

The Analysis of Organometallic Compounds Using Electrospray Ionization Mass Spectrometry: Part I

Highlights: Electrospray mass spectrometry (ESI-MS) is useful for confirming the molecular weight of organometallic compounds. ESI, when used in conjunction with "Up-Front" Collision Induced Dissociation can also confirm an expected structure of a compound.

This study demonstrates the analysis of synthetic compounds using ESI on a Platform LC detector. Unlike the more routine Fast Atom Bombardment (FAB) ionization for organometallics, ESI requires no matrix to aid the ionization process which means that the background ions relating to chemical noise are much lower in intensity. ESI analysis of organometallics simply requires that a compound be dissolved in a suitable solvent, and then can be introduced directly into the ionization source. ESI is compatible with solvents used in reverse phase chromatography, such as water, methanol and acetonitrile, but it is also possible to use a wider range of solvents, such as dichloromethane and toluene. The last two may be more suitable for organometallic compounds which are either insoluble in other solvents, or require careful choice of solvent to prevent ligand exchange reactions. Conventional ESI can be operated at flows as low as 5μ L/min, such that a 100µl aliquot of a sample solution can be infused for 20 minutes allowing easy optimization and data acquisition. Since ESI is a soft ionization technique which tends to keep analytes intact and provide molecular weight information, it can be used to confirm the molecular weight of synthetic organometallic compounds. However, ESI has an added advantage of allowing fragmentation to be produced when required. By utilizing "In-Source" Collision Induced Dissociation (CID), it may be possible to produce controlled and reproducible fragmentation, giving useful information for the elucidation or confirmation of the structure of the sample.

Experimental

For each sample, a suitable solvent was chosen and a solution was prepared in the concentration range 25-50 ng/µL. The solution was then introduced into the ESI source at a flow rate of 5µL/min using a Harvard Apparatus 22 syringe pump. The ESI source conditions were optimized for the generation of the molecular related ion and data were acquired by accumulating several continuum spectra over a suitable mass range. Subsequent spectra were acquired at higher CID voltages to generate in-source fragmentation.

Sample 1

Formula : C 43 H 30 N 8 RuReCIO 3 .2PF 6 Average molecular weight = 1319.4 Solvent : acetonitrile Concentration : 25ng/µL (note : bipy = 2,2'-bipyridine, C 10 H 8 N 2)

Sample 1 contains ruthenium, rhenium and chlorine atoms so the expected isotope pattern is complex. When using ESI in positive ion mode with a CID voltage of 30V, the compound loses a PF 6 - counter ion to give a singly charged cation with an average mass to charge ratio (m/z) of 1174.5. Continuum spectra for the singly charged molecular ions and the isotope

model^{*} (figure 1) show that the isotope profile for the acquired data closely matches that predicted by the isotope model.

*Isotope Models : As organometallic compounds often contain metals with complex isotope patterns, the expected isotope pattern of the compound can be used to help confirm its structure. The MassLynx software, which controls the Platform LC detector, has an isotope pattern calculator which can model the expected isotope distribution. By entering the expected chemical formula of the compound, a model of the isotopes can be produced in either continuum or centroid format which can then be compared to the data acquired by ESI to confirm the presence of the expected atoms.





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Figure 1 : The calculated and acquired isotope profiles for sample 1

Resolution of Doubly Charged ions : The sample also loses the second PF 6 - counter ion to give intense doubly charged ions with an average mass of 1029.5 and thus an average mass to charge (m/z) ratio of 515.7. Due to having two charges, the resulting spectrum shows isotopes which are separated by only m/z 0.5. The Waters Alliance LC/MS System featuring the Platform LC detector is easily able to resolve doubly charged isotopes as shown in figure 2.

Gaining Structural Information : As stated previously, it is possible to induce some fragmentation in the source in order to gain some structural information about the sample. By increasing the sample cone voltage in the source to a value of 55V the doubly charged ion was completely dissociated to give a number of fragment ions as shown in figure 3. The peaks centered around m/z 362 are due to a doubly charged fragment (charge state determined by the isotope separation) produced by the loss of the two PF 6 - counter ions and rhenium with its associated ligands, [M - 2(PF 6 -) - Re(CO)3 CI]2+ . A further loss of a 2,2'-bipyridine ligand from the ruthenium center gives the intense group of doubly charged ions centered around m/z 284 and loss of the second (bipy) ligand gives a group of ions around m/z 206. The ions around m/z 304.6 are again due to a doubly charged species which has a mass of 609. The odd mass indicates that the fragment contains an odd number of nitrogen atoms and is likely to be due to the cleavage of the compound backbone to lose one nitrogen. There is also a singly charged peak at m/z 157 which can be assigned as protonated 2,2'-bipyridine.





Figure 2 : Doubly charged ion produced by the loss of two counter ions from sample 1



Summary

The data presented show that electrospray is a suitable technique for the analysis of organometallic compounds. Like FAB, electrospray can be used to confirm the molecular weight of a compound, but it has the added advantage of controlled and reproducible fragmentation which can confirm an expected structure or can help with the elucidation of an unknown. The data were acquired on a benchtop mass spectrometer equipped with an electrospray ionization source which offers an advantage in cost while maintaining the required performance. The high performance of this instrument allows the facility to resolve multiply charged ions to help with interpretation of the data.

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