On the catalytic activity of cluster anions in styrene hydrogenation: considerable enhancements in ionic liquids compared to molecular solvents

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Abstract

Many low oxidation state transition metal (carbonyl) clusters are salts and are highly soluble in ionic liquids. Since many are also effective catalysts/precatalysts for hydrogenation reactions, we have conducted a catalytic study of these compounds in ionic liquids and found that the activity of certain clusters to hydrogenate alkene substrates, when immobilised in ionic liquids, is up to 3.6-fold faster than that observed in organic solvents. Using high-pressure NMR it has been possible to trace the improvements in activity to the increased stability of the cluster species in the ionic liquid. The ionic liquid also gives rise to higher regioselectivity in the hydrogenation of cyclic dienes to monoenes compared to that observed in organic solvents.

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1. Introduction

In recent years, one of the major directions in molecular catalysis has been to find ways to support catalysts so that their separation from reaction products is facile, like in heterogeneous catalysis. Many ingenious protocols have been developed including the immobilisation of molecular catalysts in liquid supports (biphasic catalysis) and on solid supports. The liquid immobilisation media used in biphasic or multiphasic processes that are under most intensive investigation include water, ionic liquids, supercritical fluids and fluorocarbon solvents [1]. A plethora of different catalysts, either off-the-shelf, or modified specifically for immobilisation in the support solvent, have been evaluated, but only very few low oxidation state transition metal carbonyl clusters have been examined in such solvents.

The catalytic activity of clusters has been extensively studied as it was thought that they might fill the void between mononuclear species and colloidal (or heterogeneous) catalysts and open up new possibilities in catalysis and organic synthesis [2]. In general, the catalytic activity of clusters has been evaluated in organic solvents, although they often fragment to give mononuclear species which serve as the catalyst or recombine to form colloidal/nanoparticle catalysts. In addition, immobilisation of clusters on solid supports is a well developed field. Various solid supports have been used to immobilise clusters including silica, alumina, clays and nanotubes and the resulting catalytic activity of these materials has been extensively studied and reviewed [3]. Perhaps the most recent advance in this field concerns the use of heteronuclear clusters anchored to silica or alumina, then decomposed, to give very small nanoparticles which results in highly selective catalysts [4].

As mentioned above, clusters have not been widely studied in alternative solvents such as ionic liquids, supercritical fluids and fluorocarbons. although their catalytic activity has been examined in some detail in water, which can not only be used as an immobilisation solvent, but also as a source of hydrogen in the water-gas shift reaction, i.e. the conversion of CO and H2O to CO2 and H2 [5]. If the reaction is conducted in the presence of alkenes then hydroformylation or hydrohydroxymethylation can take place, the former being
the predominant reaction. Clusters have also been used to
catalyse hydrogenation reactions using water as a substrate
[6] and they have also been employed in phase transfer re-
actions, for example, a mixture of the carbonyls Ru3(CO)12
and CO2(CO)4 catalysts the carbonation of alkynes with
methyl iodide in a solvent system composed of benzene and
5 M aqueous NaOH with an ammonium salt used as the
phase transfer catalyst [7].

While many examples of reactions utilising water as a
hydrogen source are known, the vast majority are catalysed
by clusters that are not naturally (or preferentially) water
soluble, but take place in the presence of CO and a base or
phase transfer reagent [8]. It would seem that cluster anions
often form, and that these are moderately soluble in water,
but the cluster may also be a source of colloids or nanopar-
ticles. However, some cluster-carbonyl compounds have
been derivatised with hydrophilic phosphines in order to
provide high water solubility, including P(m-C6H4SO3Na)
acids [14], and while supercritical fluids are under intensive
evaluation as solvents in which to conduct catalysis, very
few carbonyl clusters have been screened in room temperature ionic liquids (see above), although
Ir2(CO)13 has been used to catalyse the reduction of CO
in a mixture of the inorganic salts AlCl3 and NaCl at tem-
peratures in excess of 100 °C [19]. However, since charged
compounds are generally highly soluble and well retained
in ionic liquids [20], there is considerable potential for
cluster catalysis using ionic liquids as immobilisation me-
dia for anionic clusters. Ionic liquids also provide a polar,
non-nucleophilic reaction environment which can increase
catalyst lifetimes in certain biphasic processes [21]. Such
an observation is important because biphasic catalysis has
been criticised since homogeneous catalyst lifetime is often
short and it is possibly not worth finding ways to recycle
and reuse them [22]. In this paper, we describe the use
of cluster-carbonyl anions as catalyst precursors to active
hydrogenation catalysts that in some cases give rise to
very different activities and selectivities to the same cluster
operating in organic solvents.

