very large. This is due to the fact that a high charge density in the gas-phase is relatively unstable.

Analogous to protonation, complexes with acidic sites can be deprotonated in the negative-ion mode. Dimerization $[(N - H)N]^-$ and multiple deprotonation $[N\text{-}nH]^{n-}$ are also possible.

3.1.4 | Cationized species

Cations such as Na^+, K^+, or NH_4^+ from glassware or solvents are often present as persistent contaminants in sample solutions or in the ESI-MS instrument itself. Acetonitrile, specifically, can contain significant amounts of NH_4^+, NH_3, and CN^-. These ions can adventitiously bind to basic/acidic sites on the species of interest (often in the backbone of a ligand) to create a charged adduct. Common examples are: $[N + NH_4]^+$ (+18 *m/z*), $[N + Na]^+$ (+23 *m/z*), or $[N + K]^+$ (+39 *m/z*).

Alternatively, cations may be intentionally added to a sample to promote these ionization pathways if the species of interest is not inherently charged. This is a good option for moisture or acid sensitive compounds which cannot be charged by protonation. KI, for example, has good solubility in many polar aprotic solvents.

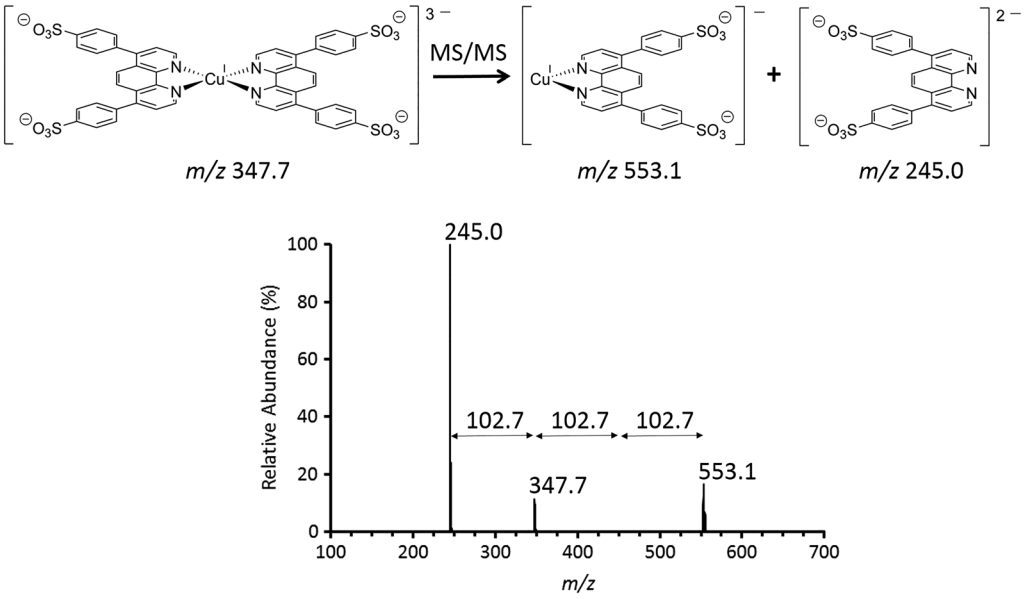


FIGURE 8 Scheme (top) and MS/MS spectrum (bottom) of the fragmentation of a triply-charged copper complex (*m/z* 347.7)

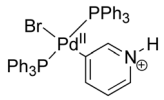


FIGURE 9 In 1994 Canary et al. employed pyridyl bromide as a substrate in a palladium catalyzed Suzuki reaction. This allowed the observation of catalytic intermediates by electrospray ionization mass spectrometry through protonation of nitrogen in the substrate

Even if the species of interest does not have any available basic sites, cationized species are often observed in the form of cationization of free ligand $[L + Na]^+$, or solvated cation clusters $[Na + nH_2O]^+$.

