A Comparison of Ruthenium-Catalysed Arene Hydrogenation Reactions in Water and 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids

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Received: June 3, 2002; Accepted: October 5, 2002

Abstract: The hydrogenation of benzene and other arene substrates under biphasic conditions is evaluated using the catalyst precursor Ru(η^6-$C_{10}H_{14}$)(pta)Cl_2 (pta = 1,3,5-triaza-7-phosphaadamantane) immobilised in water and 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids. The effect that contamination of the 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids with chloride has on the hydrogenation reaction has also been examined. Of the immobilisation solvents tested the optimum solvent was found to be chloride-free 1-butyl-3-methylimidazolium tetrafluoroborate. Catalytic turnovers in this solvent are highest, and in general, turnovers for the hydrogenation reactions follow the trend: chloride-free 1-butyl-3-methylimidazolium tetrafluoroborate > water > chloride-contaminated 1-butyl-3-methylimidazolium tetrafluoroborate.

Keywords: arenes; biphasic catalysis; hydrogenation; ionic liquids; ruthenium; water as solvent

Introduction

Ionic liquids were originally developed as highly conducting electrolytes for electrochemical use,[1] but subsequently, it was found that they have a number of properties that make them ideally suited to immobilisation of catalysts for biphasic synthesis. These properties have been described in detail elsewhere,[2] but in brief:

- They are good solvents for a range of both inorganic and organic species.
- Although they are polar (due to their ionic nature), the component ions are poorly co-ordinating and they are unlikely to interfere chemically with any solute.
- A number of organic solvents display little or very limited miscibility with these liquids.
- From an environmental perspective they exhibit negligible vapour pressure allowing volatile organic contaminants to be easily removed, but also preventing their escape to the atmosphere by evaporation.

There is considerable interest in the use of room temperature ionic liquids in biphasic catalysis and many elegant examples of ionic liquid-organic catalysis have been reported.[3] Although ionic liquids offer certain advantages in biphasic catalysis they are not without their own problems. One of the main problems faced by those using ionic liquids composed of tetrafluoroborate anions is that the purity of ionic liquids has hampered research.[4] Tetrafluoroborate-based ionic liquids are most frequently prepared *via* a metathesis reaction between the appropriate dialkylimidazolium halide salt and sodium tetrafluoroborate.[5] This method provides a relatively cheap and effective way to produce ionic liquids of a moderate purity. Alternative reagents to sodium tetrafluoroborate have been explored[6] and completely different routes have also been reported.[7] Any organic impurities can be removed *via* a combination of high vacuum and filtration through a column of activated alumina, but it proves extremely difficult to remove final traces of chloride impurities from the ionic liquid. It is well known that halide ions can coordinate to transition metal centres so their presence in a catalyst support solvent is undesirable as they can block reactive co-ordination sites which can lead to side reactions and catalyst deactivation.[8] In addition, trace amounts of chloride impurities, which may be present at levels between 0.1–0.5 mol kg^{-1}, have significant effects on the physical properties of the ionic liquid such as viscosity and density. Increases in viscosity are a particular concern in biphasic processes as the formation of an emulsion and hence the interface of the two phases is effected.

We previously described the biphasic hydrogenation of arene substrates using a cationic ruthenium cluster catalyst supported in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] ionic liquid.[9] During an extension to these studies we noticed that certain catalysed reactions carried out in tetrafluoroborate ionic liquids showed a variance in turnovers of ± 10% which depended on the batch of ionic liquid used. With this in mind, we set about establishing the optimum 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquid for conducting arene hydrogenation reactions, explored the effect of chloride contamination on the catalyst and compared the ionic liquids with water as an immobilisation solvent. In this paper we describe the outcome of these studies.

