APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 495–500 **Materials, Nanomaterials and Synthesis** **AOC**

Review

Synthesis of organometallics and catalytic hydrogenations in ionic liquids†

Paul J. Dyson*

Department of Chemistry, The University of York, Heslington, York YO10 5DD, UK

Received 12 November 2001; Accepted 15 February 2002

New solvents provide synthetic chemists with the opportunity of conducting new reactions and carrying out new processes. In this paper the author's own work on organometallic chemistry in ionic liquids is reviewed and placed in context with studies from other groups in this area. Specifically, the paper will describe the use of ionic liquids in the synthesis of organometallic complexes and clusters and the use of ionic liquids in hydrogenation catalysis. The synthesis and reactivity of ionic liquids with organometallic anions will also be discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: ionic liquid; organometallic; clusters; catalysis; hydrogenation

INTRODUCTION

Ionic liquids are often defined as ionic compounds that melt below 100 °C, although the ones of most use to synthetic chemists melt at room temperature or below. Many ionic compounds, or mixtures of ionic compounds, have melting points around 100 °C, but ionic compounds that are actually liquid at room temperature are comparatively rare. The first truly ionic liquid, $[EtNH_3][NO_3]$, with a melting point of 12 °C, was discovered in 1914.[1] About 30 years later the next ionic liquid was discovered; the liquid was composed of an alkylpyridinium cation with a tetrachloroaluminate(III) anion.[2] The newest class of ionic liquids, however, are based on 1,3-dialkylimidazolium cations; many of these have very low melting points, some considerably below 0 °C.[3] In order to achieve low melting points the two alkyl groups must be different, presumably because this lowers the symmetry of the cation and helps to prevent crystallization. The 1,3-dialkylimidazolium-based ionic liquids most frequently encountered in synthetic and catalytic applications incorporate a methyl group in combination with a C_2–C_9 alkyl chain. The physical properties of a wide range of these liquids are listed elsewhere,[4] but the general properties of ionic liquids that make them suited to chemical synthesis and catalysis include:

- they have no (or negligible) vapour pressure and, therefore, do not evaporate;
- they have favourable thermal properties;
- they dissolve many metal complexes, catalysts, organic compounds, and gases;
- they are immiscible with many organic solvents and water.

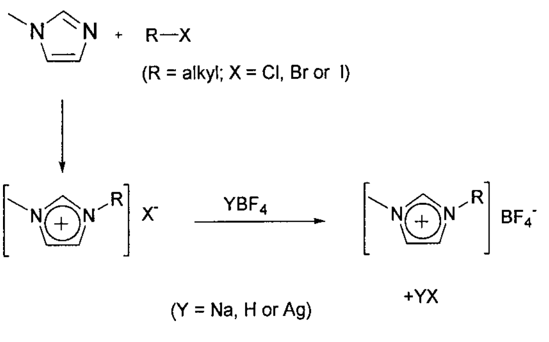
However, what really makes ionic liquids such fascinating solvents for synthetic chemists is that there is no limit to the number of different liquids that can be made, and, as our understanding of them increases, it should be possible to design specific ionic liquids for specific reactions and processes. For example, ionic liquids composed of 1,3-dialkylimidazolium cations interact with water in different ways according to the anion. With chloroaluminate anions, the resulting liquid is extremely water-sensitive; with the hexafluorophosphate anion the liquid is hydrophobic; and with the tetrafluoroborate anion the ionic liquid is hydrophilic. Furthermore, as the alkyl groups attached to the cation are increased in length, the amount of water that dissolves in the hydrophilic ionic liquid decreases. Based on this simple example, one can envisage how ionic liquids

---

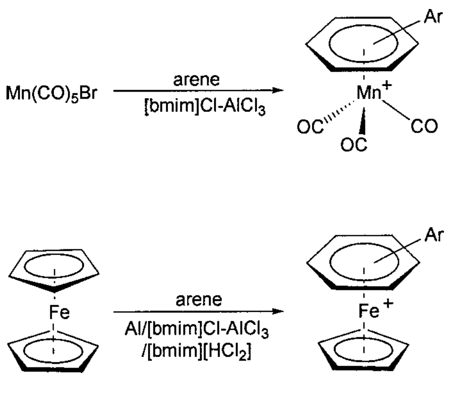
*Correspondence to: P. J. Dyson, Institut de chimie moléculaire et biologique, Ecole polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland.
E-mail: pjd14@york.ac.uk.