2. Results and discussion

Four different transition metal carbonyl cluster anions,
[HFe(CO)11]−, [HWOs3(CO)14]−, [H3Os4(CO)12]− and
[Ru6C(CO)16]2−, shown in Fig. 1, were evaluated as cata-
lysts/precatalysts for the hydrogenation of styrene in
[bmim][BF4] ionic liquid, octane and methanol for compar-
ison purposes. Octane was selected as a reference organic
solvent as hydrocarbon solvents are most widely used in
catalyst evaluation as solvents in which to conduct catalysis, very
different activities and selectivities to the same cluster
operating in organic solvents.

(a) (b)

Fig. 1. The solid-state structures of (a) [HFe(CO)11]−, (b) [HWOs3
(CO)14]−, (c) [H3Os4(CO)12]− and (d) [Ru6C(CO)16]2− (hydride
ligands are not shown).
preliminary screening reactions are summarised in Table 1 and depicted graphically in Fig. 2.

From the data presented in Table 1 and Fig. 2, two features are worth some comment. First, the activity for two of the clusters, [HFe(CO)\(_{11}\)]\(^{-}\) and [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\), is essentially the same in the ionic liquid and the molecular solvents, although the tri-iron cluster is almost inactive whereas the hexaruthenium cluster shows the highest activity. Second, the two tetraneuclear clusters [HWOs\(_3\)(CO)\(_{14}\)]\(^{-}\) and [H\(_3\)Os\(_4\)(CO)\(_{12}\)]\(^{-}\) are considerably more active in the ionic liquids compared to octane and methanol, although they are both less active than [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\).

Since [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\) is the most active compound further studies were undertaken on this compound. The activity of this cluster remains almost unchanged irrespective of the solvent in which catalysis was examined, suggesting that a similar active catalyst species operates in all solvents. Using high pressure NMR spectroscopy a [bmim][BF\(_4\)] solution of [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\) was placed under 100 bar of H\(_2\) and shaken vigorously. No signals corresponding to hydrides were observed, and after three days the experiment was stopped, although no cluster decomposition had taken place. Repeating this experiment in methanol, since it has a similar polarity to [bmim][BF\(_4\)], no hydride signals were observed, but cluster decomposition was clearly visible, although carbide centred clusters tend to be quite robust [24]. Such an observation is not unreasonable, given that methanol is a nucleophilic solvent, whereas [bmim][BF\(_4\)] is essentially non-nucleophilic and has previously been shown to stabilise homogeneous catalysts and accordingly increase catalyst lifetimes [20]. However, when the substrate was included in the high-pressure NMR experiment, decomposition of the catalyst to a heterogeneous species was observed in both solvents. Subsequent tests using mercury as a selective poison for colloids [25] showed that the active catalyst species in the ionic liquid and organic solvents was not homogeneous (although caution must be applied to this test with anionic clusters [26], see below), and hence it is not unreasonable that similar reaction rates are observed independent of the nature of the solvent. The slight differences in activity could be due to different particle sizes of the resulting colloids/nanoparticles, but we have no evidence for this proposition, and substrate solubility or rate of colloid formation in the different solvents could also give rise to the differences in activity.

