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A Highly Fluorous Room-Temperature Ionic Liquid Exhibiting Fluorous Biphasic Behavior and Its Use in Catalyst Recycling

Joep van den Broeke,[†] Ferry Winter,[†] Berth-Jan Deelman,*[†,‡] and Gerard van Koten[†]

Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands, and ATOFINA Vlissingen B.V.,
P.O. Box 70, 4380 AB Vlissingen, The Netherlands

berth-jan.deelman@atofina.com

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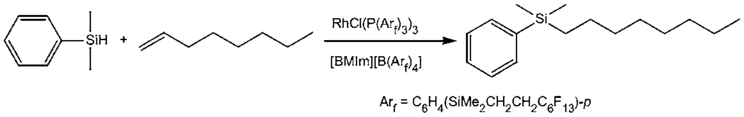
ABSTRACT



A novel fluorous room-temperature ionic liquid, 1-butyl-3-methyl-imidazolium tetrakis[*p*-{dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]-borate (1), was used as a solvent for the homogeneous hydrosilylation of 1-octene catalyzed 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 behavior with organic solvents.

The use of air- and water-stable imidazolium-based ionic liquids as a solvent for transition metal catalysts has received growing attention[1] since their preparation was first reported in 1992.[2] This interest was particularly sparked by the fact that these ionic liquids are highly stable and show limited miscibility with most of the common organic solvents, offering potential for efficient catalyst recovery by facile phase separation.[1] This approach has been successfully applied in a wide range of catalytic processes, for example, hydrogenation,[3a,b] hydroformylation,[3a] Heck reactions,[3c] oligomerizations,[3d] epoxidations,[3e] and polymerizations.[3f] A serious limitation for the application of ionic liquids is their poor solubility of apolar organic substrates, especially saturated hydrocarbons and in some cases neutral metal catalysts (vide infra).[1,4] 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.[3a,5]

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 ionic liquids with improved solvating properties for apolar compounds, as this might allow more efficient catalysis with

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[†] Utrecht University.

[‡] ATOFINA Vlissingen B.V..

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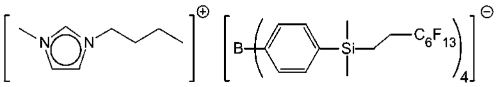
apolar substrates. In this respect, the introduction of perfluoroalkyl moieties as lipophilic groups could be of special interest, as this could lead to ionic liquids exhibiting fluorous biphasic behavior, i.e., biphasic conditions at lower temperatures and monophasic at higher temperatures. Such a fluorous ionic liquid could well be an alternative to perfluoroalkane-based fluorous biphasic systems (FBSs), the fluorous phase of which appears to be less suitable for the immobilization of ionic catalysts.[6]

Recently, we reported the synthesis of highly fluorous tetraphenylborate anions.[6a] We now present the use of these anions in the preparation of imidazolium borate ionic liquids and their performance in fluorous biphasic catalyst recycling.

Synthesis and Physical Properties of [BMIm][B{C_6H_4-($SiMe_2CH_2CH_2C_6F_{13}$)-*p*}$_4$]. The imidazolium salt [BMIm]-[B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-*p*}$_4$] (**1**) (BMIm = 1-butyl-3-methylimidazolium) (Scheme 1) was obtained by metathesis of [BMIm]I[7] and Na[B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-*p*}$_4$][6a] in CH_2Cl_2. This salt is an air-stable, nonhygroscopic viscous yellow liquid (ρ = 1.38 g/mL) at 25 °C that is transformed into a glasslike substance at subambient 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 × 10^{-5} S m^{-1} at 25 °C, and it increases as viscosity decreases at elevated temperatures (1.1 × 10^{-3} S m^{-1} at 95 °C). These values are low for room temperature ionic liquids, which usually have conductivities in the range of 0.1−1.0 S m^{-1}.[8] The relative polarity of the ionic liquid was assessed using the solvatochromatic dye Nile Red.[9] Measurement of λ^{abs}_{max} of Nile Red dissolved in **1** and determination of the molar transition energy (E_{NR}) for this dye in the solution show that **1** can be considered as a polar solvent (Figure 1).