†This paper is based on work presented at the XIVth FECHEM Conference on Organometallic Chemistry held at Gdansk, Poland, 2–7 September 2001.

Contract/grant sponsor: EPSRC.
Contract/grant sponsor: ICI.



Scheme 1.



Scheme 2.

could be tailored to give desirable properties for specific reactions and processes.

This paper describes aspects of organometallic synthesis and hydrogenation catalysis conducted in ionic liquids. It includes a section on cluster synthesis in ionic liquids that has not been reported previously.

CLASSIFICATION OF 1,3-DIALKYLIMIDAZOLIUM-BASED IONIC LIQUIDS

Ionic liquids can be classified as either inert or reactive, depending on the type of anion present. This is not to say that the 1,3-dialkylimidazolium cation is completely unreactive. The proton in the 2-position is acidic, and under certain basic conditions it may be lost with the formation of a carbene. These carbenes have been trapped by reaction with metals (see below) and have also been found to be produced during certain catalytic reactions that require base.

Reactive ionic liquids contain anionic metal halides, such as the chloroaluminates, chlorocuprates, and chlorostannates. These ionic liquids are made from the direct reactions of the solid [cation]Cl and metal chloride, which collapse to form a liquid.[5,6] The identity of the anion present depends upon the stoichiometry (mole fraction) of the reactants used. When the mole fraction of [cation]Cl:$AlCl_3$ is 0.5 the $AlCl_4^-$ anion is essentially the only species present. If the mole fraction of $AlCl_3$ employed is greater than 0.5, then multinuclear species such as $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ are formed and the ionic liquid is referred to as (Lewis) acidic. When the mole fraction is less than 0.5 the ionic liquid is basic. For this reason, chloroaluminate ionic liquids are often written as [cation]Cl–$AlCl_3$, rather than [cation]$AlCl_4$. These features can be exploited in synthesis and catalysis and, in general, acidic ionic liquids have proved to be the most useful. Ionic liquids based on chlorocuprates are also prepared from the direct reaction of the [cation]Cl and CuCl.[7] Like the chloroaluminates, they also contain a complex mixture of anions, and several have been shown to be present, including $[CuCl_2]^-$, $[Cu_2Cl_3]^-$, and $[Cu_3Cl_4]^-$.

Inert ionic liquids are produced when anions such as BF_4^-, PF_6^-, or SbF_6^- are employed.[8] Many other anions have also been used, but these are among the most popular. These ionic liquids are made in exchange reactions (e.g. see Scheme 1). One of the main difficulties of the preparation is removing all the chloride by-product, and elaborate purification procedures have been devised.[9] The presence of chloride contamination can markedly affect the physical properties of the ionic liquid, such as melting point, density, and viscosity. In addition, the chemical properties of the ionic liquid can be affected by chloride, e.g. certain catalysts are deactivated by nucleophilic chloride ions.

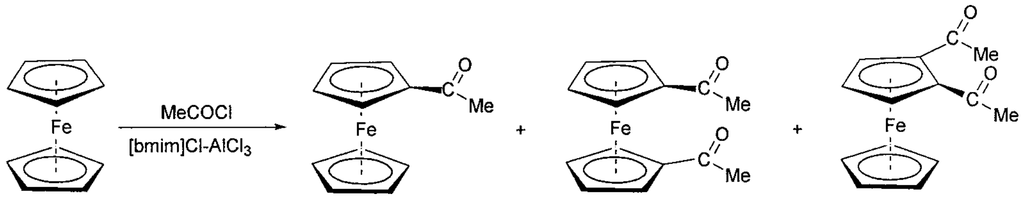
Although these ionic liquids are referred to as inert, the anions can react under certain conditions. In particular, the PF_6^- anion is prone to oxidation with the formation of HF, and care must be taken to avoid this problem.