Nanoparticle catalysts have previously been shown to be very effective in ionic liquids. For example, iridium nanoparticles generated from organometallic precursors [27], rhodium nanoparticles produced from RhCl\(_3\) [28] and palladium nanoparticles protected by phenanthroline ligands [29] have all been characterised (or generated directly) in ionic liquids and evaluated as hydrogenation catalysts. Benzenes or even hydrogenated using nanoparticles catalysts in ionic liquids [25], which is in keeping with related catalysts that operate in water [30]. However, we found that while the heterogeneous catalyst formed from the decomposition of [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\) was active for a range of alkene substrates, benzene could not be reduced under related conditions. The substrates hydrogenated using [Ru\(_6\)C(CO)\(_{16}\)]\(^{2-}\) as a catalyst precursor in [bmim][BF\(_4\)] are listed in Table 2.

Perhaps the most interesting feature to emerge from the hydrogenation of the substrates listed in Table 2 is that regioselective (partial) reduction of the cyclic dienes takes place, with, for example, the hydrogenation of 1,3-cyclohexadiene yielding only cyclohexene under the conditions used. The same catalyst in organic solvents is considerably less selective, and the high regioselectivity is a direct consequence of the ionic liquid. It has previously been proposed that the partial reduction of dienes to mono-ones, which takes place in ionic liquids, is a consequence of the lower solubility of the monone in the ionic liquid relative to the diene [31,42]. If the reaction is conducted under homogeneous conditions in an organic solvent then the cyclohexene can easily re-associate with the catalyst.

Table 1
<table>
<thead>
<tr>
<th>Cluster Solvent</th>
<th>Yield (%)</th>
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<tr>
<td>[HFe(CO)(_{11})](^{-}) Octane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Methanol</td>
<td>&lt;1</td>
</tr>
<tr>
<td>[bmim][BF(_4)]</td>
<td>&lt;1</td>
</tr>
<tr>
<td>[HWOs(<em>3)(CO)(</em>{14})](^{-}) Octane</td>
<td>2</td>
</tr>
<tr>
<td>Methanol</td>
<td>8</td>
</tr>
<tr>
<td>[bmim][BF(_4)]</td>
<td>29</td>
</tr>
<tr>
<td>[H(_3)Os(<em>4)(CO)(</em>{12})](^{-}) Octane</td>
<td>3</td>
</tr>
<tr>
<td>Methanol</td>
<td>14</td>
</tr>
<tr>
<td>[bmim][BF(_4)]</td>
<td>27</td>
</tr>
<tr>
<td>[Ru(<em>6)C(CO)(</em>{16})](^{2-}) Octane</td>
<td>90</td>
</tr>
<tr>
<td>Methanol</td>
<td>&gt;99</td>
</tr>
<tr>
<td>[bmim][BF(_4)]</td>
<td>93</td>
</tr>
</tbody>
</table>

Conditions: H\(_2\) (50.7 bar), 100 °C. Cluster concentration 5 × 10\(^{-4}\) M, solvent (1 ml), styrene (1 ml), total reactor volume 30 ml.
and undergo further hydrogenation to the fully saturated product. A similar mechanism can be envisaged for the hydrogenation of the cyclic dienes in [bmm][BF4] ionic liquid. The relative polarities of cyclic dienes versus cyclic monoenes relative to [bmm][BF4] supports this hypothesis as the cyclic monoenes should be less soluble than the cyclic dienes. The stirrer rate had no effect on the selectivity of the reaction, although it has a significant effect on the yield, the yield increasing with increasing stirrer rates.

