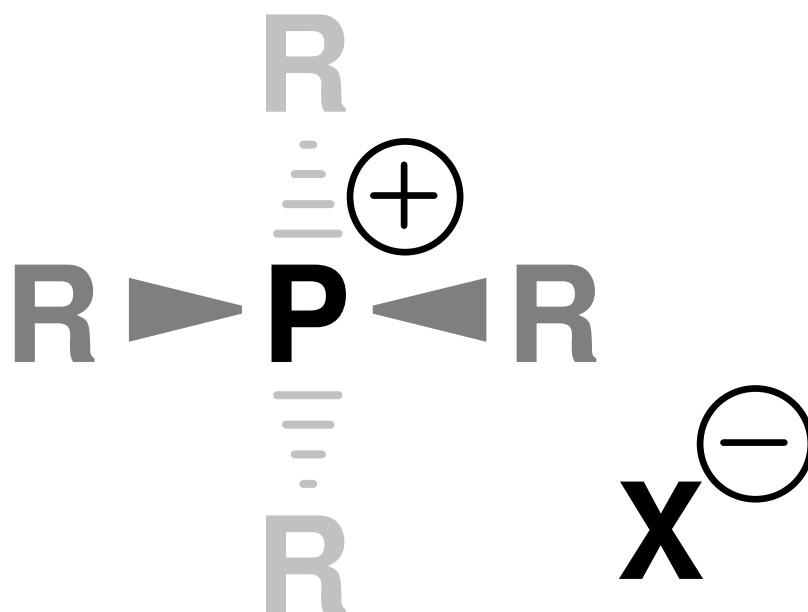


# Ionic Liquids Today

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Issue 3-06, Monday, 11<sup>th</sup> December, 2006.

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>>> **Phosphonium-based ionic liquids: a forgotten class of materials?**

>>> **How pure do ionic liquids have to be?**



## **Content:**

- I. Editorial: How pure do ionic liquids have to be?**
- II. Applications of ionic liquids**
- III. Phosphonium-based ionic liquids: wake up from the beauty sleep!**
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## **I. Editorial**

By Thomas Schubert.

On this occasion, I'd like to thank all co-operation partners from universities, institutes and the industry, researchers and scientists (whether they purchased our high purity materials or not) and last but not least all friends from the community.

There are some truly interesting applications on the horizon to be commercialised within the next few years. In addition, the number of publications about ionic liquids is still increasing. Whereas five years ago publications about synthesis and catalysis dominated, we have seen the main focus of interest shifting more to physical data of ionic liquids in 2006. I really welcome this – simply because it agrees well with our company's philosophy: to provide solid data that enables scientists and engineers to design new processes and devices. After more than five years of answering questions concerning ionic liquids applications I can tell you: there's at least one enquiry each week about a potential use of ionic liquids I would never have thought of!

But we have to be honest: some applications, e.g. thermal fluids for solar thermal devices, are more difficult to realize than expected.<sup>1</sup>

Let's look forward to another successful year 2007!

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<sup>1</sup> This was shown in a feasibility study by the Fraunhofer Institute for Solar Energy Systems (FhG ISE, Freiburg, Germany), the Institute for Environmental Research and Technology (UFT, Bremen, Germany), Tyforop Chemie GmbH (Hamburg, Germany) and IOLITEC, funded by the Deutsche Bundesstiftung Umwelt e.V.



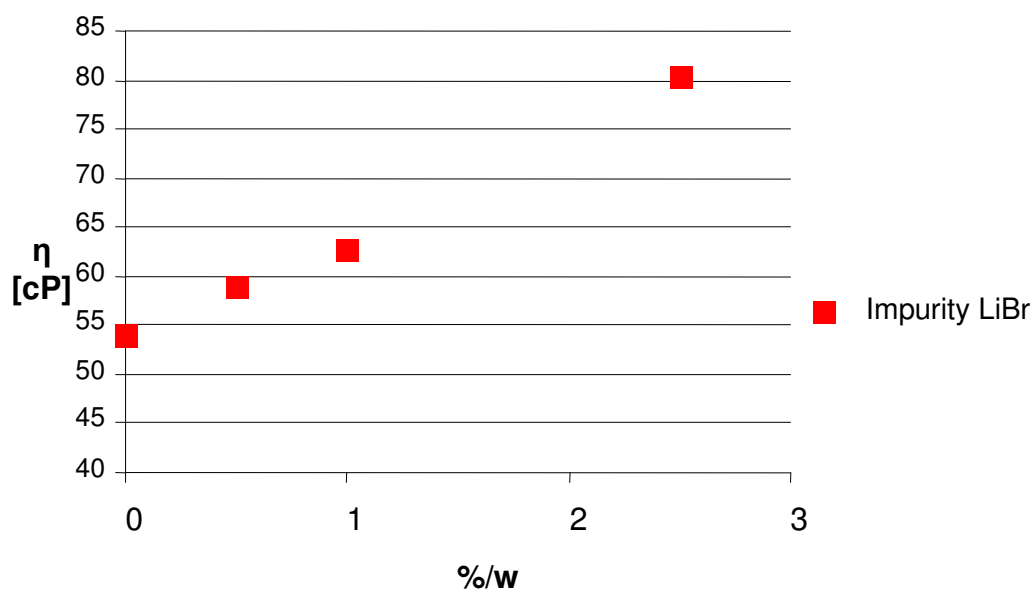
## How pure do ionic liquids have to be?

In the previous issue I discussed (my very personal and completely subjective view of) ionic liquids' commercialisation. Driven by a number of discussions with chemists and engineers, I'll try to give a statement from the view of an ionic liquids developer and supplier.

### The effect of impurities on the physical properties

The physical properties of ionic liquids show a strong dependency on both ionic impurities, e.g. halides, and non-ionic impurities, e.g. water. In order to gain more insight we investigated the influence of these typical impurities systematically.

In a first series of experiments we contaminated a high-purity sample of the easy-to-handle ionic liquid *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide with varying amounts of lithium bromide and measured the corresponding viscosity (Fig. 1):



**Fig. 1.** Effect of a typical impurity on the viscosity of an ionic liquid.

The message from this experiment is obvious at the first glance: only 2.5% of added lithium bromide resulted in an increase in viscosity by 48%. As a consequence, the corresponding conductivity surely will be lower, too. This result for ionic liquids is



definitely different from the known behaviour observed in aqueous media, where the conductivity increases, if we also increase the number of charge carriers.

But to be honest, this is just half of the truth: if we use molar fractions instead of % by weight, we added  $x = 0.108$  or 10.8% lithium bromide, since the difference of the molecular weight is small compared to the ionic liquid. How this "hard" lithium cation is "solvated" by the ionic liquid is, or surely will be subject matter of current or future research.

Another interesting aspect was demonstrated in an impressive way by *Ken Seddon* and co-workers by simply comparing published melting points of the common ionic liquid 1-ethyl-3-methyl-imidazolium tetrafluoroborate:

**"Influence of chloride, water and organic solvents on the physical properties of ionic liquids."**

K.R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275-2287.

**"[...] This can be illustrated by melting points reported for the same ionic liquid, e.g. [EMIM] [BF<sub>4</sub>]:**

**15°C:** J.S. Wilkes, M.J. Zaworotko, *J. Chem. Soc., Chem. Comm.* **1992**, 965-967.

**5.8°C:** J.D. Holbrey, K.R. Seddon, *J. Chem. Soc., Dalton Trans.* **1999**, 2133-2139.

**12.5°C:** J. Fuller, R.T. Carlin, R.A. Osteryoung, *J. Electrochem. Soc.* **1997**, *144*, 3881-3886.

**11°C:** A.B. McEwen, H.L. Ngo, K. Lecompte, J.L. Goldman, *J. Electrochem. Soc.* **1999**, *146*, 1687-1695.

**14.6°C:** A. Noda, M. Watanabe, *Electrochim. Acta.* **2000**, *45*, 1265-1270

In other words: five references, five different melting points! A truly frustrating result, especially for potential users of ionic liquids. Since melting points are typically lowered by impurities (leading often to supercooling and/or glass transitions), I personally prefer *Wilkes'* or *Watanabe's* numbers.

