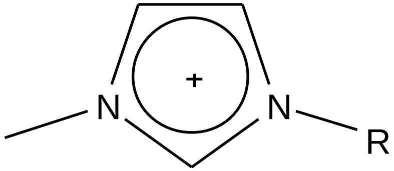
How to select the best ionic liquid for a given application?

Koen Binnemans

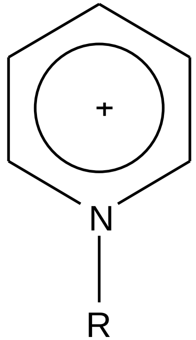
Catholic University of Leuven (Belgium)

Cations of ionic liquids



1

imidazolium



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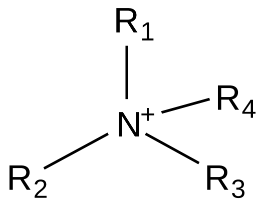
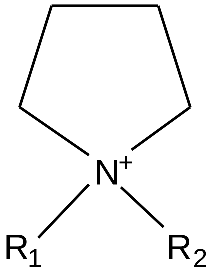
pyridinium



3

ammonium



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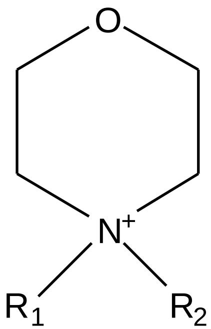
pyrrolidinium



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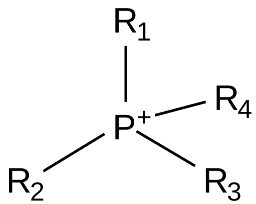
morpholinium



6

phosphonium

Anions of ionic liquids

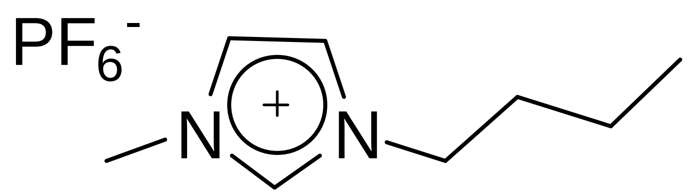
- $[AlCl_4]^-$, $[Al_2Cl_7]^-$
- Cl^-, Br^-, I^-
- SCN^-, $[N(CN)_2]^-$
- $[NO_3]^-$, $[SO_4]^{2-}$
- $[CH_3COO]^-$, $[CF_3COO]^-$
- $[CF_3SO_3]^-$ (= OTf)
- $[BF_4]^-$
- $[PF_6]^-$, $[SbF_6]^-$
- $[(CF_3SO_2)_2N]^-$ (= Tf_2N)
- $[Co(CO)_4]^-$
- ….. many more other anions

Number of possible ionic liquids?

- By combination of cations, anions, chains lengths, substitution pattern, chirality, …:
  - About one million (10^6) simple ionic liquids
  - About one billion (10^{12}) binary ionic liquids
  - About one trillion (10^{18}) ternary ionic liquids

  According to Ken Seddon (QUILL, Belfast)

- But: until quite recently more than 50% of all publications were about one class of ionic liquids!!! [$C_n$mim][PF_6]
  and in particular:
  [C_4mim][PF_6]
  [BMIM][PF_6]



Why was [BMIM][PF_6] so popular?

- Relatively cheap
- Easy synthesis and purification
- Excellent model compound for fundamental studies (high symmetry of anion, weak hydrogen bonding)
- Hydrophobic: not miscible with water
- …. Everyone was using it ("me too" mentality)

…. The ionic liquid [BMIM][PF_6] is a strong candidate for use as a recyclable solvent, the Belfast team suggests. It is readily prepared at room temperature, is stable to moisture, and has **no detectable vapor pressure**. Furthermore, it is immiscible with water and hexane but dissolves many organic compounds and transition-metal complexes. And it is a liquid from just above 0 °C to more than 200 °C. "This is my favorite room-temperature ionic liquid since it is **water stable** and water immiscible," comments **Robin Rogers** chemistry professor at the University of Alabama, Tuscaloosa. "The big advantage I see here is product recovery and no solvent loss through evaporation. Seddon's work furthers the idea that room-temperature ionic liquids can be used as replacements for volatile organic compounds. I see an almost infinite variety of potential reactions in these liquids."

(*Chemistry and Engineering News, 4 Jan. 1999*)

Things can change…

Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate

Richard P. Swatloski, John D. Holbrey and Robin D. Rogers

Green Chemistry, 2003, **5**, 361–363

Why is [BMIM][PF_6] problematic?

- $[PF_6]^-$ is hydrolytically unstable.
- Contact with water above 50°C leads to HF formation
  Every mole of [BMIM][PF_6] produces 5 moles of HF!!

$$[PF_6]^- + 4H_2O \leftrightarrows 5HF + F^- + H_3PO_4$$

- Measurements above 50°C lead to HF formation.
- High viscosity (371 cP at 25 °C)
- Because of its instability, [BMIM][PF_6] will never be used as a solvent by the chemical industry.
- [BMIM][PF_6] is now considered as the « *Antichrist* » of ionic liquids

Is there still a future for hexafluorophosphate ionic liquids?

- [BMIM][PF_6] must not be used as:
  - solvent for chemical reactions
  - organic phase for solvent extraction

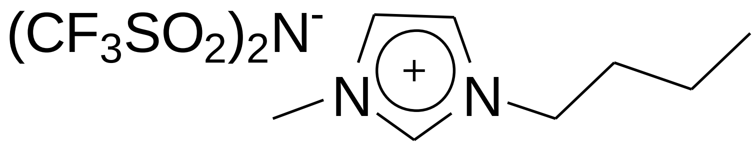
- But: $LiPF_6$ is still widely used as electrolyte in Li-ion batteries
  Hexafluorophosphate can be used in electrochemical devices (anhydrous electrolytes)
- PF_6^- is a useful ion for the design of **ionic liquid crystals**

1-Alkyl-3-methylimidazolium salts, [$C_n$mim][X]

[$C_n$mim][PF_6]: liquid-crystalline for C_{14} chain and longer
[$C_n$mim][Tf_2N]: not liquid-crystalline

What is a good alternative for [BMIM][PF_6] ?

