Arene hydrogenation in a room-temperature ionic liquid using a ruthenium cluster catalyst

Paul J. Dyson,[a] **David J. Ellis,**[b] **David G. Parker**[c] **and Thomas Welton**[b]

[a] *Department of Chemistry, The University of York, Heslington, York, UK YO10 5DD. E-mail: pjd14@york.ac.uk*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: t.welton@ic.ac.uk*
[c] *ICI Group R & T Affairs, PO Box 90, Wilton Centre, Middlesbrough, Cleveland, UK TS90 8JE*

The air and moisture stable system [bmim][BF$_4$]–[Ru$_4$(η^6-C$_6$H$_6$)$_4$][BF$_4$] {[bmim]$^+$ = 1-butyl-3-methylimidazolium cation} presents a novel medium for conducting hydrogenations of arenes; the environmental problems associated with related aqueous–organic biphasic regimes are eliminated.

The heterogenisation of homogenous catalysts is rapidly becoming an important area of chemistry.[1] It is hoped that the advantages of both homogeneous (greater efficiency, all metal centres being involved in the process) and heterogeneous (ease of catalyst separation, greater selectivity) catalysts can be combined in one system. One increasingly attractive route to greater catalyst separation exploits the use of biphasic liquid reaction systems.[2,3] Not surprisingly, aqueous–organic biphasic systems have emerged as an important class of catalysts and have found several industrial applications.[4] However, the method is not without problems; it precludes the use of water sensitive catalysts and reagents and, from an environmental perspective, trace amounts of organic compounds in water are notoriously difficult to remove.

An alternative system that will allow the use of water sensitive reagents and catalysts and solves some of the containment problems associated with aqueous–organic systems is that based on biphasic ionic liquid–organic systems. The development of a variety of air and moisture stable ionic liquids in recent years has lead to their deployment in a number of processes.[4] Building on our previous results with the chloroaluminate(III) ionic liquids,[5] we have been investigating the [bmim][BF$_4$] ionic liquid {[bmim]$^+$ = 1-butyl-3-methylimidazolium cation}, which has received some attention as a solvent for the hydrogenation of olefins using Wilkinson's and related catalysts.[6] Whilst these catalysts are moderately effective they are deactivated by trace quantities of chloride ions remaining in the ionic liquid from its preparation.

The hydrogenation of arenes is an important industrial process, particularly for the generation of cleaner diesel fuels,[7] and is dominated by the use of heterogeneous catalysts. In an attempt to develop biphasic methodologies for the hydrogenation of arenes we describe herein the use of a [bmim][BF$_4$]–organic system. Many catalysts, especially neutral species, are not soluble in [bmim][BF$_4$] and therefore careful choice of catalyst is required. Ionic inorganic and organometallic compounds tend to be highly soluble in [bmim][BF$_4$] and for this reason we chose to investigate the cluster, [H$_4$Ru$_4$(η^6-arene)][BF$_4$]$_2$, which proved to be both soluble and stable. Clusters of this type were first reported by Maitlis and coworkers[8] and then later by Süss–Fink and coworkers who went on to fully characterise these intriguing electronically unsaturated cluster cations.[9] Süss-Fink and coworkers then went on to show that they could be used as catalyst precursors for the hydrogenation of fumeric acid and arenes under aqueous–organic biphasic conditions.[9–11] This provides an ideal opportunity to compare the two systems directly. Table 1 lists a number of biphasic hydrogenation reactions of arenes employing the [bmim][BF$_4$] ionic liquid and water with [H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$][BF$_4$]$_2$ as the catalyst precursor.†

The turnover frequencies obtained in the ionic liquid and aqueous regimes are similar. This would suggest that the active catalytic species is the same in both systems. It has been clearly shown that [H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$]$^{2+}$ can oxidatively add hydrogen to give [H$_6$Ru$_4$(η^6-C$_6$H$_6$)$_4$]$^{2+}$, which is the hydrogenating species.[10] This contrasts with many cluster-based catalyst precursors that are believed to fragment into mononuclear species during reaction.[12] Few other effective hydrogenation catalysts are known and most of these cannot be used in biphasic processes and they tend to be air and moisture sensitive.[11,13] The turnover frequencies compare well to other homogeneous arene hydrogenation systems, such as [(η^6-C$_6$Me$_6$)$_2$Ru$_2$(μ-Cl)]Cl$_2$ which will hydrogenate benzene at 50 °C and 50 atm with a catalytic turnover of 246 mol mol^{-1} h^{-1}.[14] However, the main advantage of the ionic liquid–organic system arises from the ease of separation of the catalyst from the starting material/product stream and the subsequent purification of the solvent, allowing different compounds to be hydrogenated without contamination. The aqueous phase in a biphasic hydrogenation processes cannot be used for different arenes or returned to the environment without expensive treatment to remove trace quantities of organic compounds. Since the [bmim][BF$_4$] ionic liquid has no vapour pressure, organic compounds (and water) may be removed by merely placing the liquid under a high vacuum. Using this technique we have been able to repeatedly use the same batch of ionic liquid for the catalytic hydrogenation of several different arenes.