In conclusion, these observations lead to an important result: in order to measure reliable values for physical properties of ionic liquids, exact specifications, like halide



and water content, have to be determined before in a reliable way, too. But how can we determine inorganic halide impurities dissolved in another salt? The answer is simple: ion chromatography!

### ***The influence of impurities on applications***

In a number of publications it was described that residual halide can cause problems in catalysis. Furthermore, it's quite obvious that in electrochemical applications residual halide as well as water can lead to a significant loss of performance, since values of important physical properties change dramatically, e.g. conductivity or the electrochemical window. But also in thermodynamic applications, like the use as thermal fluids or sorption cooling media, halides can cause serious trouble like a significant increase in viscosity and, of course, an increased corrosiveness.

If we go from R&D chemicals to industrial chemicals, the price criterion becomes more and more important. Since each purification step of the starting materials or the raw ionic liquid produces additional costs, we have to ask again: how pure do ionic liquids have to be? If commercialisation of a certain ionic liquid-based process becomes more and more concrete, both users and suppliers have to find a balance between necessary specifications, i.e. colour and acceptable impurities like halides or water, and of course the price. At least one thing is trivial: a material produced on a multi-tonne scale will be much cheaper than one produced for lab scale applications.

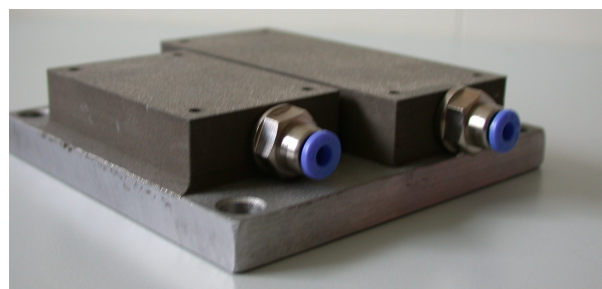
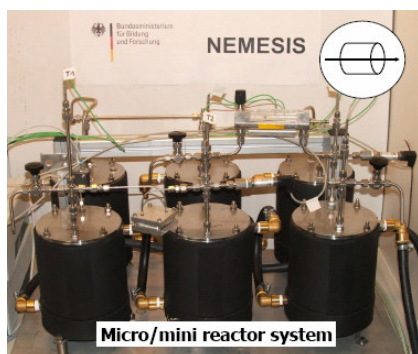
### ***The synthetic pathway***

Many problems with impurities are caused by the synthetic pathway. Since ionic liquids have a low to negligible vapour pressure, it is difficult to purify them once they have been produced. As a consequence, the use of very pure starting materials is extremely important.

The first step is an alkylation reaction of N, S or P with an alkylating agent. In many cases the resulting materials are already ionic liquids by definition. The chemist has to fight with some truly difficult problems, because kinetics and thermodynamics of such reactions can be extremely tricky. In typical batch processes many problems are caused by so-called "hot-spots", leading to by-products and thus to impurities. These problems become even more dramatic if the reaction is scaled up.



At IOLITEC we have realised that controlling reaction temperatures and efficient mixing of reactants can avoid hot spots. This leads directly to *microreactor technology*. In the project funded by the German BMBF, we developed together with a team of experts from universities, research institutes and the industry a microreactor system capable of producing ultrapure ionic liquids in a continuous process. In 2007 production of ionic liquids using this new technology will start, which puts IOLITEC in the position to produce quantities up to 100 kg per week.



## ***Quality control***

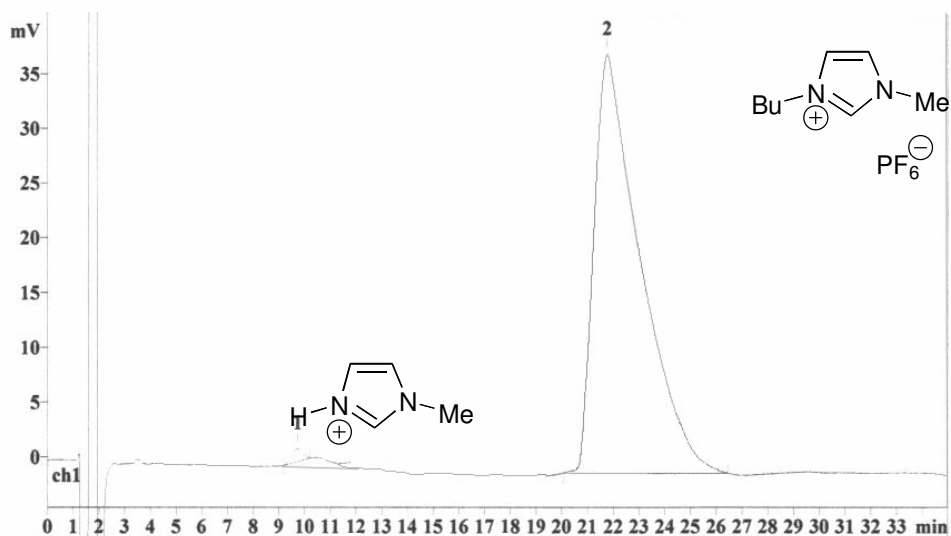
A novel class of materials needs novel methods for their analysis and, with regard to their commercial production and distribution, novel methods for quality control. In this context, ionic liquids are a real challenge, since they combine organic with inorganic chemistry, resulting in a number of materials. Many of them are synthesized using the so-called "metathesis route", which simply means ion exchange and which should not be confused with the organic metathesis reaction.

At IOLITEC we decided right from the start to use ion chromatography (IC) to detect halide impurities next to larger, sometimes more complex anions, but also alkali metal ions next to other cations. IC is a liquid chromatography very similar to HPLC. The main differences between IC and HPLC are the detection system and the columns, which are designed for the separation of ions. The measured physical property is conductivity, but UV/VIS detection is also possible.

A really important and labour-intensive point is the development of methods for the detection of new cations and anions, which are typically larger and more complex than "normal" ions measured by using IC. An interesting point worth mentioning is



the possibility of detecting amines using IC: samples containing traces of amines are acidified to form cations which can then be detected by IC (Fig. 2).



**Fig.**

## 2. Detection of amine impurities using IC.

In our quality control lab, we have developed a number of specific methods for different cations and anions. The future challenges are to optimise these methods using columns that are designed for larger cations and anions and thus of course for ionic liquids. In this interesting field of research we co-operate with one of the world's leading specialists in ion analytics, Metrohm.

### **Conclusions**

In my opinion there are two answers to the introductory question. On the one hand, there is the research and development level, where it is necessary to know the exact specifications of the ionic liquid used, in particular if physical and chemical data are determined. On the other hand, there are and there will be industrial applications, where suppliers (such as IOLITEC) and users have to find the right balance between minimum costs and minimum specifications without the loss of performance. Modern production techniques will help to produce premium qualities at reasonable prices.

Finally, the more we learn about impurities, the more we learn about how to influence the properties of neat ionic liquids by adding other compounds as additives. So, let's get back to work again!



## **II. Applications of Ionic Liquids**

By Tom Beyersdorff, Marcin Gonsior & Thomas Schubert.

### **Highlighted publication of this issue**

#### **Why are Ionic Liquids Liquid?**

I. Krossing, J. M. Slattery, C. Dagueuet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427-13434.

Original title: "Why are Ionic Liquids Liquid? A simple Explanation Based on Lattice and Solvation Energies"

*Krossing et al.* describe a simple quantitative explanation for the comparably low melting points of ionic liquids. Their concept was to assess the Gibbs free energy of fusion for the process  $IL_{(s)} \rightarrow IL_{(g)}$ , which relates very well to the melting of ionic liquids. The basic principle is to use the Born-Fajans-Haber-cycle. The necessary data were determined by experimental work (melting points and dielectric constants), or estimated and calculated by using quantum chemical methods (lattice free energies: volume based thermodynamics and COSMO solvation model).