Scheme 1



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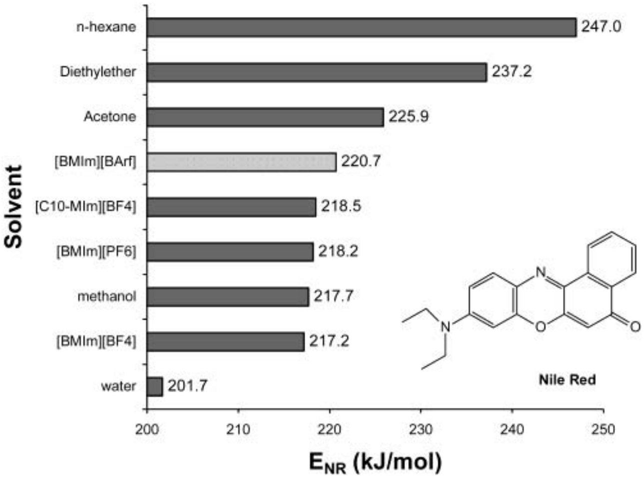

Figure 1. E_{NR} values for [C_n−MIm]X ionic liquids and common organic solvents. $E_{NR} = (hcN_A/\lambda_{max}) \times 10^6$, where *h* is Planck's constant, *c* is the speed of light, N_A is Avogadro's number, and λ_{max} is the wavelength at maximum absorbance (nm). [BArf] = [B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-*p*}$_4$].

Table 1. Solubility of [BMIm][B{$C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-*p*}$_4$] (**1**) in Various Solvents

solvent	DN[a]	dielectric constant (ϵ_r)[a]	solubility (g/L)[b]
FC-72		1.6[c]	3.7 × 10^{-1}
benzene	0.1	2.3	8.0
hexane	0.0	1.9	1.9 × 10^1
pentane		1.8	2.7 × 10^1
toluene	0.1	2.4	4.1 × 10^1
Et_2O	19.2	4.2	5.1 × 10^2
acetone	17.0	20.6	5.8 × 10^2
methanol	30.0	32.7	3.3 × 10^1
methanol:H_2O (1:1)			2.5
H_2O	18.0	78.4	<0.2

[a] Donor number, taken from ref 24. [b] Solubility in g/L of pure solvent at 25 °C. [c] A mixture of perfluorohexanes, the ϵ_r given is that of perfluoro-*n*-hexane, a major component of FC-72.

The solubility properties of **1** were investigated; it was found to be insoluble in water and very soluble in polar and to some extent in apolar organic solvents (Table 1). As alkenes are important substrates in various catalytic processes, the behavior of various mixtures of 1-alkenes and **1** was also studied. Solubilities of 1-hexene (16.7 mol/mol, 9.3 × 10^2 g/L) and 1-octene (4.7 mol/mol, 3.5 × 10^2 g/L) in **1** are much higher than those reported for closely related ionic liquids [BMIm][PF_6] (1-octene: 0.026 mol/mol)[10] and [MeN-(*n*-Hex)$_3$]Tos (1-octene: 1.5 mol/mol).[11] Furthermore, mixtures of 1-hexene or 1-octene and **1** ($\phi_{v(1-alkene)}$ = 0.63) give a biphasic system at room temperature but display low consolute temperatures (*T* = 60 and 84 °C, respectively). They transform into clear homogeneous liquids above these temperatures. The phase behavior of **1** with toluene was investigated more thoroughly; a critical temperature (T_c) of 62 °C at a toluene volume fraction ($\phi_{v(toluene)}$) of 0.90 was found (Figure 2).

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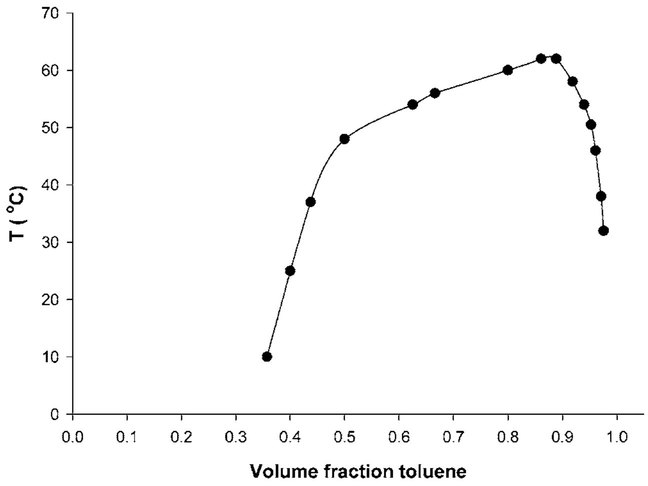


Figure 2. Phase diagram of $[BMIm][B\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}p\}_4]$ and toluene.