ORGANOMETALLIC SYNTHESIS IN CHLOROALUMINATE IONIC LIQUIDS

As mentioned above, the chloroaluminate ionic liquid [bmim]Cl–$AlCl_3$, with a mole fraction of $AlCl_3 = 0.65$, contains significant concentrations of the Lewis acid $[Al_2Cl_7]^-$. The Lewis acidity of this ionic liquid has been exploited in the synthesis of organometallic compounds traditionally carried out in organic solvents in the presence of $AlCl_3$ (see Scheme 2).

The piano-stool complexes $[Mn(CO)_3(\eta\text{-arene})]^+$ are useful intermediates in organic synthesis.[10] They can be prepared in a number of ways, and perhaps the most straightforward route is the direct reaction between $Mn(CO)_5Br$ and an appropriate arene in an organic solvent containing a slurry of $AlCl_3$.[11] The $AlCl_3$ acts as a Lewis acid, removing the bromide ion, which initiates the formation of the Manganese–arene bond. We have shown that the organic solvent–$AlCl_3$ slurry may be replaced with acidic [bmim]Cl–$AlCl_3$ to afford $[Mn(CO)_3(\eta\text{-arene})]^+$ products in good yield.[12]

Although less widely used in organic synthesis, the sandwich complexes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$ have attracted



Scheme 3.

much interest.[13] Typically, these complexes are made from the direct reaction of ferrocene, with the arene in an organic solvent containing $AlCl_3$ and aluminium powder.[14] A Brønsted acid is also required to initiate loss of one of the cyclopentadienyl rings of the ferrocene, and in some cases the fortuitous presence of water produced this acid, *viz.* $HAlCl_4$, from water and aluminium trichloride. In the alternative synthesis using acidic [bmim]Cl–$AlCl_3$ in place of an organic solvent, the Brønsted acid [bmim][HCl_2] is used to initiate loss of the cyclopentadienyl ring.[15]

Isolation of both the manganese and iron complexes from the acidic ionic liquid involves the addition of an aqueous solution of HBF_4 that also destroys the ionic liquid. Though this is clearly undesirable, the high reaction rates and yields that can be obtained by virtue of the Lewis acid constituting the solvent may be advantageous.

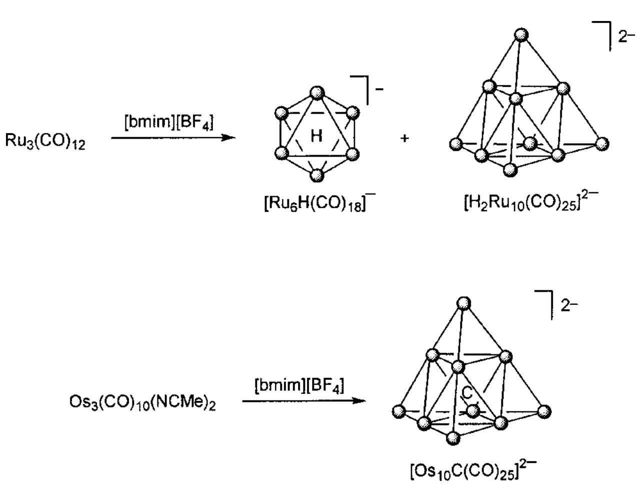
The acylation of ferrocene has also been conducted in acidic choroaluminate ionic liquids. In [emim]I–$AlCl_3$, ferrocene reacts with acylating reagents $(RCO)_2O$ and RCOCl (where R = Me, Ph, Pr, nBu and tBu) to afford mono-substituted and 1,1′-bis-substituted products.[16] Under slightly different conditions, using acidic [bmim]Cl–$AlCl_3$ and ethanoyl chloride as the acylating reagent, a further product, 1,2-diethanoylferrocene, is isolated in low yield (see Scheme 3).[17]