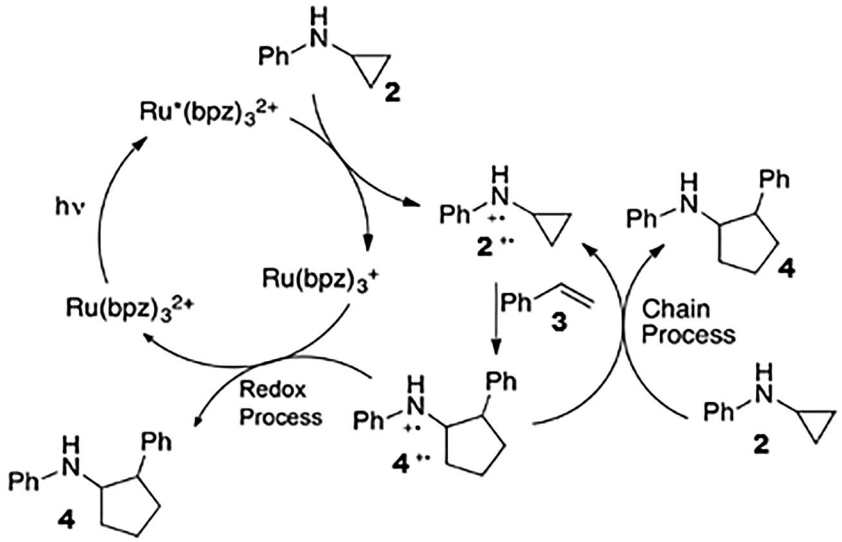
3.2 | Odd-electron ions

3.2.1 | Inherently charged radical cations

Stable or metastable radical cations that exist in solution may be observed by

ESI-MS. This can be especially useful in identifying short-lived key reaction intermediates in metal-catalyzed reactions. A recent example involves the detection of amine radical cations in the ruthenium-catalyzed light-mediated annulation shown below (Scheme 1).[24]

Both radical cation intermediates were observed along with the ruthenium catalyst in both the 1+ and 2+ states. Figure 10 shows the concurrent appearance of radical cation $\mathbf{2}^{+\bullet}$ (inset, *m/z* 133) and



SCHEME 1 Proposed mechanism for the [3 + 2] annulation reaction of N-cyclopropylaniline **2** and styrene **3** catalyzed by Ru (II)$(bpz)_3(PF_6)_2$. Bpz = 2,2′-bypyrazine. Adapted with permission from the study of Cai et al[24]

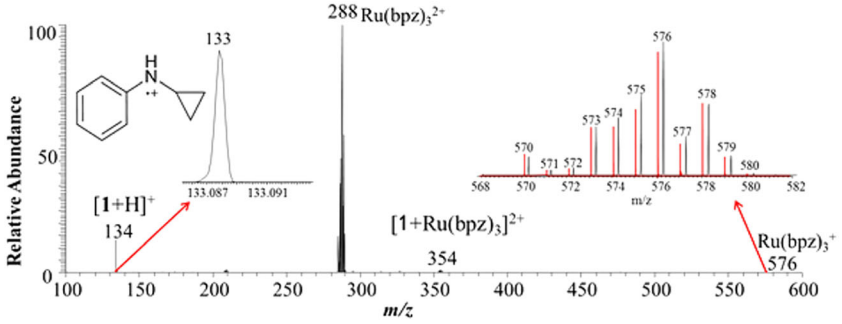


FIGURE 10 ESI-MS spectrum of Ru (II) $(bpz)_3(PF_6)_2$ and N-cyclopropylaniline acquired with light irradiation of the sample. Adapted with permission from study of Cai et al[24] [Colour figure can be viewed at wileyonlinelibrary.com]

Ru $(bpz)_3^+$ (inset, *m/z* 576) when the reaction solution is irradiated with visible light providing strong evidence for the photo-oxidation of cyclopropylaniline by photoexcited Ru (II)*$(bpz)_3^{2+}$.

