

TECHNISCHE UNIVERSITÄT MÜNCHEN

Fachgebiet Molekulare Katalyse

**Epoxidation and Sulfoxidation Mediated by
Ionic Liquids**

Bo Zhang

Vollständiger Abdruck der von der Fakultät für Chemie der Technischen Universität München zur
Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften

genehmigten Dissertation.

Vorsitzende: Univ. – Prof. Dr. K. Köhler

Prüfer der Dissertation: 1. Univ. – Prof. Dr. F. E. Kühn

2. Prof. Dr. J. Mink, Hungarian Academy of Sciences,
Budapest / Ungarn

Die Dissertation wurde am 18.11.2013 bei der Technischen Universität München eingereicht und
durch die Fakultät für Chemie am 11.12.2013 angenommen.

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This thesis has been performed in the time between November 2010 and November 2013 at the research group Molecular Catalysis of Technische Universität München.

I would like to express my deep gratitude to my academic supervisor

Herrn Prof. Dr. Fritz E. Kühn

For his continuous supervision, encouragement and trust in my work.

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Munich

*To my family
With deep gratitude and love*

Abstract

Ionic liquids (ILs) have received great attention in recent years as solvents or catalysts due to their unique properties. This work focused on developing a cheap, environmentally benign, recyclable ILs system for epoxidation and sulfoxidation.

This thesis is divided into three parts, which present the results that have been discovered within three years of research.

Imidazolium perrhenate ionic liquids

Imidazolium-based ionic liquids (ILs) containing perrhenate anions were synthesized and characterized. In addition, their catalytic activity was examined in epoxidation of olefins and oxidation of sulfides. The results show that ILs containing perrhenate are very efficient reaction media and catalysts for these two oxidation reactions with hydrogen peroxide as oxidant, thus affording good yield of the corresponding product. A deeper understanding of the mechanism of the oxidation systems was obtained by investigations with Raman, IR, NMR spectroscopy and DFT calculation. Hydrogen bonds between the oxidant and perrhenate activate the oxidant, thereby leading to the transfer of an oxygen atom to the substrates such as olefins or sulfides, demonstrating the special features of ILs as a reaction environment.

Ionic liquids with weakly coordinating anions

A protocol for oxidation of sulfides to sulfoxides mediated by ILs with weakly coordinating anions ($[\text{BF}_4]^-$ and $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5, 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$) was established. Besides their catalytic performance, the mechanism of oxidation system was also investigated. The hydrogen bond formation between the IL anion and the oxidant appears to be the crucial step during the oxidation reaction.

Transition metal catalysts in ionic liquids

New transition metal compounds, Schiff-base complexes of methyltrioxorhenium (VII) and polyoxometalates salts are used as catalysts for epoxidation and sulfoxidation with ILs as solvents under mild conditions. Currently available catalytic systems provide an environmentally benign and sustainable way for oxidation reactions.

Contents

1 Introduction	1
1.1 Ionic liquids	1
1.1.1 Metal-containing ILs	3
1.1.2 Industrial applications	4
1.2 Epoxidation of olefins	5
1.2.1 Methyltrioxorhenium (VII) in olefin epoxidation	5
1.2.2 Polyoxometalates in olefin epoxidation	8
1.2.3 Industrial processes	10
1.3 Oxidation of sulfides	11
1.3.1 Catalyst-free sulfoxidation	12
1.3.2 Transition-metal catalysts in sulfoxidation	13
1.4 Objective	14
1.5 References	15
2 Activation of hydrogen peroxide by ionic liquids: mechanistic studies and application in the epoxidation of olefins.....	21
2.1 Introduction	21
2.2 Results and discussion.....	22
2.2.1 Epoxidation in perrhenate-containing ILs.....	22
2.2.2 Mechanistic considerations of the activation of H ₂ O ₂	24
2.2.3 Spectroscopic and DFT studies of the activation of H ₂ O ₂ with perrhenate and subsequent epoxidation	26
2.3 Conclusion.....	34
2.4 Experimental section	34
2.4.1 General	34
2.4.2 Synthesis of perrhenate-based ILs.....	35
2.4.3 Preparation of the ¹⁷ O-labeled ILs	37
2.4.4 Oxidation of cyclooctene to cyclooctene oxide in ILs	37
2.4.5 Computational details.....	37
2.5 References	38
3 Imidazolium perrhenate ionic liquids as efficient catalysts for the selective oxidation of sulfides to sulfones	41
3.1 Introduction	41

3.2 Results and discussion.....	42
3.2.1 Characterization of the IPILs	42
3.2.2 Influence of solvent, oxidant and catalyst.....	43
3.2.3 Influence of the reaction temperature.....	45
3.2.4 Influence of the substrate/catalyst ratio.....	45
3.2.5 Selective oxidation of different sulfides.....	46
3.2.6 Recycling of the catalyst	47
3.3 Conclusion.....	48
3.4 Experimental section	48
3.4.1 General	48
3.4.2 Synthetic method and characterization data.....	49
3.4.3 General procedure for the oxidation of sulfides.....	51
3.5 References	53
4 Oxidation of sulfides to sulfoxides mediated by ionic liquids.....	57
4.1 Introduction	57
4.2 Results and discussion.....	58
4.2.1 Influence of different solvents and oxidants	58
4.2.2 Selective oxidation of different sulfides.....	59
4.2.3 Reaction mechanism	60
4.2.4 Recycle ability of IL system.....	64
4.3 Conclusion.....	65
4.4 Experimental section	65
4.4.1 General	65
4.4.2 Typical procedure for the oxidation of the sulfides in [Bmim][BF ₄]	66
4.5 References	68
5 Synthesis and characterization of imidazolium salts with the weakly coordinating [B(C₆F₅)₄]⁻ anion	71
5.1 Introduction	71
5.2 Results and discussion.....	72
5.2.1 Synthesis of [Li(NCCH ₃) ₄][B(C ₆ F ₅) ₄]	72
5.2.2 Crystal structure of [Li(NCCH ₃) ₄][B(C ₆ F ₅) ₄].....	73
5.2.3 Synthesis of the new imidazolium-BAr ^F compounds	74
5.2.4 Crystal structures of imidazolium-BAr ^F compounds	75
5.2.5 Thermal characterization	76

5.3 Conclusion.....	77
5.4 Experimental section.....	77
5.4.1 General.....	77
5.4.2 Synthetic method and characterization data.....	78
5.4.3 Single-crystal X-ray structure determination.....	79
5.5 References.....	82
6 Ionic liquids with weakly coordinating anions: synthesis, properties and application	85
6.1 Introduction.....	85
6.2 Results and discussion.....	87
6.2.1 Synthesis of WCAILs.....	87
6.2.2 Solid-state structures.....	88
6.2.3 Characterization of WCAILs.....	92
6.2.4 Application for oxidation of sulfides to sulfoxides.....	93
6.2.5 Reaction mechanism.....	95
6.3 Conclusion.....	98
6.4 Experiment section.....	99
6.4.1 Gernal.....	99
6.4.2 Synthetic method and characterization data.....	99
6.4.3 Single-crystal X-ray structure determination.....	104
6.4.4 Catalysis studies.....	106
6.5 References.....	106
7 Oxidation reactions catalyzed by polyoxomolybdate salts	111
7.1 Introduction.....	111
7.2 Results and discussion.....	113
7.2.1 Synthesis of WCC-POMs.....	113
7.2.2 Characterization of the WCC-POMs.....	113
7.2.3 Crystal structures of WCC-POMs.....	114
7.2.4 Catalytic epoxidation of olefins.....	115
7.2.5 Selective catalytic oxidation of sulfides to sulfoxides.....	119
7.3 Conclusion.....	122
7.4 Experimental section.....	122
7.4.1 General.....	122
7.4.2 Synthetic method and characterization data.....	123
7.4.3 Single-crystal X-ray structure determination.....	124

7.4.4 General procedure for the epoxidation of olefins.....	125
7.4.5 General procedure for the oxidation of sulfides.....	126
7.5 References	126
8 Schiff base complexes of methyltrioxorhenium (VII): synthesis and catalytic application.....	131
8.1 Introduction	131
8.2 Results and discussion.....	132
8.2.1 Synthesis and spectroscopic characterization	132
8.2.2 X-ray crystal structure of complex 2	134
8.2.3 Catalytic application.....	135
8.3 Conclusion.....	138
8.4 Experimental section	138
8.4.1 General	138
8.4.2 Synthetic methods and characterization data	139
8.4.3 Single-crystal X-ray structure determination	140
8.4.4 Catalytic reactions	142
8.5 References	143
9 New ionic liquids with [Ni^{II}(CN)₄]²⁻ anion: synthesis, characterization and catalytic performance.....	147
9.1 Introduction	147
9.2 Results and discussion.....	148
9.2.1 Synthesis of ILs with [Ni(CN) ₄] ²⁻ anion	148
9.2.2 Characterization of ILs with [Ni(CN) ₄] ²⁻ anion	149
9.2.3 Catalytic epoxidation of olefins	149
9.3 Conclusion.....	151
9.4 Experimental section	151
9.4.1 General	151
9.4.2 Synthetic method and characterization data.....	151
9.4.3 Catalytic reaction.....	153
9.5 References	153
10 Summary	155
11 Appendix.....	159
12 Permissions for reuse of publications	229

Abbreviations

Bz	benzyl
d	doublet
DCM	dichloromethane
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
EA	elemental analysis
EtOAc	ethyl acetate
FAB	fast atom bombardment
GC	gas chromatography
h	hour
ILs	ionic liquids
im	imidazole
iPr	<i>iso</i> -Propyl
IR	infrared spectroscopy
L	liter
m	multiplet
M	molar
MeCN	acetonitrile
min	minute
mL	milliliter
MS	mass spectrometry
MTO	methyltrioxorhenium
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl
POM	polyoxometalates
r.t.	room temperature
q	quartet
t	triplet
TBHP	<i>tert</i> -butyl hydroperoxide
TGA	thermogravimetric analysis
TOF	turn-over frequency
UHP	urea hydrogen peroxide
XRD	X-ray diffraction
WCA	weakly coordinating anion
WCC	weakly coordinating cation

Glossary of ionic liquids

Cations

[Bmim] ⁺	1-butyl-3-methylimidazolium
[C ₄ mim] ⁺	1-butyl-3-methylimidazolium
[C ₈ mim] ⁺	1-octyl-3-methylimidazolium
[C ₈ Py] ⁺	1-octyl-pyridinium
[C ₁₂ mim] ⁺	1-dodecyl-3-methylimidazolium
[C ₁₂ Py] ⁺	1-dodecyl-pyridinium
[Dbim] ⁺	1,2-dimethyl-3-butylimidazolium
[Emim] ⁺	1-ethyl-3-methylimidazolium
[N _{4,4,4,4}] ⁺	<i>tetra</i> -butyl-ammonium
[P _{4,4,4,4}] ⁺	<i>tetra</i> -butyl-phosphonium
[P _{4,4,4,14}] ⁺	tributyl-(tetradecyl)-phosphonium
[TMG] ⁺	1,1,3,3-tetramethylguanidium

Anions

[B[3,5-(CF ₃) ₂ -C ₆ H ₃] ₄] ⁻	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
[B(C ₆ F ₅) ₄] ⁻	tetrakis(pentafluorophenyl)borate
[BF ₄] ⁻	tetrafluoroborate
[PF ₆] ⁻	hexafluorophosphate
[HSO ₄] ⁻	hydrogen sulfate
[NTf ₂] ⁻	bis(trifluoromethylsulfonyl)imide
[Ni(CN) ₄] ²⁻	tetracyanonickelate
[ReO ₄] ⁻	perrhenate

1 Introduction

1.1 Ionic liquids

In recent years, the growing awareness of environmental issues has brought attention on the need for “greener” and more sustainable technologies in chemical industry.^[1] The chemistry community has been urged to develop new reaction pathways that are less hazardous to human health and environment.^[2] Due to the necessity of solvents for most homogeneous reactions, alternative, less harmful solvents have been developed. The ideal solvent should have very low volatility, be easy to handle and recycle, have a wide liquid range, and be chemical and physical stable. In these respects ionic liquids (ILs) appear to be good candidates.

Ionic liquids (ILs) have received great attention due to their unique properties, such as non-volatile nature, non-measurable vapor pressure, broad liquid temperature ranges, ability to dissolve a wide range of inorganic and organic compounds.^[3] Thus, ILs have commonly been quoted as “green” replacements for organic solvents for industrial process and their overall environmental impact.^[4]

The first IL, [Et₄N][NO₃], was reported by Walden already in 1914.^[5] Later, Hurely *et al.* developed the first room temperature IL from [Emim]Cl-AlCl₃ system for aluminium electroplating in 1948.^[6] However, these chloroaluminate-based IL systems were brought to a more general audience by the groups of Osteryoung and Wilkes only in the 1970s. The scope was extended by the groups of Hussey and Seddon in 1980s, mainly for electrochemical and spectroscopic studies.^[7] In 1972, Parshall *et al.* developed ILs based on tetraalkylammonium chlorostannate with dissolved PtCl₂ as a reaction medium for several homogeneous catalytic reactions of olefins.^[8] In 1992, Wilkes’ group again received a major breakthrough in IL chemistry by the discovery of air- and moisture-stable imidazolium salts with anions such as [BF₄]⁻ and [PF₆]⁻,^[9] leading to the diversification of ILs with numerous combinations of cations and anions. At the onset of the new millennium, the concept of task-specific ionic liquids was introduced by Davis.^[10] These compounds are defined as ionic liquids in which the anion, cation, or both covalently incorporate a functional group (designed to endow them with particular properties, either physical or chemical or in terms of reactivity) as a part of the ion structures. Today, there are up to 10¹⁸ kinds of ionic liquids that can in principle be produced, which present enormous opportunities to design or optimize the most suitable system for specific catalytic processes (Figure 1).

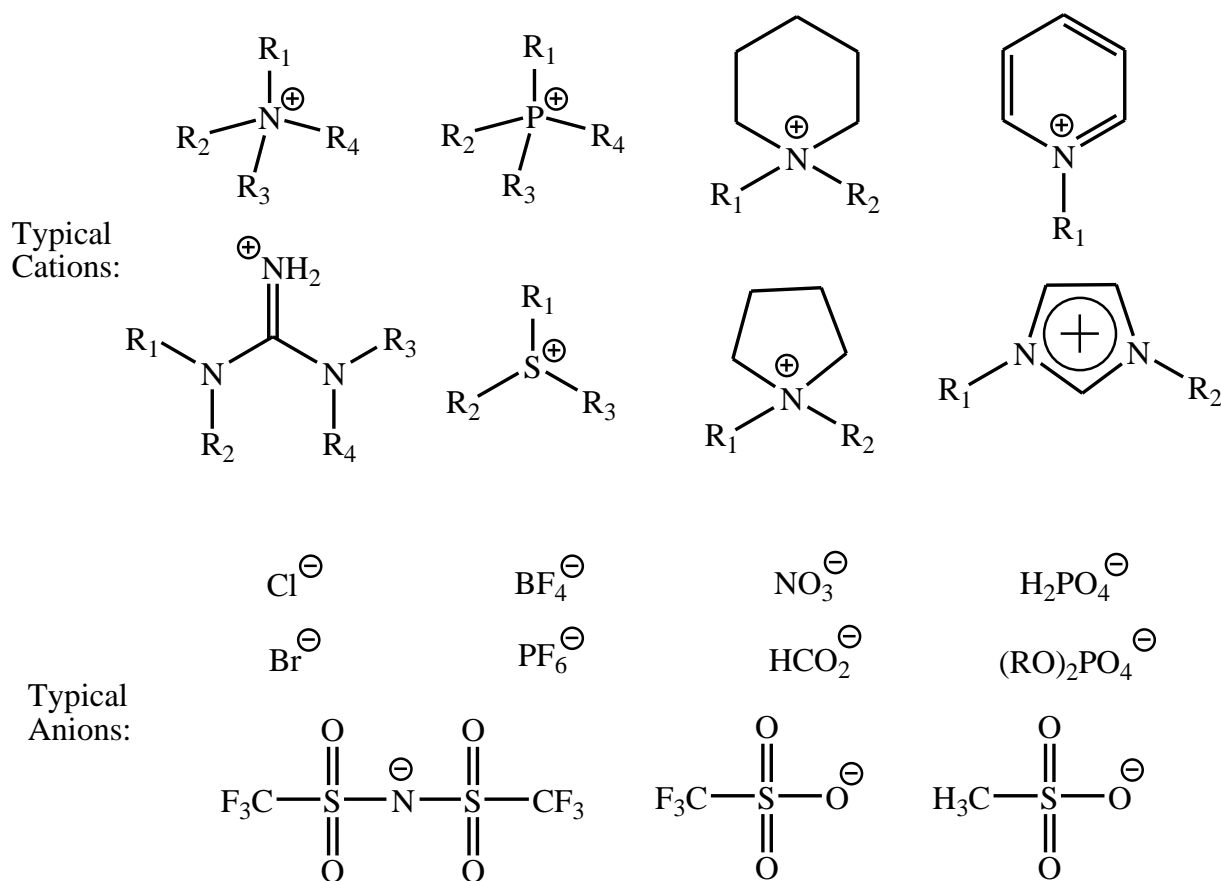


Figure 1. Typical cations and anions in ionic liquids.

Ionic liquids are not only used as green solvent, but also act as catalysts, catalysts activator, or co-catalysts for different reactions. In some of the more recent examples found in the literature, ILs are deliberately prepared so that one of the ions serves as the catalyst for a specific reaction.^[11] Cole and co-workers designed a series of water-stable Brønsted acidic ionic liquids in 2002,^[12] and many organic reactions involving esterification,^[13] nitration,^[14] and acetylation^[15] have been performed with these ionic liquids, resulting in excellent yields and selectivity. Functionalized ionic liquids containing anionic selenium species, $[\text{SeO}_3\text{Me}]^-$, have been prepared.^[16] These salts have been used as selenium catalysts for the oxidative carbonylation of anilines. Analogously, ionic liquids bearing acid counteranions ($[\text{HSO}_4]^-$ or $[\text{H}_2\text{PO}_4]^-$) have been used in catalyzing esterifications as recyclable reaction media.^[17] Ionic liquids, containing the function SO_3H , have recently been employed in the oligomerization of various alkenes to produce branched alkene derivatives with high conversions and excellent selectivities.^[18] All of these studies offer the possibility of designing suitable catalysts for special reactions.

Another advantage of ILs in catalysis is the immobilization of the catalyst. Besides the

tunable solubility to most organic chemicals, ILs are also able to dissolve a wide range of inorganic and organometallic compounds, and therefore large numbers of catalysts having polar or ionic character can be immobilized in ILs, which can greatly facilitate the separation and subsequent reuse of the catalyst. In addition, the technological integration of ILs with other advanced technologies, including supercritical fluids, electrochemistry, biocatalysis, and nanotechnology, with great potential for growth, has received more and more attention in green catalysis, and for a long period to come, the importance of the ILs as excellent process solvents in these integrated technologies will be gradually recognized.^[19]

1.1.1 Metal-containing ILs

Metal-containing ionic liquids have been used as versatile reaction media, catalysts, catalyst precursors and reagents for various chemical processes.^[20] Some metal-based imidazolium salts with m.p. above 100 °C were also included to provide information about solid state ionic interactions and catalytic properties. Additionally, the presence of metal ions provides many additional properties such as color, geometry, magnetism and the weaker anion-cation interactions.^[21] For example, Welton *et al.* developed imidazolium salts [Emim]₂[MCl₄] (M = Co or Ni) with m. p. 90-100 °C by mixing the corresponding metal chloride with [Emim]Cl under dry nitrogen atmosphere. The crystal structure of [Emim][CoCl₄] and [Emim][NiCl₄] showed that extended hydrogen bonding networks observed between the [MCl₄]²⁻ and ring hydrogens.^[22] The [Rmim][ZnX₂Y₂] (R = Me, Et, n-Bu, benzyl; X = Y = Cl or Br or X = Cl, Y = Br) systems are used for the coupling reaction of CO₂ and ethylene or propylene oxide to produce cyclic carbonates.^[23] The catalytic activities increase with the increasing nucleophilicity of the halide ion.

On the other hand, metal-NHCs-containing ILs with their recent advances in catalytic reactions enrich their potential applications. For example, Shreeve and co-workers synthesized pyrazolyl-functionalized N-heterocyclic carbene complexes of palladium (II) (Pd(Me)(3-mesityl-1-(pyrazolylmethylene)imidazolium)chloride) by using a silver (I) N-heterocyclic carbene complex as a ligand transfer reagent. The obtained complex is air- and moisture- stable and was investigated in the Heck reaction of iodobenzene and *n*-butyl acrylate at 120 °C with a catalyst loading of 2 mol %. The reaction yielded *n*-butyl (E)-cinnamate in excellent yields. The catalyst was recycled three times without an evident loss of activity. The high catalytic activity and recyclability was obtained due to the strong Pd (II)-carbene bond and the weak Pd (II)-nitrogen bond. The Pd (0) intermediate can easily be formed and is additionally stabilized and activated by the strong σ -bond between the carbene

electron pair and the Pd centre.^[24]

It is obvious that ILs provide high reaction rates and specific selectivity in different fields of catalytic applications. However, the problem of leaching effects in the catalysis reaction is produced. In order to avoid this problem, modifying the metal-complex catalyst to make it more alike to IL solvent medium becomes necessary. In this regard, tagging of the IL-functionality (imidazolium cation) to the ligand of metal complex catalysts has been confirmed as a useful technique to prevent catalyst leaching due to the increased ionophilicity towards ILs.^[25]

1.1.2 Industrial applications

The most successful example for an industrial process using ionic liquids technology is probably the BASIL (Biphasic acid scavenging utilizing ionic liquid) process established by BASF in 2002.^[26] The BASIL process is used for the production of the generic photoinitiator precursor alkoxyphenylphosphines (Figure 2).

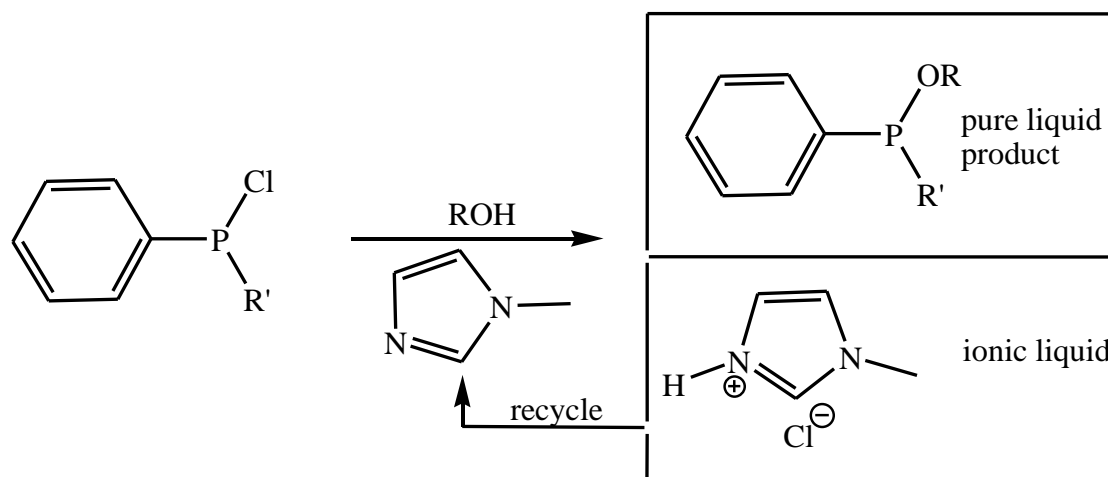


Figure 2. The BASIL process

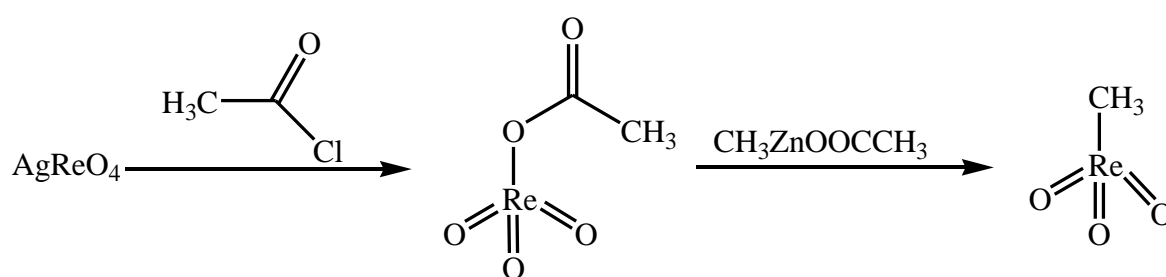
In the conventional process, triethylamine was used to scavenge the acid that was formed in the course of the reaction, but this method made the reaction mixture difficult to handle due to the waste by-product (triethylammonium chloride formed a dense insoluble paste). Thus, a new idea replacing triethylamine with 1-methylimidazole was produced. Forming 1-methylimidazolium chloride ionic liquid can be easily separated out of the reaction mixture as a discrete phase due to form two liquid phases. Additionally, this new process uses a much smaller reactor than the original technology and the space-time yield is increased from $8 \text{ kg m}^{-3} \text{ h}^{-1}$ to $690,000 \text{ kg m}^{-3} \text{ h}^{-1}$, as well as the yield increased from 50 % to 98 %.

1.2 Epoxidation of olefins

The epoxidation of olefins is of high interest in both industry and academia. Epoxides are very important intermediates in the synthesis of numerous fine chemicals, such as perfumes or pharmaceutical compounds, particularly for the synthesis of various polymers.^[27] The epoxidation of olefins using peracids RCO_3H as oxidant was firstly discovered by Russian chemist N. Prileschajew in 1909.^[28] However, peracides are often dangerous (explosive) and must be handled with greatest care. Subsequently, it was found that Lewis acidic transition metal oxo complexes can transfer one oxygen atom to olefins. Therefore, many transition metal complexes have been successfully used to be catalysts toward olefin epoxidation in order to obtain kinds of epoxides.

1.2.1 Methyltrioxorhenium (VII) in olefin epoxidation

Among the multitude of organometallic oxidation catalysts, methyltrioxorhenium (CH_3ReO_3 , MTO) has been recognized to be the most active catalyst for olefin epoxidation. Aside from its application as an oxidation catalyst, MTO is also used to catalyze the other reactions, such as olefin epoxidation, oxidation of conjugated dienes, allylic alcohols and alkynes, aldehyde olefination and olefin metathesis.^[29] However, the synthesis of MTO suffers from some disadvantages with respect to large scale applications:^[30] 1) direct alkylation of dirhenium heptoxide (Re_2O_7) with the non-reducing alkyl-transfer reagent tetramethyltin wastes half of the rhenium by concomitant formation of (catalytically inactive) trimethyltin perrhenate; 2) the very toxic reagent tetramethyltin is necessary to be used. Therefore, the new method replacing the toxic reagent by the methyl zinc acetate as a methylating reagent was developed by Herrmann (Scheme 1).^[31]



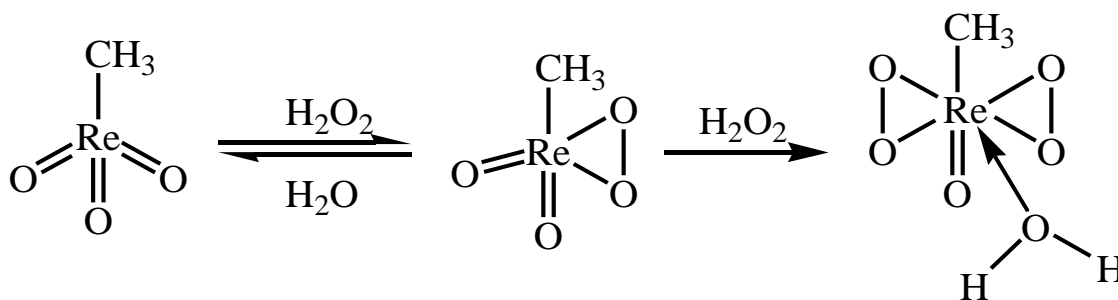
Scheme 1. Formation of MTO employing organozinc compound.

Among all applications of MTO, olefin epoxidation is the most widely investigated reaction. MTO can catalyze the epoxidation of various olefins with hydrogen peroxide which is

environmentally friendly oxidant since water is produced as only byproduct. Moreover the concentration of MTO used in the epoxidation of simple olefins is 0.1 mol % at different temperature.^[32]

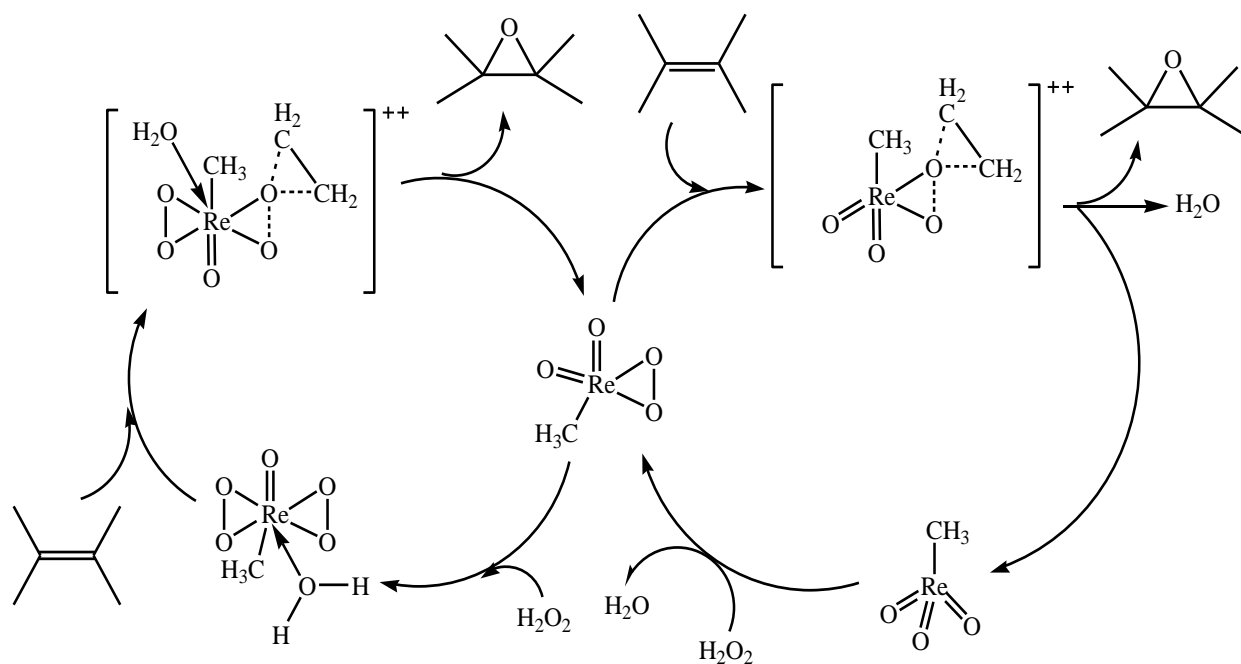
Recently, MTO showed high catalytic activity in epoxidation system with urea hydrogen peroxide (UHP) as oxidant and ILs as solvent.^[33] The advantages of this oxidation system in ILs are numerous: 1) This system is a homogenous oxidation solution due to good solubility of ILs; 2) The oxidation solution is nearly water-free, so conversion of the substrate yields only the epoxides and not by-product diols; 3) The system of ionic liquids can be recycled for several times, which present a high interest for industrial applications.^[34]

With respect to mechanistic studies in the epoxidation reaction using MTO as catalyst in different solvent, Herrmann *et al.* found MTO formed mono- and bis-peroxide complexes with 1 or 2 equivalents of H₂O₂. Moreover, the bis-peroxo complex has also been isolated and structurally characterized (Scheme 2).^[35]



Scheme 2. Formation of the mono- and bis-peroxo species

Experiments with the isolated bis (peroxo) complex (CH₃)Re(O₂)₂O•H₂O have shown that it is the active species in olefin epoxidation catalysis and several other catalytic reactions.^[36] In situ experiments show that the mon-peroxo complex exists solely in equilibrium with MTO and is also catalytically active in epoxidation processes. Kinetic experiments indicate that the rate constants for the transformation of substrate into their oxidation products by catalysis with the mono- and bis-peroxo complex are of a comparable order of magnitude.^[37] The most acknowledge mechanism of the epoxidation of MTO is a bicyclic mechanism involving both mono- and bis-peroxo complexes (Scheme 3).

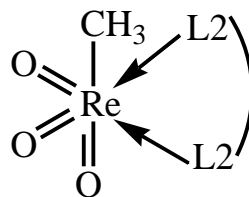
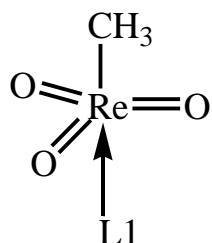


Scheme 3. Mechanism of the epoxidation of olefin catalyzed by MTO

The results of both cycles indicate that of key mechanistic importance is the formation of the bis (peroxo) rhenium (VII) complex $(\text{CH}_3)\text{Re}(\text{O}_2)_2\text{O}\cdot\text{H}_2\text{O}$ from MTO and two equivalents of H_2O_2 in a clean reaction, which seems to be one of the most reactive peroxo metal complexes for epoxidation of olefins. For other rhenium oxides such as Re_2O_7 , have lower activities for epoxidation due to subsequent hydrolysis (HReO_4) which does not occur with MTO under the conditions of catalysts.^[38] It is interesting to point out that for both cycles, a concerted mechanism is suggested in which the electron rich double bond of the alkene attacks a peroxidic oxygen of $(\text{CH}_3)\text{Re}(\text{O}_2)_2\text{O}\cdot\text{H}_2\text{O}$, which has been inferred from experimental data that system may involve a spiro arrangement.^[39]

However, a drawback of MTO for the epoxidation of olefin was soon discovered: the Lewis acidity of the rhenium center causes hydrolysis and concomitant cleavage of the epoxide ring leading to the formation of by-product diols in the presence of water.^[40] Several methods have been suggested to overcome this problem. An efficient procedure developed to avoid this side reaction requires the use of urea hydrogen peroxide adduct (UHP) as oxidant, which enables epoxidation to be carried out in non-aqueous media.^[41-42] Another method is that the aromatic N-base ligands work by coordinating to the Re center, thereby reducing the Lewis acidity of the catalyst and accelerating the catalytic reactions additionally.^[43] Nevertheless, the activity of MTO-Lewis base adducts was originally found to be significantly lower than that of MTO itself.^[44] Surprisingly, K. B. Sharpless found the excess use of pyridine did not only hamper

the formation of by-product diols but also increased the reaction velocity in comparison to MTO itself as catalyst precursor.^[45] Subsequently, 3-cyanopyridine and particularly pyrazole as Lewis bases are found to be more effective and less problematic for epoxidation.^[42d, 46] Therefore, many N-base adducts of MTO were isolated and characterized and in several cases employed for olefin epoxidation catalysis.^[39] Scheme 4 represents some examples of Lewis base adducts of MTO.



L1 = quinclidine

N,N'-dimethylpiperazine

p-methoxyaniline

urotropine

2,6-dimethylaniline

2-(*p*-tolyliminomethyl) phenol

Pyridine-*N*-oxide

L2 = 2,2'-bipyridine

2-(aminomethyl) pyridine

piperazine

2,2'-bipyridine-*N*-oxide

1,10'-phenanthroline

2,2'-bipyrimidine

2,2'-bipyridine-*N*-oxide

Scheme 4. Lewis base adducts of MTO

The activity of the catalytic Lewis base adducts of MTO depends on the choice of Lewis base ligand, most likely due to the ligands stability against oxidation by H₂O₂ and the contribution of ligand basicity to the catalytic systems.^[47]

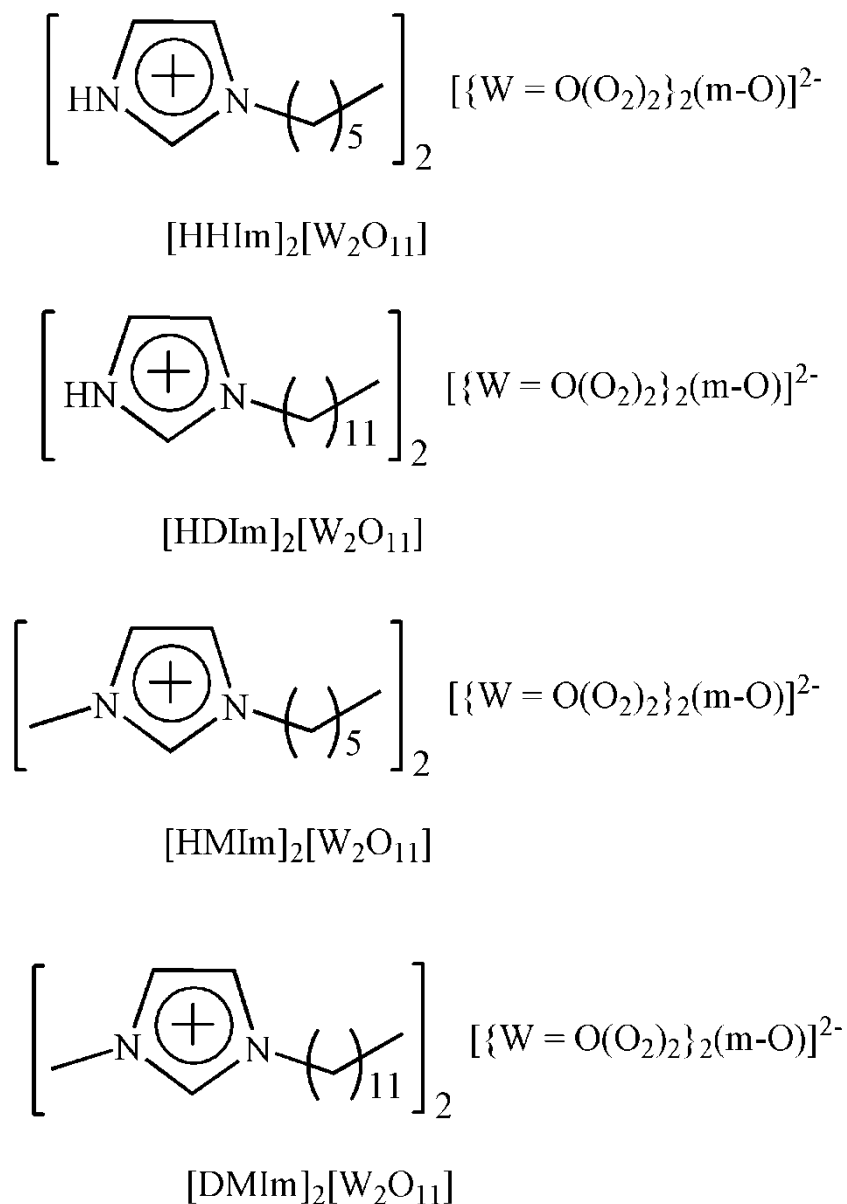
1.2.2 Polyoxometalates in olefin epoxidation

Polyoxometalates (POMs) are a subset of metal oxides that represent a diverse range of molecular clusters with an almost unmatched range of physical properties and the ability to form dynamic structures.^[48] POMs were firstly discovered by Berzelius in 1826,^[49] and then has been expanded to a huge family. In addition to its fundamental importance, POMs are ubiquitous in chemical research with numerous applications ranging, such as nanotechnology,^[50] biology,^[51] surfaces,^[52] catalysis,^[53] supramolecular materials,^[54] electronic materials^[55] and molecular materials.^[56] Generally, the synthesis of POMs clusters

Chapter 1

is often very simple synthetic manipulations requiring a small number of steps, or even just one step (one-pot syntheses).^[57] Some greatest importance synthetic variables in synthesizing such clusters should be attention: 1) concentration/type of metal oxide anion, 2) PH and type of acid, 3) ionic strength, 4) hetroatom concentration, 5) presence of additional ligands, 6) reducing agent and 7) temperature and solvent of the reaction.

It is also well known that POM catalysts are widely used for organic reactions due to catalytic features such as good catalytic activity and selectivity, the feasible design of catalytically active sites and controllable redox and acidic properties at atomic or molecular levels.^[58] These characteristics make them economical and environmentally attractive in both academic and industrial applications. For example, ester hydrolysis in water can be greatly enhanced by the catalysis of the POM, $H_3PW_{12}O_{40}$, immobilized on organomodified mesoporous silica. This design overcomes the difficulty involved with the use of solid acides by which catalytic activity is often severely deactivated by water.^[59] The epoxidation of *cis*-cyclooctene was investigated with $[W_2O_{11}]^{2-}$ as catalyst and hydrogen peroxide as oxidant by Hou and co-workers (Scheme 5).^[60]



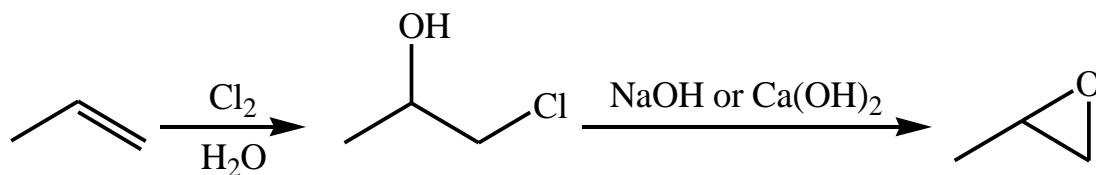
Scheme 5. The anion $[\text{W}_2\text{O}_{11}]^{2-}$ functionalized catalysts

It was found that $[\text{HDIm}]_2[\text{W}_2\text{O}_{11}]$ can be regarded as a reaction-induced phase-separation catalyst, which was proved to be the most active catalyst. A noteworthy fact is that the catalytic system switched the reaction mixture from triphase to emulsion, then to a biphasic system, leading the catalyst self precipitated from the reaction at the end of the reaction.

1.2.3 Industrial processes

Epoxides, particularly ethylene and propene oxide, are key raw materials of a wide variety of chemicals and are often applied as building blocks for polymers. In 1993, the worldwide production capacity for propylene oxide was about 4.0×10^6 tonnes per year of which 1.7, 1.4 and 0.36×10^6 tonnes per year in the USA, Western, Europe and Japan, respectively.^[61] The

traditional route proceeds *via* the conversion of propylene to chloropropanols (Scheme 6).



Scheme 6. The chlorhydrine process

The reaction is performed at 30-35 °C and 2-3 bar of pressure using aqueous solution chlorine as oxidant. The resulting chlorhydrine is in situ dehydrochlorinated to propylene oxide using basic solution of NaOH or Ca(OH)₂. Afterwards, the propylene oxide is distilled out of the reaction mixture to avoid direct hydration. Due to the environmental pressure (toxic chlorine) and huge amount of by-products, a new direct oxidation route was developed in 1967 using organic hydroperoxides as oxidant agent and different transition-metal catalysts.^[62] Until 1983, the breakthrough was made by Enichem.^[63] The system using a titanium-substituted silicalite (TS-1) catalyst which has a hydrophobic surface was developed, moreover, this catalyst has been proved to be effective to a variety of liquid-phase oxidation with the environmental hydrogen peroxide. Based on this technology, BASF, Dow and Solvay developed the HPPO (hydrogen peroxide to propylene oxide) process for the production of propylene oxide. Water is the co-product of this reaction. Hydrogen peroxide is converted completely and the propylene conversion is nearly quantitative. The crude propylene oxide product is purified by distillation. Additionally, methanol can be recycled.

HPPO has significant environmental benefits versus the conventional processes: 1) wastewater is reduced by up to 80 %; 2) energy use is reduced by 35 %; 3) the simple raw material integration and avoidance of co-products reduces the infrastructure and physical footprint of the plant significantly.

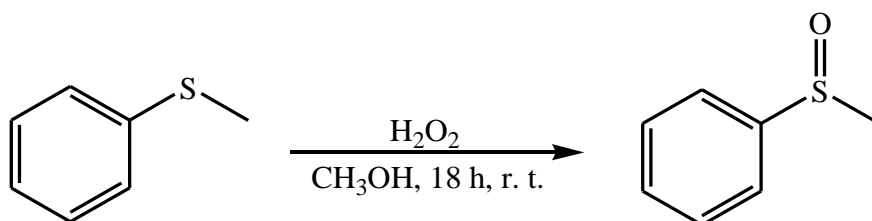
1.3 Oxidation of sulfides

Organic sulfoxides and sulfones are useful synthetic intermediates for the construction of various chemically and biologically active molecules, including drugs,^[64] flavors,^[65] germicides,^[66] cardiotoxic agents,^[67] vasodilators,^[68] and catabolism regulators.^[69] The oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones. The sulfur atom can be easily oxidized by different electrophilic oxidants, but special conditions must be set up to chemoselectively obtain sulfoxides or sulfones.^[70] Due to a great interest of these compounds, different synthetic methods have been developed for

chemoselective oxidation of sulfides.

1.3.1 Catalyst-free sulfoxidation

The oxidation of sulfides to the corresponding the sulfoxides by the use of hydrogen peroxide in acetone and acetic acid were initially developed by Gazdar in 1908.^[71] Since that time, many sulfoxides were obtained through their procedure.^[72] In 1981, Drabowica *et al.* observed that use of methanol instead of acetone as the solvent for oxidation of sulfides to sulfoxides with H₂O₂ as oxidant agent decreased the reaction time from 24 h to 18 h (Scheme 7).^[73]



Scheme 7. Oxidation of sulfides to sulfoxides in methanol

However, many functional groups in the sulfides were easily destroyed in this system. In this case, Ravikumar *et al.* found the transformation of various sulfides into sulfoxides by H₂O₂ in hexafluoro-2-propanol (HFIP) as solvent.^[74] The results showed that the oxidation reactions in HFIP proceed smoothly with high yield of sulfoxides. However, this system was severely restricted in practical organic synthesis by using poisonous HFIP as solvent due to environmental pressure. After several years, Xu *et al.* developed a new, convenient and selective oxidation method of some alkyl phenyl sulfides to the corresponding sulfoxides using hydrogen peroxide as oxidant agent in phenol at room temperature.^[75] This system was proved to be a highly efficient and selective for the oxidation of various sulfides within a short reaction time. Additionally, the functional groups, even including the highly reactive aldehyde group, were not affected. Recently, a simple and environmentally benign method for oxidation of sulfides with hydrogen peroxide as oxidant agent was introduced by Liu and co-workers.^[76] This method can achieve approximately stoichiometric transformation for some sulfides, resulting an excellent selectivity for sulfoxides under mild conditions.

1.3.2 Transition-metal catalysts in sulfoxidation

A wide variety of transition metal-catalysts are utilized for oxidative transformations in oxidation of sulfides to sulfoxides or sulfones. Transition metals are activated by, or serve to activate a terminal oxidant, such as dioxygen, superoxide, radicals and peroxides. This section focused on the some transition metal-catalyzed oxidation of sulfides with peroxides.

The catalysts containing molybdenum and tungsten such as MoO_2Cl_2 ,^[77] LiNbMoO_6 ,^[78] $[\text{n-C}_4\text{H}_9]_4\text{N}[\alpha\text{-Mo}_8\text{O}_{26}]$,^[79] $[\text{C}_5\text{H}_5\text{N}(\text{n-C}_{16}\text{H}_{33})]_3\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4$ ^[80] and $\text{W}(\text{CO})_6$ ^[81] have been widely used for the oxidation of sulfides. Additionally, the neutral hexamethylphosphoric triamide complexes of both molybdenum and tungsten diperoxo species, were extensively studied for the oxidation of sulfides.^[82] It is important to note that the differences in the speciation and acidity of these two metal ions can lead to minor variations in the reactivity. For example, the tungsten complex has a greater catalytic efficiency for sulfide oxidations by H_2O_2 in the presence of strong acid, whereas the molybdenum complexes lead to a higher rate of sulfoxidation without any acid.^[80a, 83] This difference in reactivity can be attributed to the differences in Lewis acidity of molybdenum and tungsten, where the harder Lewis acid, molybdenum, forms a stronger coordination bond with the dianionic peroxo moiety, thus activating it for the oxidation of a nucleophile in the absence of acid.^[84]

Polyoxomolybdenum and polyoxotungsten were found to be very efficient catalysts for the oxidation of sulfides due to form oxobridged clusters in the presence of hydrogen peroxide. In recent years, the concept combination of POM anions with IL cations is regarded feasible way to afford green POM catalyst since they might possess the advantages of both IL and POM in the same material, which has been investigated quite intensively. In this case, Zhao *et al.* developed a heterogeneous process for selective oxidation of sulfides with hydrogen peroxide, catalyzed by alky-tethered imidazolium IL-based polyoxomolybdenum salt catalysts. The results showed that the process almost exclusively produces sulfoxide at room temperature within a very short time of 0.5 h; while sulfone can be selectively obtained at a higher temperature of 45 °C with excess hydrogen peroxide.^[85]

1.4 Objective

Developing green chemistry methodologies is one of the main themes of modern synthetic chemistry. ILs have received great attention as environmentally benign solvents to replace volatile organic solvents in a wide variety of chemical reactions. The main objective of this work was to develop a cheap, environmental benign and reusable metal containing ILs or a green system for oxidation reactions.

In a first study, functional ILs containing imidazolium cations with Lewis acidic group can be used as green organocatalysts. Based on our pervious work, perrhenates which is the decomposition products of well-examined epoxidaton catalysts such as MTO should be the best candidate for synthesizing functional ILs. Therefore, a series of imidazolium-based ILs containing perrhenate anions were synthesized and used as solvents as well as catalysts for epoxidation of olefin and sulfoxidation. In addition, theoretical studies were also performed to better study the reaction mechanism of the catalytic reaction.

In a second study, in order to save the cost the metal-free ILs with weakly coordinating anions were synthesized and applied for the sulfoxidation. Then catalysis tests are conducted as well. This is especially interesting as no ILs system without any catalyst for sulfoxidation has been reported so far.

In a third study, development of transition metal catalysts in ionic liquids should be established in order to obtain the green and recycle system. The Schiff-base complexes of methyltrioxorhenium (VII) and polyoxometalates were used as catalysts for sulfoxidation and epoxidation in ILs.