The other main class of organometallic complexes that have been prepared in chloroaluminate (and other ionic liquids) are carbene complexes, since the acidic proton on the 2-position of the imidazolium cation may be removed with base to form a carbene. For example, heating a mixture of $PtCl_2$ and $PtCl_4$ under a high pressure of ethylene affords *cis*-Pt(η-C_2H_4)(1-ethyl-3-methylimidazol-2-ylidene)Cl_2 in moderate yield.[18,19] Carbene complexes may also be isolated from inert ionic liquids and have also been identified during palladium-catalysed Heck reactions that employ base as a co-catalyst.[20,21]

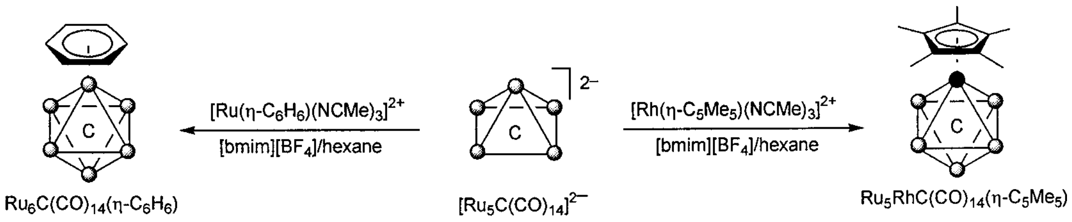
CLUSTER SYNTHESIS IN TETRAFLUOROBORATE IONIC LIQUIDS

High temperatures can be reached in ionic liquids because they do not evaporate, and this property has been exploited in the synthesis of transition metal carbonyl cluster compounds, as shown in Scheme 4. The thermolysis of $Ru_3(CO)_{12}$ in [bmim][BF_4] at 250 °C for several hours affords $[Ru_6H(CO)_{18}]^-$ and $[H_2Ru_{10}(CO)_{25}]^{2-}$. These reactions suggest that the ionic liquid behaves more like an alcohol than a hydrocarbon solvent, although it is not clear from where the hydride ligands originate. The polarity of [bmim][BF_4] is comparable to that of methanol.[22] Ruthenium-hydride clusters like these are conveniently made from thermolysis reactions in methanol,[23] whereas related reactions of $Ru_3(CO)_{12}$ in hydrocarbon solvents give ruthenium-carbide clusters.[24,25]

Interestingly, the high nuclearity decaosmium cluster, $[Os_{10}C(CO)_{24}]^{2-}$, can also be prepared from $Os_3(CO)_{10}(NCMe)_2$ in high yield. Usually, this cluster is isolated from solid-state pyrolysis reactions,[26] which suggests that the inert ionic liquid mimics the pyrolysis environment to some extent. At this stage it is not possible to say why the thermolysis with ruthenium affords the hydride-containing products whereas the corresponding reaction with osmium gives the carbide-containing product. However, in cluster chemistry it is well known that the type of product isolated from a thermolysis reaction is very solvent dependent. Recently, it has been found that these types of cluster reaction can be studied by electrospray mass spectrometry in order to optimize the yield of the products.[27,28] Attempts to apply this procedure to reactions conducted in ionic liquids, either neat or by dilution in electrospray-friendly solvents, proved unsuccessful, although it has been shown that ionic



Scheme 4.



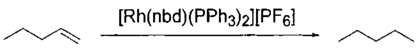
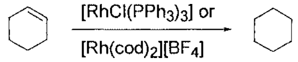
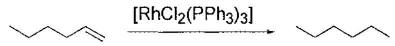
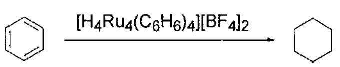
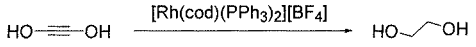
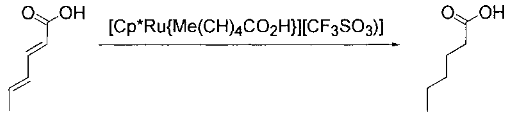
Scheme 5.

