

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) cata-

lysts 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 have 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

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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 reactions, for example, a mixture of the carbonyls $\text{Ru}_3(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ catalyses the carbonylation 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 nanoparticles. However, some cluster-carbonyl compounds have been derivatised with hydrophilic phosphines in order to provide high water solubility, including $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ derivatives of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}$ and Os), $\text{Ir}_4(\text{CO})_{12}$ [9], $\text{Ru}_6\text{C}(\text{CO})_{17}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ [10]. Some of these clusters were shown to act as catalyst precursors in water-gas shift [10] and hydrogenation [11] reactions and could be used several times without any decrease in activity. In addition, the cluster $\text{Ru}_3(\text{CO})_9\{\text{PPh}_2(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})\}_3$ has been shown to be a catalyst precursor for the hydrogenation of acrylic acid and the hydroformylation of propylene under water-gas shift conditions [12]. The $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ derivatised clusters were also evaluated in the ionic liquid $[\text{bmim}][\text{BF}_4]$ (bmim is the 1-butyl-3-methylimidazolium cation), but their catalytic activity was very low. Similarly, the ruthenium cubane cluster $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4(\text{OH})_4]^{4+}$, an active pre-catalyst for the hydrogenation of benzene in aqueous solution, is almost inactive in $[\text{bmim}][\text{BF}_4]$, which is thought to be due to activation of the cluster by reaction with water [13].

Metal carbonyl compounds are soluble in supercritical fluids [14], and while supercritical fluids are under intensive evaluation as solvents in which to conduct catalysis, very little catalysis using clusters has been carried out in these fluids. $\text{Fe}_3(\text{CO})_{12}$ catalyses the isomerisation of 1-hexene to 2-hexene in supercritical CO_2 [15]. The hydroformylation of ethylene using $\text{Ru}_3(\text{CO})_{12}$ as the catalyst precursor has also been conducted in supercritical CO_2 [16]. The reaction was conducted at pressures ranging from 224 to 408 atmospheres, with turnover frequencies increasing rapidly with pressure. The same catalyst precursor was found to be only slightly active for hydrogenation reactions under similar conditions [17]. Supercritical water has also been used as a solvent for the water-gas shift reaction using $\text{Rh}_6(\text{CO})_{16}$ as a catalyst precursor [18].

Only very few carbonyl clusters have been screened in room temperature ionic liquids (see above), although $\text{Ir}_4(\text{CO})_{12}$ has been used to catalyse the reduction of CO in a mixture of the inorganic salts AlCl_3 and NaCl at temperatures 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 media 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, $[\text{HFe}(\text{CO})_{11}]^-$, $[\text{HWOs}_3(\text{CO})_{14}]^-$, $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ shown in Fig. 1, were evaluated as catalysts/precatalysts for the hydrogenation of styrene in $[\text{bmim}][\text{BF}_4]$ ionic liquid, octane and methanol for comparison purposes. Octane was selected as a reference organic solvent as hydrocarbon solvents are most widely used in cluster catalysis and methanol was chosen as it has a similar polarity to $[\text{bmim}][\text{BF}_4]$ [23] and therefore dissolves a similar range of compounds. The four clusters chosen are anionic, since salts are highly soluble in ionic liquids, and they also represent a range of structural types, viz. homonuclear, heteronuclear, differing nuclearities and geometries, and a carbide centred cluster. The results from the

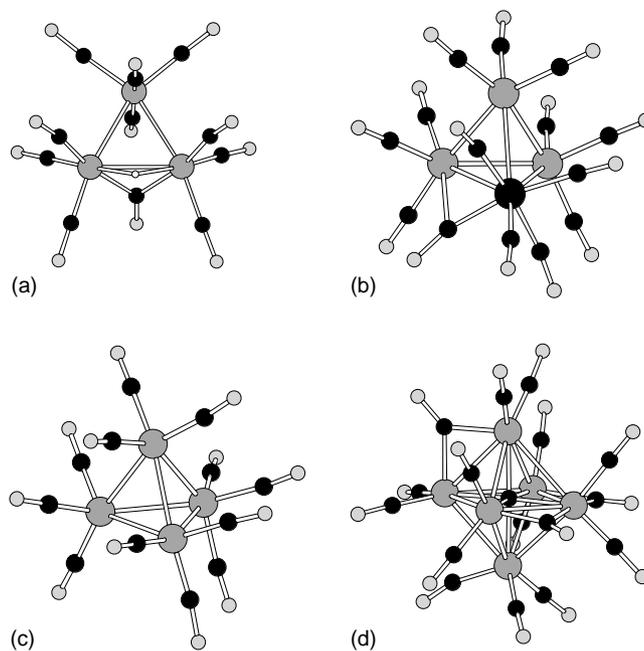


Fig. 1. The solid-state structures of (a) $[\text{HFe}(\text{CO})_{11}]^-$, (b) $[\text{HWOs}_3(\text{CO})_{14}]^-$, (c) $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ and (d) $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ (hydride ligands are not shown).