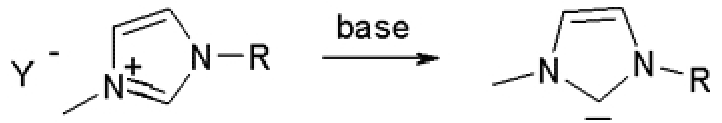
- Bistriflimide ionic liquid [BMIM][Tf_2N]



- Many names for one and the same anion:
  - Bistriflimide — $(CF_3SO_2)_2N^-$
  - Triflimide — PMS
  - **Bis(trifluoromethylsulfonyl)imide** — Tf_2N^-
  - Bis(trifluoromethylsulfonyl)amide — BTA
  - Bis(perfluoromethylsulfonyl)imide — TFSI
  - Bis(trifluoromethanesulfonyl)imide

Is [BMIM][Tf_2N] the ideal ionic liquid?

- [BMIM][Tf_2N] is now often considered as the standard ionic liquid for general use:
  - Solvent for chemical reactions
  - Organic phase in solvent extraction
  - Electrolyte for electrodeposition of metals
- However.....
  - Imidazolium not stable against strong bases (carbene formation)



  - Limited cathodic stability (reduction)
  - Limited stability against oxidation (ozonolysis)
  - Many metal salts and biopolymers (cellulose) are poorly soluble in ionic liquids with Tf_2N^- anions

Electrochemical windows of $[Tf_2N]^-$ salts

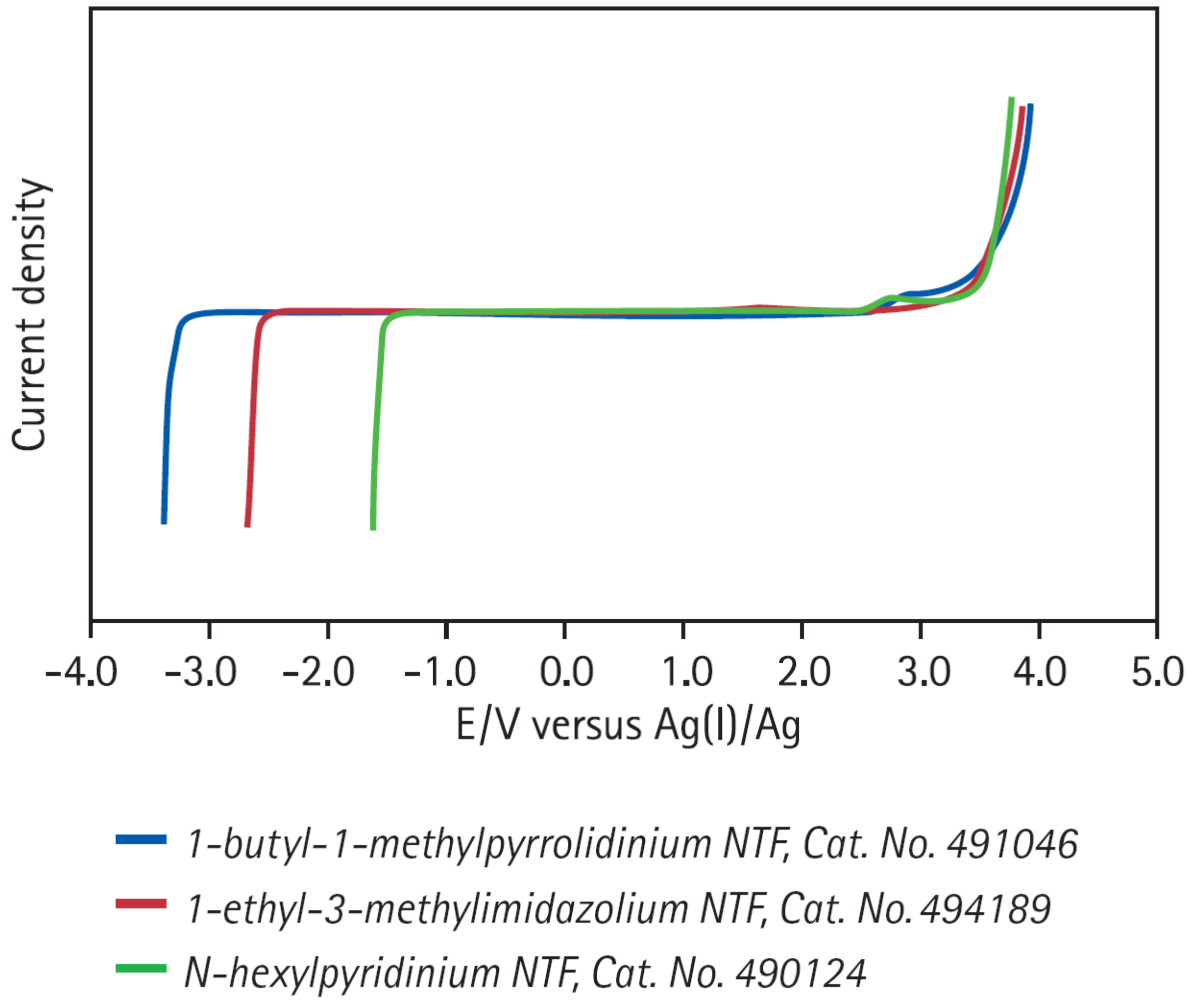
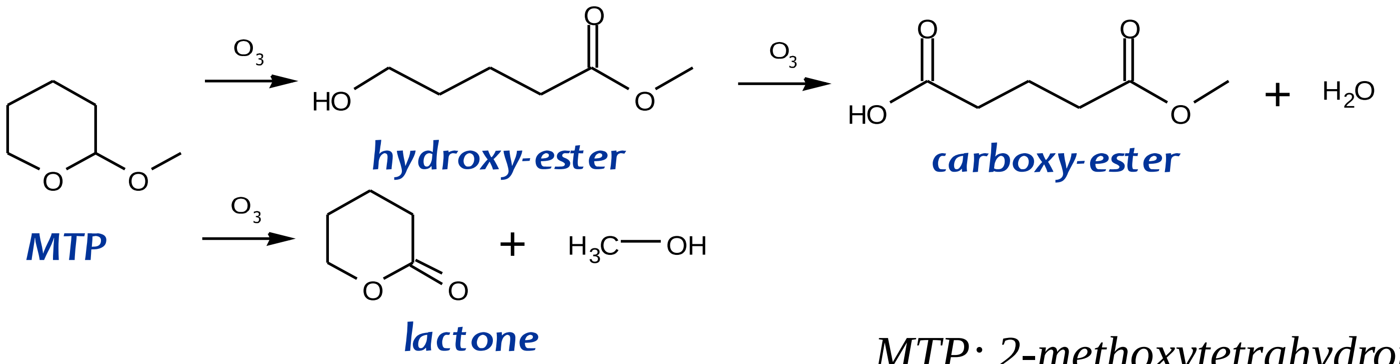