liquids can be used as matrices for laser desorption mass spectrometry.[29]

Ionic coupling reactions are widely used in cluster chemistry as a way to build up clusters in a step-wise fashion, and also to introduce ligands other than CO in a controlled manner. The pentaruthenium dianionic cluster $[Ru_5C(CO)_{14}]^{2-}$ undergoes ionic coupling with a range of mononuclear dicationic species to afford neutral hexaruthenium clusters.[30,31] Traditionally, these reactions are carried out in polar organic solvents, typically CH_2Cl_2. For example, $[Ru_5C(CO)_{14}]^{2-}$ reacts with $[Ru(\eta\text{-}C_6H_6)(NCMe)_3]^{2+}$ or $[Rh(\eta\text{-}C_5H_5)(NCMe)_3]^{2+}$ in dichloromethane under reflux to afford the hexanuclear clusters $Ru_6C(CO)_{14}(\eta\text{-}C_6H_6)$[32] and $Ru_5RhC(CO)_{14}(\eta\text{-}C_5H_5)$.[33] We have repeated these reactions using the two-phase ionic liquid–organic approach (Scheme 5). The starting materials are dissolved in [bmim][BF$_4$] and stirred gently. As the neutral product is formed it migrates into the organic phase and is isolated without the need for any further purification. Although the reactions of clusters in ionic liquids reveal some interesting possibilities, the main aim is to be able to make new compounds, and, as yet, this goal has not been reached.

Clearly, there is considerable potential for ionic liquids in the synthesis of transition metal complexes. The ionic coupling reactions appear to be particularly suited to these types of solvent, and perhaps this is where most benefits lie. One can envisage ionic protecting groups in organic and organometallic intermediates that, once removed to give the desired (neutral) product, release the product into the organic phase, allowing its immediate extraction and purification in a single step.

Table 1. Hydrogenation of alkene, arene, and alkyne substrates in ionic liquids using transition metal catalysts and H_2

Solvent	Hydrogenation reaction/catalyst	Comment	Ref.
[bmim][BF$_4$] or [bmim][PF$_6$] or [bmim][SbF$_6$]		Considerably higher turnover frequencies compared to acetone	7
[bmim][BF$_4$] or [bmim][PF$_6$]		Good recovery	39
[bmim][BF$_4$]		Slightly higher turnover frequencies compared with aqueous–organic system	40
[bmim][BF$_4$]	acrylonitrile-butadiene rubber $\xrightarrow{[RuHCl(CO)(PCy_3)_2]}$ hydrogenated acrylonitrile-butadiene rubber	Achieved under mild conditions	41
[bmim][BF$_4$]		Slightly higher turnover frequencies compared with aqueous–organic system	42
[bmim][BF$_4$]		Two-phase to one-phase system with water	43
[bmim][PF$_6$]		Activation energies determined	44

HYDROGENATION CATALYSIS IN IONIC LIQUIDS

The first reports of transition-metal-catalysed reactions in ionic liquids were carried out in acidic chloroaluminates.[34,35] Since the chloroaluminates are extremely air- and moisture-sensitive, catalytic studies have tended to move away from these liquids, to those that contain more inert anions, such as BF_4^- and PF_6^-. Although ionic liquids have been used as biphasic support solvents in a wide range of different catalysed reactions,[36–38] only hydrogenation reactions will be discussed here, as this is where the author's own interests lie. Key hydrogenation reactions carried out in ionic liquids that do not involve prochiral or chiral substrates are summarized in Table 1. Asymmetric reductions have also been demonstrated using rhodium and ruthenium catalysts incorporating chiral bis-phosphine ligands.[7,45–47]

Some general features of 1,3-dialkylimidazolium ionic liquids with BF_4^- or PF_6^- anions that are useful in hydrogenation catalysis have emerged in the last few years. First, compared with water, they dissolve high concentrations of hydrogen, which leads to increased reaction rates in biphasic reactions. Second, they are non-nucleophilic and present an inert environment that often increases the lifetime of the catalyst and subsequent reaction rates.

