

## Direct analysis of catalysts immobilised in ionic liquids using electrospray ionisation ion trap mass spectrometry

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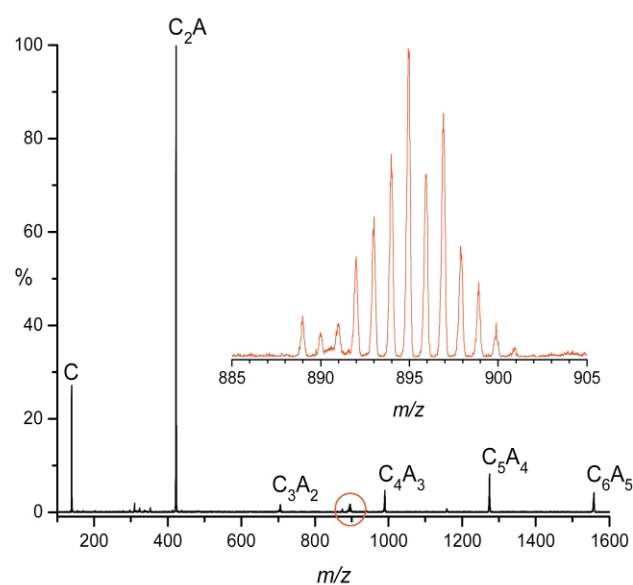
Catalysts immobilised in ionic liquids have been analysed using electrospray ionisation ion trap mass spectrometry, which allows identification of the catalyst without contamination from the ionic liquid; additionally, a new ionic liquid containing the Monsanto catalyst as the anionic component,  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ , has been characterised using the same method.

Ionic liquids are currently undergoing extensive study as media for catalyst immobilisation in multiphasic catalysis.<sup>1</sup> A wide range of reactions are under investigation and notable examples include hydrogenation,<sup>2</sup> hydroformylation<sup>3</sup> and C–C coupling<sup>4</sup> reactions. Although a wide range of catalysts have been examined in many different reactions very little information concerning transformations of the catalyst is available, in part because *in situ*  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis necessitates deuterated ionic liquids which are extremely expensive. Furthermore, extraction of the catalyst after reaction is often not possible (at least for catalysts that do not easily leach) which prevents post-reaction analysis by spectroscopic techniques. It has become apparent that the optimum catalysts for operation in ionic liquids are those that are themselves ionic, with the charge either located on the metal centre or on a ligand.<sup>2e</sup> Such species lend themselves to electrospray ionisation mass spectrometric (ESI-MS) analysis,<sup>5</sup> but since the solvent is also ionic and present in vast excess, aggregation of the solvent ions, swamping of the compound of interest and saturation of the detector, makes analysis problematic. In this paper we show how ESI-MS can be combined with quadrupole ion trap methods to analyse catalysts dissolved in ionic liquids.

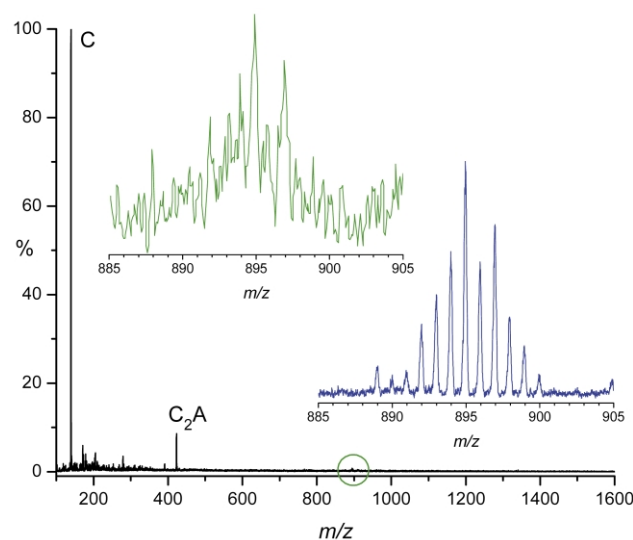
The ionic liquid active catalysts  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-triphos})\text{Cl}][\text{PF}_6]$  (**1**),  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})\text{Cl}][\text{BF}_4]$  (**2**),  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{pta})\text{Cl}_2]$  (**3**) and  $[\text{PPN}][\text{HOS}_3\text{W}(\text{CO})_{14}]$  (**4**) were analysed in liquid  $[\text{C}_4\text{mim}][\text{PF}_6]$  ( $\text{C}_4\text{mim}$  = the 1-butyl-3-methylimidazolium cation).<sup>6</sup> The concentration of ions in the pure ionic liquids is typically 3–4 mol L<sup>-1</sup>, vastly in excess of that required for ESI-MS, which routinely characterises analytes at picomolar levels or less, *i.e.*, nine orders of magnitude less concentrated. As such, it is crucial that the ionic liquid is diluted by a molecular solvent, but this necessarily lowers the concentration of the catalyst by a corresponding amount. A balance has to be struck such that the catalyst is present at detectable levels but the ionic liquid is diluted sufficiently that the problems previously described are not fatal to the experiment.