We decided to highlight this paper, because it gives an answer to a very fundamental question. With this work it is possible very important properties such as melting points and dielectric constants of ionic liquids.

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### **Inorganic Synthesis**

#### **Ionothermal Synthesis of Molecular Sieves using ionic liquids**

E. R. Parnham, R. E. Morris, *Chem. Mater.* **2006**, *18*, 4882-4887.

Original title: "1-Alkyl-3-methyl-imidazolium Bromide Ionic Liquids in the Ionothermal Synthesis of Aluminium Phosphate Molecular Sieves"\*

The synthesis of new types of molecular sieves seems to be an important field in ionic liquids research: In the last issue, we already reported that *Wang et al.* (*Angew. Chem.* 2006, *118*, 4069-4074.) used ionic liquids to synthesize aluminophosphates. In this issue there's another interesting contribution on a very similar topic. *Morris et al.* were able to show that





chain length and as well branching of the alkyl side chains effected different structures of the aluminium phosphates.

**\* IOLITEC distributes any patent-free 1,3-Dialkyl-imidazolium halide.**

## **Catalysis**

### **Direct conversion of methane to methanol**

J. Cheng, Z. Li, M. Haught, Y. Tang, *Chem. Comm.* **2006**, 4617-4619.

Original title: "Direct methane conversion to methanol by ionic liquid-dissolved platinum catalysts"

*Tang et al.* describe that Pt salts and oxides, ionic liquids and concentrated sulfuric acid catalyse the direct oxidation of methane to methanol. The use of the ionic liquid led to a better tolerance of the catalytic system against water.

**\* The ionic liquids used in this article are all available from IOLITEC.**

## **Organic Synthesis**

### **Solvent for Michael reactions**

N. Karodia, X. Liu, P. Ludley, D. Pletsas, G. Stevenson, *Tetrahedron* **2006**, *62*, 11039-11043.

Original title: "The ionic liquid ethyltri-n-butylphosphonium tosylate as solvent for the acid-catalysed hetero-Michael reaction"

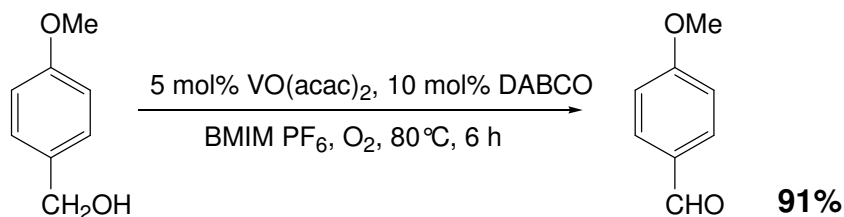
The Michael reaction of methyl vinyl ketone with a couple of Michael donor systems is described.

### **Green aerobic alcohol oxidation in ionic liquid**

N. Jiang, A. J. Ragauskas, *Tetrahedron Letters* **2006**, *48*, 273-276.

Original title: "Vanadium-catalyzed selective aerobic alcohol oxidation in ionic liquid [BMIM]PF<sub>6</sub>"

The authors describe the oxidation of aromatic alcohols in the presence of a vanadium catalyst using an ionic liquid as solvent. A couple of acid scavengers were tested. The best results were observed with DABCO, without an over-oxidation to the corresponding carboxylic acid. The reaction protocol works best with benzylic alcohols.



**\* This material (IL-011) is offered for a very special price until 31<sup>st</sup> January 2007!**

## Physical Chemistry

### **Dissolving metal oxides in ionic liquids**

P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner, K. Binnemanns, *J. Phys. Chem. B* **2006**, *110*, 20978-20992.

Original title: "High Performance Carbon Composite Electrode Based on an Ionic Liquid as Binder"

*Binnemanns et al.* describe that a protonated betaine bis(trifluoromethylsulfonyl)imide is an ionic liquid able to dissolve large quantities of metal oxides. Soluble are trivalent rare earths, uranium(IV)oxide, zinc(II)oxide, cadmium(II)oxide, mercury(II)oxide, nickel(II)oxide, copper(II)oxide, palladium(II)oxide, lead(II)oxide, manganese(II)oxide and silver(I)oxide. The dissolved oxides can be stripped by treatment of the ionic liquid with an acidic aqueous solution. Insoluble or poorly soluble are iron(III), manganese(IV) and cobalt oxides, as well as aluminium oxide and silicon dioxide.

## Biocatalysis

### **Enzymatic resolution of cycloalkyl acetates:**

E. Xantathakis, M. Zarevúcka, D. Saman, M. Wimmerova, F. N. Kollis, Z. Wimmer, *Tetrahedron: Asymmetry* **2006**, *17*, 2987-2992.

Original title: „Application of ionic liquids in enzymatic resolution by hydrolysis of cycloalkyl acetates“

*Wimmer et al.* reported the enzymatic resolution of cycloalkyl acetates using commercially available lipases and ionic liquids. The enantiomeric purities were high or acceptable.

**\* All cited materials are available on request.**



## **Enzymatic resolution of amino acids:**

H. Zhao, L. Jackson, Z. Song, O. Olubajo, *Tetrahedron: Asymmetry* **2006**, *17*, 2491-2498.

Original title: "Using ionic liquid [EMIM] [CH<sub>3</sub>COO] as an enzyme friendly co-solvent for resolution of amino acids"

The authors describe the successful use of 1-ethyl-3-methyl-imidazolium acetate in the enzymatic resolution of amino acids (DL-phenylalanine methylester). The lyophilised *B. licheniformis* protease showed a very high enantioselectivity and activity at concentrations of [EMIM] [CH<sub>3</sub>COO] up to 4.0 M. The best results were observed in 2.0 M [EMIM] [CH<sub>3</sub>COO].

## **Nano-particle synthesis**

### **Synthesis of very small TiO<sub>2</sub> particles via sol-gel-synthesis**

H. Choi, Y. J. Kim, R. S. Varma, D. Dionysiou, *Tetrahedron Lett.* **2006**, *47*, 4619-4622.

Original title: "Thermally Stable Nanocrystalline TiO<sub>2</sub> Photocatalysts Synthesized via Sol-Gel Methods Modified with Ionic Liquid and Surfactant Molecules"

*Dionysiou et al.* give another example that ionic liquids are useful solvents for the sol-gel-synthesis of well-defined nanostructured inorganic materials: The authors report that 1-butyl-3-methyl-imidazolium hexafluorophosphate, when used together with polyoxyethylensorbitan monooleate as templating material, leads to TiO<sub>2</sub>-nano-particles with a pore size distribution only from 2.0 to 7.5 nm.

**\* This material (IL-011) is offered for a very special price until 31<sup>st</sup> January 2007!**

## **Reviews**

### **Ion Pairing**

Y. Marcus, G. Hefter, *Chem. Rev.* **2006**, *106*, 4585-4621.



### III. Phosphonium-based ionic liquids: wake up from the beauty sleep!

By Tom Beyersdorff.

During the last decade many publications described the manifold applications of ionic liquids as solvents in organic synthesis and (bio-)catalysis, electrolytes in dye-sensitized solar-cells and batteries or solvents for electrochemical applications. Most of the ionic liquids discussed were in fact based on aromatic and aliphatic ammonium salts. Phosphonium-based ionic liquids have stood in the shadow of these materials for many years. The main reason for the lack of phosphonium-based ionic liquids was the poor availability of the starting materials: trialkylphosphines. Cytec Industries Inc. is experienced in manufacturing trialkylphosphines and quaternary phosphonium salts and has thus filled this gap. Over the past years a variety of new products have been developed by pairing tetraalkylphosphonium cations with various anions (Figure 1). At the moment about 20 different phosphonium-based ionic liquids traded under the brand name CYPHOS<sup>®</sup> are available, many of them even on a tonne scale. Herein we will first give a short overview of the synthesis of phosphonium-based ionic liquids before we discuss selected applications of these materials published during the last years without being exhaustive.