Our own interests are largely concerned with the hydrogenation of aromatic substrates to their corresponding cyclohexanes, a process important for the production of cleaner fuels[48] and prevention of yellowing of paper.[49] The ruthenium-cluster $[H_4Ru_4(\eta\text{-}C_6H_6)_4]^{2+}$ is highly soluble in ionic liquids; it is also a precatalyst that has been used to hydrogenate aromatic compounds under aqueous–organic biphasic conditions.[50–52] The active catalyst is $[H_6Ru_4(\eta\text{-}C_6H_6)_4]^{2+}$, which is readily formed from $[H_4Ru_4(\eta\text{-}C_6H_6)_4]^{2+}$ under an atmosphere of hydrogen. We have compared the activity of this catalyst in water and $[bmin][BF_4]$ ionic liquid using neat arene substrates without any co-solvent.[42] The turnover frequencies obtained in the ionic liquid are higher than those obtained in the aqueous system, arising from the higher concentration of dissolved hydrogen gas and the arene substrates in the ionic liquid compared with water. The solubility of the products is also lower than that of the starting materials in the $[bmim][BF_4]$ ionic liquid, which facilitates separation.

We have found that ionic liquids are not always superior to other solvents for conducting hydrogenation reactions. The ruthenium clusters $Ru_3(CO)_{12-x}(tpptn)_x$ ($x = 1$–3) and $H_4Ru_4(CO)_{11}(tpptn)$ (where $tpptn = P\{m\text{-}C_6H_4SO_3Na)_3)$[53] and the cubane[54] $[Ru_4(\eta^6\text{-}C_6H_6)_4(OH)_4]^{4+}$ catalyse hydrogenation of alkene and arene substrates in water, but they are far less effective catalysts in ionic liquids. This is because the water reacts with the clusters and cubane to generate the active catalyst species, and a similar process cannot take place in dry ionic liquids.

All the biphasic ionic liquid–organic processes illustrated in Table 1, except that taken from Ref. 43, involve rapidly mixing the two phases so that they form an emulsion. The reaction is not truly homogeneous, and the rate of reaction depends on the rate at which the reaction is stirred. We have developed an ionic liquid–water catalyst system that undergoes a temperature-controlled, and reversible, two-phase–single phase transition.[43] At room temperature the ionic liquid 1-octyl-3-methylimidizolium tetrafluoroborate, $[omim][BF_4]$, forms a separate layer to water. On heating to 80 °C, the two phases become completely miscible, allowing homogeneous reactions to occur. Using this solvent system, the water-soluble substrate butyne-1,4-diol was hydrogenated with $[Rh(\eta\text{-}C_7H_8)(PPh_3)_2][BF_4]$ as the catalyst. The reaction was carried out at 80 °C, giving a homogeneous single-phase solution; on cooling to room temperature, the two phases reform, with the ionic liquid phase containing the catalyst and the aqueous phase containing a mixture of 2-butene-1,4-diol and butane-1,4-diol that were extracted without contamination of the catalyst. The rhodium(I) catalyst was selected for this reaction as it is highly ionic-liquid soluble (since it is a salt) and it is also hydrophobic by virtue of the phosphine ligands.

ORGANOMETALLIC IONIC LIQUIDS

Ionic liquids containing some rather exotic anions have been prepared; notable examples include gold chloride,[55] carboranes,[56] and transition metal carbonyl[57] anions. The transition-metal-carbonyl-based ionic liquid $[bmim][Co(CO)_4]$ catalyses the debromination of 2-bromoacetophenones to their corresponding ketones. Such a system in which the ionic liquid is also the catalyst could prove to be a very clean way of conducting reactions, and there are many anionic compounds that could be converted into ionic liquids by combining them with 1,3-dialkylimidazolium cations.