Figure from Merck catalogue

Ozonolysis in ionic liquids

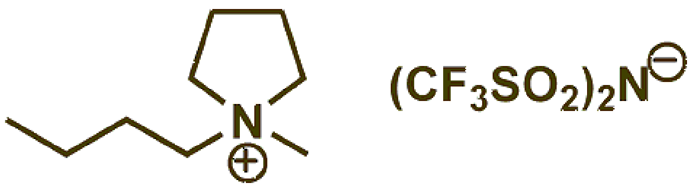


MTP: 2-methoxytetrahydropyran

- Ozone = interesting alternative for less green oxidants
- Disadvantages ozone:
  - explosive mixtures with organic solvents
  - aerosol formation upon bubbling of ozone through solution
- Ionic liquids offer solution
  - very low vapor pressure
  - high viscosity

Ozonolysis in ionic liquids

- Ozonation stability test
  (0.42 mmol O_3 per minute for 2 hours at 100 °C)
- Ozone resistance evaluated at the molecular level by ^{1}H and ^{13}C NMR and macroscopically by colour and viscosity changes
- Fast degradation of imidazolium ionic liquids
  sensitivity of double bonds to ozone
- Good ozone stability for pyrrolidinium salts
  [BMPyr][$(CN)_2N$] and [BMPyr][Tf_2N]



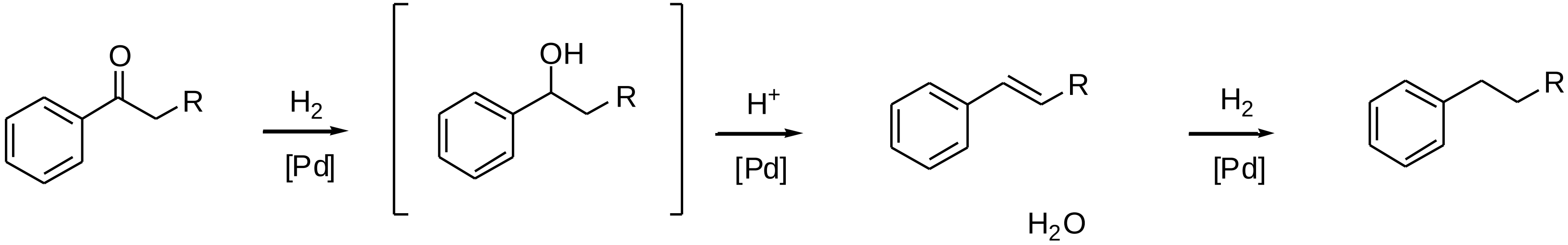
Van Doorslaer et al., *Chem. Commun.* (2009) 6439

Selection criteria for ionic liquids

- Miscibility with water or organic solvents (temperature dependent)
- (Electro)chemical stability
- Solubility of solutes
- *Melting point*
- *Viscosity*

- Some ionic liquids have wide applicability
  - [BMIM][Tf_2N] for organic synthesis
  - [BMPyr][Tf_2N] for electrodeposition of reactive metals
  - [EMIM][OAc] for dissolution of cellulose
- In other cases, series of ionic liquids have to be screened
- Mixtures of ionic liquids can have unexpected properties

Hydrogenolysis of aromatic ketones to alkylbenzenes



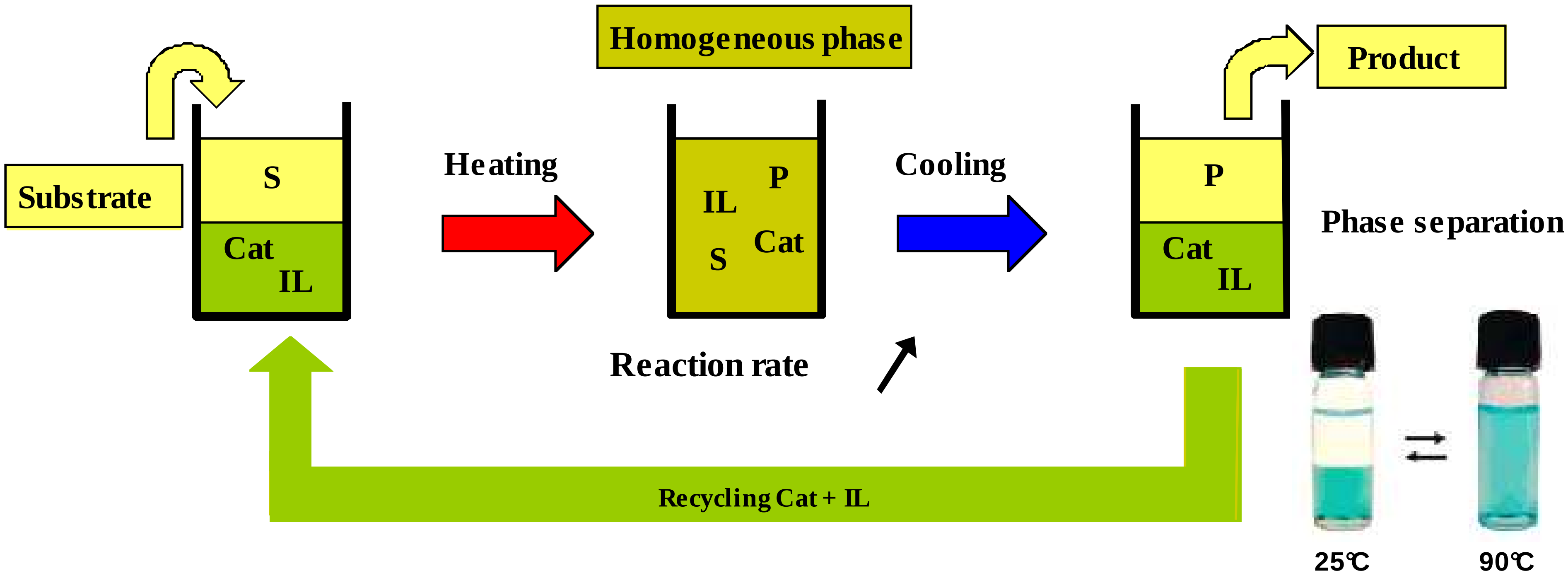
Alkylbenzenes: intermediates for alkylbenzene sulfonate surfactants