1.5 References

- [1] R. Mestres, *Green Chem.* **2004**, *6*, G10.
- [2] J. A. Linthorst, *Found. Chem.* **2010**, *12*, 55.
- [3] V. I. Pârvăulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.
- [4] Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619.
- [5] P. Walden, *Bull. Acad. Imper. Sci. (St. Petersburg)* **1914**, 1800.
- [6] (a) F. H. Hurley, US patent 2, 446, 331, **1948**; (b) F. H. Hurley, *Chem. Abstr.* **1949**, *43*, P7645b3; (c) F. H. Hurley, T. P. Weir Jr., *J. Electrochem. Soc.* **1951**, *98*, 207.
- [7] (a) H. L. Chum, V. R. Koch, L. L. Miller, R. A. Osteryoung, *J. Am. Chem. Soc.* **1975**, *97*, 3264; (b) J. Robinson, R. A. Osteryoung, *J. Am. Chem. Soc.* **1979**, *101*, 323; (c) J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263; (d) D. Appleby, C. L. Hussey, K. R. Seddon, J. E. Turp, *Nature* **1986**, *323*, 614.
- [8] G. W. Parshall, *J. Am. Chem. Soc.* **1972**, *94*, 8716.
- [9] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, 965.
- [10] J. H. Davis Jr., *Chem. Lett.* **2004**, *33*, 1072.
- [11] (a) A. Kamal, G. Chouhan, *Tetrahedron Lett.* **2005**, *46*, 1489; (b) L. D. S. Yadav, R. Patel, V. K. Rai, V. P. Srivastava, *Tetrahedron Lett.* **2007**, *48*, 7793.
- [12] A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis, Jr., *J. Am. Chem. Soc.* **2002**, *124*, 5962.
- [13] Y. L. Gu, F. Shi, Y. Q. Deng, *J. Mol. Catal. A: Chem.* **2004**, *212*, 71.
- [14] K. Qiao, H. Hagiwara, C. Yokoyama, *J. Mol. Catal. A: Chem.* **2006**, *246*, 65.
- [15] W. Wang, W. Cheng, L. Shao, J. Yang, *Catal. Lett.* **2008**, *121*, 77.
- [16] H. S. Kim, Y. J. Kim, H. Lee, K. Y. Park, C. Lee, C. S. Chin, *Angew. Chem. Int. Ed.* **2002**, *41*, 4300.
- [17] J. F. Dubreuil, K. Bourahla, M. Rahmouni, J. P. Bazureau, J. Hamelin, *Catal. Commun.* **2002**, *3*, 185.
- [18] Y. Gu, F. Shi, Y. Deng, *Catal. Commun.* **2003**, *4*, 597.
- [19] Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619.
- [20] (a) R. J. C. Brown, P. J. Dyson, D. J. Ellis, T. Welton, *Chem. Commun.* **2001**, 1862; (b) H. S. Kim, J. J. Kim, H. Kim, H. G. Jang, *J. Catal.* **2003**, *220*, 44; (c) N. Audic, H. Clavier, M. Mauduit, J. C. Guillemin, *J. Am. Chem. Soc.* **2003**, *125*, 9248; (d) R. D. Tilve, M. V. Alexander, A. C. Khandekar, S. D. Samant, V. R. Kanetkar, *J. Mol. Catal. A: Chem.* **2004**, *223*, 237; (e) K. M. Lee, C. K. Lee, I. J. B. Lin, *Angew. Chem. Int. Ed.*

Chapter 1

- Engl.* **1997**, *17*, 1850.
- [21] (a) C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin, *Chem. Mater.* **1999**, *11*, 1237; (b) C. K. Lee, H. H. Peng, I. J. B. Lin, *Chem. Mater.* **2004**, *16*, 530; (c) D. K. Lee, K. M. Lee, I. J. B. Lin, *Organometallics* **2002**, *21*, 10; (d) H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972; (e) C. K. Lee, K. M. Hsu, C. H. Tsai, C. K. Lai, I. J. B. Lin, *Dalton Trans.* **2004**, 1120.
- [22] P. B. Hitchcock, K. R. Seddon, T. Welton, *J. Chem. Soc., Dalton Trans.* **1993**, 2639.
- [23] J. Palgunadi, O. S. Kwon, H. Lee, J. Y. Bae, B. S. Ahn, N-Y. Min, H. S. Kim, *Catal. Today* **2004**, *98*, 511.
- [24] R. Wang, B. Twamley, J. M. Shreeve, *J. Org. Chem.* **2006**, *71*, 426.
- [25] L. Graser, D. Betz, M. Cokoja, F. E. Kühn, *Curr. Inorg. Chem.* **2011**, *1*, 166.
- [26] (a) WO 03/062171, WO03/062251, WO05/061416 (BASF AG); (b) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123; (c) M. Masse, *Chem. Unserer Zeit* **2004**, 434; (d) R. D. Rogers, K. R. Seddon, *Nature Mater.* **2003**, *2*, 363; (e) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
- [27] F. Cavani, J. H. Teles, *ChemSusChem.* **2009**, *2*, 508.
- [28] D. Astruc, *Organometallic Chemistry and Catalysis*, Springer Berlin / Heidelberg, **2007**, p. 399.
- [29] (a) C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197; (b) G. S. Owens, J. Arias, M. M. Abu-Omar, *Catal. Today* **2000**, *55*, 317; (c) J. H. Espenson, *Chem. Commun.* **1999**, *6*, 479; (d) K. P. Gable, *Adv. Organomet. Chem.* **1997**, *41*, 127; (e) W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169.
- [30] (a) A. M. J. Rost, W. A. Herrmann, F. E. Kühn, *Tetrahedron Lett.* **2007**, *48*, 1775; (b) F. E. Kühn, K. R. Jain, M.-D. Zhou, *Rare Met.* **2006**, *25*, 411.
- [31] (a) W. A. Herrmann, A. M. J. Rost, J. K. M. Mitterpleininger, N. Szesni, S. Sturm, R. W. Fischer, F. E. Kühn, *Angew. Chem. Int. Ed.* **2007**, *46*, 7301; (b) E. Tosh, J. K. M. Mitterpleininger, A. M. J. Rost, D. Veljanovski, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2007**, *9*, 1296.
- [32] W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638.
- [33] G. S. Owens, M. M. Abu-Omar, *Chem. Commun.* **2000**, 1165.
- [34] (a) D. Betz, W. A. Herrmann, F. E. Kühn, *J. Organomet. Chem.* **2009**, *694*, 3320; (b) D. Betz, A. Raith, M. Cokoja, F. E. Kühn, *ChemSusChem.* **2010**, *3*, 559.
- [35] W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem. Int. Ed. Engl.*

- 1993**, 32, 1157.
- [36] W. A. Herrmann, J. D. G. Correia, G. R. J. Artus, R. W. Fischer, C. C. Romão, *J. Organomet. Chem.* **1996**, 520, 139.
- [37] (a) A. M. Al-Ajlouni, J. H. Espenson, *J. Am. Chem. Soc.* **1995**, 117, 9243; (b) J. H. Espenson, *Chem. Commun.* **1999**, 479; (c) W. Adam, C. R. Saha-Möller, O. Weichold, *J. Org. Chem.* **2000**, 65, 5001.
- [38] W. A. Herrmann, *J. Organomet. Chem.* **1995**, 500, 149.
- [39] (a) P. Gisdakis, N. Rösch, *Eur. J. Org. Chem.* **2001**, 4, 719; (b) P. Gisdakis, I. V. Yudanov, N. Rösch, *Inorg. Chem.* **2001**, 40, 3755; (c) P. Gisdakis, W. Antonczak, S. Köstlmeier, W. A. Herrmann, N. Rösch, *Angew. Chem. Int. Ed.* **1998**, 37, 2211; (d) O. Pestovski, R. V. Eldik, P. Huston, J. H. Espenson, *J. Chem. Soc. Dalton Trans.* **1995**, 133.
- [40] (a) C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, 97, 3197; (b) W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, 30, 169.
- [41] E. da P. Carreiro, A. J. Burke, M. J. M. Curto, A. J. R. Teixeira, *J. Mol. Catal. A: Chem.* **2004**, 217, 69.
- [42] R. Saladino, R. Bernini, U. Neri, C. Crestini, *Appl. Catal. A: Gen.* **2009**, 360, 171.
- [43] (a) W. A. Herrmann, F. E. Kühn, C. C. Romão, H. T. Huy, M. Wang, R. W. Fischer, P. Kiprof, W. Scherer, *Chem. Ber.* **1993**, 126, 45; (b) W. A. Herrmann, F. E. Kühn, M. U. Rauch, J. D. G. Correia, G. Artus, *Inorg. Chem.* **1995**, 34, 2914; (c) W. A. Herrmann, F. E. Kühn, M. R. Mattner, G. R. J. Artus, M. R. Geisberger, J. D. G. Correia, *J. Organomet. Chem.* **1997**, 538, 203; (d) W. A. Herrmann, H. Ding, R. M. Kratzer, F. E. Kühn, J. J. Haider, R. W. Fischer, *J. Organomet. Chem.* **1997**, 549, 319; (e) M. D. Zhou, J. Zhao, J. Li, S. Yue, C. Bao, J. Mink S. L. Zang, F. E. Kühn, *Chem. Eur. J.* **2007**, 13, 158; (f) Z. Xu, M. D. Zhou, M. Drees, H. C. Millar, E. Herdweck, W. A. Herrmann, F. E. Kühn, *Inorg. Chem.* **2009**, 48, 6812; (g) A. Capapé M. D. Zhou, S. L. Zang, F. E. Kühn, *J. Organomet. Chem.* **2008**, 693, 3240.
- [44] (a) W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal. A: Chem.* **1994**, 86, 243; (b) W. A. Herrmann, F. E. Kühn, M. R. Mattner, G. R. J. Artus, M. R. Geisberger, J. D. G. Correia, *J. Organomet. Chem.* **1997**, 538, 203; (c) W. A. Herrmann, F. E. Kühn, M. U. Rauch, J. D. G. Correia, G. Artus, *Inorg. Chem.* **1995**, 34, 2914.
- [45] (a) J. Rudolph, K. L. Reddy, J. P. Chiang, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, 119, 6189; (b) A. K. Yudin, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, 119, 11536.
- [46] (a) C. Copéret, H. Adolfsson, K. B. Sharpless, *Chem. Commun.* **1997**, 1565; (b) W. A. Herrmann, R. M. Kratzer, H. Ding, H. Glas, W. R. Thiel, *J. Organomet. Chem.* **1998**,

Chapter 1

- 555, 293.
- [47] F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudanov, C. Di Valentin, N. Rösch, *Chem. Eur. J.* **1999**, *5*, 3603.
- [48] (a) D. L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1736; (b) J. Yan, D. L. Long, E. F. Wilson, L. Cronin, *Angew. Chem. Int. Ed.* **2009**, *48*, 4376; (c) D. M. Way, J. B. Cooper, M. Sadek, T. Vu, P. J. Mahon, A. M. Bond, R. T. C. Brownlee, A. G. Wedd, *Inorg. Chem.* **1997**, *36*, 4227.
- [49] J. J. Berzelius, *Poggendorfs Ann. Phys. Chem.* **1826**, *6*, 369.
- [50] D. L. Long, L. Cronin, *Chem. Eur. J.* **2006**, *12*, 3699.
- [51] (a) H. Y. Ma, J. Peng, Z. G. Han, X. Yu, B. X. Dong, *J. Solid State Chem.* **2005**, *178*, 3735; (b) T. Yamase, *J. Mater. Chem.* **2005**, *15*, 4773.
- [52] R. J. Errington, S. S. Petkar, B. R. Horrocks, A. Houlton, L. H. Lie, S. N. Patole, *Angew. Chem. Int. Ed.* **2005**, *44*, 1254.
- [53] (a) M. V. Vasylyev, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 884; (b) R. Neumann, A. M. Khenkin, I. Vigdergauz, *Chem. Eur. J.* **2000**, *6*, 875; (c) N. Mizuno, K. Yamaguchi, K. Kamata, *Coord. Chem. Rev.* **2005**, *249*, 1944; (d) I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, K. I. Hardcastle, C. L. Hill, T. M. Anderson, *Inorg. Chem.* **2003**, *42*, 1163.
- [54] (a) D. Volkmer, B. Bredenkötter, J. Tellenbröcker, P. Kögerler, D. G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, M. Piepenbrink, B. Krebs, *J. Am. Chem. Soc.* **2002**, *124*, 10489; (b) S. Liu, D. Volkmer, D. G. Kurth, *J. Cluster Sci.* **2003**, *14*, 405.
- [55] G. Chaidogiannos, D. Velessiotis, P. Argitis, P. Koutsolelos, C. D. Diakoumakos, D. Tsamakidis, N. Glezos, *Microelectron. Eng.* **2004**, *73-74*, 746.
- [56] (a) E. Coronado, C. Gimenez-Saiz, C. J. Gomez-Garcia, *Coord. Chem. Rev.* **2005**, *249*, 1776; (b) E. Coronado, S. Curreli, C. Giménez-Saiz, C. J. Gómez-García, J. Roth, *Synth. Met.* **2005**, *154*, 241; (c) L. Xu, E. B. Wang, Z. Li, D. G. Kurth, X. G. Du, H. Y. Zhang, C. Qin, *New J. Chem.* **2002**, *26*, 782.
- [57] D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105.
- [58] (a) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113; (b) N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199.
- [59] K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara, S. Yamanaka, *Angew. Chem. Int. Ed.* **2007**, *46*, 7625.
- [60] Y. Qiao, Z. Hou, H. Li, Y. Hu, B. Feng, X. Wang, L. Hua, Q. Huang, *Green Chem.* **2009**, *11*, 1955.
- [61] M. McCoy, M. S. Reisch, A. H. Tullo, P. L. Short, J. F. Tremblay, W. J. Storck, M. Voith,

Chapter 1

- Chem. Eng. News* **2008**, 86, 35.
- [62] Halcon, US patent 3350422, 10/1967; ARCO, GB patent 1136923, 12/1968.
- [63] B. Notari, *Catal. Today* **1993**, 18, 163.
- [64] (a) D. Mctavish, M. Buckley, K. C. Hell, *Drugs* **1991**, 47, 138; (b) P. Richardson, C. J. Hawkey, W. A. Stack, *Drugs* **1998**, 56, 307; (c) K. C. Lai, S. K. Lam, K. M. Chu, B. C. Y. Wong, W. M. Hui, W. H. C. Hu, G. K. K. Lau, W. M. Wong, M. F. Yuen, A. O. O. Chan, C. L. Lai, J. Wong, *N. Engl. J. Med.* **2002**, 346, 2033.
- [65] R. Kubec, M. Svobodová, J. Velíšek, *J. Agric. Food Chem.* **2000**, 48, 428.
- [66] K. H. Kyung, D. C. Han, H. P. Fleming, *J. Food. Sci.* **1997**, 62, 406.
- [67] R. Schmied, G. X. Wang, M. Korth, *Circ. Res.* **1991**, 68, 597.
- [68] S. Padmanabhan, R. C. Lavin, G. J. Darant, *Tetrahedron: Asymmetry* **2000**, 11, 3455.
- [69] W. Komatsu, Y. Miura, K. Yagasaki, *Lipids* **1998**, 33, 499.
- [70] F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, *J. Mol. Catal. A: Chem.* **2008**, 286, 124.
- [71] M. Gazdar, S. Smiles, *J. Chem. Soc.* **1908**, 93, 1833.
- [72] (a) R. Pummerer, *Chem. Ber.* **1910**, 43, 1406; (b) P. Karrer, E. Scheitlin, H. Siegrist, *Helv. Chim. Acta* **1950**, 33, 1237; (c) A. C. Cope, D. E. Morrison, L. Field, *J. Am. Chem. Soc.* **1950**, 72, 59; (d) R. L. Shriner, H. C. Struck, W. J. Jorison, *J. Am. Chem. Soc.* **1930**, 52, 2060.
- [73] J. Drabowica, M. Mikolajczyk, *Synth. Commun.* **1981**, 11, 1025.
- [74] K. S. Ravikumar, J. P. Bogue, D. Bonnet-Delpon, *Tetrahedron Lett.* **1998**, 39, 3141.
- [75] W. L. Xu, Y. Z. Li, Q. S. Zhang, H. S. Zhu, *Synthesis* **2004**, 2, 227.
- [76] F. Liu, Z. Fu, Y. Liu, C. Lu, Y. Wu, F. Xie, Z. Ye, X. Zhou, D. Yin, *Ind. Eng. Chem. Res.* **2010**, 49, 2533.
- [77] K. Jeyakumar, D. K. Chand, *Tetrahedron Lett.* **2006**, 47, 4573.
- [78] S. Choi, J. D. Yang, M. Ji, H. Choi, M. Kee, K. H. Ahn, S. H. Byeon, W. Baik, S. Koo, *J. Org. Chem.* **2001**, 66, 8192.
- [79] C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. Deng, *Green Chem.* **2009**, 11, 1401.
- [80] Y. Ishii, H. Tanaka, Y. Nishiyama, *Chem. Lett.* **1994**, 1.
- [81] A. Arcoria, F. P. Ballistreri, G. A. Tomaselli, F. Di Furia, G. Modena, *J. Mol. Catal.* **1983**, 18, 177.
- [82] O. Bortolini, F. Di Furia, G. Modena, *J. Mol. Catal.* **1983**, 19, 319.
- [83] O. Bortolini, S. Campestrini, F. Di Furia, G. Modena, *J. Org. Chem.* **1987**, 52, 5093.
- [84] A. Arcoria, F. P. Ballistreri, G. A. Tomaselli, F. Di Furia, G. Modena, *J. Mol. Catal.*

Chapter 1

1984, 24, 189.

[85] P. Zhao, M. Zhang, Y. Wu, J. Wang, *Ind. Eng. Chem. Res.* **2012**, 51, 6641.

2 Activation of hydrogen peroxide by ionic liquids: mechanistic studies and application in the epoxidation of olefins

This chapter originated from the following publication:

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2.1 Introduction

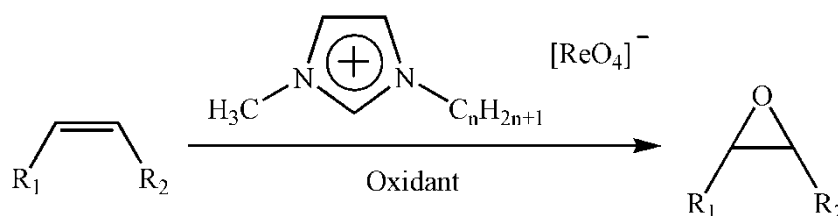
Although the compound class of (room temperature) ionic liquids, henceforth denoted as (RT)ILs, has been known since the middle of the 20th century,^[1] research on ILs has experienced an extraordinary growth during the last decade.^[2] Thus far, more than 40,000 research articles have been published on ionic liquids.^[3] Above all, their unique chemical and physical properties such as low miscibility with non-polar, organic solvents, low volatility, low flash point, thermal stability, high polarity, and at least in several cases, low toxicity^[4] render ILs attractive and “green” alternatives to organic solvents.^[5] Pioneering contributions of the groups of Rogers,^[6] Wasserscheid,^[7] Seddon,^[8] Welton,^[9] Dupont,^[10] among many others^[11] to the studies of SILP^[12] (Supported Ionic Liquid Phase) as reaction media for two-phase catalyzed reactions have made the catalytic application of ILs a prominent research area.^[13] In several cases, ILs have already found applications as solvents for extractants in industrial catalytic syntheses,^[14] such as the BASF-BASIL process.^[15] However, they also exhibit a templating effect in the synthesis of inorganic materials (nanoparticles, metal oxides, metal-organic frameworks).^[16] The beneficial effect on a reaction in terms of reaction rates is ascribed to a low degree of interactions (e.g. solvent cages) with the dissolved molecules. Recently, many groups focused on the functionalization of ILs, in particular those that contain imidazolium cations with Lewis acidic or basic groups, which can act as organocatalysts.^[17] Among many catalyzed processes that have been performed in ionic liquids are epoxidation reactions.^[18] The original purpose of applying ILs to this reaction was for facile

product/catalyst separation, which indeed could be achieved more easily in several cases than in the original processes. In addition, it was observed that ILs greatly affected the activity of the epoxidation catalysts, thereby leading to very active systems in several cases.^[19] Surprisingly, some typically catalytically inactive inorganic compounds, such as perrhenates (the usual decomposition products of well-examined epoxidation catalysts, such as methyltrioxorhenium (MTO)),^[20-22] displayed activity in olefin epoxidation, when applied as anions of ILs, thus showing very good yields of the epoxides and reusability of the IL. These observations led to the study reported herein. The activation of hydrogen peroxide by perrhenate, which was enabled solely by the ionic liquids environment, is to the best of our knowledge, reported for the first time. This new mode of activation allows for easy epoxidation of olefins.

2.2 Results and discussion

2.2.1 Epoxidation in perrhenate-containing ILs

Several perrhenate-containing ILs of the general formula $[\text{C}_n\text{mim}][\text{ReO}_4]$ (C_nmim = 1- C_nH_{n+1} -3-methylimidazolium, C_n = butyl (C_4), octyl (C_8), dodecyl (C_{12})) were synthesized and used to study the epoxidation of cyclooctene with different oxidants: H_2O_2 , urea hydrogen peroxide (UHP) and *tert*-butyl hydroperoxide (TBHP) (Scheme 1).



Scheme 1. Olefin epoxidation in ionic liquids with the perrhenate anion.

Equimolar amounts of the IL and cyclooctene, as well as 2.5 equivalents of the oxidant, were mixed together at room temperature, thus giving a three-phase medium, which as heated at 70 °C for 4 h under vigorous stirring. After the reaction had been completed, the epoxide was dissolved in the IL, giving a two-phase medium IL + Product/water + H_2O_2 . The epoxide was extracted with *n*-hexane (5 x 1 mL) and the yield of the epoxide was determined by GC. Nearly quantitative cyclooctene oxide was obtained when aqueous H_2O_2 is used as oxidant (see Table 1, Entry 1).

Chapter 2

Table 1. Effect of oxidants on the yield of cyclooctene oxide (in percent) in imidazolium-based ILs with $[\text{ReO}_4]^-$ as anion.

Entry	IL	Oxidation agent		
		$\text{H}_2\text{O}_2/\text{H}_2\text{O}$	UHP	TBHP
1	$[\text{C}_4\text{mim}][\text{ReO}_4]$	99	42	5
2	$[\text{C}_8\text{mim}][\text{ReO}_4]$	99	66	6
3	$[\text{C}_{12}\text{mim}][\text{ReO}_4]$	99	80	5

Reaction conditions: 1 mmol IL, 1 mmol cyclooctene, 2.5 mmol oxidation agent, 4 h reaction time, 70 °C.

However, with UHP, yields are lower, and with TBHP, no significant yield of epoxide was obtained. In the case of UHP, the yield of cyclooctene oxide was higher when the alkyl moiety at the imidazolium cation is longer. This effect can be attributed to the increased solubility of the oxidizing agent in $[\text{C}_{12}\text{mim}][\text{ReO}_4]$ (Entry 3). Other substrates, such as cyclohexene, styrene and 1-octene show good conversions in $[\text{C}_{12}\text{mim}][\text{ReO}_4]$ with UHP as oxidant (see Table 2). However, the solubility of UHP in $[\text{C}_{12}\text{mim}][\text{ReO}_4]$ rendered the recycling of the IL more difficult than with hydrogen peroxide.

Table 2. Epoxidation of various olefins in $[\text{C}_{12}\text{mim}][\text{ReO}_4]$ and UHP as oxidation agent. In all cases, the conversion of the olefins are equal to the epoxide yields, i.e. the selectivity is in each case 100 %.

Entry	Substrate	Product	Yield (%)
1	cyclooctene	cyclooctene oxide	80
2	cyclohexene	cyclohexene oxide	63
3	styrene	epoxystyrene	37
4	1-methyl hexane	1-methyl cyclohexane-2-on	59
5	1-octene	1-octene oxide	15

These promising findings of new peroxide chemistry were a motivation to further experimentally examine whether the addition of catalytic amounts of perrhenate to standard ILs with different polarities, such as $[\text{C}_8\text{mim}][\text{BF}_4]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$, would also lead to cyclooctene epoxidation (Table 3). Notably, different cation with $[\text{ReO}_4]^-$ had a tremendous effect on the activity. Whereas NH_4ReO_4 does not provide a significant yield of the epoxide, with potassium perrhenate, yields of up to 53 % (Table 3, entry 2) can be achieved. When the concentration of perrhenate is decreased to 10 mol % (relative to the substrate), the activity also drops notably (Table 3, entry 3). From Table 3, it is clear that ammonium ions inhibit the epoxidation of an olefin. Similarly to peroxides, these cations interact with $[\text{ReO}_4]^-$ and / or the IL ions. Presumably, this interaction causes the inactivity of NH_4ReO_4 (Table 3, entries 4 and 5), whereas K^+ ions behave very differently (Table 3, entries 2 and 3). This comparison also highlights the role of the IL as an environment, which is able to dissolve polar species, such as perrhenate salts, without the need to include a protic solvent shell (e.g., water; Table 3, entry 8) which would disturb the perrhenate-peroxide complexation. This argument allows a rationalizing of why perrhenates are inactive in aqueous medium, where the hydration “shell”

passivates the complex.

Table 3. Yields of cyclooctene oxide for various perrhenate concentrations (PC).

Entry	Solvent	Perrhenate salt	PC [mol %]	Yield [%]
1	[C ₈ mim][BF ₄]	–	–	13
2	[C ₈ mim][BF ₄]	KReO ₄	100	53
3	[C ₈ mim][BF ₄]	KReO ₄	10	10
4	[C ₈ mim][BF ₄]	NH ₄ ReO ₄	100	17
5	[C ₈ mim][BF ₄]	NH ₄ ReO ₄	10	5
6	[C ₈ mim][NTf ₂]	KReO ₄	100	3
7	[C ₈ mim][NTf ₂]	NH ₄ ReO ₄	100	7
8	H ₂ O	NH ₄ ReO ₄	100	8

Reaction conditions: 0.5 ml IL, 1 mmol cyclooctene, 2.5 mmol H₂O₂ (50 % solution in water), reaction time 4 h, 70 °C.

By comparing the use of two ILs, [C₈mim][NTf₂] and [C₈mim][BF₄] as solvents (Entries 2, 4, 6 and 7), we can clearly conclude that the solubility of the perrhenate salt in the respective IL has a significant influence on the activity towards epoxidation. A more polar IL like [C₈mim][BF₄] will facilitate the solubility of the perrhenate salt, leading to formation of hydrogen bonds between perrhenate and H₂O₂. A reciprocal observation is made with [C₈mim][NTf₂], wherein NH₄ReO₄ and KReO₄ are entirely insoluble, leading to yields of 7 % and 3 %, respectively.

Recycling experiments were carried out on samples of the IL [C₈mim][ReO₄] (Figure 1). Constant yields of 98–99 % were obtained for at least 8 runs, which demonstrates the high stability of the IL under oxidative conditions, thus rendering it a good candidate for efficient olefin epoxidation.

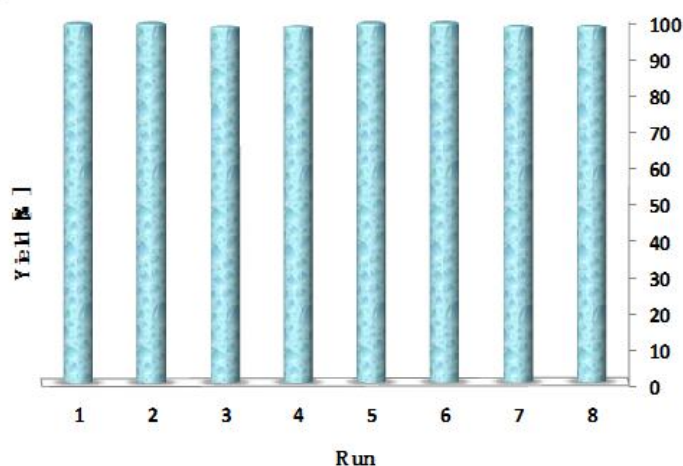


Figure 1. Yields of cyclooctene oxide after eight reaction runs in [C₈mim][ReO₄].

2.2.2 Mechanistic considerations of the activation of H₂O₂

The reactivity of the perrhenate-containing IL is intriguing. In contrast, by using [C₈mim][BF₄] without the addition of a metal oxide, cyclooctene epoxide is obtained in 13 % yield (Table 2,

Entry 1), thus pointing to the pivotal role of perrhenate in the conversion of the olefin into the corresponding epoxide. However, this fundamental-yet surprising-activity of $[\text{BF}_4]^-$ can be rationalized by the formation of hydrogen bonds between $[\text{BF}_4]^-$ with hydroxides.^[9b, 23] To verify whether the $[\text{BF}_4]^-$ anion is responsible for the activation of hydrogen peroxide, or whether they even react with the peroxide or water, in situ ^{19}F -NMR spectra, $[\text{C}_4\text{mim}][\text{BF}_4]$ (see Figure 2), were recorded in the presence of perrhenate and hydrogen peroxide.

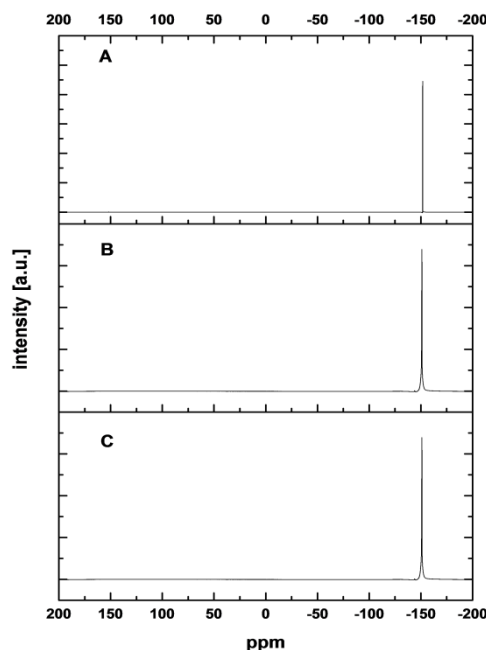


Figure 2. ^{19}F -NMR Spectra (200 – -200 ppm) of $[\text{C}_4\text{mim}][\text{BF}_4]$ at 70 °C: without NH_4ReO_4 and H_2O_2 (A), with NH_4ReO_4 and H_2O_2 after 30 min. (B) and 90 min (C).

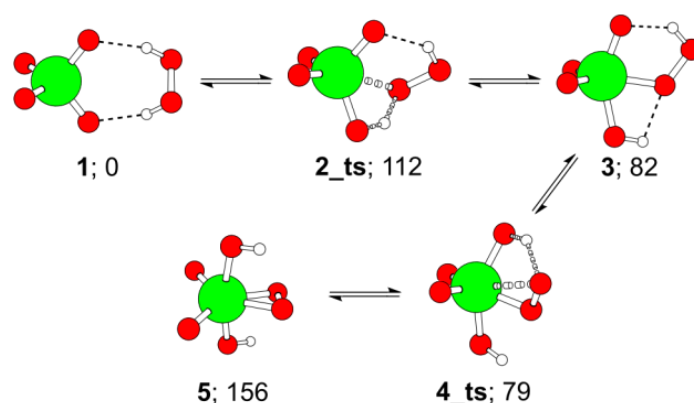
Notably, no change in the fluorine signals during epoxidation were observed, thus showing that $[\text{BF}_4]^-$ anion did not react with H_2O_2 or was hydrolyzed by water. Therefore, we can conclude that the $[\text{BF}_4]^-$ anion is not (or only to a minor degree) responsible for the activation in the presence of $[\text{ReO}_4]^-$, as also corroborated by vibrational spectroscopy.

Welton and co-workers reported the formation of hydrogen bonds between the IL anions and water molecules.^[24] Mele *et al.* observed weak H bonding of the imidazolium cation with water.^[25] Hence, in Table 2, entry 1, H_2O_2 is presumably associated with the IL anion. Hydrogen bonds to the cation probably do not form in the presence of a potent H-bond acceptor such as a perrhenate anion. The addition of metal-oxo complexes, such as $[\text{ReO}_4]^-$, accelerates the reaction, presumably through the formation of $\text{O}_3\text{Re}-\text{O} \cdots \text{H}-\text{O}-\text{OH}$ species, which activate the peroxide and hence, enable epoxidation. Seemingly, metal-oxide-mediated olefin epoxidation in ILs follows a different reaction mechanism to that with the usually metal catalysts,^[11] in which (hydro) peroxy ligands act as catalytically active species in transferring an oxo moiety to the olefin.^[26] The activation of peroxides with the carbonate anion and the

subsequent epoxidation of olefins were reported by Yao and Richardson.^[27] However, their reactions were performed in water and, thus, the substrates had to contain functional groups (carboxylate, sulfonate, ester) that would render them soluble; hence, the reactions of simple olefins were not undertaken. The mechanism has also not been examined in detail. Therefore, to shine some light onto the activation of peroxide with perrhenate, the reaction mechanism was also examined by DFT calculation.

2.2.3 Spectroscopic and DFT studies of the activation of H₂O₂ with perrhenate and subsequent epoxidation

Recent publications presented elaborate schemes for modeling ILs.^[28-29] The scope of the calculations reported herein was to elucidate and support the proposed catalytic mechanisms, in particular in terms of the trends in crucial activation barriers. Therefore, as first approximation, we refrained from directly including the effects of ILs that are often described by using molecular modeling approaches. We relied on ILs to provide a reaction cavity and we assumed that gas phase models correctly helped to identify trends. Thus, the absolute values of barrier heights should be taken with caution. Three complexes from which the oxidation may start were considered (Scheme 2): that is, encounter complex **1** between hydrogen peroxide and [ReO₄]⁻, the hydroxo-hydroperoxo rhenium species **3**, and the bishydroxo-peroxo complex **5**.^[30]



Scheme 2. Calculated equilibrium structures for the reaction of [ReO₄]⁻ with H₂O₂ including the transition states (ts). All of the complexes are monoanions. These dashed lines indicate hydrogen bonds, thick dashed lines bonds to be broken or formed in a reaction step. Free reaction energies (kJ mol⁻¹) relative to **1**, activation barriers relative to the preceding initial state. Color coding of the atomic spheres: Re green, large; O red; H white, small.

Before exploring the actual mechanism, it is important to identify active species that are formed with peroxide in the IL. Therefore, the reactions were monitored *via* in situ IR and Raman spectroscopy. Upon addition of the oxidant, the asymmetric stretching vibration splits

in both the Raman and IR spectra (Figure 3, spectrum **a**). Point group analysis shows that this is consistent with a lowering of the local symmetry of $[\text{ReO}_4]^-$ from T_d to C_{2v} .

These changes can be assigned to a distortion of the local symmetry of the anion by weak coordination, for example, hydrogen bonds. This assignment is supported by calculated vibrational spectra of the key intermediates (**1**, **3** and **5**; Figure 3). Indeed, in the IR spectra, the experimentally observed splitting ($890\text{--}920\text{ cm}^{-1}$; Figure 3, spectrum **a**) of the former asymmetric stretching mode of the pure ionic liquids, which is found at about 900 cm^{-1} (see Figure 3),^[31] is also reflected in the simulated spectra (Figure 4).

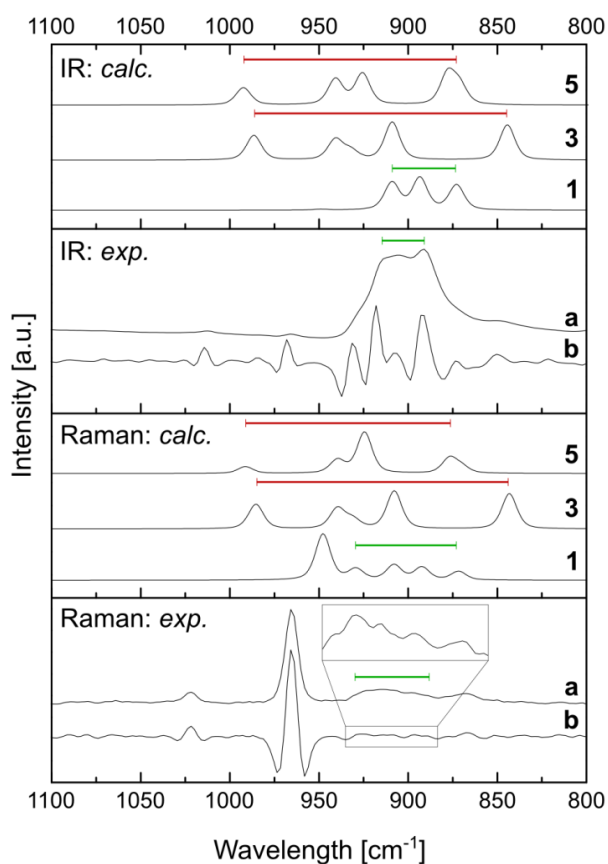


Figure 3. Raman and mid-IR spectra of $[\text{C}_8\text{mim}][\text{ReO}_4]$ ($\text{Re}=\text{O}$ asymmetric stretch vibration) after peroxide addition. Calculated: encounter complex **1**, hydroxo-hydroperoxo complex **3**, and peroxo complex **5**; **a**: measured, and **b**: 2nd derivative of the spectra. Peak broadenings indicated as horizontal bars (see text).

For structure **1**, a small splitting is calculated, with three peaks within the range $865\text{--}910\text{ cm}^{-1}$, whereas the ligands on the metal center of structures **3** and **5** induce a significant larger broadening of the spectra (**3**: $840\text{--}985\text{ cm}^{-1}$; **5**: $875\text{--}990\text{ cm}^{-1}$). Both the shift and splitting of this band, as observed experimentally (spectrum **a**), are best reproduced by the simulated for complex **1**. Thus, from IR data, structure **1** is expected to be predominantly formed. In the Raman spectra, the asymmetric stretching mode of the pure ionic liquid at about 916 cm^{-1} (see

Figure 3), is broadened to 885–930 cm^{-1} (Figure 4, spectrum **a**). Again, this finding is supported by the calculated spectrum of encounter complex **1**, which exhibits a broadening to 875–930 cm^{-1} . The splitting patterns in the Raman spectra of **3** and **5** are also significantly broadened (**3**: 840–985 cm^{-1} ; **5**: 875–990 cm^{-1}). The calculated spectrum of structure **1** has a slightly different peak pattern to the second derivative of the experimental spectrum (spectrum **b**, extended view). The simulated IR and Raman spectra of structures **3** and **5** show an additional peak at about 980 cm^{-1} , which is assigned to the hydroxyl groups but is not observed in experimentally, thus corroborating the dominance of structure **1** in the reaction. Far-IR measurements do not indicate any additional Re-O vibrations, excluding the formation of rhenium-peroxo species.

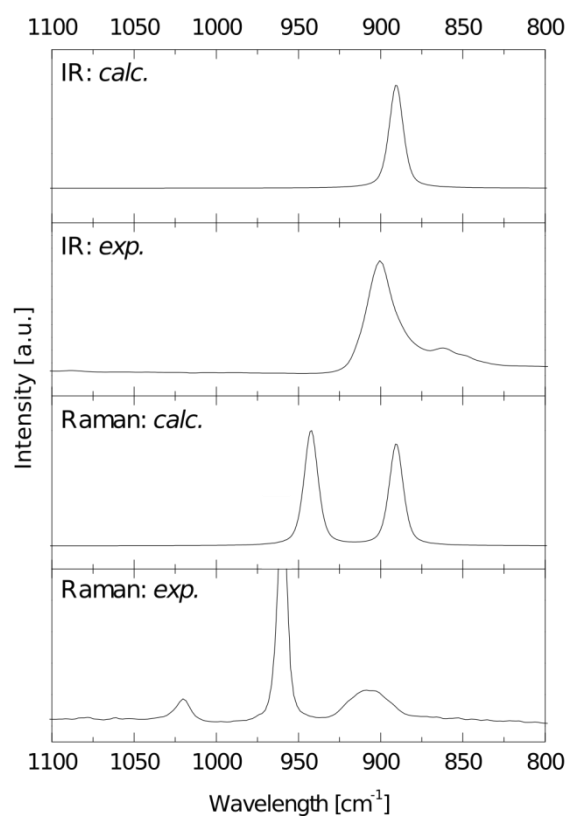


Figure 4. Comparison of calculated and measured Raman spectra of the pure ionic liquid: $[\text{ReO}_4]^-$ calculated, $[\text{C}_8\text{mim}][\text{ReO}_4]$ measured. The peak at 1020 cm^{-1} in the experimental spectrum results from the $[\text{C}_8\text{mim}]^+$ counter ion.

Thus, structure **1** can be safely addressed as the predominant equilibrium structure. The formation of the encounter complex **1** is calculated to be exothermic by -20 kJ mol^{-1} (Scheme 2), owing to the newly formed H bonds. Compound **1** can be considered as an initial state of all reaction pathways. Thus, all of the free reaction energies shown are given relative to structure **1**. A barrier of 112 kJ mol^{-1} (**2_ts**) has to be overcome to arrive at the endothermic hydroxo-hydroperoxo complex **3** (82 kJ mol^{-1}). The strongly endothermic peroxo complex **5**

(156 kJ mol⁻¹) is reachable *via* a barrier of 79 kJ mol⁻¹ (**4_ts**). Hence, these latter alternatives to structure **1** are both thermodynamically and kinetically disfavored. These computational results, together with the findings on the vibrational spectra, indicate that the equilibrium of the ionic liquid and hydrogen peroxide will be predominantly shifted towards complex **1**. As a consequence, during the reaction, [ReO₄]⁻ can be assumed to be coordinated by H₂O₂ through H bonds, thus activating the peroxide bond and making it susceptible to attack by an olefin. In contrast to MTO, the stable delocalized electronic structure of perrhenate implies a chemical inertness that requires a significant amount of energy to be disturbed, for example, by inserting H₂O₂ to yield structures **3** and **5**.

Further computational efforts addressed the question whether a single perrhenate moiety or peroxide-bridged agglomerates of such anions may act as active species (see Figure 5).

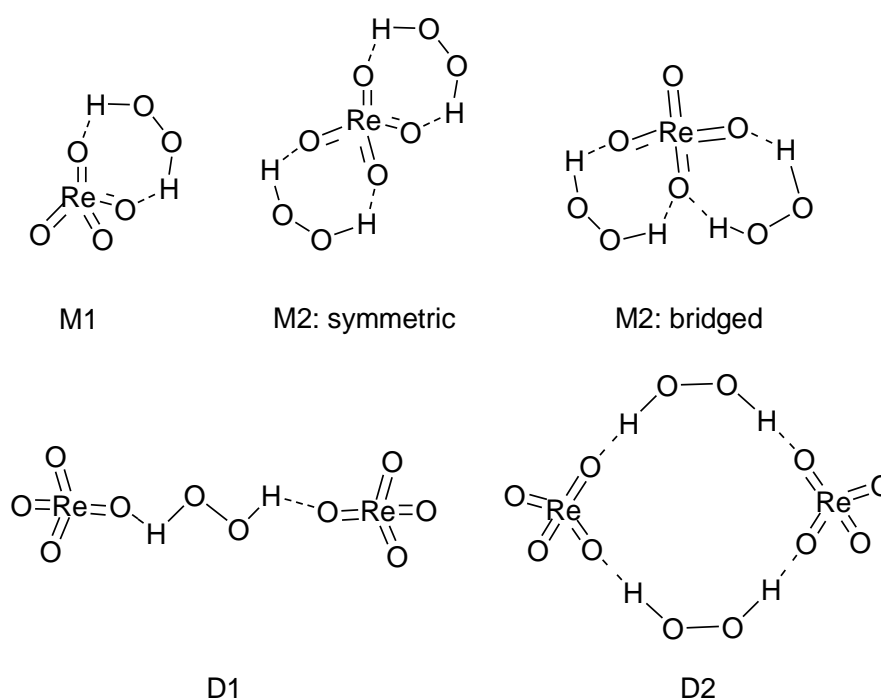


Figure 5. Possible perrhenate-peroxide complexes, either mono- (M) or dimers (D), as alternatives to M1 (structure **1** of the article).

Simulated Raman spectra did not exclude such agglomerates (see Figure 6). The formation of such structures will depend on the size and the content of the reaction cavity provided by the IL, specifically on the size of the counterion. Mono-perrhenates that contain two peroxide moieties are also conceivable as active species, thus enhancing the possibility for epoxidation.

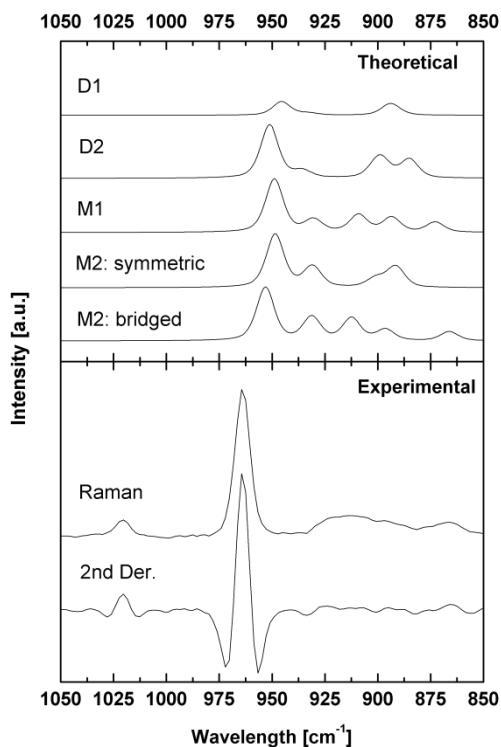


Figure 6. Calculated Raman spectra of various systems in comparison with experimental spectra of $[\text{C}_8\text{mim}][\text{ReO}_4]$.

Although our spectroscopic studies show that the equilibrium is shifted almost completely towards complex **1**, epoxidation might involve one of the minor intermediates. Therefore, we examined various plausible transition states (**ts**). Accordingly, among all of the reaction channels studied, the rate-limiting barrier (relative to structure **1**) was by far the lowest for direct oxidation by complex **1** (see Figure 7).

Chapter 2

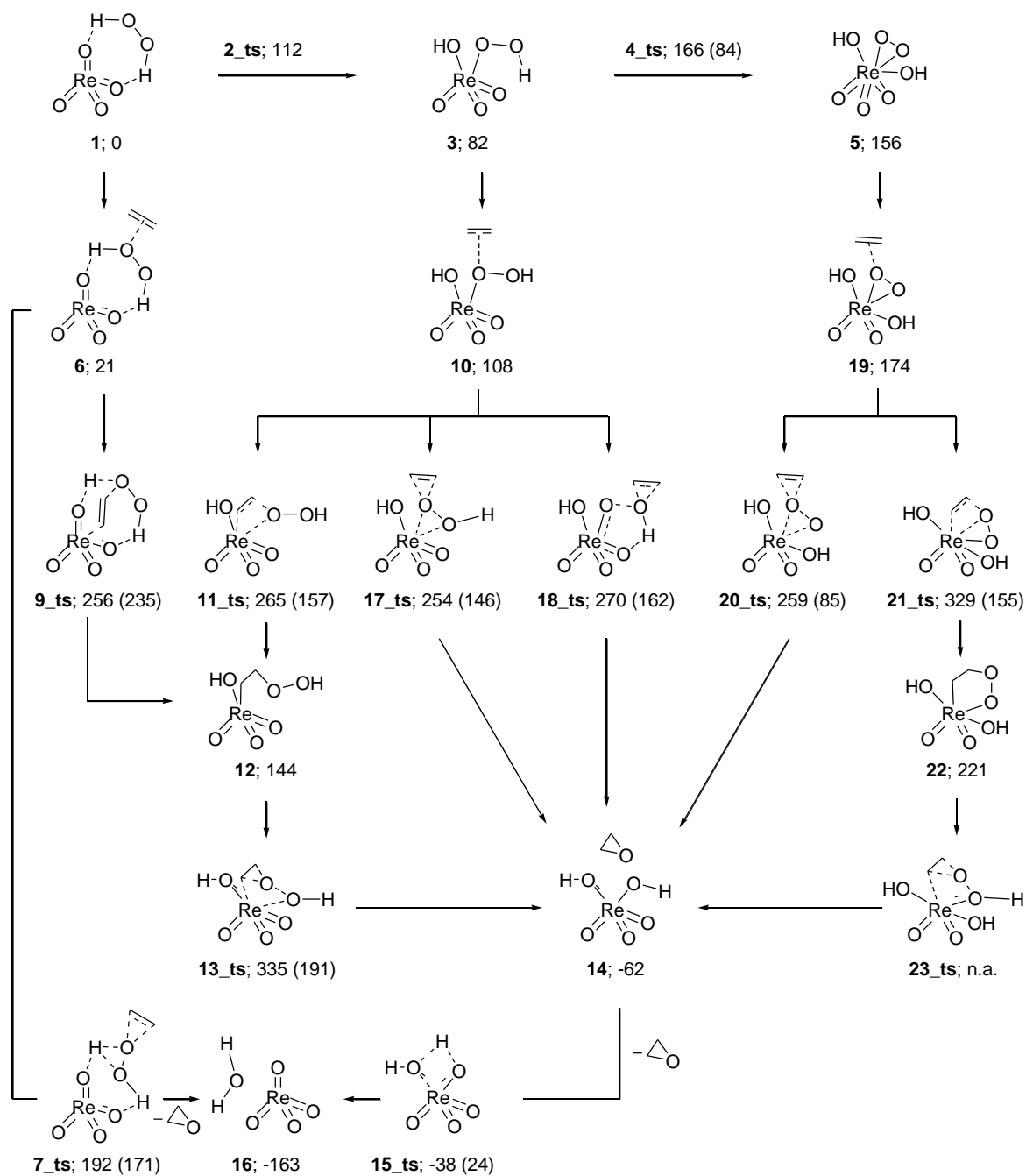
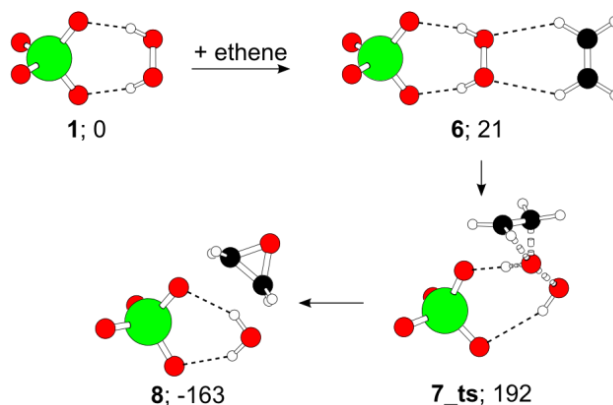


Figure 7. Alternative reaction pathways and their activation barriers. Values given are Gibbs free energies (in kJ mol^{-1}) relative to the intermediate **1**. Activation barriers in parentheses are relative to the preceding intermediate.

Transition state **7_{ts}** lies 171 kJ mol^{-1} above the preceding intermediate state (IS) **6** (Scheme 3). A second hydrogen bond does not necessarily have to form to the same $[\text{ReO}_4]^-$ unit.



Scheme 3. Calculated reaction pathway of direct epoxidation through the H-bonded complex **1**. Gibbs free energies (in kJ mol^{-1}) are relative to the separated substrates, $[\text{ReO}_4]^-$ and H_2O_2 . All of the complexes are mono-anions. Free energies calculated as in Scheme 2. Color coding of the atomic spheres: C black, small; the rest as in Scheme 2.

We were unable to identify an alternative structure for product **8** that involved a water molecule bound through H bonds to the perrhenate anion. A water ligand, which coordinated at the perrhenate through its oxygen atom, analogous to structures that have previously been found in MTO chemistry,^[32-33] immediately reorients to form structure **8**. The barrier of the corresponding back reaction was calculated to be 355 kJ mol^{-1} ; hence, the reverse step is highly unlikely. Direct insertion, starting from structure **1**, encounters a notably higher barrier (256 kJ mol^{-1} ; see Figure 7). In agreement with experimental findings that identify structure **1** as the prevailing species, alternative epoxidation pathways, starting from structures **3** or **5**, are far less likely (Scheme 2). The barriers of such alternative oxygen-transfer pathways relative to structure **1**, that is, neglecting the energy change owing to coordination of the olefin, are at least 254 kJ mol^{-1} (see Figure 7). To elucidate the origin atom in the epoxide product, the epoxidation of cyclooctene was repeated using ^{17}O -labeled $[\text{C}_8\text{mim}][\text{ReO}_4]$ and H_2O_2 as oxidant. After work up and product isolation, the recorded ^{17}O -NMR spectrum of cyclooctene oxide does not show any signal, even after 24 h of acquisition time. This result clearly excludes the formation of Re-hydroperoxo (**3**) or Re-peroxo (**5**) species, that is, a transfer of oxo ligands from Re onto the olefin. Thus, the oxygen has to originate from H_2O_2 , without prior direct coordination at the metal center, thus suggesting the pathway starting from structure **1**.

Thus far, we have only discussed mechanistic aspects only with regard to H_2O_2 as oxidant. It is the question, which effects are responsible for the poor epoxide yields when using UHP and TBHP as oxidants (Table 1). Analogous to structure **1** with oxidant H_2O_2 (Scheme 2), we examined the H-bonded encounter complexes (**1a** and **1b**) of perrhenate and the oxidants UHP and TBHP, respectively (Figure 4). Oxidant UHP, viewed as adduct of H_2O_2 and urea (see 1a), exhibits H bonds between the hydroxyl groups of H_2O_2 and the carbonyl and amino

functions of urea.^[34] In structure **1b**, the *tert*-butyl group of TBHP shields the oxygen center to be transferred. In contrast to structure **1**, both structures **1a** and **1b** can only form a single H-bond to perrhenate (Figure 8).

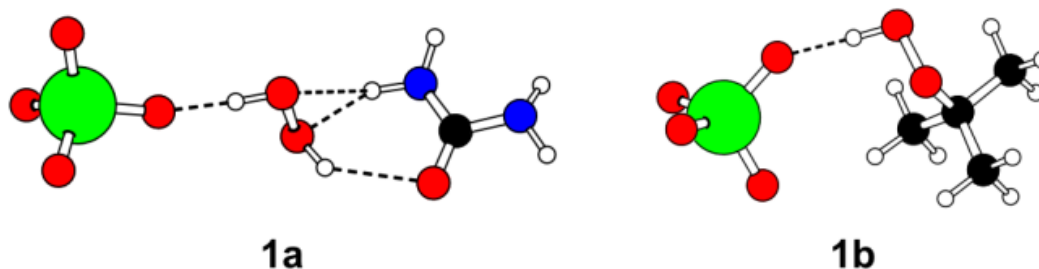


Figure 8. Encounter complexes of $[\text{ReO}_4]^-$ with UHP (**1a**) and TBHP (**1b**). Color coding of the atomic spheres: N blue, small; the rest as in Scheme 3.

According to the calculated activation barriers, relative to the corresponding ISs (**1**, **1a** or **1b**; Scheme 3, Figure 8), direct epoxidation with UHP (**7a_ts**, 173 kJ mol^{-1}) is favored over the reactions of alternative oxidants (H_2O_2 : **7_ts**, 192 kJ mol^{-1} ; TBHP: **7b_ts**, 189 kJ mol^{-1}). Thus, the electronic activation of the peroxide does not correlate with the measured trend of yields (Table 1).

Notably, the yields are affected by: 1) steric shielding of the activated center, 2) competition between the substrates, and 3) the thermodynamic driving force, in particular the activation barrier of the back reaction. Whilst the calculated free reaction energies for the overall reaction with H_2O_2 (-192 kJ mol^{-1}) and UHP (-190 kJ mol^{-1}) are similar, the reaction is far less exothermic with TBHP (-170 kJ mol^{-1}). Furthermore, the *tert*-butyl group TBHP that is coordinated to the perrhenate anion shields the oxygen center, thus (together with the slightly lower reaction free energy) rationalizing the poor yields (Table 1). Other factors may contribute to the differing activities of UHP and H_2O_2 . For instance, urea does not need to stay close to the complex of perrhenate and H_2O_2 , but may coordinate to another perrhenate ion. According to calculated energies of the H bonds between perrhenate and various substrates, urea (34 kJ mol^{-1}) binds more strongly to perrhenate than H_2O_2 (20 kJ mol^{-1}), whilst water binds weakest (8 kJ mol^{-1}). System **1** (H_2O_2) contains notable amounts of water because the oxidant is available in aqueous solution, whereas system **1a** (UHP) only incorporates urea and H_2O_2 . Thus, the epoxidation yields can be rationalized as the result of competition between forming a perrhenate complex with either urea or H_2O_2 . Notably, ammonium ions almost completely suppress the reaction (Table 3) because they form very strong H bonds with perrhenate anions (404 kJ mol^{-1}).

The cations of the IL, not accounted for in our simple models, are obviously not innocent

(Table 1). Despite its simplicity, this computational approach demonstrates the feasibility of the discussed mechanism. Clearly, more elaborate modeling of the environment that is set up by the IL will be desirable. With such more realistic modeling, the calculated activation barriers would be expected to be lower. Because the high activation barrier of 173 kJ mol^{-1} is at odds with the good observed yields (at least 50 %), the rate limiting step has been recalculated with the experimentally used substrate (cyclooctene), which is known to be more easily epoxidized than the model olefin (ethene).^[35] The resulting activation barrier of 143 kJ mol^{-1} demonstrates better agreement between the chosen computational model and the experimental data, as well as the far better reactivity of cyclooctene in comparison to ethene. Assuming a first-order reaction and a pre-exponential factor of 10^{13} s^{-1} , we estimate a barrier of about 110 kJ mol^{-1} based on the observed 50 % yield after 4 h.

2.3 Conclusion

A new synthetic concept which is based on the solvent effect of ionic liquids on polar compounds, such as perrhenate salts is presented. NMR, IR, and Raman spectroscopy, as well as by DFT studies, indicate that simple anionic metal-oxo complexes are able to activate hydrogen peroxide through hydrogen-bonding interactions, thus enabling olefin epoxidation through an outer-sphere mechanism, which does not involve the Re center. This method was shown to be very efficient, even with catalytic amounts of metal salts, which are easily separated from the product and reused without loss of activity. This reaction type opens up new possibilities for the epoxidation of olefins with compounds that are very stable, readily accessible, and cheap. These compounds have several advantages over the meanwhile commonly used, yet expensive molecular Re, Mo, Ti, and Mn compounds, which are expensive and often quite sophisticated. Further studies of this reaction system are worthwhile, particularly in view of affording longer-term stability and performance in the epoxidation of cyclooctene.

2.4 Experimental section

2.4.1 General

All syntheses and catalytic reaction were carried out in air. 1-methylimidazole, 1-bromobutyl, 1-bromooctyl, 1-bromododecyl, fluoroboric acid (50 %), hydrogen peroxide (50 % in water), *n*-hexane, acetonitrile, and ethyl acetate were purchased from Acros Organics. NaOH pellets were purchased from J. T. Baker. Cyclooctene (95 %), *tert*-butyl hydroperoxide 5.0-6.0 M

Chapter 2

solution in decane, Amberlite IRA-400 (OH), and acetone were purchased from Sigma-Aldrich. ^{17}O -enriched water (10 wt. %) was purchased from Deutero GmbH. All chemicals were used as received without further purification.

Microanalyses of the obtained products were performed in the Mikroanalytisches Labor of the Technische Universität München in Garching. ^1H , ^{13}C and ^{17}O NMR spectra were recorded in CDCl_3 with a 400-MHz Bruker Avance DPX-400 spectrometer. In-situ Mid-IR spectra were recorded with Mettler Toledo ReactIR™, ex-situ spectra were measured on a Varian IR FT670 equipped with an ATR cell (diamond crystal). Raman spectra were recorded on a Bio-Rad FTS-60A. Thermogravimetry coupled with mass spectroscopy (TG-MS) was conducted utilizing a Netzsch TG209 system; typically 10 mg of each sample were heated from 25 °C to 1000 °C at 10 K min^{-1} . Differential Scanning Calorimetry (DSC) was performed on a Q 2000 series DSC instrument, where 2 mg of each sample were heated from -100 °C to 150 °C at 10 K min^{-1} . Density was measured by an Anton Paar DMA4500 densimeter. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II.