Acknowledgements

I would like to thank Dr Tom Welton (Imperial College) who introduced me to ionic liquids, and with whom I continue to collaborate, and the students whose names appear in the references who conducted the work. I would also like to thank the Royal Society for a University Research Fellowship and the EPSRC and ICI for financial support in ionic liquid chemistry.

REFERENCES

1. Sugden S and Wilkins H. *J. Chem. Soc.* 1929; 1291, and references cited therein.
2. Hurley FH and Wier Jr TP. *J. Electrochem. Soc.* 1951; **98**: 207.
3. Wilkes JS, Levisky JA, Wilson RA and Hussey CL. *Inorg. Chem.* 1982; **21**: 1263.
4. Hagiwara R and Ito Y. *J. Fluorine Chem.* 2000; **105**: 221.
5. Øye HA, Jagtoyen M, Oksefjell T and Wilkes JS. *Mater. Sci. Forum* 1991; **73–75**: 183.
6. Bonhôte P, Dias A-P, Papageoriou N, Kalyanasundaram K and Grätzel M. *Inorg. Chem.* 1996; **35**: 1168.
7. Chauvin Y and Olivier-Bourbigou H. *CHEMTECH* 1995; **25**: 26.

8. Chauvin Y, Mußmann L and Olivier H. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 2698.
9. Seddon KR, Stark A and Torres MJ. *Pure Appl. Chem.* 2000; **72**: 2275.
10. Pearson AJ and Bruhn PR. *J. Org. Chem.* 1991; **56**: 7092.
11. Winkhaus G, Pratt L and Wilkinson G. *J. Chem. Soc.* 1961; 3807.
12. Crofts D, Dyson PJ, Sanderson KM, Srinivasan N and Welton T. *J. Organomet. Chem.* 1999; **573**: 292.
13. Bambridge K and Roberets RMG. *J. Organomet. Chem.* 1991; **401**: 125.
14. Neseyanov AN, Vol'kenau NA and Bolesova IN. *Tetrahedron Lett.* 1963; 1725.
15. Dyson PJ, Grossel MC, Srinivasan N, Vine T, Welton T, Williams DJ, White AJ and Zigras T. *J. Chem. Soc., Dalton Trans.* 1997; 3465.
16. Stark A, MacLean BL and Singer RD. *J. Chem. Soc., Dalton Trans.* 1999; 63.
17. Crofts D, Dyson PJ, Sanderson KM, Srinivasan N and Welton T. In *Advances in Molten Salts: From Structural Aspects to Waste Processing*, Gaune-Escard M (ed.). Begell House Inc.: New York, 1999; 624–633.
18. Hasan M, Kozhevnikov IV, Siddiqui MRH, Steiner A and Winterton N. *J. Chem. Res. (S)* 2000; 392.
19. Hasan M, Kozhevnikov IV, Siddiqui MRH, Femoni C, Steiner A and Winterton N. *Inorg. Chem.* 2001; **40**: 795.
20. Xu L, Chen W and Xiao J. *Organometallics* 2000; **19**: 1123.
21. Mathews CJ, Smith PJ, Welton T, White AJP and Williams DJ. *Organometallics* 2001; **20**: 3848.
22. Carmichael AJ and Seddon KR. *J. Phys. Org. Chem.* 2000; **13**: 591.
23. Bailey PJ, Charalambous E, Hoyle J, Johnson BFG, Lewis J and McPartlin M. *J. Chem. Soc., Chem. Commun.* 1990; 1443.
24. Braga D, Grepioni F, Dyson PJ, Johnson BFG, Frediani P, Bianchi M and Piacenti F. *J. Chem. Soc., Dalton Trans.* 1992; 2565.
25. Dyson PJ, Johnson BFG and Martin CM. *Coord. Chem. Rev.* 1998; **175**: 59.