#### **Synthesis**

Tertiary phosphines  $PR_3$  are generally prepared by the free radical addition of phosphine  $PH_3$  to olefins<sup>2</sup>. Nucleophilic addition ( $S_N2$ ) of the tertiary phosphines to haloalkanes  $R'-X$  ( $X = Cl, Br, I$ ) results in the formation of tetraalkylphosphonium halides with the general formula  $[R'PR_3]^+ X^-$  ( $X = Cl, Br, I$ ). In contrast to the corresponding amines, the larger radii and more polarizable ion pair of trialkylphosphines  $PR_3$  make them more nucleophilic. Therefore the formation of phosphonium salts is in general much faster than for amines<sup>3</sup>.

The resulting phosphonium halides can easily be converted into the corresponding materials containing other anions (see Figure 1) by metathesis<sup>4</sup> (Scheme 2).

<sup>2</sup> M. M. Rahmut, H. A. Currier, A. M. Semsel, V. P. Wystrach, *J. Org. Chem.* **1961**, *26*, 5138-5145.

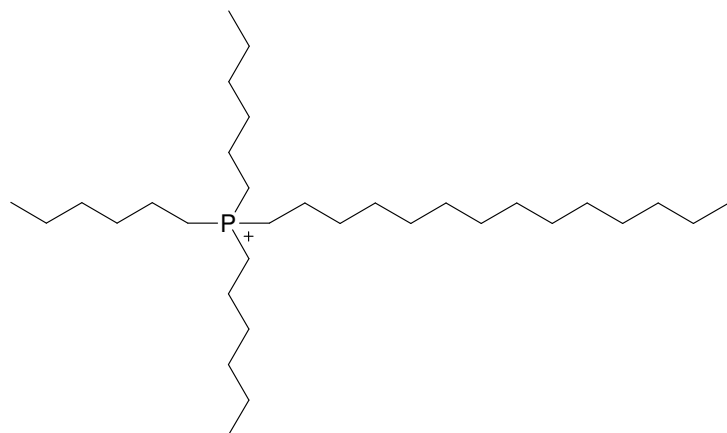
<sup>3</sup> S. A. Buckler, W. A. Henderson, *J. Am. Chem. Soc.* **1960**, *82*, 5791-5794.

<sup>4</sup> A. J. Robertson, WO0187900, **2001**, Cytec Industries.

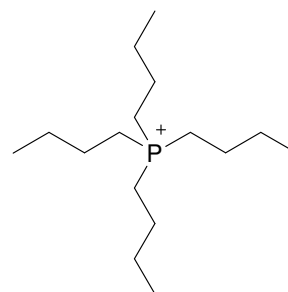


**Figure 1:**

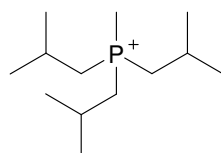
examples of cations:



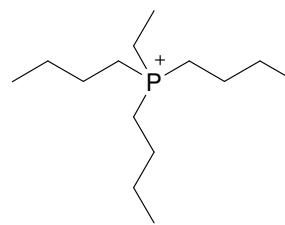
Trihexyl(tetradecyl)phosphonium



Tetrabutylphosphonium



Triisopropylmethylphosphonium



Tributylethylphosphonium

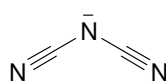
examples of anions:



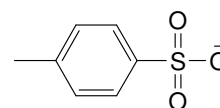
chloride



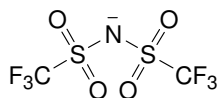
bromide



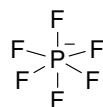
dicyanamide



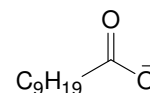
tosylate



bis(trifluoromethylsulfonyl)imide

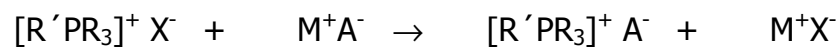


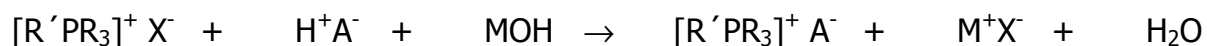
hexafluorophosphate



decanoate

**Scheme 2:**





All ionic liquids containing the anions shown in Figure 1 can be prepared by one of these methods.

### ***Properties of phosphonium-based ionic liquids***

The biggest difference between phosphonium and ammonium ionic liquids is their thermal stability. Even though both can decompose at higher temperatures by retro-alkylation, in general phosphonium salts are more stable than their ammonium analogues<sup>5</sup>. Thermogravimetric analysis (TGA) indicates dynamic thermal stabilities for many of these products up to 300°C.

In contrast to ammonium salts which undergo the Hoffmann elimination in the presence of base<sup>6</sup>, phosphonium salts decompose by formation of a tertiary phosphine oxide and an alkane under alkaline conditions<sup>7</sup>. Depending on the structure of the substituents R and R', phosphoranes such as the well known Wittig reagents can be formed alternatively.

One of the most characteristic properties of ionic liquids is the viscosity. Phosphonium-based ionic liquids typically have higher viscosities than their ammonium analogues at room temperature. As for all other ionic liquids the viscosity decreases upon heating to higher temperatures.

### **Applications**

#### **Phase-Transfer-Catalysts**

The traditional application of phosphonium salts is their use as phase transfer catalysts (PTCs). Even though they are typically more expensive than comparable ammonium salts, the biggest advantage is their higher thermal and chemical stability. A typical example for the higher stability is the biphasic conversion of aromatic chlorides to fluorides using KF at temperatures above 130°C.

<sup>5</sup> M. O. Wolff, K. M. Alexander, G. Belder, *Chimica Oggi* **2000**, 29.

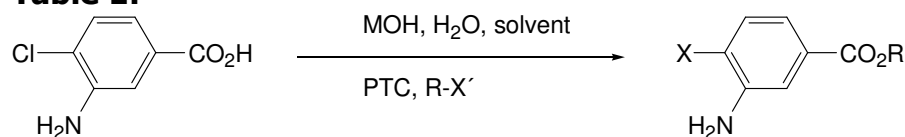
<sup>6</sup> C. K. Ingold, O. Schumacher, *J. Chem. Soc.* **1928**, 3125.

<sup>7</sup> M. Zanger, C. A. VanderWerf, W. E. McEwen, *J. Am. Chem. Soc.* 1959, 81, 3806-3808



Recently *Shanks et al.* patented a process for the preparation of esters from 3-amino-4-halobenzoic acid via phase-transfer catalysis (Table 1)<sup>8</sup>.

**Table 1:**



Entry	R-X'	MOH	Solvent	PTC	Temp./°C	Time/h	Yield/%
1	C <sub>12</sub> H <sub>25</sub> Oms	NaOH	Xylene	P <sub>4444</sub> Br	140	5	100
2	C <sub>16</sub> H <sub>33</sub> Br	KOH	MeCO <sup>i</sup> Bu	P <sub>4444</sub> Br	120	5	95
3	C <sub>12</sub> H <sub>25</sub> Br	KOH	Xylene	P <sub>4444</sub> Br	140	5	100
4	C <sub>16</sub> H <sub>33</sub> Br	KOH	Xylene	N <sub>222</sub> Benz Br	120	3	83

From the few examples given, it is obvious that the phosphonium salts in this case show a better performance than the ammonium salts as PTCs.

### **Phosphonium-based ionic liquids as solvents for strong bases**

Probably the most extensively studied ionic liquids as solvents for catalysis are those based on the 1,3-dialkylimidazolium cation. Regardless of the stability of the anions, these ionic liquids facilitate many unusual chemical reactions. Nevertheless these materials are not suitable for reactions involving active metals such as sodium or potassium or for reactions involving strong bases such as Grignard or organolithium reagents since these react with the ionic liquids to form *N*-heterocyclic carbenes (NHCs)<sup>9</sup>.