Advantages of ionic liquids in catalytic hydrogenolysis

- improving recyclability Pd catalyst: immobilization of Pd catalyst in IL
- improved product separation by change in polarity
  aromatic ketone (polar) → alkylbenzene (nonpolar)
- acidic solvent for promoting hydrogenolysis: IL with acidic functional group

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Biphase catalysis in ionic liquids



S = substrate P = product
Cat = catalyst IL = ionic liquid

Product must be less polar than substrate

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Miscibility of ionic liquids with aromatic ketones and alkylbenzenes

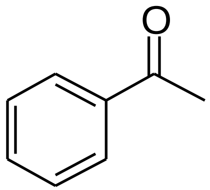
- Ideal ionic liquid:
  - homogeneous mixture at reaction temperature (80 °C)
  - phase separation after cooling to RT
    (product isolation by decantation)

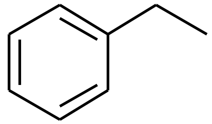
    or
  - miscible with aromatic ketone substrates at 80 °C
  - immiscible with derived alkylbenzene products at RT

- Reaction mixture composition at 70 % conversion was simulated with a 30 mol% ketone/70 mol% alkylbenzene mixture (‘30/70’)
- Water was added to closely simulate reaction conditions : water generated as by-product in alkylbenzene formation.

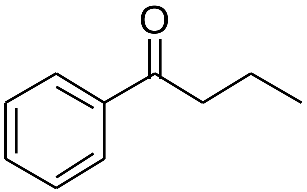
Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

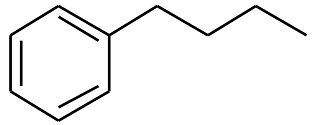
Selected ketones and alkylbenzenes



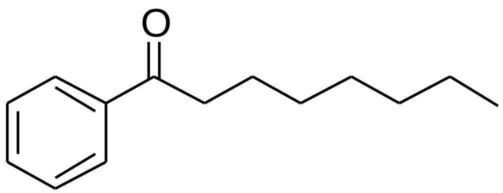


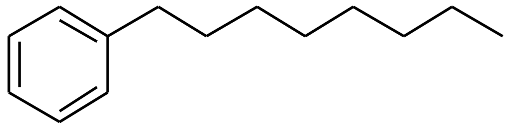
C_2





C_4





C_8

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

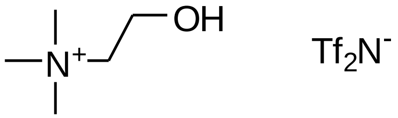
Selected ionic liquids

- **Screening of more than 30 different ionic liquids**
- Cations:
  - Methyltrioctylammonium ($MOct_3N$)
  - Choline (Chol)
  - 1-Ethyl-3-methylimidazolium (EMIM)
  - 1-Butyl-3-methylimidazolium(BMIM)
  - 1-Butyl-2,3-dimethylimidazolium (BMMIM)
  - *N*-butyl-*N*-methylpyrrolidinium (BMPyr)
  - *Different cations functionalized with COOH function*
- Anions: Cl^-, BF_4^-, Tf_2N^-, CF_3COO^-, CH_3COO^-, $CH_3SO_3^-$, $CF_3SO_3^-$, Tosylate, $EtSO_4^-$, HSO_4^-, $N(CN)_2^-$
- No hexafluorophosphate (PF_6) salts: hydrolyze with HF formation in the presence of water at 80 °C

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Results of miscibility tests

- Limited number of tests successful.
- **Methyltrioctylammonium salts**: negative results.
- **Imidazolium salts**: positive results for [BMIM][Tf_2N] and [BMMIM][Tf_2N], but only for tests with octanophenone.
- **Pyrrolidinium salts**: positive results for ([BMPyr][CF_3CO_2] in combination with butyrophenone and for [BMPyr][$(CN)_2N$] in combination with all ketones.
- Good results for *choline bistriflimide* [Chol][Tf_2N]



- Good results for most COOH-functionalized ionic liquids and especially for *betainium bistriflimide* [Hbet][Tf_2N]

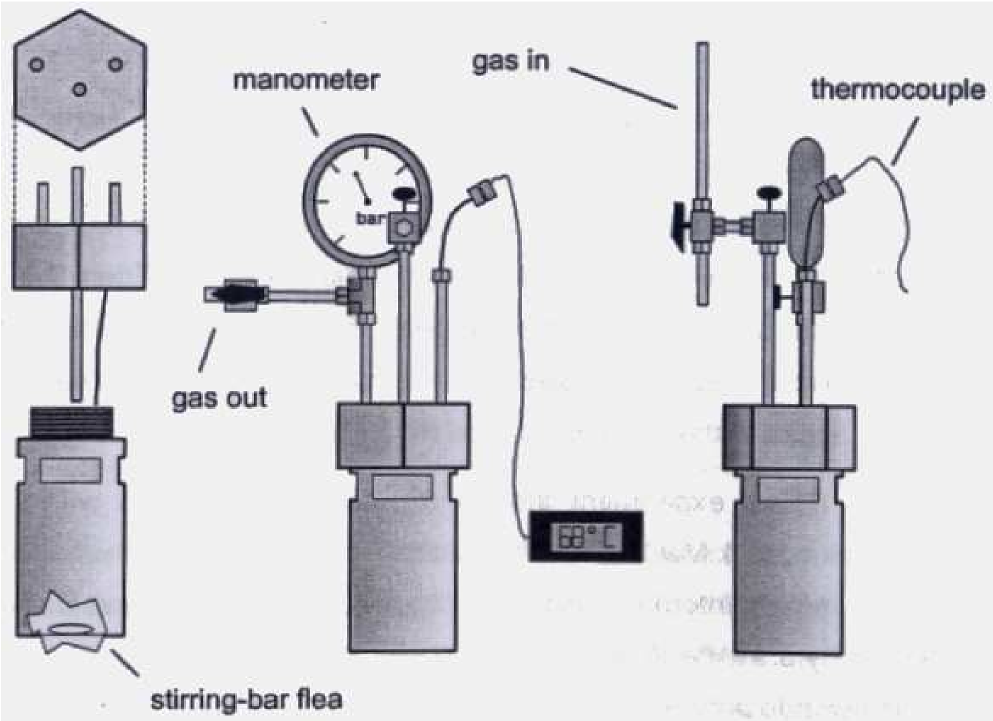
Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Catalytic experiments