Results and Discussion

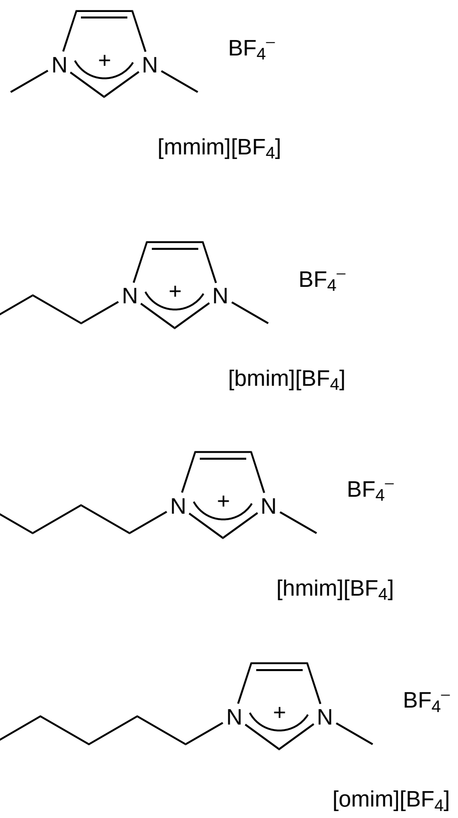
Many catalysts are soluble in ionic liquids, especially ionic compounds, although neutral species, such as Wilkinson's catalyst, are also soluble to some extent.[10] While the solubility of the catalyst is clearly important, in a biphasic process the nature of the interaction between the catalyst solution and the substrates and products are also significant. In the ideal process, the substrates will be completely miscible with the catalyst support solution and the products should be completely immiscible. Such a situation is very rare although the synthesis of butyraldehyde from propylene, CO and H_2 involves an aqueous-organic biphasic process that operates under such conditions.[11] In this process the substrates are all gases under normal conditions, but in general, if the substrates are more soluble than the products in a catalyst support solvent then the process may still be advantageous.

Dialkylimidazolium tetrafluoroborate ionic liquids are miscible with polar organic solvents such as chlorinated solvents and alcohols, and immiscible with nonpolar solvents such as ethers and alkanes.[12] Solvents with intermediate polarity, however, have a degree of miscibility. Table 1 compares polarities of some dialkylimidazolium tetrafluoroborate ionic liquids with conventional organic solvents including benzene and cyclohexane that are relevant to this work. The ionic liquids exhibit similar polarities to one another and are similar to the polarities of lower alcohols.[13] The polarity of benzene is intermediate between that of dichloromethane (a miscible solvent) and diethyl ether (an immiscible solvent) and exhibits a limited degree of miscibility. Cyclohexane, on the other hand, has a polarity lower than that of diethyl ether. Clearly, the difference in polarity between benzene and cyclohexane could facilitate biphasic arene hydrogenation reactions using these ionic liquids since the substrate will be more soluble in the ionic liquid thereby increasing the rate of the catalytic reaction and the product should be less soluble making extraction more straightforward.

Table 1. Solvatochromic shifts of the dye Nile Red in various solvents. Data for ionic liquids are taken from ref.[13]

Solvent	λ_{max} [nm]
[bmim][BF_4]	550.8
[hmim][BF_4]	551.9
[omim][BF_4]	549.5
methanol	549.6
dichloromethane	535.2
benzene	525.4
diethyl ether	504.4
cyclohexane	487.6

The concentration of benzene and cyclohexane in a range of ionic liquids (Scheme 1) has been determined at 20 °C and the results from these experiments are summarised in Figure 1. As the length of the alkyl group increases from a methyl group in [mmim][BF_4] to an octyl group [omim][BF_4] the solubility of benzene rapidly increases. In contrast, the solubility of cyclohexane, which has a lower polarity than benzene, remains effectively constant. Since the solubility of benzene is greatest in [omim][BF_4] and the solubility of cyclohexane is almost as low as it is for [mmim][BF_4] then selection of [omim][BF_4] for hydrogenation reactions seems reasonable. In this solvent the interface between a benzene substrate and an ionic liquid is



Scheme 1.

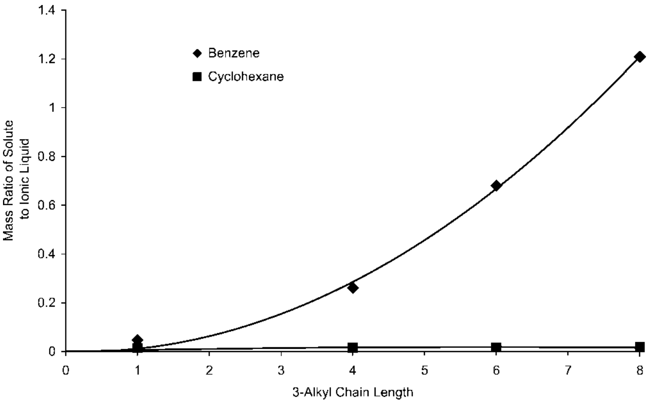
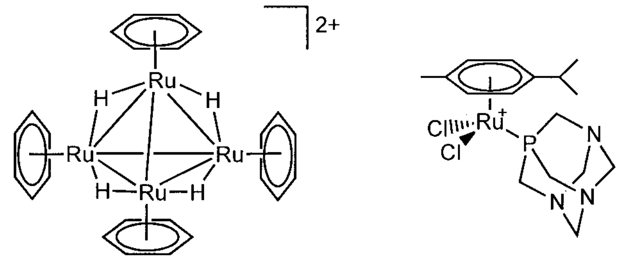