Recently Clyburne et al. reported that phosphonium ionic liquids form clear solutions of low viscosity upon treatment with PhMgBr/THF which show no sign of degradation after one month<sup>10</sup>. Quenching of such a solution after one month with anhydrous Br<sub>2</sub> resulted in the formation of PhBr in 98% yield which indicated the stability of the solutions. It has to be mentioned that Grignard reagents dissolved in phosphonium ionic liquids are still air and moisture sensitive. Unfortunately, the attempt to

<sup>8</sup> T. E. Shanks, R. J. Maleski, US2006/0135807 A1

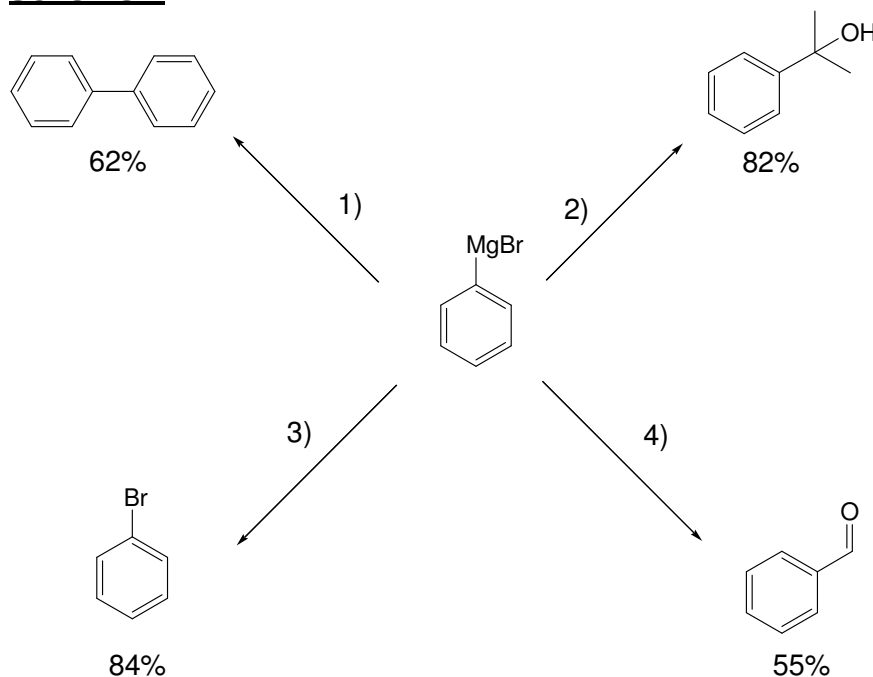
<sup>9</sup> B. Gorodetsky, T. Rammial, N. R. Branda, J. A. C. Clyburne, *Chem. Comm.* **2004**, 1972-1973.

<sup>10</sup> T. Rammial, D. D. Ino, J. A. C. Clyburne, *Chem. Comm.* **2005**, 325-327.



generate the Grignard reagent in phosphonium ionic liquids as the only solvent failed. In addition, a number of reactions was carried out in the ionic liquid including addition to carbonyl, benzyne reaction, halogenation and coupling reactions (Scheme 1).

### Scheme 1



*Reaction conditions:* 1)  $\text{CuCl}_2$ ; 2) acetone; 3)  $\text{Br}_2$ ; 4) DMF; all reaction were followed by an aqueous work-up and extraction with hexane.

As a consequence of the unique solvent properties of phosphonium salts, product isolation was made easy. After quenching the reaction by the addition of water and hexane, a three-phase system was formed and the products were isolated from the upper organic layer.

These results suggest that phosphonium-based ionic liquids may be more suitable for reactions involving strong bases than imidazolium-based ionic liquids.

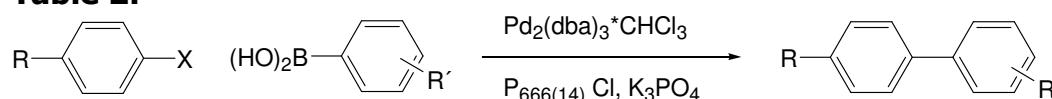




## Solvents for catalysis

Recently a Suzuki cross-coupling reaction has been reported in imidazolium-based ionic liquids which required ultrasonic irradiation to proceed at 30°C<sup>11</sup>. Another drawback observed during this reaction was the formation of inactivated Pd black during the reaction which resulted in lower conversion rates. In contrast, *McNulty et al.* reported Suzuki cross-coupling reactions performed in trihexyl(tetradecyl)-phosphonium chloride at slightly elevated temperature with high yield and recovery of the the catalyst after work-up<sup>12</sup>. It was shown that various substituted iodobenzenes including electron rich derivatives could be cross-coupled with a variety of arylboronic acids efficiently within 1 h at 50°C. Various bases (Et<sub>3</sub>N, iPr<sub>2</sub>NEt, etc.) have been used for this study but the best results were obtained when potassium phosphate and water were employed. Arylbromides were also coupled under the same conditions but the reactions were somewhat more sluggish but could be enhanced by the addition of triphenylphosphine (Table 2).

**Table 2:**



Entry	X	R	R'	Ligand	Temp./°C	Time/h	Isolated Yield%
1	I	H	H	None	50	1	95
2	I	Ac	H	None	50	1	100
3	I	Ac	4-OMe	None	50	1	99
4	I	OMe	4-OMe	None	50	1	86
5	Br	Ac	H	PPH <sub>3</sub>	50	1	99
6	Br	Ac	4-OMe	PPH <sub>3</sub>	50	1	98
7	Br	OMe	4-OMe	PPH <sub>3</sub>	50	3	95

<sup>11</sup> R. Rjagopal, D. V. Jarikote, K. V. Srinivasan, *Chem. Comm.* 2002, 616-

<sup>12</sup> J. McNulty, A. Capretta, J. Wilson, J. Dyck, G. Adjabeng, A. Robertson, *Chem. Comm.* 2002, 1986-1987.



Product isolation was achieved in all cases by the addition of water and hexane to the reaction mixture which resulted in the formation of a triphasic system. The palladium catalyst remained fully dissolved in the central phosphonium layer while the products were extracted into the upper organic layer and inorganic salts (phosphates, borates) into the lower aqueous layer. It was shown that the catalyst dissolved in the phosphonium layer could be reused several times without loss of activity.

### ***Solvents for biocatalysis***

The use of ionic liquids in biocatalysis has previously been investigated<sup>13</sup>. In many cases the reactivity of enzymes was investigated, whereas the possibility of whole-cell transformations remains mainly unexplored.

*Baumann et al.* tested six phosphonium-based ionic liquids for their biocompatibility with three xenobiotic-degrading bacteria (*Pseudomonas putida*, *Achromobacter xylosoxidans*, *Sphingomonas aromaticivorans*)<sup>14</sup>. From the 18 pairings 7 were found to be biocompatible with trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide P<sub>666(14)</sub>N Tf<sub>2</sub> being compatible with all three organisms. This IL was then used for the further experiments in a two-phase partitioning bioreactor (TPPB). The reactor was charged with an initially toxic aqueous solution of phenol (1 L H<sub>2</sub>O, 1.58 mg phenol), 0.25 L of P<sub>666(14)</sub> N Tf<sub>2</sub> and the phenol degrader *P. putida*. The toxic level of phenol was initially reduced by partitioning into the IL phase which allowed the cells to utilize the reduced phenol concentration. It was shown that the partitioning of phenol was accelerated by cellular demand and thermodynamic equilibrium. Eventually, all of the phenol was consumed at a rate that is comparable to that of organic aqueous TPPB systems. For the first time the successful use of an IL with a cell system was demonstrated.

<sup>13</sup> U. Krugl, M. Eckstein, N. Kaftzik, **2003**, *Biocatalytic reactions in Ionic Liquids*, in P. Wasserscheid, T. Welton "Ionic Liquids in Synthesis", Wiley, Weinheim, 336-355.

<sup>14</sup> M. D. Baumann, A. J. Daugulis, P. G. Jessop, *Appl. Microbiol. Biotechnol.*, **2005**, 67, 131-137.