3.2.2 | ESI-oxidized or ESI-reduced metal centers

In most cases, the ESI process does not produce new ions. Instead, ions that are present in solution are separated from their counterions and transferred into the gas phase. However, in some cases, ESI can act as a true ionization method. In the positive ion mode, electron-rich metal centers like metalloporphyrins, ferrocines, or zero-valent metal complexes, may be oxidized by the ESI process to create $[M^{\bullet}]^+$. In an analogous fashion, electron-poor metal complexes may be reduced by the ESI process in the negative ion mode to $[M^{\bullet}]^-$.This occurs because ESI is an electrochemical process: in the positive ion mode, something must be oxidized within the spray capillary to create excess positive ions for analysis. Then, to complete the electrolytic cell, ions are reduced when they impact a surface within the MS (eg, the spray baffle, a focusing lens, one of the quadrupoles, or the detector). Most often iron from a stainless steel ESI capillary or solvent from the sample is sacrificially oxidized to provide the required current; however, if an easily oxidizable metal complex exists in the sample, it may also be oxidized. For example, in the positive ion mode Pd(0) can lose an electron and form the corresponding Pd(I) complex.

By the same mechanism, easily reduced ions like Ag^+, which are analyzed in the negative ion mode, may have abnormally low signal intensities because of reduction of Ag^+ to Ag(0) metal within the ESI capillary.

In cases like these, the charge state of the ion in solution (before ESI) is ambiguous. If information about the charge state is required and it is desirable to avoid electrochemical oxidation or reduction, the sample may be doped with a more easily oxidized or reduced additive or the sample may be run in the opposite ion mode.

3.3 | Contaminant ions

It is likely that some of the signals observed in the mass spectrum are not related to the compound of interest. Some species are known to linger in mass spectrometers or in shared tubing. The best way to quickly dismiss such peaks is to always run a solvent blank on the MS before sample analysis. Some of the most common types of contaminants are given in Table 1 below with examples.

TABLE 1 Possible contaminants in ESI mass spectra of organometallic or coordination compounds

Compound	Ion	*m/z*
Metal ions		
Lithium	Li^+	7.01600
Sodium	Na^+	22.98977
Potassium	K^+	38.96371
Copper	Cu^+	62.92960 62.92779
Silver	Ag^+	106.90509 108.90476
Solvents		
Methanol	$[MeOH + H]^+$	33.03404
Acetonitrile	$[MeCN + H]^+$	42.03437
Dimethylformamide	$[Me_2NCHO + H]^+$	73.05276
DMSO	$[Me_2SO + H]^+$	79.02176
Triethylamine	$[Et_3N + H]^+$	102.12827
Anions		
Acetate	$[CH_3CO_2]^-$	59.01330
Sulfate	$[SO_4]^{2-}$	47.97641
Tetrafluoroborate	$[BF_4]^-$	87.00292
Iodide	I^- $[I_3]^-$	126.90447 380.71341
Hexafluorophosphate	$[PF_6]^-$	144.96418
Fluorinated tetraphenyl borates (BAr^F)	$[B\{C_6H_3(CF_3)_2\}_4]^-$ $[B(C_6F_5)_4]^-$	863.06488 678.97737
Cations		
Ammonium	NH_4^+	18.03437
Tetrabutylammonium	$[Bu_4N]^+$	242.28478
Triphenylphosphine oxide	$[Ph_3POH]^+$	279.09388
Phosphonium ions Ammonium ions	$[R_4P]^+$ $[R_4N]^+$	Various

Abbreviation: ESI, electrospray ionization.

The listed species can be observed on their own (if they bear a charge and have a mass-to-charge ratio greater than the low mass cut-off of the instrument) or as clusters or adducts. For example, triphenylphosphine oxide can form clusters with metal ions,

$[(OPR_3)_{1-4} + Na]^+$; iodide may be observed as the more surface active I_3^-, and solvent adducts of metal ions are commonplace.