We are currently investigating the hydrogenation of functionalized arenes and heteroaromatics using a series of ionic clusters in the full range of available ionic liquids.

Table 1 Biphasic hydrogenation reactions of arenes in the [bmim][BF$_4$] ionic liquid and water with [H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$][BF$_4$]$_2$ as the catalyst precursor

Substrate	Reaction system	Reaction conditions	Conversion (%)	Catalytic turnover[a]/ mol mol^{-1} h^{-1}
Benzene	Ionic liquid	60 atm H$_2$, 90 °C, 2.5 h	91	364
	Water	60 atm H$_2$, 90 °C, 2.5 h	88	352
Toluene	Ionic liquid	60 atm H$_2$, 90 °C, 3 h	72	240
	Water	60 atm H$_2$, 90 °C, 3 h	78	261
Cumene	Ionic liquid	60 atm H$_2$, 90 °C, 2.5 h	34	136
	Water	60 atm H$_2$, 90 °C, 2.5 h	31	124

[a] Catalytic turnover is calculated on the assumption that the tetra-ruthenium catalyst does not break down into monoruthenium fragments which is entirely consistent with the data.

Notes and references

† The ionic liquid [bmim][BF$_4$] was prepared using the literature method.[6] [H$_4$Ru$_4$(η-C$_6$H$_6$)][BF$_4$]$_2$ is very soluble and stable in this ionic liquid and is readily characterised in the ionic liquid using ^{1}H NMR spectroscopy which revealed and spectrum similar to that in conventional solvents.

Hydrogenations were carried using a Parr stainless steel autoclave (300 ml) fitted with either a glass or PTFE liner. The catalyst [H$_4$Ru$_4$(η^6-C$_6$H$_6$)][BF$_4$]$_2$ was added together with the required amount of [bmim][BF$_4$] ionic liquid. The autoclave was then sealed and purged with hydrogen gas (99.9995% purity) and the appropriate reaction pressure was then set at room temperature. The autoclave was then sealed and heated to the required reaction temperature and stirred for the time period required. After reaction the contents were then separated into organic and ionic liquid phases and the products analysed by ^{1}H NMR spectroscopy and GC. The only products observed were the perhydrogenated cycloalkanes, there was no evidence for the formation of partially hydrogenated products or polymeric by-products.

1 J. H. Clark and D. J. Macquarrie, *Chem. Commun*., 1998, 853.

2 *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*, ed. B. Cornils and W. A. Herrmann, Wiley–VCH, Weinheim, 1998.
3 P. J. Dyson, D. J. Ellis and T. Welton, *Platinum Met. Rev*., in press.
4 Y. Chauvin, L. Mussmann and H. Olivier, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2698.
5 P. J. Dyson, M. C. Grossel, N. Srinivasan, T. Vine, T. Welton, D. J. Williams, A. J. P. White and T. Zigras, *J. Chem. Soc., Dalton Trans.*, 1997, 3465.
6 P. A. Z. Suarez, J. E. L. Dullis, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217.
7 A. Stanislaus and B. H. Cooper, *Catal. Rev.-Sci. Eng*., 1994, **36**, 73.
8 J. A. Cabeza, A. Nutton, B. E. Mann, C. Brevard and P. M. Maitlis, *Inorg. Chim. Acta*, 1986, **115**, L47.
9 G. Meister, G. Rheinwald, H. Stoecki-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, 1994, 3215.
10 L. Plasseraud and G. Süss-Fink, *J. Organomet. Chem*., 1997, **539**, 163.
11 E. G. Fidalgo, L. Plasseraud and G. Süss-Fink, *J. Mol. Catal. A*, 1998, **132**, 5.
12 B. F. G. Johnson, *Transition metal clusters*, Wiley, Chichester, 1980.
13 I. P. Rothwell, *Chem. Commun*., 1997, 1331 and references therein.
14 M. A. Bennett, T.-N. Huang and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 312.

Communication 8/07447J