Supporting information

Water free metathesis reaction: a route to ionic liquids

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Experimental

We worked at the melting point of the halide salts. All the ionic liquids were synthesised following this experimental procedure: 1-butyl-3-methylimidazolium chloride heated gently at 70°C. Then the salt of lithium or sodium of each anion were added under argon and stirred for 24h. The resultant product was dissolved in THF or CH₂Cl₂ (based on the nature of the anion) and stirred for 20 min to precipitate the resulting salt which was filtered off (0.2µm filter). The resulting filtrate was placed in the fridge (-5°C) for one night for complete precipitation of the salt, in case of salt precipitation another filtration was performed and the resulting filtrate evaporated to dryness.

RK: N-butyl-N-metylpyrrolidinium chloride and tetrabutylphosponium bromide melts at 120°C. THF used for dicyanamide anion while CH₂Cl₂ was used for the other anions.

The possible presence of residual Cl⁻ was examined via inspection of the appreciate mass regions of the respective mass spectra. In case of ionic liquids based on: (C₄H₄Im)⁺ the chloride peak appears at m/z=313, (C₆H₄Im)⁺ at m/z=369, (C₈H₈Im)⁺ at m/z=425, (P₁₄)⁺ at m/z= 319 and (P₄₄₄₄)⁺ at m/z= 553.5.

NMR spectroscopy and ESI-MS analysis

NMR spectra were recorded on BRUKER AVANCE 300 spectrometer (¹H: 300.1 MHz, ¹³C: 75.4, ¹¹B: 96.2 MHz, ¹⁹F:282.2 MHz and ³¹P 121.4 MHz). Deuterated solvents (CD₂Cl₂, D₂O and d₆-DMSO) were used as internal standards. The chemical shift are noted in parts per million (ppm), the coupling constant in Hz.

The high resolution mass spectra were recorded in a positive and negative ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The gas flow of spray gas is 0.6bar and the capillary voltage is +/-4.5kV. The solutions are infused at 180µL/h. The mass range of the analysis is 50-1000m/z and the calibration was done with sodium formate.

1-butyl-3-methylimidazolium tetrafluoroborate: [C₄H₄Im][BF₄]
**1-butyl-3-methylimidazolium thiocyanate** : \([\text{C}_4\text{H}_9\text{Im}][\text{SCN}]\)

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<tbody>
<tr>
<td>Mass calculated</td>
<td>226.1</td>
<td>139.1</td>
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Chloride peak at m/z=313

ESI\(^+\) mass spectrum

ESI\(^-\) mass spectrum
Entire Cation Anion

Mass calculated 197.1 139.1 57.9

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: \([\text{C}_4\text{Im}][\text{NTf}_2]\)
1-butyl-3-methylimidazolium dicyanamide: \([C_1C_4Im][N(CN)_2]\)

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<td>419.0</td>
<td>139.1</td>
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**ESI**\(^{+}\) mass spectrum

**ESI**\(^{-}\) mass spectrum

Electronic Supplementary Material (ESI) for Green Chemistry
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**1H NMR in d6-DMSO**

**13C NMR in d6-DMSO**
1-hexyl-3-methylimidazolium tetrafluoroborate: \([\text{C}_6\text{C}_4\text{Im}][\text{BF}_4]\)
$^1$H NMR in CD$_2$Cl$_2$

$^{13}$C NMR in CD$_2$Cl$_2$
$^{19}$F NMR in CD$_2$Cl$_2$

$^{11}$B NMR in CD$_2$Cl$_2$
1-hexyl-3-methylimidazolium thiocyanate: [C₆H₁₃Im][SCN]

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<tr>
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<td>167.1</td>
<td>87</td>
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### ESI+ mass spectrum

- m/z 167.11
- m/z 392.34

### ESI− mass spectrum

- m/z 58.02
- m/z 283.12

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1-hexyl-3-methylimidazolium dicyanamide: [C$_6$C$_4$Im][N(CN)$_2$]
1-octyl-3-methylimidazolium tetrafluoroborate: [C₈C₃Im][BF₄]

Electronic Supplementary Material (ESI) for Green Chemistry
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$^1$H NMR in CD$_2$Cl$_2$

$^{13}$C NMR in CD$_2$Cl$_2$
ESI+ mass spectrum

ESI− mass spectrum

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<td>195.1</td>
<td>87.0</td>
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1-octyl-3-methylimidazolium dicyanamide: \([\text{C}_8\text{Im}]\text{[CN]}_2\)
N-butyl-N-methylpyrrolidinium dicyanamide: [P₄][N(CN)₂]

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<td>195.1</td>
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$^1\text{H NMR in d}_6\text{-DMSO}$
\[^{13}\text{C} \text{ NMR in d6-DMSO}\]

![Graph showing NMR spectrum with peaks at 142.15, 350.32, and 319.32 m/z.]

\[\text{ESI}^+ \text{ mass spectrum}\]

![Graph showing ESI+ mass spectrum with peaks at 142.15, 350.32, and 319.32 m/z.]

\[\text{ESI}^- \text{ mass spectrum}\]

![Graph showing ESI- mass spectrum with peaks at 66.00 and 274.17 m/z.]

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\text{N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide: } [\text{P}_{14}][\text{NTf}_2] \]
$^1$H NMR in CD$_2$Cl$_2$
$^{13}$C NMR in CD$_2$Cl$_2$

ESI$^+$ mass spectrum
ESI mass spectrum

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Tetrabutylphosphonium bis(trifluoromethylsulfonyl)imide: [P_{4444}][NTf_{2}]
$^{31}$P NMR in CD$_2$Cl$_2$

ESI$^+$ mass spectrum
ESI mass spectrum

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Tetrabutylphosphonium tetrafluoroborate: [P$_{4444}$][BF$_4$]
$^{31}$P NMR in CD$_2$Cl$_2$

$^{19}$F NMR in CD$_2$Cl$_2$
$^{11}$B NMR in CD$_2$Cl$_2$

ESI$^+$ mass spectrum
**ESI mass spectrum**

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