1. Reactor

10 mL reactor

2 mL ionic liquid
50 bar H_2
80 ℃
2 hours



2. Analysis

➢ *Procedure*

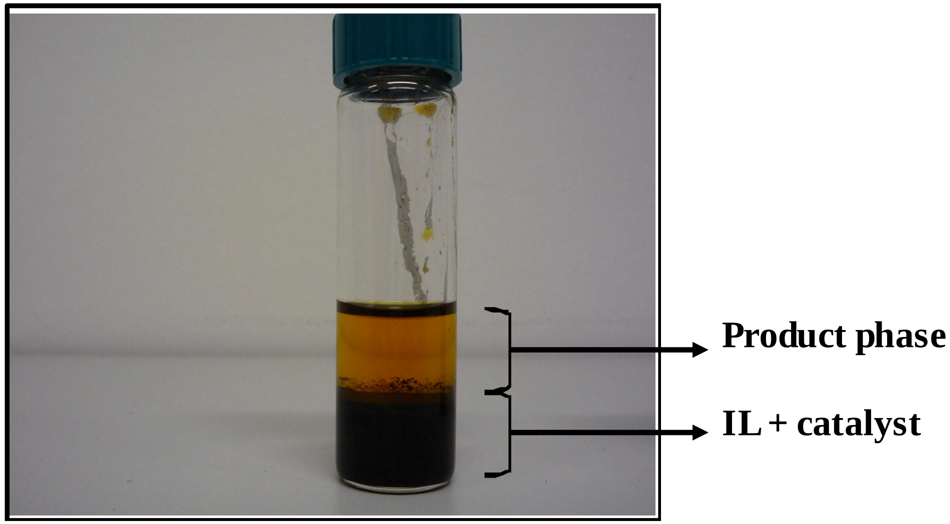
Upper layer reaction mixture (diluted in toluene) is injected in GC with FID and apolar column (CB-sil 5)

➢ *Identification components*

Injection pure components + GC-MS

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Product isolation

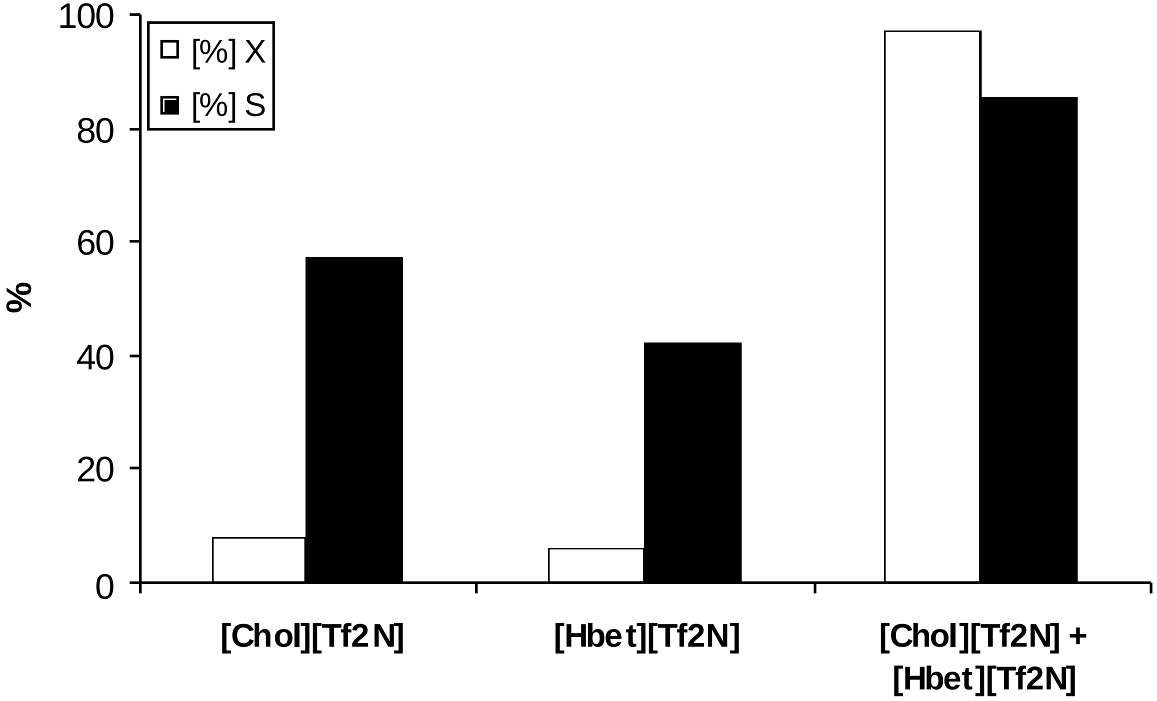


Phase separation after hydrogenolysis of octanophenone

Product phase: less than 0.01mol% IL leaching (NMR)
No measurable Pd leaching (ICP-AES)

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Mixtures of ionic liquids



Reaction conditions: acetophenone (6 mmol), 0.08 g of 5 wt.% Pd-C, [Chol][Tf$_2$N] (2 mL), [Hbet][Tf$_2$N] (1 mL), 80 ° C, 50 bar H_2, 2 h; X [%] = conversion of ketone; S [%] = selectivity towards ethylbenzene;

1 + 1 ≠ 2 Synergism in ionic liquid mixtures

Van Doorslaer et al., *ChemSusChem* **1** (2008) 997.

