Low-Temperature Fast Atom Bombardment Mass Spectrometry – Application to the Characterization of Molecular Catalysts

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Aims and Hope......................

Molecular catalysts are delicate..............................

Molecular catalysts inherently are highly reactive species not easily allowing for mass spectrometric characterization by conventional methods. Thus, a method ideally suited for that purpose would enable their examination directly from their solution in aprotic solvents, i.e., from the chemical environment where they have been prepared.

Conventional mass spectrometry............................

Mass spectrometry without prior removal of the solvent or other manipulations that might cause decomposition can in principal be achieved by either electrospray ionization (ESI) or by fast atom bombardment (FAB). In the beginning of this work, only the latter technique was available at our institute and thus, needed adaptation to the above requirements. An often overseen advantage of the FAB method is that it can also handle non-charged analytes – a property missing in case of the highly appraised ESI.

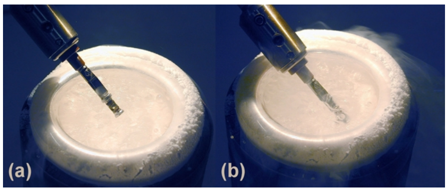
Solvent has to act as FAB matrix..............................

The simple but highly efficient procedure allows to employ almost any solvent as matrix in LT-FAB-MS. The spectrum of the analyte is then obtained during thawing of the frozen solution within the ion source of the mass spectrometer. Consequently, the choice of the matrix is not restricted any longer, neither by volatility nor by unwanted chemical reactions. Instead, the solvent matrix may be tailored to the analyte's requirements [1, 2].

Methodology of LT-FAB-MS..

Freezing the „matrix“...

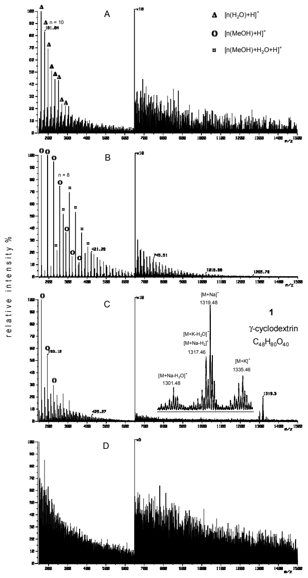
Typical organic solvents are highly volatile under the high vacuum conditions of a mass spectrometer. The way to control their evaporation is to freeze a solution of the analyte directly on the FAB target (a), simply by immersing it into liquid nitrogen for about 30 seconds (b). The target is then rapidly transferred into the vacuum lock.



Instrumental settings...

A Jeol JMS-700 sector instrument was used in the positive-ion FAB mode. Resolution was set to $R = 2000$ by tuning to the m/z 460 ion of 3-NBA. The magnet was scanned over the mass range of interest at a rate of about 8 s per cycle; mass accuracy of 0.05 amu could be obtained. The FAB gun was operated with Xe gas at an emission current of 8 mA and at an acceleration voltage of 6 kV. The analytes were dissolved in the respective solvent to yield 0.5–3.0 mg/mL solutions. 3–4 µL of that solution were deposited on the stainless steel FAB probe tip and frozen.

A peak coming out of the cold................................

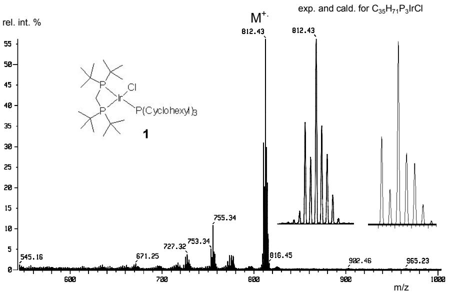


The measurement is conducted while the sample is melting in the ion source. This example shows the measurement of γ-cyclodextrin from solution in methanol. In the beginning, some water and water-methanol cluster ions are observed. The analyte is being detected while the drop is melting. After evaporation of the solvent the signal of the analyte vanishes. The cycle can be repeated by re-dissolving the solid residue.

Reaction Monitoring...............

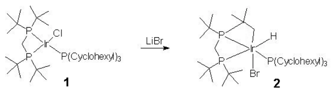
The precursor complex..

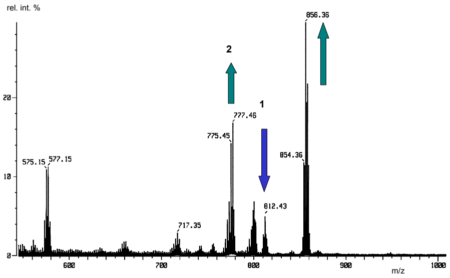
The iridium complex **1** was intended to be a precursor for further reactions. Due to its high reactivity towards water and air it could only be characterized by LT-FAB-MS from toluene, whereas EI, CI and FD did only yield decomposition products. As seen below, **1** yielded an intense molecular ion peak, M$^{+\cdot}$, showing the correct isotopic pattern [3].