2.4.2 Synthesis of perrhenate-based ILs

The original synthesis of the perrhenates involved a mixture of imidazolium bromide and $[\text{NH}_4][\text{ReO}_4]$ in acetone, which was stirred for 48 h at room temperature and subsequently worked up. Elemental analysis showed that a significant amount of the bromide was present in the ionic liquid after purification. Because the purity of the new ILs has a dramatic effect on the epoxidation of olefins, a new strategy was used for the synthesis of the IL perrhenates, which involved the exchange of bromide by hydroxide on an ion exchange resin and subsequent addition of $[\text{NH}_4][\text{ReO}_4]$ and stirring at 70 °C for 24 h. The only byproducts are ammonia and water, which can easily be removed in vacuo at elevated temperatures. The ionic liquids were characterized by FT-IR, Raman, ^1H -, ^{13}C -, ^{17}O -NMR spectroscopy and elemental analysis. In Addition, physical data such as density, melting point and decomposition temperature were determined. According to differential scanning calorimetry (DSC) data, the compounds $[\text{C}_4\text{mim}][\text{ReO}_4]$ and $[\text{C}_8\text{mim}][\text{ReO}_4]$ were liquid and contain a glass-transition temperature below room temperature having a glass transition temperature below room temperature. Owing to its high molecular mass, $[\text{C}_{12}\text{mim}][\text{ReO}_4]$ shows a melting point at 48 °C. Thermogravimetric analysis (TGA) data indicate that all ionic liquids show negligible volatility and high thermal stability with a decomposition onset temperature

near to 400 °C.

Equimolar amount of alkyl bromide and 1-methylimidazole (0.5 mol) were heated for 1 h at 40 °C in THF (40 ml). Afterwards, the mixture was heated at reflux for 24 h. After cooling to room temperature, a mixture of EtOAc and MeCN (40 mL, 3:1 v/v) were added and the mixture was heated at reflux for 1 h to afford the pure product after drying at 80 °C under high vacuum for 8 h.

Preparation of 3-alkyl-1-methyl imidazolium perrhenate: A solution of 3-alkyl-1-methyl imidazolium bromide (0.08 mmol) in water (10 mL) was slowly added onto the ion-exchange resin (PH 7). The product was slowly washed off the column with water until PH value of the eluent remained at 7, thus affording the desired product ($c = 0.26 \text{ mol L}^{-1}$). Subsequently, $[\text{NH}_4][\text{ReO}_4]$ (1.2 equiv) was added and the solution was heated to 70 °C for 24 h, followed by the complete removal of the residual water under reduced pressure. Excess $[\text{NH}_4][\text{ReO}_4]$ was removed by extraction of the ionic liquid with CH_2Cl_2 (30 mL) to afford the pure product after removal of the solvent under reduced pressure (98 % yield).

3-butyl-1-methyl-1H-imidazolium perrhenate

$\text{C}_8\text{H}_{15}\text{N}_2\text{O}_4\text{Re}$ (389.42), $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 8.92$ (1H, s), 7.32 (1H, d), 7.34 (1H, d), 4.30 (2H, t), 3.68 (3H, s), 1.75 (2H, q), 1.26-1.17 (2H, m), 0.79 ppm (3H, t); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 135.9, 123.6, 122.3, 49.7, 36.3, 31.7, 19.1, 13.2$ ppm; IR (ATR, diamond crystal, neat): $\nu = 900$ (Re=O asym.), 916 cm^{-1} (Re=O sym.); elemental analysis calc. (%) for $\text{C}_8\text{H}_{15}\text{N}_2\text{O}_4\text{Re}$: C, 24.67; H, 3.88; N, 7.19; O, 16.43; Re, 47.82; found: C, 25.19; H, 4.05; N, 7.29; Re, 46.50; $T_g = -76.5$ °C; $d = 1.963$; $T_d = 399$ °C.

3-octyl-1-methyl-1H-imidazolium perrhenate

$\text{C}_{12}\text{H}_{23}\text{N}_2\text{O}_4\text{Re}$ (445.53), $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 8.82$ (1H, s), 7.40 (1H, d), 7.36 (1H, d), 4.16 (2H, t), 3.95 (3H, s), 1.84 (2H, t), 1.27-1.19 (10H, m), 0.79 ppm (3H, t); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t., ppm): $\delta = 136.1, 123.9, 122.4, 50.3, 36.5, 31.6, 30.1, 28.9, 28.8, 26.2, 22.5, 13.98$ ppm; $^{17}\text{O-NMR}$ (CDCl_3 , 100 MHz, r.t.) $\delta = 564$ ppm; IR (ATR, diamond crystal, neat): $\nu = 916$ (Re=O asym.), 900 (Re=O sym.), 320 cm^{-1} (Re=O deform.) Raman (cm^{-1}): $\nu = 959$ (Re=O sym.), 908 (Re=O asym.) 331 cm^{-1} (Re=O deform.); elemental analysis calc. (%) for $\text{C}_{12}\text{H}_{23}\text{N}_2\text{O}_4\text{Re}$: C, 32.35; H, 5.20; N, 6.29; O, 14.36; Re, 41.79; found: C, 31.85; H, 5.31; N, 6.29; Re, 40.03; $M_p: 9.2$ °C; $d = 1.658$; $T_d = 380$ °C.

3-dodecyl-1-methyl-1H-imidazolium perrhenate

$\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{Re}$ (501.64): $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 8.85$ (1H, s), 7.40 (1H, d), 7.34 (1H, d), 4.21 (2H, t), 4.01 (3H, s), 1.89 (2H, t), 1.33-1.24 (18H, m), 0.86 ppm (3H, t); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 136.4, 123.9, 122.4, 50.6, 36.7, 32.0, 30.3, 29.7, 29.7,$

29.6, 29.5, 29.4, 29.1, 26.4, 22.8, 14.2 ppm; IR (ATR, diamond crystal, neat): $\nu = 900$ (Re=O asym.), 916 cm^{-1} (Re=O sym.); elemental analysis calc. (%) for $\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{Re}$: C, 38.31; H, 6.23; N, 5.58; O, 12.76; Re, 37.12; found: C, 38.19; H, 6.16; N, 5.63; Re, 36.84; M.p: $48.2\text{ }^\circ\text{C}$; $d = 1.433$; $T_d = 383\text{ }^\circ\text{C}$.

2.4.3 Preparation of the ^{17}O -labeled ILs

^{17}O -labeled water (100 μL , 10 atom %) was added to 1,3-methyl-octyl-imidazolium perrhenate (3.7 mmol) and the solution was stirred at room temperature for 16 h. Afterwards, water was removed under reduced pressure.

2.4.4 Oxidation of cyclooctene to cyclooctene oxide in ILs

The ionic liquid (1 mmol) was placed in a round bottom flask equipped with a magnetic bar, followed by the addition of substrate (1 mmol). Finally, the oxidant (2.5 mmol) was added and the reaction mixture was heated up to $70\text{ }^\circ\text{C}$ for 4 h. Afterwards, the epoxide was extracted with *n*-hexane (5 x 1 ml) and a solution of epoxide in *n*-hexane (100 μL) was mixed with 1000 μL of internal standard and measured by means of GC.

2.4.5 Computational details

All electronic structure calculations were carried out with the program package Gaussian 0336 with the hybrid DFT functional B3LYP.^[37] For the description of rhenium, we employed the MWB-60 energy-averaged Stuttgart/Dresden pseudopotential;^[38] all other atoms were represented by the 6-311+G(d,p)^[39] basis set. In general, we invoked simple models that focus on perrhenate. These models did not account for the environment provided by the ionic liquid; in particular, all effects of the 1R-3-methylimidazolium ($[\text{RMIM}]^+$) counter ions (R = butyl, octyl, or dodecyl) were neglected. This model approach assumes the environment provided by the ionic liquid (IL) will not prevent the formation of weak hydrogen (H) bonds between a perrhenate anion and peroxide (typically about 1.5 kJ mol^{-1}). These H bonds are not stable in a common organic solvent due to strong coordination of the substrate by a solvent. Such solvent effects are assumed to be absent in an IL. $[\text{RMIM}]^+$ counter ions, known as H bond donors,^[40] are not expected to participate as H bond acceptors in the reaction mechanism, e.g. the complexation and activation of peroxides, in view of their cationic character and the complete lack of lone-pair bearing atoms.^[41]

2.5 References

- [1] J. S. Wilkes, J. A. Levinsky, R. A. Wilson, C. A. Hussey, *Inorg. Chem.* **1982**, *21*, 1263.
- [2] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, *13*, 965.
- [3] Thomson ISI web of science topic search “Ionic Liquid”, September 7th **2012**
- [4] (a) J. Ranke, S. Stolte, R. Störmann, J. Arning, B. Jastorff, *Chem. Rev.* **2007**, *107*, 2183; (b) M. Matzke, S. Stolte, K. Thiele, T. Juffernholz, J. Arning, J. Ranke, U. Welz-Biermann, B. Jastorff, *Green Chem.* **2007**, *9*, 1198; (c) S. Stolte, J. Arning, U. Bottin-Weber, M. Matzke, F. Stock, K. Thiele, M. Uerdingen, U. Welz-Biermann, B. Jastorff, J. Ranke, *Green Chem.* **2006**, *8*, 621; (d) R. P. Swatowski, J. D. Holbrey, R. D. Rogers, *Green Chem.* **2003**, *5*, 361.
- [5] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.
- [6] (a) J. G. Huddleston, H. D. Willauer, R. P. Swatowski, A. E. Visser, R. D. Rogers, *Chem. Commun.* **1998**, 1765; (b) K. E. Gutowski, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2003**, *125*, 6632.
- [7] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
- [8] (a) M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chem.* **1999**, *1*, 23; (b) C. J. Adams, M. J. Earle, G. Roberts, K. R. Seddon, *Chem. Commun.* **1998**, 2097; (c) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1291.
- [9] (a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; (b) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508; (c) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459.
- [10] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.
- [11] (a) R. Sheldon, *Chem. Commun.* **2001**, 2399; (b) Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619; (c) S. Liu, J. Xiao, *J. Mol. Catal. A: Chem.* **2007**, *270*, 1.
- [12] (a) C. R. Mehnert, *Chem. Eur. J.* **2005**, *11*, 50; (b) H.-P. Steinrück, J. Libuda, P. Wasserscheid, T. Cremer, C. Kolbeck, M. Laurin, F. Maier, M. Sobota, P. S. Schulz, M. Stark, *Adv. Mater.* **2011**, *23*, 2571.
- [13] V. I. Pâulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.
- [14] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.
- [15] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
- [16] Z. Ma, J. Yu, S. Dai, *Adv. Mater.* **2010**, *22*, 261.
- [17] Z.-Z. Yang, Y.-N. Zhao, L.-N. He, *RSC Advances* **2011**, *1*, 545.

Chapter 2

- [18] (a) M. Crucianelli, R. Saladino, F. Angelis, *ChemSusChem*. **2010**, *3*, 524; (b) D. Betz, P. Altmann, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Coord. Chem. Rev.* **2011**, *255*, 1528; (c) L. Graser, D. Betz, M. Cokoja, F. E. Kühn, *Curr. Inorg. Chem.* **2011**, *1*, 166.
- [19] (a) D. Betz, A. Raith, M. Cokoja, F. E. Kühn, *ChemSusChem*. **2010**, *3*, 559; (b) D. Betz, W. A. Herrmann, F. E. Kühn, *J. Organomet. Chem.* **2009**, *694*, 3320.
- [20] (a) W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638; (b) J. Rudolph, K. L. Reddy, J. P. Chiang, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, *119*, 6189; (c) F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudanov, C. Di Valentin, N. Rösch, *Chem. Eur. J.* **1999**, *5*, 3603; (d) P. Ferreira, W.-M. Xue, E. Bencze, E. Herdtweck, F. E. Kühn, *Inorg. Chem.* **2001**, *40*, 5834; (e) M. Zhou, J. Zhao, J. Li, S. Yue, C. Bao, J. Mink, S. Zang, F. E. Kühn, *Chem. Eur. J.* **2007**, *13*, 158.
- [21] (a) A. M. Al-Ajlouni, J. H. Espenson, *J. Org. Chem.* **1996**, *61*, 3969; (b) J. H. Espenson, *Chem. Commun.* **1999**, 479; (c) M. M. Abu-Omar, P. J. Hansen, J. H. Espenson, *J. Am. Chem. Soc.* **1996**, *118*, 4966.
- [22] F. E. Kühn, A. M. Santos, I. S. Gonçalves, C. C. Romão, A. D. Lopes, *Appl. Organomet. Chem.* **2001**, *15*, 43.
- [23] Y. Wang, H. Li, S. Han, *J. Phys. Chem. B* **2006**, *110*, 24646.
- [24] L. Cammarata, S. G. Kazarin, A. P. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.
- [25] A. Mele, C. D. Tran, S. H. De Paoli Lacerda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4364.
- [26] W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem. Int. Ed.* **1993**, *32*, 1157.
- [27] H. Yao, D. E. Richardson, *J. Am. Chem. Soc.* **2000**, *122*, 3220.
- [28] M. Klöhn, A. Seduraman, P. Wu, *J. Phys. Chem. B* **2008**, *112*, 10989.
- [29] M. Klöhn, C. Stüber, A. Seduraman, P. Wu, *J. Phys. Chem. B* **2010**, *114*, 2856.
- [30] (a) P. Gisdakis, S. Antonczak, S. Köstlmeier, W. A. Herrmann, N. Rösch, *Angew. Chem. Int. Ed.* **1998**, *37*, 2211; (b) C. Di Valentin, R. Gandolfi, P. Gisdakis, N. Rösch, *J. Am. Chem. Soc.* **2001**, *123*, 2365; (c) N. Rösch, C. Valentin, I. V. Yudanov, Vol. 25 (Eds.: F. Maseras, A. Lledós), Computational modeling of homogeneous catalysis, Springer US, **2002**, pp. 289; (d) D. V. Deubel, G. Frenking, P. Gisdakis, W. A. Herrmann, N. Rösch, J. Sundermeyer, *Acc. Chem. Res.* **2004**, *37*, 645.
- [31] (a) L. A. Woodward, H. L. Roberts, *Trans. Faraday. Soc.* **1965**, *52*, 615; (b) M. R. Mohammad, W. F. Sherman, *J. Phys. C: Solid State Phys.* **1981**, *14*, 283.

Chapter 2

- [32] (a) C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197; (b) F. E. Kühn, A. M. Santos, M. Abrantes, *Chem. Rev.* **2006**, *106*, 2455.
- [33] W. A. Herrmann, J. D. G. Correia, F. E. Kühn, G. R. J. Artus, C. C. Romão, *Chem. Eur. J.* **1996**, *2*, 168.
- [34] J. A. Dobado, J. Molina, D. Portal, *J. Phys. Chem. A* **1998**, *102*, 778.
- [35] P. Altmann, M. Cokoja, F. E. Kühn, *J. Organomet. Chem.* **2012**, *701*, 51.
- [36] *Gaussian 03*, Rev. C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, **2004**.
- [37] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454.
- [38] D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.
- [39] (a) A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033; (b) P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377; (c) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639; (d) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.
- [40] K. Fumino, T. Peppel, M. Geppert-Rybczyńska, D. H. Zaitsau, J. K. Lehmann, S. P. Verevkin, M. Köckerling, R. Ludwig, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14064.
- [41] A. Aggarwal, N. L. Lancaster, A. R. Sethi, T. Welton, *Green Chem.* **2002**, *14*, 517.

3 Imidazolium perrhenate ionic liquids as efficient catalysts for the selective oxidation of sulfides to sulfones

This chapter originated from the following publication:

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3.1 Introduction

The synthesis of sulfoxides and sulfones is of interest due to their valuable applications as intermediates during the preparation of various chemically and biologically important molecules.^[1-7] The selective oxidation of sulfides is the most straightforward method for synthesis of sulfones. A plethora of procedures are available using transition-metals such as V-,^[8] Re-,^[9] Mn-,^[10] Ti-,^[11] Mo-^[12-14] and W-^[15-16] based catalysts for the preparation of sulfones in organic solvents. However, most of these procedures are not satisfactory due to high cost, difficult catalyst preparation and separation, and due to the formation of large volumes of toxic waste. Therefore, a high demand for the development of low cost, green, efficient and durable homogeneous catalysts for oxidation of sulfides to sulfones exists. In this respect, ionic liquids (ILs) are environmentally benign reaction media for reactions, separations, and manufacturing processes due to their favorable physical and chemical properties.^[17-24] In particular, metal-containing ILs may be particularly interesting candidates as reaction media or catalysts because of their special characteristics, such as easy preparation and separation, catalyst stability, solubility and reusability.^[17, 21, 25-26]

Since more than two decades, methyltrioxorhenium (MTO) has been known to be a very efficient catalyst for the oxidation of organic compounds.^[27-32] The catalyst recycling and hence reusability of the system is, however, intrinsically difficult, since both catalyst and product are soluble in the same phase. Immobilization of MTO on heterogeneous carrier materials has been proven to be difficult as well. Notorious leaching quickly leads to significant catalyst losses in almost all examined cases.^[33-34] It is known that certain other

rhenium (VII) compounds, such as acetyl perrhenate ($\text{O}_3\text{Re-OAc}$) and immobilized benzyltrioxorhenium (VII), are also displaying catalytic activities under special conditions.^[28, 35-37] Furthermore, perrhenate itself has so far only been known as a mediocre catalyst for the reaction of diols to olefins,^[38-39] but it has not been applied as catalyst or initiator in the epoxidation of olefins, unlike its Re (VII) congener MTO. These results were tempting enough to extend our investigations to design perrhenate containing ionic liquids since they might possess the advantages of both of ILs and catalyst (perrhenate). Initial work in this field has been focused on the epoxidation that imidazolium perrhenate ionic liquids (IPILs) of the general type $[\text{C}_n\text{mim}][\text{ReO}_4]$ ($\text{C}_n\text{mim} = 1\text{-C}_n\text{H}_{2n+1}\text{-3-methylimidazolium}$; $n = 2$ (**1**), 4 (**2**), 5 (**3**), 6 (**4**), 8 (**5**), 10 (**6**), 12 (**7**), see Figure 1) are very efficient reaction media for the epoxidation of simple olefins (cyclooctene, 1-octene, styrene) using aqueous hydrogen peroxide and UHP as oxidants.^[40] Due to negligible solvent-perrhenate interactions in these ILs, H_2O_2 can form hydrogen bonds with the Re-oxo ligands, which activates H_2O_2 and makes it susceptible for epoxidation. Further research, summarized in this paper, shows that IPILs can be used in catalytic amounts for the oxidation of sulfides to sulfones with hydrogen peroxide as oxidant and conventional $[\text{C}_4\text{mim}][\text{BF}_4]$ (1-butyl-3-methylimidazolium tetrafluoroborate) ionic liquid as solvent under mild conditions.

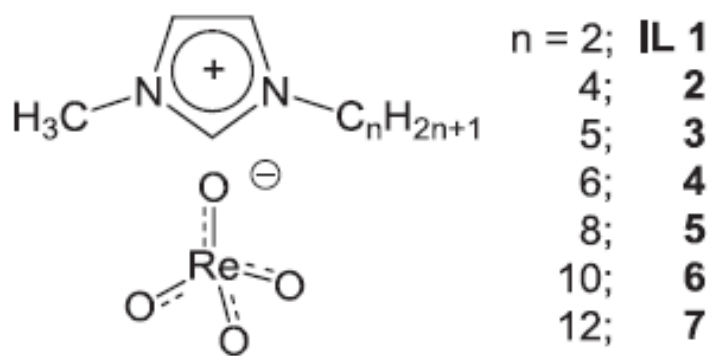


Figure 1. Imidazolium perrhenate ILs **1-7** (IPILs).

3.2 Results and discussion

3.2.1 Characterization of the IPILs

Physical data such as density, melting point and decomposition temperature were determined (see Table 1). Compounds **1-5** are liquids at room temperature and a glass transition process can be detected below room temperature according to differential scanning calorimetry (DSC) data. Compounds **6** and **7** show melting points of 38.3 and 48.3 °C, respectively. The

thermogravimetric analysis (TGA) data indicate that all compounds show negligible volatility and high thermal stability with a decomposition onset temperature near 400 °C (see Table 1).

Table 1. Physical data of ionic liquids **1-7**.

Compounds	Melting point/Glass transition temperature [°C]	Density [g / cm ³]	Decomposition temp. onset [°C]
1	-15.2	2.157	395.2
2	-76.5	1.963	399.3
3	-73.9	1.851	396.7
4	-61.1	1.794	393.9
5	9.2	1.658	380.2
6	38.3	1.527	381.3
7	48.3	1.433	383.5

3.2.2 Influence of solvent, oxidant and catalyst

We studied the catalytic properties of IPILs **2**, **5** and **7** for the oxidation of thioanisole using aqueous H₂O₂ and UHP as oxidants. For comparison, various oxidants and catalysts in different reaction media were also tested. The results are given in Table 2. Several organic solvents and ILs, such as [C₄mim][NTf₂] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), [C₄mim][HSO₄] (1-butyl-3-methylimidazolium hydrogen sulfate) and [C₄mim][PF₆] (1-butyl-3-methylimidazolium hexafluorophosphate) were applied as solvents. Oxidation of thioanisole with aqueous H₂O₂ as oxidant was found to be strongly solvent dependent. When using conventional solvents, such as *n*-hexane and toluene (Entries 1-2) the yield of sulfone is below 60 %, and the selectivity toward sulfone is less than 80 %, due to the low solubility of the catalyst in these solvents. Higher yields (> 60 %) were obtained in MeOH and the examined ILs as solvents, since the solvent/substrate/oxidant mixture is homogeneous (Entries 3-7). [C₄mim][BF₄] (1-butyl-3-methylimidazolium tetrafluoroborate) turned out to be the best solvent providing the highest yield (96 %) and the best selectivity (98 %) (Entry 4). Other ILs such as [C₄mim][NTf₂] and [C₄mim][HSO₄] exhibited also high yields (Entries 5 and 6). For sake of comparison, *tert*-butyl hydroperoxide (TBHP) and urea hydrogen peroxide (UHP) were also used as oxidants under the same conditions. The catalytic activity decreases significantly with TBHP as oxidant (Entry 10). In the case of UHP, the low solubility appears to affect the reaction negatively, leading to a low yield (Entry 9). A blank experiment without oxidant was carried out under the same conditions and no significant oxidation was observed within 24 h, indicating that the oxygen

source in the oxidation reaction was not air (Entry 8). Based on these results, H₂O₂ appears to be superior to TBHP and UHP as oxidizing agent.

Various easily available rhenium compounds, such as K[ReO₄] and [NH₄][ReO₄] have been applied as catalysts in the oxidation of thioanisole with aqueous hydrogen peroxide (Entries 12 and 13). [NH₄][ReO₄] and K[ReO₄] provide a yield of up to 93 %. Compared to [NH₄][ReO₄] and K[ReO₄], compound **2** exhibits a better performance for the oxidation of thioanisole (Entry 4) due to the better solubility in [C₄mim][BF₄]. Besides, the more lipophilic IPIs **5** and **7** were examined as catalysts for oxidation of thioanisole. The results show that increasing the carbon chain length in the imidazolium had little effect on yield and selectivity (Entries 14 and 15). Importantly, in the absence of perrhenate, the sulfone yield decreased to mere 13 %. The sulfoxide yield, however, is 86 % (Entry 11), which is in good accord with the method selectively oxidizing sulfides to sulfoxides in [C₄mim][BF₄].^[44] This result shows that the “over-oxidation” to sulfones can only be induced by perrhenate and not by BF₄. Regarding the mechanism of this reaction, it has previously been shown that [ReO₄]⁻ activates H₂O₂ *via* hydrogen bonds, facilitating the epoxidation of olefins.^[40] Analogously, the oxidation of sulfides to sulfones is assumed to take place through the same mechanism.

Table 2. Catalytic oxidation of thioanisole under different reaction conditions.^[a]

Entry	Solvent	Oxidant	Catalyst	Yield ^[b] [%]	Selectivity ^[b] [%]
1	<i>n</i> -hexane	H ₂ O ₂	2	57	58
2	Toluene	H ₂ O ₂	2	50	78
3	MeOH	H ₂ O ₂	2	62	63
4	[C ₄ mim][BF ₄]	H ₂ O ₂	2	96	98
5	[C ₄ mim][NTf ₂]	H ₂ O ₂	2	85	85
6	[C ₄ mim][HSO ₄]	H ₂ O ₂	2	92	96
7	[C ₄ mim][PF ₆]	H ₂ O ₂	2	64	66
8	[C ₄ mim][BF ₄]	---	2	---	---
9	[C ₄ mim][BF ₄]	UHP	2	44	45
10	[C ₄ mim][BF ₄]	TBHP	2	<1	<1
11	[C ₄ mim][BF ₄]	H ₂ O ₂	---	13	13
12	[C ₄ mim][BF ₄]	H ₂ O ₂	NH ₄ ReO ₄	92	93
13	[C ₄ mim][BF ₄]	H ₂ O ₂	KReO ₄	93	94
14	[C ₈ mim][BF ₄]	H ₂ O ₂	5	90	91
15	[C ₁₂ mim][BF ₄]	H ₂ O ₂	7	92	93

^[a] Reaction conditions: 10 mmol substrate, 5 mol % catalyst, 40 mmol oxidant in 2 mL solvent at 60 °C, t = 1.5 h;

^[b] Determined by GC on the crude reaction mixture using internal standard technology.

It is important to note that both the sulfides and hydrogen peroxide are completely soluble in [C₄mim][BF₄]/**2**, therefore being a more efficient and completely homogeneous oxidation system. Reactants and products are both easily removed from the reaction mixture *via* extraction with diethyl ether, which is immiscible with ILs used in this work.

3.2.3 Influence of the reaction temperature

The oxidation of thioanisole under different temperatures was investigated as well. As shown in Figure 2, a higher reaction temperature leads to an acceleration of the thioanisole oxidation. A lower temperature, however, is disadvantageous for the oxidation reaction and the yield is less than 10 % at 0 °C. Therefore, a reaction temperature of 60 °C was chosen for the further improvement of the reaction conditions.

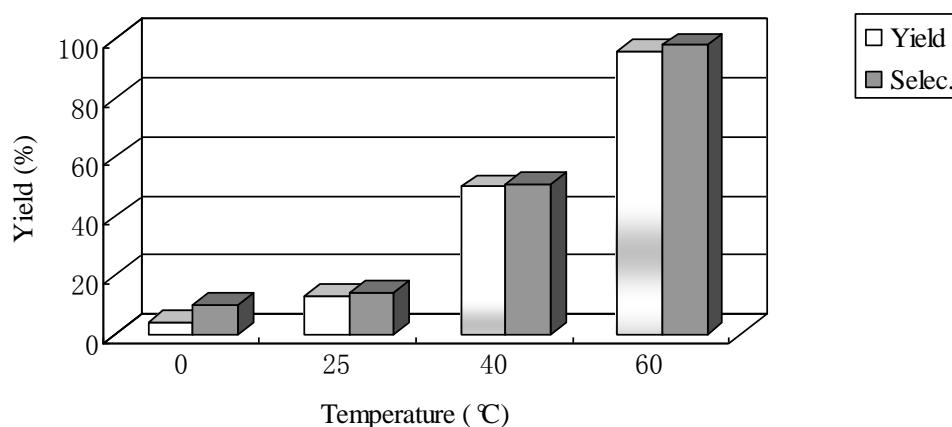


Figure 2. Catalytic oxidation of thioanisole in the $[C_4mim][BF_4]/\mathbf{2}$ system at different temperatures. Reaction condition: 10 mmol substrate, 5 mol % **2**, 40 mmol H_2O_2 (35 %) in 2 mL $[C_4mim][BF_4]$; $t = 1.5$ h.

3.2.4 Influence of the substrate/catalyst ratio

The influence of the substrate to catalyst ratio was also studied (Figure 3). The reaction led to a yield of 75 % within 90 min when a substrate to catalyst ratio of 100:1 was applied. Lowering the ratio of substrate to catalyst led to higher yields. In this case, in order to obtain the actual catalytic activity of compound **2** and complete oxidation reaction in a short period of time, 20:1 appears to be the optimal ratio.

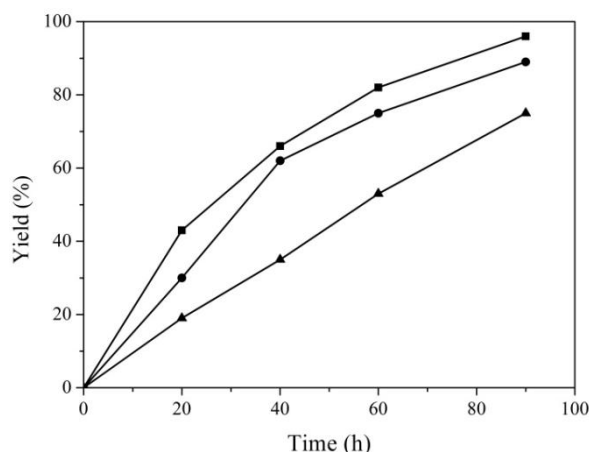
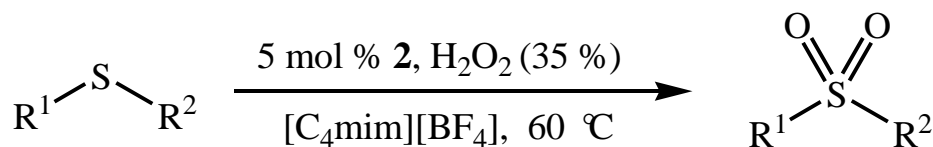


Figure 3. Reaction kinetics of thioanisole in $[\text{C}_4\text{mim}][\text{BF}_4]/\mathbf{2}$ at $60\text{ }^\circ\text{C}$ using different substrate-to-catalyst (S/C) ratios; $t = 1.5\text{ h}$. S/C:100/1 (▲), 100/3 (●), 100/5 (■).

3.2.5 Selective oxidation of different sulfides

The optimized reaction was carried out using **2** as catalyst for oxidation of sulfides to sulfones in the conventional ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ at $60\text{ }^\circ\text{C}$ (Scheme 1).



Scheme 1. Oxidation of sulfides to sulfones with H_2O_2 using $[\text{C}_4\text{mim}][\text{ReO}_4]$ (**2**) as catalyst.

To generalize the developed protocol, a wide range of sulfides with different functional groups was oxidized under the same conditions. The results are listed in Table 3 and show that sulfones can be obtained in high yields using 35 % hydrogen peroxide at $60\text{ }^\circ\text{C}$. Good catalytic activity and selectivity were obtained for all tested sulfides. Interestingly, dialkyl sulfides (Entries 8 and 14) were more easily oxidized (within 1 h) than diaryl sulfides (Entries 9-11, 15), indicating that the steric hindrance was an important factor in this reaction. For the oxidation of various phenyl-ring substituted sulfides to corresponding sulfones, the electronic nature and the position of the substituents had less effect on the yield and selectivity of the product sulfones (Entries 2-4). Furthermore, another useful feature of the presented protocol is that functional groups, such as double bonds, hydroxyl groups and esters are also tolerated and no epoxidation and aldehyde formation is observed (Entries 7, 12 and 13).

The oxidation of dibenzothiophene is of current interest because of its presence in diesel fuels. It is regarded as a possible cause of acid rain and aerosols.^[45-47] In the conventional process, hydrodesulfurization is used to remove sulfur e.g. from dibenzothiophene, a process that is far from the requirements of environmental legislations.^[48-49] Oxidation of thiophenes in fuels

followed by extraction of the sulfone products is one of the few better methods available for sulfur removal.^[50-52] In the present protocol, involving a recyclable medium and catalyst allows a relatively easy catalytic oxidation of dibenzothiophene to sulfone in a one-pot reaction with quantitative yields under mild conditions (Entry 15). This methodology could be adapted to the removal of sulfur-containing compounds from petroleum-derived fuels.

Table 3. Oxidation of sulfides to sulfones with H₂O₂ using **2** as catalyst in [C₄mim]BF₄ at 60 °C.^[a]

Entry	R ¹	R ²	Time (h)	Yield ^[b] (%)	Selectivity ^[c] (%)
1	Ph	Me	1.5	96	98
2	<i>p</i> -MePh	Me	2.5	95	96
3	<i>p</i> -BrPh	Me	2	94	97
4	<i>p</i> -OMePh	Me	2	94	97
5	Ph	Et	1.5	95	96
6	Ph	CH(CH ₃) ₂	1.5	95	96
7	Ph	CH ₂ -CH=CH ₂	4	93	97
8	n-Butyl	n-Butyl	1	96	98
9	Ph	Ph	4	83	94
10	Ph	Bz ^[d]	5.5	82	94
11	Bz	Bz	5.5	83	95
12	Ph	CH ₂ CH ₂ OH	5	87	97
13	Ph	CH ₂ COOCH ₃	6	84	95
14	Tetrahydrothiophene		1	97	99
15	Dibenzothiophene		8	56	93

^[a] Reaction conditions: 10 mmol substrate, 5 mol % catalyst **2**, 40 mmol H₂O₂ (35 %) in 2 mL [C₄mim][BF₄] at 60 °C;

^[b] Isolated yield after column chromatography;

^[c] Determined by GC or ¹H-NMR on the crude reaction mixture using internal standard technology;

^[d] Bz = benzyl.

3.2.6 Recycling of the catalyst

It is noteworthy that the system described in this work can be reused for at least ten cycles (Table 4). Ten consecutive preparations of methyl phenyl sulfone showed no significant loss in yield compared with the fresh catalyst, proving that this system had consistent activity during the recycling experiments. In addition, the catalyst is very well soluble in conventional ionic liquids, which is a very important feature for practical and efficient applications of catalytic processes.

Table 4. The recycling of [C₄mim][BF₄]/**2** in the oxidation of thioanisole.^[a]

Cycle	1	2	3	4	5	6	7	8	9	10
Conv. ^[b] [%]	99	99	99	98	98	97	97	97	98	97
Yield ^[c] [%]	96	95	96	93	94	91	90	92	93	92

^[a] Reaction conditions: 10 mmol thioanisole, 5 mol % of catalyst **2**, 40 mmol of H₂O₂ (35 %) at 60 °C;

^[b] Determined by GC on the crude reaction mixture using internal standard technology;

^[c] Isolated yields after column chromatography.

This approach is a significant improvement in comparison to the procedure reported by McKervey *et al.* using homogeneous Re(V) catalysts and UHP for oxidation of sulfides in acetonitrile, where the reaction times are considerably higher and the catalyst can not be reused.^[53] The IPILs are more efficient catalysts and recycling provides environmental benefits and economic viability.

3.3 Conclusion

A simple, efficient and green method for oxidation of sulfides to sulfones was developed using novel perrhenate-containing ionic liquids as catalysts and hydrogen peroxide as oxidant. Perrhenate has so far merely been regarded as deactivated decomposition product of MTO or related catalytically active compounds during oxidation reactions. This is very first report on the catalytic activity of perrhenate for the oxidation of sulfides with peroxides in homogeneous phase. The IPILs exhibit good catalytic abilities; a series of sulfones were obtained with high yields under mild reaction conditions. It was demonstrated that IPILs could be reused at least ten times without considerable loss of activity. The conversion and yield did not decrease on recycling and the products obtained were the desired sulfones, providing an environmentally benign chemical process with potential for industrial applications.

3.4 Experimental section

3.4.1 General

All preparations and manipulation involving air sensitive materials were performed using standard Schlenk techniques under argon atmosphere. Solvents were dried by standard procedures (Et₂O over Na/benzophenone; CH₂Cl₂ over CaH₂), distilled under argon and kept over 4 Å molecular sieves. All chemicals (purchased from Acros Organics or Aldrich) were of analytical grade and used as received. ¹H-NMR, ¹³C-NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer and chemical shifts are reported relative to the residual signal deuterated solvent. IR spectra were recorded on Varian FTIR - 670 spectrometer, using a

GladiATR accessory with a diamond ATR element. Thermogravimetry coupled with mass spectroscopy (TG-MS) was conducted utilizing a Netzsch TG209 system; typically about 10 mg of each sample were heated from 25 °C to 1000 °C at 10 K min⁻¹. Differential Scanning Calorimetry (DSC) was performed on a Q2000 series DSC instrument; typically about 2 mg of each sample were heated from -100 °C to 150 °C at 10 K min⁻¹. Density was measured by an Anton Paar DMA4500 densimeter. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Melting points were determined by MPM-H2 melting point meters. TLC was performed on silica gel 60F254 plates procured from E. Merck. Silica gel (0.06–0.2 mm 60A) was used for column chromatography. [C₄mim][BF₄], [C₄mim][NTf₂], [C₄mim][HSO₄] and [C₄mim]PF₆ were synthesized according to literature procedures.^[41-43]

3.4.2 Synthetic method and characterization data

The imidazolium perrhenates **1–7** are prepared according to a published procedure.^[40] The exchange of 1-alkyl-3-methylimidazolium bromide [C_nH_{2n+1}mim]Br (n = 2, 4, 5, 6, 8, 10, 12; mim = 3-methylimidazolium) is achieved by hydroxide *via* ion exchange resin and subsequent addition of NH₄ReO₄ and stirring at 70 °C for 24 h. The only byproducts are ammonia and water, which can easily be removed in vacuo at elevated temperatures. The ionic liquids **1–7** are characterized by FT-IR, ¹H-, ¹³C-NMR spectroscopy and elemental analysis.

1: ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.08 (1H, s, m_z-H₂), 7.75 (1H, d, m_z-H₄), 7.66 (1H, d, m_z-H₅), 4.16 (2H, q, -CH₂-), 3.85 (3H, s, N-CH₃), 1.42 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 136.74 (m_z-C₂), 124.10 (m_z-C₄), 122.48 (m_z-C₅), 44.75 (-CH₂-), 36.22 (N-CH₃), 15.61 ppm (-CH₃); IR: ν = 893 (Re=O), 863 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₆H₁₁N₂O₄Re: C 19.94, H 3.07, N 7.75; found: C 19.85, H 2.98, N 7.71.

2: ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.04 (1H, s, m_z-H₂), 7.71 (1H, d, m_z-H₄), 7.65 (1H, d, m_z-H₅), 4.17 (2H, t, -CH₂-), 3.85 (3H, s, N-CH₃), 1.80 (2H, m, -CH₂-), 1.29 (2H, m, -CH₂-), 0.89 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 137.00 (m_z-C₂), 124.11 (m_z-C₄), 122.76 (m_z-C₅), 49.17 (-CH₂-), 36.22 (N-CH₃), 31.93, 19.36 (-CH₂-), 13.77 ppm (-CH₃); IR: ν = 898 (Re=O), 863cm⁻¹ (Re=O); elemental analysis calcd (%) for C₈H₁₅N₂O₄Re: C, 24.67, H, 3.88, N, 7.19; found: C, 25.21, H, 4.12, N, 7.17.

3: ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.03 (1H, s, m_z-H₂), 7.71 (1H, d, m_z-H₄), 7.64 (1H, d, m_z-H₅), 4.13 (2H, t, -CH₂-), 3.86 (3H, s, N-CH₃), 1.81 (2H, m, -CH₂-), 1.33(4H,

m, 2-CH₂-), 0.85 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 136.99 (mz-C₂), 124.10 (mz-C₄), 122.74 (mz-C₅), 49.47 (-CH₂-), 36.21 (N-CH₃), 29.64, 28.20, 22.07 (-CH₂-), 14.20 ppm (-CH₃); IR: ν = 893 (Re=O), 858 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₉H₁₇N₂O₄Re: C, 26.79, H, 4.25, N, 6.94; found: C, 26.48, H, 4.24, N, 6.90.

4. ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.04 (1H, s, mz-H₂), 7.72 (1H, d, mz-H₄), 7.65 (1H, d, mz-H₅), 4.13 (2H, t, -CH₂-), 3.86 (3H, s, N-CH₃), 1.78 (2H, m, -CH₂-), 1.25 (6H, m, 3-CH₂-), 0.84 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 137.00 (mz-C₂), 124.11 (mz-C₄), 122.76 (mz-C₅), 49.47 (-CH₂-), 36.22 (N-CH₃), 31.11, 29.93, 25.73, 22.42 (-CH₂-), 14.31 ppm (-CH₃); IR: ν = 898 (Re=O), 849 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₁₀H₁₉N₂O₄Re: C, 28.77, H, 4.59, N, 6.71; found: C, 28.74, H, 4.69, N, 6.64;

5. ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.05 (1H, s, mz-H₂), 7.76 (1H, d, mz-H₄), 7.69 (1H, d, mz-H₅), 4.13 (2H, t, -CH₂-), 3.85 (3H, s, N-CH₃), 1.82 (2H, m, -CH₂-), 1.26 (10H, m, 5-CH₂-), 0.86 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 136.90 (mz-C₂), 124.07 (mz-C₄), 122.72 (mz-C₅), 49.26 (-CH₂-), 36.21 (N-CH₃), 31.61, 29.83, 28.92, 28.78, 25.96, 22.51 (-CH₂-), 14.39 ppm (-CH₃); IR: ν = 903 (Re=O), 858 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₁₂H₂₃N₂O₄Re: C, 32.35, H, 5.20, N, 6.29; found: C, 31.69, H, 4.92, N, 5.80.

6. ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.14 (1H, s, mz-H₂), 7.75 (1H, d, mz-H₄), 7.68 (1H, d, mz-H₅), 4.13 (2H, t, -CH₂-), 3.85 (3H, s, N-CH₃), 1.77 (2H, m, -CH₂-), 1.22 (14H, m, 7-CH₂-), 0.84 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 137.02 (mz-C₂), 124.12 (mz-C₄), 122.77 (mz-C₅), 49.43 (-CH₂-), 36.22 (N-CH₃), 31.88, 30.01, 29.50, 29.42, 29.27, 28.99, 26.11, 22.68 (-CH₂-), 14.41 ppm (-CH₃); IR: ν = 903 (Re=O), 863 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₁₄H₂₇N₂O₄Re: C, 35.51, H, 5.75, N, 5.92; found: C, 35.91, H, 5.88, N, 6.07.

7. ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 9.09 (1H, s, mz-H₂), 7.76 (1H, d, mz-H₄), 7.70 (1H, d, mz-H₅), 4.13 (2H, t, -CH₂-), 3.85 (3H, s, N-CH₃), 1.77 (2H, m, -CH₂-), 1.23 (18H, m, 9-CH₂-) 0.86 ppm (3H, t, -CH₃); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 137.01 (mz-C₂), 124.14 (mz-C₄), 122.80 (mz-C₅), 49.41 (-CH₂-), 36.27 (N-CH₃), 31.86, 29.96, 29.59, 29.57, 29.51, 29.39, 29.27, 28.95, 26.08, 22.65 (-CH₂-), 14.46 ppm (-CH₃); IR: ν = 903 (Re=O), 858 cm⁻¹ (Re=O); elemental analysis calcd. (%) for C₁₆H₃₁N₂O₄Re: C, 38.31, H, 6.23, N, 5.58; found: C, 37.93, H, 6.28, N, 5.52.

3.4.3 General procedure for the oxidation of sulfides

To a stirred solution of sulfide (10 mmol) and [C₄mim][ReO₄] (0.1952 g, 5 % mol) in [C₄mim][BF₄] (2 mL), an aqueous solution of hydrogen peroxide (35 % in water) (3.5 mL, 40 mmol) is added in 2 to 3 portions at 60 °C. The progress of the reaction is followed by TLC. The reaction mixture is extracted with diethyl ether (5 × 10 mL) and the extract is dried over anhydrous MgSO₄. The yield and selectivity of methyl phenyl sulfone are calculated from calibration curves ($r^2 > 0.999$) recorded using 3-methylanisole and 1,4-diacetylbenzene as internal standard. The crude product is obtained by rolling evaporation and purified by column chromatography separation (silica gel using hexane/ethyl acetate 90:10 v/v). The RTIL phase is diluted with CH₂Cl₂ and then treated with MnO₂ to destroy the excess peroxide. The obtained liquid is firstly dried over anhydrous MgSO₄ and then in vacuo for 4 h at 50 °C to remove CH₂Cl₂. Fresh substrate and hydrogen peroxide are then added for a new reaction cycle. All products are characterized by melting point, ¹H-NMR, ¹³C-NMR and IR spectroscopy.

Methyl phenyl sulfone: white solid, m.p.: 84–86 °C; IR: $\nu = 1283, 1143 \text{ cm}^{-1}$; ¹H-NMR (CDCl₃, 400 MHz, r.t.): $\delta = 3.07$ (s, 3H, CH₃), 7.59–7.67 (m, 3H, Ar-H), 7.95–7.97 ppm (m, 2H, Ar-H); ¹³C-NMR (CDCl₃, 100 MHz, r.t.): $\delta = 44.42$ (CH₃), 127.25, 129.38, 133.72, 140.53 ppm (Ar-C).

1-methyl-4-(methylsulfonyl)benzene: white solid; m.p.: 85–97 °C; IR: $\nu = 1286, 1144 \text{ cm}^{-1}$; ¹H-NMR (CDCl₃, 400 MHz, r.t.): $\delta = 2.46$ (s, 3H, CH₃), 3.05 (s, 3H, *p*-CH₃), 7.37–7.39 (m, 2H, Ar-H), 7.83–7.85 ppm (m, 2H, Ar-H); ¹³C-NMR (CDCl₃, 100MHz, r.t.): $\delta = 21.60$ (CH₃), 44.60 (*p*-CH₃), 127.35, 129.95, 137.73, 144.67 ppm (Ar-C).

1-bromo-4-(methylsulfonyl) benzene: white solid; m.p.: 103–105 °C; IR: $\nu = 1304, 1142 \text{ cm}^{-1}$; ¹H-NMR (CDCl₃, 400 MHz, r.t.): $\delta = 3.07$ (s, 3H, CH₃), 7.72–7.74 (m, 2H, Ar-H), 7.81–7.83 ppm (m, 2H, Ar-H); ¹³C-NMR (CDCl₃, 100 MHz, r.t.): $\delta = 44.50$ (CH₃), 128.97, 132.70, 139.58 ppm (Ar-C).

1-methoxy-4-(methylsulfonyl) benzene: white solid; m.p.: 199–212 °C; IR: $\nu = 1312, 1139 \text{ cm}^{-1}$; ¹H-NMR (CDCl₃, 400 MHz, r.t.): $\delta = 3.04$ (s, 3H, CH₃), 3.89 (s, 3H, OCH₃), 7.02–7.04 (m, 2H, Ar-H), 7.86–7.88 ppm (m, 2H, Ar-H); ¹³C-NMR (CDCl₃, 100 MHz, r.t.): $\delta = 44.84$ (CH₃), 55.71 (OCH₃), 144.50, 129.52, 132.30, 163.70 ppm (Ar-C).

Ethyl phenyl sulfone: white solid; m.p.: 38–40 °C; IR: $\nu = 1303, 1140 \text{ cm}^{-1}$; ¹H-NMR (CDCl₃, 400 MHz, r.t.): $\delta = 1.08$ –1.10 (t, 3H, CH₃), 2.93–2.98 (m, 2H, CH₂), 7.41–7.49 (m, 3H, Ar-H), 7.73–7.75 ppm (m, 2H, Ar-H); ¹³C-NMR (CDCl₃, 100 MHz, r.t.): $\delta = 7.63$ (CH₃), 50.81 (CH₂), 128.37, 129.52, 133.92, 138.92 ppm (Ar-C).

Chapter 3

Isopropyl phenyl sulfone: pale yellow liquid; IR: $\nu = 1301, 1139 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 1.08\text{--}1.10$ (d, 6H, 2 CH_3), 3.00 – 3.07 (m, 1H, CH), 7.37–7.50 (m, 3H, Ar–H), 7.69–7.71 ppm (m, 2H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 15.48$ (CH_3), 55.26 (CH), 128.76, 129.01, 133.58, 136.86 ppm (Ar–C).

Phenyl allyl sulfone: pale yellow liquid; IR: $\nu = 1306, 1141 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 3.75\text{--}3.76$ (d, 2H, CH_2), 5.05–5.10 (d, 1H, $\text{CH}=\text{CH}_2$), 5.23–5.25 (d, 1H, SO_2CH_2), 5.67–5.73 (m, 1H, SO_2CH_2), 7.47–7.58 (m, 3H, Ar–H), 7.79–7.81 ppm (m, 2H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 60.69$ (CH_2), 124.58 (CH), 124.68 (SO_2CH_2), 128.34, 129.07, 133.80, 138.25 ppm (Ar–C).

Dibutyl sulfone: white solid; m.p.: 45–47 °C; IR: $\nu = 1313, 1124 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 0.95\text{--}0.98$ (m, 6H, 2 CH_3), 1.45–1.51 (m, 4H, 2 CH_2), 1.78–1.85 (m, 4H, 2 CH_2), 2.93–2.97 ppm (t, 4H, SO_2CH_2); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 13.52$ (CH_3), 21.75 (CH_2), 23.91 (CH_2), 52.44 ppm (SO_2CH_2).

Diphenyl sulfone: white solid; m.p.: 124–126 °C; IR: $\nu = 1312, 1151 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 7.40\text{--}7.58$ (m, 6H, Ar–H), 7.96–7.98 ppm (m, 4H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 127.64, 129.28, 133.18, 141.61$ ppm (Ar–H).

Benzyl phenyl sulfone: white solid; m.p.: 149–151 °C; IR: $\nu = 1287, 1151 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 4.33$ (s, 2H, CH_2), 7.09–7.11 (m, 2H, Ar–H), 7.30–7.36 (m, 3H, Ar–H), 7.45–7.49 (m, 2H, Ar–H), 7.60–7.67 ppm (m, 3H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 62.91$ (CH_2), 128.13, 128.56, 128.63, 128.75, 128.86, 130.81, 133.68, 137.89 ppm (Ar–C).

Dibenzyl sulfone: white solid; m.p.: 150–152 °C; IR: $\nu = 1297, 1111 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 4.16$ (s, 4H, 2 CH_2), 7.40–7.46 ppm (m, 10H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 58.04$ (CH_2), 127.55, 128.99, 129.04, 130.85 ppm (Ar–C).

2-(Phenyl sulfonyl)ethanol: pale yellow liquid; IR: $\nu = 1287, 1135 \text{ cm}^{-1}$; $^1\text{H-NMR}$ ($[\text{D}_6]\text{-DMSO}$, 400 MHz, r.t.): $\delta = 3.49\text{--}3.52$ (t, 2H, CH_2), 3.76–3.79 (t, 2H, CH_2), 4.86–4.99 (t, 1H, OH), 7.61–7.73 (m, 3H, Ar–H), 7.95–7.96 ppm (m, 2H, Ar–H); $^{13}\text{C-NMR}$ ($[\text{D}_6]\text{-DMSO}$, 100 MHz, r.t.): $\delta = 55.58$ (CH_2), 58.19 (CH_2), 128.11, 129.71, 134.08, 140.4 ppm (Ar–C).

Methyl 2-(phenylsulfonyl) acetate: pale yellow liquid; IR: $\nu = 1323, 1147 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 3.53$ (s, 3H, CH_3), 4.09 (s, 2H, CH_2), 7.45–7.59 (m, 3H, Ar–H), 7.82–7.84 ppm (m, 2H, Ar–H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 52.90$ (CH_3), 60.63 (CH_2), 128.33 (COO) 129.52, 134.32, 138.68, 162.85 ppm (Ar–C).

Tetramethylene sulfone: pale yellow liquid; IR: $\nu = 1295, 1106 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 2.02\text{--}2.03$ (m, 2H, Ar-H), 2.82–2.83 ppm (m, 2H, r-H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 22.58, 51.02$ ppm (Ar-C).

Dibenzothiophene sulfone: white solid; mp: 233–235 °C; IR: $\nu = 1282, 1153 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, r.t.): $\delta = 7.53\text{--}7.57$ (m, 2H, Ar-H), 7.64–7.68 (m, 2H, Ar-H), 7.81–7.86 (m, 4H, Ar-H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, r.t.): $\delta = 121.59, 122.17, 130.18, 131.61, 133.88, 137.74$ ppm (Ar-C).

3.5 References

- [1] I. Fernández, N. Khiar, *Chem. Rev.* **2003**, *103*, 3651.
- [2] P. Kowalski, K. Mitka, K. Ossowska, Z. Kolarska, *Tetrahedron* **2005**, *61*, 1933.
- [3] K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315.
- [4] E. Baciocchi, C. Chiappe, T. D. Giacco, C. Fasciani, O. Lanzalunga, A. Lapi, B. Melai, *Org. Lett.* **2009**, *11*, 1413.
- [5] F. Liu, Z. Fu, Y. Liu, C. Lu, Y. Wu, F. Xie, Z. Ye, X. Zhou, D. Yin, *Ind. Eng. Chem. Res.* **2010**, *49*, 2533.
- [6] P. K. Khatri, S. L. Jain, B. Sain, *Ind. Eng. Chem. Res.* **2011**, *50*, 701.
- [7] V. Hulea, P. Moreau, F. D. Renzo, *J. Mol. Catal. A: Chem.* **1996**, *111*, 325.
- [8] F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, *J. Mol. Catal. A: Chem.* **2008**, *286*, 124.
- [9] S. Yamazaki, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2955.
- [10] F. Hosseinpoor, H. Golchoubian, *Tetrahedron Lett.* **2006**, *47*, 5195.
- [11] C. V. Reddy, J. G. Verkade, *J. Mol. Catal. A: Chem.* **2007**, *272*, 233.
- [12] C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. Deng, *Green Chem.* **2009**, *111*, 1401.
- [13] K. Jeyakumar, D. K. Chand, *Tetrahedron Lett.* **2006**, *47*, 4573.
- [14] N. Gharah, S. Chakraborty, A. K. Mukherjee, R. Bhattacharyya, *Inorg. Chim. Acta* **2009**, *362*, 1089.
- [15] S. X. Ying, W. J. Fa, *J. Mol. Catal. A: Chem.* **2008**, *280*, 142.
- [16] B. M. Choudary, B. Bharathi, C. V. Reddy, M. L. Kantam, *J. Chem. Soc. Perkin Trans.* **2002**, *1*, 2069.
- [17] R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834.
- [18] S. G. Lee, *Chem. Commun.* **2006**, 1049.
- [19] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.

