

# Waters Alliance<sup>™</sup> Systems for LC/MS ESI/APCI Applications

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

**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.

The analysis of organometallic compounds by mass spectrometry has traditionally been carried out using Fast Atom bombardment (FAB) as the mode of ionization. The advent of ESI-MS offers an alternative method of analysis with a number of inherent advantages. This study demonstrates the analysis of synthetic compounds using ESI on a Platform LC detector. Unlike FAB ionization, ESI requires no matrix to aid the ionization process which means that the background ions relating to chemical noise are much lower in intensity. All that is required for ESI analysis is a suitable solvent for the compound, and then a solution at the required concentration can be introduced directly into the ionization source. As ESI is an Atmospheric Pressure Ionization (API) technique, it has a further advantage over FAB in that there is no need to insert the sample via a vacuum lock. ESI is well known for use 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 5µL/min, such that a 100µl aliquot of a sample solution can be infused for 20 minutes allowing easy optimization and data acquisition. Several spectra, using different conditions, can be acquired in a short period of time using less than a microgram of sample. 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.

Sample 2 Formula : C 36 H 35 O 2 BrMoP 2 Average molecular weight = 737.5 Solvent : dichloromethane Concentration : approx 50ng/µL



### Experimental

For each sample, a suitable solvent was chosen and a solution was prepared in the concentration range 25-50 ng/ $\mu$ L. The solution was then introduced into the ESI source at a flow rate of 5 $\mu$ L/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.

**Molecular Weight Information:** Sample 2 gives a molecular ion at m/z 738 (figure 4) which matches the expected isotope pattern generated by the software. The base peak of the spectrum at m/z 659 is due to the facile loss of bromine from the complex which occurs even at a low cone voltage of 18V. Indeed, this fragmentation occurs so easily that the intact molecular ion for this complex has not previously been observed using FAB.



#### 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.

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