Figure 1. Graph showing the miscibilty of benzene and cyclohexane in [C_x-mim][BF_4] ionic liquids (where x = 1 mmim; x = 4 bmim; x = 6 hmim and x = 8 omim). Measurements were conducted at 20 °C on pure ionic liquids without catalyst present since the catalyst is present in low concentration and therefore should not effect solubility.

greatest allowing optimum mixing of the benzene substrate and catalysts without compromising the efficiency of the extraction of the cyclohexane product after reaction. We have found, however, that differences in turnovers for reactions carried out in [bmim][BF_4], [hmim][BF_4] and [omim][BF_4] are indistinguishable and this is because at the temperature of the reaction, *viz.* 90 °C, all the solutions are essentially homogeneous.

We have previously shown that the cluster pre-catalyst [$H_4Ru_4(\eta^6\text{-}C_6H_6)$][$BF_4$]$_2$, (Scheme 2) originally developed for biphasic aqueous-organic arene hydrogenation reactions,[14] operates effectively in [bmim][BF_4].[9] At the time we ascribed slight improvements in catalytic activity to increased solubility of hydrogen gas in the ionic liquid; the Henry coefficient solubility constant of hydrogen in [bmim][BF_4] is 3.0×10^{-3} mol L^{-1} atm^{-1} which is much higher than water.[15] Based on the above results it seems likely that the improvement is also due to increased solubility of the benzene substrate in the [bmim][BF_4] ionic liquid, although other factors such as viscosity, which is higher for the ionic liquid, are important. The effect of the increased solubility of benzene in the ionic liquid has been confirmed by comparing the effect of stirrer speed on turnover in the two solvents. The results are presented in Figure 2 which demonstrates that the ionic liquid solution is less sensitive to stirrer rate exhibiting close to the maximum turnover at a lower stirrer rate than the analogous reaction in water.

The complex $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ (pta = 1,3,5-triaza-7-phosphaadamantane) has also been shown to be a pre-catalyst for the hydrogenation of arenes.[16] Since it is soluble in ionic liquids we screened it in arene hydrogenation reactions and found it to be less effective in [bmim][BF_4] than in water. Surprised by this result we proposed that the poorer result for was due to impurities in the ionic liquid that deactivated the catalyst. From the literature,[4] the most likely culprit is chloride, known to be present at levels between 0.1 – 0.5 mol kg^{-1}, and also known to deactivate homogeneous catalysts. The importance of the purity of ionic liquids has been discussed previously,[17] and much work has been devoted to studying the effect of chloride impurities on the physical properties ionic liquids and in designing ways in removing all the residual chloride from the metathesis synthesis of [bmim][BF_4] and related ionic liquids. We used a modification of a synthesis described previously in which 1-butylimidazole is methylated with the simultaneous formation of the tetrafluoroborate anion using trimethyloxonium tetrafluoroborate, Me_3OBF_4, which avoids halide precursors.[18] The original synthesis is conducted in an organic solvent, whereas we conducted the reaction under solvent-free conditions at low temperature.



Scheme 2.

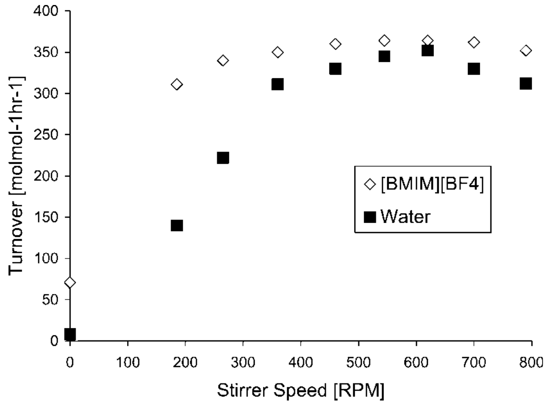


Figure 2. Relationship between catalytic turnover and stirring rate for the hydrogenation of benzene to cyclohexane using [$H_4Ru_4(\eta^6\text{-}C_6H_6)$][$BF_4$]$_2$. *Reaction conditions:* catalyst (30 mg) in solvent (10 mL), substrate (2 mL), H_2 (60 atm) 90 °C, 1 h.