Contaminants that are problematic to other techniques are not necessarily significant in ESI-MS. For example, silicone grease has strong signals in ^1H NMR but is largely invisible to ESI-MS because it is not appreciably basic (a notable exception, the strongly Lewis acidic dimethylaluminum cation, $[Me_2Al]^+$, coordinates strongly to silicone grease).[25,26]

It is important to remember that the ESI signal intensity of an ion does not necessarily depend linearly on that ion's concentration in solution. For example, ions with a high surface activity in solution will be over represented in the resulting mass spectrum. Thus, a contaminant (or indeed any ion in solution) with a high ESI activity can give major signals in a mass spectrum even if they are present in only trace quantities.

4 | ASSIGNMENT METHODOLOGY

Below are the key steps to take when assigning peaks in a new system:

4.1 | Before analysis

1. Determine the *m/z* value of any expected signal. Also, write a list of every chemical species contained in your sample and its nominal molecular weight and charge. Do not forget solvents and reagents that were used in an earlier synthetic step. This information will help you to quickly identify any obvious important signals or adducts thereof during analysis.
2. Have on hand a complete list of possible contaminants from sample handling.[27] MS is a very sensitive technique and can pick up trace contaminants. Be sure to consider the material of your storage container. For example, if you store you sample in glass, Na^+ ions from the glass may leach into your sample. If you store your sample in plastic, phthalates can be observed.
3. Prepare dry and oxygen-free solvents for reactive compounds. Normal solvent purification methods work well in most cases,[28] but the additional precaution of leaving solvents over activated molecular sieves for several days prior to use is highly recommended for particularly reactive compounds.[29] Normal Schlenk and glovebox handling methods are appropriate. Reactive samples are best introduced to the instrument via gas-tight syringe or from a Schlenk flask using the pressurized sample infusion method.[30,31]
4. Samples need to be diluted to concentrations suitable for MS analysis prior to analysis to avoid saturation, although of course avoiding decomposition is also important. The tension between saturation (low concentrations desirable) and decomposition (high concentrations desirable) is ever present, but erring on the side of starting at low concentration (micromolar or lower) and only increasing it when decomposition is problematic is the best practice.
5. Calibrate. A well-calibrated instrument makes the task of unknown assignment considerably easier and high mass accuracy, and resolution can even provide an empirical solution to the elemental composition of an ion.

4.2 | During analysis

1. Collect a blank spectrum of pure solvent before introducing your sample solution into the instrument. This will allow you to rule out any contaminants from previous samples or from the solvent.
2. Collect a full MS spectrum at a number of different spray voltages/temperatures and desolvation and sample flowrates. Look for any major changes in the spectrum (eg, a new major peak or peaks or significant loss in signal). If there are no significant changes you can move on using only one set of ESI parameters. If you do see significant changes stick to using the more mild ESI conditions as this should avoid most in-source fragmentation, oxidation, or reduction, but be aware that mild conditions may promote adduct or cluster formation or incomplete desolvation.
3. Check for the most obvious *m/z* ratios that would correspond to your ion(s) of interest. Collect accurate mass measurements on these peaks and perform MS/MS experiments on each. An MS/MS experiment that includes the full isotope pattern of the peak of interest is useful to identify which product peaks still contain a given metal. However, to determine the exact difference in mass between two fragments, set an isolation window width that includes only the most abundant peak within an isotope pattern and use that for the MS/MS experiment. Use a collision energy that reduces the precursor ion intensity to 10% to 20% of the total ion current.
4. Make a note of all major signals in the spectrum and perform MS/MS experiments on each following the same guidelines as above.
5. Identify any minor peaks in the spectrum that have an isotope pattern consistent with your ions of interest and perform MS/MS experiments on each of these signals as well.
6. Collect a final full MS scan to check that the overall spectrum has not changed significantly over the course of your experiments. If it has, you may have problems with spray instability or ongoing reactions in your solution.

4.3 | Spectrum assignment

At this point, you should have a full MS spectrum and one MS/MS spectrum for each major, or otherwise interesting, peak.

1. Check for obvious matches based on the molecular weights and isotope patterns calculated using a molecular formula finder (eg, *ChemCalc*[9] or proprietary MS software). This may be the only step you need if the sample behaves simply. If not, continue.