Mass spectrometry also confirmed, at least indirectly, the presence of colloidal catalysis. Transition metal carbonyl cluster anions are readily studied using electrospray ionisation mass spectrometry [32] and a methanol solution of [Ru6(CO)16]2− shows the characteristic parent peak. Mass spectrometric analysis of compounds in ionic liquids is problematic given that the liquid is composed of ions. However, by dilution in a co-solvent, in this case methanol, cluster anions are readily studied using electrospray ionisation mass spectrometry [32] and a methanol solution of [Ru6(CO)16]2− shows the characteristic parent peak. Mass spectrometric analysis of compounds in ionic liquids is problematic given that the liquid is composed of ions. However, by dilution in a co-solvent, in this case methanol, using a literature procedure [33], a spectrum corresponding to [Ru6(CO)16]2− was observed. Association of the solvent cation is entirely expected given that it is present in vast excess. Peaks corresponding to the ruthenium isotope, were not observed in post-catalyst solutions indicating that the cluster had been consumed and was no longer present.

The tetranuclear clusters [HWOs4(CO)12]− and [H2Os4 (CO)12]− are considerably more active in the ionic liquids compared to the organic solvents evaluated, suggesting that different catalyst species are present in the different solvents, and so the latter cluster was subjected to a more detailed examination. The 1H NMR spectrum of [H2Os4(CO)12]− in methanol gives rise to a singlet resonance at −14.3 ppm, in [bmm][BF4] the resonance is observed at −14.8 and is characteristic of three equivalent hydrides. When the system is placed under 100 bar of H2 and shaken vigorously, no change in the spectrum is observed and after three days no decomposition of the cluster appeared to take place. On addition of the styrene substrate, also under 100 bar of H2, the peak at −14.8 disappears and a new peak at −20.0 appears. Although there has been a considerable debate in the literature surrounding homogeneous catalysis by intact clusters, with many clusters simply being precursors to mononuclear species or colloids/nanoparticles which are the active catalysts, it is not unreasonable to assume that the new peak corresponds to a cluster in which a CO ligand has been substituted by the substrate. The concept of intact cluster catalysis has been contested despite some convincing examples of heteronuclear systems which exhibit properties suggesting that there is a through bond synergy between the different metal centres [34]. However, direct evidence for intact cluster catalysis has only recently been provided using parahydrogen (p-H2) NMR spectroscopy. Fluxional processes and transfer of hydrides into organic groups coordinated to clusters were initially demonstrated with p-H2 [35], with subsequent studies employing Os3(m-H2(CO)10) [36], Ru3(CO)10(PMe2Ph)2 and Ru3(CO)10(PPh3)2 [37], previously shown to be homogeneous hydrogenation catalysts [38], provided direct evidence for intact cluster catalysis. Using p-H2 NMR methods the active catalyst intermediates, which include both intact clusters and a mononuclear species, have been identified [39]. The route taken depends on the nature of the substrate and the solvent, with intact cluster catalysis preferred in polar solvents and fragmentation to the mononuclear intermediate being facilitated by non-polar solvents. If the cluster stays intact, CO loss or slower phosphine loss leads to hydrogenation, with the substrate binding to the vacant site (as proposed for [H3Os4(CO)12]− above in [bmm][BF4]). Although we have not probed the mechanism of hydrogenation by [H2Os4(CO)12]− using parahydrogen methods, it is not unreasonable to assume a mechanism involving intact cluster catalysis takes place (in the high-pressure NMR spectrum there are some peaks of low relative intensity that might also correspond to other active species). However, since cluster catalysis is facilitated by polar solvents, and [bmm][BF4] has a polarity similar to methanol [22], such a mechanism would be favoured. The improved catalytic activity of [H2Os4(CO)12]− in [bmm][BF4] compared to methanol might be due to the non-nucleophilic nature of the ionic liquid which protects the catalyst and prevents it from decomposing, similar observations have been made elsewhere [20]. The very low catalytic activity of [H2Os4(CO)12]− in octane could be due to poor solubility of the cluster or the active catalyst being a mononuclear species (since it is a non-polar solvent) or due to a combination of both. In the parahydrogen experiments described above, catalysis involving mononuclear species showed lower activity than that involving intact clusters.

