Abstract. A novel fluorous room-temperature ionic liquid, 1-butyl-3-methyl-imidazolium tetrakis{4-(dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl)phenyl}borate (1), was used as a solvent for the homogeneous hydrosilylation of 1-octene catalysed by a fluorous version of Wilkinson’s catalyst. The catalyst was recycled by biphasic separation with an average retention of catalyst activity of 94%. As opposed to other ionic liquids, 1 exhibits high miscibility with apolar compounds such as alkenes and resembles fluorous solvents in its phase behaviour with organic solvents.

7.1 Introduction

The use of air- and water-stable imidazolium-based ionic liquids as a solvent for transition-metal catalysts has received growing attention since their preparation was first reported in 1992. This interest was particularly sparked by the fact that these ionic liquids (IL’s) are highly stable and show limited miscibility with most of the common organic solvents, offering potential for efficient catalyst recovery by facile phase separation. This approach has been successfully applied in a wide range of catalytic processes, for example, hydrogenation, hydroformylation, Heck reactions, oligomerisations, epoxidations, and polymerisations. A serious limitation for the application of IL’s is the poor solubility of apolar organic substrates, especially saturated hydrocarbons and in some cases neutral metal catalysts (vide infra), in these liquids. As in aqueous biphasic systems, the limited solubility of substrates and catalysts can result in reduction or even complete loss of activity when compared with truly homogeneous conditions.

The nature of ionic liquids, being composed of discrete anions and cations, makes it possible to fine-tune both lipophilicity and polarity through the choice of suitable cation-anion combinations. In view of the considerations above, we reasoned that it would be interesting to design IL’s with improved solvating properties for apolar compounds, as this might allow more efficient catalysis with apolar substrates. In this respect, the introduction of perfluoroalkyl moieties as lipophilic groups could be of especial interest, as this could lead to IL’s exhibiting fluorous biphasic behaviour, i.e., biphasic conditions at lower temperatures and monophasic at higher temperatures. Such a fluorous ionic liquid could well be an alternative to perfluoroalkane-based fluorous biphasic systems (FBS’s), the fluorous phase of which appears to be less suitable for the immobilisation of ionic catalysts.

In Chapter 3 of this thesis the synthesis of highly fluorous tetraphenylborate anions was described. In this chapter the use such an anion in the preparation of an imidazolium borate ionic liquid, and performance thereof, in fluorous biphasic catalyst recycling is presented.

7.2 Results and Discussion

Synthesis and Physical Properties of \([\text{BMIm}]\text{[B}(\text{C}_6\text{H}_4\{\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}-4)\text{]}\). The imidazolium salt \([\text{BMIm}]\text{[B}(\text{C}_6\text{H}_4\{\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}-4)\text{]}\) (BMIm = 1-butyl-3-methylimidazolium) was obtained by metathesis of \([\text{BMIm}]\text{I}\) and Na[B(C6H4{SiMe2(CH2CH2C6F13)}-4)] in CH2Cl2. The resulting salt is an air-stable, non-hygroscopic and viscous yellow liquid at 25 °C (ρ = 1.38 g/mL) that is transformed into a glasslike substance at sub-ambient temperatures. No distinct phase-transition enthalpy could be determined using DSC; however, during repeated heating cycles a slight change in the slope of the DSC trace was observed, pointing to a possible glass transition at −10 °C. The
conductivity of neat 1 is $1.9 \times 10^{-5}$ S m$^{-1}$ at 25 °C, and it increases as viscosity decreases at elevated temperatures ($1.1 \times 10^{-3}$ S m$^{-1}$ at 95 °C). These values are low for a room-temperature IL, which usually have conductivities in the range of 0.1 - 1.0 S m$^{-1}$. The relative polarity of 1 was assessed using the solvatochromatic dye Nile Red. Measurement of $\lambda_{\text{abs max}}$ of Nile Red dissolved in 1 and determination of the molar transition energy ($E_{\text{NR}}$) for this dye in the solution showed that 1 can be considered as a polar solvent (Figure 1).

**Figure 1.** $E_{\text{NR}}$ values for [C$_{10}$-MIm]BF$_4$ (C$_{10}$ = 1-decyl) and [BMIm]X ionic liquids and common organic solvents. $E_{\text{NR}} = (hcN_A/\lambda_{\text{max}}) \times 10^6$, where $h$ is Planck’s constant, $c$ is the speed of light, $N_A$ is Avogadro’s number and $\lambda_{\text{max}}$ is the wavelength at maximum absorbance (nm).