- [20] K. X. Li, L. Chen, Z. C. Yan, H. L. Wang, *Catal. Lett.* **2010**, *139*, 151.
- [21] V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.
- [22] F. V. Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757.
- [23] P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238.
- [24] J. H. Davis Jr., *Chem. Lett.* **2004**, *33*, 1072.
- [25] C. S. Vasam, I. J. B. Lin, *J. Organomet. Chem.* **2005**, *690*, 3498.
- [26] Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619.
- [27] W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169.
- [28] C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197.
- [29] F. E. Kühn, A. M. Santos, W. A. Herrmann, *Dalton Trans.* **2005**, 2483.
- [30] F. E. Kühn, K. R. Jain, M. D. Zhou, *Rare Met.* **2006**, *25*, 411.
- [31] G. S. Owens, A. Durazo, M. M. Abu-Omar, *Chem. Eur. J.* **2002**, *8*, 3053.
- [32] G. S. Owens, M. M. Abu-Omar, *Chem. Commun.* **2000**, 1165.
- [33] K. R. Jain, F. E. Kühn, *J. Organomet. Chem.* **2007**, *692*, 5532.
- [34] D. Veljanovski, A. Sakthivel, W. A. Herrmann, F. E. Kühn, *Adv. Synth. Catal.* **2006**, *348*, 1752.
- [35] W. A. Herrmann, J. D. G. Correia, F. E. Kühn, G. R. J. Artus, C. C. Romão, *Chem. Eur. J.* **1996**, *2*, 168.
- [36] A. Sakthivel, G. Raudaschl-Sieber, F. E. Kühn, *Dalton Trans.* **2006**, 468.
- [37] D. Mandelli, M. C. A. van Vliet, U. Arnold, R. A. Sheldon, U. Schuchardt, *J. Mol. Catal. A: Chem.* **2001**, *168*, 165.
- [38] M. Shiramizu, F. D. Toste, *Angew. Chem. Int. Ed.* **2012**, *51*, 8082.
- [39] I. Ahmad, G. Chapman, K. M. Nicholas, *Organometallics* **2011**, *30*, 2810.
- [40] I. I. E. Markovits, W. A. Eger, S. Yue, M. Cokoja, C. Münchmeyer, B. Zhang, M.-D. Zhou, A. Genest, J. Mink, S. L. Zang, N. Rösch, F. E. Kühn, *Chem. Eur. J.* **2013**, *19*, 5972.
- [41] S. Park, R. J. Kazlauskas, *J. Org. Chem.* **2001**, *66*, 8395.
- [42] V. Singh, S. Kaur, V. Sapehiya, J. Singh, G. L. Kad, *Catal. Commun.* **2005**, *6*, 57.
- [43] J. Li, L. Wang, F. Shi, S. Liu, Y. He, L. Lu, X. Ma, Y. Deng, *Catal. Lett.* **2011**, *141*, 339.
- [44] B. Zhang, M. D. Zhou, M. Cokoja, J. Mink, S. L. Zang, F. E. Kühn, *RSC Adv.* **2012**, *2*, 8416.
- [45] I. V. Babich, J. A. Moulijn, *Fuel* **2003**, *82*, 607.
- [46] L. Lu, S. Cheng, J. Gao, G. Gao, M. Y. He, *Energy Fuels* **2007**, *21*, 383.

Chapter 3

- [47] H. Li, X. Jiang, W. Zhu, J. Lu, H. Shu, Y. Yan, *Ind. Eng. Chem. Res.* **2009**, *48*, 9034.
- [48] R. Shafi, G. J. Hutchings, *Catal. Today* **2000**, *59*, 423.
- [49] J. Esser, P. Wasserscheid, A. Jess, *Green Chem.* **2004**, *6*, 316.
- [50] W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He, J. Xia, *Green Chem.* **2008**, *10*, 641.
- [51] W. S. Zhu, H. M. Li, X. Jiang, Y. S. Yan, J. D. Lu, J. X. Xia, *Energy Fuels* **2007**, *21*, 2514.
- [52] H. Y. Lü, J. B. Gao, Z. X. Jiang, F. Jing, Y. X. Yang, G. Wang, C. Li, *J. Catal.* **2006**, *239*, 369.
- [53] H. Q. N. Gunaratne, M. A. Mckerverey, S. Feutren, J. Finlay, J. Boyd, *Tetrahedron Lett.* **1998**, *39*, 565.

4 Oxidation of sulfides to sulfoxides mediated by ionic liquids

This chapter originated from the following publication:

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4.1 Introduction

The oxidation of sulfides is of considerable significance for industrial chemistry. The removal of sulfur-containing compounds is an important process in fuel industry.^[1] Therefore, research efforts focus on cost-efficient liquid phase processes, such as the oxidation of sulfides, which are corrosive agents for car engines and problematic for the environment. Furthermore, the selective transformation of organic sulfides to sulfoxides is of high interest in the synthesis of fine chemicals. Sulfoxides are valuable intermediates for the construction of various fine chemicals as useful building blocks in asymmetric synthesis.^[2] Thus, there is high demand for a low cost, efficient and highly selective method for the oxidation of sulfides to sulfoxides. There are numerous reports on the oxidation of sulfides to sulfoxides using molecular V-,^[3] Re-,^[4] Fe-,^[5] Mn-,^[6] Ti-,^[7] Mo-^[8] and W-^[9] based catalysts in organic solvents. However, these catalysts bear several disadvantages: firstly, the syntheses of the catalysts are often quite demanding, which renders them expensive. Secondly, over-oxidation to sulfones can often not be prevented. Some catalyst-free oxidations of sulfides were reported before.^[10] However, these reactions are usually quite time-consuming and accompanied by destruction of functional groups.

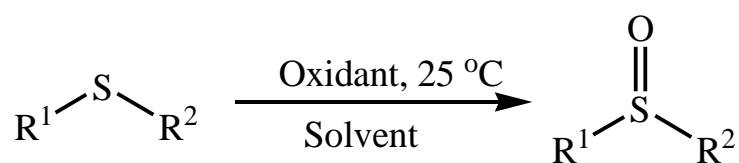
Room temperature ionic liquids (RTILs) have received much attention due to their unique properties, such as negligible volatility, broad liquid temperature ranges and the ability to dissolve a wide range of inorganic and organic compounds.^[11] In the last 10 years, RTILs were applied as alternative reaction media for a plethora of catalyzed reactions,^[12] including the oxidation of sulfides to sulfones.^[13] Previously, we and others have shown that ILs are very convenient reaction media for the epoxidation of olefins catalyzed by organometallic Re-^[14] and Mo-compounds.^[15] The catalytic activities in ILs surpass those achieved in organic solvents.^[16] More recently, we discovered that ILs may have a beneficial effect on the activation of H₂O₂ in olefin epoxidation.^[17] In this work, a novel, efficient, highly selective

and catalyst-free approach for the oxidation of sulfides to sulfoxides in ILs is reported.

4.2 Results and discussion

4.2.1 Influence of different solvents and oxidants

Thioanisole was treated in a preliminary study with various oxidants in different reaction media to elucidate optimal reaction conditions (Scheme 1). It is known that the oxidant selection is very important for the oxidation of sulfide to sulfoxide and a variety of oxidants such as KMnO_4 ,^[18] NaClO_4 ,^[19] molecular halogens,^[20] NBS ^[21] and *tert*-butyl hydroperoxide (TBHP).^[22] However, these oxidants are disadvantageous due to their low oxygen content, which not only makes product isolation difficult, but also leads to the formation of harmful byproducts. H_2O_2 is a good alternative oxidant for such a process not only due to its low cost and high oxygen content but also for being an environmental benign reagent, forming only water as byproduct. In this study, the activity of H_2O_2 for the oxidation of various sulfides using several ILs such as $[\text{Bmim}][\text{BF}_4]$ (Bmim = 1-butyl-3-methylimidazolium), $[\text{Emi}][\text{SE}]$ (1-ethyl-3-ethylimidazolium ethyl sulfate), $[\text{Bmim}][\text{HSO}_4]$ and $[\text{Dbim}][\text{BF}_4]$ (1,2-dimethyl-3-butylimidazolium) both as solvent and promoter was examined. For sake of comparison, several other reactions using organic solvents, or different oxidants such as UHP and TBHP were also examined. All these results are summarized in Table 1.



Scheme 1. Oxidation of sulfides to sulfoxides.

It is seen in Table 1 that solvent selection is very important for sulfide oxidation. A high yield can be obtained only if the H_2O_2 solution can be dissolved in the selected solvent forming a homogeneous reaction system. In the case of using *n*-hexane, toluene or CH_2Cl_2 as solvent (Entries 1-3), a clear biphasic solution was observed, leading to a low sulfoxide yield (< 30 %). Conversely, a high yield (> 65 %) can be obtained when using CH_3CN , methanol and ILs as solvent since all of them form a homogeneous phase with the H_2O_2 containing phase (Entries 5, 7, 10-12). Additionally, the polarity of the reaction medium may also be an important factor for the oxidation of sulfides. Methanol, despite very good conversion and yield, allows only quite long reaction time (18 h) and functional group decomposition

occurs.^[10b] The reaction becomes much faster when using ILs as reaction media (4 h) (Entries 7, 10-12). A high conversion (98 %) and good yield (95 %) within 4 h reaction time can be achieved in [Bmim]BF₄ as solvent (Entry 7). This is mainly because that the applied IL acts not only as a solvent but also an activator in the reaction system. A more detailed discussion of the interaction between IL and H₂O₂, will be given in the spectroscopic part. Although most ILs in Table 1 represent high conversions (> 89 %) and yields (> 80 %), [Bmim][BF₄] exhibits better stability than other ILs (such as [Bmim][HSO₄], [Emi][SE]). The oxidation of thioanisole is completed within 4 h and less than 3 % of sulfone is formed, even if the reaction time of 24 h is allowed. Therefore, [Bmim][BF₄] was selected as solvent. The oxidation behavior in the IL system was also investigated (Entries 6-9). A blank experiment without oxidant was carried out and no significant oxidation was observed within 24 h (Entry 6), indicating that the oxygen source for the synthesis of sulfoxide is not air. For different oxidants such as TBHP and UHP, very low conversions (6 % for TBHP, 13 % for UHP) and yields (5 % for TBHP, 12 % for UHP) were obtained (Entries 8, 9).

Table 1. Oxidation of thioanisole in different solvents with different oxidants at 25 °C.^a

Entry	Solvent	Oxidant	Time / h	Conv. (%) ^b	Yield (%) ^c
1	n-hexane	H ₂ O ₂	24	10	7
2	Toluene	H ₂ O ₂	24	24	21
3	CH ₂ Cl ₂	H ₂ O ₂	24	29	28
4	CH ₃ CN	H ₂ O ₂	24	72	69
5	Methanol	H ₂ O ₂	18	>99	99 ^{10b}
6	[Bmim][BF ₄]	---	24	---	---
7	[Bmim][BF ₄]	H ₂ O ₂	4	98	95
8	[Bmim][BF ₄]	UHP	24	13	12
9	[Bmim][BF ₄]	TBHP	24	6	5
10	[Dbim][BF ₄]	H ₂ O ₂	4	89	86
11	[Bmim][HSO ₄]	H ₂ O ₂	4	91	83
12	[Emi][SE]	H ₂ O ₂	4	92	80

^a Reaction conditions: 4 mL of solvent, 10 mmol of thioanisole, 20 mmol of oxidant;

^b Determined by GC-MS on the crude reaction mixture;

^c Isolated yield after column chromatography.

4.2.2 Selective oxidation of different sulfides

To generalize the developed protocol, a series of sulfides with different functional groups were selected (see Table 2) and all oxidation reactions were performed under the same conditions as Entry 7 in Table 1. Among all investigated substrates, dimethyl sulfide (Entry 6) was more easily oxidized (within 2 h) than other substrates with bulkier substituents. This indicates that the steric hindrance is an important factor for this reaction. In general, sulfides

bearing strong electron-donating alkyl and alkene groups (Entries 1, 2, 5, 6, 9 and 11) display very good yields (> 80 %). On the other hand, the oxidation of sulfides containing electron-withdrawing groups such as alcoholate (Entry 7), ester (Entry 8), acetyl (Entry 10) or less electron-donating groups (Entries 3, 4 and 12–14) lead to lower yields. Presumably, electron-donating groups increase the nucleophilicity of the sulfur atom and hence the reactivity of the substrates. Notably, neither epoxidation of the double bond of allyl phenyl sulfide (Entry 9) nor oxidation of the hydroxy group (Entry 7) was observed. Although the oxidation of diphenyl sulfide (Entries 3) requires a higher temperature compared to other aryl sulfides, the presented method still exhibits a relatively easy way to obtain diphenyl sulfoxides in a one-pot reaction. The reactivity of thioethers is affected by the nucleophilicity of the sulfur atom and the steric hindrance of the substituted groups. Higher reactivity is always obtained in the case of strong electron-donating groups and with smaller substituents.

Table 2. Oxidation of sulfides to sulfoxides with aqueous H₂O₂ in [Bmim][BF₄].^a

Entry	R ¹	R ²	Time / h	Conv. (%) ^b	Yield (%) ^c
1	Ph	Me	4	98	95
2	Ph	Et	6	98	90
3	Ph	Ph	8 ^d	79	65
4	Ph	Ph	24	81	72
5	nBu	nBu	6	90	86
6	Me	Me	2	98	96
7	Ph	CH ₂ CH ₂ OH	8	81	75
8	Ph	CH ₂ COOMe	8	78	71
9	Ph	CH ₂ -CH=CH ₂	8	83	80
10	Ph	CH ₂ OCH ₃	8	85	78
11	Ph	iPr ^e	8	91	87
12	Ph	Bz ^f	8	79	73
13	Bz	Bz	6	89	85
14	Dibenzothiophene		8 ^[d]	38	36

^a Reaction conditions: 4 mL [Bmim][BF₄], 10 mmol substrate, 20 mmol H₂O₂ at 25 °C;

^b Determined by GC-MS or ¹H NMR on the crude reaction mixture;

^c Isolated yield after column chromatography;

^d Reaction conditions: 4 mL [Bmim][BF₄], 10 mmol substrate, 20 mmol H₂O₂ at 50 °C;

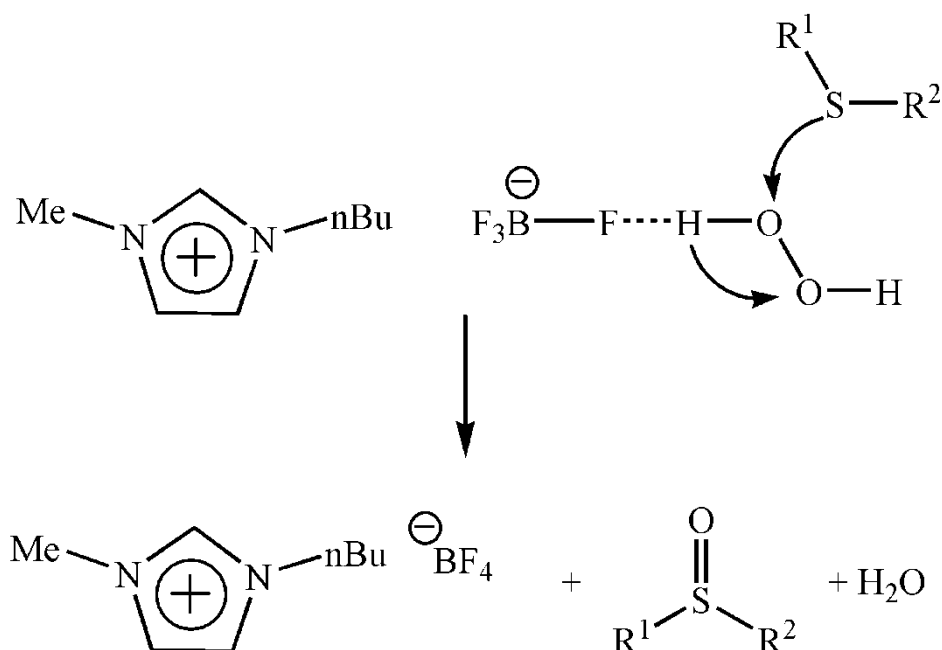
^e iPr = isopropyl;

^f Bz = benzyl.

4.2.3 Reaction mechanism

Regarding the mechanism of this reaction, the interaction between the ionic liquid and H₂O₂ appears to be crucial. Organic sulfides are oxidized by hydrogen peroxide in a heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen.^[23] This also explains the faster oxidation rate of aliphatic sulfides, which are more nucleophilic than aromatic sulfides. It may be assumed that the BF₄ anion of the ionic liquid forms a hydrogen bond with H₂O₂ and increases the electrophilic ability of a peroxide oxygen atom of H₂O₂,

and at the same time assists the leaving group H₂O in departing from the reaction intermediate (Scheme 2).^[10c] However, it is very important to exclude other possible interactions with hydrogen peroxide. A thinkable scenario would be the reaction of hydrogen peroxide with the BF₄ anion, which would generate hydrofluoric acid, or protons, respectively, which are also known to catalyze the oxidation of sulfides.^[24] Further, hypothetically, an oxygen atom could interact with the imidazolium cation. The interaction of H₂O₂ would be strongest with the hydrogen atom in the C₂ position of the imidazolium ring, since the two neighboring N atoms have a relatively strong electron withdrawing ability, rendering the C–H bond more acidic.



Scheme 2. Suggested mechanism

A number of spectroscopic examinations of the interactions between water and ionic liquids were performed to date.^[25] Lendl *et al.* found that water interacts with [BF₄][−] *via* hydrogen bonding.^[26] A similar interaction between the anion of the IL and hydrogen peroxide could be expected. IR, Raman and NMR spectroscopy are convenient tools to support this hypothesis.

Chapter 4

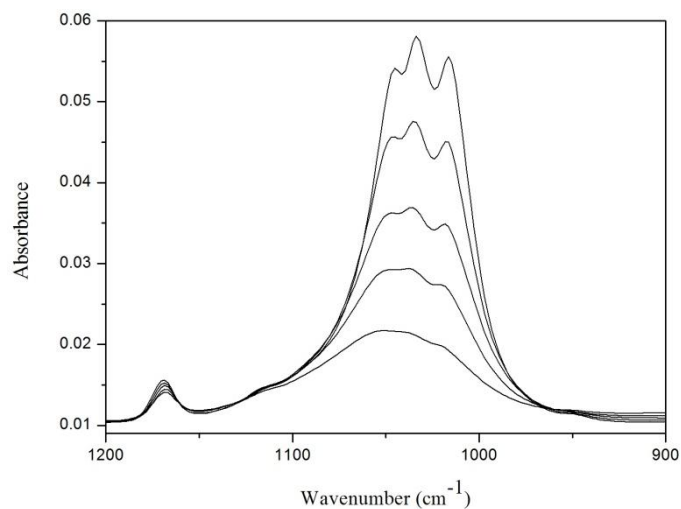


Figure 1. IR spectra in the range of 900 to 1200 cm⁻¹ for the treatment of [Bmim]BF₄ with different H₂O₂ concentrations. The lines represent the spectra for 0.23, 0.53, 1.5, 3.8, mol L⁻¹ H₂O₂ concentrations from top to bottom (the topmost line represents pure [Bmim]BF₄).

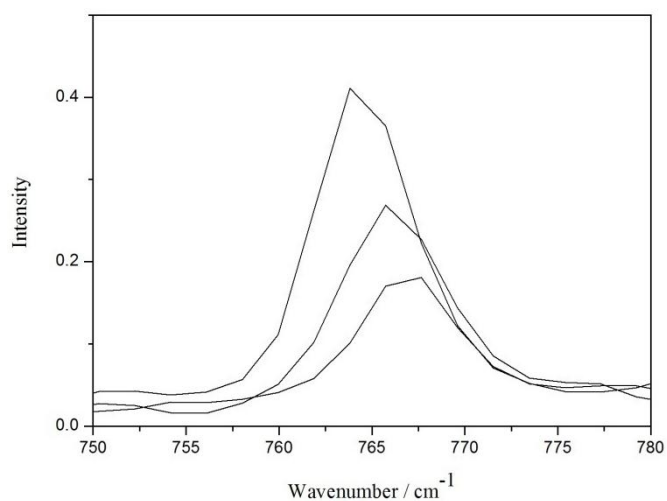


Figure 2. Raman spectra in the range of 750 to 780 cm⁻¹ for the treatment of [Bmim]BF₄ with different H₂O₂ concentrations. The lines represent spectra for 3.4 and 4.1 mol L⁻¹ H₂O₂ concentrations from top to bottom (the topmost line represents pure [Bmim]BF₄).

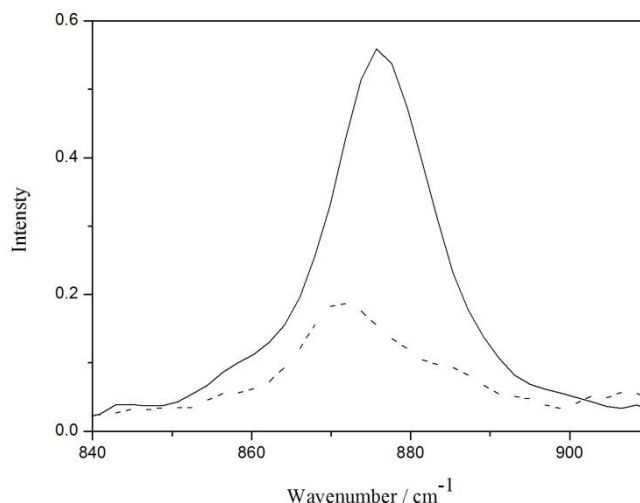


Figure 3. Raman spectra of H_2O_2 (solid curve), $[\text{Bmim}][\text{BF}_4] + \text{H}_2\text{O}_2$ (35 %) (dashed curve) in the range of 840 to 950 cm^{-1} .

In order to answer the question, which type of interaction is most likely responsible for the activation of hydrogen peroxide, we performed vibration and nuclear magnetic resonance spectroscopic studies of the ionic liquid $[\text{Bmim}][\text{BF}_4]$ before and after treatment with hydrogen peroxide. Figures 1 and 2 show the IR and Raman spectra of the B–F region of $[\text{Bmim}][\text{BF}_4]$ at different H_2O_2 concentrations. Pure $[\text{Bmim}][\text{BF}_4]$ has been examined in this range as well, bands were assigned as in previous reports.^[25i] In this study, we concentrated on BF stretching vibrations regions of 900–1200 cm^{-1} for IR and 750–780 cm^{-1} for Raman as they are representative of structural changes in H_2O_2 (35 %).

When increasing the H_2O_2 molar fraction, the symmetric BF_4 stretching band only slightly shifts to a higher wavenumber (Fig. 1). Three bands have been observed at $\sim 1045 \text{ cm}^{-1}$, $\sim 1033 \text{ cm}^{-1}$, $\sim 1016 \text{ cm}^{-1}$ for the pure ionic liquid.^[25i] The BF_4 anion displays T_d symmetry resulting in four bands. Two of these bands are polarized two are depolarized in Raman, and one band should be triplet in IR. However the three bands change into two (at $\sim 1068 \text{ cm}^{-1}$, $\sim 1025 \text{ cm}^{-1}$) after the addition of H_2O_2 , due to the interaction between H_2O_2 and the BF_4 anion. A B–F...H hydrogen bond may be assumed thus leading to a widening of the corresponding band (as compared to B–F). The original three bands have changed into two with the increasing concentration of H_2O_2 , accordingly. In the Raman spectra, the symmetric stretching mode (B–F) of the ionic liquid is shifted from $\sim 764 \text{ cm}^{-1}$ (pure form) to 767 cm^{-1} (Figure 2). This finding is matched with the IR spectra, which also gives only a minor shift on the B–F vibrational band after the addition of H_2O_2 . The O–O vibration band of H_2O_2 were also studied with Raman techniques (Figure 3). The shift difference of $\nu(\text{O–O})$ is about 5 cm^{-1} between pure H_2O_2 ($\sim 876 \text{ cm}^{-1}$) and IL + H_2O_2 ($\sim 871 \text{ cm}^{-1}$), suggesting the H_2O_2 is weakly

interacting. Furthermore, ^{11}B NMR and ^{19}F NMR were also performed to show hydrogen bonding in this system. The ^{11}B NMR spectrum showed one resonance at -1.86 ppm ($[\text{BF}_4]$). According to the isotope effect of the boron atom (^{10}B , 19.9 % and ^{11}B , 80.1 %), two singlets were observed in the ^{19}F NMR with an integral ratio of $\sim 1:4$ at -148.66 and -148.71 ppm. When adding H_2O_2 to the IL, the ^{11}B NMR resonance showed a slight shift to -2.16 ppm. The corresponding ^{19}F NMR showed signals at -150.42 and -150.47 ppm.

The spectroscopic investigations further show that the symmetry of the tetrafluoroborate anion has not changed and that no new species such as HF and BF_3 are observed, which could in principle be formed by a reaction of BF_4 with H_2O_2 . The slight shift of the BF_4 signals points to a change in the coordination sphere of the anion, such as a weak $\text{H}\dots\text{F}$ interaction, but not to the formation of BF_3 , which would lead to a significantly different peak position due to the symmetry change. On the other hand, the stretching modes of the imidazolium ring C–H groups (Raman and IR scattering contributions in the range of $3000\text{--}3500\text{ cm}^{-1}$) should be affected by this replacement. Yet, the measurements did not show appreciable changes in positions, maybe as a consequence of the difficulty of the spectral deconvolution due to the overlap between the C–H and the O–H stretching regions, especially for a high water content. To better address this issue, substitution of the C_2 proton in the imidazolium ring with a CH_3 group has been performed for oxidation of thioanisole under the same conditions, using $[\text{Dbim}][\text{BF}_4]$ as solvent for oxidation of thioanisole (Table 1, Entry 10), yielding sulfoxides in 86 %, which proves that an interaction of H_2O_2 with imidazolium protons does not take place.^[25e] However, there is no possibility to exclude a situation in which they would interact with each other because of strong electrostatic forces, when the number of “free” cations and anions reaches a certain content.^[25a] With the applied amount of aqueous H_2O_2 , the interaction between H_2O_2 and the BF_4 anion is much stronger and more stable than that between H_2O_2 and the cation.^[25e] Based on the above described experimental and spectroscopic findings and in combination with published literature,^[25e] a hydrogen bond formation between a peroxide oxygen and a BF_4 anion appears to be the crucial step during the oxidation reaction in the $[\text{Bmim}][\text{BF}_4] + \text{H}_2\text{O}_2$ (35 %) system.

4.2.4 Recycle ability of IL system

Besides the activity and selectivity, the recyclability and stability of ILs for sulfide oxidations were also investigated. ^{19}F NMR ($\delta = -148.70$ and -148.76 ppm) and ^{11}B NMR ($\delta = -1.86$ ppm) spectra of the $[\text{Bmim}][\text{BF}_4]$ were recorded after four recycling runs, confirming that the IL is stable and no structural change or decomposition took place. Furthermore, as shown in Fig.6,

no significant change of conversion, selectivity and yield were observed. The diphenyl sulfide has been oxidized using recycled [Bmim][BF₄] as solvent under the same reaction conditions (Table 2, Entry 4). The obtained yield is 68 % after 24 h, proving that this system has constant activity and stability during the recycling experiments.

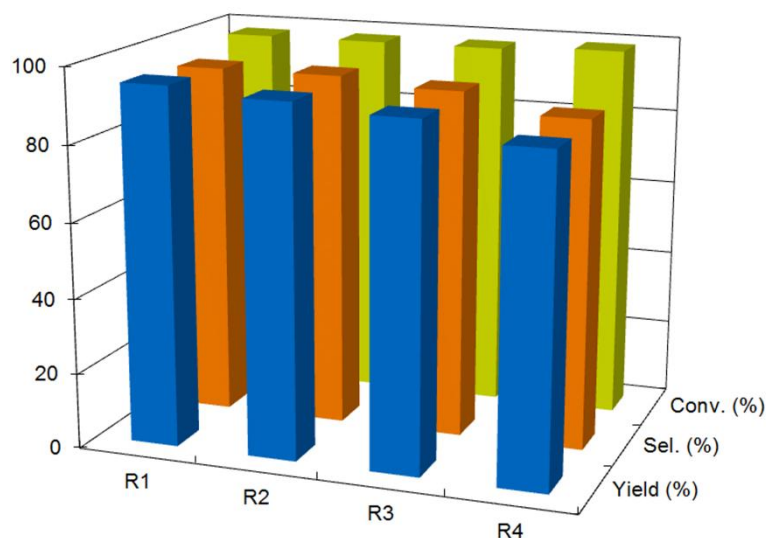


Figure 6. Oxidation of thioanisole with H₂O₂ in [Bmim][BF₄] at 25 °C after four reaction runs.

4.3 Conclusion

A selective and efficient method for the oxidation of sulfides to the corresponding sulfoxides has been developed. The sulfoxidation can be performed under mild conditions without any catalyst or additional activation reagent when hydrogen peroxide is present. The good stability of this system is supported by ¹⁹F- and ¹¹B- NMR spectroscopic results. No significant decrease of activity has been observed after four runs. According to IR, Raman and NMR examinations, the IL used in this system assists the nucleophilic attack of the sulfur atom by hydrogen bond formation between a OH group and a [BF₄]⁻ anion. High selectivity and seemingly good recyclability, as well as the absence of classical (and often quite expensive) molecular catalysts together with mild conditions make this method useful for the oxidation of sulfides to sulfoxides.

4.4 Experimental section

4.4.1 General

All reactions were performed in oven-dried glassware under an argon atmosphere using standard Schlenk techniques. All solvents were collected from purification systems and kept

over molecular sieves. ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra were recorded on a Bruker Avance DPX-400 spectromete. IR spectra were recorded on Varian FTIR-670 spectrometer, using a GladiATR accessory with a diamond ATR element. Gas chromatography-mass spectroscopy (GC-MS) analysis was performed on an Agilent 6890 instrument using a capillary column (30 m \times 0.25 mm \times 0.25 μm) with MS detector. Raman spectra were recorded on a Bio-Rad FTS-60A. Melting Pointing was measured by melting point meters MPM-H2. TLC was performed on silica gel 60F254 plates procured from E. Merck. Silica gel (0.06-0.2 mm 60A) was used for column chromatography. All chemicals were purchased from Acros and ABCR and used without further purification. [Bmim][BF₄], [Emi][SE] and [Bmim][HSO₄] were synthesized according to literature procedures.^[27-29]

4.4.2 Typical procedure for the oxidation of the sulfides in [Bmim][BF₄]

To the stirred solution of thioanisole (1.18 mL, 10 mmol) in 4 mL [Bmim][BF₄], an aqueous solution of H₂O₂ (1.75 mL, 20 mmol, 35 %) was added at room temperature forming a homogeneous reaction solution. The progress of the reaction was followed by TLC. The reaction mixture was extracted with diethyl ether (5 \times 10 mL) and the extractant was dried over anhydrous MgSO₄. The crude product was obtained by rolling evaporation and purified by column chromatography separation (silica gel using hexane/ethyl acetate 90:10 v/v). The RTIL phase was diluted with CH₂Cl₂ and treated with MnO₂ to destroy the excess peroxide and dried over anhydrous MgSO₄, filtrated, and then dried in vacuo for 4 h at 50 °C to remove CH₂Cl₂. Fresh substrate and hydrogen peroxide were then added for a new reaction cycle. All products were characterized by ^1H NMR, ^{13}C NMR and IR spectroscopy .

Methyl phenyl sulfoxide: pale yellow oil; M.p.: 30 °C, found 28-30 °C; IR (cm⁻¹): 1032vs (SO); ^1H NMR (CDCl₃, 400Hz, r.t. ppm): 2.60 (3H, s, Me), 7.39 (5H, m, Ph), 7.53 (2H, m, Ph); ^{13}C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 43.75, 123.29, 129.17, 130.81, 145.62.

Ethyl phenyl sulfoxide: yellow oil; B.p.: 284 °C; found 285-287 °C; IR (cm⁻¹): 1018vs (SO); ^1H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 1.05 (3H, t, Me), 2.73 (2H, m, CH₂), 7.37 (3H, m, Ph), 7.48 (2H, m, Ph); ^{13}C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 6.06, 50.49, 124.38, 129.33, 131.08, 143.78.

Diphenyl sulfoxide: white crystal; M.p.: 70 °C; found 70-72 °C; IR (cm⁻¹): 1034vs (SO); ^1H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 7.38 (6H, m, Ph), 7.57 (4H, m, Ph); ^{13}C NMR(CDCl₃, 100Hz, r.t. ppm): δ = 123.80, 128.31, 130.02, 144.69.

Dibutyl sulfoxide: white solid; M.p.: 31 °C; found 31-33 °C; IR (cm⁻¹): 1023vs (SO); ^1H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 0.99 (6H, t, Me), 1.49 (4H, m, CH₂), 1.85 (4H, m, CH₂),

Chapter 4

2.97 (4H, m, CH₂); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 13.53, 21.78, 23.95, 52.50.

Dimethyl sulfoxide: colorless liquid; B.p.: 189 °C, found 190-192 °C; IR (cm⁻¹): 1015vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 2.47 (6H, s, Me); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 41.30.

2-(Phenylsulfinyl)ethanol: pale yellow oil; B.p.: 362 °C, found 360-363 °C; IR (cm⁻¹): 3343s (OH), 1018vs (SO); ¹H NMR ([D₆]-DMSO, 100Hz, r.t. ppm): δ = 2.97 (1H, m, CH₂OH), 3.67 (1H, m, CH₂SO), 3.84 (1H, m, CH₂SO), 5.10 (1H, t, OH), 7.54 (3H, m, Ph), 7.62 (2H, m, Ph); ¹³C NMR ([D₆]-DMSO, 100Hz, r.t. ppm): δ = 54.32, 59.92, 123.78, 129.20, 130.65, 144.66.

Methyl 2-(phenylsulfinyl) acetate: pale yellow oil; B.p.: 341 °C, found 342-344 °C; IR (cm⁻¹): 1043vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 3.54 (3H, s, Me), 3.69 (1H, m, CH₂), 7.39 (3H, m, Ph), 7.54-7.56 (2H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 52.63, 61.34, 124.03, 129.37, 131.73, 142.92, 165.17.

Phenyl allyl sulfoxide: yellow oil; B.p.: 297 °C, found 297-300 °C; IR (cm⁻¹): 1037vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 3.45 (2H, m, CH₂), 5.11 (1H, d, CH=CH₂), 5.24 (1H, d, SOCH₂), 5.56 (1H, m, SOCH₂), 7.43 (3H, m, Ph), 7.52 (2H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 59.76, 122.85, 123.27, 124.19, 128.01, 130.06, 141.85.

Methoxymethyl phenyl sulfoxide: yellow oil; B.p.: 296 °C, found 295-298 °C; IR (cm⁻¹): 1015vs; ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 3.68 (3H, s, OMe), 4.53 (2H, s, SOCH₂), 7.60 (2H, m, Ph), 7.66 (1H, m, Ph), 7.95 (2H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 61.19, 87.78, 128.74, 129.23, 134.07, 137.39

Phenyl isopropyl sulfoxide: yellow oil; B.p.: 290 °C, found 292-294 °C; IR (cm⁻¹): 1020vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 1.05 (3H, d, Me), 1.14 (3H, d, Me), 2.75 (1H, m, SOCH), 7.41-7.44 (3H, m, Ph), 7.51 (2H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 13.82, 15.84, 54.45, 124.91, 128.83, 130.93, 141.68.

Benzyl phenyl sulfoxide: white solid; M.p.: 124-126 °C, found 123-125 °C; IR (cm⁻¹): 1027vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 4.10 (2H, m, SOCH₂), 7.02 (2H, m, Ph), 7.35 (3H, m, Ph), 7.46 (5H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 63.57, 124.47, 128.26, 128.46, 128.86, 129.13, 130.37, 131.19, 142.72.

Dibenzyl sulfoxide: white crystalline powder. M.p.: 135 °C, found 135-137 °C; IR (cm⁻¹): 1028vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 3.94 (4H, m, CH₂SOCH₂), 7.31-7.38 (4H, m, Ph), 7.43 (6H, m, Ph); ¹³C NMR (CDCl₃, 100Hz, r.t. ppm): δ = 57.18, 128.42, 128.99, 130.16, 130.86.

Dibenzothiophene oxide: off-white to pale yellow solid. M.p.: 194-196 °C, found 195-197 °C; IR (cm⁻¹): 1018vs (SO); ¹H NMR (CDCl₃, 400Hz, r.t. ppm): δ = 7.56 (m, 2H, Ph), 7.65 (2H, m,

Ph), 7.87 (2H,m, Ph), 8.03-8.05 (2H,m, Ph); ^{13}C NMR (CDCl_3 , 100Hz, r.t. ppm): δ = 120.89, 126.55, 128.55, 131.55, 136.10, 144.12.

4.5 References

- [1] I. V. Babich, J. A. Moulijn, *A. Fuel* **2003**, *82*, 607.
- [2] (a) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315. (b) F. Brebion, B. Delouvrie, F. Najera, L. Fensterbank, M. Malacria, J. Vaissermann, *Angew. Chem. Int. Ed.* **2003**, *42*, 5342; (c) M. S. Chen, M. C. White, *J. Am. Chem. Soc.* **2004**, *126*, 1346.
- [3] (a) A. V. Anisimov, E. V. Fedorova, A. Z. Lesnugin, V. M. Senyavi, L. A. Aslanov, V. B. Rybakov, A. V. Tarakanova, *Catal. Today* **2003**, *78*, 319; (b) V. Conte, F. Fabbianesi, B. Floris, P. Galloni, D. Sordi, I. W. C. E. Arends, M. Bonchio, D. Rehder, D. Bogdal, *Pure Appl. Chem.* **2009**, *81*, 1265; (c) G. P. Romanelli, D. O. Bennardi, V. Palermo, P. G. Vázquez, P. Tundo, *Lett. Org. Chem.* **2007**, *4*, 544; (d) R. Trivedi, P. Lalitha, *Synth. Commun.* **2006**, *36*, 3777.
- [4] (a) J. H. Espenson, *Chem. Commun.* **1999**, 479; (b) H. Q. N. Gunaratne, M. A. McKervey, S. Feutren, J. Finlay, J. J. Boyd, *Tetrahedron Lett.* **1998**, *39*, 5655; (c) K. J. Stanger, J. W. Wiench, M. Pruski, J. H. Espenson, G. A. Kraus, R. J. Angelici, *J. Mol. Catal. A: Chem.* **2006**, *243*, 158.
- [5] (a) J. Legros, C. Bolm, *Angew. Chem. Int. Ed.* **2003**, *42*, 5487; (b) M. Bagherzadeh, M. Amini, *Inorg. Chem. Commun.* **2009**, *12*, 21; (c) H. Egami, T. Katsuki, *J. Am. Chem. Soc.* **2007**, *129*, 8940; (d) A. Marques, M. Marin, M. F. Ruasse, *J. Org. Chem.* **2001**, *66*, 7588; (e) J. Legros, C. Bolm, *Angew. Chem. Int. Ed.* **2004**, *43*, 4225.
- [6] (a) M. Bagherzadeh, R. Latifi, L. Tahsini, M. Amini, *Catal. Commun.* **2008**, *10*, 196; (b) F. Xie, Z. Fu, H. S. Zhong, Z. P. Ye, X. P. Zhou, F. L. Liu, C. Y. Rong, L. Q. Mao, D. L. Yin, *J. Mol. Catal. A: Chem.* **2009**, *207*, 93.
- [7] M. Iwamoto, Y. Tanaka, J. Hirosumi, N. Kita, S. Triwahyono, *Microporous Mesoporous Mater.* **2001**, *48*, 271.
- [8] (a) K. Jeyakumar, D. K. Chand, *Tetrahedron Lett.* **2006**, *47*, 4573; (b) N. Gharah, S. Chakraborty, A. K. Mukherjee, R. Bhattacharyya, *Inorg. Chim. Acta* **2009**, *362*, 1089; (c) C. Yang, Q. P. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. G. Deng, *Green Chem.* **2009**, *11*, 1401.
- [9] (a) V. V. Thakur, A. Sudalai, *Tetrahedron: Asymmetry* **2003**, *14*, 407; (b) M. Ciclosi, C. Dinoi, L. Gonsalvi, M. Peruzzini, E. Manoury, R. Poli, *Organometallics* **2008**, *27*, 2281.

Chapter 4

- [10] (a) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315; (b) J. Drabowicz, M. Mikolajczyk, *Synth. Commun.* **1981**, *11*, 1025; (c) W. L. Xu, Y. Z. Li, Q. S. Zhang, H. S. Zhu, *Synthesis* **2004**, *2*, 227; (d) K. S. Ravikumar, F. Barbier, J-P. Bégué, D. Bonnet-Delpon, *J. Fluorine Chem.* **1999**, *95*, 123; (e) T. Noguchi, Y. Hirai, M. Kirihaara, *Chem. Comm.* **2008**, 3040.
- [11] (a) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508; (b) J. Tong, M. Hong, W. Guan, J. B. Li, J. Z. Yang, *J. Chem. Thermodyn.* **2006**, *38*, 1416.
- [12] (a) S. L. Jain, S. Singhal, B. Sain, *J. Organomet. Chem.* **2007**, *692*, 2930; (b) I. P. Vasile, H. Christopher, *Chem. Rev.* **2007**, *107*, 2615; (c) L. Lu, S. F. Cheng, J. B. Gao, G. H. Gao, M. Y. He, *Energy Fuels* **2007**, *21*, 383; (d) W. S. Zhu, H. M. Li, X. Jiang, Y. S. Yan, J. D. Lu, L. N. He, J. X. Xia, *Green Chem.* **2008**, *10*, 641; (e) Y. Chao, H. Li, W. Zhu, G. Zhu, Y. Yan, *Pet. Sci. Technol.* **2010**, *28*, 1242; (f) Y. Mochizuki, K. Sugawara, *Energy Fuels* **2008**, *22*, 3303; (g) S. G. Zhang, Q. L. Zhang, Z. C. Zhang, *Ind. Eng. Chem. Res.* **2004**, *43*, 614.
- [13] (a) D. Betz, P. Altmann, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Coord. Chem. Rev.* **2011**, *255*, 1518; (b) A. A. Lindén, M. Johansson, N. Hermanns, J-E. Bäckvall, *J. Org. Chem.* **2006**, *71*, 3849.
- [14] D. Betz, W. A. Herrmann, F. E. Kühn, *J. Organomet. Chem.* **2009**, *694*, 3320.
- [15] F. E. Kühn, J. Zhao, M. Abrantes, W. Sun, C. A. M. Afonso, L. C. Branco, I. S. Gonçalves, M. Pillinger, C. C. Romão, *Tetrahedron Lett.* **2005**, *46*, 47.
- [16] D. Betz, A. Raith, M. Cokoja, F. E. Kühn, *ChemSusChem.* **2010**, *3*, 559.
- [17] I. I. E. Markovits, W.A. Eger, S. Yue, M. Cokoja, C. Münchmeyer, B. Zhang, M.-D. Zhou, A. Genest, J. Mink, S. L. Zang, N. Rösch, F. E. Kühn, *Chem. Eur. J.* **2013**, *19*, 5972.
- [18] G. W. Gokel, H. M. Gerdes, D. M. Dishong, *J. Org. Chem.* **1980**, *45*, 3634.
- [19] J. M. Khurana, A. K. Panda, A. Ray, A. Gogia, *Org. Prep. Proced. Int.* **1996**, *28*, 234.
- [20] (a) G. Kar, A. K. Saikia, U. Bora, S. K. Dehury, M. K. Chaudhuri, *Tetrahedron Lett.* **2003**, *44*, 4503; (b) A. Shaabani, M. B. Teimouri, H. R. Safaei, *Synth. Commun.* **2000**, *30*, 265; (c) K. Choudhary, D. Suri, S. Kothari, K. K. Banerji, *J. Phys. Org. Chem.* **2000**, *13*, 283; (d) J. Drabowicz, W. Midura, M. Mikolajczyk, *Synthesis* **1979**, 39.
- [21] K. Surendra, N. S. Krishnaveni, V. P. Kumar, R. Sridhar, K. R. Rao, *Tetrahedron Lett.* **2005**, *46*, 4581.
- [22] P. J. Kropp, G. W. Breton, J. D. Fields, J. C. Jung, B. R. Loomis, *J. Am. Chem. Soc.* **2000**, *122*, 4280.

Chapter 4

- [23] (a) V. Hulea, P. Moreau, F. D. Renzo, *J. Mol. Catal. A: Chem.* **1996**, *111*, 325; (b) B. M. Choudary, B. Bharathi, C. V. Reddy, M. L. Kantam, *J. Chem. Soc. Perkin Trans.* **2002**, *1*, 2069;
- [24] G. Modena, L. Maioli, *Gazz. Chim. Ital.* **1957**, *87*, 1306.
- [25] (a) B. J. Sun, Q. Jin, L. S. Tan, P. Y. Wu, F. Yan, *J. Phys. Chem. B* **2008**, *112*, 14251; (b) A. Mele, C. D. Tran, S. H. de Paoli Lacerda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4364; (c) D. W. Kim, D. J. Hong, J. W. Seo, H. S. Kim, H. K. Kim, C. E. Song, D. Y. Chi, *J. Org. Chem.* **2004**, *69*, 3186; (d) Y. Jeon, J. Sung, D. Kim, C. Seo, H. Cheong, Y. Ouchi, R. Ozawa, H. Hamaguchi, *J. Phys. Chem B* **2008**, *112*, 923; (e) L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192; (f) A. Engdahl, B. Nelander, G. Karlström, *J. Phys. Chem. A* **2001**, *105*, 8393; (g) M. Pettersson, S. Tuominen, M. Räsänen, *J. Phys. Chem. A* **1997**, *101*, 1166; (h) N. E. Heimer, R. E. D. Sesto, Z. Z. Meng, J. S. Wilkes, W. R. Carper, *J. Mol. Liq.* **2006**, *124*, 84; (i) S. A. Katsyuba, E. E. Zvereva, A. Vikiš, P. J. Dyson, *J. Phys. Chem. A* **2007**, *111*, 352.
- [26] M. López-Pastor, M. J. Ayora-Cañada, M. Valcárcel, B. Lendl, *J. Phys. Chem. B* **2006**, *110*, 10896.
- [27] S. Park, R. J. Kazlauskas, *J. Org. Chem.* **2001**, *66*, 8395.
- [28] J. Z. Yang, X. M. Lu, J. S. Gui, W. G. Xu, H. W. Li, *J. Chem. Thermodynamics* **2005**, *37*, 1250.
- [29] V. Singh, S. Kaur, V. Sapehiya, J. Singh, G. L. Kad, *Catal. Commun.* **2005**, *6*, 57.

5 Synthesis and characterization of imidazolium salts with the weakly coordinating $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion

This chapter originated from the following publication:

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5.1 Introduction

Weakly coordinating anions (WCAs) have been a subject of intensive research in the past decade due to their increasing importance in coordination chemistry and catalysis.^[1-6] These applications have grown out of basic research into the special properties of anions containing hydrocarbon and fluorocarbon functionality such as $[\text{SO}_3\text{CF}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{OTeF}_5]^-$.^[7] Owing to the importance of WCAs both in fundamental and applied chemistry, a new class of WCAs has recently been developed. Robert *et al.* reported the anions $[(\text{C}_6\text{F}_5)_3\text{M-LN-M}(\text{C}_6\text{F}_5)_3]^-$, with $\text{M} = \text{B}$ or Al and the linking group LN being azide, dicyanamide, and imidazolid, which were found to be the most stable and effective activators for olefin polymerization reaction.^[8-9] $[\text{CB}_{11}\text{H}_{12}]^-$ and related carborane anions developed by Reed *et al.* were applied in many systems, despite the expensive and time consuming multistep procedures of their preparation.^[10]

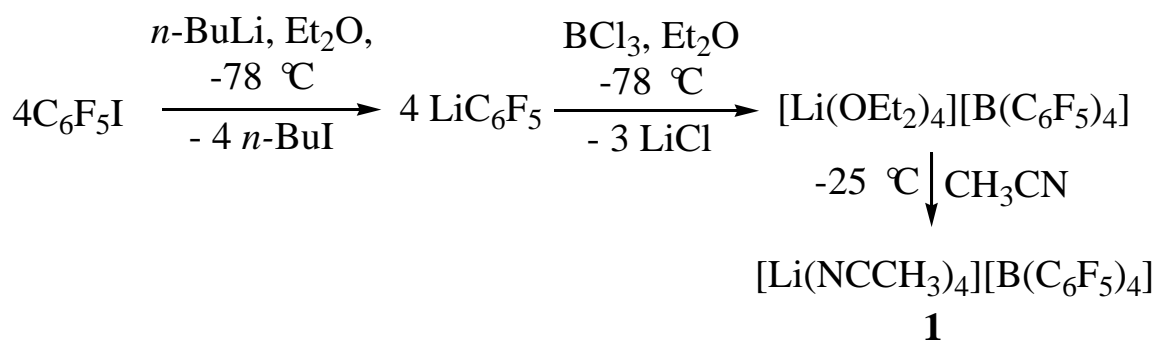
The $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, commonly abbreviated as BAr^{F} , is much more stable as compared to the other anions and frequently used as a counteranion for electrophilic cations.^[7, 11] It can be introduced by salt metathesis reaction of reagents such as $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$, which was first reported in 1963,^[12] $[\text{Mn}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{F}_5)_4]_2$,^[13] $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$,^[14] $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$,^[15] $[\text{HN}^n\text{Bu}_3][\text{B}(\text{C}_6\text{F}_5)_4]$,^[16] $[\text{B}^n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$,^[17] the superacid $[\text{C}_6\text{Me}_3\text{H}_4][\text{B}(\text{C}_6\text{F}_5)_4]$,^[18] $[\text{Cp}_2\text{Zr}(\text{CH}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$,^[19-20] $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ^[21] and $[\text{M}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{F}_5)_4]_2$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}$)^[22-23] with labile or sometimes even covalently bound halides. Recently, imidazolium-based ionic liquids (ILs) have received considerable attention in different research fields.^[24-30] The synthesis of ILs bearing $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions and organic cations such as imidazolium could represent an approach to

combine the advantages of unreactive and stabilizing WCAs and eco-friendly ILs with low vapor pressure. Since $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -based organic salts with imidazolium cations are quite rare,^[31-32] we focused on the synthesis of new ionic compounds consisting of imidazolium cations and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions *via* metathesis reactions. In this report, we present the precursors $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) and $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) as metathesis reagents for the conversion of imidazolium bromides $[\text{Bmim}]\text{Br}$ and $[\text{Dbim}]\text{Br}$ (Bmim = 1-butyl-3-methylimidazolium; Dbim = 1,2-dimethyl-3-butylimidazolium) to yield the imidazolium-based salts $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**) and $[\text{Dbim}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**) with the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion.

5.2 Results and discussion

5.2.1 Synthesis of $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$

The alkali metal salt $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared according to literature procedures,^[23] but using $\text{C}_6\text{F}_5\text{I}$ instead of $\text{C}_6\text{F}_5\text{Br}$. The reaction of 1 equiv. LiC_6F_5 with 0.25 equiv. BCl_3 in a mixture of diethyl ether and *n*-hexane at low temperatures leads to the formation of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ under precipitation of LiCl . Subsequent crystallization of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ from a concentrated solution in acetonitrile yields $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) as colorless crystals in a moderate yield of 41 % (Scheme 1).



Scheme 1. Synthesis of the precursor $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**).

Compound **1** exhibits very good solubility in polar organic solvents such as acetonitrile and diethyl ether. It is stable at room temperature and can be handled in air for a short period of time (5 min). The ^1H NMR spectrum shows one broad singlet at 1.96 ppm originating from free acetonitrile, as a consequence of a fast scrambling with CD_3CN solvent molecules. The ^{19}F NMR spectrum exhibits one broad singlet at -133.8 ppm (arising from 8 *o*-F atoms), one

triplet at -164.0 ppm (attributed to 4 *p*-F atoms) and one multiplet which can be assigned to 8 *m*-F atoms. According to elemental analysis, the number of coordinated acetonitrile molecules to the lithium cation is four (see Experimental Section). Compound **1** has further been characterized by means of IR spectroscopy. The ν_{CN} absorption band in the IR spectra is shifted from 2254 cm^{-1} for free acetonitrile to 2279 cm^{-1} for compound **1**. The higher energy vibration in the ν_{CN} region (2293 and 2306 cm^{-1} for free acetonitrile and **1**, respectively) can be assigned to combination of the symmetrical CH_3 deformation and the C-C stretch that borrows its intensity from the ν_{CN} band. These results are in good agreement with what has previously been reported for related $\text{Cu(I)}^{[33]}$ and $\text{Ag(I)}^{[21]}$ complexes.

5.2.2 Crystal structure of $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$

The molecular structure of compound **1** is presented in Figure 1. The compound crystallizes in the monoclinic space group $P2_1/n$ with one ion pair in the asymmetric unit. Both central atoms (lithium and boron) exhibit a tetrahedral coordination environment. Selected bond lengths are given in Table 1. The Li-N bond lengths (in average 2.03 Å) are longer than the Li-O bond lengths of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ described by Martin *et al.* (in average 1.95 Å),^[15] which are also listed in Table 1. According to the non-coordinating nature of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, the B-C bond lengths in **1** and $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ are similar. Since the steric demand of the “end-on” - coordinated linear acetonitrile molecules is lower than that of the “side-on” - coordinated diethyl ether molecules, the N-Li-N bond angles in **1** exhibit a broader range (103 to 122 °) than the related O-Li-O bond angles in Martin’s diethyletherate (104 to 117 °).

Table 1. Comparison of selected bond lengths (Å) and angles (deg) in **1** and $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ^[15]

Selected bond lengths _{min-max}	1	$[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ^[15]
Li-O	—	1.936(4)-1.957(4)
Li-N	2.010(3)-2.044(3)	—
B-C	1.654(2)-1.657(2)	1.651(3)-1.658(3)
Selected bond angles _{min-max}		
O-Li-O	—	104.2(2)-116.9(2)
N-Li-N	103.0(2)-121.6(2)	—
C-B-C	100.8(1)-114.5(1)	101.6(2)-114.5(2)

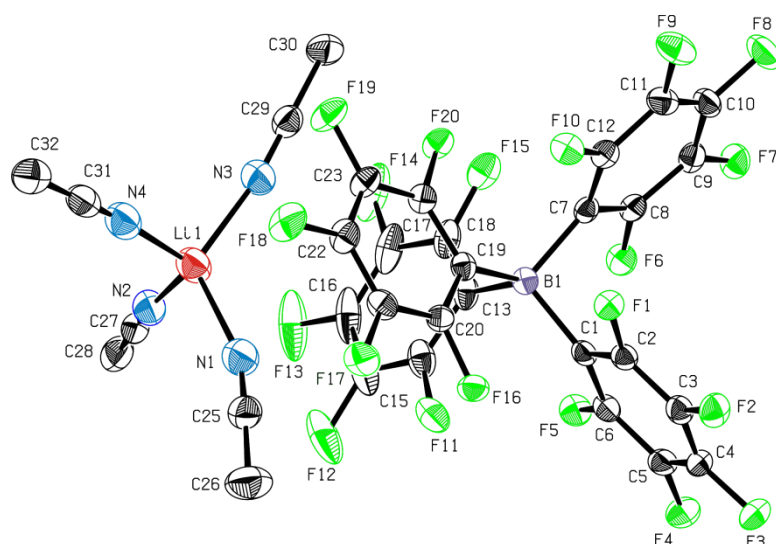
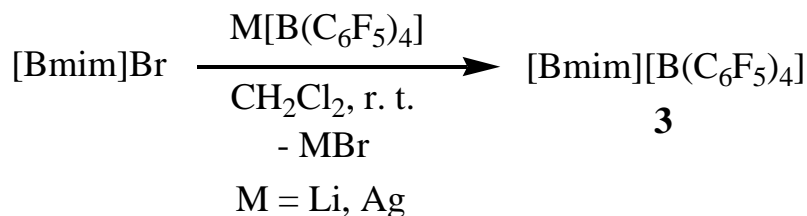


Figure 1. ORTEP view of **1** with displacement ellipsoids at the 50 % probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li1–N1 2.033(3), Li1–N2 2.041(3), Li1–N3 2.010(3), Li1–N4 2.044(3), Li1–N1–C25 160.2(2), Li1–N2–C27 169.1(2), Li1–N3–C29 169.9(2), Li1–N4–C31 175.5(2), N1–Li1–N2 104.6(2), N2–Li1–N3 103.2(2), N3–Li1–N4 105.5(2), N1–Li1–N4 103.0(2), N1–Li1–N3 121.6(2), N2–Li1–N3 103.2(2).

