Tetrahedron Letters 57 (2016) 3453-3456

Contents lists available at ScienceDirect

**Tetrahedron Letters** 

journal homepage: www.elsevier.com/locate/tetlet

# Tunable aryl alkyl ionic liquids with weakly coordinating bulky borate anion

Maria Kaliner, Thomas Strassner\*

Physikalische Organische Chemie, Technische Universität Dresden, 01169 Dresden, Germany

#### ARTICLE INFO

Article history: Received 24 March 2016 Revised 16 June 2016 Accepted 20 June 2016 Available online 21 June 2016

Keywords: Ionic liquids Imidazolium cations Borate anions TAAILs ESP

## ABSTRACT

A series of 1-aryl 3-alkyl imidazolium tetrakis[bis-3,5(trifluoromethyl)phenyl]borate [BArF<sub>3,5</sub>] ionic liquids were synthesized and characterized. Increasing the alkyl chain length leads to lower melting points even resulting in room temperature ionic liquids (RTILs). In comparison to their corresponding alkyl imidazolium [BArF<sub>3,5</sub>] counterparts these aryl imidazolium [BArF<sub>3,5</sub>] ionic liquids show significantly lower melting points.

© 2016 Elsevier Ltd. All rights reserved.

### Introduction

Tetraarvlborate anions with many fluoro or fluoromethyl groups on the phenyl part have attracted great interest as weakly coordinating bulky counterions.<sup>1,2</sup> The tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [BArF<sub>3.5</sub>] anion was first introduced in 1983 by Kobayashi et al. and was originally used for anion catalyzed phase transfer catalysis for diazo-coupling reactions.<sup>3-5</sup> In contrast Brookhart et al. prepared oxonium acid [H(OEt<sub>2</sub>)<sub>2</sub>][BArF<sub>3.5</sub>] from Na[BArF<sub>3.5</sub>] in ether and HCl and used the [BArF<sub>3.5</sub>] anion as stabilization reagent for electrophilic cationic transition metal complexes,<sup>6</sup> e.g., to stabilize the palladium catalyst in the synthetic copolymerization of olefins and carbon monoxide.<sup>7,8</sup> Also in organometallic chemistry the bulky [BArF] anions have frequently been used.<sup>9–11</sup> It was observed that the generally weakly coordinating anions tetrafluoroborate ([BF<sub>4</sub>]) or hexafluorophosphate ([PF<sub>6</sub>]) reacted with highly reactive electrophilic complexes and that abstraction of fluorine from the anion to the cationic complex occurred. By using bulky fluorinated tetraarylborate anions the fluoro transfer onto the metal center could be avoided.<sup>2,9–11</sup>

Weakly coordinating anions recently became more and more important for ionic liquids (ILs) because they show a much lower tendency to coordinate to the cation than the halide counterions.<sup>2</sup> Due to the weaker interaction between the cation and the bulky anion the properties of ILs like melting point, viscosity, high thermal stability, or acidity can be modified.<sup>12</sup> By definition ionic liquids are salts that contain organic cations and inorganic or organic anions and have a melting point below 100 °C. ILs which are even liquid below 25 °C are called room temperature ionic liquids (RTILs).<sup>12</sup> ILs attract interest in a lot of different applications like plating,<sup>13–18</sup> as solvents in organic synthesis or catalysis,<sup>12,19–24</sup> as extracting agents,<sup>25–28</sup> for the dissolution of cellulose,<sup>29–34</sup> or as electrolytes in dye sensitized solar cells.<sup>35–41</sup> In 2006 the first ionic liquids with the [BArF<sub>3,5</sub>] anion were synthesized based on ammonium, imidazolium, pyridinium, and isochinolinium cations.<sup>42</sup>

These [BArF<sub>3,5</sub>] ILs were used in the investigation of ion transfer across polarized water/IL interfaces,<sup>42,43</sup> as ionic liquid salt bridges<sup>44,45</sup> that isolate the working from the reference electrode in electrochemistry cells or to prepare poly(IL) functionalized particles<sup>46</sup> where the polymerization is carried out via the functional



Figure 1. General structure of the investigated aryl alkyl imidazolium [BArF<sub>3,5</sub>] ILs.





<sup>\*</sup> Corresponding author. Tel.: +49 0351 46338571; fax: +49 351 46339679. *E-mail address*: thomas.strassner@chemie.tu-dresden.de (T. Strassner).



Scheme 1. Synthesis of borate TAAILs by anion metathesis.

group at the cation. Even redox active  $[{\sf BArF}_{3,5}]$  ILs containing a ferrocenyl alkyl ammonium cation were synthesized.  $^{47}$ 

We focus on imidazolium based ILs, so-called tunable arvl alkvl ionic liquids (TAAILs) that feature a (substituted) phenyl ring together with an alkyl chain on the other nitrogen atom of the heterocycle.<sup>48–50</sup> Through the aryl ring additional mesomeric and steric effects change the properties of the ionic liquids. Variation of the substituent at the phenyl ring leads to different melting points using the same alkyl chain length and anion depending on the mesomeric or inductive effects of the substituent. Generally, electron donating substituents show lower melting points than electron withdrawing substituents as previously reported.<sup>49</sup> The exchange of the anion also has an influence on the properties of the TAAILs. Coordination of small anions (Br, I) leads to higher melting points compared to the bigger anions ([BF<sub>4</sub>], [PF<sub>6</sub>]).<sup>48</sup> Ionic liquids with N,N-dialkyl imidazolium cations and [BArF<sub>3,5</sub>] anion have been found to exhibit interesting properties. Therefore we investigated the influence of the [BArF<sub>3,5</sub>] anion on different aryl alkyl imidazolium cations by combining the large cations with bulky weakly coordinating anions. In this Letter we report the syntheses and characterization of 1-aryl 3-alkyl imidazolium [BArF<sub>3,5</sub>] ILs. The acronym [Ph<sub>R</sub>C<sub>n</sub>Im][BArF<sub>3,5</sub>] describes TAAILs 4a-6d where Ph<sub>R</sub> characterizes type and position of the substituent R at the phenyl ring and  $C_n$  the length of the alkyl chain at the imidazolium core (Im). The general structure is given in Figure 1.