Ionic liquid 1 is insoluble in water but very soluble in polar and to some extent even in apolar organic solvents (Table 1). As alkenes are important substrates in various catalytic processes, the behaviour of various mixtures of 1-alkenes and 1 was also studied. The solubilities of 1-hexene (16.7 mol/mol, $9.3 \times 10^2$ g/L) and 1-octene (4.7 mol/mol, $3.5 \times 10^2$ g/L) in 1 at 25 °C are much higher than the solubility of these alkenes in the closely related IL’s [BMIm]PF$_6$ (1-octene: 0.026 mol/mol)$^{10}$ and [MeN(n-Hex)$_3$]Tos (1-octene: 1.5
Table 1: Solubility of [BMIm][B{C₆H₄(SiMe₂CH₂CH₂C₆F₁₃)-4}₄] (1) in various solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>DN⁴</th>
<th>dielectric constant (ε_r)ᵇ</th>
<th>solubility (g/L)ᶜ</th>
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<tbody>
<tr>
<td>FC-72</td>
<td></td>
<td>1.6ᵈ</td>
<td>3.7 × 10⁻¹</td>
</tr>
<tr>
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<td>2.3</td>
<td>8.0</td>
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<tr>
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<td>1.9 × 10¹</td>
</tr>
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</tr>
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</tr>
<tr>
<td>H₂O</td>
<td>18.0</td>
<td>78.4</td>
<td>&lt; 0.2</td>
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</table>

⁴ Donor number, taken from ref. 11. ⁵ Taken from ref. 11. ⁶ Solubility in g/L of pure solvent at 25 °C. ⁷ A mixture of perfluorohexanes, the ε_r given is that of perfluoro-n-hexane, a major component of FC-72.

Furthermore, mixtures of 1-hexene or 1-octene and 1 (φᵥ(1-alkene) = 0.63) yielded a biphasic system at room temperature, but displayed low consolute temperatures (T = 60 °C and 84 °C, respectively). Furthermore, when assessing the miscibility of 1 with toluene, a critical temperature (T_c) of 62 °C at a toluene volume fraction (φᵥ(toluene)) of 0.90 was found (Figure 2).

![Figure 2. Phase diagram of [BMIm][B(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃})₄] and toluene.](image)

The physical properties of 1 differ considerably from those of the ionic liquids reported previously. Whereas other [BMIm]-based IL’s display polarities close to that of methanol,³ and have considerable solubility in water (exceptions are [BMIm]PF₆ and [BMIm][(CF₃SO₂)₂N])³,⁴ and essentially no solubility in alkanes,¹,⁴ the polarity and solubility of 1 correspond with those for less polar solvents. It is well known that an increase
solubility of 1 correspond with those for less polar solvents. It is well known that an increase in the size of the anion is accompanied by a decrease in the polarity of ionic liquids.\textsuperscript{13a} Our results correspond with this trend, 1 being less polar than [BMIm]PF\textsubscript{6} or [C\textsubscript{10}MIm]BF\textsubscript{4} (C\textsubscript{10}MIm = 1-decyl-3-methyl-imidazolium). The determined value for $E_{\text{NR}}$ shows a polarity for 1 that is comparable to that of acetone and diethyl ether, which corresponds with the data in Table 1; the solubility of 1 is highest in these solvents. Furthermore, large ion size in general results in high viscosity, which in turn causes low conductivity.\textsuperscript{8} Both these properties were observed for 1.

Ionic liquids, in general, are highly soluble in polar solvents, especially in MeOH,\textsuperscript{4a} and virtually insoluble in apolar solvents.\textsuperscript{4} The high solubility in proton-donor solvents, e.g., H\textsubscript{2}O and MeOH, is predominantly the result of hydrogen-bond formation between the anions of the ionic liquid and the solvent.\textsuperscript{14} As the fluorous anion of 1 offers little possibility for hydrogen-bonding interactions, low solubility in water and, to some extent, methanol results. On the other hand, the lipophilic anion, which moderates the ionic character of 1, enhances its solubility in apolar solvents. As a result, in 1 the solvent properties of both an ionic liquid and a fluorous solvent are combined. The low critical temperature of mixtures of 1 with toluene confirms this observation.\textsuperscript{15}