2. If your compound of interest contains a metal with a distinctive isotope pattern, focus only on signals with that underlying pattern. Start with the highest intensity signal. Based on the distance between peaks in the isotope pattern, determine if the signal is from a singly or doubly charged ion (even if the metal of interest is monoisotopic, there will be a minor isotope pattern because of the presence of ^{12}C and ^{13}C for organometallic ions). Look at the MS/MS spectrum for that signal, and use the fragmentation pattern at moderate collision energy to identify any obvious ligands or molecular fragments that must exist in the complex. Add up the mass of the metal atoms (check the isotope pattern to determine if there is one or more metal atom present) plus the mass of any known fragments and subtract this value from the *m/z* value of the peak (assuming a singly charged signal). Try to assign the leftover mass based on other ligands, solvents, or contaminants that may be in the sample. Again, use a molecular formula finder; do not rely on nominal mass. For any match, remember to check that the oxidation state and coordination number of the metal center are reasonable, the overall charge of the ion is correct, and the experimental isotope pattern matches the calculated pattern.
3. Repeat step 2 for any signals of interest. Note that once you identify one signal, other signals may be related by ligand loss, ligand substitution, or adduct formation. Checking the distance between different signals can identify such relatives and simplify analysis.
4. If possible, collect MS/MS data on known, pure samples, and compare with the MS/MS data collected from your sample to further support peak assignments. Be aware that the MS/MS process can sometimes cause isomerization in complexes before fragmentation, so to unambiguously distinguish between isomers, matching fragmentation patterns are not enough. Density Functional Theory (DFT) calculations can help here. See the study of Vikse et al[32] for an example.

If key signals remain unassigned,

1. Check the full MS for repeating patterns. These can be a sign of cluster formation (eg, Na_2I^+, $Na_3I_2^+$, $Na_4I_3^+$, and so on) or the presence of oligomers (eg, polyethyleneglycol). If you can assign one of these peaks, you can likely assign all others in the series.
2. Develop a spreadsheet. For complex spectra with many peaks and repeating patterns it may be useful to create an excel spreadsheet to calculate the *m/z* ratio of all likely permutations that may appear in the spectrum. The MS assignment of methylaluminoxane is a good example of this method[33]; in this case, the masses of all ions with the formula $[(MeAlO)_n(Me_3Al)_mMe]^-$ (n = 0–30, m = 0–20) were generated in a matrix in order to assign the observed species.
3. Run some more samples under different conditions. Change solvents and check for changes in peak position. If cationization seems to be happening, deliberately add an excess of one of the additives (eg, Na^+).
4. If possible, run a related complex. For example, a complex with a different organyl substituent or an isotopically labelled complex. Compare this spectrum with your original spectrum, and look for peaks that shift by the appropriate amount.
5. Reconsider possible contaminants in your procedure and within the mass spectrometer itself. For example, the rubber used in septa contain antioxidants that are generally substituted phenols, and these often provide a strong negative ion signal.

If you do not see anything you are looking for and no peaks are easily assigned, there may have been a problem during analysis. Go back, and test the operation of the MS using a calibration solution; try varying the concentration of your sample; use a freshly prepared sample; widely adjust the MS source conditions; check that the inlet line is not plugged; check that there is no arcing within the source, and that the spray current is stable and non-zero.

5 | CASE STUDIES

Below, the first case study demonstrates the assignment of a simple inorganic sample with a complicated spectrum. It provides a particularly good example of how simple systems can produce complex spectra. The second case study demonstrates the assignment of various species observed in real-time from a solution-phase metal-catalyzed reaction.

5.1 | A pure complex with a complicated spectrum—Lanthanum trichloride

Data for this case study were taken with permission from the study of McQuinn et al[34] and discuss the analysis of a pure, 5-mM aqueous sample of lanthanum chloride.

5.1.1 | Before analysis

Determine the *m/z* ratio of the expected ions. In this case, one might expect La^{3+} (*m/z* 46), $LaCl^{2+}$ (*m/z* 87/88), or $LaCl_2^+$(*m/z* 209/211/213). Water adducts $[La(H_2O)_n]^{3+}$ also seem likely.