The ionic liquid  $[\text{C}_4\text{mim}][\text{PF}_6]$ , containing the catalyst  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-triphos})\text{Cl}]^+$  (**1**)<sup>7</sup> was diluted in methanol to concentrations of 10, 1, 0.1, 0.01 and 0.001 mmol L<sup>-1</sup>. The corresponding concentration of catalyst was 4 orders of magnitude lower in each case, *i.e.* 1000, 100, 10, 1 and 0.1 pmol L<sup>-1</sup>. The spectrum collected at the highest concentration is depicted in Fig. 1. Despite the overwhelming dominance of ionic liquid species (the cation itself and aggregates of the cation with the anion), the presence of the catalyst can easily be detected.

Furthermore, it is clear that even the lowest concentration analysed (Fig. 2) is perfectly sufficient to detect the catalyst. Any signals suspected as possible species of interest (green inset) may be checked by using a slow scan across the specific area of interest.



**Fig. 1** The positive ion ESI mass spectrum of **1** in the ionic liquid  $[\text{C}_4\text{mim}][\text{PF}_6]$ , diluted in methanol to a concentration of 1000 pmol L<sup>-1</sup> in **1**. 'C' corresponds to the cation, 'A' to the anion, so 'C<sub>5</sub>A<sub>4</sub>' is the aggregated ion  $\{[\text{C}_4\text{mim}]_5[\text{PF}_6]_4\}^+$ . The circled peak and enlarged isotope pattern correspond to **1**.



**Fig. 2** The positive ion ESI mass spectrum of **1** in the ionic liquid  $[\text{C}_4\text{mim}][\text{PF}_6]$ , diluted in methanol to a concentration of 0.1 pmol L<sup>-1</sup> in **1**. The green isotope pattern of **1** is the raw data from the full scan; the blue isotope pattern is a slow scan of the 885–905 *m/z* region.

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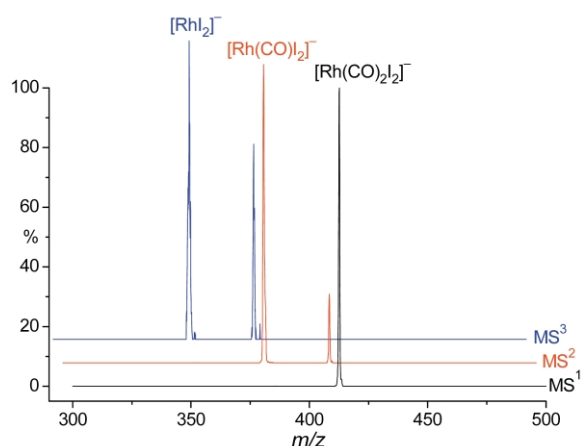
These two spectra demonstrate that the range of concentrations that can be analysed is wide. While ionic liquid aggregates of the form  $\{[C_4mim]_{n+1}[PF_6]_n\}^+$  extend to greater masses at higher concentrations, the catalyst remains easily identifiable, assisted by the characteristic isotope pattern. There is a tradeoff at low concentrations between signal-to-noise ratio and reduced interference from ionic liquid aggregates. Similar observations were made for all the other cationic and anionic catalysts examined, including the high molecular weight anion  $[HOS_3W(CO)_{14}]^-$ . The ionic liquids  $[C_4mim][BF_4]$ ,  $[C_6mim][BF_4]$  and  $[C_8mim][BF_4]$  were examined with essentially analogous results. Overlap of aggregates with signals of interest is extremely unlikely to occur in different ionic liquids, so changing the counterion is a straightforward solution to suspected interference.