Design your own ionic liquid: Liquid metal salts

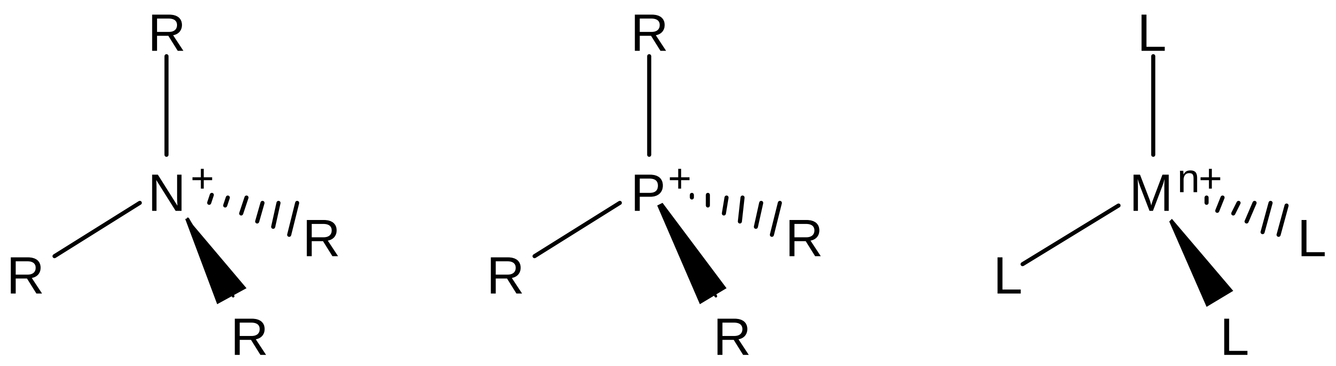
- Need for high concentrations of metal ions in electrolytes for electrodeposition
- New approach: make metal part of ionic liquid
  - No longer a need to dissolve metal salts
  - High metal concentrations
- Until now most metal-containing ILs had metal in anion

  e.g. $[AlCl_4]^-$ or $[CoCl_4]^{2-}$

  these anions are not electro-active: not interesting for electrodeposition
- **Metal in cation** is attracted toward cathode where electrodeposition takes place.
- Try to design low-melting metal salts (***liquid metal salts***) with the metal an integral part of the cation.

Liquid metal salts

- Tetrahedral metal ions with four ligands are analogues of tetraalkylammonium or phosphonium ions
- For example, copper(I) with four neutral ligands



- Choice of anion important for lowering the melting point
- Metal preferably in lowest available oxidation state

Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

$[Cu(MeCN)_4][Tf_2N]$

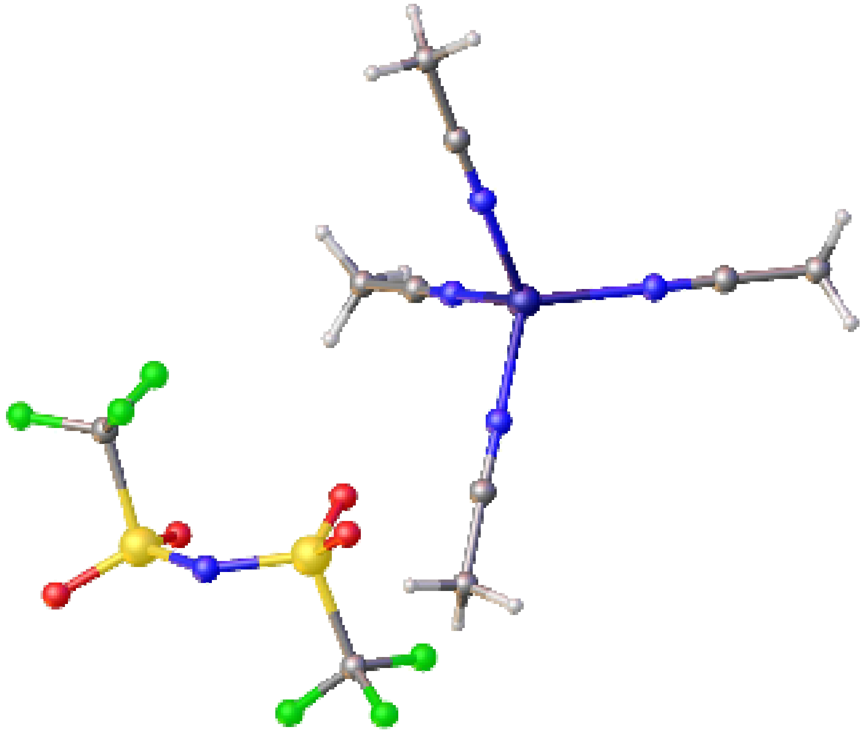
- Synthesis:

  $CuO + 2\ HTf_2N \rightarrow Cu(Tf_2N)_2 + H_2O$

  $Cu(Tf_2N)_2 + Cu(s) + 8\ CH_3CN \rightarrow 2\ [Cu(CH_3CN)_4][Tf_2N]$

- Melting point: 66 °C
- For comparison:
  - $[NMe_4][Tf_2N]$ 133 °C
  - $[NEt_4][Tf_2N]$ 109 °C
  - $[NPr_4][Tf_2N]$ 105 °C