5.1.2 | MS analysis

This is a case where the source conditions in the mass spectrometer dramatically affect the resulting spectrum. The conditions in the spectrum presented here (Figure 11) involved a relatively high solution flowrate, cool source, and desolvation gas temperatures.

5.1.3 | Spectrum analysis

While the sample solution ($LaCl_3$ in water) is simple, the resulting mass spectrum is not (Figure 11). The simple ions predicted originally are clearly not the major peaks, and the observed pattern of equally spaced peaks indicates a significant amount of cluster formation.

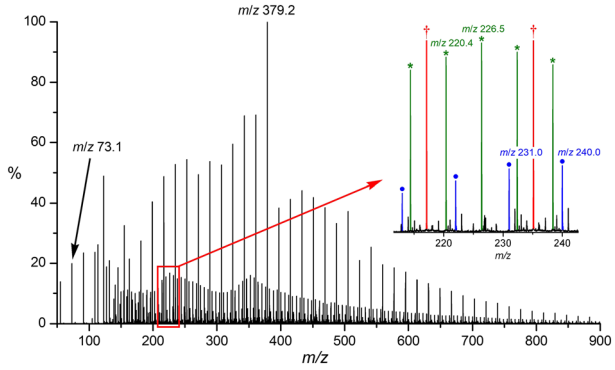


FIGURE 11 Positive ion electrospray ionization mass spectrum of an aqueous solution of $LaCl_3$ before peak assignment. Adapted from the study of McQuinn et al[34] [Colour figure can be viewed at wileyonlinelibrary.com]

The first step is to identify a set of peaks that all belong to the same series. This is done by finding peaks that are all separated by the same *m/z* ratio. In this case, there are three patterns as show in the inset in Figure 11.

The dominant pattern, shown in red (†), has peaks separated by increments of *m/z* 18. This is consistent with a singly charged species containing a varying number of water molecules. From the *m/z* ratio of some of the smaller clusters in this series, it is clear that the series is due to protonated water clusters. For example, *m/z* 73.1 is $[H(H_2O)_4]^+$. The spectrum is dominated by these water clusters and in particular the most abundant cluster is $[H(H_2O)_{21}]^+$ (*m/z* 379.2).

The repeating pattern shown in green (*) is separated by increments of *m/z* 6. This is consistent with a triply charged species that contains varying numbers of water molecules (the mass of water is 18 Da, divided by a charge of 3+ will give peaks separated by *m/z* 6). For example, the peaks at *m/z* 220.4 and *m/z* 226.5 must correspond to $[X + (H_2O)_n]^{3+}$ and $[X + (H_2O)_{n+1}]^{3+}$. X must have a charge of 3+ and is therefore most likely La^{3+}. Thus, *m/z* 220.4 corresponds to $[La(H_2O)_{29}]^{3+}$; *m/z* 226.5 corresponds to $[La(H_2O)_{30}]^{3+}$, and the green series of peaks in general corresponds to $[La(H_2O)_n]^{3+}$.

The blue (•) series has peaks in increments of *m/z* 9, consistent with a doubly charged ion containing varying numbers of water molecules. The masses of the blue series could be attributed to $[LaCl(H_2O)_n]^{2+}$ or $[La(OH)(H_2O)_{n-1}]^{2+}$ since both ^{35}Cl and $(OH + H_2O)$ have a nominal mass of 35 Da. The lack of a chlorine isotope pattern rules out $[LaCl(H_2O)_n]^{2+}$.

MS/MS studies can also be performed on individual peaks to verify their composition and the reader is referred to the original manuscript for a detailed description of these experiments.

5.2 | A solution-phase reaction mixture—Rhodium-catalyzed hydroacylation

Data for this case study were taken with permission from the study of Theron et al[35] and follow the hydroacylation of aldehyde 2-(methylthio)benzaldehyde and alkyne 1-octyne to a ketone (Scheme 2).

5.2.1 | Before analysis

A list is generated of all components of the reaction mixture including potential products and their molecular weight and charge (Table 2).