5.2.3 Synthesis of the new imidazolium-BAr^F compounds

In order to obtain the imidazolium salts **3** and **4**, two different starting materials, [Li(NCCH₃)₄][B(C₆F₅)₄] and [Ag(NCCH₃)₄][B(C₆F₅)₄], were used (Scheme 2). The latter was prepared according to the literature.^[21]



Scheme 2. Synthesis of [Bmim][B(C₆F₅)₄] (**3**)

The metathesis reaction of **1** with [Bmim]Br leads to the formation of **3** in a yield of 62 % within 2 h at room temperature. In order to increase the yield and reduce the reaction time, we selected [Ag(NCCH₃)₄][B(C₆F₅)₄] as precursor for the synthesis of the imidazolium-BAr^F compounds. In the metathesis reaction, silver cations were exchanged by imidazolium cations. The metathesis was performed using dry CH₂Cl₂ in the dark at room temperature. The reaction mixture was stirred for 10 min, and then filtered through siliceous earth on a Schlenk frit. The solvent was removed under high vacuum. The product was washed with dry *n*-hexane and then dried in vacuo. Typical yields of the purified product were around 89 %. In the ¹⁹F NMR spectra of compounds [Bmim][B(C₆F₅)₄] and [Dbim][B(C₆F₅)₄] the fluorine

signals are shifted about 2 ppm toward low field, compared to those of $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (Table 2), indicating that the bromide salts ($[\text{Bmim}]\text{Br}$ and $[\text{Dbim}]\text{Br}$) have reacted with $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$.

Table 2. ^{19}F NMR chemical shifts (ppm) of $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Dbim}][\text{B}(\text{C}_6\text{F}_5)_4]$ in d_6 -DMSO.

Compound	δ (^{19}F) (ppm)		
$[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$	-168.4	-164.0	-133.8
$[\text{Bmim}]\text{B}(\text{C}_6\text{F}_5)_4$	-165.6	-161.7	-131.3
$[\text{Dbim}]\text{B}(\text{C}_6\text{F}_5)_4$	-166.0	-161.5	-132.4

5.2.4 Crystal structures of imidazolium- BAR^{F} compounds

Crystals of $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Dbim}][\text{B}(\text{C}_6\text{F}_5)_4]$ suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the corresponding compounds **3** and **4** are very stable in air for a long time (at least one day) and soluble in polar organic solvents such as ether and dichloromethane. The molecular structures of **3** and **4** are presented in Figures 2 and 3. Both compounds crystallize in the monoclinic space group $P2_1/c$. The asymmetric unit consists of one anion and one $[\text{Bmim}]^+$ cation (**3**) or of two ion pairs $[\text{Dbim}]^+[\text{B}(\text{C}_6\text{F}_5)]^-$ (**4**). No significant cation...anion contacts are observed.

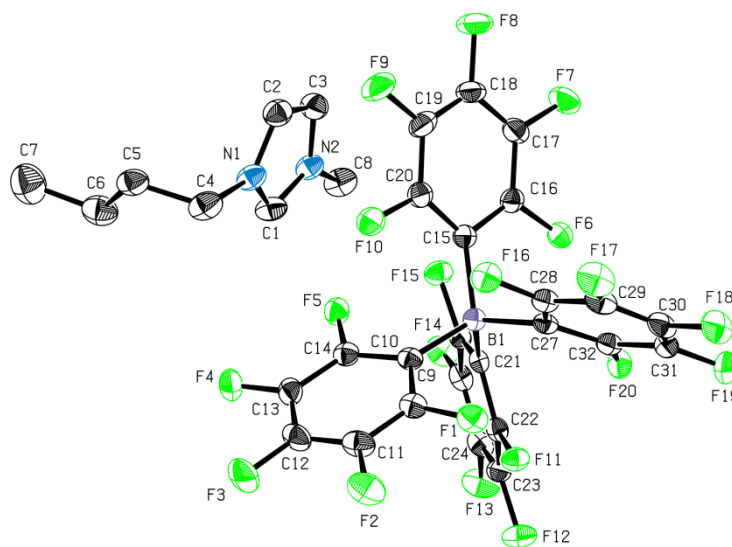


Figure 2. ORTEP view of **3** showing vibrational ellipsoids at the 50 % probability level. H atoms are omitted for clarity.

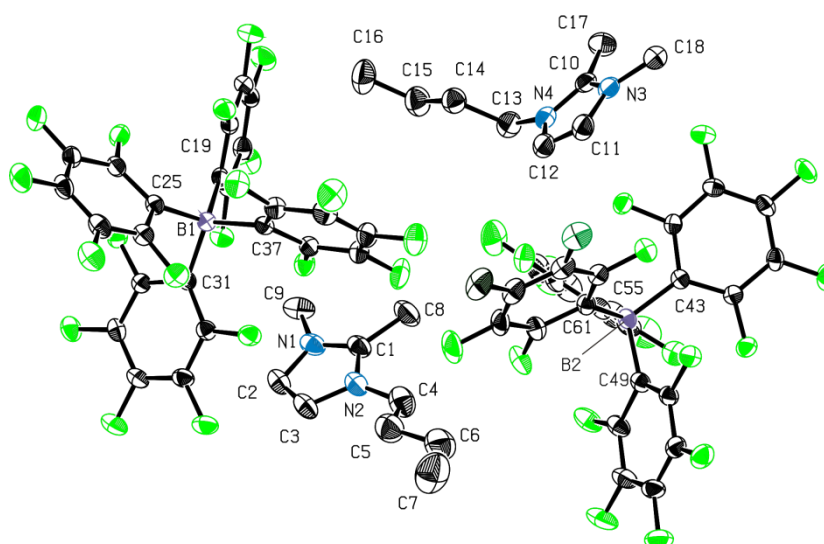


Figure 3. ORTEP view of **4** showing vibrational ellipsoids at the 30 % probability level. H atoms are omitted for clarity.

5.2.5 Thermal characterization

Samples of compounds **1**, **3** and **4** were examined by thermogravimetric analysis (TGA) in combination with online fragment detection *via* coupled mass spectroscopy (MS), applying a temperature program with a heating rate of 10 °C min⁻¹ between 30 and 1000 °C. For compound **1**, a total weight loss of about 87 % of the original mass was detected. Compound **1** shows its first decomposition onset at 135 °C and is associated with a weight loss of *ca.* 9 % of the original mass. The second and final decomposition starts at 220 °C and corresponds to a weight loss of 70 % at 400 °C. The first step originates from the loss of CH₃CN molecules as indicated by detection of CH₃⁺ and CN⁻ fragments. The second maximum in the MS curves of CH₃CN, CH₃⁺ and CN⁻ fragments is at 285 °C. Simultaneously, maxima in the MS curves of Li(CH₃CN)⁺ and C₆F₅⁺ fragments, resulting from the stepwise decomposition of the [B(C₆F₅)₄]⁻ anion, are observed at 285 °C. The ionic compounds **3** and **4** exhibit a thermal stability beyond 240 °C (245 °C for **3**, 270 °C for **4**). Furthermore, the thermal behavior of the salts was studied by differential scanning calorimetry (DSC), as shown in Figure 4. Both crystalline salts displayed a sharp melting transition on heating, and crystallized on cooling from the melt. The melting points and crystallization points of **3** and **4** are 145.0, 97.0 °C and 150.8, 70.0 °C, respectively.

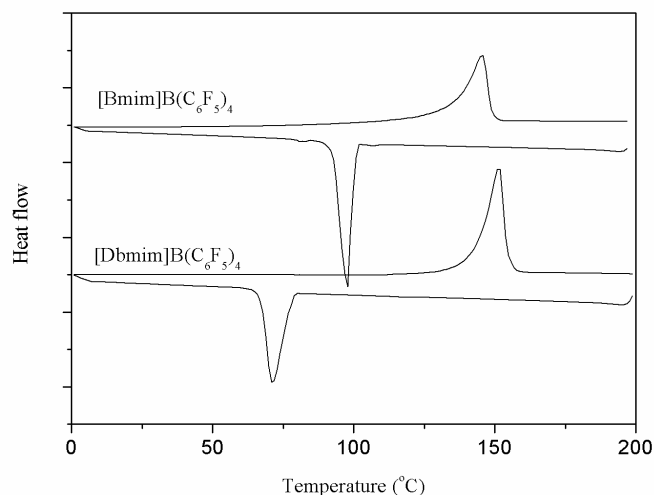


Figure 4. Characteristic DSC traces for **3** and **4** showing the characteristic melting and crystallization points.

5.3 Conclusion

In summary, the imidazolium-BAr^F compounds **3** and **4** were synthesized using two different precursors. Compounds **3** and **4** are imidazolium salts bearing the BAr^F anion characterized by X-ray single crystal structure analysis. Whereas the yield of **3** is about 62 % when using **1** as starting material (after 2 h at 25 °C), the yield increases to 89 % when **2** is employed (after 10 min at 25 °C). The crystal structure of **1** was also elucidated by single-crystal X-ray diffraction. The two new imidazolium salts **3** and **4** have decomposition temperatures (at 245 °C for **3** and at 270 °C for **4**) indicative of high thermal stability.

5.4 Experimental section

5.4.1 General

All reactions were performed in an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures (*n*-hexane and diethyl ether over Na/benzophenone; CH₂Cl₂ over CaH₂), distilled under argon and used immediately or stored over molecular sieves. ¹H, ¹¹B and ¹⁹F NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer and referenced to deuterated solvent in the case of the ¹H NMR, C₆F₆ for the ¹⁹F NMR, BF₃·OEt₂ for ¹¹B NMR respectively. IR spectra were recorded on a Varian FTIR-670 spectrometer, using a GladiATR accessory with a diamond ATR element. Elemental analyses were performed with a Flash EA 1112 series elemental analyzer. Thermogravimetric analysis in combination with online fragment detection *via* coupled mass

spectroscopy (TGA-MS) was conducted utilizing a Netzsch-STA 409 PC system. Typically, about 10 mg of each sample was heated from 30 to 1000 °C at 10 °C min⁻¹. Differential scanning calorimetric analysis (DSC) was performed on a DSCQ2000 from TA instrument (Waters) in the temperature range from 0 to 200 °C at 10 °C min⁻¹. Fast atom bombardment mass spectrometry (FAB-MS) was carried out with a Finnigan MAT 90 mass spectrometer. The compound [Ag(NCCH₃)₄][B(C₆F₅)₄] was synthesized according to the literature.^[21] All chemicals were purchased from Aldrich, Acros Organics and ABCR and used without further purification.

5.4.2 Synthetic method and characterization data

Synthesis of [Li(NCCH₃)₄][B(C₆F₅)₄] (1): A 2.5 M solution of *n*-BuLi in *n*-hexane (6.8 mL, 17 mmol) is slowly added to a mixture of C₆F₅I (5.0 g, 17 mmol) in 15 mL diethyl ether *via* syringe at -78 °C. After 1 h of stirring at -78 °C, a 1 M solution of BCl₃ in *n*-hexane (4.3 mL, 4.3 mmol) is transferred to the pale yellow reaction mixture *via* a syringe within 5 min. The resulting suspension (LiCl is precipitating immediately) is allowed to warm to room temperature. After filtration the solution is dried under vacuum to yield a sticky colorless solid that is washed several times with pentane. A concentrated solution in acetonitrile is stored at -25 °C to yield colorless crystals of **1**. The crystalline product is collected and washed with *n*-hexane. Upon drying under vacuum, 1.5 g (41 % yield, 1.8 mmol) of a colorless solid **1** is isolated. - ¹H NMR (400 MHz, CD₃CN, 298 K, ppm): δ = 1.96 (s, 12H, 4 CH₃CN); - ¹⁹F NMR (377 MHz, CD₃CN, 298 K, ppm): δ = -133.8 (s, 8F, *o*-F), -164.0 (t, 4F, *p*-F) and -168.4 (m, 8F, *m*-F); - C₃₂H₁₂BF₂₀LiN₄ (850.2): calcd. C 45.21, H 1.42, N 6.59; found C 44.21, H 1.36, N 6.22; - Selected IR: ν = 2279 (w, CN), 2306 (w) cm⁻¹.

Method 1 for the synthesis of 3 and 4: In a Schlenk tube, [Li(NCCH₃)₄][B(C₆F₅)₄] (72 mg, 90 μmol) and [Bmim]Br (20 mg, 90 μmol) are dissolved in 10 mL CH₂Cl₂. The mixture is stirred at room temperature for 2 h, and then filtered *via* a cannula. After removal of the solvent under high vacuum, the product washed with dry *n*-hexane three times and then dried in a high vacuum for 4 h.

Method 2 for the synthesis of 3 and 4: To a solution of [Ag(NCCH₃)₄][B(C₆F₅)₄] (0.738 g, 1 mmol) in CH₂Cl₂, a solution of imidazolium bromide ([Bmim]Br: 0.218 g, 1 mmol; [Dbim]Br: 0.223 g, 1 mmol) in CH₂Cl₂ is added at room temperature and the mixture stirred for 10 min under exclusion of light, where upon a colorless precipitate forms. The solution is filtered *via* a cannula and the solvent removed in vacuo. The product is washed with dry *n*-hexane three times and then dried in a high vacuum for 4 h.

[Bmim][B(C₆F₅)₄]: 0.73 g (89 %); - ¹H NMR (400 MHz, [D₆]DMSO, 296 K, ppm): δ = 0.89 (t, 3H, CH₂CH₃), 1.25 (m, 2H, CH₂), 1.76 (m, 2H, CH₂), 3.85 (s, 3H, NCH₃), 4.16 (t, 2H, NCH₂), 7.71 (m, 1H, NCH), 7.77 (m, 1H, NCH), 9.12 (s, 1H, NCHN); - ¹⁹F NMR (377 MHz, [D₆]DMSO, 296 K, ppm): δ = -165.6 (m, 8F, *m*-F), -161.7 (t, 4F, *p*-F), -131.3 (s, 8F, *o*-F); - ¹¹B NMR (128 MHz, [D₆]DMSO, 296 K, ppm): δ = -16.7 (s); - C₃₂H₁₄N₂BF₂₀ (818.3): calcd. C 46.91, H 1.97, N 3.42; found C 46.25, H 2.10, N 3.87; - IR: ν = 480 (w), 573 (w), 660 (m), 683 (m), 739 (m), 772 (m), 974 (vs), 1082 (vs), 1272 (m), 1373 (w), 1486 (vs), 1513 (s), 1642 (m), 1953 (w), 2159 (w), 2545 (vw) cm⁻¹; - FAB-MS: m/z (%) = 138.8 ([Bmim]⁺), 678.8 ([B(C₆F₅)₄]⁻).

[Dbim]B(C₆F₅)₄: 0.76 g (92 %); - ¹H NMR (400 MHz, [D₆]DMSO, 296 K, ppm): δ = 0.89 (t, 3H, CH₂CH₃), 1.27 (m, 2H, CH₂), 1.68 (m, 2H, CH₂), 2.58 (s, 3H, NCH₃), 3.75 (s, 3H, NC(CH₃)N), 4.11 (t, 2H, NCH₂), 7.61 (m, 1H, NCH), 7.64 (m, 1H, NCH); - ¹⁹F NMR (377 MHz, [D₆]DMSO, 296 K, ppm): δ = -166.0 (m, 8F, *m*-F), -161.5 (t, 4F, *p*-F), -132.4 (s, 8F, *o*-F); - ¹¹B NMR (128 MHz, [D₆]DMSO, 296 K, ppm): δ = -16.8 (s); - C₃₃H₁₇N₂BF₂₀ (832.3): calcd. C 47.56, H 2.18, N 3.36; found C 46.63, H 2.48, N 3.89; - IR: ν = 477 (vw), 573 (w), 621 (w), 659 (m), 683 (w), 830 (m), 975 (vs), 1081 (s), 1163 (m), 1274 (m), 1374 (w), 1458 (vs), 1512 (s), 1567 (w), 1592 (w), 1642 (m), 1957 (m), 2158 (m), 2547 (w) cm⁻¹; - FAB-MS: m/z (%) = 152.9 ([Dbim]⁺), 678.8 ([B(C₆F₅)₄]⁻).

5.4.3 Single-crystal X-ray structure determination

Intensity data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ -CCD), a rotating anode (Bruker AXS, FR591) or a fine-focus sealed tube with MoK α radiation (λ = 0.71073 Å), and a graphite monochromator using the SMART software package.^[34] The measurements were performed on single crystals coated with Paratone oil and mounted on glass capillaries. Each crystal was frozen under a stream of nitrogen. A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.^[35] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^[36] Space group assignments were based upon systematic absences and successful refinement of the structures. The structures were solved using the Bruker APEX suite of programs^[37] and were refined against all data using SHELXLE-97^[38] in conjunction with SHELXLE.^[39] Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic displacement parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned

Chapter 5

otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.^[40] Images of the crystal structures were generated by PLATON.^[41] Details are summarized in Table 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-889186 (**1**), -889187 (**3**) and -889188 (**4**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Single crystal X-ray structure determination of complexes

Table 3. Crystallographic details of **1**, **3** and **4**.

	1	3	4
Formula	C ₃₂ H ₁₂ BF ₂₀ LiN ₄	C ₃₂ H ₁₅ BF ₂₀ N ₂	C ₃₃ H ₁₇ BF ₂₀ N ₂
M_r	850.21	818.27	832.30
Cryst. size, mm ³	0.45×0.62×0.74	0.36×0.54×0.65	0.18×0.22×0.72
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.4260(5)	18.53177(5)	32.4863(10)
<i>b</i> , Å	16.3172(7)	11.0850(3)	11.0613(3)
<i>c</i> , Å	19.1740(9)	17.8002(5)	18.7999(6)
β , deg	106.537(2)	104.890(2)	105.476(2)
<i>V</i> , Å ³	3426.9(3)	3533.81(17)	6510.6(3)
<i>Z</i>	4	4	8
D_{calcd} , g cm ⁻³	1.65	1.54	1.70
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.2	0.2	0.2
<i>F</i> (000), e	1680	1624	3312
<i>hkl</i> range	±13, ±19, ±23	±22, ±13, ±21	±39, ±13, ±22
$((\sin\theta)/\lambda)_{\text{max}}$, Å ⁻¹	0.604	0.603	0.603
Refl. measured	78515	70191	202926
Refl. unique	6347	6486	11919
R_{int}	0.021	0.022	0.037
Param. refined	526	500	1015
$R(F)/wR(F^2)^a$ (all refls.)	0.0312/0.0788	0.0356/0.0847	0.0468/0.1061
GoF (F^2) ^b	0.93	1.04	1.02
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.28 / -0.21	0.31 / -0.19	0.46 / -0.28

^a $R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, $wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^b GoF = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$

5.5 References

- [1] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.
- [2] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169.
- [3] M. Bochmann, *Acc. Chem. Res.* **2010**, *43*, 1267.
- [4] Y. Li, M. Cokoja, F. E. Kühn, *Coord. Chem. Rev.* **2011**, *255*, 1541.
- [5] T. D. Shaffer, J. R. Ashbaugh, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3775.
- [6] K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1025.
- [7] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133.
- [8] R. E. LaPointe, G. R. Roof, K. A. Abboud, J. Klosin, *J. Am. Chem. Soc.* **2000**, *122*, 9560.
- [9] S. J. Lancaster, D. A. Walker, M. Thornton-Pett, M. Bochman, *Chem. Commun.* **1999**, 1533.
- [10] K. Shelly, C. A. Reed, Y. J. Lee, W. R. J. Scheidt, *J. Am. Chem. Soc.* **1986**, *108*, 3117.
- [11] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325.
- [12] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212.
- [13] M. Vierle, Y. Zhang, A. M. Santos, K. Köhler, C. Häfner, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F. E. Kühn, *Chem. Eur. J.* **2004**, *10*, 6323.
- [14] P. Jutzi, C. Müller, A. Stammler, H. G. Stammler, *Organometallics* **2000**, *19*, 1442.
- [15] E. Martin, D. L. Hughes, S. J. Lancaster, *Inorg. Chim. Acta* **2010**, *363*, 275.
- [16] X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840.
- [17] F. Schödel, H.-W. Lerner, M. B. Roig, M. Bolte, *Acta Crystallogr.* **2006**, *E62*, 372.
- [18] C. A. Reed, N. L. P. Fackler, K. C. Kim, D. Stasko, D. Evans, P. D. W. Boyd, C. E. F. Rickard, *J. Am. Chem. Soc.* **1999**, *121*, 6314.
- [19] W. E. Piers, T. Chivers. *Chem. Soc. Rev.* **1997**, *26*, 345.
- [20] X. Wang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840.
- [21] Y. Zhang, A. M. Santos, E. Herdtweck, J. Mink, F. E. Kühn, *New J. Chem.* **2005**, *29*, 366.
- [22] A. K. Hijazi, A. A. Hmaideen, S. Syukri, N. Radhakrishnan, E. Herdtweck, B. Voit, F. E. Kühn, *Eur. J. Inorg. Chem.* **2008**, 2892.
- [23] Y. Li, L. T. Voon, H. Y. Yeong, A. K. Hijazi, N. Radhakrishnan, K. Köhler, B. Voit, O. Nuyken, F. E. Kühn, *Chem. Eur. J.* **2008**, *14*, 7997.
- [24] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
- [25] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508.
- [26] T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459.
- [27] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.
- [28] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.

Chapter 5

- [29] V. L. Parvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.
- [30] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.
- [31] P. A. Chase, A. L. Gille, T. M. Gilbert, D. W. Stephan, *Dalton Trans.* **2009**, 7179.
- [32] C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, J. F. Brennecke, *J. Chem. Eng. Data* **2004**, *49*, 954.
- [33] H. C. Liang, E. Kim, C. D. Incarvito, A. L. Rheingold, K. D. Karlin, *Inorg. Chem.* **2002**, *41*, 2209.
- [34] SMART (version 7.56a), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.
- [35] SAINT (version 4.15), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.
- [36] G. M. Sheldrick, SADABS (VERSION 2008/1). Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2008**.
- [37] APEX 2 suite of crystallographic software (version 2008.4), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.
- [38] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**, *Acta Crystallogr.* **2008**, *A46*, 112.
- [39] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, SHELXLE, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.
- [40] A. J. C. Wilson (Ed.), International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Kluwer Academic Publishers, Dordrecht, **1992**.
- [41] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2010**. See also: A. L. Spek, *J. Appl. Crystallogr.* **2009**, *D65*, 148.

6 Ionic liquids with weakly coordinating anions: synthesis, properties and application

This chapter contains unpublished results

6.1 Introduction

One of the growing awareness of environmental issues in the 21st century has focused attention on the need for greener and more sustainable ionic liquids (ILs) technologies in chemical industry.^[1] ILs make a unique designed platform on which, it is possible to explore different functional attributes in the corresponding cationic and anionic components for different purposes,^[2] while retaining the core desirable features of the IL state of matter.^[3] It is not surprising that ILs have tremendous applications in a variety of chemical processes and play an important role in green and sustainable chemistry.^[4]

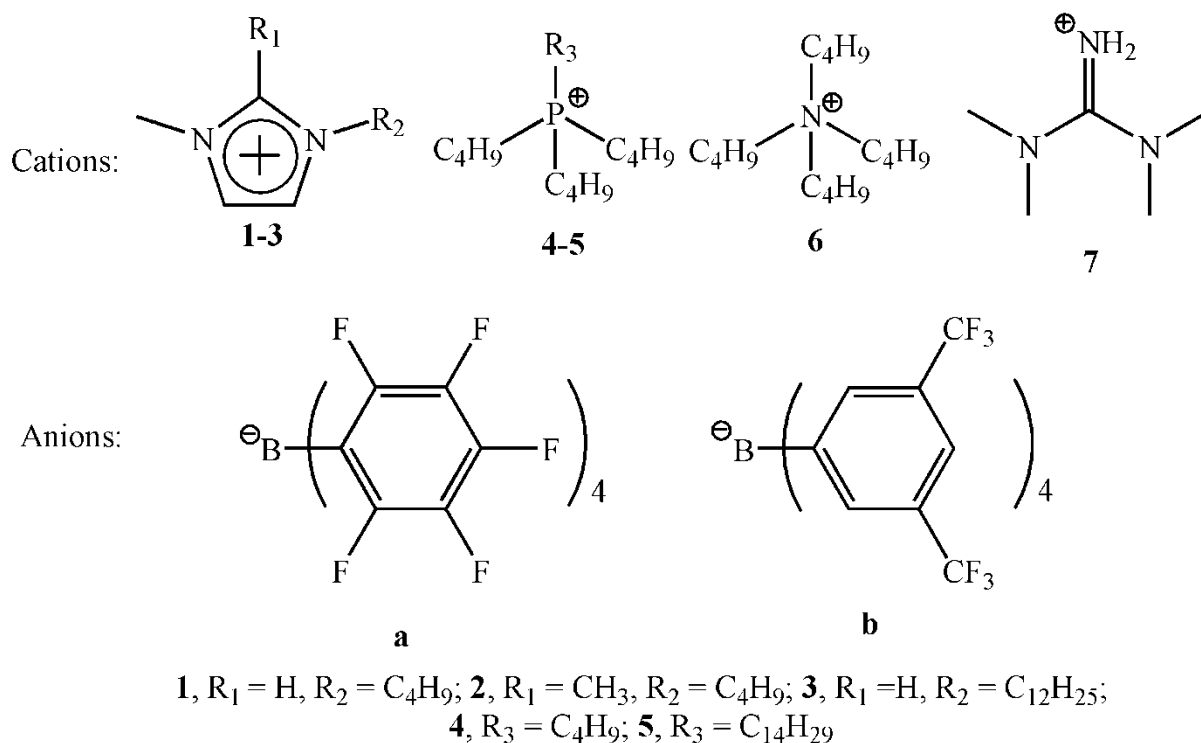
The physical properties of ILs are connected to many physical observables, but the weaker anion-cation interactions and the size of the ions as measured by the molecular volume V_m probably lead to lower melting salts with lower viscosities and higher conductivities.^[5] The strength of these anion-cation interactions is correlated to some extent with the coordination ability and Lewis basicity of the anion.^[6] In this case, weakly coordinating anions (WCAs) are good candidates for the synthesis of ILs.^[7] In general, traditional ILs usually use WCAs such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{AlCl}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$ with imidazolium or pyridinium cation.^[1-2] Recently, a new class ionic liquids with weakly coordinating anions (ILWCAs) have been developed. For example, ILs with $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ($\text{R}^{\text{F}} = \text{C}(\text{Ph})(\text{CF}_3)_2$, $\text{C}(\text{CF}_3)_3$, $\text{C}(\text{H})(\text{CF}_3)_2$, $\text{C}(\text{CH}_3)(\text{CF}_3)_2$)-imidazolium melts for electrochemical applications were discovered and $[\text{Al}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4]^-$ was used for hydrovinylation reaction and had been confirmed to be the most effective in enhancing the conversion.^[8] Matsumoto prepared and characterized low melting and low viscous ILs with perfluoroalkyltrifluoroborates.^[9] A comprehensive examination of ILs based on carborane^[10] or azolate^[11] anions were also developed. However, in terms of anion stability, it was shown that the $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$, $-\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2$) were much more stable than above anions,^[6, 12] which promoted their use in many different research fields.^[13] It is known that $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ were shown to stabilize reactive cations since they have been discovered in our group.^[14] For instance, the complex $[\text{Ag}(\text{MeCN})_4][\text{B}(\text{Ar}^{\text{F}})_4]$

exhibited catalytic activity in coupling reactions of terminal alkynes with aldehydes and amines.^[15] The complexes $[M(\text{MeCN})_6][\text{B}(\text{Ar}^{\text{F}})_4]_2$ ($M = \text{Mn}^{2+}, \text{Cu}^{2+}, \text{Ar}^{\text{F}} = \text{C}_6\text{F}_5, -\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2$; $M = \text{Cr}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$) can be used as initiators for the polymerization of 2-methylpropene yielding polyisobutylenes at moderate temperatures.^[16] Moreover, $[\text{Mn}(\text{MeCN})_6][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]_2$ served for the synthesis of paramagnetic solids.^[17] Owing to the importance of WCAs catalysis application and green chemistry, we focused our study on ILs with $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5, -\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2$) as the anions, probably representing an approach to combine the advantages of stabilizing WCAs and eco-friendly ILs with low vapor pressure.

Surprisingly, the investigation of potential ILs containing $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ anions has been largely neglected. For catalysis application, there is quite rare in this field so far. To extend the scope of these promising results, ILs with $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ as the anion are thus of interest due to the high electrochemical stability of this anion as well as the stabilization of highly reactive.

Here we present the synthesis and characterization of a series of ILs which prepared by combining the organic cations (1-butyl-3-methylimidazolium ($[\text{Bmim}]^+$), 1,2-dimethyl-3-butylimidazolium ($[\text{Dbim}]^+$), 1-dodecyl-3-methylimidazolium ($[\text{C}_{12}\text{mim}]^+$), tetra-butyl-phosphonium ($[\text{P}_{4,4,4,4}]^+$), tributyl-(tetra-decyl)-phosphonium ($[\text{P}_{4,4,4,14}]^+$), tetra-butyl-ammonium ($[\text{N}_{4,4,4,4}]^+$) and 1,1,3,3-tetramethylguanidium ($[\text{TMG}]^+$)) with two different $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ anions (Scheme 1), including the solid state structures determined by single crystal X-ray diffraction. These salts enhanced thermal stability, which provided and exploited new chemical materials.

The oxidation of sulfides is of considerable significance for industrial chemistry. The removal of sulfur-containing compounds minimizes the negative health and environmental effects from reducing the sulfur content in fuels.^[18] In this aspect, the compound **5b** offers practical advantages without seriously jeopardizing their ultimate application for oxidation of sulfides to sulfoxides. Furthermore, this system can be cycled five times without loss of activity. This method was confirmed to be a green, safe, operationally simple and cost-effective system, which can be further development in industry technology.

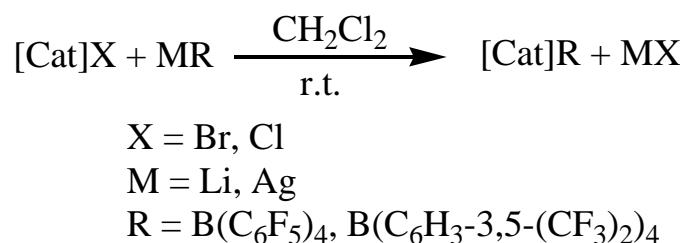


Scheme 1. Structures and abbreviations for the cations and anions in this work

6.2 Results and discussion

6.2.1 Synthesis of WCAILs

WCAILs were synthesized according to the modified literature procedures.^[19] Two different strategies were used to prepare the WCAILs (Scheme 2).



Scheme 2. Synthesis of WCAILs

In the first step, $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Li}[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ was synthesized by literature procedure.^[19-20] WCAILs **1a-7a** and **1b-7b** were obtained by the reaction of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Li}[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ with $[\text{Cat}]\text{X}$ in dry CH_2Cl_2 at room temperature for 2 h. However, great care must be taken to insure that all materials were free of moisture and air because $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{Li}[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ would get to be viscous liquid in the presence water and air. After filtration, the solvent was removed under vacuum. The remaining product

was washed with dry pentane, and then dried under high vacuum for one day until a constant weight was achieved. Typical yields of the purified product were 55-62 %. In order to increase the yield and reduce the reaction time, Ag[B(C₆F₅)₄] or Ag[B(3,5-(CF₃)₂-C₆H₃)₄] was selected as precursor for the synthesis of the WCAILs. Ag[B(C₆F₅)₄] or Ag[B(3,5-(CF₃)₂-C₆H₃)₄] was prepared according to the literature procedure.^[14] The metathesis was performed in the darkness at room temperature with dry CH₂Cl₂ as solvent. The reaction mixture was stirred for 10 min before it was filtered. The filtrate was removed under high vacuum to obtain the rough product. The product was washed with dry pentane and then dried under vacuum for one day. Typical yields of the pure product (spectra, elemental analyses) were up to 85-95 %. Under these conditions, satisfactory separation of the byproduct (lithium or silver halides) was usually achieved with filtration. From above results, the best routes typically involved silver salts rather than lithium salts in dry dichloromethane. All WCAILs can be handled in air. The salt **5a** is pale yellow liquid and **5b** is pale yellow crystalline liquid at room temperature. All salts have high solubility in polar organic solvents such as CH₂Cl₂, CH₃CN, common alcohols, but low solubility in *n*-hexane.

6.2.2 Solid-state structures

Crystals of **4a**, **7a**, **2b** and **5b** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the corresponding compounds at -10 °C in a refrigerator (See Experiment Section for crystallographic details). The diffraction measurements were carried out at low temperatures (between 100 to 200 K) in order to minimize rotation of the CF₃ groups and ensure the accuracy of the evaluation of intermolecular interactions involving F and H atoms.

The compound **4a** crystallizes in the orthorhombic space group *Pca*2₁ with two formula units per cell. The asymmetric unit consists of two [P_{4,4,4,4}]⁺ ions and two [B(C₆F₅)₄]⁻ ions. The ORTEP of the molecule is shown in the Figure 1 with atom labeling. Furthermore, the B-C bond lengths (1.656(2)-1.664 (2)) are shorter than the B-C bond lengths (1.657(4)-1.681(4)) of similar structure [N_{4,4,4,4}][B(C₆F₅)₄] described by M. Bolte due to different cation,^[21] which are listed in Table 1.

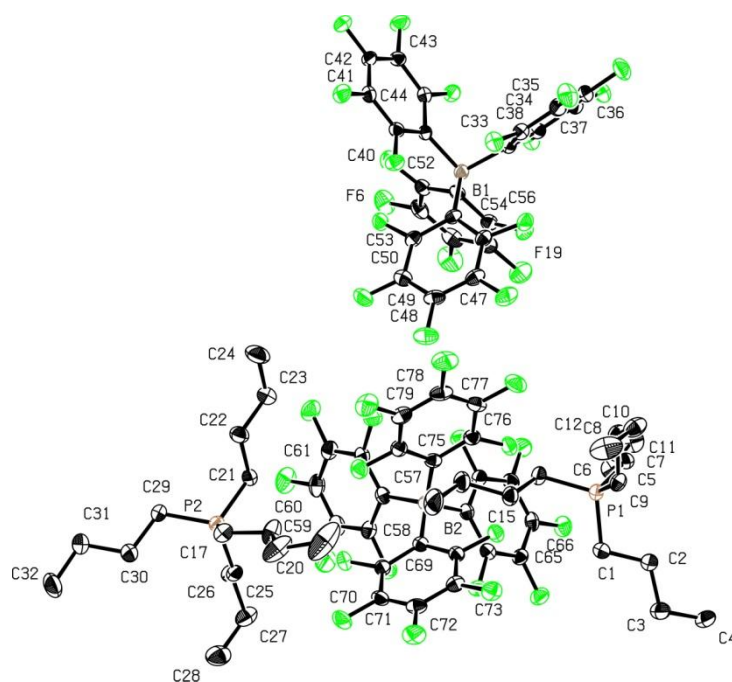


Figure 1. ORTEP style plot of compound **4a** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Table 1. Comparison of selected bond lengths (Å) and angles (°).

Entry	Compound	Bond lengths (B-C) (min-max)/ (Å)	Bond angles (C-B-C) (min-max)/ [°]
1	[Bmim][B(C ₆ F ₅) ₄]	1.652 (2)-1.655 (2) ¹⁹	101.26(11)-114.60 (12) ¹⁹
2	[Dbim][B(C ₆ F ₅) ₄]	1.653 (3)-1.659 (3) ¹⁹	101.23 (14)-114.19 (15) ¹⁹
3	[N _{4,4,4,4}][B(C ₆ F ₅) ₄]	1.657 (4)-1.681 (14) ²¹	---
4	[P _{4,4,4,4}][B(C ₆ F ₅) ₄]	1.656 (2)-1.664 (2)	101.39 (12)-115.59 (13)
5	[TMG][B(C ₆ F ₅) ₄]	1.393 (19)-1.661 (2)	102.29 (10)-113.30 (10)
6	[Dbim][B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄]	1.635 (2) – 1.640 (2)	101.85 (2) – 122.66 (14)
7	[P _{4,4,4,14}][B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄]	1.649(2)-1.653(19)	107.53(10)-111.06(10)

The compound **7a** was crystallized in triclinic centrosymmetric space group $P\bar{1}$ with $Z = 2$. It is striking that hydrogen atoms could be located in the difference fourier maps and were allowed to refine freely. Furthermore, the structure of the compound **7a** exhibits hydrogen-bonding interactions between the F atom from [B(C₆F₅)₄] anion and hydrogen atoms from the NH₂ group of 1,1,3,3-tetramethylguanidine (TMG) cation (Figure 2). Thus, the anion and cation are both restabilized by the extensive hydrogen bond. Representative hydrogen bonds are N1-H1...F3 and N1-H2...F13, whose H-bonds lengths are 2.375, 2.541 Å, respectively. The angle of N1-H1...F3 and N1-H...F13 are 158.33, 103.27 °, respectively (Table 2). The interactions between cation and anion *via* hydrogen bond maybe attribute to the hydrogen atom (-NH₂ group) which has the partial positive charge because of relatively stronger electronwithdrawing ability of N atom, is easier to attract to F atom which has the partial negative charge. This is also explained that other compound **4a** is difficult to form

hydrogen bond between cation and anion. According to the non-coordinating nature of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, the B-C bond lengths of **7a** are much shorter than the structure $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Dbim}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{N}_{4,4,4,4}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{P}_{4,4,4,4}][\text{B}(\text{C}_6\text{F}_5)_4]$ due to the hydrogen bond between the cation and anion, while the bond angles are similar, which are also shown in Table 1.

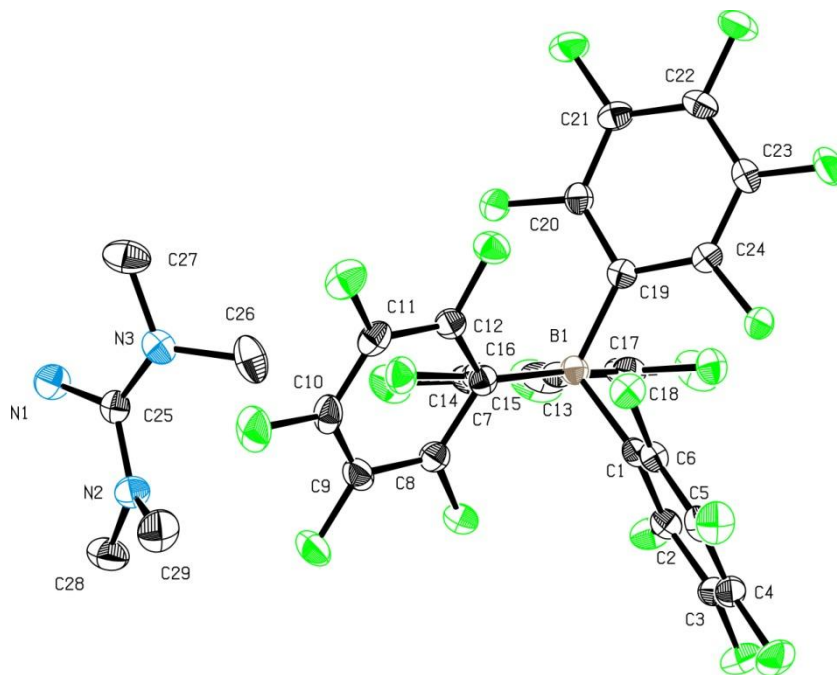


Figure 2. ORTEP style plot of compound **7a** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Table 2. Interatomic distances (Å) and angle [°] involving hydrogen bonded atoms in compound **7a**.

Entry	Hydrogen type	D-H...A	D-H (Å)	H...A (Å)	D-H...A [°]
1	NH ₂ -C ₆ F ₅	N1-H1...F3	3.199	2.357	158.33
2	NH ₂ -C ₆ F ₅	N1-H2...F13	2.862	2.541	103.27

The crystal structure of **2b** is crystallized in monoclinic space group $\text{P}2_1/\text{c}$ with $Z = 4$. The ORTEP of the molecule is shown in Figure 3. It was found that four CF_3 groups are disordered over two positions and the butyl-group of the cation is disordered over two positions. Furthermore, no significant cation...anion contacts was observed. This is in coincidence previous observations that the bands that related to hydrogen bonds disappeared when the proton atoms on imidazolium-ring were replaced by the $-\text{CH}_3$ groups.^[6b] Interestingly, the B-C bond lengths (1.635 (2) – 1.640 (2)) are much shorter than the compounds containing $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion (Table 1), probably indicating that there is a little effect of substitution on the bond lengths in the phenyl ring such as CF_3 group.

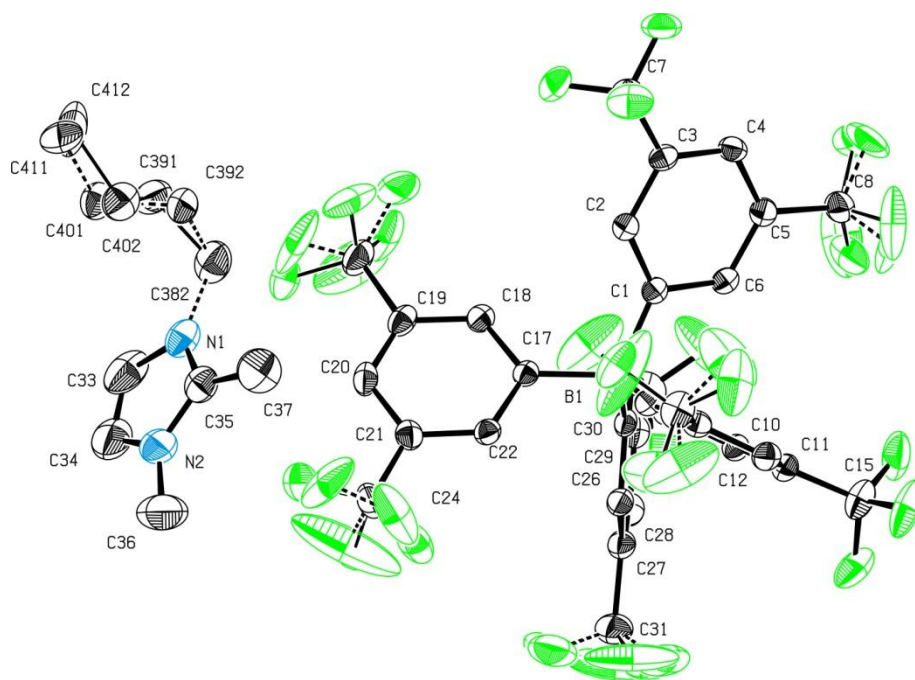


Figure 3. ORTEP style plot of compound **2b** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

The compound **5b** was crystallized in triclinic space group $P\bar{1}$ with $Z = 2$. The structure is shown in Figure 4 and the crystallographic data are summarized in the Experimental Section. It was found that three CF_3 groups are disordered over two positions. Interestingly, bond angle $(\text{C-B-C})_{\text{min}}$ ($107.53(10)^\circ$) is much bigger than any other compounds containing $[\text{B}(\text{C}_6\text{F}_5)_4]$ anion (Table 1), probably due to the steric hindrance effects of longer carbon chain of the cation.

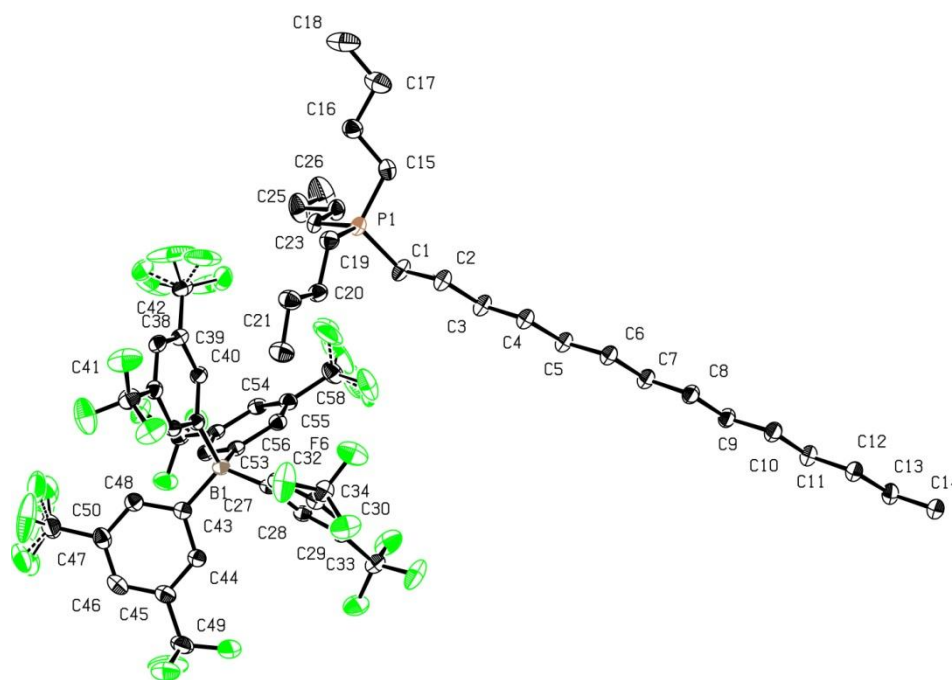


Figure 4. ORTEP style plot of compound **5b** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

5.2.3 Characterization of WCAILs

A series of salts **1a-7a** and **1b-7b** have been synthesized and characterized by FT-IR, NMR spectroscopy and elemental analysis (see Experiment Section). Melting points (T_m) were determined from differential scanning calorimetry (DSC) experiments. The results are summarized in Table 3. There is a significant lowering of the melting points for all salts with the $[B(3,5-(CF_3)_2-C_6H_3)_4]$ anion (**1b-7b**) compared to the corresponding $[B(C_6F_5)_4]$ anion salts (**1a-7a**), indicating that increasing anion size is connected with a significant decrease in melting point.^[22] The reduction in melting point is most pronounced with $[P_{4,4,4,14}]^+$ cation. In this case, the melting points of salts (**5a** and **5b**) are reduced from $\sim 120^\circ C$ to less than $50^\circ C$. While high symmetry compounds (**4a**, **6a**, **7a**, **4b**, **6b** and **7b**) lead to high melting points. Therefore, symmetry-breaking (in cations) is considered to be a key driver to the formation of lower melting ionic liquid.^[23] Similarly, the melting points for the **2a** and **2b** decreased with increasing alkyl chain length from butyl to dodecyl due to the increasing the cation size and decreasing the cation symmetry. Furthermore, the hydrogen bond between cation and anion maybe another factor for determining the properties, such as melting point.^[5, 24] The melting point of **5b** is lower compared to the similar salts containing the same anion due to the hydrogen bond. It can be clearly seen that the liquid range for these WCAILs is governed principally by the choice of cation, which has the greatest influence on the lower melting point, IL with $[P_{4,4,4,14}]^+$ cation (**5a** and **5b**) showing the lowest temperatures of all.

Thermal stability was measured by using thermogravimetric analysis (TGA), with isocratic heating at $10\text{ }^{\circ}\text{C min}^{-1}$ under an inert argon atmosphere. All salts prepared were thermally stable to greater than $240\text{ }^{\circ}\text{C}$ (Table 3). Interestingly, the salts show slight increase in upper stability temperature on increasing the cation alkyl chain from butyl to dodecyl, as well as on changing from phosphonium to imidazolium cations. In general, **a** and **b** anion with other type of cations decompose below $200\text{ }^{\circ}\text{C}$,^[15e] indicating that this kind of ionic liquids have good thermal stability.

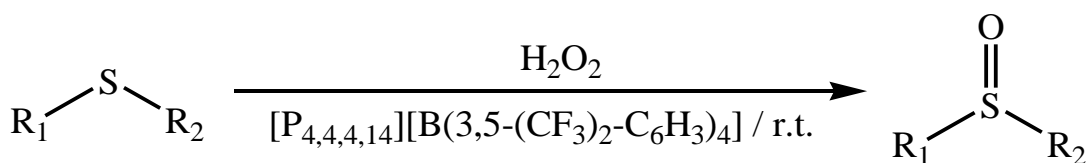
Table 3. Decomposition temperature (T_d) and melting points (T_m) of WCAILs

Entry	Compounds	T_d ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
1	[Bmim] [B(C ₆ F ₅) ₄] (1a)	245	145
2	[Dbim] [B(C ₆ F ₅) ₄] (2a)	270	151
3	[C ₁₂ mim] [B(C ₆ F ₅) ₄] (3a)	287	120
4	[P _{4,4,4,4}] [B(C ₆ F ₅) ₄] (4a)	330	114
5	[P _{4,4,4,14}] [B(C ₆ F ₅) ₄] (5a)	337	-39 ^a
6	[N _{4,4,4,4}] [B(C ₆ F ₅) ₄] (6a)	220	159
7	[TMG] [B(C ₆ F ₅) ₄] (7a)	255	152
8	[Bmim] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (1b)	260	106
9	[Dbim] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (2b)	255	91
10	[C ₁₂ mim] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (3b)	284	73
11	[P _{4,4,4,4}] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (4b)	300	121
12	[P _{4,4,4,14}] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (5b)	318	49
13	[N _{4,4,4,4}] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (6b)	238	92
14	[TMG] [B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄] (7b)	250	156

^aGlass transition temperature.

6.2.4 Application for oxidation of sulfides to sulfoxides

The oxidation of sulfides to sulfoxides was carried out using WCAILs **5a** and **5b** as reaction media and H₂O₂ as oxidant agent at room temperature. The details concerning the catalytic reaction are given in the experiment part. Oxidation of thioanisole with aqueous H₂O₂ as oxidant was found to be strongly solvent dependent. When using **5a** as solvent, the yield of sulfoxide is 18 % within 4 h, and the selectivity toward sulfoxide is 90 % probably due to the high viscosity. Higher yields were obtained using **5b** as media. Therefore, **5b** was chosen as media for oxidation of sulfides to sulfoxides with H₂O₂ at room temperature (Scheme 3). A blank experiment without oxidant was also investigated and no considerable oxidation was observed within 24 h, indicating that the oxygen source for the synthesis of sulfoxide is not air.



Scheme 3. Oxidation of sulfides to sulfoxides

It can be seen in Figure 5 that with increasing the reaction time, the yield of methyl phenyl sulfoxide increased greatly, while the selectivity of methyl phenyl sulfoxide kept steadily during the reaction. The maximum yield could be achieved after 4 h and no further increase in the yields of methyl phenyl sulfoxides was observed with prolonged reaction time.

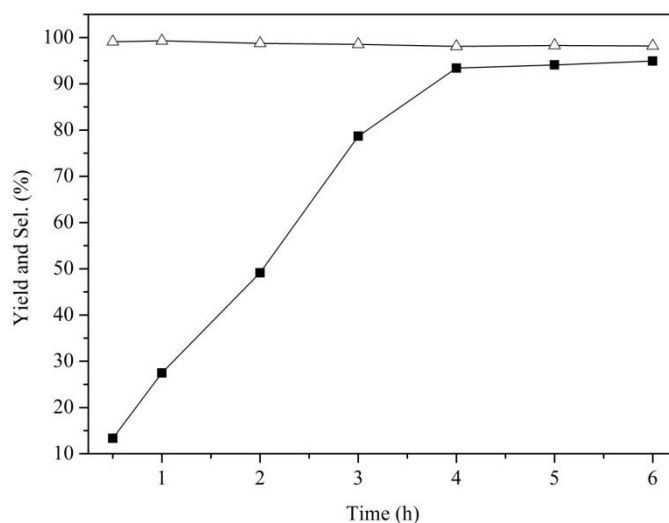


Figure 5. Time dependent yield (■) and selectivity (Δ) of methyl phenyl sulfoxide in the oxidation of thioanisole with H₂O₂ in [P_{4,4,4,14}][B(3,5-(CF₃)₂-C₆H₃)₄].

To generalize the developed methodology, a wide range of sulfides with different substituted groups were selected to oxidize under the same condition. The results are shown in Table 4. All sulfides were effectively oxidized to the corresponding sulfoxides with good to excellent yields using 35 % hydrogen peroxide at room temperature. Interestingly, a dialkyl sulfide (Entries 3) is more active, affording a very high sulfoxide yield (within 3 h) than diaryl sulfides (Entries 1, 3-7) due to the steric hindrance. For the oxidation of various phenyl-ring substituted sulfides to corresponding sulfoxides, the electronic nature of the substituents has less effect on the yield and selectivity of the product sulfoxides (Entries 4-7). It is important to note that another useful feature of the presented protocol is that neither epoxidation of the double bond of allyl phenyl sulfide (Entry 6) nor oxidation of the hydroxo group (Entry 7) was observed.

Table 4. Oxidation of sulfides to sulfoxides with aqueous H₂O₂ in [P_{4,4,4,14}][B(3,5-(CF₃)₂-C₆H₃)₄]^a

Entry	R ¹	R ²	Time (h)	Yield ^b (%)	Selectivity ^c (%)
1	Ph	Me	4	93	97
2	Me	Me	3	94	98
3	<i>n</i> -Butyl	<i>n</i> -Butyl	4	91	97
4	Ph	Ethyl	5	84	96
5	Ph	CH(CH ₃) ₂	5	80	97
6	Ph	CH ₂ CH=CH ₂	6	82	96
7	Ph	CH ₂ CH ₂ OH	5	86	97

^a Reaction conditions : 0.5 mL [P_{4,4,4,14}][B(3,5-(CF₃)₂-C₆H₃)₄], 2 mmol substrate, 5 mmol H₂O₂ (30 %) at 25 °C;

^b Isolated yield after column chromatography;

^c Determined by GC-MS or ¹H NMR on the crude reaction mixture.