The neutral compound  $[Ru(\eta^6-p\text{-cymene})(pta)Cl_2]$ , shown to be a pre-catalyst in hydrogenation reactions,<sup>8</sup> could also be analysed in the presence of a large excess of ionic liquid. The ion observed was  $[M + C_4mim]^+$ , the neutral catalyst having associated itself with the ionic liquid cation. This phenomenon relies on the high basicity of the pta ligand,<sup>9</sup> resulting in an ionisation efficiency sufficiently high enough that the nominally neutral complex can be observed in the mass spectrum.

An ionic liquid composed of the Monsanto catalyst anion  $[Rh(CO)_2I_2]^-$  combined with the  $[C_4mim]$  cation was prepared in the reaction between  $[Rh_2(CO)_4I_2]$  and  $[C_4mim]I$  in methanol<sup>10</sup> using a modified route to that used to prepare a cobalt-carbonyl ionic liquid.<sup>11</sup> The advantage of this new synthesis is that no byproducts are formed which contaminate the resulting ionic liquid. Analysis of the liquid, dissolved in methanol, produced the expected spectra for the anion, 413  $m/z$  and the cation, 139  $m/z$ . The ion trap has the facility for fragmenting the parent ion to obtain structural information, and this process is depicted in Fig. 3. The  $MS^1$  spectrum shows selection of the  $[Rh(CO)_2I_2]^-$  parent ion at 413  $m/z$ . The  $MS^2$  spectrum is the daughter ion spectrum, after colliding the parent with He in the ion trap. The major product of this process is  $[Rh(CO)I_2]^-$  at 385  $m/z$ , which may be further fragmented in the  $MS^3$  step to generate  $[RhI_2]^-$  at 357  $m/z$ . No further fragmentation of this species was possible, even at high collision energies.

Dilution of the  $[C_4mim][Rh(CO)_2I_2]$  ionic liquid to a catalytic amount in  $[C_4mim][PF_6]$  followed by ESI-MS analysis according to the method described above affords spectra of sufficient quality to allow *in situ* determination of reaction intermediates.

In summary, recent advances in mass spectrometric instrumentation mean that the detection limits are extremely low, which allows catalysts to be easily characterised in ionic liquids.



**Fig. 3** Negative ion ESI- $MS^n$  spectra of a dilute methanol solution of the ionic liquid  $[C_4mim][Rh(CO)_2I_2]$ .  $MS^1$  selected the parent ion at 413  $m/z$ ;  $MS^2$  and  $MS^3$  show second and third generation daughter ions at 385 and 357  $m/z$ . No further fragmentation of the complex was possible.

Interferences from the relatively high concentrations of the ionic liquid are essentially inconsequential. Ionic liquids have previously been used as matrices in MALDI mass spectrometry. The results, while promising, were most successful for high molecular weight biological compounds.<sup>12</sup> We attempted to analyse metal complexes using MALDI with the ionic liquid as the matrix, but with only limited success, possibly due in part to the general problems associated with the analysis of metal complexes by this technique. The electrospray method described herein is considerably easier to conduct from an experimental standpoint and the results are far more reliable. However, some catalysts are likely to react with MeOH and alternative dilution solvents may be required.

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- Synthesis of  $[C_4mim][Rh(CO)_2I_2]$ :  $[Rh_2(CO)_4I_2]$  (0.24 g, 0.42 mmol) in methanol (6 ml) was treated with a solution of  $[C_4mim]I$  (0.224 g, 0.84 mmol) in methanol (5 ml) with stirring for 24 h. The methanol was removed from the resulting deep brown-red solution under high vacuum over a period of 24 h yielding a brown air sensitive liquid. Spectroscopic data: IR ( $\nu_{CO}$ ,  $CH_2Cl_2$ ) 2062, 1990  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $CDCl_3$ ): 1.0292(s, 3H,  $NCH_2CH_2CH_2CH_3$ ), 1.4684(s, 2H,  $NCH_2CH_2CH_2$ ), 1.9664(s, 2H,  $NCH_2CH_2$ ), 4.0175(s, 3H,  $NCH_3$ ), 4.7638(s, 2H,  $NCH_2$ ), 7.6106(m, 1H,  $HC=CH$ ), 7.6890(m, 1H,  $HC=CH$ ), 9.0570(s, 1H,  $NC(H)N$ ).
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