Based on the components of the reaction mixture, the most obvious potential signal is the cationic catalyst (*m/z* 462). Complexes of the catalyst with various ligands, substrate, or product are also likely. Instead of calculating all possible permutations in advance, Table 2 will be used to solve for major signals once MS data are collected.

TABLE 2 Components of the reaction mixture

Component	Mass (Da)
Reactant aldehyde (C_8H_8OS)	152.02959
Reactant alkyne (C_8H_{14})	110.10955
Product ketone ($C_{16}H_{22}OS$)	262.13914
Catalyst $[C_{19}H_{36}FNP_2Rh]^+$	462.13621
Rh^+	102.90550
Phosphine ligand ($C_{13}H_{31}NP_2$)	263.19317
Fluorobenzene (C_6H_5F)	96.03753
Solvent (1,2-$Cl_2C_2H_4$)	97.96901

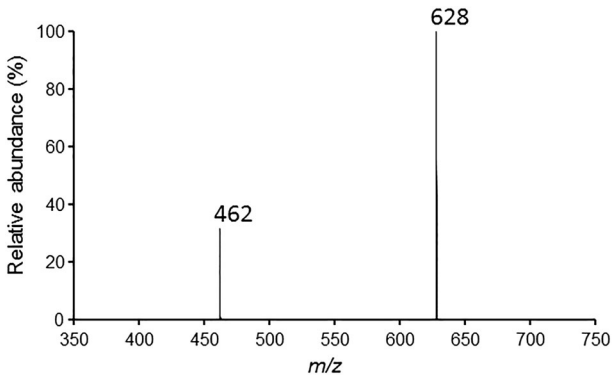
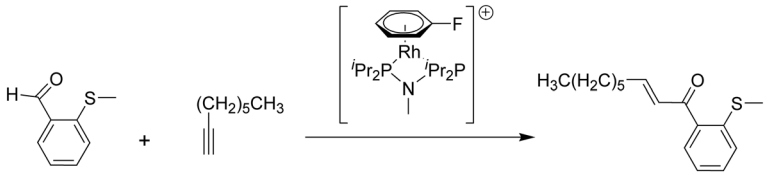


FIGURE 12 Full mass spectrum of the reaction mixture after a reaction time of 2 minutes. Adapted from the study of Theron et al[35]



SCHEME 2 Overall reaction scheme. Adapted from the study of Theron et al[35]

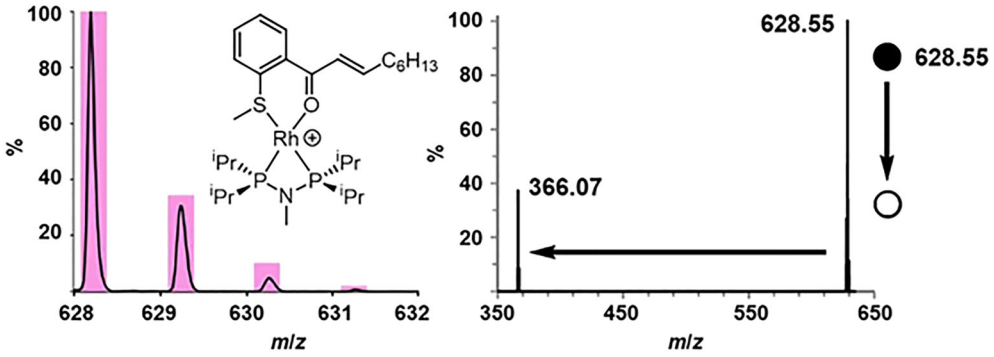
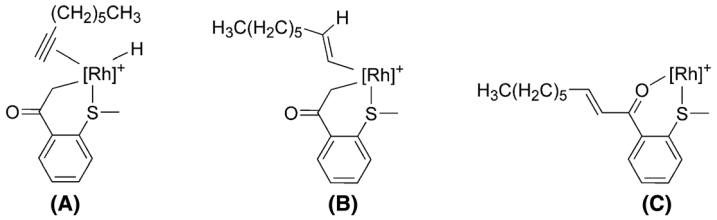