## **Electrochemistry**

Ionic liquids have been widely investigated for their application as electrolytes in supercapacitors. Two phosphonium salts, namely trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide  $P_{666(14)}NTf_2$  and trihexyl(tetradecyl)phosphonium dicyanamide  $P_{666(14)}N(CN)_2$ , have been selected for this purpose by *Frackowiak et al.*<sup>15</sup>. They were able to design a supercapacitor operating at 3.4 V with high energy values of  $\sim 40$  Wh/kg by using a solution 25 wt% solution of  $P_{666(14)}NTf_2$  in acetonitrile and electrodes made of 85 wt% activated carbon, 10 wt% polyvinylidene fluoride and 5 wt% acetylene black. It has to be mentioned that this is one of a few examples where capacity measurements have been performed on porous carbon electrodes which are close to real supercaps but significantly decrease the the operating potential range. In addition *Frackowiak et al.* showed that stable capacity values were maintained over 1000 cycles at 200 mA/g current load.

**The capacitor could also be charged and discharged with high current load of 2 A/g with capacitance values of 40 F/g**

### *Conclusions*

As well as other ionic liquids, phosphonium-based ionic liquids are no longer curiosities. Over the past years it has been shown that phosphonium ILs are attractive materials for a number of applications. These are derived from their physico-chemical properties, e.g. high thermal, chemical and electrochemical stability and extraordinary solvent properties. Finally, an important point worth mentioning is that phosphonium-based ionic liquids are available on a tonne scale.

All materials mentioned are available from IoLiTec. Send your request to: [order@iolitec.de](mailto:order@iolitec.de) or call Dr. Tom Beyersdorff: ++49 7666 9129591.

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<sup>15</sup> E. Frackowiak, G. Lota, J. Pernak, *Appl. Phys. Lett.* **2005**, *86*, 164104.



## IV. Analytical Chemistry Services

By Andreas Reisinger.

Over the last three years of working with ionic liquids, we have gained wide experience and practical knowledge in the field of analytical chemistry of these materials. Therefore we now offer an analytical service including various analytical methods related to the field of ionic liquids chemistry. This gives you the opportunity to benefit from our expertise in this field and order the analysis you need. Of course, our analytical service is not restricted to ionic liquids but open for any sample that can be analysed with our equipment.

### 1. Electrochemical parameters



Many important properties related to the stability or electrochemistry of an ionic liquid are based on electrochemical parameters. Thus our analytical laboratory is equipped with a Metrohm 712 Conductometer for conductivity measurements and a Metrohm/Eco Chemie Autolab Potentiostat/Galvanostat for the determination of electrochemical stabilities, corrosion and electrochemical noise as well as Tafel analyses.



### 2. Ion chromatography

Being a subdivision of High Performance Liquid Chromatography (HPLC), a general definition of Ion Chromatography (IC) can be given as follows: Ion chromatography includes all rapid liquid chromatography separations of ions in columns coupled online with detection and quantification in a flow-through detector. Therefore it is best suitable for qualitative and quantitative determination of anions and cations in ionic liquids as well as elsewhere.





In our labs we use an IC system from our partner Metrohm, the world's leading company in the field of ion chromatography. With respect to IC, we also offer the development of analytical methods for the determination of new ions.

### 3. Water content (Karl-Fischer titration)

Water determination is one of the most frequently performed analyses in laboratories around the world. This is not really surprising, as the water content directly influences the quality, processability, shelf life and stability of a wide range of products including ionic liquids. Thus we offer quantitative determination of water content by Karl-Fischer titration using the Metrohm 795 KFT-Titrino.



### 4. Viscosity

The viscosity of an ionic liquid directly influences the material's characteristics such as pumpability or pourability. Most ionic liquids have a relatively high viscosity, which may affect or limit their applicability in industrial processes. Therefore we routinely determine viscosities of ionic liquids using a Brookfield, DV-E viscosimeter and also offer this service in a temperature range of -15°C to 130°C.

### 5. Stability

Especially for compounds and materials that are made for laboratory use, very little is usually known about long term stabilities. Therefore we offer controlled atmosphere tests using a Thunder Scientific Humidity generator. This generator runs at relative humidities of 5 to 95 % over a temperature range of -10°C to 70°C. Furthermore, we offer thermal stability analyses with a VLM Thermostat.



For questions concerning methodologies, prices and quotations look at IoLiTec's Homepage ([www.iolitec.de](http://www.iolitec.de)) or contact Iolitec's Team via phone: (+49 (0)7666 9129591) or email ([info@iolitec.de](mailto:info@iolitec.de)).



## **V Community**

By Marcin Gonsior and Thomas Schubert.

### **News**

#### **September, 15<sup>th</sup>-18<sup>th</sup>: 232<sup>rd</sup> ACS Meeting, San Francisco, USA:**

At the fall meeting of the American Chemical Society the session "Physical chemistry of ionic liquids" took place for the first time. Many interesting talks about some fundamental questions, like "Why are ionic liquids liquid?" were presented and discussed at a high scientific level.

One important point in this context was purity of ionic liquids and the influence of impurities on the physicochemical properties. IOLITEC's Managing Director demonstrated in his talk how sensitive important properties of ionic liquid are to the influence of impurities. This talk is available from the download area on IOLITEC's Web-site [www.iolitec.com](http://www.iolitec.com).

#### **Nano Tech Taiwan 2006, Taipei September 27-29**

For the second time the international NanoTech exhibition took place in Taipei, the capital of Taiwan. The exhibition held in the Taiwan World Trade Center (TWTC) was



accompanied by a conference and exhibition Taiwan Nano-X 2006 – a scientific contribution to the Nano Tech's commercial program. The show has brought together 89 (in 139 booths) domestic and foreign exhibitors. The booths were arranged in several

thematic groups: Academy & Research Institutes, Foreign Exhibitors, Nano Application Products, Nano Materials. IOLITEC as a supplier of nano powders and chemical specialities for Europe established contacts with several innovative Asian companies providing nanoscaled metal, metal oxides and non-oxide ceramic. Apart from variety of "raw" nano materials, several application were presented there, e.g. polymer composites, displays based on CNTs, nanotech anti-fogging and anti-scratch



coatings, UV absorbing coatings etc. Nanomaterial processing equipment like grinding and dispersing equipment, nanotechnologically oriented analytical instruments were also of our interests from a user view. During the exhibition participants could get themselves acquainted with exhibitors' offers in the announcement centre. Interesting presentations were accompanied by a lively discussion and comments.

### **October, 8<sup>th</sup>-11<sup>th</sup>: Green Solvents for Processes, Friedrichshafen, Germany:**

Organized by the German DECHEMA the international conference GSFP took place. With about 200 participants the number was as high as 2 years ago at Bruchsal (Green Solvents for catalysis). Ionic liquids as green solvents dominated the conference again.

### **NanoSolution 2007:**

IOLITEC visited for the first time the 2<sup>nd</sup> European Exhibition for Nano Applications "NanoSolutions" in Cologne, Germany. With more than 100 domestic and international exhibitors accompanied by a conference, NanoSolutions 2006 was an event that brought together nanotechnological companies and their customers. Selected materials will soon be available from IOLITEC.

### **Congratulations: Prof. Dr. Ingo Krossing, member of IOLITEC's scientific advisory board, wins the Otto-Klung-Weberbank Award.**

The Otto-Klung-Weberbank Award is endowed with a price money of 50.000 €. The award was introduced as the Otto-Klung-Award in 1973. Five former winners received the Nobel-price after receiving this award.



## Two new employees strengthen IOLITEC's team:

**Dr. Andreas Reisinger**, 28, finished his PhD thesis in the group of Prof. Dr. I. Krossing at the University of Freiburg. During his PhD at the University of Karlsruhe, the Ecole Polytechnique Fédérale de Lausanne (EPFL) and the University of Freiburg, he worked in the field of weakly coordinating anion chemistry. In particular, the thesis covered the synthesis and stabilisation of strong Brønsted acids, weakly bound silver(I) complexes with gaseous ligands and donor-free binary silver(I) alkoxides. With his start at IoLiTec, he is heading our microsystem technology division.