**Recycling of a Fluorous Wilkinson's Catalyst Dissolved in Fluorous Ionic Liquid**

1. To assess the suitability of 1 as a medium for immobilisation of a homogeneous catalyst, the rhodium-catalysed hydrosilylation of 1-octene was studied.\textsuperscript{16} Wilkinson’s complex, [RhCl(PPh\textsubscript{3})\textsubscript{3}], which is a well-known catalyst for this reaction, forms stable solutions in [BMIm]BF\textsubscript{4} and [BMIm]PF\textsubscript{6}.\textsuperscript{3b} However, as Wilkinson’s complex displays a higher affinity for the organic rather than for the ionic phase, the latter ionic liquids turned out to be unsuitable for the immobilisation of the catalyst. Furthermore, whereas [RhCl(PPh\textsubscript{3})\textsubscript{3}] proved to be insoluble in 1, a lightly fluorous derivative of Wilkinson’s catalyst, [RhCl{P(C\textsubscript{6}H\textsubscript{4}{SiMe\textsubscript{2}(CH\textsubscript{2}CH\textsubscript{2}C\textsubscript{6}F\textsubscript{13})-4)}\textsubscript{3}] (2),\textsuperscript{17} exhibited interesting solubility in 1. Concentrations of 2 in 1 of at least, $1.4 \times 10^{-2}$ M were attainable.

The hydrosilylation reaction of 1-octene with dimethylsilane catalysed by 2 in the ionic liquid 1 at 84 °C afforded dimethylphenyloctysilane (Table 2). Selective anti-Markovnikov addition of the silane occurred, while formation of PhMe\textsubscript{2}SiSiMe\textsubscript{2}Ph was not observed.\textsuperscript{18} Some isomerisation of the excess 1-octene (ca. 30% by GC) took place. This results are similar to those reported for this reaction.\textsuperscript{19}

At 84 °C the reaction-mixture was an emulsion. When the temperature was raised to 100 °C (entry 8 in Table 2) a homogeneous phase was obtained, however, this did not result in an increase in the reaction rate observed. This indicates that at 84 °C, despite the non-homogeneous conditions, neither the concentration of the substrates in the ionic phase nor their phase transfer into the ionic phase are rate limiting.
Table 2: Comparison of the hydrosilylation of 1-octene using either non-fluorous or fluorous Wilkinson’s catalysts in ionic liquids.\(^a\)

\[
\begin{array}{cccccc}
\text{entry} & \text{catalyst} & \text{solvent} & \text{cycle (no.)} & \text{TOF}\(^b\) (h\(^{-1}\)) & r^c \\
1 & [\text{RhCl}(\text{PPh}_3)_3] & \text{benzene} & & 1.8 \times 10^3 & \\
2 & [\text{RhCl}(\text{PPh}_3)_3] & [\text{BMIm}]\text{BF}_4 & 1 & 4.0 \times 10^2 & \\
3 & & & 1 & <1 & \\
4 & 2 & 1 & 1 & 4.0 \times 10^2 & \\
5 & 2 & 1 & 2 & 3.1 \times 10^2 & 0.77 \\
6 & 2 & 1 & 3 & 2.8 \times 10^2 & 0.91 \\
7 & 2 & 1 & 15 & 1.3 \times 10^2 & <0.94^f \\
8 & 2^g & 1 & & 3.2 \times 10^2 & \\
\end{array}
\]

\(\text{Ar}_1 = C_6H_4(SiMe_2(CH_2CH_2C_6F_{13}))^{-4}\)

\(^{a}\) Conditions: 17 µmol (0.2 mol%) of catalyst, 1.2 mL of ionic liquid, 8.75 mmol of 1-octene, 7.85 mmol of dimethylphenylsilane \(t = 60\) min, \(T = 84\) °C (unless stated otherwise). \(^b\) Average Turn Over Frequency (TOF) determined after 1 hour and defined as mol of silane per mol of initial Rh per hour. \(^c\) Retention of catalyst activity = activity in cycle \(n\) / activity in cycle (\(n-1\)). \(^d\) Reaction was 99% complete after 15 min. \(^e\) Blank run. \(^f\) Average retention per cycle for cycles 4-15. \(^g\) At \(T = 100\) °C, homogeneous conditions.

Whereas the turn-over frequencies (TOF) observed do not make a strong case for the use of 1 in hydrosilylation catalysis, the total turn-over number (TON) obtained after multiple cycles clearly does. Reasonably efficient catalyst recycling was possible by phase separation at 0 °C (Figure 3). A single aliquot of pre-catalyst was used 15 times with a retention of catalyst activity of 92% per cycle (94% when the first cycle is disregarded, Figure 4).\(^{20}\) This resulted in a TON of \(4.0 \times 10^3\) mol per mol of catalyst, which is significantly higher than corresponding values reported for the conventional system under monophasic conditions (first bar in Figure 4).\(^{16,21}\)