FIGURE 13 Isotope pattern (left) and MS/MS spectrum (right) of the signal at *m/z* 628. Adapted from the study of Theron et al[35] [Colour figure can be viewed at wileyonlinelibrary.com]



SCHEME 3 Possible structures for *m/z* 628

Rhodium has only one naturally occurring isotope, and none of the other main reaction ingredients have significant isotope patterns; therefore, the isotope patterns for signals of interest should consist of one major peak with small subsequent peaks 1 *m/z* apart for a singly charged ion (because of contributions from carbon-13).

5.2.2 | MS analysis

Full MS spectra of the reaction mixture were recorded over time. A spectrum is shown below after a reaction time of 2 minutes (Figure 12). MS/MS spectra for the two dominant peaks (and some minor peaks) were also recorded.

5.2.3 | Spectrum assignment

The major peaks in the spectrum are at *m/z* 628 and *m/z* 462. The signal at *m/z* 462 is easily assigned to the cationic catalyst. After zooming in on the peak at 628 in the full spectrum (Figure 13 left), the spacing of the peaks at m/z 628, 629, and 630 suggest a singly charged ion. Next, the MS/MS spectrum is examined (Figure 13, right). The dot system for labelling sequential MS/MS experiments can be seen on the right of the spectrum. A sequence of dots and arrows depicts the experimental process that occurred in order to generate the displayed spectrum. A closed dot and associated *m/z* value represent a single ionic species that was isolated in the collision chamber. The vertical arrow represents the fragmentation process (collision induced dissociation unless otherwise noted) and an open dot represents collection of a full product ion spectrum.[36]

The peak at *m/z* 628.55 undergoes a neutral loss of 262.48 Da and leaves an ion at *m/z* 366.07. 262.48 Da is consistent with the product ketone, and *m/z* 366.07 is consistent with $[Rh(L)]^+$ where L is the phosphine ligand in Table 2. A tentative assignment of $[Rh(L)(prod)]^+$ is proposed for the signal at *m/z* 628. The isotope pattern for this signal is consistent with the assignment (Figure 13, left); the charge is correct and the metal oxidation state and coordination number is chemically reasonable.

The assignment seems good; however, there are other options that also have an *m/z* value of 628 as shown in Scheme 3.

To distinguish between these possibilities, the product ketone was independently mixed with the precatalyst and analyzed by MS/MS. The MS/MS spectrum of *m/z* 628 of the premade complex matched the MS/MS spectrum obtained under reaction conditions suggesting that $[Rh(L)(prod)]^+$ was in fact the observed species. Further evidence comes from supporting experiments, and a full discussion is provided in the original manuscript.

One of the main benefits of using ESI-MS to study reaction mixtures is its ability to detect reaction components over 3 to 5 orders of magnitude. This allows observation of the main reaction components (substrates and products) while at the same time revealing low concentration intermediates or catalytic species. In this case study, a variety of other much less intense signals were observed in the full spectrum upon magnification. The reader is referred to the original manuscript for a detailed description of the assignment of these other minor but catalytically important signals.

6 | CONCLUSIONS

The ESI mass spectra of organometallic species or coordination compounds can be mystifying at first glance, but a clear understanding of how these complexes behave during ESI-MS and a methodical plan

of attack for spectrum acquisition and assignment can simplify characterization. When characterization is straightforward, ESI-MS becomes a truly powerful technique to tackle characterization problems in organometallic and coordination chemistry.

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36. An example: consider an MS^3 experiment in which an ion of mass 400 Da was isolated, subjected to collision induced dissociation (CID) and one of the product ions (200 Da) was further isolated and subjected to CID. The full product spectrum resulting from CID of the 200 Da ion is displayed. The dot notation in this case would read: ● *m/z* 400 ⟶ ● *m/z* 200 ⟶ ○. Note: it is convention to display the dot notation vertically next to the spectrum as in Figure 13 (right) and it is shown horizontally here only for space considerations.

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