## **Results and discussion**

The imidazolium halide salts 1a-3d were synthesized from the commercially available anilines using previously described reactions.<sup>48</sup> The aryl imidazoles were accessible via a ring closing reaction using a one-pot procedure with glyoxal, formaldehyde, ammonium chloride, and the respective anilines, followed by a nucleophilic substitution with an alkyl halide. The aryl imidazolium [BArF<sub>3,5</sub>] salts 4a-6d were synthesized by anion metathesis with Na[BArF<sub>3,5</sub>] from the aryl imidazolium halide salts 1a-3d as shown in Scheme 1. After addition of an equimolar amount of Na  $[BArF_{3,5}]^{51}$  to the solution of the halide salts **1a-3d** in dichloromethane the reaction mixture was stirred at room temperature for 24 h. After removal of the sodium halide salt and solvent, TAAILs 4a-6d were obtained in excellent yields between 88% and 99%.<sup>52</sup> The synthesized TAAILs show no transformation when exposed to air and can be washed with water. They are air and water stable and do not need to be handled or stored in a glovebox. The sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[BArF<sub>3.5</sub>]) was synthesized through a modified route according to Smith et al. using a Grignard reaction.<sup>53</sup> Because of the high and sometimes explosive reactivity of the Grignard reactant the reaction should be handled with care. No problems with the reaction could be observed following the instructions. The azeotropic distillation was carried out with toluene instead of benzene and provided the Na[BArF<sub>3.5</sub>] salt as a colorless solid.

We investigated the influence of the substituent at the aryl ring and the alkyl chain length of the cations in comparison to the influence of the anion on the melting points of the TAAILs. We used different alkyl chain lengths (small, medium, and long) and three different electron donating substituents (2-Me, 4-OMe, 2,4,6-Me [Mes]) which have a different influence of the electron density of the phenyl ring. The methyl and mesityl groups exhibit an +I effect that donates electrons through the sigma bonds into the ring, while mesityl also has an additional steric influence. The +M effect of the methoxy group results in an electron donation through the  $\pi$ -system. To visualize the electronic effects we calculated the electrostatic surface potential (ESP)<sup>54</sup> of the substituted 1-aryl 3-butyl imidazolium cations 4b, 5b, and 6b as shown in Figure 2. To compare the ESP's of the imidazolium cations with different substituents (2-Me, 4-OMe, Mes) we kept the chain length  $(C_4H_9)$ constant. Cations carry a positive charge all over the molecule, the ESP representations differentiate between a more positive potential at the imidazolium core (blue) and a negative potential at the end of the alkyl chain and/or at the functional groups (red). Substituents in para position at the aryl ring, especially OMe, show a more negative potential than the methyl group at the ortho position.

TAAILs with mesityl substituents **6a–d** lead to higher melting points due to the steric influence of the methyl groups at the phenyl ring (Table 1). If there are two methyl groups in *ortho* position to the imidazolium ring the planes of the phenyl ring and of the imidazolium ring<sup>55</sup> are orthogonal to each other as could be demonstrated by quantum chemical calculations (Fig. 2). [BArF<sub>3,5</sub>] ILS **4a–5d** with mono substituted 2-Me and 4-OMe show lower melting points than the sterically hindered mesityl [BArF<sub>3,5</sub>] ILS, certainly due to minor steric influences between the aryl ring and the imidazolium core.

The melting points of the imidazolium halide salts with 2-Me **1a–d** and 4-OMe **2a–d** show a minimum for the medium sized hexyl chain length whereas for the mesityl imidazolium halide salts **3a–d** the melting points decrease by increasing alkyl chain length.

By exchanging the halide anion with  $[BArF_{3,5}]$  the behavior of the methyl imidazolium ILs **4a–d** changed, leading to generally lower melting points with increasing chain length as can also be

Table 1

Melting points of 1-aryl 3-alkyl imidazolium [BArF<sub>3,5</sub>] ionic liquids 4a-6d and 1-aryl 3-alkyl-imidazolium halide salts 1a-3d

Anion	R	Me (C <sub>1</sub> )	Bu (C <sub>4</sub> )	Hex $(C_6)$	Undec (C <sub>11</sub> )
[BArF <sub>3,5</sub> ]	2-Me 4-OMe 2,4,6-Me	71 83 102	70 44 86	41 68 70	-27 <sup>d</sup> -23 <sup>d</sup> -21 <sup>d</sup>
Halide	2-Me 4-OMe 2,4,6-Me	119 <sup>a</sup> 127 <sup>a</sup> 160 <sup>a</sup>	61 <sup>b</sup> 56 <sup>a</sup> 90 <sup>a</sup>	l <sup>b,c</sup> l <sup>a,c</sup> 68 <sup>a</sup>	$\begin{array}{l} 47^{\mathrm{b}} \\ 46^{\mathrm{b}} \\ 60^{\mathrm{b}} \end{array}$

<sup>a</sup> Imidazolium salts with iodide counterions.

<sup>b</sup> Imidazolium salts with bromide counterions.

<sup>c</sup> Ionic liquids are liquid (*l*) at room temperature.

<sup>d</sup> Glass transition temperature upon cooling; all melting points are given in °C.

Download English Version:

https://daneshyari.com/en/article/5258766

Download Persian Version:

https://daneshyari.com/article/5258766

Daneshyari.com