Figure 3. Fluorous biphasic catalyst recycling using a fluorous ionic liquid.
The drop in conversion upon recycling (Table 2) is most likely caused by catalyst leaching. After separation from the ionic liquid, the product layers were slightly orange, suggesting some leaching of the rhodium catalyst. ICP-AAS analyses of the product phases of the cycles 2 and 3 confirmed this view. Both phosphine (1.5 × 10^{-3} wt%) and rhodium (3.6 × 10^{-3} wt%) were found in the product layer, corresponding to a loss of 4% of initial rhodium and 2% of initial phosphine per cycle. Phosphine oxidation caused by traces of oxygen, which can never be completely excluded in experiments on this scale, might be an additional source of activity loss. This low loss of Rh and phosphine contrast with the Rh leaching of 12% per cycle observed when catalyst 2 was used in the hydrosilylation of 1-hexene under fluorous biphasic conditions (perfluoromethylcyclohexane and 1-hexene, 1:2 (v:v)). It is interesting to note that efficient recycling of Wilkinson’s catalyst using [BMIm]BF_{4} was not practical because the catalyst dissolved preferentially in the product phase. Consequently, the approach presented here, involving the use of fluorous catalyst 2 in fluorous ionic liquid 1, is a most efficient one. It allows the efficient recycling of a Wilkinson’s-type catalyst used for the hydrosilylation of olefins.

7.3 Conclusions

In conclusion, we have developed a fluorous ionic liquid with the characteristics of both conventional ionic liquids and perfluorinated solvents. This fluorous ionic liquid can be used in fluorous biphasic catalyst recycling and offers a higher solubility of apolar substrates compared with existing ionic liquids. Along with the fact that it forms a homogeneous phase with organic solvents above the consolute temperature, this makes this solvent especially attractive for use in catalytic processes that suffer from phase transfer limitations in other
biphasic solvent systems. Non-volatile fluorous ionic liquids of this kind could also be an alternative for the more commonly used perfluorocarbons in fluorous biphasic catalyst recycling.

7.4 Experimental Section

General Procedures. All reactions were performed under dry N₂ atmosphere using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, CH₂Cl₂ from CaH₂ and benzene from sodium. 1-Butyl-3-methylimidazolium iodide,²⁵ Na[B(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)] and [RhCl{P(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)}₃] were prepared according to literature procedures. 1-Octene was purified by flash chromatography over basic alumina followed by distillation from CaH₂ prior to use. PhMe₂SiH was stored over molecular sieves (3Å). All other chemicals were used as received. NMR spectra were recorded on a Varian Inova 300 spectrometer with TMS (1H, 13C{1H}, CFCl₃ (19F) and BF₃·Et₂O (11B{1H}) as external references. Elemental analyses and ICP/AAS analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr. DSC traces were recorded on a Mettler-Toledo DSC-821. Conductivity measurements were performed using a Consort C832 Multiparameter Analyser equipped with a two platinum electrode conductivity cell. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer.

1-Butyl-3-methylimidazolium tetrakis{4-(dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl)phenyl}borate (1). A mixture of Na[B(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)] (10.00 g, 5.11 mmol) and [BMIm]I (1.29 g, 4.86 mmol) was stirred in CH₂Cl₂ (200 mL) for 2 days. The mixture was washed with demineralised water (3 x 50 mL), dried over MgSO₄ and volatiles were removed in vacuo. The residue was taken up in benzene and traces of solid material were separated by centrifugation. Removal of solvents in vacuo yielded 8.60 g (81%) of a yellow oil. ¹H NMR (acetone-d₆, 300.1 MHz): δ 8.68 (s, 1H, NC₃H), 7.72 (bs, 1H, NC₃H), 7.67 (bs, 1H, NCH), 7.44 (m, 8H, Ar-Ho), 7.25 (d, 8H, ³JHH = 7.5 Hz, Ar-Hm), 4.30 (t, 2H, ³JHH = 7.2 Hz, NC₃H₂), 3.99 (s, 3H, NC₃H₃), 2.17 (m, 8H, CH₂CF₂), 1.85 (tt, 2H, CH₂(CH₂), 1.36 (tq, 2H, CH₂(CH₂), 0.99 (m, 8H, SiCH₃), 0.94 (t, 3H, ³JHH = 7.1 Hz CH₂CH₂), 0.31 (s, 24H, SiCH₃). ¹³C{¹H} NMR (acetone-d₆, 75.5 MHz): δ 166.0 (q, ¹JC = 49.1 Hz), 136.2 (s), 135.9 (s), 131.5 (s), 128.7 (s), 123.8 (s), 122.3 (s), 120.7 (m), 117.6 (m), 113.3 (m), 113.0 (m), 112.2 (m), 110.2 (m), 49.6 (s), 35.8 (s), 32.2 (s), 26.2 (t, ²JC = 23.8 Hz), 19.5 (s), 12.9 (s), 5.5 (s), -4.0 (s). ¹¹B{¹H} NMR (acetone-d₆, 96.3 MHz): δ -12.2 (s, ¹JC = 49.1 Hz). ¹⁹F NMR (acetone-d₆, 282.5 MHz): δ -87.9 (m, 12F, CF₃), -122.6 (m, 8F, CF₂CF₃), -128.8 (m, 8F, CF₂), -129.7 (m, 8F, CF₂), -130.0 (m, 8F, CF₂), -133.0 (m, 8F, CH₂CF₂). Anal. Calced. for C₇₂H₇₁BF₅₂N₄Si₄: C, 41.67; H, 3.42; F, 47.28; I, 0.00. Found: C, 41.58; H, 3.42; F, 47.28; I, 0.00. DSC: possible glass transition at -10 °C.