Table 1
Hydrogenation of styrene to ethylbenzene using clusters as catalysts/catalyst precursors

Cluster	Solvent	Yield (%)
[HFe(CO) ₁₁] ⁻	Octane	<1
	Methanol	<1
	[bmim][BF ₄]	<1
[HWOs ₃ (CO) ₁₄] ⁻	Octane	2
	Methanol	8
	[bmim][BF ₄]	29
[H ₃ Os ₄ (CO) ₁₂] ⁻	Octane	3
	Methanol	14
	[bmim][BF ₄]	27
[Ru ₆ C(CO) ₁₆] ²⁻	Octane	90
	Methanol	>99
	[bmim][BF ₄]	93

Conditions: H₂ (50.7 bar), 100 °C, 4 h. Cluster concentration 5×10^{-4} M, solvent (1 ml), styrene (1 ml), total reactor volume 30 ml.

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 [Ru₆C(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 tetranuclear clusters [HWOs₃(CO)₁₄]⁻ and [H₃Os₄(CO)₁₂]⁻ are considerably more active in the ionic liquids compared to octane and methanol, although they are both less active than [Ru₆C(CO)₁₆]²⁻.

Since [Ru₆C(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][BF₄] solution of

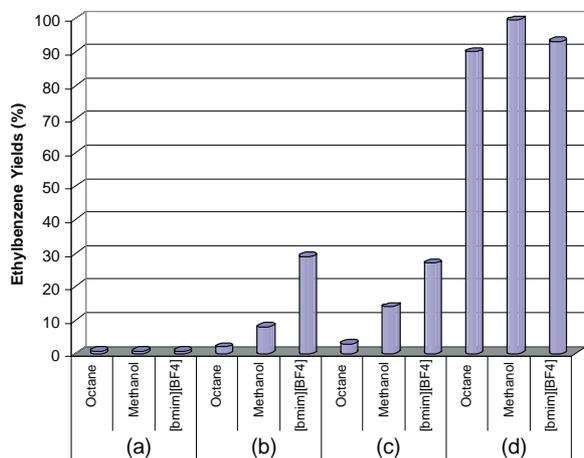


Fig. 2. Comparison of the catalytic activity of (a) [HFe(CO)₁₁]⁻, (b) [HWOs₃(CO)₁₄]⁻, (c) [H₃Os₄(CO)₁₂]⁻ and (d) [Ru₆C(CO)₁₆]²⁻ in octane, methanol and [bmim][BF₄].

[Ru₆C(CO)₁₆]²⁻ was placed under 100 bar of H₂ 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][BF₄], 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][BF₄] 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 RhCl₃ [28] and palladium nanoparticles protected by phenanthroline ligands [29] have all been characterised (or generated directly) in ionic liquids and evaluated as hydrogenation catalysts. Benzene may even be 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 [Ru₆C(CO)₁₆]²⁻ was active for a range of alkene substrates, benzene could not be reduced under related conditions. The substrates hydrogenated using [Ru₆C(CO)₁₆]²⁻ as a catalyst precursor in [bmim][BF₄] 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 monoenes, which takes place in ionic liquids, is a consequence of the lower solubility of the monoene 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 2
Hydrogenation of various substrates using $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ as a catalyst precursor in $[\text{bmim}][\text{BF}_4]$

Substrate	Product(s)	Yield (%)
1-Hexene	Hexane	31
1-Octene	Octane	18
Cyclohexene	Cyclohexane	26
1,3-Cyclohexadiene	Cyclohexene	31
1,4-Cyclohexadiene	Cyclohexene	45
	Cyclohexane	4
1,5-Cyclooctadiene	Cyclooctene	40
	Cyclooctane	4
Benzene		No reaction