The advantage of this oxidation system is their potential recovery for multiple uses. After oxidation of thioanisole was completed in **5b** IL, the IL phase was diluted with CH₂Cl₂ after extraction sulfide and sulfoxide, and then treated with MnO₂ to destroy the excess peroxide. The obtained liquid was dried over anhydrous MgSO₄, and then dried under high vacuum until a constant weight was achieved. Five recycling tests were carried out and the results are summarized in Figure 6. It can be seen that no significant loss of yield and selectivity was observed after five runs when thioanisole was used at the test substrate. This system provides the advantage of recycle and stable compared to the other systems which using the organic solvent as media for oxidation of sulfides have been previously reported.^[25]

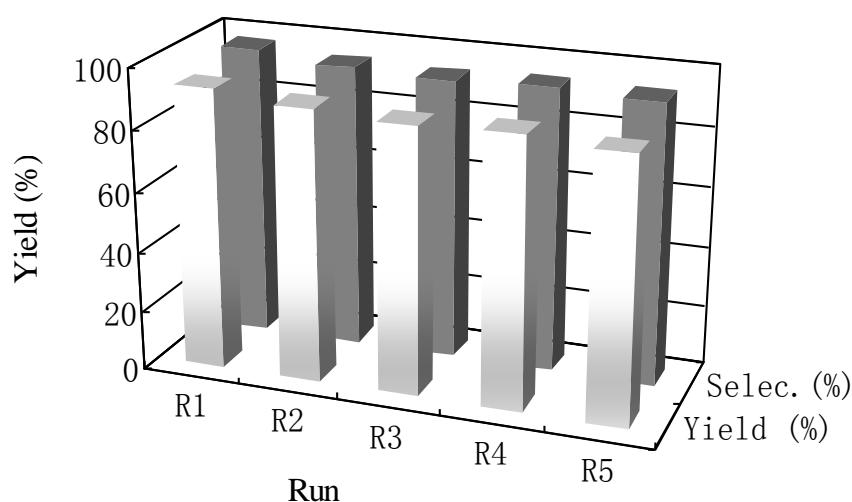


Figure 6. Oxidation of thioanisole with H₂O₂ in **5b** at 25 °C after five reaction runs.

6.2.5 Reaction mechanism

Regarding the mechanism of this reaction, the interaction between the ionic liquid and H₂O₂ and H₂O appear to be crucial. It is known that organic sulfides are oxidized by hydrogen

peroxide in an heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen.^[26] This also explains the dialkyl sulfides are indeed more easily oxidized than the diaryl sulfides. Concerning the efficiency of our oxidizing system, it can be explained by a specific feature of **5b** ionic liquid which not only act as a solvent but also can be viewed as a promoter for the catalysis. Because of the electron withdrawing character of the CF₃ group, the hydrogen bond between the **5b** ionic liquid and H₂O₂ or H₂O is formed and prevents from any further oxidation into sulfone.^[27] Furthermore, **5b** ionic liquid is more stable in catalysis reaction compared to the common ILs such as [BF₄]⁻ or [PF₆]⁻ as anion. Because the hydrofluoric acid HF which comes from the decomposition of [BF₄]⁻ or [PF₆]⁻ as anion ILs in oxidation reaction in the presence of water or hydrogen peroxide was producing.^[28]

In order to further study the interaction between ILs and H₂O or H₂O₂ and support above points as well, several techniques such as infrared vibration and nuclear magnetic resonance have been used to monitor interaction between the donors and anionic species. In order to understand which hydrogen participated in the hydrogen bonds, deuterium has been instead of the pure water for IR measurements. Figures 7 and 8 show the IR spectra of the CF stretching region of **5b** ionic liquid in D₂O and H₂O₂. As can be seen from the Figures, the CF₃ stretching modes are expected to be very prominent in the infrared spectrum. Due to the non-equivalence CF bands to interpret as antisymmetric and symmetric stretching mode has no sense. The exact C_{3v} local symmetry should produce only two bands ν_a (higher) and ν_s (lower). Instead, three well developed bands at 1355, 1275 and 1119 cm⁻¹ have been observed in 1a spectrum. The first two bands can be interpreted as individual localized CF stretchings which shows different CF band length and the multiply structure broad band near 1119 cm⁻¹, is a kind of symmetric stretching mode of different CF bands. This explanation is in agreement with the literature data of announced CF₃ derivatives.^[29] And accordingly, we can name them as $\nu > \nu' > \nu''$, respectively. As can be seen from Figure 7, the bands ν and ν' are not shifted, while new bands are formed in the region of CF₃ symmetric stretching mode. To obtain fine spectral differences between samples, the second derivative showed in Figure 8. When adding the D₂O or H₂O₂ into the IL, two new bands at 1115 and 1124 cm⁻¹ or 1114 and 1123 cm⁻¹ are formed, respectively. Furthermore, clear developing of a shoulder near 1085 cm⁻¹ can be seen in Figure 7 for spectrum 2a and 3a which are more clearly identified by second derivatives. In Figure 8, the band at 1085 cm⁻¹ in 2b and 3b spectra is getting stronger compared to the pure ionic liquid. These changes can be ascribed to a further distortion of the CF₃ local symmetry from C_{3v} to C₁ which lead to formation of new spectra features by weak coordination, such as hydrogen bond between F from ionic liquid and hydrogen from D₂O or

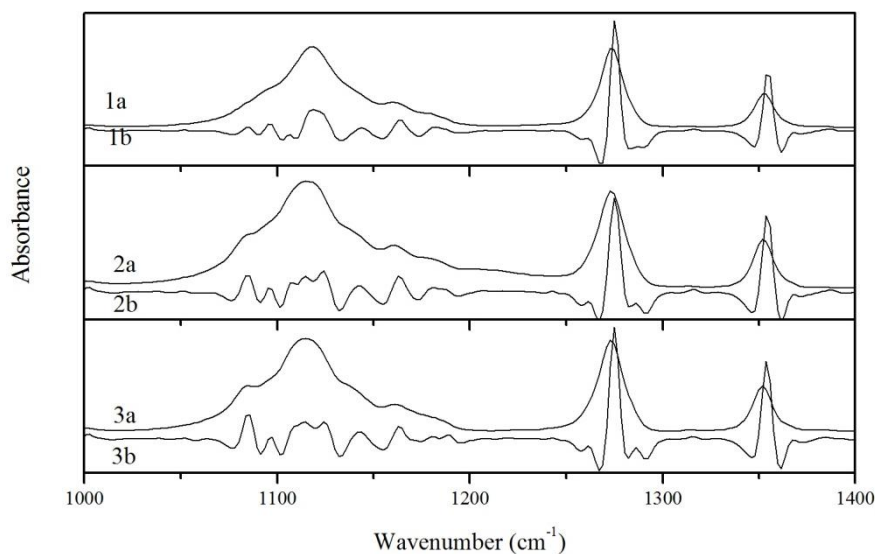
H₂O₂.

Figure 7. Band CF stretching region of pure IL [P_{4,4,4,14}][B(C₆H₃-3,5-(CF₃)₂)₄] (1a, 1b), IL with D₂O (2a, 2b) and IL with H₂O₂ (3a, 3b).

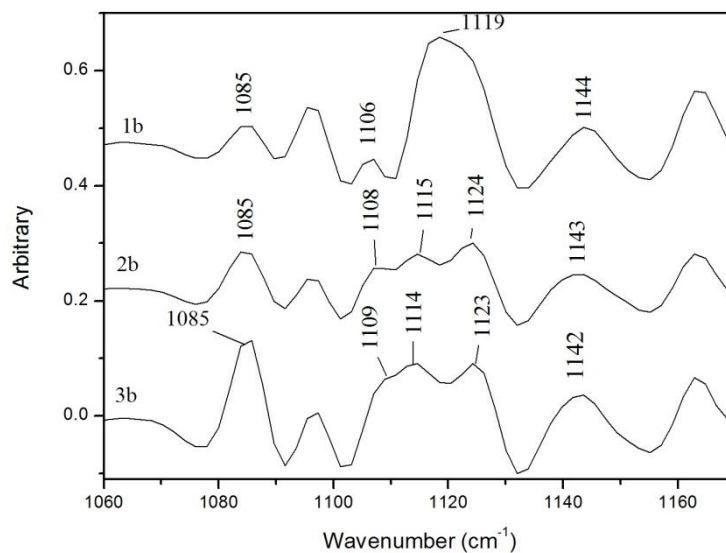


Figure 8. Second derivative of bond CF symmetric stretching region of pure IL [P_{4,4,4,14}][B(3,5-(CF₃)₂-C₆H₃)₄] (1b), IL with D₂O (2b) and IL with H₂O₂ (3b) (The derivative curves were multiplied by -10).

It is known that NMR is sufficiently advanced that, approximate chemical shifts can be predicted for compounds of a known structure and, vice versa, the approximate coordination environment of unknown compounds can be predicted on the basis of chemical shift

values.^[28d] Therefore, ^{11}B , ^{19}F and ^{31}P NMR were also performed to show hydrogen-bonding in the absence and in the presence of water or hydrogen peroxide. The ^{11}B NMR spectrum shows one resonance at -6.58 ppm with pure ionic liquid. The spectra recorded exhibits a slight shift to -6.84 ppm after addition H_2O into IL and -6.75 ppm after H_2O_2 (30 %) addition. The corresponding ^{19}F NMR shows one signal at -59.55 ppm for the pure IL. The spectroscopic investigations shifts to -61.29 ppm or two signals -60.64 and -61.23 ppm when adding the H_2O or H_2O_2 into IL. The slight shift of the CF_3 signal points to a change in the coordination sphere of the anion, such as a weak H...F interaction, but not to the formation of BF_3 or HF , which would lead to a significantly different peak position due to the symmetry change. On the other hand, the behavior of cation when the environment was changed was also studied. As it can be seen, the ^{31}P NMR pattern of two different mixtures is quite different. The signal at 34.95 ppm for the pure IL significantly has been shifted to 33.43 ppm for the mixture with H_2O and to 33.50 ppm for the mixture with H_2O_2 , indicating the cation of IL is not changed as well. Based on above described experimental and spectroscopic findings, a hydrogen bond formation between CF_3 group of IL and hydrogen peroxide or water appears to be the crucial step during the oxidation reaction.

6.3 Conclusion

In continuation of our studies of ionic liquids utilizing N, N'-Dialkylimidazolium, tetrabutylammonium, tetralkylphosphonium, 1,1,3,3-tetramethylguanidium cations with new family $[\text{B}(\text{Ar}^{\text{F}})_4]$ species have been synthesized and structurally characterized. The synthesis is optimized and simple, and the products can be obtained in high yield. All salts have high thermal stability. It has been shown that the $[\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]^-$ anion salts (**2b**, **3b**, **5b** and **6b**) melting points are reduced by below 100 °C compared to the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salts, which lead to opportunities to form ILs materials. The melting points of the salts using the tetrabutylammonium and 1,1,3,3-tetramethylguanidium as cation are higher than any other salts due to the high symmetry structure. Increasing the size of the salts has been identified as a common and potentially general characteristic of low melting points with large cation, such as **5a** and **5b**. The systematic variation of alkyl substituent on the cation led to usefully predictive trends in melting points. It is important to mention that hydrogen-bonding interactions between $[\text{TMG}]^+$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ has been discovered.

The ionic liquid $[\text{P}_{4,4,4,14}][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ can be successfully applied for oxidation of sulfides to sulfoxides without any catalyst. Furthermore, this system can be recycled five

times without any loss of activity. This methodology with mentioned advantages is an improved and environmentally benign way for catalytic process.

6.4 Experiment section

6.4.1 Gernal

All preparations and manipulation involving air-sensitive materials were performed using standard Schlenk techniques under argon atmosphere. Solvents were dried by standard procedures (Et₂O over Na/benzophenone; CH₂Cl₂ over CaH₂), distilled under argon and kept over 4 Å molecular sieves. All chemicals (purchased from Acros Organics or Aldrich) were of analytical grade and used as received. NMR spectra were recorded on a Bruker Avance DPX-400 instrument and referenced to deuterated solvent in the case of the ¹H NMR, C₆F₆ for the ¹⁹F NMR, BF₃ OEt₂ for ¹¹B NMR and H₃PO₄ (85 %) for ³¹P NMR spectra, respectively. IR spectra were recorded on Varian FTIR - 670 spectrometer, using a GladiATR accessory with a diamond ATR element. Elemental analyses were obtained from the microanalytical laboratory in Technische Universität München. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Thermogravimetry analysis (TGA) was conducted utilizing a Netzsch TG209 system; typically about 10 mg of each sample were heated from 25 °C to 1000 °C at 10 K min⁻¹. Differential scanning analysis (DSC) was performed on a DSCQ2000 from TA instrument (Waters) in temperature range from -150 °C to 200 °C at 10 K min⁻¹. Melting points were measured by MPM-H2 melting point meters. TLC was performed on silica gel 60F254 plates procured from E. Merck. Silica gel (0.06–0.2 mm 60A) was used for column chromatography.

6.4.2 Synthetic method and characterization data

General procedure Li[B(C₆F₅)₄], Li[B(C₆H₃-3,5-(CF₃)₂)₄], Ag[B(C₆F₅)₄] and Ag [B(C₆H₃-3,5-(CF₃)₂)₄]: A 2.5 M solution of *n*-butyl lithium in *n*-hexane (17.82 mL) was added slowly to a solution of bromopentafluorobenzene (5 mL, 40 mmol) or 3,5-bis(trifluoromethyl)-5-bromobenzene (7 mL, 40 mmol) in a mixture of diethyl ether (40 mL) at -78 °C and stirred for 1 h. This was followed by the dropwise addition of BCl₃ (11.8 mL, 11.8 mmol) dissolved in diethyl ether (20 mL). After 1 h, the resulting suspension was warmed slowly to room temperature. The product Li[B(C₆F₅)₄] or Li[B(C₆H₃-3,5-(CF₃)₂)₄] was separated by filtration, washed with pentane several times, and then dried under vacuum

for one day. $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{Ag}[\text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4]$ were prepared according to literature procedures.^[14]

General procedure 1 for the synthesis of 1a-7a: 1 equiv $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ and 1 equiv $[\text{Cat}]\text{X}$ were weighed in two different Schlenk tubes and were dissolved in a mixture CH_2Cl_2 . The two solutions were mixed and stirred for 2 h at room temperature, and then filtered. The solvent is removed under high vacuum for 4 h. The product was washed with dry *n*-hexane three times and then dried in vacuum for one day.

General procedure 2 for the synthesis of 1a-7a: Equimolar amounts of $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Cat}]\text{X}$ were weighed into a Schlenk vessel. Dry 20 mL CH_2Cl_2 was added. The mixture was stirred in darkness at room temperature for 10 min. The precipitate was removed by filtration, and the filtrate was vacuumed for 4 h. The product was washed several times with *n*-hexane and dried in vacuum for one day.

Experimental data for 1a: $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.787 g, 1 mmol), $[\text{Bmim}]\text{Br}$ (0.218 g, 1 mmol); isolated yield: 0.73 g (89 %). $^1\text{H-NMR}$ ($[\text{D}_6]$ -DMSO, 400Hz, 298K, ppm): $\delta = 0.89$ (t, 3H, CH_2CH_3), 1.25 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 3.85 (s, 3H, NCH_3), 4.16 (t, 2H, NCH_2), 7.71 (m, 1H, NCH), 7.77 (m, 1H, NCH), 9.12 (s, 1H, NCHN); $^{19}\text{F-NMR}$ ($[\text{D}_6]$ -DMSO, 377Hz, 298K, ppm): $\delta = -131.26$ (s, 8F, *o*-F), -161.66 (t, 4F, *p*-F), -165.60 (t, 8F, *m*-F); $^{11}\text{B-NMR}$ ($[\text{D}_6]$ -DMSO, 128Hz, 298K, ppm): $\delta = -16.7$ (s); elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{14}\text{N}_2\text{BF}_{20}$ (818.3): calcd. C 46.91, H 1.97, N 3.42; found C 46.25, H 2.10, N 3.87; IR (cm^{-1}): $\nu = 480$ (w), 573 (w), 660 (m), 683 (m), 739 (m), 772 (m), 974 (vs), 1082 (vs), 1272 (m), 1373 (w), 1486 (vs), 1513 (s), 1642 (m), 1953 (w), 2159 (w), 2545 (vw).

Experimental data for 2a: $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.787 g, 1 mmol), $[\text{Dbim}]\text{Br}$ (0.223 g, 1 mmol); isolated yield: 0.76 g (92 %). $^1\text{H-NMR}$ ($[\text{D}_6]$ -DMSO, 400Hz, 298K, ppm): $\delta = 0.89$ (t, 3H, CH_2CH_3), 1.27 (m, 2H, CH_2), 1.68 (m, 2H, CH_2), 2.58 (s, 3H, NCH_3), 3.75 (s, 3H, $\text{NC}(\text{CH}_3)\text{N}$), 4.11 (t, 2H, NCH_2), 7.61 (m, 1H, NCH), 7.64 (m, 1H, NCH); $^{19}\text{F-NMR}$ ($[\text{D}_6]$ -DMSO, 377Hz, 298K, ppm): $\delta = -132.42$ (s, 8F, *o*-F), -161.54 (t, 4F, *p*-F), -166.02 (t, 8F, *m*-F); $^{11}\text{B-NMR}$ ($[\text{D}_6]$ -DMSO, 128Hz, 298K, ppm): $\delta = -16.8$ (s); elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{17}\text{N}_2\text{BF}_{20}$ (832.3): calcd. C 47.56, H 2.18, N 3.36; found C 46.63, H 2.48, N 3.89; IR (cm^{-1}): $\nu = 477$ (vw), 573 (w), 621 (w), 659 (m), 683 (w), 830 (m), 957 (vs), 1081 (s), 1163 (m), 1274 (m), 1374 (w), 1458 (vs), 1512 (s), 1567 (w), 1592 (w), 1642 (m), 1957 (m), 2158 (m), 2547 (w).

Experimental data for 3a: $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.787 g, 1 mmol), $[\text{C}_{12}\text{mim}]\text{Br}$ (0.331 g, 1 mmol); isolated yield: 0.87 g (93 %). $^1\text{H-NMR}$ ($[\text{D}_6]$ -DMSO, 400Hz, 298K, ppm): $\delta = 0.78$ (t, 3H, CH_3), 1.20 (m, 18H, 9 CH_2), 1.75 (m, 2H, CH_2), 3.83 (3H, NCH_3), 4.13 (t, 2H, NCH_2), 7.68 (s,

1H, NCH), 7.73 (s, 1H, NCH), 9.09 (s, 1H, NCHN); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -130.28(s, 8F, *o*-F), -159.55 (t, 4F, *p*-F), -164.01 (t, 8F, *m*-F); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -16.51 (s); elemental analysis calcd (%) for C₄₀H₃₂N₂BF₂₀ (931.47): calcd. C 51.58, H 3.46, N 3.01; found C 51.39, H 3.63, N 3.16; IR (cm⁻¹): 475 (vw), 573 (m), 610 (w), 623 (m), 660 (s), 682 (m), 734 (w), 756 (m), 773 (m), 800 (vw), 831 (w), 976 (vs), 1080 (vs), 1165 (m), 1274 (m), 1461 (vs), 1514 (s), 1563 (w), 1589 (w), 1644 (m), 2856 (w), 2927 (w).

Experimental data for 4a: Ag[B(C₆F₅)₄] (0.787 g, 1 mmol), [P_{4,4,4,4}]Br (0.338 g, 1 mmol); isolated yield: 0.82 g (87 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.86 (m, 12H, 4CH₃), 1.38 (m, 16H, 8CH₂), 2.14 (m, 8H, 4CH₂); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -130.20(s, 8F, *o*-F), -159.07 (t, 4F, *p*-F), -163.72(t, 8F, *m*-F); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -16.47 (s); ³¹P-NMR ([D₆]-DMSO, 162Hz, r.t., ppm): δ = 29.74 (s); elemental analysis calcd (%) for C₄₀H₃₆BF₂₀P (938.47): calcd. C 51.19, H 3.87; found C 50.27, H 4.03; IR (cm⁻¹): 574 (w), 660 (m), 683 (w), 755 (m), 772 (m), 906 (m), 975 (vs), 1082 (vs), 1273 (w), 1382 (vw), 1459 (vs), 1512 (s), 1642 (m), 1958 (vw), 2159 (vw), 2873 (w), 2932 (w), 2960 (w).

Experimental data for 5a: Ag[B(C₆F₅)₄] (0.787 g, 1 mmol), [P_{4,4,4,14}]Cl (0.434 g, 1 mmol); isolated yield: 0.92 g (85 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.78 (t, 3H, CH₃), 0.88 (t, 9H, 3CH₃), 1.21 (m, 20H, 10CH₂), 1.43 (m, 16H, 8CH₂), 2.17 (m, 8H, 4CH₂); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -130.23 (s, 8F, *o*-F), -160.21 (t, 4F, *p*-F), -164.35 (t, 8F, *m*-F); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -16.51 (s); ³¹P-NMR ([D₆]-DMSO, 162Hz, 298K, ppm): δ = 33.77 (s); elemental analysis calcd (%) for C₅₀H₅₆BF₂₀P (1078.73): calcd. C 55.67, H 5.23, found C 55.66, H 5.96; IR (cm⁻¹): 475 (vw), 573 (w), 602 (w), 610 (w), 660 (m), 683 (w), 726 (vw), 755 (m), 774 (vs), 909 (vw), 977 (vs), 1083 (vs), 1274 (m), 1373 (vw), 1461 (vs), 1512 (s), 1642 (m), 2857 (w), 2929 (w).

Experimental data for 6a: Ag[B(C₆F₅)₄] (0.787 g, 1 mmol), [N_{4,4,4,4}]Br (0.322 g, 1 mmol); isolated yield: 0.86 g (93 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.97 (t, 12H, 4CH₃), 1.25 (m, 8H, 4CH₂), 1.53 (m, 8H, 4CH₂), 3.05 (m, 8H, 4NCH₂); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -131.08 (s, 8F, *o*-F), -160.51 (t, 4F, *p*-F), -161.40 (t, 8F, *m*-F); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -16.37 (s); elemental analysis calcd (%) for C₄₀H₃₆BF₂₀N (921.5): calcd. C 52.14, H 3.94, N 1.52, found C 51.07, H 4.10, N 1.66; IR (cm⁻¹): 476 (w), 574 (w), 660 (m), 682 (m), 773 (w), 977 (vs), 1085 (s), 1272 (m), 1461 (vs), 1513 (s), 1643 (w), 1960 (w), 2169 (w), 2878 (w), 2963 (w).

Experimental data for 7a: Ag[B(C₆F₅)₄] (0.787 g, 1 mmol), [TMG]Cl (0.151 g, 1 mmol); isolated yield: 0.75 g (94 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 1.89 (s, 12H, 4CH₃), 7.89 (s, 2H, NH₂); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -130.32 (s, 8F, *o*-F), -159.30 (t, 4F, *p*-F), -163.91 (t, 8F, *m*-F); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -16.49 (s); elemental analysis calcd (%) for C₂₉H₁₄N₃BF₂₀ (795.2): calcd. C 43.80, H 1.77, N 5.28, found C 43.52, H 1.86, N 5.38; IR (cm⁻¹): 440 (w), 661 (s), 756 (w), 774 (m), 976 (vs), 1080 (s), 1276 (m), 1460 (vs), 1511 (s), 1628 (s), 1958 (w), 2158 (w), 3433 (vw).

General procedure for the synthesis of 1b-7b: Equimolar amounts of Ag[B(C₆H₃-3,5-(CF₃)₂)₄] and [Cat]X were weighed into a Schlenk vessel. Dry 20 mL CH₂Cl₂ was added. The mixture was stirred in darkness at room temperature for 10 min. The precipitate was removed by filtration, and the filtrate was vacuumed for 4 h. The product was washed several times with *n*-hexane and dried in vacuum for one day.

Experimental data for 1b: Ag[B(3,5-(CF₃)₂-C₆H₃)₄] (0.971 g, 1 mmol), [C₄mim]Br (0.218 g, 1 mmol); isolated yield: 0.95 g (95 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.89 (t, 3H, CH₂CH₃), 1.26 (m, 2H, CH₂), 1.75 (m, 2H, CH₂), 3.84 (s, 3H, NCH₃), 4.15 (t, 2H, NCH₂), 7.62 (m, 8H, Ar-H), 7.70 (m, 4H, Ar-H), 7.73(m, 1H, NCH), 7.71 (m, 1H, NCH), 9.11 (s, 1H, NCHN); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -59.96 (s, CF₃); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -6.58 (s); elemental analysis calcd (%) for C₄₀H₂₈N₂BF₂₄ (1003.44): caclcd. C 47.88, H 2.81, N 2.79, found C 47.54, H 2.84, N 3.08; IR (cm⁻¹): 448 (w), 621 (m), 669 (s), 712 (s), 743 (m), 837 (m), 887 (m), 1109 (vs), 1272 (vs), 1353 (s), 1568 (vw), 1608 (vw), 2961 (vw).

Experimental data for 2b: Ag[B(C₆H₃-3,5-(CF₃)₂)₄] (0.971 g, 1 mmol), [C₄C₄mim]Br (0.223 g, 1 mmol); isolated yield: 0.97 g (95 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.87 (t, 3H, CH₂CH₃), 1.25 (m, 2H, CH₂), 1.64 (m, 2H, CH₂), 2.48 (s, 3H, NCH₃), 3.73 (s, 3H, NC(CH₃)N), 4.08 (t, 2H, NCH₂), 7.61 (m, 12H, Ar-H), 7.62 (m, 2H, 2NCH); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -59.55 (s, CF₃); ¹¹B-NMR ([D₆]-DMSO, 128Hz, 298K, ppm): δ = -6.59 (s); elemental analysis calcd. (%) for C₄₁H₃₀N₂BF₂₄ (1017.46): caclcd. C48.40, H 2.97, N 2.75, found C 47.70, H 2.96, N 3.03; IR (cm⁻¹): 669 (vs), 715 (s), 742 (m), 838 (m), 889 (s), 1115 (vs), 1274 (vs), 1352 (s), 1462 (w), 1535 (vw), 2193 (w), 2959 (vw).

Experimental data for 3b: Ag[B(C₆H₃-3,5-(CF₃)₂)₄] (0.971 g, 1 mmol), [C₁₂mim]Br (0.331 g, 1 mmol); isolated yield: 1.03 g (93 %). ¹H-NMR ([D₆]-DMSO, 400Hz, 298K, ppm): δ = 0.72 (t, 3H, CH₃), 1.16 (m, 18H, 9CH₂), 1.75 (m, 2H, CH₂), 3.84 (3H, NCH₃), 4.13(t, 2H, NCH₂), 7.69 (m, 12H, Ar-H), 7.74 (s, 1H, NCH), 7.75 (s, 1H, NCH), 9.11 (s, 1H, NCHN); ¹⁹F-NMR ([D₆]-DMSO, 377Hz, 298K, ppm): δ = -60.03(s, CF₃); ¹¹B-NMR ([D₆]-DMSO,

Chapter 6

128Hz, 298K, ppm): $\delta = -6.54$ (s); elemental analysis calcd (%) for $C_{48}H_{44}N_2BF_{24}$ (1115.65): calcd. C 51.68, H 3.98, N 2.51, found C 51.81, H 3.90, N 2.52; IR (cm^{-1}): 446 (m), 580 (vw), 622 (w), 667 (s), 682 (m), 707(m), 715(m), 742 (w), 838(m), 888 (s), 899 (m), 949 (vw), 1114 (vs), 1158 (vs), 1272 (vs), 1353 (vs), 1466 (vw), 1570 (vw), 1610 (vw), 2860 (w), 2934 (w).

Experimental data for 4b: $Ag[B(C_6H_3-3,5-(CF_3)_2)_4]$ (0.971 g, 1 mmol), $[P_{4,4,4,4}]Br$ (0.338 g, 1 mmol); isolated yield: 1.02 g (91 %). 1H -NMR ($[D_6]-DMSO$, 400Hz, 298K, ppm): $\delta = 0.82$ (m, 12H, 4CH₃), 1.36 (m, 16H, 8CH₂), 2.10 (m, 8H, 4CH₂); 7.57 (m, 12H, Ar-H); ^{19}F -NMR ($[D_6]-DMSO$, 377Hz, 298K, ppm): $\delta = -59.66$ (s, CF₃); ^{11}B -NMR ($[D_6]-DMSO$, 128Hz, 298K, ppm): $\delta = -6.59$ (s); ^{31}P -NMR ($[D_6]-DMSO$, 162Hz, r.t., ppm): $\delta = 33.76$ (s); elemental analysis calcd (%) for $C_{48}H_{48}BF_{20}P$ (1122.64): calcd. C 51.35, H 4.31; found C 51.07, H 4.46; IR (cm^{-1}): 447 (vw), 667 (m), 712 (m), 837 (w), 886 (m), 1114 (vs), 1272 (vs), 1353 (s), 1465 (w), 1610 (vw), 2542 (vw), 2875 (vw), 2963 (vw).

Experimental data for 5b: $Ag[B(C_6H_3-3,5-(CF_3)_2)_4]$ (0.971 g, 1 mmol), $[P_{4,4,4,14}]Cl$ (0.434 g, 1 mmol); isolated yield: 1.15 g (91 %). 1H -NMR ($[D_6]-DMSO$, 400Hz, 298K, ppm): $\delta = 0.73$ (t, 3H, CH₃), 0.84 (t, 9H, 3CH₃), 1.16 (m, 20H, 10CH₂), 1.40 (m, 16H, 8CH₂), 2.13 (m, 8H, 4CH₂), 7.57 (m, 12H, Ar-H); ^{19}F -NMR ($[D_6]-DMSO$, 377Hz, 298K, ppm): $\delta = -59.55$ (s,CF₃); ^{11}B -NMR ($[D_6]-DMSO$, 128Hz, 298K, ppm): $\delta = -6.58$ (s); ^{31}P -NMR ($[D_6]-DMSO$, 162Hz, 298K, ppm): $\delta = 33.54$ (s); elemental analysis calcd (%) for $C_{58}H_{68}BF_{24}P$ (1262.91): calcd. C 55.16, H 5.43, found C 55.79, H 5.81; IR (cm^{-1}): 403 (w), 450 (w), 618 (vw), 669 (s), 681 (m), 710 (s), 744 (vw), 838 (m), 887 (m), 934 (vw), 1001 (vw), 1112 (vs), 1161 (vs), 1274 (vs), 1351 (s), 1468 (w), 1608 (w), 2858 (w), 2927 (w).

Experimental data for 6b: $Ag[B(C_6H_3-3,5-(CF_3)_2)_4]$ (0.971 g, 1 mmol), $[N_{4,4,4,4}]Br$ (0.322 g, 1 mmol); isolated yield: 1.04 g (94 %). 1H -NMR ($[D_6]-DMSO$, 400Hz, 298K, ppm): $\delta = 0.88$ (t, 12H, 4CH₃), 1.27 (m, 8H, 4CH₂), 1.55 (m, 8H, 4CH₂), 3.15 (m, 8H, 4NCH₂), 7.58 (m, 12H, Ar-H); ^{19}F -NMR ($[D_6]-DMSO$, 377Hz, 298K, ppm): $\delta = -59.87$ (s, CF₃); ^{11}B -NMR ($[D_6]-DMSO$, 128Hz, 298K, ppm): $\delta = -6.81$ (s); elemental analysis calcd (%) for $C_{48}H_{48}BF_{24}N$ (921.5): calcd. C 52.14, H 4.38, N 1.27, found C 51.81, H 4.70, N 1.44; IR (cm^{-1}): 450 (vw), 670 (s), 712 (s), 799 (m), 838 (m), 889 (m), 1117 (vs), 1271 (vs), 1353 (s), 1470 (w), 1608 (vw), 2179 (w), 2964 (w).

Experimental data for 7b: $Ag[B(C_6H_3-3,5-(CF_3)_2)_4]$ (0.971 g, 1 mmol), $[TMG]Cl$ (0.151 g, 1 mmol); isolated yield: 0.93 g (95 %). 1H -NMR ($[D_6]-DMSO$, 400Hz, 298K, ppm): $\delta = 2.86$ (s, 12H, 4CH₃), 7.66 (m, 12H, Ar-H), 7.80 (s, 2H, NH₂); ^{19}F -NMR ($[D_6]-DMSO$, 377Hz, 298K, ppm): $\delta = -60.02$ (s, CF₃); ^{11}B -NMR ($[D_6]-DMSO$, 128Hz, 298K, ppm): $\delta = -6.58$ (s);

elemental analysis calcd (%) for $C_{37}H_{26}N_3BF_{24}$ (979.4): calcd. C 45.37, H 2.68, N 4.29, found C 45.20, H 2.72, N 4.35; IR (cm^{-1}): 449 (w), 669 (m), 709 (m), 837 (w), 885 (m), 1109 (vs), 1274 (vs), 1353 (s), 1415 (w), 1635 (m), 2210 (w), 2548 (vw).

6.4.3 Single-crystal X-ray structure determination

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II, CCD), a rotating anode (Bruker AXS, FR591) with MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator by using the SMART software package.^[30] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.^[31] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^[31] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX^[32] based on SIR-92.^[33] If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were refined as part of rigid rotating groups, with $C-H = 0.98 \text{ \AA}$ and $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic $C-H$ distances of 0.99 and 0.95 \AA , respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o - F_c)^2$ with SHELXL-97^[34] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.^[35] Images of the crystal structures were generated by PLATON.^[36] CCDC 956711 (**4a**), CCDC 956713 (**7a**), CCDC 956714 (**2b**) and CCDC 956712 (**5b**) contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or [via https://www.ccdc.cam.ac.uk/services/structure_deposit/](https://www.ccdc.cam.ac.uk/services/structure_deposit/)

Single crystal X-ray structure determination on compound 4a: Crystal data: formula: $C_{40}H_{36}BF_{20}P$; $M_r = 938.47$; crystal color and shape: colorless fragment, crystal dimensions: $0.48 \times 0.56 \times 0.61 \text{ mm}$; crystal system: orthorhombic; space group: $Pca2_1$ (no. 29); $a = 18.9591(7)$, $b = 22.2987(8)$, $c = 19.2449(7) \text{ \AA}$, $V = 8136.0(5) \text{ \AA}^3$, $Z = 8$, $\lambda (MoK_{\alpha}) = 0.71073$

Chapter 6

\AA , $\mu = 0.190 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.532 \text{ gcm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 3808$; θ -range = $0.91\text{--}25.40^\circ$; data collected: 231060; independent data [$I_o > 2\sigma(I_o)$ /all data/ R_{int}]: 14524/14933/0.036; data/restraints/parameter: 14933/1/1126; $R1$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0245/0.0257; $wR2$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0667/0.0682; GOF = 1.046; $\Delta\rho_{\text{max/min}}$: 0.27/-0.22 e\AA^{-3} . For detailed information see Appendix.

Single crystal X-ray structure determination on compound 7a: Crystal data: formula: $\text{C}_{29}\text{H}_{14}\text{BF}_{20}\text{N}_3$; $M_r = 795.24$; crystal color and shape: colorless fragment, crystal dimensions: $0.10 \times 0.25 \times 0.36 \text{ mm}$; crystal system: triclinic; space group: $P\bar{1}$ (no. 2); $a = 8.1571(2)$, $b = 12.7109(4)$, $c = 14.5597(4) \text{ \AA}$, $\alpha = 89.4091(12)^\circ$, $\beta = 83.9006(12)^\circ$, $\gamma = 81.7908(12)^\circ$, $V = 1485.66(7) \text{ \AA}^3$, $Z = 2$, $\lambda (\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 0.194 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.778 \text{ gcm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 788$; θ -range = $1.41\text{--}25.43^\circ$; data collected: 51233; independent data [$I_o > 2\sigma(I_o)$ /alldata/ R_{int}]: 5014/5423/0.039; data/restraints/parameter: 5423/0/534; $R1$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0296/0.0322; $wR2$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0778/0.0808; GOF = 1.031; $\Delta\rho_{\text{max/min}}$: 0.29/-0.19 e\AA^{-3} . For detailed information see Appendix.

Single crystal X-ray structure determination on compound 2b: Crystal data: formula: $\text{C}_{41}\text{H}_{29}\text{BF}_{24}\text{N}_2$; $M_r = 1016.47$; crystal color and shape: colorless block, crystal dimensions: $0.38 \times 0.51 \times 0.51 \text{ mm}$; crystal system: monoclinic; space group: $P2_1/c$ (no. 14); $a = 20.1391(5)$, $b = 13.9355(3)$, $c = 16.2559(4) \text{ \AA}$, $\beta = 111.2143(9)^\circ$, $V = 4253.03(18) \text{ \AA}^3$, $Z = 4$, $\lambda (\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 0.167 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.587 \text{ gcm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 2040$; θ -range = $1.82\text{--}25.50^\circ$; data collected: 133524; independent data [$I_o > 2\sigma(I_o)$ /all data/ R_{int}]: 6806/7872/0.019; data/restraints/parameter: 7872/0/785; $R1$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0396/0.0472; $wR2$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0937/0.1006; GOF = 1.020; $\Delta\rho_{\text{max/min}}$: 0.47/-0.43 e\AA^{-3} . For detailed information see Appendix.

Single crystal X-ray structure determination on compound 5b: Crystal data: formula: $\text{C}_{58}\text{H}_{68}\text{BF}_{24}\text{P}$; $M_r = 1262.90$; crystal color and shape: colorless fragment, crystal dimensions: $0.56 \times 0.59 \times 0.59 \text{ mm}$; crystal system: triclinic; space group: $P\bar{1}$ (no. 2); $a = 12.9732(4)$, $b = 14.0401(4)$, $c = 18.0389(5) \text{ \AA}$, $\alpha = 105.4144(14)^\circ$, $\beta = 97.8526(13)^\circ$, $\gamma = 97.5892(13)^\circ$, $V = 3088.64(16) \text{ \AA}^3$, $Z = 2$, $\lambda (\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 0.153 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.358 \text{ gcm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 1304$; θ -range = $1.19\text{--}25.43^\circ$; data collected: 95414; independent data [$I_o > 2\sigma(I_o)$ /all data/ R_{int}]: 10444/11372/0.030; data/restraints/parameter: 11372/0/845; $R1$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0363/0.0399; $wR2$ [$I_o > 2\sigma(I_o)$ /all data]: 0.0889/0.0929; GOF = 1.015; $\Delta\rho_{\text{max/min}}$: 0.53/-0.50 e\AA^{-3} . For detailed information see Appendix.

6.4.4 Catalysis studies

To a stirred solution of sulfide (2 mmol, 0.24 mL) in $[P_{4,4,4,14}][B(3,5-(CF_3)_2-C_6H_3)_4]$ (0.50 mL), an aqueous solution of hydrogen peroxide (30 % in water) (0.51 mL, 5 mmol) was added in 2 to 3 portions at room temperature. The progress of the reaction was followed by TLC. The reaction mixture was extracted with *n*-hexane/diethyl ether 2:1 v/v (5 × 5 mL) and the extract was dried over anhydrous $MgSO_4$. The crude product was obtained by rolling evaporation and purified by column chromatography separation (silica gel using *n*-hexane/ethyl acetate 90:10 v/v). The yield and selectivity of methyl phenyl sulfoxide in kinetic experiment and recycle experiment was calculated from calibration curves ($r^2 > 0.999$) recorded using 3-methylanisole and 1,4-diacetylbenzene as internal standard. The RTIL phase was diluted with CH_2Cl_2 and then treated with MnO_2 to destroy the excess peroxide. The obtained liquid was dried over anhydrous $MgSO_4$, and then dried for 4 h in vacuo at 50 °C to remove CH_2Cl_2 . Fresh substrate and hydrogen peroxide were then added for a new reaction cycle.

6.5 References

- [1] (a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; (b) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508; (c) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; (d) R. Sheldon, *Chem. Commun.* **2001**, 2399; (e) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667; (f) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123; (g) R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977; (h) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459.
- [2] (a) V. I. Pârulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615; (b) K. Binnemans, *Chem. Rev.* **2007**, *107*, 2592; (c) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206; (d) M. A. P. Martins, C. P. Frizzo, D. N. Moreira, N. Zanatta, H. G. Bonaccorso, *Chem. Rev.* **2007**, *107*, 2592;
- [3] (a) R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834; (b) S. G. Lee, *Chem. Commun.* **2006**, 1049; (c) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; (d) J. T. Tindale, K. D. Hartlen, A. Alizadeh, M. S. Workentin, P. J. Ragoon, *Chem. Eur. J.* **2010**, *16*, 9068; (e) A. Ouadi, B. Gadenne, P. Hesemann, J. J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, *Chem. Eur. J.* **2006**, *12*, 3704; (f) T. Inagaki, T. Mochida, M. Takahashi, C. Kanadan, T. Saito, D. Kawahara, *Chem. Eur. J.* **2012**, *18*, 6795; (g) Z. R. Fei, T. J. Geldbach, D. B. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *8*, 156.

- [4] I. Krossing, J. M. Slattery, C. Daguinet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427; (b) P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238; (c) I. J. B. Lin, C. S. Vasam, *J. Organometal. Chem.* **2005**, *690*, 3498; (d) Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619.
- [5] (a) I. Krossing, J. M. Slattery, C. Daguinet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427; (b) U. Preiss, J. M. Slattery, I. Krossing, *Ind. Eng. Chem. Res.* **2009**, *48*, 2290; (c) J. M. Slattery, C. Daguinet, P. J. Dyson, T. J. S. Schubert, I. Krossing, *Angew. Chem. Int. Ed.* **2007**, *46*, 5384.
- [6] (a) I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066; (b) K. Dong, S. Zhang, *Chem. Eur. J.* **2012**, *18*, 2748; (c) A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, K. A. Johnson, *J. Am. Chem. Soc.* **2005**, *127*, 16792; (d) A. R. Choudhury, T. N. G. Row, *CrystEngComm.* **2006**, *8*, 265; (e) W. M. Reichert, J. D. Holbery, R. P. Swatloski, K. E. Gutowski, A. E. Visser, M. Nieuwenhuyzen, K. R. Seddon, R. D. Rogers, *Crystal Growth&Design.* **2007**, *7*, 1106; (f) J. D. Holbrey, W. M. Reichert, R. D. Rogers, *Dalton Trans.* **2004**, 2267; (g) K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2008**, *47*, 3830; (h) R. P. Swatloski, J. D. Holbrey, R. D. Rogers, *Green Chem.* **2003**, *5*, 361; (i) C. Roth, T. Peppel, K. Fumino, M. Köckerling, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 10221.
- [7] (a) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927; (b) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133.
- [8] (a) A. Bösmann, G. Francio, E. Janssen, W. Leitner, P. Wasserscheid, *Angew. Chem. Int. Ed.* **2001**, *40*, 2697; (b) A. Reisinger, I. Krossing, *Coord. Chem. Rev.* **2006**, *250*, 2721; (c) I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. S. Quiñones, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 1966; (d) T. Timofte, S. Pitula, A. V. Mudring, **2007**, *46*, 10938.
- [9] (a) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* **2004**, *10*, 6581; (b) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, *33*, 680; (c) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, *33*, 1636; (d) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, *33*, 886; (e) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* **2005**, *11*, 752; (f) H. Matsumoto, Z. B. Zhou, H. Sakaebe, K. Tatsami, *Electrochemistry.* **2005**, *73*, 633; (g) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *ChemPhysChem.* **2005**, *6*, 1324.
- [10] (a) A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7264; (b) J. Dymon, R. Wibby, J. Kleingardner, J. M. Tanski, I. A. Guzei, J. D. Holbrey, A. S. Larsen, *Dalton Trans.* **2008**, 2999; (d) M. Bürchner, A. M. T. Erle, H. Scherer, I. Krossing, *Chem. Eur. J.* **2012**, *18*, 2254.

- [11](a) A. R. Katritzky, S. Singh, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert, S. K. Spear, R. D. Rogers, *Chem. Eur. J.* **2006**, *12*, 4630; (b) M. Smiglak, C. C. Hines, T. B. Wilson, S. Singh, A. S. Vincek, K. Kirichenko, A. R. Katritzky, R. D. Rogers, *Chem. Eur. J.* **2011**, *16*, 1572.
- [12](a) M. Finze, E. Bernhardt, H. Willner, *Angew. Chem. Int. Ed.* **2007**, *46*, 9180; (b) P. Jutzi, C. Müller, A. Stämmler, H. G. Stämmler, *Organometallics* **2000**, *19*, 1442.
- [13](a) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391; (b) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325; (c) R. E. LaPointe, G. P. Roof, K. A. Abboud, J. Klosin, *J. Am. Chem. Soc.* **2000**, *122*, 9560; (d) S. J. Lancaster, D. A. Walker, M. Thornton-Pett, M. Bochmann, *Chem. Commun.* **1999**, 1533.
- [14] S. F. Rach, F. E. Kühn, *Chem. Rev.* **2009**, *109*, 2061.
- [15] Y. Zhang, A. M. Santos, E. Herdtweck, J. Mink, F. E. Kühn, *New. J. Chem.* **2005**, *29*, 366.
- [16](a) M. Vierle, Y. Zhang, E. Herdtweck, Martin Bohnenpoll, O. Nuyken, F. E. Kühn, *Angew. Chem. Int. Ed.* **2003**, *42*, 1307; (b) A. K. Hijazi, A. Al Hmaideen, S. Syukri, N. Radhakrishnan, E. Herdtweck, B. Voit, F. E. Kühn, *Eur. J. Inorg. Chem.* **2008**, 2892; (c) M. Vierle, Y. Zhang, A. M. Santos, K. Köhler, C. Häßner, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F. E. Kühn, *Chem. Eur. J.* **2004**, *10*, 6323; (d) A. K. Hijazi, H. Y. Yeong, Y. Zhang, E. Herdtweck, O. Nuyken, F. E. Kühn, *Macromol. Rapid. Commun.* **2007**, *28*, 670; (e) Y. Li, L. T. Voon, H. Y. Yeong, A. K. Hijazi, N. Radhakrishnan, K. Köhler, B. Voit, O. Nuyken, Köhler, *Chem. Eur. J.* **2008**, *14*, 7997; (f) Y. Zhang, W. Sun, A. M. Santos, F. E. Kühn, *Catal. Lett.* **2005**, *101*, 35.
- [17] J. L. Manson, W. E. Buschmann, J. S. Miller, *Angew. Chem. Int. Ed.* **1998**, *37*, 783.
- [18](a) I. V. Babich, J. A. Moulijn, *A. Fuel* **2003**, *82*, 607; (b) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315; (c) B. Zhang, M. D. Zhou, M. Cokoja, J. Mink, S. L. Zang, F. E. Kühn, *RSC adv.* **2012**, *2*, 8416; (d) F. Brebion, B. Delouvrie, F. Najera, L. Fensterbank, M. Malacria, J. Vaissermann, *Angew. Chem. Int. Ed.* **2003**, *42*, 5342; (e) M. S. Chen, M. C. White, *J. Am. Chem. Soc.* **2004**, *126*, 1346.
- [19] B. Zhang, M. Köberl, A. Pöthig, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Z. Naturforsch. B: J. Chem. Sci.* **2012**, *67*, 1030.
- [20] E. Martin, D. L. Hughes, S. J. Lancaster, *Inorg. Chim. Acta* **2010**, *363*, 275.
- [21] F. Schödel, H. W. Lerner, M. B. Roig, M. Bolte, *Acta Cryst.* **2006**, *E62*, 372.
- [22] A. R. Katritzky, S. Singh, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert, S. K. Spear, R. D. Rogers, *Chem. Eur. J.* **2006**, *12*, 4630.
- [23] J. Dymon, R. Wibby, J. Kleingardner, J. M. Tanski, I. A. Guzer, J. D. Holbrey, A. S.

- Larsen, *Dalton Trans.* **2008**, 2999.
- [24](a) T. Peppel, C. Roth, K. Fumino, D. Paschek, M. Möckerling, R. Ludwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 6661; (b) K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2009**, *48*, 3184; (c) A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 449.
- [25](a) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315; (b) J. Drabowicz, M. Mikolajczyk, *Synth. Commun.* **1981**, *11*, 1025.
- [26](a) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315; (b) J. Drabowicz, M. Mikolajczyk, *Synth. Commun.* **1981**, *11*, 1025; (c) W. L. Xu, Y. Z. Li, Q. S. Zhang, H. S. Zhu, *Synthesis* **2004**, 227.
- [27] V. Hulea, P. Mordau, F. D. Renzo, *J. Mol. Catal. A: Chem.* **1996**, *111*, 325.
- [28] K. S. Ravikumar, F. Barbier, J. P. Bégué, D. B. Delpon, *J. Fluorine Chem.* **1999**, *95*, 123.
- [29](a) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667; (b) J. W. Wiench, C. Michon, A. Ellern, P. Hazendonk, A. Luga, R. J. Angelici, M. Pruski, *J. Am. Soc. Chem.* **2009**, *131*, 11801; (c) C. Wamser, *J. Am. Soc. Chem.* **1951**, *73*, 409; (d) I. Bányai, V. Conte, L. Pettersson, A. Silvagni, *Eur. J. Inorg. Chem.* **2008**, 5373; (e) K. Kwon, J. Park, C. K. Lee, H. Kim, *Int. J. Electrochem. Sci.* **2012**, *7*, 9835.
- [30](a) Y. S. Li, R. A. Larsen, F. O. Cox, J. R. Durig, *J. Raman Spectrosc.* **1989**, *20*, 1; (b) J. Mihály, S. Sterkel, H. M. Ortner, L. Kocsis, L. Hajba, É. Furdyga, J. Mink, *Croat. Chem. Acta.* **2006**, *79*, 497; (c) S. Eltayeb, G. A. Guirgis, A. R. Fanning, J. R. Durig, *J. Raman Spectrosc.* **1996**, *27*, 111; (d) J. Murto, A. Kivinen, K. Kajander, J. Hyömmäki, J. K. Tommola, *Acta Chem. Scand.* **1973**, *27*, 96; (e) B. C. Matuszewicz, S. Pilorz, D. Bieńko, D. Michalska, *Vibrational Spectroscopy* **2008**, *47*, 44; (f) J. F. Kang, A. Ulman, R. Jordan, *Langmuir* **1999**, *15*, 5555; (g) U. Lappan, U. Geißler, U. Scheler, K. Lunckwitz, *Radiation. Physics and Chem.* **2003**, *67*, 447; (h) W. Grochala, M. K. Cytański, M. Derzsl. T. Michalowski, P. J. Malinowski, Z. Mazej, D. Kurzydłowski, W. Koźmiński, A. Budzianowski, P. J. Leszyński, *Dalton. Trans.* **2012**, *41*, 2034; (i) N. P. G. Roeges, *A guide to the complex interpretation of infrared spectra of organic structures*, Wiley Chichester, **1994**, 29.
- [31] APEX suite of crystallographic software. APEX 2 Version 2008. 4. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [32] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [33] L. J. Farrugia, "WinGX (Version 1.70.01 January 2005)", *J. Appl. Cryst.* **1999**, *32*, 837.
- [34] Altomare, A.; Casciarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.;

Chapter 6

Camalli M. "SIR92", *J. Appl. Cryst.* **1994**, 27, 435-436.

[35] Sheldrick, G. M. "SHELXL-97", University of Göttingen, Göttingen, Germany, (**1998**).

[36] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**.

[37] Spek, A. L. "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (**2010**).

7 Oxidation reactions catalyzed by polyoxomolybdate salts

This chapter originated from the following publication:

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7.1 Introduction

Polyoxometalates (POMs) are an important and structurally diverse class of inorganic metal oxide clusters,^[1] which are not only used as inorganic components for novel materials, but also recognized as “green” industrial catalysts.^[2-3] Recently, ionic liquids (ILs) have received enormous attention in both academic and industrial research due to their unique physicochemical properties and the resulting applicability in various fields.^[4-10] We and others have shown that certain anions exhibit an increased (catalytic) activity in ionic liquid media.^[11-14] The concept of combining POM anions with “weakly coordinating cations” (WCC), such as those typically used for ionic liquids (tetraalkyl-ammonium and -phosphonium, -pyridinium, -imidazolium and others), is thus regarded as a feasible way to increase the reactivity of POMs in ionic liquids. So far, some examples of WCC-POM compounds (e. g. [Bmim]₃[PW₁₂O₄₀] (Bmim = 1-butyl-3-methylimidazolium), [Bmim]₄[SiM₁₂O₄₀] and [Bmim]₄[S₂M₁₈O₆₂] (M = Mo, W), [(n-C₄H₉)N]₄[Mo₈O₂₆] and [(n-C₄H₉)N]₂[W₆O₁₉]) have been described and mainly used as electrochemicals.^[15-20] However, only few POM salts have been investigated as catalysts. For example, the Keggin-type POM anion [PW₁₂O₄₀]³⁻ can be used as catalyst for esterification^[21] and for epoxidation reactions in ionic liquids.^[22] The compound [(n-C₄H₉)N]₂[W₆O₁₉] was found to be a catalyst for the synthesis of biscoumarins, which was investigated by Davoodna.^[23] From these results it appears that tungsten-based WCC-POMs can exhibit excellent catalytic performance because of controllable redox and acidic properties,^[24-26] which make them economical and environmentally acceptable. In contrast to tungsten-based WCC-POMs, which were widely used as catalysts for oxidation reactions, molybdenum-based congeners, such as the Lindqvist-type POM [Mo₆O₁₉]²⁻, are rather rare and have not been often used in

oxidation catalysis so far. The findings of our previous report on the catalytic oxidation of sulfides to sulfoxides using imidazolium tetrafluoroborate- and perrhenate-based ionic liquids using H_2O_2 ^[11-14] prompted us to investigate the catalytic properties of Mo-based WCC-POMs for the epoxidation of olefins and the selective oxidation of sulfides to sulfoxides.