The activation of the C-H bond..............................

Selective activation of C–H bonds is rarely observed in saturated alkyl groups. Nevertheless, **1** reacted by C–H insertion of the metal into a ligand bond upon treatment with LiBr in THF. The reaction could be tracked by LT-FAB-MS. A decreasing intensity of the m/z 812 peak was observed while an increase of m/z 856, i.e., M$^{+\cdot}$ of **2**, occured. Furthermore, the changing isotopic pattern yielded clear evidence of the halogen exchange.

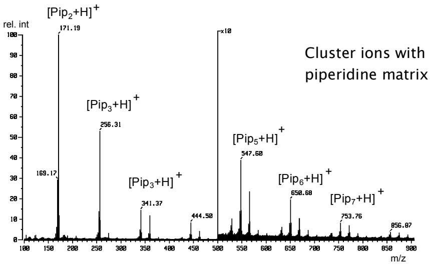




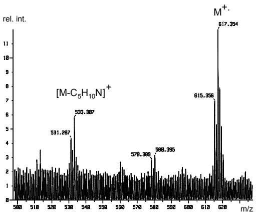
Amine Adducts of Iridium(I)....

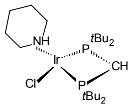
Piperidine, morpholine, diethylamine.......................

Experiments with iridium(I) complexes in presence of piperidine, morpholine, and diethylamine have been conducted by dissolving the precursor complex in the respective amines under inert conditions [4]. At the onset of desorption from the thawing solutions the corresponding [amine$_x$+H]$^+$ and sometimes [amine$_x$+H$_2$O+H]$^+$ cluster ions were observed in LT-FAB mass spectra.



Cluster ions with piperidine matrix.





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After melting of the drop the molecular ion of the iridium amine complex **3** occured.

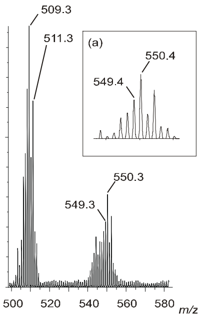
Summary................................

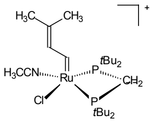
- LT-FAB-MS has been developed and successfully applied to highly reactive molecular catalysts.
- LT-FAB-MS allows for the characterization of ionic and neutral species as well.
- By LT-FAB the analytes can by analyzed directly from solutions in the solvent where they have been prepared.
- Even solvent-coordinated and other weakly bonded species can be desorbed into the gas phase by LT-FAB.
- LT-FAB can overcome restrictions of mutual solubility of analyte and matrix [6,7].
- In some instances even HR-LT-FAB experiments have been performed by use of a dual target FAB probe [6,7].

Solvent Coordination.............

Catalytically active species in olefin metathesis.......

Monomeric solvent-coordinated cationic complexes of the type [(η^2-dtbpm)ClRu=C-HR(solv)]$^+$, formed by dissociation of dinuclear units, presumably represent the catalytically active species in olefin metathesis. The isolation and characterization by NMR and MS of such a species, [(η^2-^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)ClRu=CH–CH=C(CH$_3$)$_2$(CH$_3$CN)]$^+$ (**4**), could be achieved [5].





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The inset shows the isotopic pattern calculated for the cationic complex [C$_{24}$H$_{49}$ClNP$_2$Ru]$^+$ (**4**). The cation **4** is observed at m/z 550, the solvent-free catalyst at m/z 509.

The acetonitrile ligand could only be detected by positive-ion LT-FAB-MS from CH$_2$Cl$_2$ solution containing stoichiometric amounts of CH$_3$CN. LT-FAB from pure acetonitrile as well as ESI under such conditions failed. Obviously, the low temperature employed is also advantageous for the detection of solvent-coordinated species.

Further Reading..................

[1] J. H. Gross, *Rapid. Commun. Mass Spectrom.* **12**, 1833 (1998).

[2] C.-H. Wang, M.-W. Huang, C.-Y. Lee, H.-L. Chei, J.-P. Huang, J. Shiea, *J. Am. Soc. Mass Spectrom.* **9**, 1168 (1998).

[3] V. R. Sporys, Doctoral Thesis, University of Heidelberg, 1999, pp. 113-115.

[4] P. Schöcker, Diploma Thesis, University of Heidelberg, 1998, pp. 21-24.

[5] P. Hofmann, M. A. O. Volland, S. M. Hansen, F. Eisenträger, J. H. Gross, K. Stengel, *J. Organomet. Chem.* **606**, 88-92 (2000).

[6] S. Giesa, J. H. Gross, W. E. Hull, S. Lebedkin, A. Gromov, W. Krätschmer, R. Gleiter, *Chem. Commun.* 465 (1999).

[7] Giesa, J. H. Gross, W. Krätschmer, *Rapid Commun. Mass Spectrom.* **13**, 815 (1999).

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