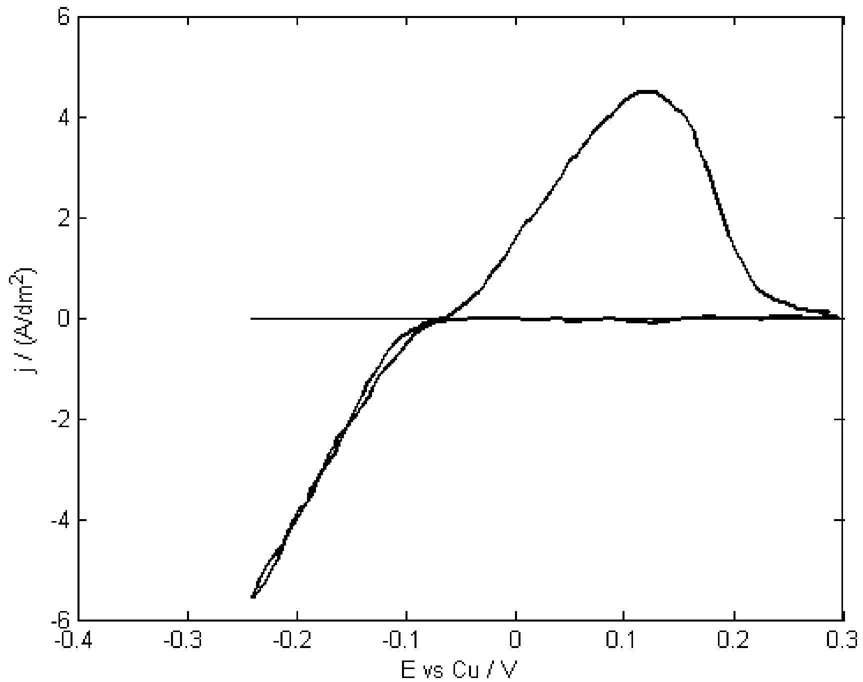
  - $[Cu(MeCN)_4][OTf]$ 124 °C

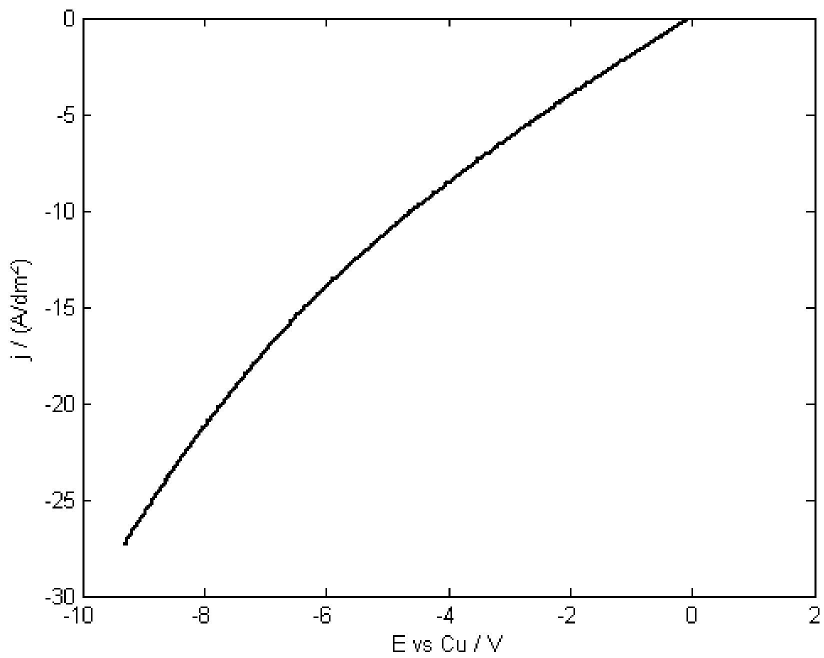


Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Electrochemistry of $[Cu(MeCN)_4][Tf_2N]$

- Because cathodic decomposition reaction of ionic liquid is the reduction of the metal ion to the metallic state, high current densities can be obtained.
- Anodic reaction is stripping of copper from sacrificial electrode

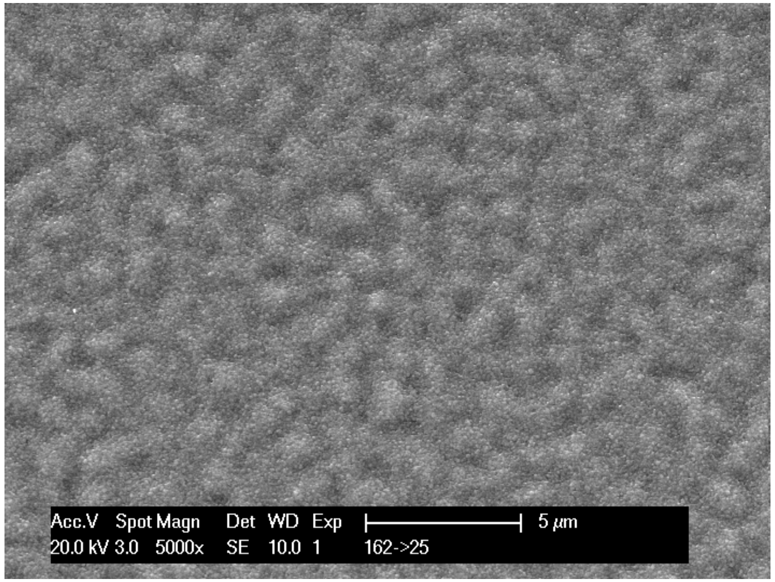


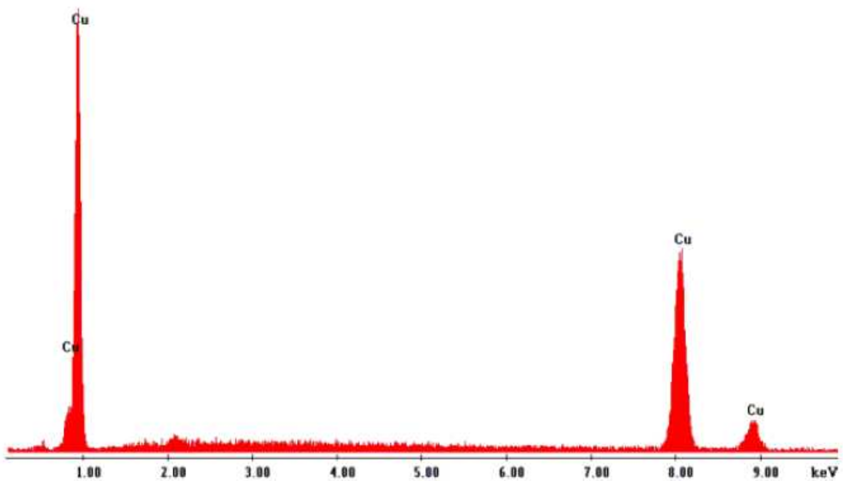


Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Deposit from $[Cu(MeCN)_4][Tf_2N]$

- Current density: 25 $A.dm^{-2}$
- Deposit average thickness: 1 μm
- Time for deposit: 5s