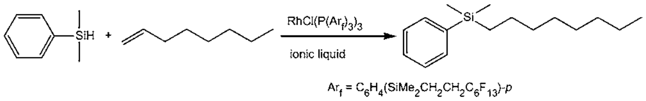
The physical properties of **1** show that it differs considerably from the ionic liquids reported previously. Whereas other [BMIm]-based compounds display polarities close to that of methanol[12] and have considerable solubility in water (exceptions are $[BMIm][PF_6]$ and $[BMIm][(CF_3SO_2)_2N]$)[3e,4] and essentially no solubility in alkanes,[1a,4] the polarity and 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,[12a] and our results correspond with this trend, **1** being less polar than $[BMIm][PF_6]$ or $[C_{10}MIm][BF_4]$ ($C_{10}MIm$ = 1-decyl-3-methyl-imidazolium). The determined E_{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 results in high viscosity, which in turn causes low conductivity,[8] and both of these properties were observed for **1**.

The fact that **1** is insoluble in water, dissolves best in solvents with a high dielectric constant and a high donor number, and exhibits some solubility in hydrocarbons is remarkable. Ionic liquids, in general, are highly soluble in polar solvents, especially in MeOH,[4a] and virtually insoluble in apolar solvents.[4] The high solubility in a solvent capable of acting as a hydrogen bridge donor (e.g., H_2O, MeOH) is predominantly the result of interactions between the anions of the ionic liquid and the solvent.[13] However, as the strength of the hydrogen bonding decreases, the solubility of the ionic liquid will be reduced as well. Because the fluorous anion in **1** offers no possibility for hydrogen bonding interactions, low solubility in water and, to some extent, methanol results. On the other hand, the lipophilic anion enhances solubility in apolar solvents, indicating that the perfluoroalkyl groups moderate the ionic character of **1**. This makes the behavior of **1** resemble that of both an ionic liquid and a fluorous solvent. The low critical temperature with toluene confirms this observation.[14]

Recycling of a Fluorous Wilkinson's Catalyst Dissolved in the Fluorous Ionic Liquid. To assess the suitability of **1** for use as a catalyst immobilization medium, rhodium-catalyzed hydrosilylation of 1-octene was studied.[15] Wilkinson's complex, $[RhCl(PPh_3)_3]$, a well-known catalyst for this reaction, is known to form stable solutions in $[BMIm][BF_4]$ and $[BMIm][PF_6]$.[3b] However, as Wilkinson's complex displayed a higher affinity for the organic rather than for the ionic phase, the latter ionic liquids turned out to be unsuccessful for the immobilization of the catalyst. Surprisingly, whereas $[RhCl(PPh_3)_3]$ proved to be insoluble in **1**, a lightly fluorous derivative of Wilkinson's catalyst, $RhCl[P\{C_6H_4(SiMe_2CH_2CH_2C_6F_{13})\text{-}p\}_3]_3$ (**2**),[16] exhibited interesting solubility in **1**; concentrations of at least 1.4×10^{-2} M were attainable.

The hydrosilylation reaction of 1-octene with dimethylsilane catalyzed by **2** in **1** afforded dimethylphenyloctylsilane (Table 2), with addition of the silane occurring in a selective anti-Markovnikov fashion. Formation of $PhMe_2SiSiMe_2Ph$ was not observed,[17] but some isomerization of the remaining 1-octene (ca. 30% by GC) took place. Similar behavior was

Table 2. Comparison of the Hydrosilylation of 1-Octene Using Either Non-Fluorous or Fluorous Wilkinson's Catalysts in Ionic Liquids[a]



catalyst	solvent	cycle	TOF[b] (h^{-1})	r[c]
$RhCl(PPh_3)_3$	benzene		1.8×10^3 [d]	
$RhCl(PPh_3)_3$	$[BMIm][BF_4]$		4.0×10^2	
[e]	**1**		<1	
2	**1**	1	4.0×10^2	
2	**1**	2	3.1×10^2	0.77
2	**1**	3	2.8×10^2	0.91
2	**1**	15	1.3×10^2	⟨0.94⟩ [f]
2[g]	**1**		3.2×10^2	

[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 turnover frequency (TOF) determined after 1 h 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] T = 100 °C, homogeneous conditions.