26. Gade LH, Johnson BFG, Lewis J, McPartlin M, Powell HR, Raithby PR and Wong WT. *J. Chem. Soc., Dalton Trans.* 1994; 521.
27. Dyson PJ, Johnson BFG, McIndoe JS and Langridge-Smith PRR. *Inorg. Chem.* 2000; **39**: 2430.
28. Dyson PJ, Hearley AK, Johnson BFG, McIndoe JS and Langridge-Smith PRR. *Organometallics* 2001; **20**: 3970.
29. Armstrong DW, Zhang L-K, He L and Gross ML. *Anal. Chem.* 2001; **73**: 3679.
30. Braga D, Dyson PJ, Grepioni F and Johnson BFG. *Chem. Rev.* 1994; **94**: 1585.
31. Dyson PJ. *Adv. Organomet. Chem.* 1999; **43**: 43.
32. Dyson PJ, Johnson BFG, Reed D, Braga D, Grepioni F and Parisini E. *J. Chem. Soc., Dalton Trans.* 1993; 2817.
33. Bailey PJ, Blake AJ, Dyson PJ, Johnson BFG, Lewis J and Parisini E. *J. Organomet. Chem.* 1993; **452**: 175.
34. Chauvin Y, Gilbert B and Guibard I. *J. Chem. Soc., Chem. Commun.* 1990; 1715.
35. Carlin RT and Osteryoung RA. *J. Mol. Catal.* 1990; **63**: 125.
36. Welton T. *Chem. Rev.* 1999; **99**: 2071.
37. Wesserscheid P and Keim K. *Angew. Chem. Int. Ed. Engl.* 2000; **39**: 3773.
38. Sheldon RA. *Chem. Commun.* 2001; 2399.
39. Suarez PAZ, Dullius JEL, Einloft S, de Souza RF and Dupont J. *Polyhedron* 1996; **15**: 1217.
40. Suarez PAZ, Dullius JEL, Einloft S, de Souza RF and Dupont J. *Inorg. Chim. Acta* 1997; **255**: 207.
41. Müller LA, Dupont J and de Souza RF. *Macromol. Rapid Commun.* 1998; **19**: 409.
42. Dyson PJ, Ellis DJ, Parker DG and Welton T. *Chem. Commun.* 1999; 25.
43. Dyson PJ, Ellis DJ and Welton T. *Can. J. Chem.* 2001; **79**: 705.
44. Steines S, Wasserscheid P and Drießen-Hölscher B. *J. Prakt. Chem.* 2000; **342**: 348.
45. Monteiro AL, Zinn FK, de Souza RF and Dupont J. *Tetrahedron Asymm.* 1997; **8**: 177.
46. Berger A, de Souza RF, Delgado MR and Dupont J. *Tetrahedron Asymm.* 2001; **12**: 1825.
47. Brown RA, Pollet P, McKoon E, Eckert CA, Liotta CL and Jessop PG. *J. Am. Chem. Soc.* 2001; **123**: 1254.
48. Stanislaus A and Cooper BH. *Catal. Rev.* 1994; **36**: 75.
49. Hu TQ, James BR, Rettig S and Lee C-L. *Can. J. Chem.* 1997; **75**: 1234.
50. Meister G, Rheinwald G, Stoecki-Evans H and Süss-Fink G. *J. Chem. Soc., Dalton Trans.* 1994; 3215.
51. Plasseraud L and Süss-Fink G. *J. Organomet. Chem.* 1997; **539**: 163.
52. Fidalgo EG, Plasseraud L and Süss-Fink G. *J. Mol. Catal. A* 1998; **132**: 5.
53. Dyson PJ, Ellis DJ, Parker DG and Welton T. *J. Mol. Catal. A: Chem.* 1999; **150**: 71.
54. Dyson PJ, Russell K and Welton T. *Inorg. Chem. Commun.* 2001; **4**: 571.
55. Hasan M, Kozhevnikov IV, Siddique MRH, Steiner A and Winterton N. *Inorg. Chem.* 1999; **38**: 5637.
56. Larsen AS, Holbrey JD, Tham FS and Reed CA. *J. Am. Chem. Soc.* 2000; **122**: 7264.
57. Brown RJC, Dyson PJ, Ellis DJ and Welton T. *Chem. Commun.* 2001; 1862.