**Dr. Marco Klingele**, 31, is a far-travelled native of the Freiburg region. He studied chemistry at the University of Freiburg (Germany) and at Trinity College Dublin (Ireland) where he was awarded an MSc degree for his work in the field of natural product synthesis in 2001. For his PhD he changed both country and subject and went to University of Otago in Dunedin (New Zealand) to study the coordination chemistry of new 1,2,4-triazole-based ligands with a focus on iron(II) spin crossover materials. He returned to Germany in 2004 to get married and to do a one-year postdoc at the University of Göttingen (bioinorganic chemistry) before he took up a position in a small analytical company. At the beginning of October 2006 he joined the team of IOLITEC as Head of Energy & Cleantech.

### Students Corner:

Having the idea of becoming an interdisciplinary journal for Ionic Liquids, we thought about guest authors for „Ionic Liquids Today“ starting with the first issue in 2007.

Well knowing that every academic has a lot of work to do, we decided to direct our invitations to PhD students or post-docs to give them the opportunity to present their work to a selected community of almost 1500 researchers from academia and the industry working on ionic liquids.

Even though ILT is not an international refereed journal every interested young scientist is invited to contribute to our newsletter with a 1-2 pages article on a topic of choice which could either be about their own work or a comment on an interesting publication from the recent literature.

We appreciate your co-operation!





Please send your contribution written in English as word file including a short CV to:  
[info@iolitec.de](mailto:info@iolitec.de)

Don't hesitate to contact us if you have questions concerning your participation.

## VI. Interesting New Materials

By Tom Beyersdorff.

**Finally – now that the soccer World Cup 2006 is over – I got my head free of football again and realised the dramatic mistake in price setting for the salts of the weakly coordinating anions in “Ionic Liquids Today, Issue 02-06” from Friday, June 30<sup>th</sup>.**

All prices were one order of magnitude too high! With this corrigendum I would like to introduce these materials again – giving the correct prices!

### **IOLITEC supports strategic research in the DFG-funded program SPP1191: 10% discount for all participants!**

With the beginning of the program every participant of the DFG-program SPP 1191 receives a discount of 10% on our ionic liquids and key intermediates (except our special offers).

### **New materials:**

#### **Weakly coordinating anions: WCAs**

In co-operation with **Professor Crossing** from the University of Freiburg/Germany, we expanded our portfolio by 4 salts of weakly-coordinating anions (WCAs), namely salts of the tetrakis(perfluoro-t-butoxy)aluminate-anion  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ . In contrast to other WCAs e.g.  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ , or  $[\text{Sb}(\text{OTeF}_5)]^-$ , which are sensitive against moisture, these anions are stable in the presence of water and even of  $\text{HNO}_3$ !



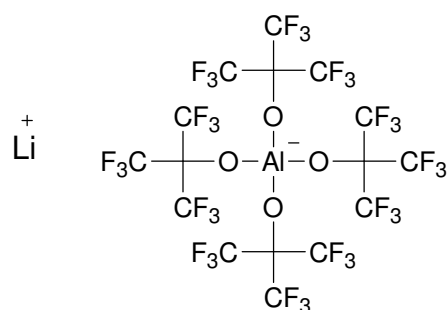
WCAs play an important role in i.e. catalysis since they are able to stabilize highly reactive cationic species due to their low basicity.

Krossing *et al.*<sup>16</sup> were able to stabilize a large number of reactive cations such as  $PX_4^+$ ,  $P_2X_5^+$  and  $P_5X_2^+$  ( $X=Br, I$ ) in the presence of the  $[Al(OC(CF_3)_3)_4]^-$  anion.

They were also able to isolate complexes cations such as  $Ag(P_4S_3)^+$  and  $Ag(P_4S_3)_2^+$  in combination with the the  $[Al(OC(CF_3)_3)_4]^-$  anion.<sup>17,18</sup>

In addition, RT stable salts of the tris(ethene)silver-cation were obtained by stabilization with the  $[Al(OC(CF_3)_3)_4]^-$ -anion.<sup>19</sup> Krossing *et al.*<sup>20</sup> also synthesized and characterized various cationic Bronsted acid complexes of the perfluorinated alkoxyaluminates.

### Lithium tetrakis(perfluoro-t.-butoxy)aluminate: Li $[Al(pftb)_4]$



The salt  $Li[Al(pftb)_4]$  is a useful precursor for the introducing of the  $[Al(pftb)_4]^-$ -anion into various other salts by metathesis.

Li-Salts of WCAs are used as substitute for  $LiClO_4$  in Li-catalysed Diels-Alder-reactions, 1,4-conjugate-additions and pericyclic rearrangement-reactions.<sup>21,22,23</sup> Also radical polymerisations have been catalysed by these kind of salts.

The use of  $Li [Al(pftb)_4]$  as electrolyte support in the Li-ion-batteries is limited since the mobility of large ions are insufficient for this application. However, a good

<sup>16</sup> M. Gonsior, I. Krossing, L. Müller, I. Raabe, *Chem. Eur. J.* **2002**, 4475-4492.

<sup>17</sup> I. Krossing, A. Adolf, M. Gonsior, *J. Am. Chem. Soc.* **2002**, 7111-7116.

<sup>18</sup> I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, 700-711.

<sup>19</sup> I. Krossing, A. Reisinger, *Angew. Chem.* **2003**, 5903.

<sup>20</sup> I. Krossing, A. Reisinger, *Eur. J. Inorg. Chem.* **2005**, 1979-1989.

<sup>21</sup> R. Braun, J. Sauer, *Chem. Ber.*, **1986**, 119, 1269.

<sup>22</sup> P. A. Grieco, J. J. Nunes, M. D. Gaul, *J. Am. Chem. Soc.*, **1990**, 112, 4595.

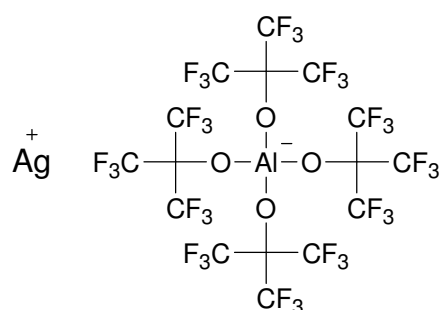
<sup>23</sup> A. Flohr, H. Waldmann, *J. Prakt. Chem.*, **1995**, 337, 609



performance has been achieved in polymer-based Li-ion-batteries using a Poly(ethylenoxide)-matrix.<sup>24</sup>

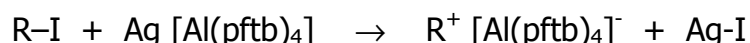
<b>Li [Al(pftb)<sub>4</sub>] (99%):</b>	<b>KI-018-1 g</b>	<b>55,00 €</b>
	<b>KI-018-5 g</b>	<b>247,50 €</b>
	<b>KI-018-10 g</b>	<b>445,50 €</b>

### Silver tetrakis(perfluoro-*t*-butoxy)aluminate: Ag [Al(pftb)<sub>4</sub>]



**This silver salt is a facile starting material to introduce the [Al(pftb)<sub>4</sub>] anion and it can be used in most chlorinated alkanes. It has also been described to catalyse a variety of hetero-Diels-Alder-reactions.<sup>25,26</sup>**

If combined with various alkyl iodides synthetic useful alkyl-cations can be generated *in situ* by precipitation of AgI.



Gonsior<sup>27</sup> used this silver complex among others to stabilize a large number of reactive phosphonium- and arsenium-intermediates during his PhD-studies.

<sup>24</sup> H. Tokuda, S. Tabata, M. A. B. H. Susan, H. Hayamizu, M. Watanabe, *J. Phys. Chem. B*, **2004**.

<sup>25</sup> S. Saitoin, *Lewis Acids in Organic Synthesis*, Ed. H. Yamamoto, Wiley-VCH Weinheim, Germany, **2000**, 9.