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(17) The formation of disilanes is catalyzed by Wikinson's complex but can be suppressed by using an excess of olefin: (a) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590−1591. (b) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885−1893.

reported for Wilkinson's catalyst in conventional solvents.[18] When the reaction was performed at 84 °C, the temperature at which a mixture of 1-octene ($\phi_{v(1-\text{octene})} = 0.63$) in **1** becomes homogeneous, the reaction mixture was still an emulsion. Although it did not affect the catalytic activity, raising the reaction temperature to 100 °C resulted in fully homogeneous conditions. This suggests that neither the concentration of the substrates in the ionic phase nor their phase transfer into the ionic phase are rate limiting at 84 °C. Furthermore, as the catalytic activities of both $RhCl(PPh_3)_3$ in [BMIm][BF_4] and **2** in **1** are similar, albeit lower than that of $RhCl(PPh_3)_3$ in benzene, it can be concluded that the perfluoro tail substitution of both the ionic liquid and the catalyst does not influence the reaction rates and selectivity.

Whereas the turnover frequencies (TOF) observed do not make a strong case for the use of **1** in hydrosilylation catalysis, the total turnover numbers (TON) obtained after multiple cycles clearly do. Reasonably efficient catalyst recycling was possible by phase separation at 0 °C. A single aliquot of precatalyst was used 15 times with a retention of catalyst activity of 92% per cycle (94% when the first cycle is disregarded, Figure 3).[19] This resulted in a TON of 4.0×10^3 mol per mol of catalyst, which is significantly higher than corresponding values reported for the conventional system under monophasic conditions (first bar in Figure 3).[15,20]

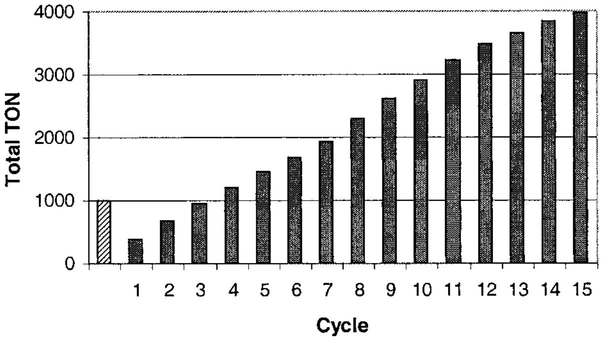

Figure 3. Turnover numbers achieved in hydrosilylation of 1-octene by catalyst **2** in fluorous ionic liquid **1**. The lightly shaded box represents the common turnover number achieved with $RhCl(PPh_3)_3$. Darkly shaded boxes represent the cumulative turnover number achieved with **2** after each cycle.

The drop in conversion (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.[21] ICP-AAS analyses of the product phases of cycles 2 and 3 confirmed this view. Both phosphine (1.5×10^{-5} wt %) and rhodium (3.6×10^{-5} wt %) were found in the product layer, corresponding to a loss of 4% of initial rhodium and 2% of initial phosphine per cycle.[22] 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.[23]

Previously, **2** was used in the hydrosilylation of 1-hexene under fluorous biphasic conditions; Rh leaching was 12% per cycle under these conditions,[15] and Wilkinson's catalyst in the conventional ionic liquid [BMIm][BF_4] could not be recycled efficiently (because the catalyst dissolved preferentially in the product phase). Therefore, the use of fluorous catalyst **2** in fluorous ionic liquid **1** is the most efficient combination thus far for recycling of a Wilkinson-type catalyst in the hydrosilylation of olefins.

In conclusion, we have developed a fluorous ionic liquid with characteristics of both conventional ionic liquids and fluorous solvents. It was shown that this fluorous ionic liquid can be used in fluorous biphasic catalyst recycling and that it 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 limitation in other biphasic solvent systems. Nonvolatile fluorous ionic liquids of this kind could also be an alternative for the more commonly used perfluorocarbons in fluorous biphasic catalyst recycling.

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Supporting Information Available: Experimental procedures and characterization data for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] 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.

[22] The ratio of Rh and P observed was 1:1.5 but is known to be 1:2 in the spent catalyst (ref 15). 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.

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