Benzene hydrogenation using $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ as the pre-catalyst was carried out in the 'halide – free' [bmim][BF_4] and the results are displayed in Table 2 together with comparisons with water, and [bmim][BF_4], [hmim][BF_4] and [omim][BF_4] prepared by the metathesis route. The catalytic activity in water is greater than that obtained for the ionic liquids made by the metathesis route. However, this trend is reversed when the chloride-free [bmim][BF_4] ionic liquid is

Table 2. Hydrogenation of benzene using $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ or $[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$ in various solvents.

Catalyst	Solvent	Turnover* [mol mol^{-1} h^{-1}]
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	H_2O	170
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	[bmim][BF_4][a]	140
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	[hmim][BF_4]	137
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	[omim][BF_4]	141
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	[bmim][BF_4][b]	206
$Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$	CH_2Cl	54
$[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$	H_2O	352
$[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$	[bmim][BF_4][a]	364
$[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$	[bmim][BF_4][b]	406

Reaction conditions: catalyst (30 mg) in solvent (10 mL), substrate (2 mL), H_2 (60 atm) 90 °C, 1 h. Product in each case is cyclohexane.

* Turnovers are quoted in number of moles of substrate converted per mole of catalyst per hour.

[a] Made *via* metathesis route, [Cl^-] 0.2 mol kg^{-1}.

[b] Made *via* alkylimidazolium methylation, chloride content zero.

Table 3. The hydrogenation of various arene substrates using $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ immobilised water and in [bmim][BF_4].

Substrate	Reaction Conditions	Turnover* (mol mol^{-1} h^{-1})
Toluene	water	130
Toluene	[bmim][BF_4][a]	54
Toluene	[bmim][BF_4][b]	136
Ethylbenzene	water	122
Ethylbenzene	[bmim][BF_4][a]	53
Ethylbenzene	[bmim][BF_4][b]	145
Chlorobenzene	water	11
Chlorobenzene	[bmim][BF_4][a]	6
Chlorobenzene	[bmim][BF_4][b]	18

Reaction conditions: catalyst (30 mg) in solvent (10 mL), substrate (1 mL), H_2 (60 atm) 90 °C, 1 h. Products formed were completely hydrogenated cyclohexane or alkane analogues of substrate.

* Turnovers are quoted in number of moles of substrate converted per mole of catalyst per hour.

[a] Made *via* metathesis route, [Cl^-] 0.2 mol kg^{-1}.

[b] Made *via* alkylimidazolium methylation, chloride content zero.

employed as the immobilisation solvent; resulting in a *ca.* 50% increase in the activity for the catalytic hydrogenation of benzene. The cluster pre-catalyst $[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$ is not expected to be prone to poisoning by halide impurities, but there is still a significant increase in turnover when the cluster is immobilised in the 'halide – free' [bmim][BF_4].

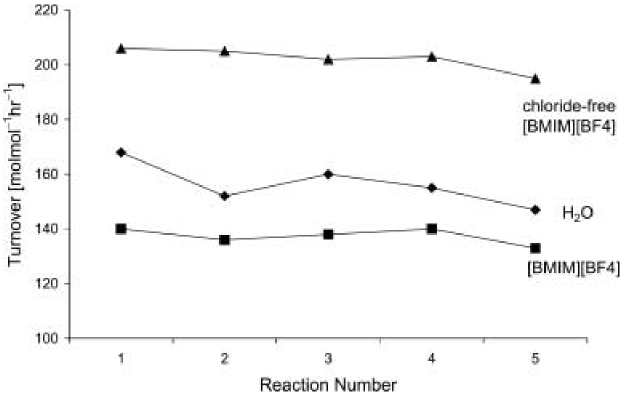


Figure 3. Reuse of $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ for the hydrogenation of benzene to cyclohexane in water, [bmim][BF_4] and halide-free [bmim][BF_4] solution. *Reaction conditions:* catalyst (30 mg) in solvent (10 mL), substrate (2 mL), H_2 (60 atm) 90 °C, 1 h.

The stability of $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ in different immobilisation solvents has been studied by exploring the sequential reuse of the catalyst to hydrogenate benzene and the results are presented in Figure 3. Over a series of five batch reactions the turnovers remain effectively constant in all three solvents, although in water there are signs of a slight decrease in activity. $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ has also been used as a pre-catalyst for the hydrogenation of some arene substrates in water and chloride-containing and chloride-free [bmim][BF_4] and the results are presented in Table 3. For each arene substrate the turnover is lowest when immobilised in [bmim][BF_4] prepared by the metathesis route and greatest in chloride-free [bmim][BF_4]. This trend is once again likely to be due to catalyst deactivation by chloride ions present in the former solvent. The decrease in turnover number as the number of alkyl groups or chlorines attached to the ring increases is typical for homogeneous catalysed reductions of arenes. In water the active catalyst generated from $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ is believed to be a triruthenium cluster.[16] Mass spectrometric and spectroscopic studies would suggest that a similar species is generated in ionic liquids.