The activity of [H2Os4(CO)12]− towards styrene hydrogenation was also evaluated in the three solvents in the presence of mercury, resulting in complete inactivity. At first glance this result would suggest that the active catalyst is a colloidal/nanoparticle, which conflicts with the high-pressure NMR study. However, it was subsequently found that [H2Os4(CO)12]− decomposes in the presence of mercury under ambient conditions, viz. not under the reducing conditions.
shows the presence of the anionic tetraosmium cluster. The highest turnover frequency is obtained for the ionic liquids composed of the 1-butyl-2,3-dimethylimidazolium (bdmim) cation and these are the most viscose of the ionic liquids. The turnover frequencies are somewhat lower than the others and in one it is somewhat higher. The lower turnover frequencies are obtained in ionic liquids that are quite similar although in three the values over 4h.

The influence of the ionic liquid on the $[\text{H}_3 \text{Os}_4 (\text{CO})_{12}]^-$ catalysed hydrogenation of styrene was also studied and the results are shown in Table 3. The turnover frequencies in all ionic liquids were measured and some related cluster-carbonyl compounds as a catalyst precursor. The clusters $[\text{PPN}][\text{HFe(CO)}_{11}]$ [48], $[\text{PPN}][\text{HWO}_3 (\text{CO})_{14}]$ [49], $[\text{PPN}][\text{H}_3 \text{Os}_4 (\text{CO})_{12}]$ [50] and $[\text{PPN}]_2[\text{Ru}_6 \text{C} (\text{CO})_{18}]$ [51] were prepared using literature methods. The identity of the compounds was confirmed using IR and $^1$H NMR spectroscopy and mass spectrometry. The data obtained was in excellent agreement with the literature data with the exception of the $^1$H NMR spectrum of $[\text{PPN}][\text{H}_3 \text{Os}_4 (\text{CO})_{12}]$ which shows chemical shift of hydride at $-14.3$ (methanol-d$_4$), while the literature value is reported to be around $-18$ppm, but the exact value is not given. The ionic liquids $[\text{bmmim}][\text{BF}_4]$, $[\text{bmmim}][\text{PF}_6]$, $[\text{bmmim}][\text{CF}_3\text{SO}_2\text{N}]$, $[\text{bmmim}][\text{PF}_6]$, $[\text{bmmim}][\text{BF}_4]$ and $[\text{ompy}][\text{BF}_4]$ were prepared by literature methods [52] and $[\text{ompy}][\text{BF}_4]$ was provided by Lonza (Visp, Switzerland).

### 2.1. Concluding remarks

Ionic liquids are becoming widely used to immobilise catalysts for hydrogenation reactions [42]. It is still too early to say whether such systems will be used on an industrial scale, but there certainly seem to be some benefits compared to the other alternative solvents such as water, fluorous solvents and supercritical fluids that are also under intensive investigation [43]. For example, although not cluster carbonyl compounds, $[\text{H}_3 \text{Ru}(\text{η}^3-\text{arene})_2]^2^-$ and some related clusters, catalyse, or act as pre-catalysts, for the hydrogenation of arenes under biphase aqueous–organic [44] and ionic liquid–organic conditions [45] since they are highly soluble in both immobilisation solvents. It was found that the purity of the ionic liquid was critical with chloride impurities impeding activity [46].

From the studies presented herein, it would appear that ionic liquids can help to direct the mechanism of catalyst activity, protect the catalyst from deactivation and provide regioselective control over a reaction. These are all extremely important features and are certainly worth studying further. Furthermore, in terms of cluster catalysts, there is a huge range of compounds available for study and they do not require any modification in order to be highly soluble in ionic liquids, while remaining highly insoluble in non-polar organic solvents. Hence, the solubility properties of cluster anions should lead to excellent catalyst retention and reuse. Neutral clusters can also be immobilised in ionic liquids following derivatisation with suitable ligands to induce the appropriate solubility properties. In addition, a strategy for making liquid metal carbonyl anions has been reported and this might be applicable to cluster-carbonyl compounds as well [47].