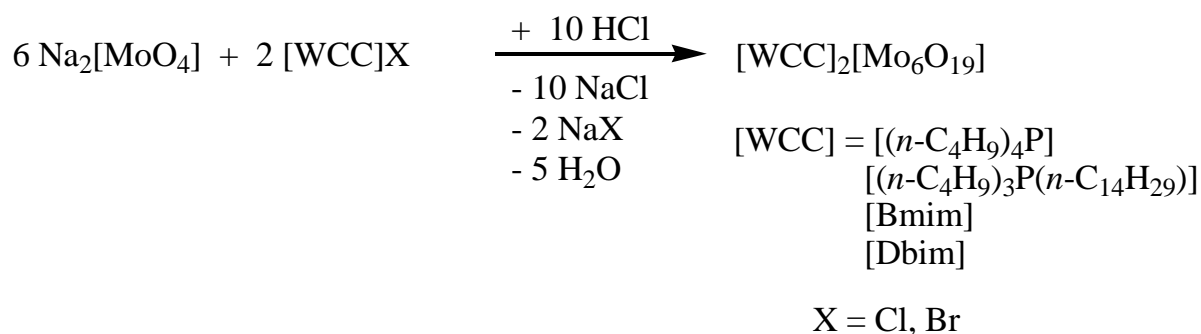
The catalytic olefin epoxidation is of high importance in the chemical industry and also valuable for the synthesis of fine chemicals such as pharmaceuticals, flavor and fragrance components.^[27-30] A vast number of coordination compounds have been applied as catalysts for this type of reaction.^[31-33] However, the typical molecular transition metal catalysts are too expensive for a broad use and for upscaling, so that cheaper and recyclable catalysts are required. Organic sulfoxides are also important synthetic intermediates for the synthesis of various chemically and biologically active molecules.^[34-36] Numerous reports on the oxidation of sulfides to sulfoxides using homogeneous transition metal catalysts in organic solvents have been published to date.^[37-45] However, in most cases, the synthesis protocols involved formation of environmentally unfavorable byproducts, and the catalysts are rather difficult to recycle and to separate from the products. We have now found that WCC-POMs not only overcome the above mentioned drawbacks, but also can be confirmed as a good catalyst for oxidation reactions.

In this work, we present the synthesis and characterization of a series of WCC-POMs containing tetrabutylphosphonium, tributyl (tetradecyl) phosphonium, 1-butyl-3-methylimidazolium and 1,2-dimethyl-3-butyl-imidazolium cations along with the $[\text{Mo}_6\text{O}_{19}]$ dianion, including three X-ray single-crystal structure determinations. The WCC-POMs show high stability and selectivity for epoxidation of olefins with anhydrous urea hydrogen peroxide (UHP) as oxidant in the ionic liquid $[\text{Bmim}]\text{PF}_6$. Additionally, a highly efficient method for selective oxidation of a series of sulfides to produce the corresponding sulfoxides in excellent yield using aqueous hydrogen peroxide as oxidant and WCC-POMs as catalyst under mild reaction conditions was also investigated. The WCC-POMs can be reused several times without significant loss of activity.

7.2 Results and discussion

7.2.1 Synthesis of WCC-POMs

The WCC-[Mo₆O₁₉]²⁻ salts with [(*n*-C₄H₉)₄P]⁺, [(*n*-C₄H₉)₃P(*n*-C₁₄H₂₉)]⁺, [Bmim]⁺ and [Dbim]⁺ cations were prepared by a modified literature procedure, which involves acid condensation in aqueous solution followed by addition of the precipitating cation (see Scheme 1).^[46-48] The success of the synthesis of WCC-POMs strongly depends on the pH of the reaction solution, the solvent and the temperature. The byproduct (sodium halide) can easily be removed by extraction with water. Recrystallization was performed from acetonitrile. More detailed procedures are given in the Experimental Section. All synthesized WCC-POMs are very stable and can be handled in air. They are highly soluble in CH₃CN, but insoluble in water and methanol.



Scheme 1. Synthesis of the WCC-POMs

7.2.2 Characterization of the WCC-POMs

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and IR spectroscopy data of compounds **1-4** are given in Table 1. TGA indicates that all compounds show negligible volatility and high thermal stability with a decomposition temperature near 300 °C. [(*n*-C₄H₉)₃P(*n*-C₁₄H₂₉)]₂[Mo₆O₁₉] (**2**) is the only compound having a melting point below 100 °C (68 °C). The melting points of [(*n*-C₄H₉)₄P]₂[Mo₆O₁₉] (**1**), [Bmim]₂[Mo₆O₁₉] (**3**) and [Dbim]₂[Mo₆O₁₉] (**4**) are 196, 128 and 193 °C, respectively. Notably, the melting points of the phosphonium salts **1** and **2** decrease with increasing alkyl chain length from butyl to tetradecyl. The lower degree of crystal packing and long-range order, caused by the long alkyl chain in **2**, is most presumably the reason for the significantly different melting points of compounds **1** and **2**. The different melting points of compounds **3** and **4** are a consequence of the substitution of a proton in the 2-position of the imidazolium ring by a methyl group. A

comparison of the structures of compounds **3** and **4** via Hirshfeld surface analysis^[49-50] revealed that in compound **4**, the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anions form more attractive contacts to the cations than in compound **3** (see chapter 11 Appendix). Furthermore, the degree of hydrogen-oxygen interactions in **4** is also higher, hence leading to a higher melting point.

Table 1. Melting points (T_m), decomposition temperatures (T_d) and IR data of compounds **1-4**.

Compound	T_m ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)	IR (cm^{-1})			
1	196	341	949	920	791	720
2	68	338	950	914	785	718
3	128	290	961	908	801	741
4	193	293	948	902	787	754

IR spectroscopy was used to identify the structure of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion. In the region of $700\text{--}1100\text{ cm}^{-1}$, four characteristic bands at around 960 and 790 cm^{-1} are ascribed to $\nu(\text{Mo}\text{--}\text{O}_t)$ and $\nu(\text{Mo}\text{--}\text{O}_b\text{--}\text{Mo})$ modes of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion (O_t and O_b mark terminal and bridging oxo ligands, respectively).^[18,51-53]

7.2.3 Crystal structures of WCC-POMs

Crystals of the new compounds **1**, **3** and **4** were grown by slow evaporation of an acetonitrile solution at room temperature. Unfortunately, we were so far not able to obtain crystals of compound **2** of a quality which is suitable for single-crystal X-ray diffraction. The structures of compounds **1**, **3** and **4** reveal that the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion consists of six distorted MoO_6 octahedra, which are connected by edges and a common vertex (Figure 1).^[54-56] There are three types of oxygen atoms in the anion (terminal oxygen O_t , μ_2 -bridging oxygen O_b , and central oxygen O_c). Thus, the Mo–O bond lengths can be grouped into three sets (Table 2). Interestingly, the bond lengths of Mo– O_b ($1.8740(2)\text{--}1.967(1)\text{ \AA}$) for **4** are longer than in the WCC-POMs **1** ($1.868(1)\text{--}2.002(1)\text{ \AA}$) and **3** ($1.862(2)\text{--}2.015(2)\text{ \AA}$), but the bond lengths of Mo– O_t and Mo– O_c are similar. Further, a number of charge-assisted hydrogen bonds $\text{CH}\dots\text{O}$ exist between the cation $-\text{CH}_n$ functions and the anion oxygen atoms of $[\text{Mo}_6\text{O}_{19}]^{2-}$ (Figure 1).

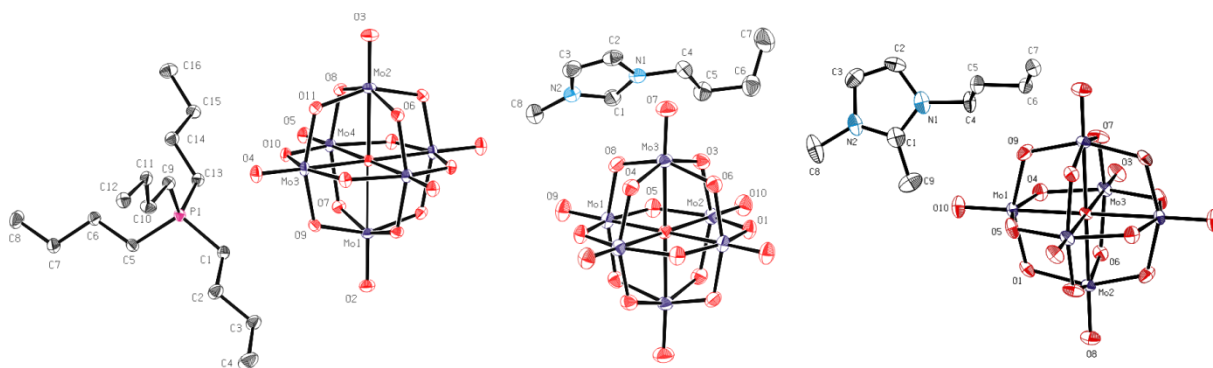


Figure 1. ORTEP views of $[(n\text{-C}_4\text{H}_9)_4\text{P}]_2[\text{Mo}_6\text{O}_{19}]$ (**1**) (left, symmetry code: (a) $-x, y, \frac{1}{2} - z$), $[\text{Bmim}]_2[\text{Mo}_6\text{O}_{19}]$ (**3**) (middle, symmetry code: (a) $-x, y + \frac{1}{2}, \frac{1}{2} - z$) and $[\text{Dbim}]_2[\text{Mo}_6\text{O}_{19}]$ (**4**) (right, symmetry code: (a) $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$) showing vibrational ellipsoids at the 50 % probability level. H atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) of **1**, **3** and **4**.

	1	3	4
Mo-O _t	1.672(2)-1.688(1)	1.678(2)-1.68(2)	1.6780(3)-1.686(1)
Mo-O _b	1.868(1)-2.002(1)	1.862(2)-2.015(2)	1.8740(2)-1.967(1)
Mo-O _c	2.313(2)-2.319(1)	2.318(1)-2.329(1)	2.3157(3)-2.324(1)

Each polyoxoanion is surrounded by $[(n\text{-C}_4\text{H}_9)_4\text{P}]^+$, $[\text{Bmim}]^+$ or $[\text{Dbim}]^+$ cations, respectively, exhibiting H...O distances in the range of 2.254 to 2.680 (Å) for **1**, 2.493 to 2.665 (Å) for **3** and 2.358 to 2.680 (Å) for **4**, which indicate interactions between the polyoxoanions and cations *via* Coulomb forces and CH...O hydrogen bonds. For compound **1**, contacts between the CH₂ and CH₃ groups of the butyl moieties and the O(O_t, O_b) atoms of $[\text{Mo}_6\text{O}_{19}]^{2-}$ can be observed. Compounds **3** and **4** also exhibit contacts between the anion and the imidazolium ring hydrogen atoms and the alkyl substituents of the cation.

7.2.4 Catalytic epoxidation of olefins

Compounds **1-4** were examined as catalysts for the epoxidation of *cis*-cyclooctene. The organic and ionic liquid solvents, as well as the oxidants were varied in order to determine the optimal reaction conditions (Table 3). The epoxide yield was indeed found to be strongly dependent on these parameters. Noteworthy, the (usually undesired) byproduct 1,2-cyclooctane diol was not found in the entire set of experiments. The observed conversion was very low (< 30 %) with CH₃CN and $[\text{Bmim}]\text{BF}_4$ as solvents (entries 1-2 and 4-6). On the other hand, when the reaction was carried out in methanol and in the ionic liquids $[\text{Bmim}]\text{PF}_6$ and $[\text{Bmim}]\text{NTf}_2$ ($\text{NTf}_2 = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$) as solvents, the epoxide yield was significantly higher (entries 3, 7-9 and 11-13). The nature of the oxidant also plays a crucial role in the reaction. Three different oxidants (aqueous H₂O₂, *tert*-butyl hydroperoxide (TBHP) in *n*-decane and urea-hydrogen peroxide (UHP)) were examined under the same

conditions. From the results shown in Table 3, entries 7-13, it can be stated that a) aqueous hydrogen peroxide solutions inhibit the catalytic reaction to some extent, and b) UHP is superior to both TBHP and H₂O₂. Obviously, the olefin conversion significantly depends on the content of water in the solution. The catalytic reaction in ionic liquid [Bmim]PF₆ with UHP exhibited both a high yield of 89 % and a selectivity of > 99 % within 4 h (entry 9). Therefore, the usage of water-free UHP is crucial for successful epoxidation. Furthermore, in the blank experiments, no reaction occurred in the absence of oxidant UHP, indicating that the oxygen source of epoxides is not air (entry 10). Epoxidation of *cis*-cyclooctene at different temperatures was investigated as well. The reaction conditions were the same as those of entry 9 in Table 3.

Table 3. Epoxidation of *cis*-cyclooctene in different oxidants and solvents at 60 °C using WCC-POM **1** as catalyst.^a

Entry	Solvent	Oxidant	Conv. (%) ^b	Yield (%) ^c
1	CH ₃ CN	H ₂ O ₂ (35 %)	29	29
2	CH ₃ CN	TBHP	30	30
3	MeOH	H ₂ O ₂ (35 %)	70	70
4	[Bmim]BF ₄	H ₂ O ₂ (35 %)	17	17
5	[Bmim]BF ₄	TBHP	9	9
6	[Bmim]BF ₄	UHP	9	9
7	[Bmim]PF ₆	H ₂ O ₂ (35 %)	49	49
8	[Bmim]PF ₆	TBHP	69	69
9	[Bmim]PF₆	UHP	89	89
10	[Bmim]PF ₆	----	----	----
11	[Bmim]NTf ₂	H ₂ O ₂ (35 %)	54	54
12	[Bmim]NTf ₂	TBHP	56	56
13	[Bmim]NTf ₂	UHP	63	63

^a Reaction conditions: *cis*-cyclooctene (2 mmol), catalyst **1** (1 mol %), oxidant (4 mmol), solvent (1 mL), 60 °C, t = 4 h;

^b The conversion to cyclooctene oxide was determined by GC analysis;

^c The yield was determined by GC analysis.

As indicated in Figure 2, a lower temperature was disadvantageous to the oxidation reaction. The yield was only 69 % within 4 h, and 72 % after 24 h at 50 °C. Because of the high yield (93 % within 4 h, 97 % after 24 h) at 70 °C, we chose 70 °C as reaction temperature for further experiments.

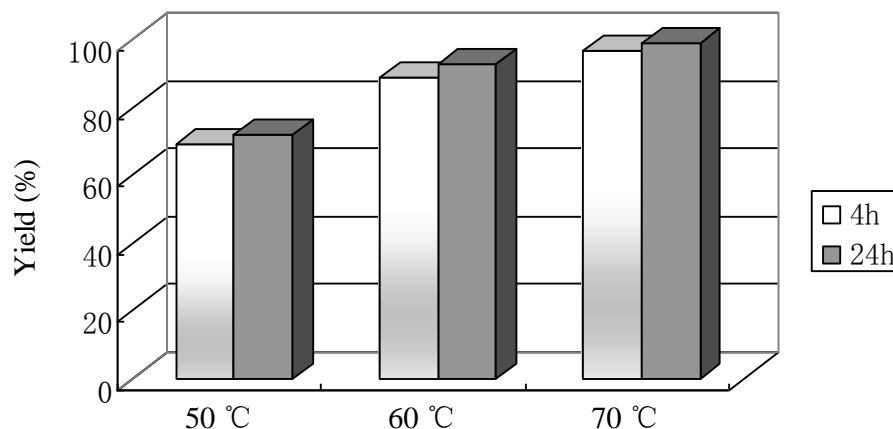


Figure 2. Effect of temperature and reaction time for the catalytic epoxidation of *cis*-cyclooctene with compound **1** as catalyst. Reaction conditions: *cis*-cyclooctene (2 mmol), catalyst **1** (1 mol %), UHP (4 mmol), [Bmim]PF₆ (1 mL).

Subsequently, in a comparative study the other synthesized WCC-POMs **2-4** were also used as catalysts in the epoxidation of *cis*-cyclooctene with UHP at 70 °C for 2 h. The results are shown in Table 4. Compound **3** exhibits the highest reactivity and conversion for the epoxidation of *cis*-cyclooctene (entry 3), most presumably due to the highest solubility in [Bmim]PF₆ at 70 °C. The other catalysts **1**, **2** and **4** also exhibited good results and the yields were 93 %, 90 % and 94 %, respectively (entries 1-2, 4).

Table 4. Epoxidation of *cis*-cyclooctene with different catalysts in [Bmim]PF₆ at 70 °C.^a

Entry	Catalyst	Conv. (%) ^b	Yield (%) ^c	TOF (h ⁻¹) ^d
1	1	93	93	47
2	2	90	90	45
3	3	97	97	49
4	4	94	94	47

^a Reaction conditions: *cis*-cyclooctene (2 mmol), catalyst (1 mol %), UHP (4 mmol), [Bmim]PF₆ (1 mL), 70 °C, t = 2 h;

^b The conversion is determined by GC analysis;

^c The yield is determined by GC analysis;

^d Determined after 2 h reaction time.

WCC-POM catalyst recycling was studied as well. First, the product was extracted with *n*-hexane and the ionic liquid phase containing the catalyst was washed with water to remove urea ([Bmim]PF₆ and WCC-POMs are insoluble in water). The IL was then dried in high vacuum and used for the next catalytic run. The WCC-POMs remained active for at least three catalytic runs. However, a slight decrease of conversion and yield was observed (Figure 3). Most presumably, this is resulting from the workup procedure, since the IL-catalyst solution is washed several times with *n*-hexane and there after with water. Hence, it is reasonable to assume that phase separation and subsequent decantation of the *n*-hexane and water phase

might have led to unintentional extraction of small amounts of the IL.

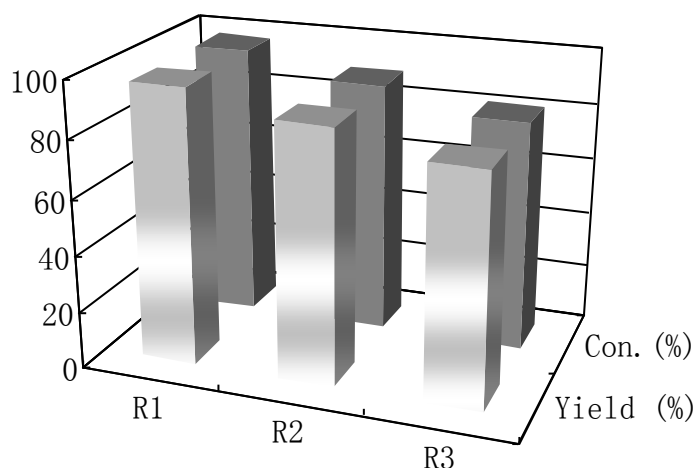
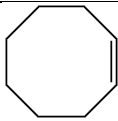
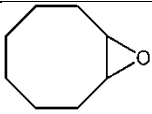
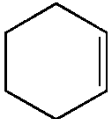
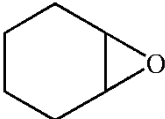
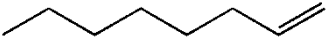
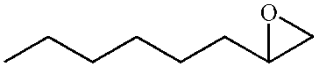
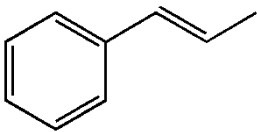
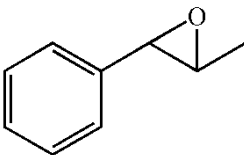
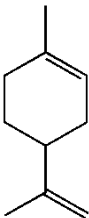
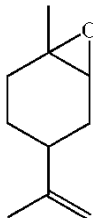
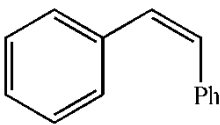
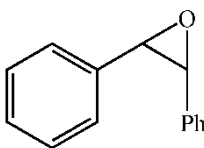
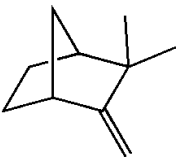
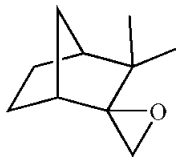


Figure 3. Recycling studies of the IL-catalyst mixture for the epoxidation of *cis*-cyclooctene.

Catalyst **3** was applied for the epoxidation of various olefins with UHP as oxidant (Table 5). Cyclohexene was readily epoxidized into the epoxide within 1.5 h with 88 % yield (entry 2). Only moderate conversion (46 %) was observed for 1-octene (entry 3), which is less prone to epoxidation than *cis*-cyclooctene. The epoxidations of *trans*- β -methylstyrene (entry 4), limonene (entry 5), *cis*-stilbene (entry 6) and (+)-camphene (entry 7) were rather challenging due to steric hindrance (26 % after 3 h, 24 % after 7 h, 25 % after 4 h, 9 % after 8 h, respectively). The turnover frequencies (TOFs) are in the range of 16-182 h⁻¹. It is noteworthy that no diol is detected during the course of all investigated reactions.

Table 5. Epoxidation of olefins with UHP catalyzed by **3** at 70 °C.^a

Entry	Substrate	Product	Time (h)	Conv. (%) ^b	Yield (%) ^c	TOF (h ⁻¹) ^d
1			2	97	97	148
2			1.5	88	88	182
3			4	46	46	30
4			3	26	26	48
5			7	24	24	16
6			4	25	25	32
7			8	9	9	---

^a Reaction conditions: *cis*-cyclooctene (2 mmol), **3** (1 mol %), UHP (4 mmol), [Bmim]PF₆ (1 mL), 70 °C;

^b The conversion is determined by GC analysis;

^c The yield is determined by GC analysis;

^d Determined after 15 min reaction time.

7.2.5 Selective catalytic oxidation of sulfides to sulfoxides

We investigated the oxidation reaction of thioanisole as model substrate in different oxidants and solvents. The results are presented in Table 6 and showed that the reaction was sensitive to the solvent. When using *n*-hexane (entry 1), CH₂Cl₂ (entry 2) and water (entry 4) as solvents, very low conversions and yields were obtained due to the poor solubility of the catalyst in these solvents. When the reaction was carried out in acetonitrile (entry 3), high conversion (97 %) and yield (82 %) were obtained within 40 min, but the selectivity of sulfoxide was relatively lower than when using methanol, which was found to be a more efficient reaction medium (95 % yield, 97 % conversion, entry 5). Note that methanol itself

can act as catalyst of the oxidation of thioanisole.^[57-59] However, the reaction time is usually significantly longer (18 h), whereas in our experiments using catalyst **3** as catalyst in methanol, high conversion (97 %) was obtained after 40 min (entry 5). In the blank experiment, the conversion was only 41 % without any catalyst (entry 9).

Table 6. Oxidation of thioanisole with different oxidants in different solvents at 25 °C.^a

Entry	Solvent	Oxidant	Time (h)	Conv. (%) ^b	Yield (%) ^c
1	<i>n</i> -hexane	H ₂ O ₂ (35 %)	4	82	57
2	CH ₂ Cl ₂	H ₂ O ₂ (35 %)	4	16	14
3	CH ₃ CN	H ₂ O ₂ (35 %)	0.67	97	82
4	H ₂ O	H ₂ O ₂ (35 %)	4	80	67
5	MeOH	H₂O₂ (35 %)	0.67	97	95
6	MeOH	TBHP	3	73	71
7	MeOH	-----	24	28	27
8	-----	H ₂ O ₂ (35 %)	4	93	46
9	MeOH	H ₂ O ₂ (35 %)	8	52 ^d	41

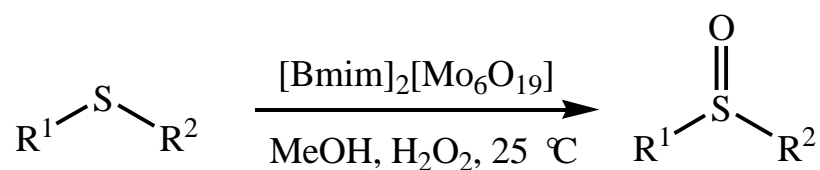
^a Reaction conditions: thioanisole (2 mmol), **3** (1 mol %), H₂O₂ (35 %, 2.1 mmol), solvent (1 mL) 25 °C;

^b Determined by GC on the crude reaction mixture;

^c Isolated yield after column chromatography.

Thus, it can safely be concluded that methanol is not catalyzing the oxidation in our case. The absence of oxidant leads to a significant decrease of conversion (28 %, entry 7). An obvious decrease of oxidation activity was observed by adding TBHP as oxidant (entry 6). The yield decreased to 46 % after 4 h without any solvent (entry 8).

In an effort to establish the scope of our protocol, a series of sulfides with different substituents were used (Scheme 2) in methanol. All oxidation reactions were performed under the same conditions (Table 7) and showed nearly quantitative conversions within a very short time (< 3 h). The sulfoxides were obtained in very good selectivities (> 80 %), as well as TOFs were in the range of 165-380 h⁻¹.



Scheme 2. Oxidation of sulfides to sulfoxides with aqueous hydrogen peroxide as oxidant and [Bmim]₂[Mo₆O₁₉] (**3**) as catalyst in methanol.

Interestingly, sulfides with methyl groups (entry 1) were found to be more easily oxidized within short time (ca. 30 min) compared to other substrates with bulky substituents, indicating that the steric hindrance is an important factor for the oxidation reaction. It was a significant observation that functional groups such as allyl (entry 6), hydroxo (entry 7) and ester moieties (entry 9) were not affected in this oxidation procedure. Noteworthy, the WCC-POM catalyst **3** was very easily recovered by filtration when the reaction was completed. Therefore, the

WCC-POMs-H₂O₂ system offered a facile, rapid, highly selective method to obtain sulfoxides.

Table 7. Oxidation of sulfides to sulfoxides with H₂O₂ as oxidant and **3** as catalyst in MeOH.^a

Entry	R ¹	R ²	Time (min)	Conv. (%) ^b	Yield (%) ^c	TOF (h ⁻¹) ^d
1	Me	Me	30	96	95	190 ^e
2	<i>n</i> -Bu	<i>n</i> -Bu	40	96	94	141
3	Ph	Me	40	97	95	143
4	Ph	Et	40	93	92	138
5	Ph	CH(CH ₃) ₂	40	95	94	141
6	Ph	CH ₂ -CH=CH ₂	40	95	93	138
7	Ph	CH ₂ CH ₂ OH	45	90	87	125
8	Ph	CH ₂ OMe	60	88	87	120
9	Ph	CH ₂ COOMe	70	87	86	140
10	Ph	Ph	150	93	83	83
11	Ph	Bz ^f	70	90	85	98
12	Bz	Bz	60	89	86	110

^a Reaction conditions: thioanisole (2 mmol), **3** (1 mol %), H₂O₂ (35 %, 2.1 mmol), MeOH (1 mL) at 25 °C;

^b Determined by GC or ¹H - NMR on the crude reaction mixture;

^c Isolated yield after column chromatography;

^d TOFs of the catalyst were calculated over 40 min;

^e TOFs of the catalyst were calculated over 30 min;

^f Bz = benzyl.

The reusability of the catalyst WCC-POMs for oxidation of sulfides to sulfoxides was also studied. After the oxidation of thioanisole using **3** as catalyst was completed, ethyl acetate was added to the reaction mixture and the catalyst was precipitated, filtered, washed with ethyl acetate, and dried in vacuum at room temperature. Five catalytic runs were carried out and the results are shown in Figure 4. It has to be noted that no significant loss of conversion and yield was observed after five runs, indicating a rather steady reusability of the WCC-POM catalyst. In comparison to the recycling of the IL-catalyst mixture for the epoxidation of olefins, in this case the catalyst precipitation is a more convenient method to recover the catalyst without a loss after each cycle.

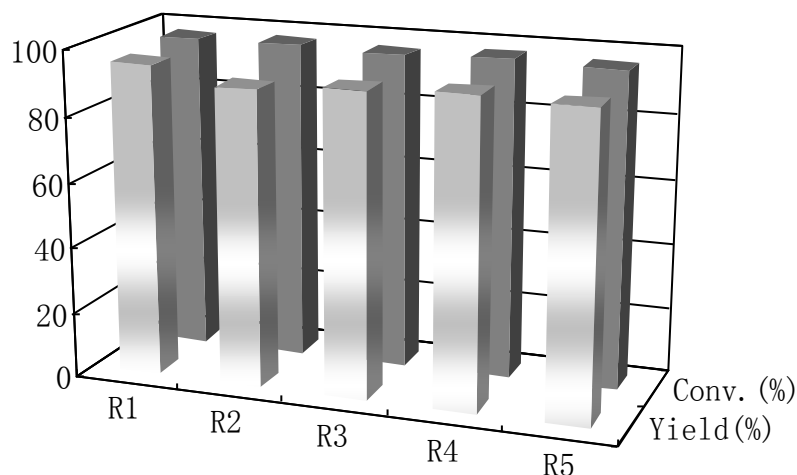


Figure 4. Recycling of the catalyst **3** in the oxidation of thioanisole with H_2O_2 .

7.3 Conclusion

The epoxidation of olefins and oxidation of sulfides to sulfoxides catalyzed by polyoxomolybdate salts containing weakly coordinating cations was achieved under mild conditions. The preparation of the catalysts is simple and convenient, and they can be recycled several times. The WCC-POM catalysts show high stability and selectivity for the epoxidation of olefins in ionic liquid $[\text{Bmim}]\text{PF}_6$ with anhydrous urea hydrogen peroxide (UHP) as oxidant. A method for the selective oxidation of sulfides to the corresponding sulfoxides using aqueous hydrogen peroxide as oxidant has also been developed. It is noted that both catalytic reactions are cost-efficient.

7.4 Experimental section

7.4.1 General

All reactions were performed using standard Schlenk techniques under an argon atmosphere. All solvents were collected from purification systems and kept over molecular sieves. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer and referenced to deuterated solvent in the case of the ^1H NMR and ^{13}C NMR, C_6F_6 for the ^{19}F NMR, H_3PO_4 (85 %) for ^{31}P NMR, respectively. IR spectra were recorded on a Varian FTIR-670 spectrometer, using a GladiATR accessory with a diamond ATR element. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. Elemental analyses were performed with a Flash EA 1112

series elemental analyzer. Thermogravimetric (TG) and differential scanning (DSC) analysis was conducted utilizing a Netzsch-STA 409 PC system. Typically about 10 mg of each sample was heated from 25 to 1000 °C at 10 K min⁻¹. Melting points were determined by MPM-H2 melting point meters. TLC was performed on silica gel 60F254 plates procured from E. Merck. Silica gel (0.06-0.2 mm 60 A) was used for column chromatography. All chemicals were purchased from Acros and ABCR and used without further purification. [Bmim]PF₆, [Bmim]BF₄ and [Bmim]NTf₂ were synthesized according to literature procedures.^[60-61]

7.4.2 Synthetic method and characterization data

Synthesis of [(n-C₄H₉)₄P]₂[Mo₆O₁₉] (1): Na₂MoO₄ · 2H₂O (4.8 g, 20 mmol) in H₂O (20 mL) was mixed with acetonitrile, and HCl (37 %, 10 mL) was added. The resulting mixture was refluxed for 1 h. After cooling, the lower aqueous layer was discarded and the upper layer was treated with [(n-C₄H₉)₄P]Br (2.7 g, 10.4 mmol) in water (100 mL). The precipitate was filtered and thoroughly washed successively three times with water and ethanol. Recrystallization of the solid from acetonitrile afforded yellow crystals of [(n-C₄H₉)₄P]₂[Mo₆O₁₉]. ¹H NMR (400 MHz, [D₆]-DMSO, r. t., ppm): δ = 0.93 (d, 12H), 1.42 (m, 16H), 2.19 (m, 8H); ³¹P NMR (162 MHz, [D₆]-DMSO, r. t., ppm): δ = 33.78; Elemental analysis (%): calcd. C 27.48, H 5.19; found C 27.55, H 5.20; IR (cm⁻¹): ν = 434.9 (s), 594.8 (m), 720.6 (m), 920.2 (w), 949.0 (vs), 1003.8(w), 1100.9 (w), 1085.4 (w), 1378.8 (w), 1462.5 (w), 1919.5 (w), 2157.9 (w), 2871.1 (w), 2929.5 (w), 2959.6 (w).

Synthesis of [(n-C₄H₉)₃P(n-C₁₄H₂₉)]₂[Mo₆O₁₉] (2): Na₂MoO₄ · 2H₂O (4.8 g, 20 mmol) in H₂O (20 mL) was mixed with acetonitrile, and HCl (37 %, 10 mL) was added. The resulting mixture was refluxed for 1 h. After cooling, the lower aqueous layer was discarded and the upper layer was treated with [(n-C₄H₉)₃P(n-C₁₄H₂₉)]Cl (4.99 g, 10.4 mmol) in water (100 mL). The precipitate was filtered and thoroughly washed successively three times with water and ethanol. Recrystallization of the solid from acetonitrile afforded pale-green crystals of [(n-C₄H₉)₃P(n-C₁₄H₂₉)]₂[Mo₆O₁₉]. ¹H NMR (400 MHz, [D₆]-DMSO, r. t., ppm): δ = 0.89 (d, 3H), 1.00 (d, 9H), 1.29 (m, 18H), 1.39 (d, 2H), 1.56 (m, 8H), 1.70 (m, 8H), 2.40 (m, 8H); ³¹P NMR (162 MHz, [D₆]-DMSO, r. t., ppm): δ = 33.95; Elemental analysis (%): calcd. C 37.15, H 6.84; found C 36.67, H 6.43; IR (cm⁻¹): ν = 436.3 (s), 591.4 (s), 718.9 (w), 785.5 (vs), 914.6 (w), 950.2 (vs), 1098.6 (w), 1459.6 (m), 1902.5 (w), 2850.2 (m), 2920.2 (m), 2956 (w).

Synthesis of [Bmim]₂[Mo₆O₁₉] (3): Na₂MoO₄ · 2H₂O (4.8 g, 20 mmol) was dissolved into 10 mL H₂O, and an aqueous solution of HCl (37 %, 5 mL) was added. After stirring for 10 min,

[Bmim]Br (1.6 g, 3.75 mmol) was added with vigorous stirring. The precipitate was filtered and thoroughly washed successively three times with water and ethanol. Recrystallization of the solid from acetonitrile afforded yellow crystals of [Bmim]₂[Mo₆O₁₉]. ¹H NMR (400 MHz, [D₆]-DMSO, r. t., ppm): δ = 0.91 (d, 3H), 1.27 (m, 2H), 1.78 (m, 2H), 3.87 (s, 3H), 4.17 (t, 2H), 7.69 (s, 1H), 7.75 (s, 1H), 9.10 (s, 1H); ¹³C NMR (100 MHz, [D₆]-DMSO, r. t., ppm): δ = 13.76, 19.28, 31.87, 36.23, 49.04, 122.70, 124.08, 136.95; Elemental analysis (%): calcd. C 16.57, H 2.78, N 4.83; found C 16.69, H 2.61, N 4.64; IR (cm⁻¹): ν = 437.1 (m), 614.5 (m), 753.6 (s), 786.2 (vs), 878.6 (w), 911.8 (m), 952.3 (vs), 1164.3 (m), 1462.0 (w), 1568.3 (w), 1906.3 (w), 2870.2 (w), 2930.9 (w), 2959.3 (w), 3115.6 (w), 3144.8 (w).

Synthesis of [Dbim]₂[Mo₆O₁₉] (4): Na₂MoO₄ · 2H₂O (4.8 g, 20 mmol) was dissolved in 10 mL H₂O, and an aqueous solution of HCl (37 %, 5 mL) was added. After stirring for 10 min, [Dbim]Br (1.75 g, 3.75 mmol) was added with vigorous stirring. The precipitate was filtered and thoroughly washed successively three times with water and ethanol. Recrystallization of the solid from acetonitrile afforded pale-yellow crystals of [Dbim]₂Mo₆O₁₉. ¹H NMR (400 MHz, [D₆]-DMSO, r. t., ppm): δ = 0.92 (t, 3H), 1.29 (m, 2H), 1.70 (m, 2H), 2.59 (s, 3H), 3.76 (s, 3H), 4.11 (t, 2H), 7.61 (s, 1H), 7.64 (s, 1H); ¹³C NMR (100 MHz, [D₆]-DMSO, r. t., ppm): δ = 9.60, 13.87, 19.37, 31.64, 35.14, 47.79, 121.32, 122.78, 144.64; Elemental analysis (%): calcd. C 18.20, H 3.05, N 4.72; found C 18.14, H 2.94, N 4.65; IR (cm⁻¹): ν = 434.3 (s), 592.2 (s), 753.7 (s), 787.0 (vs), 948.6 (vs), 1093.2 (w), 1133.9 (w), 1247.0 (w), 1417.3 (w), 15334.6 (w), 1588.1 (w), 1901.0 (w), 2962.2 (w), 3140.6 (w).

7.4.3 Single-crystal X-ray structure determination

The data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ-CCD), a rotating anode (Bruker AXS, FR591) or a fine-focused sealed tube with Mo-*K*_α radiation (λ = 0.71073 Å), and a graphite monochromator by using the SMART software package.^[62] The measurements were performed on single crystals coated with Paratone oil and mounted on glass capillaries. Each crystal was frozen under a stream of nitrogen. A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT 4.15.^[63] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^[63] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved using Bruker APEX suite,^[64] and were refined against all data using SHELXL.^[65] Hydrogen atoms were assigned to ideal positions and refined using a riding

model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme.^[66] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.^[67] Images of the crystal structures were generated by PLATON^[68] and Mercury.^[69]

1: pale-yellow fragment, $2(\text{C}_{16}\text{H}_{36}\text{P}) \text{Mo}_6\text{O}_{19}$, $M_r = 1398.48$, monoclinic, space group $C2/c$ (No. 15), $a = 16.0547(3)$, $b = 16.0680(3)$, $c = 19.7281(4) \text{ \AA}$, $\beta = 106.248(1)^\circ$, $V = 4885.94(16) \text{ \AA}^3$, $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.625 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.90 \text{ g cm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 2792$, $\theta_{\text{max}} = 25.44^\circ$, $R_I = 0.0156$ (4133 observed data), $wR_2 = 0.0370$ (all 4475 data), $\text{GOF} = 1.053$, 414 parameters, $\Delta\rho_{\text{max/min}} = 0.34 / -0.34 \text{ e \AA}^{-3}$.

3: light-yellow fragment, $2(\text{C}_8\text{H}_{15}\text{N}_2) \text{Mo}_6\text{O}_{19}$, $M_r = 1158.08$, monoclinic, space group $P21/c$ (No. 14), $a = 8.546(2)$, $b = 17.085(3)$, $c = 11.075(2) \text{ \AA}$, $\beta = 106.248(1)^\circ$, $V = 1529.5(5) \text{ \AA}^3$, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 2.471 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 2.52 \text{ g cm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 1116$, $\theta_{\text{max}} = 25.62^\circ$, $R_I = 0.0165$ (2584 observed data), $wR_2 = 0.0395$ (all 2836 data), $\text{GOF} = 1.064$, 208 parameters, $\Delta\rho_{\text{max/min}} = 0.34 / -0.27 \text{ e \AA}^{-3}$.

4: light-yellow fragment, $2(\text{C}_9\text{H}_{17}\text{N}_2) \text{Mo}_6\text{O}_{19}$, $M_r = 1186.13$, monoclinic, space group $P21/n$ (No. 14), $a = 11.0074(2)$, $b = 10.7827(2)$, $c = 13.5900(3) \text{ \AA}$, $\beta = 91.045(1)^\circ$, $V = 1612.72(5) \text{ \AA}^3$, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 2.347 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 2.44 \text{ g cm}^{-3}$, $T = 123(1) \text{ K}$, $F(000) = 1148$, $\theta_{\text{max}} = 25.47^\circ$, $R_I = 0.0256$ (2902 observed data), $wR_2 = 0.0660$ (all 2989 data), $\text{GOF} = 1.161$, 218 parameters, $\Delta\rho_{\text{max/min}} = 1.36 / -0.58 \text{ e \AA}^{-3}$. For more detailed information see Appendix.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication Nr. CCDC-892238 ($[(\text{n-C}_4\text{H}_9)_4\text{P}]_2[\text{Mo}_6\text{O}_{19}]$), CCDC-892239 ($[\text{Bmim}]_2[\text{Mo}_6\text{O}_{19}]$), and CCDC-892240 ($[\text{Dbim}]_2[\text{Mo}_6\text{O}_{19}]$). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cifs.

7.4.4 General procedure for the epoxidation of olefins

In a typical reaction, the catalyst (20 μmol) was dissolved in solvent (1 mL). Substrate (2 mmol) was added, followed by the addition of UHP (4 mmol, 0.3762 g). The reaction mixture was extracted with *n*-hexane ($5 \times 1 \text{ mL}$) and then monitored by quantitative GC analysis. Samples were taken at regular time intervals. The resulting slurry was filtered and the filtrate

injected onto a GC column. The conversion of olefins and the formation of epoxides were calculated from calibration curves ($r^2 > 0.999$) recorded prior to the reaction. For the recycling experiment, 3 mL of water was added to the mixtures after extracting substrate and product with *n*-hexane. The upper phase was removed from the reaction by means of cannulation. The IL phase was washed three times with water and then dried in vacuum for 4 h. Fresh substrate and UHP were then added for a new reaction cycle.

7.4.5 General procedure for the oxidation of sulfides

Catalyst (20 μmol) and 2 mmol of sulfide (2 mmol) were dissolved in MeOH (1 mL), followed by dropwise adding H_2O_2 (35 %) (0.19 mL, 2.1 mmol) at room temperature. The progress of the reaction was followed by TLC. After completion of the reaction, 3 mL of ethyl acetate was added to the mixture to obtain the catalyst by filtration. The solvent was removed under vacuum for 4 h and then the crude products were analyzed by GC or ^1H NMR using internal standard technology. The sulfoxides were purified by column chromatography (silica gel using hexane/ethyl acetate 90:10 v/v). For the recycling experiment, ethyl acetate was added to the reaction mixture after the reaction was completed and the catalyst precipitated, filtered off, washed with ethyl acetate, and dried in high vacuum at room temperature.

7.5 References

- [1] P. G. Rickert, M. R. Antonio, M. A. Firestone, K. Kubatko, T. Szreder, J. F. Wishart, M. L. Dietz, *J. Phys. Chem. B* **2007**, *111*, 4685.
- [2] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.
- [3] L. C. W. Baker, D. C. Glick, *Chem. Rev.* **1998**, *98*, 3.
- [4] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508.
- [5] R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834.
- [6] S. G. Lee, *Chem. Commun.* **2006**, 1049.
- [7] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
- [8] V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.
- [9] F. V. Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757.
- [10] P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238.
- [11] I. I. E. Markovits, W. A. Eger, S. Yue, M. Cokoja, C. Münchmeyer, B. Zhang, M.-D. Zhou, A. Genest, J. Mink, S.-L. Zang, N. Rösch, F. E. Kühn, *Chem. Eur. J.* **2013**, *19*, 5972.

- [12] B. Zhang, S. Li, S. Yue, M. Cokoja, M. D. Zhou, S. L. Zang, F. E. Kühn, *Z. Naturforsch. B: J. Chem. Sci.* **2013**, *68* (5/6), 587.
- [13] B. Zhang, M. D. Zhou, M. Cokoja, J. Mink, S. L. Zang, F. E. Kühn, *RSC Adv.* **2012**, *2*, 8416.
- [14] E. A. Pidko, V. Degirmenci, E. J. M. Hensen, *ChemCatChem.* **2012**, *4*, 1263.
- [15] M. H. Chang, J. A. Dzielawa, M. L. Dietz, M. R. Antonio, *J. Electroanal. Chem.* **2004**, *567*, 77.
- [16] J. Zhang, A. M. Bond, D. R. MacFarlane, S. A. Bond, A. G. Wedd, *Inorg. Chem.* **2007**, *44*, 5123.
- [17] A. W. A. Mariotti, J. L. Xie, B. F. Abrahams, A. M. Bond, A. G. Wedd, *Inorg. Chem.* **2007**, *46*, 2530.
- [18] T. Rajkumar, G. R. Rao, *Mater. Lett.* **2008**, *62*, 4134.
- [19] T. Rajkumar, G. R. Rao, *Mater. Chem. Phys.* **2008**, *112*, 853.
- [20] T. Rajkumar, G. R. Rao, *Solid State Sci.* **2009**, *11*, 36.
- [21] Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge, L. Shen, *Angew. Chem. Int. Ed.* **2009**, *48*, 168.
- [22] L. Liu, C. Chen, X. Hu, T. Mohamood, W. Ma, J. Lin, J. Zhao, *New J. Chem.* **2008**, *32*, 283.
- [23] A. Davoodna, *Bull Korean Chem. Soc.* **2011**, *32*, 4286.
- [24] N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199.
- [25] M. Misono, *Chem. Commun.* **2001**, 1141.
- [26] P. Zhao, M. Zhang, Y. Wu, J. Wang, *Ind. Eng. Chem. Res.* **2012**, *51*, 6641.
- [27] S. A. Hauser, M. Cokoja, F. E. Kühn, *Catal. Sci. Technol.* **2013**, *3*, 552.
- [28] M. Herbert, F. Montilla, R. Moyano, A. Pastor, E. Álvarez, A. Galindo, *Polyhedron* **2009**, *28*, 3929.
- [29] N. Gharah, S. Chakraborty, A. K. Mukherjee, R. Bhattacharyya, *Chem. Commun.* **2004**, 2630.
- [30] M. Herbert, E. Álvarez, D. J. Cole-Hamilton, F. Montilla, A. Galindo, *Chem. Commun.* **2010**, *46*, 5933.
- [31] D. Betz, A. Raith, M. Cokoja, F. E. Kühn, *ChemSusChem.* **2010**, *3*, 559.
- [32] W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem. Int. Ed.* **1991**, *30*, 1638.
- [33] M. Zhou, J. Zhao, J. Li, S. Yue, C. Bao, J. Mink, S. Zang, F. E. Kühn, *Chem. Eur. J.* **2007**, *13*, 158.
- [34] A. A. Lindén, M. Johansson, N. Hermanns, J-E. Bäckvall, *J. Org. Chem.* **2006**, *71*, 3849.
- [35] E. Baciocchi, M. F. Gerini, A. Lapi, *J. Org. Chem.* **2004**, *69*, 3586.

- [36] E. Baciocchi, C. Chiappe, T. D. Giacco, C. Fasciani, O. Lanzalunga, A. Lapi, B. Melai, *Org. Lett.* **2009**, *11*, 1413.
- [37] A. V. Anisimov, E. V. Fedorova, A. Z. Lesnugin, V. M. Senyavi, L. A. Aslanov, V. B. Rybakov, A. V. Tarakanova, *Catal. Today* **2003**, *78*, 319.
- [38] V. Conte, F. Fabbianesi, B. Floris, P. Galloni, D. Sordi, I. W. C. E. Arends, M. Bonchio, D. Rehder, D. Bogdal, *Pure Appl. Chem.* **2009**, *81*, 1265.
- [39] G. P. Romanelli, D. O. Bennardi, V. Palermo, P. G. Vázquez, P. Tundo, *Lett. Org. Chem.* **2007**, *4*, 544.
- [40] J. H. Espenson, *Chem. Commun.* **1999**, 479.
- [41] K. J. Stanger, J. W. Wiench, M. Pruski, J. H. Espenson, G. A. Kraus, R. J. Angelici, *J. Mol. Catal. A: Chem.* **2006**, *243*, 158.
- [42] J. Legros, C. Bolm, *Angew. Chem. Int. Ed.* **2003**, *42*, 5487.
- [43] J. Legros, C. Bolm, *Angew. Chem. Int. Ed.* **2004**, *43*, 4225.
- [44] K. Jeyakumar, D. K. Chand, *Tetrahedron Lett.* **2006**, *47*, 4573.
- [45] M. Ciclosi, C. Dinoi, L. Gonsalvi, M. Peruzzini, E. Manoury, R. Poli, *Organometallics* **2008**, *27*, 2281.
- [46] D. L. Long, P. Kögerler, L. Cronin, *Angew. Chem. Int. Ed.* **2004**, *43*, 1817.
- [47] A. Thakur, A. Chakraborty, V. Ramkumar, S. Ghosh, *Dalton Trans.* **2009**, 7552.
- [48] D. L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1736.
- [49] M. A. Speckerman, D. Jayatilaka, *CrystEngComm.* **2009**, *11*, 19.
- [50] F. L. Hirshfeld, *Theor. Chim. Acta* **1977**, *44*, 129.
- [51] S. Gatard, S. Blanchard, B. Schollhorn, P. Gouzerh, A. Proust, K. Boubekour, *Chem. Eur. J.* **2010**, *16*, 8390.
- [52] M. Schulz-Dobrick, M. Jansen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2326.
- [53] T. Rajkumar, G. R. Rao, *J. Chem. Sci.* **2008**, *120*, 587.
- [54] Y. Gao, X. Wang, Y. Li, E. Wang, L. Xu, C. Hu, *J. Coord. Chem.* **2004**, *57*, 445.
- [55] V. Shivaiah, S. K. Das, *Angew. Chem. Int. Ed.* **2006**, *45*, 245.
- [56] X. Ma, Z. Yang, C. Schulzke, *Z. Kristallogr.* **2010**, 775.
- [57] K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* **2005**, *61*, 8315.
- [58] J. Drabowicz, M. Mikolajczyk, *Synth. Commun.* **1981**, *11*, 1025.
- [59] W. L. Xu, Y. Z. Li, Q. S. Zhang, H. S. Zhu, *Synthesis* **2004**, 227.
- [60] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.
- [61] S. Park, R. J. Kazlauskas, *J. Org. Chem.* **2001**, *66*, 8395.

- [62] APEX suite of crystallographic software. APEX 2 Version **2008.4**. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [63] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [64] APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [65] C. B. Huebschle, G. M. Sheldrick, B. Dittrich "SHELXL". *J. Appl. Cryst.* **2011**, *44*, 1281.
- [66] G. M. Sheldrick, "SHELXL-97", University of Göttingen, Göttingen, Germany, **1998**.
- [67] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199), A. J. C. Wilson (Ed.), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**.
- [68] A. L. Spek, "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2010**.
- [69] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, "Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures", **2008**.

8 Schiff base complexes of methyltrioxorhenium (VII): synthesis and catalytic application

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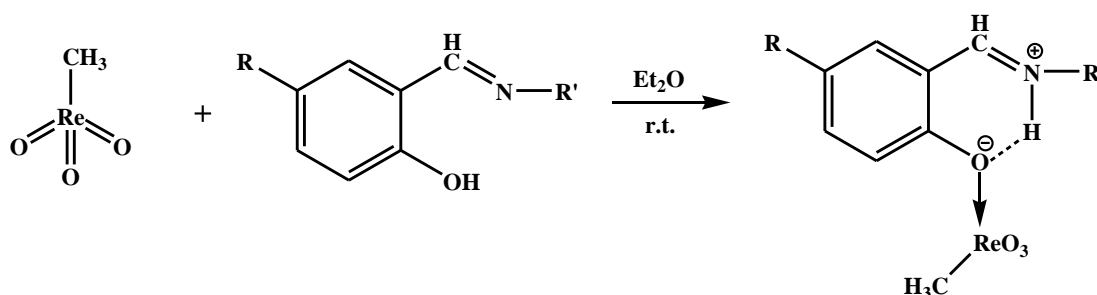
8.1 Introduction

Epoxides are valuable intermediates in organic chemistry, for fine chemicals and in pharmaceutical synthesis.^[1-3] A broad variety of catalysts for olefin epoxidation has been described.^[4-7] Among these catalysts, methyltrioxorhenium (VII) (MeReO₃, MTO) was found to be one of the most efficient and powerful for olefin epoxidation when employing hydrogen peroxide as oxidant.^[8-13] However, due to the pronounced Lewis acidity of MTO and in the presence of water (formed as by-product from hydrogen peroxide) ring opening of the epoxides to diols often takes place, particularly when more sensitive epoxides are formed.^[8-9] Several methods have been suggested to overcome this problem. An efficient procedure developed to avoid this side reaction requires the use of urea hydrogen peroxide adduct (UHP) as oxidant, which enables epoxidation to be carried out in non-aqueous media.^[14-15] Another method is the application of excess aromatic N-bases, ligating the Re center in an equilibrium reaction and thereby reducing the Lewis acidity of the catalyst and accelerating the catalytic reaction additionally.^[16-21] However, separation of the catalyst, containing the expensive element rhenium is an additional issue. Two-phase reactions are often chosen to achieve this purpose. Among such solvents non-volatile ionic liquids (ILs) have received a great deal of attention in recent years due to their unique properties.^[22-25] It has already been noted that some Schiff base adducts of MTO display high catalytic activity in organic solvent.^[26-30] With the aim of developing more sustainable procedures for olefin epoxidation, Schiff base adducts of MTO are combined with ILs as solvent and UHP as oxidant.

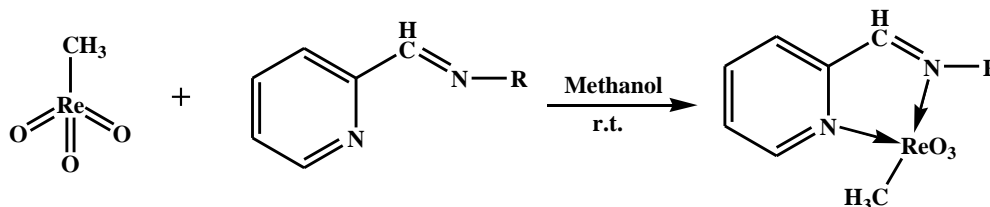
8.2 Results and discussion

8.2.1 Synthesis and spectroscopic characterization

Complexes **1-4** (Scheme 1) were synthesized by treatment of MTO with the respective Schiff bases in diethyl ether at room temperature, while complexes **5-8** were prepared in methanol. The product formation can be easily followed due to the appearance of orange-yellow color. The product can be purified by re-crystallization from Et₂O/*n*-hexane or methanol. In comparison to many N-coordinated Lewis base adducts, being considerably less stable against moisture and temperature than MTO itself,^[31-33] complexes **1-8** show good stability in air at room temperature for several days and can be handled without decomposition.



R = CH₃, R' = ethylbenzyl (**1**), R = CH₃, R' = *p*-Methylphenyl (**2**), R = CH₃, R' = *p*-Chlorophenyl (**3**),
R = H, R' = (R)-(+)-alpha-methylbenzyl (**4**)



R = (s)-(-)-alpha-methylbenzyl (**5**), (s)-(-)-1-phenylpropyl (**6**), (R)-(+)-alpha-methylbenzyl (**7**),
(s)-1-(4-chlorophenyl)ethyl (**8**)

Scheme 1. Synthesis of MTO complexes **1-8**

In the IR spectra of complexes **1-8**, the asymmetric Re=O stretching vibrations are observed in the region of 910-965 cm⁻¹, while the symmetric Re=O stretching vibrations are found between 1027 and 934 cm⁻¹ (See Table 1). It is seen that in comparison to the asymmetric stretching vibrations exhibited by non-coordinated MTO ($\nu_{\text{sym}} = 998 \text{ cm}^{-1}$, $\nu_{\text{asym}} = 965 \text{ cm}^{-1}$), the respective Re=O bands of complexes **1-8** are strongly shifted. This vibration differences reflect the donor capacity of the Schiff base ligands, reducing the bond order of the Re=O bonds.

For free MTO the difference between $\nu_{\text{sym}}(\text{Re}=\text{O})$ and $\nu_{\text{asym}}(\text{Re}=\text{O})$ is 33 cm⁻¹ (tetrahedral

coordination geometry). Complexes **1-4** and **5-8**, the difference between the symmetric and asymmetric Re=O stretching vibrations is not equally large, indicating different coordination geometries of Re center. It is 65.5-93 cm^{-1} for complexes **1-4** and 24-32 cm^{-1} for the complexes **5-8**. It has been reported that differences of 20-27 and 60-80 cm^{-1} between ν_{sym} (Re=O) and ν_{asym} (Re=O) correspond to octahedral and trigonal-bipyramidal coordination geometry, respectively.^[29-30] In some special cases, the differences can become very large (167 cm^{-1}) due to the rather asymmetric coordination of the rhenium atom.^[26] Therefore, it can be deduced that the complexes **1-4** are closer to trigonal-bipyramidal coordination geometry, while complexes **5-8** have a (slightly distorted) octahedral geometry. Additionally, the stretching vibrations of the iminic bands in the complexes **1-8** are also significantly shifted when compared to the free ligands (see below).