Conditions: H_2 (50.7 bar), 100°C , 4 h. 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 $[\text{bmim}][\text{BF}_4]$ ionic liquid. The relative polarities of cyclic dienes versus cyclic monoenes relative to $[\text{bmim}][\text{BF}_4]$ 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 $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ 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 $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{-bmim}]^-$ was observed. Association of the solvent cation is entirely expected given that it is present in vast excess. Peaks corresponding to this ion, or any others containing 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 $[\text{HWOs}_3(\text{CO})_{14}]^-$ and $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ 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 $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ in methanol gives rise to a singlet resonance at -14.3 ppm, in $[\text{bmim}][\text{BF}_4]$ the resonance is observed at -14.8 and is characteristic of three equivalent hydrides. When the system is placed under 100 bar of H_2 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 H_2 , 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 ($p\text{-H}_2$) NMR spectroscopy. Fluxional processes and transfer of hydrides into organic groups coordinated to clusters were initially demonstrated with $p\text{-H}_2$ [35], with subsequent studies employing $\text{Os}_3(\text{m-H})_2(\text{CO})_{10}$ [36], $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$ and $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [37], previously shown to be homogeneous hydrogenation catalysts [38], provided direct evidence for intact cluster catalysis. Using $p\text{-H}_2$ 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 $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ above in $[\text{bmim}][\text{BF}_4]$). Although we have not probed the mechanism of hydrogenation by $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ 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 $[\text{bmim}][\text{BF}_4]$ has a polarity similar to methanol [22], such a mechanism would be favoured. The improved catalytic activity of $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ in $[\text{bmim}][\text{BF}_4]$ 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 $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ 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 $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ 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 colloid/nanoparticle, which conflicts with the high-pressure NMR study. However, it was subsequently found that $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ decomposes in the presence of mercury under ambient conditions, viz. not under the reducing

Table 3
Hydrogenation of styrene using $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ as a catalyst precursor in various ionic liquids

Ionic liquid	TOF ($\text{mol mol}^{-1} \text{h}^{-1}$)
[bmim][BF ₄]	587
[bmim][PF ₆]	522
[bmim][(CF ₃ SO ₂) ₂ N]	587
[bdmim][PF ₆]	392
[bdmim][BF ₄]	413
[bdmim][(CF ₃ SO ₂) ₂ N]	457
[ompy][BF ₄]	718

Conditions: H₂ (50.7 bar), 100 °C, 4 h. 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 $\text{mol mol}^{-1} \text{h}^{-1}$, calculated as an average value over 4 h.

conditions presented by a hydrogen atmosphere. The reaction of metal catalysts with metallic mercury has been noted previously [26,40], and the reactions of anionic clusters with mercury salts have been extensively studied [41]. As such, the results from the mercury poisoning experiments are not surprising and can be discounted. Furthermore, electrospray ionisation mass spectrometry of a post-catalyst solution shows the presence of the anionic tetraosmium cluster.

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 the ionic liquids are quite similar although in three the values are somewhat lower than the others and in one it is somewhat higher. The lower turnover frequencies are obtained in ionic liquids composed of the 1-butyl-2,3-dimethylimidazolium (bdmim) cation and these are the most viscose of the ionic liquids. The highest turnover frequency is obtained in [ompy][BF₄] (ompy is the 1-octyl-3-methylpyridinium cation) which forms a single phase with the substrate.

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, fluorosolvents and supercritical fluids that are also under intensive investigation [43]. For example, although not cluster-carbonyl compounds, $[\text{H}_4\text{Ru}_4(\eta^6\text{-arene})_4]^{2+}$ and some related clusters, catalyse, or act as pre-catalysts, for the hydrogenation of arenes under biphasic 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 [PPN][HFe(CO)₁₁] [48], [PPN][HWOs₃(CO)₁₄] [49], [PPN][H₃Os₄(CO)₁₂] [50] and [PPN]₂[Ru₆C(CO)₁₆] [51] were prepared using literature methods. The identity of the compounds was confirmed using IR ν_{CO} and ¹H NMR spectroscopy and mass spectrometry. The data obtained was in excellent agreement with the literature data with the exception of the ¹H NMR spectrum of [PPN][H₃Os₄(CO)₁₂] which shows chemical shift of hydride at -14.3 (methanol-d₄), while the literature value is reported to be around -18 ppm, but the exact value is not given. The ionic liquids [bmim][BF₄], [bmim][PF₆], [bmim][(CF₃SO₂)₂N], [bmmim][PF₆], [bmmim][BF₄] and [bmmim][(CF₃SO₂)₂N] were prepared by literature methods [52] and [ompy][BF₄] 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 4 h 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 ($\varnothing = 10$ mm) which was closed. After the mixture had been pressurised with H₂, the tube was shaken at 20 °C. Periodically, it was placed in the NMR spectrometer and the spectra were recorded.

3.4. Mass spectrometry

ESI-MS spectra were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument under optimised conditions [54]. Samples were infused directly into the source at $5 \mu\text{l min}^{-1}$ 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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