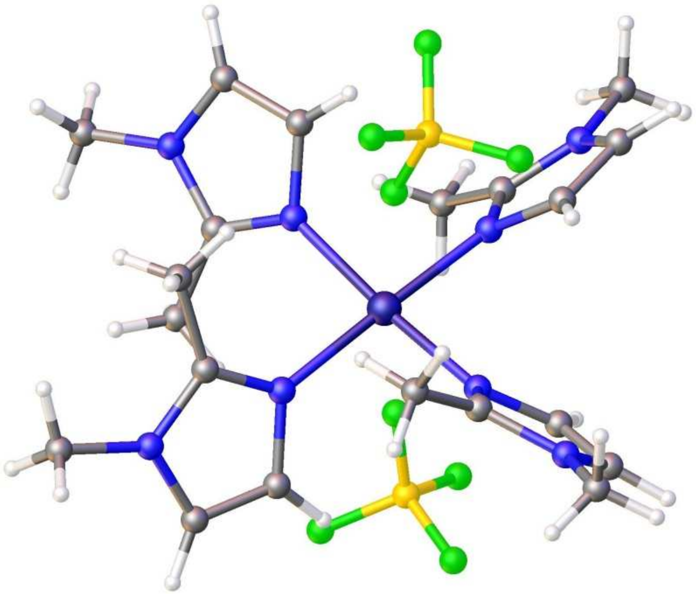


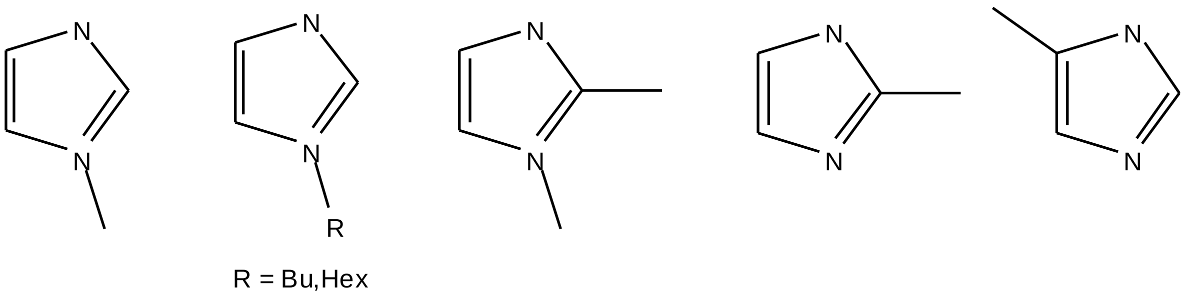
- EDX analysis shows no decomposition products included in layer

Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Copper(II)-containing Liquid Metal Salts

$[Cu(MeIz)_6][Tf_2N]_2$	50 °C
$[Cu(BuIz)_4][Cl]_2$	55 °C
$[Cu(BuIz)_4][Tf_2N]_2$	**< RT**
$[Cu(BuIz)_4][NO_3]_2$	126 °C
$[Cu(HexIz)_4][Cl]_2$	66 °C
$[Cu(MeIz)_6][Tf_2N]_2$	50 °C
$[Cu(1,2\text{-}DiMeIz)_4][BF_4]_2$	185 °C

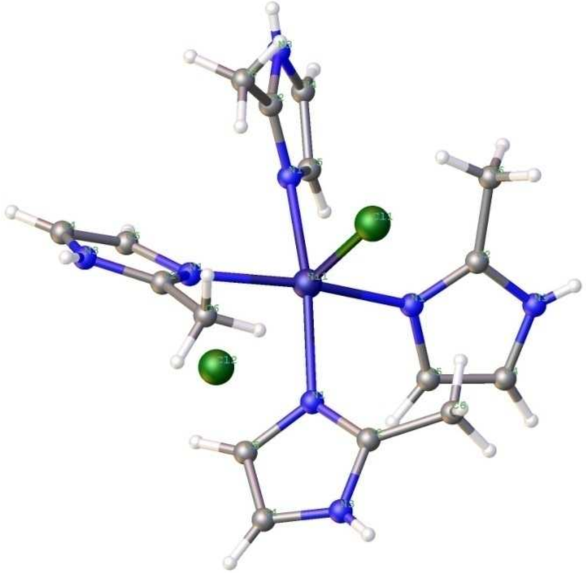




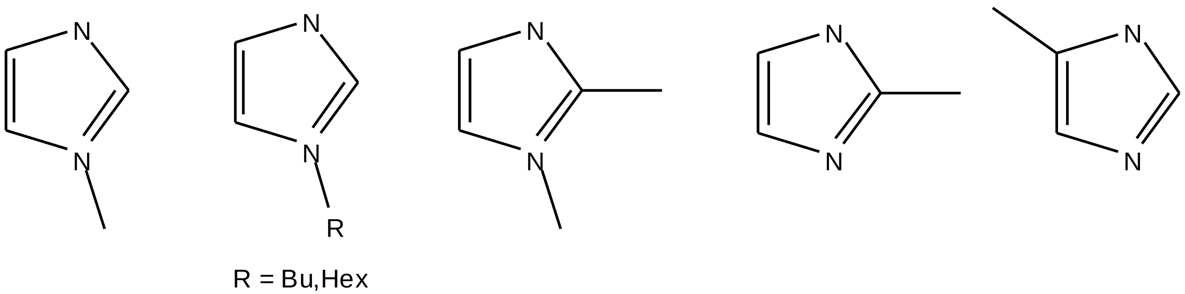
MeIz, BuIz, HexIz   1,2-DiMeIz   2-MeIz   4-MeIz

Liquid Metal Salts of other transition metals

$[Ni(2\text{-}MeIz)_4Cl][Cl]$	83 °C
$[Ni(BuIz)_6][Cl]_2$	124 °C
$[Ni(HexIz)_6][Cl]_2$	69 °C
$[Co(HexIz)_6][Cl]_2$	**34 °C**
$[Fe(MeIz)_6][NO_3]_2$	60 °C
$[Mn(BuIz)_6][Cl]_2$	58 °C
$[Mn(HexIz)_6][Cl]_2$	**45 °C**



$[Ni(2\text{-}MeIz)_4Cl][Cl]$ 83 °C



MeIz, BuIz, HexIz 1,2-DiMeIz 2-MeIz 4-MeIz

Conclusions

- [BMIM][Tf_2N] is preferred over [BMIM][PF_6] as a solvent for organic reactions and extraction studies
- There can be stability issues with imidazolium ILs
  - Stability in alkaline medium
  - Stability against oxidation and reduction
- Pyrrolidinium ionic liquids have higher electrochemical stability
- Screening of ionic liquids can be required to find best system (screening sets are commercially available)
- Mixtures often perform better than pure Ils
- Biopolymers are not soluble in Tf_2N^- ILs
- Inorganic salts are often poorly soluble in Tf_2N^- ILs
- Liquid metal salts have high metal concentration

Acknowledgments

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  - Prof. Dr. Luc Van Meervelt, Dr. Kristof Van Hecke
  - Dr. Neil Brooks
  - Prof. Dr. Dirk De Vos, Prof. Dr. Jan Fransaer, Prof. Dr. Christ Glorieux
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