<sup>26</sup> N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, A. S. Weller, *Chem. Eur. J.*, **2002**, *8*, 2088.

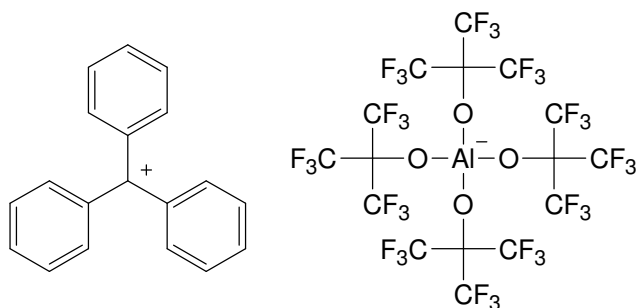
<sup>27</sup> M. Gonsior, „From cationic silver complexes to reactive Phosphonium- and Arsenium-intermediates stabilized by weakly coordinating anions”, Dissertation, Göttingen: Cuvillier, **2005**, ISBN 3-86537-583-9.



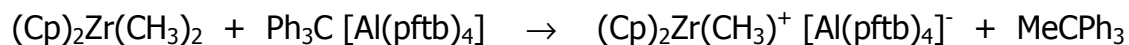
<b>Ag [Al(pftb)<sub>4</sub>] (99%):</b>	<b>KI-019-1 g</b>	<b>65,00 €</b>
	<b>KI-019-5 g</b>	<b>297,50 €</b>
	<b>KI-019-10 g</b>	<b>540,00 €</b>

**Triphenylcarbenium tetrakis(perfluoro-*tert*-butoxy)aluminate:**

**Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>]**



This compound is of great interest in homogenous catalysis. Metallocenes of the formula [(Cp)<sub>2</sub>M(CH<sub>3</sub>)]<sup>+</sup> that are active catalysts, require a stable weakly coordinating anion, which is very important for the activity and selectivity of i.e. the polymerization. Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>] generates very reactive catalysts of a well defined composition<sup>28</sup>:

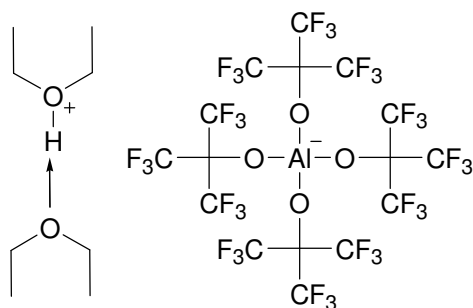


<b>Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>]:</b>	<b>KI-020-1 g</b>	<b>65,00 €</b>
	<b>KI-020-5 g</b>	<b>297,50 €</b>
	<b>KI-020-10 g</b>	<b>540,00 €</b>

<sup>28</sup> E. Y.-X. Chen, T. J. Marks, *Chem. Rev.*, **2000**, *100*, 1391.



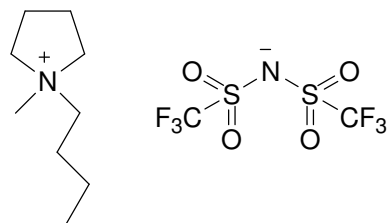
**Diethyloxonium tetrakis(perfluoro-tert.-butoxy)aluminate monoetherate:  
H(OEt<sub>2</sub>)<sub>2</sub> [Al(pftb)<sub>4</sub>]**



This protonated ether can be used as a facile H<sup>+</sup> source since the reaction by-product diethyl ether can easily be removed from the reaction mixture. With this compound the [Al(pftb)<sub>4</sub>] anion can easily be introduced to carboxylate salts.

<b>Li [Al(pftb)<sub>4</sub>] (99%):</b>	<b>KI-021-1 g</b>	<b>95,00 €</b>
	<b>KI-021-5 g</b>	<b>427,50 €</b>
	<b>KI-021-10 g</b>	<b>769,50 €</b>

**1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide:  
[BMPyrr] NTf<sub>2</sub>**



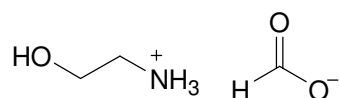
The thermal and electrochemical stability of this ionic liquid qualify it to be the perfect solvent for electrochemical applications.

**Our special offer:\***

<b>BMPyrr NTf<sub>2</sub>, 99%</b>	<b>IL-035-100 g</b>	<b>130,00 €</b>
	<b>IL-035-250 g</b>	<b>285,00 €</b>
	<b>IL-035-500 g</b>	<b>540,00 €</b>
	<b>IL-035-1 kg</b>	<b>950,00 €</b>
	<b>IL-035-5 kg</b>	<b>4.275,00 €</b>



### Ethanolammonium formate: EAF

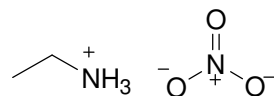


EAF has been described to have a high solvating ability for some inorganic salts such as  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  or  $\text{KBr}$ <sup>29</sup>. In addition 17 g of polyaniline were dissolved in 100 ml of the Ionic Liquid. With a meltingpoint of  $-82^\circ\text{C}$  this IL is a promising solvent for low temperature reactions.

#### Our special offer:\*

<b>EAF, 97%</b>	<b>IL-034-100 g</b>	<b>55,00 €</b>
	<b>IL-034-250 g</b>	<b>120,00 €</b>
	<b>IL-034-500 g</b>	<b>230,00 €</b>
	<b>IL-034-1 kg</b>	<b>365,00 €</b>
	<b>IL-034-5 kg</b>	<b>1.460,00 €</b>

### Ethylammonium nitrate: EAN



The first ionic liquid published in literature.

It has widely been used in protein science as for example protein crystallisation reagent<sup>30</sup>. Recently it has also been used as promoter for the Knoevenagel-Condensation of aromatic aldehydes with active methylene compounds<sup>31</sup>.

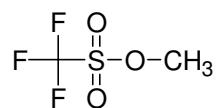
#### Our special offer\*:

<b>EAN, 98%</b>	<b>IL-043-100g</b>	<b>165,00 €</b>
	<b>IL-043-250g</b>	<b>370,00 €</b>
	<b>IL-043-500g</b>	<b>590,00 €</b>
	<b>IL-043-1kg</b>	<b>950,00 €</b>

<sup>29</sup> N. Bicak, *J. Mol. Liq.* **2005**, *116*, 15-18.

<sup>30</sup> J.A. Garlitz, C. A. Summers, R. A. Flowers II, G. E. Borgstahl, *Acta Crystallogr. D Biol. Crystallogr* **1999**, *55*, 2037-2038.

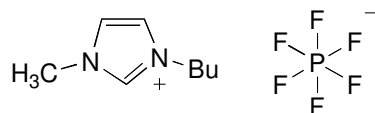
<sup>31</sup> Y. Hu, J. Chen, Z. G. Le, Q. G. Zheng, *Synthetic Communications* **2005**, *35*, 739-744.

**Trifluoromethanesulfonic acid methylester (Methyl triflate): TfOMe**

Methyl triflate is probably one of the most powerful methylating reagents for example in the synthesis of Ionic Liquids.

**Our special offer\*:**

<b>TfOMe, 98%</b>	<b>KI-002-100g</b>	<b>190,00 €</b>
	<b>KI-002-250g</b>	<b>430,00 €</b>
	<b>KI-002-500g</b>	<b>850,00 €</b>
	<b>KI-002-1kg</b>	<b>1.530,00 €</b>

**1-Butyl-3-methyl-imidazolium hexafluorophosphate: BMIM PF<sub>6</sub>****Our Special offer:\***

<b>BMIM PF<sub>6</sub> (99%):</b>	<b>IL-011-500 g</b>	<b>315,00 €</b>
	<b>IL-011-1 kg</b>	<b>535,00 €</b>
	<b>IL-011-5 kg</b>	<b>2.405,00 €</b>

**\* All special offers are valid until January 31<sup>st</sup>, 2007.  
Prices do not include costs for shipping&handling!**



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