### 3. Experimental

#### 3.1. Sample preparation

The clusters $[\text{PPN}][\text{HFe(CO)}_{11}]$ [48], $[\text{PPN}][\text{HWO}_3 (\text{CO})_{14}]$ [49], $[\text{PPN}][\text{H}_3 \text{Os}_4 (\text{CO})_{12}]$ [50] and $[\text{PPN}]_2[\text{Ru}_6 \text{C} (\text{CO})_{18}]$ [51] were prepared using literature methods. The identity of the compounds was confirmed using IR and $^1$H NMR spectroscopy and mass spectrometry. The data obtained was in excellent agreement with the literature data with the exception of the $^1$H NMR spectrum of $[\text{PPN}][\text{H}_3 \text{Os}_4 (\text{CO})_{12}]$ which shows chemical shift of hydride at $-14.3$ (methanol-d$_4$), while the literature value is reported to be around $-18$ppm, but the exact value is not given. The ionic liquids $[\text{bmmim}][\text{BF}_4]$, $[\text{bmmim}][\text{PF}_6]$, $[\text{bmmim}][\text{CF}_3\text{SO}_2\text{N}]$, $[\text{bmmim}][\text{PF}_6]$ and $[\text{bmmim}][\text{BF}_4]$ were prepared by literature methods [52] and $[\text{ompy}][\text{BF}_4]$ was provided by Lonza (Visp, Switzerland).

#### 3.2. Hydrogenation reactions

All catalytic experiments were conducted using a Baskerville Multi-Cell autoclave using a modified literature method [53]. To each reaction vessel, the catalyst (1 × $10^{-3}$ mmol), substrate (1 ml) and the appropriate solvent (1 ml) were added. The autoclave was purged with hydrogen gas and then the pressure was set to 50.7 bar at room temperature. The catalytic runs were carried out at 100 °C for 4h and the % conversions determined by GC analysis to known standards using a Varian chrompack CP-3380 gas chromatograph. Metallic mercury (0.25 ml) was added as a selective poison to test for colloidal catalysis when required.

#### 3.3. High-pressure NMR spectroscopy

In a typical experiment, the cluster was dissolved in the appropriate solvent and the solution was placed into the sapphire NMR tube (Ø = 10 mm) which was closed. After the mixture had been pressurised with H$_2$, the tube was shaken at 20 °C. Periodically, it was placed in the NMR spectrometer and the spectra were recorded.

### Table 3

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>TOF (mol mol$^{-1}$ h$^{-1}$)</th>
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<tbody>
<tr>
<td>$[\text{bmmim}][\text{BF}_4]$</td>
<td>587</td>
</tr>
<tr>
<td>$[\text{bmmim}][\text{PF}_6]$</td>
<td>522</td>
</tr>
<tr>
<td>$[\text{bmmim}][\text{CF}_3\text{SO}_2\text{N}]$</td>
<td>587</td>
</tr>
<tr>
<td>$[\text{bdmim}][\text{PF}_6]$</td>
<td>392</td>
</tr>
<tr>
<td>$[\text{bdmim}][\text{BF}_4]$</td>
<td>413</td>
</tr>
<tr>
<td>$[\text{bdmim}][\text{CF}_3\text{SO}_2\text{N}]$</td>
<td>457</td>
</tr>
<tr>
<td>$[\text{ompy}][\text{BF}_4]$</td>
<td>718</td>
</tr>
</tbody>
</table>

Conditions: H$_2$ (50.7 bar), 100 °C, 4h. Cluster concentration 5 × 10$^{-4}$ M, ionic liquid (1 ml), styrene (1 ml), total reactor volume (30 ml). TOF is the turnover in units of mol mol$^{-1}$ h$^{-1}$, calculated as an average value over 4h.
3.4. Mass spectrometry

ESI-MS spectra were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument under optimized conditions [54]. Samples were infused directly into the source at 5 µl min⁻¹ using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. The MS detector was tuned automatically on the base peak, which optimised the remaining parameters.

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References

References