Hydrosilylation. Compound 1 (1.65 g, 0.80 mmol) was heated to 80 °C and degassed in vacuo for 1 h. [RhCl{P(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)}₃] (80 mg, 17 µmol) was added and the mixture was stirred at 70 °C for 5 min to ensure a homogeneous catalyst distribution. Freshly distilled 1-octene (1.38 mL, 8.75 mmol) and dimethylphenylsilane (1.20 mL, 7.85 mmol) were added. After stirring at 84 °C for 60 min the mixture was cooled to 0 °C and the upper layer was decanted and analysed by ¹H NMR and GC. A similar procedure was employed for catalysis at 100 °C.
Solubility Studies. Saturated solutions of 1 in a solvent were prepared and allowed to settle at 25 °C for 1 h until the solution was completely clear upon visible inspection. A sample of 2.0(1) mL was taken while ensuring that no undissolved material was sampled. The solvent was removed in vacuo and the residue was kept under vacuum (0.1 mbar) for 1 h after which the weight was constant within ± 1 mg. The weight of the residue was determined and the solubility calculated.

Determination of the phase diagram of a toluene - [BMIm][B(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)₄] mixture. A known amount of toluene was added to 1 (0.45 mL). The resulting mixture was stirred and heated slowly until it became a single phase. The mixture was then cooled until it became biphasic. Then an additional amount of toluene was added and the process repeated.

Solubility of alkenes in [BMIm][B(C₆H₄{SiMe₂(CH₂CH₂C₆F₁₃)}-4)₄] (1). Ionic liquid 1 (0.5 g) and alkene (0.5 g) were weighed into a Schlenk. The mixture was heated until it became homogeneous. After cooling to –20°C, the upper phase was isolated. The solubility of alkene in 1 was calculated from the weight loss in the ionic layer after removal of all volatiles in vacuo.

Polarity measurements: A Nile Red solution in methanol (1 mL, 1.89 10⁻³ M) was added to 0.5 g of 1. After the mixture had become homogeneous, the methanol was removed in vacuo. Then, the absorption maximum of Nile Red was determined by transmission UV-Vis spectroscopy in a thin film of 1. An absorption maximum of 542 nm was observed, which corresponds with an $E_{NR}$ of 220.7 kJ/mol.

References and Notes


(16) de Wolf, E.; Speets, E. A.; Deelman, B.-J.; van Koten, G. *Organometallics* 2001, 20, 3686. The authors used 1-hexene as an olefinic substrate.


(18) The formation of disilanes is catalysed by Wilkinson's complex but can be suppressed by using an excess of olefin: (a) Brown-Wensley, K. A. *Organometallics* 1987, 6, 1590. (b) Chang, L. S.; Corey, J. Y. *Organometallics* 1989, 8, 1885.


(20) The drop in activity after the first recycle is well above average.


(22) ICP-AAS analysis showed the presence of 147 mass ppm of boron in the product layer, which corresponds with a leaching of 4 wt% of ionic liquid per cycle.

(23) The ratio of Rh and P observed was 1 : 1.5, but is known to be 1 : 2 after use of the catalyst (ref 16). This can be explained by phosphine oxidation, resulting in the formation of rhodium particles and phosphine oxides. The latter will have a higher affinity for the fluorous phase, resulting in a relatively higher leaching of the metal.

(24) Substrate quality also proved to be important for the observed activity. The use of freshly distilled 1-octene resulted in increased conversions relative to aged material. Formation of epoxides, which is known to decrease the activity of Wilkinson's catalyst in hydrogenation, is a likely cause for this lower activity.