Conclusions

Arene hydrogenation is an important reaction in organic synthesis, the preparation of cleaner fuels and in paper production.[19] In this work we have shown that the mononuclear ruthenium complex $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$ acts as pre-catalyst for the hydrogenation of arene substrates. It dissolves in water and ionic liquids, but unless the ionic liquid is free from halide impurities the ionic liquids offer little advantage, in terms of activity and reusability, over water. This is in spite of the advantageous substrate-product solubility properties offered by the ionic liquid. Other pre-catalysts used in hydrogenations have been shown to be less active in ionic liquids than water, but in contrast to the pre-catalyst used here, these catalysts react with water to form the active catalyst.[20]

Experimental Section

The ionic liquids containing chloride impurities were made according to the literature method[4] and then filtered through neutral alumina prior to use. Deionised water was used without the addition of pH buffers or phase-transfer reagents. The chloride-free [bmim][BF_4] was made using a modified literature method (see below). The complexes $[H_4Ru_4(\eta^6\text{-}C_6H_6)][BF_4]_2$[13a] and $Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl_2$[21] were made according to the literature procedures. All other reagents were supplied by Aldrich and were used without further purification.

Electrospray mass spectra were obtained a VG Autospec instrument. NMR spectra were recorded on a Bruker DRX-400 spectrometer with ^1H at 400.13, ^{31}P at 161.98 and ^{13}C at 100.1 MHz. ^1H NMR chemical shifts are reported in ppm relative to residual ^1H signals in the deuterated solvents ($CDCl_3$, $\delta = 7.29$), $^{31}P\{^1H\}$ NMR spectra are reported in ppm downfield of an external 85% solution of phosphoric acid. All hydrogenation products were analysed by NMR and/or gas chromatography using a Varian gas chromatograph with a capillary carbowax column (30 m) using injection, oven and detector temperatures 10–30 °C above the boiling points of the substrate/product being studied.

Preparation of Chloride-Free [bmim][BF_4]

1-Butylimidazole (5 mL) was added dropwise to a rapidly stirred sample of trimethyloxonium tetrafluoroborate (1 mol equiv.) cooled to -78 °C over a period of 10 min. After the initial vigorous evolution of gas had ceased, the reaction mixture was allowed to warm to room temperature. Any residual dimethyl ether by-product was removed under high vacuum. The product was passed through activated charcoal and alumina columns to afford colourless [bmim][BF_4] ionic liquid in quantitative yield.

Spectroscopic data for [bmim][BF_4]: $ESMS^+$: $m/z = 139$ $[bmim]^+$; $ESMS^-$: $m/z = 87$ $[BF_4]^-$; ^1H NMR ($CDCl_3$): $\delta = 8.76$ (s, 1H), 7.51 (m, 2H), 4.24 (q, $J = 4.24$ Hz, 2H), 3.99 (s, 3H), 1.90 (quintet, $J = 7.28$ Hz, 2H), 1.39 (sextet, $J = 7.28$ Hz, 2H), 0.97 (t, $J = 7.28$ Hz, 3H); ^{13}C NMR (DEPT, $CDCl_3$): $\delta = 135.46$ (CH), 123.23 (CH), 121.94 (CH), 49.92 (CH_2), 35.50 (CH_3), 31.31 (CH_2), 18.86 (CH_2), 12.72 (CH_3) ppm; anal.: found (calcd.) C 41.44 (42.51) H 7.33 (6.69) N 12.03 (12.39) Cl 0.00 (0.00)%.

Hydrogenation Reactions

All hydrogenations were carried out in a Parr stainless steel autoclave (300 mL) fitted with a PTFE liner. The catalyst was added directly to the autoclave and the solvent was added. The autoclave was then sealed and purged with nitrogen and the reaction substrate was then added through the liquid inlet port *via* a syringe. The autoclave was then purged thoroughly with hydrogen gas (99.9995% purity) and the appropriate reaction pressure was then set at room temperature. The autoclave was then heated to the required reaction temperature and stirring was commenced for the period required. Once the desired time period had elapsed, the stirring was stopped and the autoclave allowed to cool before releasing the pressure. Substrate and catalyst layers were separated in a separating funnel.

Acknowledgements

We would like to thank the Royal Society for a University Research Fellowship (PJD), the University of York for financial support (DJE) and the University of Waikato for a travel grant (WH).

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