Table 1. Selected IR spectroscopic data of Schiff-bases and MTO adducts.

Compound	Imine	ReO ₃		
	$\nu(\text{C}=\text{N})$ (cm^{-1})	ν_{sym} (cm^{-1})	ν_{asym} (cm^{-1})	$\nu_{\text{s}}-\nu_{\text{as}}$ (cm^{-1})
MTO		998	965	33
L1	1629			
C1	1639	1027	956, 919	89.5
L2	1615			
C2	1636	1007	963, 913	69
L3	1611			
C3	1614	997	943, 920	65.5
L4	1621			
C4	1628	1029	959, 913	93
L5	1645			
C5	1639	942	911	31
L6	1646			
C6	1638	934	910	24
L7	1645			
C7	1639	942	911	31
L8	1647			
C8	1640	945	913	32

Selected NMR data of complexes **1-8** is shown in Table 2. Again, complexes **1-4** and **5-8** are clearly different with respect to their chemical shifts of the CH₃ moiety atoms. It should be noted that the magnitude of the ¹H-NMR shift is related to the electron-donating capability of the ligands. The results confirm that the better the electron donating ability of the ligand is the larger the high-field shift of the ¹H NMR signal of the Re-CH₃ group. The weaker donor capacity of the base ligands in complexes **1-4** are reflected in less pronounced shift differences to non-coordinated MTO.

Table 2. Selected ^1H and ^{13}C NMR data of MTO complexes in CDCl_3 .

Compound	MTO-CH ₃	
	δ (^1H) (ppm)	δ (^{13}C) (ppm)
MTO	2.67	19.03
1	2.50	20.35
2	2.54	21.50
3	2.64	20.31
4	2.60	20.65
5	2.01	24.31
6	1.98	23.03
7	1.74	24.30
8	1.97	23.15

8.2.2 X-ray crystal structure of complex 2

Complex **2** crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ with $Z = 4$. The molecular solid-state structure is depicted in Figure 1 and the crystallographic data are summarized in the Experimental Section. It is observed that complex **2** displays trans-configuration of the Re-bound CH_3 group with respect to the Re-bound Schiff-base oxygen atom. The Re-C bond distance for **2** is $2.098(2) \text{ \AA}$, which is significantly longer than in free MTO ($2.063(2) \text{ \AA}$).^[34] This effect results in a somewhat higher sensitivity of the Re- CH_3 and accordingly, adducts of MTO are generally somewhat less stable than non-coordinated organometallic compound alone. The Re=O bond distances of **2** are around 1.7 \AA and therefore quite similar to the other known MTO adducts in our previous work.^[26, 28, 35-36]

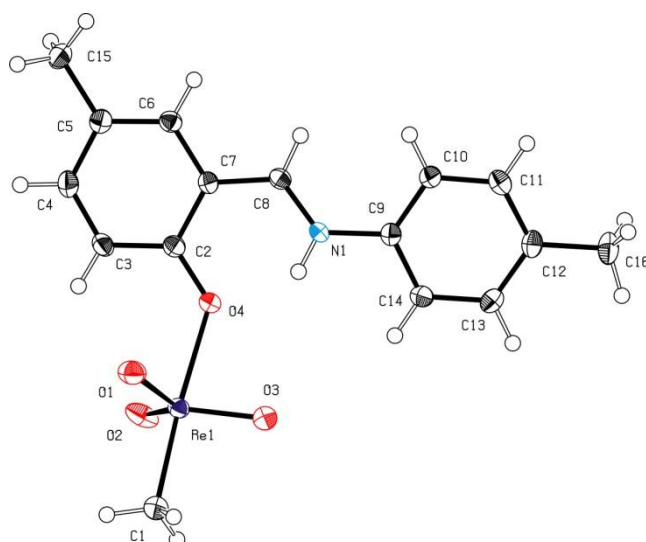


Figure 1. ORTEP style plot of **2** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (deg): Re1-O1 1.721(2), Re-O2 1.714(2), Re1-O3 1.742(2), Re-O4 2.231(2), Re1-C1 2.098(2), C2-O4 1.321(3), C8-N1 1.308(3), C9-N1 1.418(3); O1-Re1-O2 118.41(10), O1-Re1-O3 120.35(10), O1-Re1-O4 86.63(9), O1-Re1-C1 94.23(10), O2-Re1-O3 119.64(11), O2-Re1-O4 89.12(8), O2-Re1-C1 94.01(10), O3-Re1-O4 81.73(8), O3-Re1-C1 94.37(10), O4-Re1-C1 175.88(9), Re1-O4-C2 129.01(16).

8.2.3 Catalytic application

Cis-cyclooctene epoxidation catalyzed by **1** as model catalyst was examined in different ionic liquids and with different oxidants. The results are given in Figure 2. The details concerning the catalytic reaction are given in the experiment part. A catalyst: oxidant: substrate ratio of 1:200:100 was used in all experiments. Epoxidation of *cis*-cyclooctene was found to be strongly solvent dependent. When using [Emim]BF₄ (1-ethyl-3-methylimidazolium tetrafluoroborate) and [Bmim]NTf₂ (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) as solvents for epoxidation of *cis*-cyclooctene, the yield was low (< 20 %). While higher yields (79 %) were obtained after 24 h in [Bmim]PF₆ (1-butyl-3-methylimidazolium hexafluorophosphate) with UHP (urea hydrogen peroxide) as oxidant. For comparison, H₂O₂ was also used as oxidant under the same conditions. The catalytic activity is significantly lower with the latter oxidant and diol is formed as by-product. Based on this result, UHP appears to be superior to H₂O₂ as oxidizing agent.

A blank experiment without oxidant was carried out under the same conditions and no significant oxidation was observed within 24 h, indicating that the oxygen source in the oxidation reaction is not air. It is noteworthy that the advantageous properties of the Schiff-base MTO complexes-UHP oxidation system and the ionic liquid [Bmim]PF₆ have to be combined to achieve good conditions for catalytic oxidations. Remaining reactants and products are both easily removed from the reaction mixture *via* extraction with *n*-hexane,

which is immiscible with the ionic liquids used in this work. This method of removing reactants and products is also advantageous because the Schiff base MTO complexes, the peroxorhenium species, and the urea byproduct are insoluble in *n*-hexane.

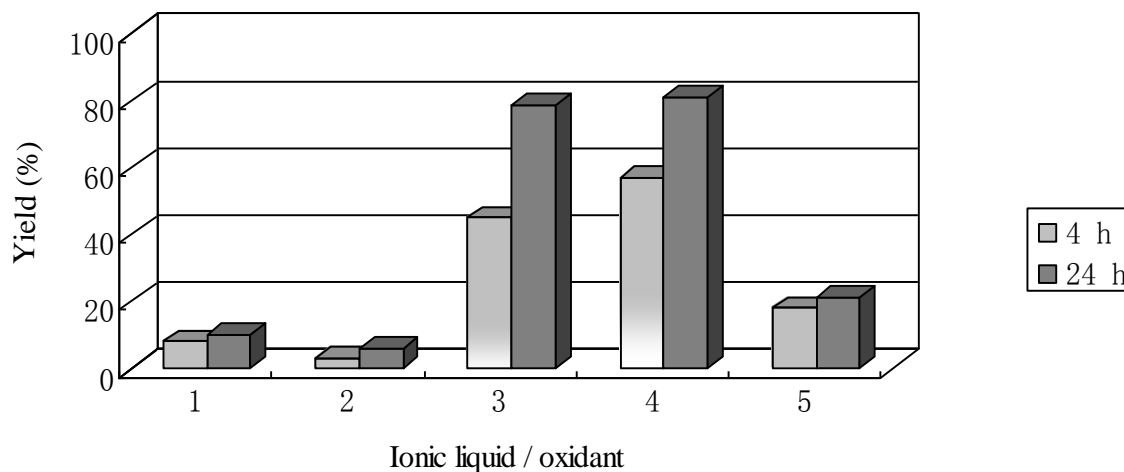


Figure 2. Epoxidation of *cis*-cyclooctene with different oxidants in different ionic liquids. 1: [Emim]BF₄/UHP, 2: [Bmim]NTf₂/UHP, 3: [Emi]SE/UHP, 4: [Bmim]PF₆/UHP, 5: [Bmim]PF₆/H₂O₂.

Complexes **1-8** were also examined as catalysts for the epoxidation of *cis*-cyclooctene using UHP as oxidant in [Bmim]PF₆ at room temperature (Table 3 and Figure 3). Complexes **2** and **4**, which have electron donating Schiff base ligands, show the highest activity and conversion of cyclooctene with almost 100 % after 2 h. Complex **3** is less catalytic active (59 % after 4 h and 70 % after 24 h). Complex **1** also leads to a good activity and conversion (63 % after 6 h and 81 % after 24 h). However it can be seen that **5-8** only show very low catalytic activity achieving yields (< 20 %) (Entries 6-9) compared with **1-4** (> 60 %) (Entries 2-5). The comparatively low conversion can be explained by the fact that the coordination of di-nitrogen Schiff bases increases the electron density of Re centre, leading to it being less prone to nucleophilic attack by an olefin. The steric hindrance of the coordinated di-nitrogen Schiff bases additionally hampers the approach of the olefin to the Re atom and appears to be another reason for a slower reaction.^[33] It is noteworthy that no diol is detected during the course of the measurements (Table 3). Additionally, figure 3 shows that all catalytic reactions follow first order kinetics. The reaction conversion increases steadily for the first four hours and then slows down.

Table 3. Epoxidation of *cis*-cyclooctene with different catalysts in [Bmim]PF₆/UHP at room temperature.^a

Entry	Catalysts	Time (h)	Conversion (%) ^b	Selectivity (%) ^b
1	MTO	2	96	>99
2	1	6	63	>99
3	2	2	97	>99
4	3	4	59	>99
5	4	4	92	>99
6	5	8	10	>99
7	6	6	4	>99
8	7	8	11	>99
9	8	6	6	>99

^a Reaction condition: *cis*-cyclooctene (2 mmol), catalyst (1 mol %), UHP (4 mmol), [Bmim]PF₆ (1 mL) at room temperature;

^b The conversion and selectivity is calculated by GC analysis.

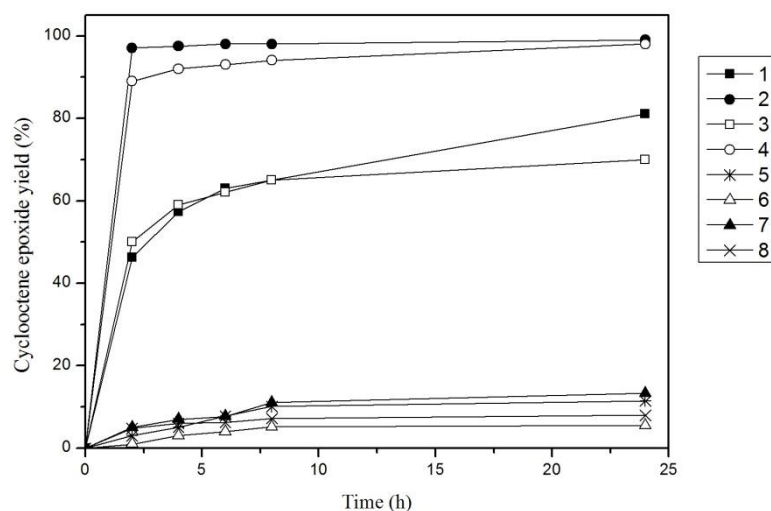


Figure 3. Time dependent yield of *cis*-cyclooctene epoxide in the presence of complexes **1-8** as catalysts (1 mol %) in ionic liquid [Bmim]PF₆ at room temperature.

Recovery of the [Bmim]PF₆/MTO, **2** or **4** mixture for the oxidation of cyclooctene was also investigated. A problem of this system is that the use of UHP as oxidant results in an accumulation of urea as the reaction medium which is not eliminated in the extraction. Two possible means of removing urea are possible and were applied. The first method is that washing the system with water and then filtration. [Bmim]PF₆ is not soluble in water. The IL phase can be dried under vacuum. The new UHP and cyclooctene were added into the IL phase for the next catalytic cycles. The yield of cyclooctene oxide is 30 % for MTO, 7 % for complex **2** and 21 % for complex **4** in the second recycle. It is obvious that washing with water would likely be very effective in removing the urea but would be likely to also remove catalyst. The other method is that dissolving ionic liquid in dichloromethane to precipitate of dissolved urea can be removed subsequently by filtration. Dichloromethane is then removed

under reduced pressure. After the new addition of UHP and *cis*-cyclooctene further catalytic cycles were attempted. The yield of cyclooctene oxide is 14 % for MTO, 11 % for complex **2** and 3 % for complex **4** using this method in the second recycle. The deactivation was probably due to leaching of the catalyst. This phenomenon is in agreement with previous investigation employing methyltrioxorhenium as an olefin epoxidation catalyst in an IL/UHP similar system.^[37-38]

8.3 Conclusion

Eight base adducts of MTO were prepared and characterized. They display good stability in air at room temperature. The complexes were applied as catalysts for the epoxidation of cyclooctene in [Bmim]BF₆ with UHP as oxidant at room temperature. The results show that the (N-salicylidene) aniline derived Schiff base complexes of MTO exhibit higher catalytic activity and selectivity than di-nitrogen Schiff bases complexes of MTO. It is noteworthy that the oxidation reaction yields only the epoxide and not by-product diol. This system provides an environmentally benign way for olefin epoxidation.

8.4 Experimental section

8.4.1 General

All reactions were performed using standard Schlenk techniques under an argon atmosphere. All solvents were collected from solvent drying systems and kept over molecular sieves. NMR spectra were recorded on a Bruker Avance DPX 400 and chemical shifts are reported relative to the residual signal of the deuterated solvent. IR spectra were recorded on Varian FTIR-670 spectrometer, using a GladiATR accessory with a diamond ATR element. Elemental analyses were obtained from the microanalytical laboratory in Technische Universität München. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II. All chemicals were purchased from Acros and ABCR and used without further purification. [Emim]BF₄, [Bmim]BF₄, [Bmim]NTf₂, [Emi]SE (1-ethyl-3-methylimidazolium ethyl sulfate) ionic liquids were synthesized according to literature procedures.^[39-40]

8.4.2 Synthetic methods and characterization data

Synthesis of compounds 1-4: MTO (0.2 g, 0.8 mmol) is dissolved in diethyl ether (10 mL) and an equally concentrated solution of ligand (0.8 mmol) in diethyl ether (10 mL) is added to the stirred solution at room temperature. After 30 min the yellow solution is concentrated in an oil pump vacuum to 3 mL, and the yellow or orange precipitate is obtained by filtration, washed with dry *n*-hexane (3 × 10 mL) and dried under reduced pressure.

1: (color: yellow) Yield: 87 %; - ¹H-NMR: (400MHz, CDCl₃, 296 K, ppm): δ = 2.19 (s, 3H, Ph-CH₃), 2.50 (s, 3H, MTO-CH₃), 4.70 (s, 2H, NCH₂), 6.76 (m, 1H, Ph), 6.96 (m, 1H, Ph), 7.01 (m, 1H, Ph), 7.21 (m, 5H, Ph), 8.28 (s, 1H, CH=N), 12.80 (s, 1H, NH); - ¹³C-NMR: (100MHz, CDCl₃, 296 K, ppm): δ = 19.55 (Ph-CH₃), 20.35 (MTO-CH₃), 63.15 (NCH₂), 118.64, 118.43, 127.33, 127.66, 127.76, 128.66, 131.47, 133.27, 138.21, 158.96 (aryl-C), 165.63 (CH=N); -C₁₆H₁₈NO₄Re (474.53): calcd. C 40.50, H 3.82, N 2.95, found C 41.34, H 3.95, N 3.11.

2: (color: orange) Yield: 89 %; - ¹H-NMR: (400MHz, CDCl₃, 296 K, ppm): δ = 2.24 (s, 3H, Ph-CH₃), 2.31 (s, 3H, Ph-CH₃), 2.54 (s, 3H, MTO-CH₃), 6.84 (m, 1H, Ph), 7.12 (m, 6H, Ph), 8.50 (s, 1H, CH=N), 13.04 (s, 1H, NH); - ¹³C-NMR: (100MHz, CDCl₃, 296 K, ppm): δ = 19.80 (Ph-CH₃), 20.81 (Ph-CH₃), 21.50 (MTO-CH₃), 117.44, 119.20, 121.40, 128.49, 130.43, 132.55, 134.31, 137.25, 146.37, 159.43 (aryl-C), 162.14 (CH=N); -C₁₆H₁₈NO₄Re (474.53): calcd. C 40.50, H 3.82, N 2.95, found C 40.68, H 3.92, N 2.94.

3: (color: yellow) Yield: 85 %; - ¹H-NMR: (400MHz, CDCl₃, 296 K, ppm): δ = 2.36 (s, 3H, Ph-CH₃), 2.64 (s, 3H, MTO-CH₃), 6.98 (m, 1H, Ph), 7.22 (m, 5H, Ph), 7.28 (m, 1H, Ph), 8.58 (s, 1H, CH=N), 12.67 (s, 1H, NH); - ¹³C-NMR: (100MHz, CDCl₃, 296 K, ppm): δ = 19.98 (Ph-CH₃), 20.31 (MTO-CH₃), 117.36, 118.47, 119.46, 127.31, 131.00, 132.62, 133.31, 138.81, 146.53, 159.29 (aryl-C), 164.20 (CH=N); -C₁₅H₁₅ClNO₄Re (494.94): calcd. C 36.40, H 3.05, N 2.83, found C 36.80, H 3.10, N 2.96.

4: (color: yellow) Yield: 81 %; - ¹H-NMR: (400MHz, CDCl₃, 296 K, ppm): δ = 1.67 (d, 3H, CH₃), 2.60 (s, 3H, MTO-CH₃), 4.59 (m, 1H, CH), 6.89 (m, 1H, Ph), 7.01 (m, 1H, Ph), 7.39 (m, 7H, Ph), 8.42 (s, 1H, CH=N), 13.62 (s, 1H, NH); - ¹³C-NMR: (100MHz, CDCl₃, 296 K, ppm): δ = 20.54 (CH₃), 20.65 (MTO-CH₃), 69.03 (CH), 117.93, 119.32, 119.46, 127.19, 128.11, 129.49, 132.27, 133.33, 144.40, 162.29 (aryl-C), 164.25 (CH=N); -C₁₆H₁₈NO₄Re (474.53): calcd. C 40.51, H 3.82, N 2.95, found C 41.43, H 4.09, N 3.05.

Synthesis of complexes 5-8: 0.8 mmol of MTO is added to 0.8 mmol of the corresponding di-nitrogen Schiff base in methanol (4 mL) at room temperature. A yellow precipitate is formed rapidly. The precipitate is isolated by filtration, washed with *n*-hexane (3 × 10 mL)

and dried under reduced pressure for one day.

5: (color: yellow) Yield: 82 %; - $^1\text{H-NMR}$: (400MHz, CDCl_3 , 296 K, ppm): $\delta = 1.80$ (d, 3H, CH_3), 2.01 (s, 3H, MTO- CH_3), 5.11 (m, 1H, CH), 7.30 (m, 3H, PhH), 7.44 (m, 2H, PhH), 7.46 (m, 1H, PyH), 7.91 (m, 2H, PyH), 8.41 (s, 1H, $\text{CH}=\text{N}$), 8.80 (m, 1H, PyH); - $^{13}\text{C-NMR}$: (100MHz, CDCl_3 , 296 K, ppm): $\delta = 22.11$ (Ph- CH_3), 24.31 (MTO- CH_3), 69.28 (CH), 121.92, 125.56, 126.39, 127.77, 128.19, 129.04, 138.46, 149.72, 152.00 (aryl-C), 159.50 ($\text{CH}=\text{N}$); - $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3\text{Re}$ (459.51): calcd. C 39.21, H 3.73, N 6.10, found C 39.85, H 3.66, N 6.27.

6: (color: yellow) Yield: 80 %; - $^1\text{H-NMR}$: (400MHz, CDCl_3 , 296 K, ppm): $\delta = 0.95$ (d, 3H, CH_3), 1.98 (s, 3H, MTO- CH_3), 2.12 (m, 2H, CH_2), 4.70 (t, 1H, CH), 7.28 (m, 1H, PhH), 7.40 (m, 4H, PhH), 7.47 (m, 1H, PyH), 7.88 (m, 1H, PyH), 7.90 (m, 1H, PyH), 8.05 (s, 1H, $\text{CH}=\text{N}$), 8.77 (m, 1H, PyH); - $^{13}\text{C-NMR}$: (100MHz, CDCl_3 , 296 K, ppm): $\delta = 11.44$ (CH_3), 23.03 (MTO- CH_3), 29.59 (CH_2), 57.53 (CH), 121.92, 126.28, 125.96, 127.46, 127.88, 128.90, 138.02, 150.34, 152.71 (aryl-C), 159.84 ($\text{CH}=\text{N}$); - $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3\text{Re}$ (473.54): calcd. C 40.58, H 4.04, N 5.92, found C 40.77, H 4.01, N 5.94.

7: (color: yellow) Yield: 81 %; - $^1\text{H-NMR}$: (400MHz, CDCl_3 , 296 K, ppm): $\delta = 1.74$ (s, 3H, MTO- CH_3), 1.80 (s, 3H, CH_3), 5.12 (m, 1H, CH), 7.32 (m, 1H, PhH), 7.40 (m, 2H, PhH), 7.46 (m, 2H, PhH), 7.48 (m, 1H, PyH), 7.91 (m, 2H, PyH), 8.42 (s, 1H, $\text{CH}=\text{N}$), 8.81 (m, 1H, PyH); - $^{13}\text{C-NMR}$: (100MHz, CDCl_3 , 296 K, ppm): $\delta = 22.10$ (Ph- CH_3), 24.30 (MTO- CH_3), 69.26 (CH), 121.91, 125.53, 126.38, 127.77, 128.19, 129.03, 138.44, 149.74, 152.00 (aryl-C), 159.45 ($\text{CH}=\text{N}$); - $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3\text{Re}$ (459.51): calcd. C 39.21, H 3.73, N 6.10, found C 39.19, H 3.85, N 6.12.

8: (color: yellow) Yield: 84 %; - $^1\text{H-NMR}$: (400MHz, CDCl_3 , 296 K, ppm): $\delta = 1.75$ (d, 3H, CH_3), 1.97 (s, 3H, MTO- CH_3), 5.01 (m, 1H, CH), 7.36 (m, 4H, PhH), 7.48 (m, 1H, PyH), 8.00 (m, 1H, PyH), 8.02 (m, 1H, PyH), 8.46 (s, 1H, $\text{CH}=\text{N}$), 8.79 (m, 1H, PyH); - $^{13}\text{C-NMR}$: (100MHz, CDCl_3 , 296 K, ppm): $\delta = 22.82$ (Ph- CH_3) 23.15, (MTO- CH_3), 68.66 (CH), 124.64, 126.15, 128.89, 129.05, 133.69, 138.08, 140.75, 149.73, 152.50 (aryl-C), 159.87 ($\text{CH}=\text{N}$); - $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{O}_3\text{Re}$ (493.96): calcd. C 36.47, H 3.26, N 5.67, found C 36.18, H 3.18, N 5.63.

8.4.3 Single-crystal X-ray structure determination

The data were collected on an X-ray diffractometer equipped with a CCD detector (Bruker AXS, APEX II, κ -CCD), a rotating anode (Bruker AXS, FR591) with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator. The measurement was performed on a single crystal stored under perfluorinated ether and mounted on glass fiber by using the SMART software package.^[41] The crystal was frozen under a stream of cold nitrogen (OXFORD

Chapter 8

CRYOSYSTEMS cooling device). A matrix scan was used to determine the initial lattice parameters. Intensities were integrated and the raw data were corrected for Lorentz, polarization, scan speed, background, and, arising from the scaling procedure, for latent decay and absorption effects using SAINT 4.15^[42] and SADABS.^[43] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier syntheses and were refined against all data using SHELXL-97.^[44] Hydrogen atoms were assigned to ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97^[44] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.^[45] Images of the crystal structures were generated by PLATON.^[46] Further details are summarized in Table 4.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-924572 (2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Table 4. Crystallographic details for complex **2**.

2	
Formula	C ₁₆ H ₁₈ NO ₄ Re
<i>M_r</i>	474.52
Color / habit	orange / needle
Crystal size, mm	0.13×0.13×0.30
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	7.4623(2)
<i>b</i> , Å	17.8241(6)
<i>c</i> , Å	12.4101(4)
<i>β</i> , deg	107.3380(12)
<i>V</i> , Å ³	1575.65(9)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	2.000
<i>μ</i> , cm ⁻¹	7.729
<i>F</i> (000)	912
<i>T</i> (K)	123
<i>hkl</i> range	±8, ±21, ±14
<i>θ</i> Range (°)	2.06 – 25.35
No. of rflns. collected	35467
No. of indep. rflns. / <i>R</i> _{int}	2866 / 0.044
No. of obsd. rflns. [<i>I</i> _o > 2σ(<i>I</i> _o)]	2825
No. of data/restraints/params	2866 / 0 / 202
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> _o > 2σ(<i>I</i> _o)] ^a	0.0143 / 0.0350
<i>R</i> 1/ <i>wR</i> 2 (all data) ^a	0.0146 / 0.0353
GOF (on <i>F</i> ²) ^b	1.161
Largest diff. peak and hole (e Å ⁻³)	0.89 / -0.91

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}, ^b GOF = \frac{[\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}}$$

8.4.4 Catalytic reactions

To a solution of *cis*-cyclooctene (2 mmol) and UHP (4 mmol) in IL (1 mL) was added the catalyst (1 mol %) at room temperature. After completion, the reaction mixture was extracted with *n*-hexane (5 × 3 mL). The organic phase was dried over Na₂SO₄. Following the evaporation of the solvent, the crude product was analyzed by GC. The conversion and the formation of cyclooctene oxide were calculated from calibration curves (*r*² > 0.999) recorded prior to the start of the reaction.

8.5 References

- [1] R. A. Sheldon, *Green Chem.* **2007**, *9*, 1273.
- [2] J. R. Monnier, *Appl. Catal. A.* **2001**, *221*, 73.
- [3] S. Yamazaki, *Tetrahedron.* **2008**, *64*, 9253.
- [4] N. Grover, F. E. Kühn, *Curr. Org. Chem.* **2012**, *16*, 16.
- [5] D. Betz, P. Altmann, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Coord. Chem. Rev.* **2011**, *255*, 1518.
- [6] K. R. Jain, F. E. Kühn, *Dalton Trans.* **2008**, 2221.
- [7] F. E. Kühn, A. M. Santos, M. Abrantes, *Chem. Rev.* **2006**, *106*, 2455.
- [8] W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169.
- [9] C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197.
- [10] F. E. Kühn, A. Scherbaum, W. A. Herrmann, *J. Organomet. Chem.* **2004**, *689*, 4149.
- [11] W. A. Herrmann, A. M. J. Rost, J. K. M. Mitterpleininger, N. Szesni, S. Sturm, R. W. Fischer, F. E. Kühn, *Angew. Chem. Int. Ed.* **2007**, *46*, 7301.
- [12] W. A. Herrmann, A. M. J. Rost, E. Tosh, H. Riepl, F. E. Kühn, *Green Chem.* **2008**, *10*, 442.
- [13] K. R. Jain, F. E. Kühn, *J. Organomet. Chem.* **2007**, *692*, 5532.
- [14] E. P. Carreiro, A. J. Burke, M. J. M. Curto, A. J. R. Teixeira, *J. Mol. Catal. A: Chem.* **2004**, *217*, 69.
- [15] R. Saladino, R. Bernini, V. Neri, C. Crestini, *Appl. Catal. A: Gen.* **2009**, *360*, 171.
- [16] W. A. Herrmann, F. E. Kühn, C. C. Romão, H. T. Huy, M. Wang, R. W. Fischer, P. Kiprof, W. Scherer, *Chem. Ber.* **1993**, *126*, 45.
- [17] W. A. Herrmann, F. E. Kühn, M. U. Rauch, J. D. G. Correia, G. Artus, *Inorg. Chem.* **1995**, *34*, 2914.
- [18] W. A. Herrmann, F. E. Kühn, M. R. Mattner, G. R. J. Artus, M. R. Geisberger, J. D. G. Correia, *J. Organomet. Chem.* **1997**, *538*, 203.
- [19] W. A. Herrmann, H. Ding, R. M. Kratzer, F. E. Kühn, J. J. Haider, R. W. Fischer, *J. Organomet. Chem.* **1997**, *549*, 319.
- [20] W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel, H. Glas, *J. Organomet. Chem.* **1998**, *555*, 293.
- [21] C. D. Nunes, M. Pillinger, A. A. Valente, I. S. Gonçalves, J. Rocha, P. Ferreira, F. E. Kühn, *Eur. J. Inorg. Chem.* **2002**, 1100.
- [22] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508.
- [23] R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834.

- [24] S. Lee, *Chem. Commun.* **2006**, 1049.
- [25] F. V. Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757.
- [26] M. D. Zhou, J. Zhao, J. Li, S. Yue, C. Bao, J. Mink, S. L. Zang, F. E. Kühn, *Chem. Eur. J.* **2007**, *13*, 158.
- [27] A. Capapé M. D. Zhou, S. L. Zang, F. E. Kühn, *J. Organomet. Chem.* **2008**, *693*, 3240.
- [28] Z. Xu, M. D. Zhou, M. Drees, H. C. Millar, E. Herdtweck, W. A. Herrmann, F. E. Kühn, *Inorg. Chem.* **2009**, *48*, 6812.
- [29] C. J. Qiu, Y. C. Zhang, Y. Gao, J. Q. Zhao, *J. Organomet. Chem.* **2009**, *694*, 3418.
- [30] Y. Gao, Y. Zhang, C. Qiu, J. Zhao, *Appl. Organomet. Chem.* **2011**, *25*, 54.
- [31] H. Rudler, J. R. Gregorio, B. Denise, J. M. Brégeault, A. Deloffre, *J. Mol. Catal. A: Chem.* **1998**, *133*, 255.
- [32] F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudanov, C. di Valentin, N. Rösch, *Chem. Eur. J.* **1999**, *5*, 3603.
- [33] P. Ferreira, W. M. Xue, É. Bencze, E. Herdtweck, F. E. Kühn, *Inorg. Chem.* **2001**, *40*, 5834.
- [34] W. A. Herrmann, *J. Organomet. Chem.* **1995**, *500*, 149.
- [35] M. D. Zhou, S. L. Zang, E. Herdtweck, F. E. Kühn, *J. Organomet. Chem.* **2008**, *693*, 2473.
- [36] M. D. Zhou, Y. Yu, A. Capapé K. R. Jain, E. Herdtweck, X. R. Li, J. Li, S. L. Zang, F. E. Kühn, *Chem. Asian J.* **2009**, *4*, 411.
- [37] M. Herbert, F. Montilla, R. Moyano, A. Pastor, E. Álvarez, A. Galindo, *Polyhedron* **2009**, *28*, 3929.
- [38] G. S. Owens, M. M. Abu-Omar, *Chem. Commun.* **2000**, 1165.
- [39] C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, J. F. Brennecke, *J. Chem. Eng. Data.* **2004**, *49*, 954.
- [40] B. Wang, Q. G. Zhang, J. Z. Yang, *Fluid Phase Equilibria* **2007**, *254*, 163.
- [41] Apex suite of crystallographic software. Apex 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [42] Saint, Version 7.56a and Sadabs Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
- [43] G. M. Sheldrick, Sadabs (version 2008/1), Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen (Germany) (**2008**).
- [44] G. M. Sheldrick, "Shelxl-97", University of Göttingen, Göttingen, Germany, (**1998**).
- [45] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp.

Chapter 8

219–222), and 4.2.4.2 (pp. 193–199), A.J. C. Wilson (Ed.), Kluwer Academic Publishers, Dordrecht, The Netherlands (**1992**).

[46] A. L. Spek, "Platon", A Multipurpose Crystallographic Tool, UtrechtUniversity, Utrecht, The Netherlands (**2010**).

9 New ionic liquids with $[\text{Ni}^{\text{II}}(\text{CN})_4]^{2-}$ anion: synthesis, characterization and catalytic performance

9.1 Introduction

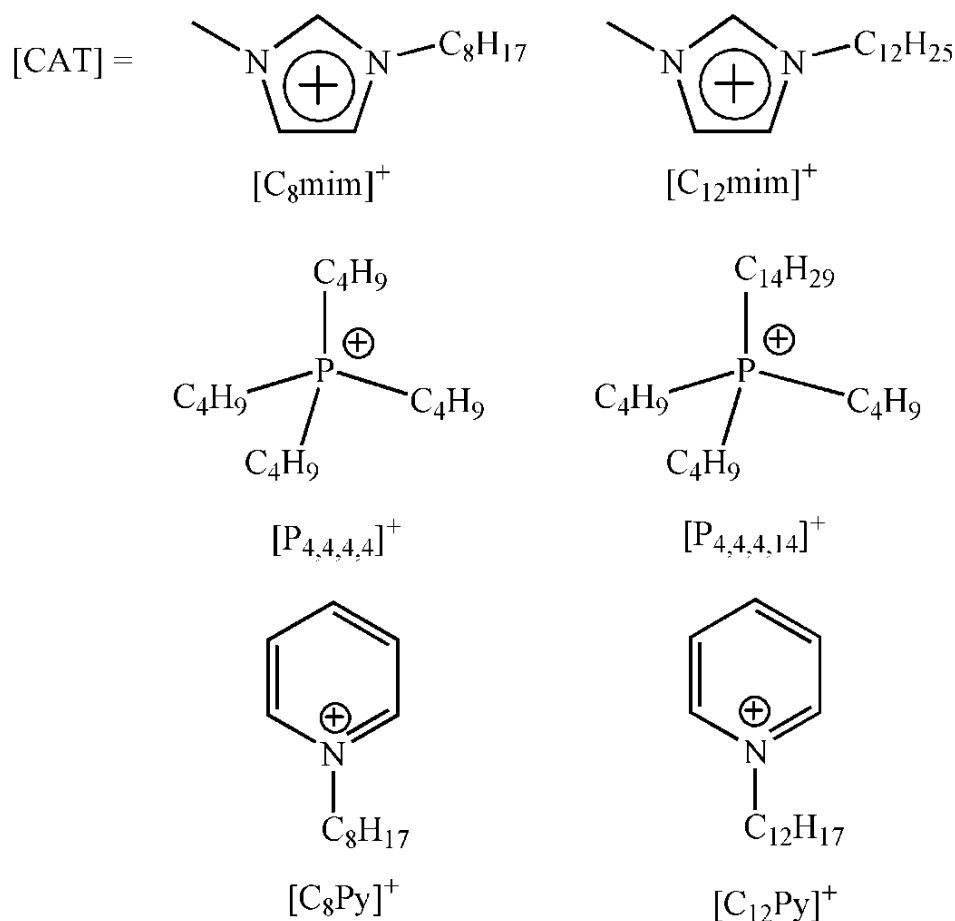
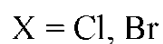
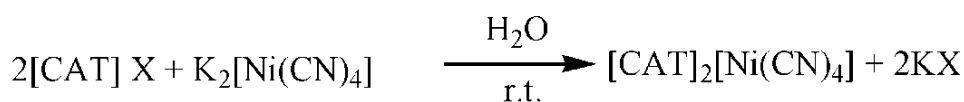
Ionic liquids (ILs) have attracted much attention as a replacement for classical solvents in many applications due to their remarkable physical and chemical properties.^[1] Most ILs are purely organic onium cations and anions such as $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ and $[\text{CF}_3\text{SO}_2]^-$, which are regarded as green media for various reactions.^[2] However, metal-containing ILs have been recently developed as new materials, which not only provides unique properties of ILs but also has additional advantages such as geometry, magnetism and catalytic properties in comparison with “organo-ILs”.^[3] Many of metal-containing ILs which prepared so far by mixing chlorine based ILs with metal chlorides in various molar ratios are capable of mediating a wide variety of synthetic reactions and exhibit great potential in catalysis.^[4] However, the investigation of potential nickel ion-containing ILs in catalysis seems largely neglected. A small number of imidazolium-based Ni ion containing ILs have been described as catalysts for the reactions. For example, Iwasawa found that this kind of ILs $[\text{C}_n\text{mim}]_2[\text{NiCl}_4]$ catalyzed Suzuki cross-coupling reactions with good yield.^[5] Kim reported pyridinium base dicationic ionic salts containing $[\text{NiCl}_4]^{2-}$ can be used as catalysts for the hydrolysis of sodium borohydride.^[6] These results promote us to investigate new nickel ion containing IL species involved the properties of ILs and potential catalytic feature. Thus, ILs with $[\text{Ni}(\text{CN})_4]^{2-}$ anion was developed recently by our group.

In this work, we prepared new ILs based on 1-octyl-3-methylimidazolium ($[\text{C}_8\text{mim}]^+$), 1-dodecyl-3-methylimidazolium ($[\text{C}_{12}\text{mim}]^+$), tetra-butyl-phosphonium ($[\text{P}_{4,4,4,4}]^+$), tributyl-(tetradecyl)-phosphonium ($[\text{P}_{4,4,4,14}]^+$), 1-octyl-pyridinium $[\text{C}_8\text{Py}]^+$ and 1-dodecyl-pyridinium $[\text{C}_{12}\text{Py}]^+$ with $[\text{Ni}(\text{CN})_4]^{2-}$. These ILs have high thermal stability and are used as catalysts for epoxidation of olefins.

9.2 Results and discussion

9.2.1 Synthesis of ILs with $[\text{Ni}(\text{CN})_4]^{2-}$ anion

A series of ILs with $[\text{Ni}(\text{CN})_4]^{2-}$ anion was prepared by mixture of cation halide ($[\text{C}_8\text{mim}]\text{Br}$, $[\text{C}_{12}\text{mim}]\text{Br}$, $[\text{P}_{4,4,4,4}]\text{Br}$, $[\text{P}_{4,4,4,14}]\text{Cl}$, $[\text{C}_8\text{Py}]\text{Br}$ and $[\text{C}_{12}\text{Py}]\text{Br}$) and dipotassium tetracyanonickelate in water (Scheme 1). The precipitation was formed immediately. After filtration, the product was washed with water and methanol for three times. The solvent was removed under vacuum. All ILs have high solubility in polar organic solvents such as CH_2Cl_2 , CH_3CN , common alcohols, but low solubility in *n*-hexane.



Scheme 1. Synthesis of ILs with different cation and $[\text{Ni}(\text{CN})_4]^{2-}$ anion.

9.2.2 Characterization of ILs with $[\text{Ni}(\text{CN})_4]^{2-}$ anion

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and IR spectroscopy data of ILs with $[\text{Ni}(\text{CN})_4]^{2-}$ are given in Table 1. TGA indicates that all ILs show negligible volatility and high thermal stability with a decomposition temperature more than 270 °C. $[\text{C}_8\text{mim}]_2[\text{Ni}(\text{CN})_4]$ (**1**), $[\text{P}_{4,4,4,14}]_2[\text{Ni}(\text{CN})_4]$ (**4**) and $[\text{C}_8\text{Py}]_2[\text{Ni}(\text{CN})_4]$ (**5**) are liquid at room temperature. The melting points of $[\text{C}_{12}\text{mim}]_2[\text{Ni}(\text{CN})_4]$ (**2**), $[\text{P}_{4,4,4,4}]_2[\text{Ni}(\text{CN})_4]$ (**3**) and $[\text{C}_{12}\text{Py}]_2[\text{Ni}(\text{CN})_4]$ (**6**) are 71 °C, 141 °C and 81 °C, respectively. In addition, IR spectroscopy was used to identify the CN group. The CN stretching vibration of ILs lies between 2106-2114 cm^{-1} , which has significant shifted compared to the vibration (2119 cm^{-1}) of starting material $\text{K}_2[\text{Ni}(\text{CN})_4]$ alone.

Table 1. Melting points (T_m), glass transition points (T_g), decomposition temperatures (T_d) and IR data of ILs.

Entry	ILs	T_m/T_g (°C)	T_d (°C)	IR (CN) (cm^{-1})
1	$[\text{C}_8\text{mim}]_2[\text{Ni}(\text{CN})_4]$	-52	354	2113
2	$[\text{C}_{12}\text{mim}]_2[\text{Ni}(\text{CN})_4]$	71	327	2114
3	$[\text{P}_{4,4,4,4}]_2[\text{Ni}(\text{CN})_4]$	141	347	2106
4	$[\text{P}_{4,4,4,14}]_2[\text{Ni}(\text{CN})_4]$	-57	352	2110
5	$[\text{C}_8\text{Py}]_2[\text{Ni}(\text{CN})_4]$	-43	286	2113
6	$[\text{C}_{12}\text{Py}]_2[\text{Ni}(\text{CN})_4]$	81	271	2109

9.2.3 Catalytic epoxidation of olefins

The ILs **1-6** were examined as catalysts for epoxidation of *cis*-cyclooctene with TBHP (*tert*-butyl hydroperoxide) as oxidant in solvent-free at 70 °C (Figure 1). Further details of the catalytic reaction are given in the experimental section. Blank reactions showed no significant amounts of epoxide were formed in the absence of catalysts. A catalyst: oxidant: substrate ratio of 5:200:100 was used in all experiments.

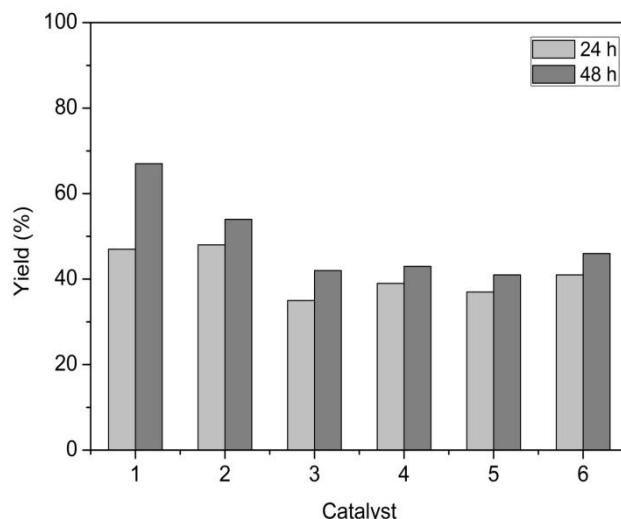


Figure 1. Yield of *cis*-cyclooctene epoxidation after 24 h (gray bars) and after 48 h (black bars) with ILs **1-6** as catalysts and TBHP as oxidant agent at 70 °C.

ILs **1-6** showed similar catalytic activity for epoxidation of *cis*-cyclooctene, indicating the cation of ILs not involved in the catalysis reaction. IL **1** displayed the best catalytic performance achieving more than 60 % yield after 48 h in all ILs. The final solution exhibited no color and no decomposition of ILs was detected in the whole reactions *via* ^1H NMR confirmation. A further catalytic experiment using 1-octene as substrate was carried out as well. The results showed that a 77 % yield of epoxide was obtained after 24 h using **2** as catalyst and TBHP as oxidant at 70 °C. It is important to note that all ILs showed high epoxidation selectivity (> 99 %) and no significant by-product such as diol was found in the whole measurements. Figure 2 shows that the catalytic reaction follows first order kinetics in which the reaction conversion increases steadily for the first 6 h and then slows down.

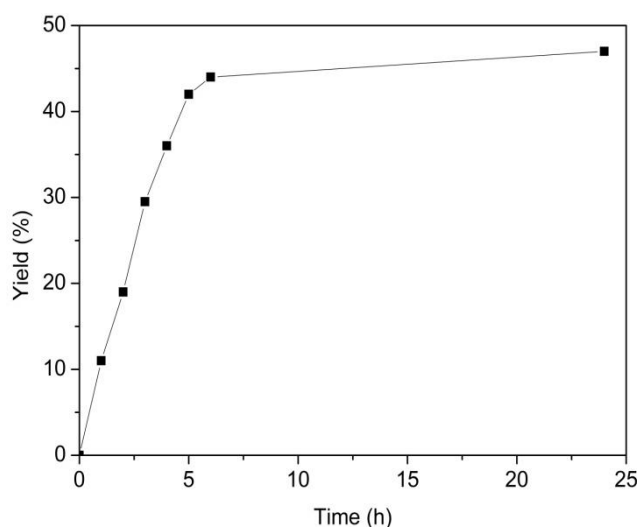


Figure 2. Kinetics of epoxidation of *cis*-cyclooctene with $[\text{C}_{12}\text{mim}]_2[\text{Ni}(\text{CN})_4]$ as catalyst and TBHP as oxidant at 70 °C.

9.3 Conclusion

A series of ILs based on different cation of ILs and $[\text{Ni}(\text{CN})_4]^{2-}$ was synthesized and characterized. The preparation of ILs was simple and convenient. All ILs showed negligible volatility and high thermal stability. It was found that these ILs can be used as catalysts for the epoxidation of olefins with TBHP as oxidant at 70 °C, as well as displaying good activity and high selectivity for epoxides. The present catalytic procedure provides a cheap, safe, easy to handle and environmentally benign alternative.

9.4 Experimental section

9.4.1 General

All preparations and manipulation involving air sensitive materials were performed using standard Schlenk techniques under argon atmosphere. Solvents were dried by standard procedures (Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and kept over 4 Å molecular sieves. All chemicals (purchased from Acros Organics or Aldrich) were of analytical grade and used as received. ^1H -NMR, ^{13}C -NMR and ^{31}P -NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer and chemical shifts are reported relative to the residual signal deuterated solvent. IR spectra were recorded on Varian FTIR – 670 spectrometer, using a GladiATR accessory with a diamond ATR element. Thermogravimetry coupled with mass spectroscopy (TG-MS) was conducted utilizing a Netzsch TG209 system; typically about 10 mg of each sample were heated from 25 °C to 1000 °C at 10 K min^{-1} . Differential Scanning Calorimetry (DSC) was performed on a Q2000 series DSC instrument; typically about 2 mg of each sample were heated from -100 °C to 150 °C at 10 K min^{-1} . Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphasex 120 and a Hewlett-Packard integration unit HP 3396 Series II.

Organic and inorganic starting materials were reagent grade from Acros or Aldrich and used as received. The preparation of 1-methyl-3-octyl-imidazolium $[\text{C}_8\text{mim}]\text{Br}$, 1-methyl-3-dodecyl-imidazolium $[\text{C}_{12}\text{mim}]\text{Br}$, tetrabutylphosphonium bromide $[\text{P}_{4,4,4,4}]\text{Br}$, tributyl(tetradecyl)phosphonium chloride $[\text{P}_{4,4,4,14}]\text{Cl}$, 1-(1-octyl)-pyridine bromide $[\text{C}_8\text{py}]\text{Br}$, 1-(1-dodecyl)-pyridine bromide $[\text{C}_{12}\text{py}]\text{Br}$ followed literature procedures.^[7]

9.4.2 Synthetic method and characterization data

$[\text{CAT}]\text{X}$ (2 mmol) was added to a water (50 mL) solution of according $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.2496g,

1 mmol). The resulting mixture was stirred for 2 h. After filtration the volatiles were removed in vacuum. The crude product was washed by methanol and water for three times. The desired product was obtained as yellow or white solid.

[C₈mim]₂[Ni(CN)₄] (**1**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.83 (m, 3H), 1.23 (m, 10H), 1.79 (m, 2H), 3.87 (s, 3H), 7.68 (s, 1H), 7.75 (s, 1H), 9.08 ppm (s, 1H); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 13.86, 22.01, 25.47, 28.45, 29.39, 31.13, 35.81, 48.80, 54.86, 122.25, 123.56, 131.32, 136.32 ppm; IR (ATR, diamond crystal, neat): ν = 2113 cm⁻¹ (CN); FAB-MS (m/z %): 195.3 (100) [C₈mim]⁺, 357.3 (19) [[C₈mim][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₂₈H₄₈N₈Ni (555.43): C, 60.55; H, 8.71; N, 20.17; found: C, 59.97; H, 8.51; N, 19.65; T_g: -52 °C; T_d: 354 °C.

[C₁₂mim]₂[Ni(CN)₄] (**2**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.85 (m, 3H), 1.25 (m, 18H), 1.78 (d, 2H), 3.86 (s, 3H), 4.15 (d, 3H), 7.69 (s, 1H), 7.76 (s, 1H), 9.08 ppm (s, 1H); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 13.68, 21.84, 25.26, 28.15, 28.46, 28.59, 28.71, 28.76, 28.78, 29.15, 31.04, 35.56, 48.55, 122.03, 123.36, 131.02, 136.17 ppm; IR (ATR, diamond crystal, neat): ν = 2114 cm⁻¹ (CN); FAB-MS (m/z %): 251.5 (100) [C₁₂mim]⁺, 413.2 (100) [[C₁₂mim][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₃₆H₄₈N₈Ni (651.51) : C, 64.37; H, 9.66; N, 16.76; found: C, 64.51; H, 9.57; N, 16.46; T_m: 71 °C; T_d: 327 °C.

[P_{4,4,4,4}]₂[Ni(CN)₄] (**3**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.92 (m, 12H), 1.47 (m, 16H), 2.19 ppm (m, 8H); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 13.74, 17.62, 18.10, 23.11, 23.16, 23.73, 23.89, 131.71 ppm; ³¹P-NMR ([D₆]-DMSO, 162 MHz, r.t.): δ = 34.43 ppm (s); IR (ATR, diamond crystal, neat): ν = 2106 cm⁻¹; FAB-MS (m/z %): 259.4 (100) [P_{4,4,4,4}]⁺, 421.1 (100) [[P_{4,4,4,4}][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₃₆H₇₂N₄Ni (681.62): C, 63.43; H, 10.65; N, 8.22; found: C, 62.73; H, 10.68; N, 8.06; T_m: 141 °C; T_d: 347 °C.

[P_{4,4,4,14}]₂[Ni(CN)₄] (**4**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.85 (d, 3H), 0.92 (d, 3H), 1.36 (m, 20H), 1.47 (m, 16H), 2.19 ppm (m, 8H); ³¹P-NMR ([D₆]-DMSO, 162 MHz, r.t.): δ = 34.94 ppm (s); IR (ATR, diamond crystal, neat): ν = 2110 cm⁻¹ (CN); FAB-MS (m/z %): 399.8 (100) [P_{4,4,4,14}]⁺, 561.3 (64) [[P_{4,4,4,14}][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₅₆H₁₁₂N₄OP₂Ni (962.16): C, 69.91; H, 11.73; N, 5.82; found: C, 69.60; H, 11.87; N, 5.83; T_g: -57 °C; T_d: 352 °C.

[C₈Py]₂[Ni(CN)₄] (**5**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.83 (d, 3H), 1.25 (m, 9H), 2.51 (m, 2H), 4.65 (m, 2H), 8.21 (m, 2H), 8.65 (m, 1H), 9.13 ppm (m, 2H); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 13.49, 13.51, 21.71, 25.06, 28.13, 28.18, 30.75, 30.82, 59.95, 127.35, 144.55, 145.54 ppm; IR (ATR, diamond crystal, neat): ν = 2113 cm⁻¹ (CN); FAB-MS

(m/z %): 192.2 (100) [C₈Py]⁺, 354.2 (26) [[C₈Py][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₃₀H₄₄N₆Ni (547.4): C, 65.82; H, 8.10; N, 15.35; found: C, 63.78; H, 8.19; N, 15.01; T_g: -43 °C; T_d: 286 °C.

[C₁₂Py]₂[Ni(CN)₄] (**6**): ¹H-NMR ([D₆]-DMSO, 400 MHz, r.t.): δ = 0.84 (d, 3H), 1.27 (m, 18H), 1.92 (d, 2H), 4.61 (m, 2H), 8.18 (m, 2H), 8.60 (m, 1H), 9.09 ppm (m, 2H); ¹³C-NMR ([D₆]-DMSO, 100 MHz, r.t.): δ = 13.86, 22.01, 25.33, 28.32, 28.63, 28.71, 28.79, 28.84, 28.93, 30.65, 31.21, 60.72, 128.06, 131.23, 144.66, 145.42 ppm; IR (ATR, diamond crystal, neat): ν = 2109 cm⁻¹ (CN); FAB-MS (m/z %): 248.4 (100) [C₁₂Py]⁺, 410.2 (19) [[C₁₂Py][Ni(CN)₄]]⁻; elemental analysis calc. (%) for C₃₈H₆₀N₆Ni (659.62): C, 69.19; H, 9.17; N, 12.74; found: C, 68.88; H, 9.30; N, 12.52; T_m: 81 °C; T_d: 271 °C.

9.4.3 Catalytic reaction

To a solution of *cis*-cyclooctene (2 mmol) and TBHP (4 mmol) was added the catalyst (5 mol %) at 70 °C. After completion, the reaction mixture was extracted with *n*-hexane (5 × 3 mL). The organic phase treated with a catalytic amount of MgSO₄ and MnO₂ to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of *cis*-cyclooctene and the formation of the according oxidewere calculated from calibration curves ($r^2 > 0.999$) recorded prior to the reaction course.

9.5 References

- [1] (a) V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615; (b) R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834; (c) S. G. Lee. *Chem. Commun.* **2006**, 1049; (d) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; (e) F. V. Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757; (f) P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238; (g) J. H. Davis, *Chem. Lett.* **2004**, *33*, 1072.
- [2] Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, *13*, 2619.
- [3] L. Graser, D. Betz, M. Cokoja, F. E. Kühn, *Curr. Inorg. Chem.* **2011**, *1*, 166.
- [4] I. J. B. Lin, C. S. Vasam, *J. Organomet. Chem.* **2005**, *690*, 3498.
- [5] C. Zhong, T. Sasaki, M. Tada, Y. Iwasawa, *J. Catal.* **2006**, *242*, 357.
- [6] A. Chinnappan, H. Kim, C. Baskar, I. T. Hwang, *Int. J. Hydrogen Energy* **2012**, *37*, 10240.
- [7] J. G. Huddleston, R. D. Rogers, *Chem. Commun.* **1998**, 1765.

10 Summary

10.1 Imidazolium perrhenate ionic liquids: synthesis, properties and catalytic applications

A series of imidazolium perrhenate ionic liquids (IPILs) $[\text{C}_n\text{mim}][\text{ReO}_4]$ ($\text{C}_n\text{mim} = 1\text{-C}_n\text{H}_{2n+1}\text{-3-methylimidazolium}$; $n = 2$ (**1**), 4 (**2**), 5 (**3**), 6 (**4**), 8 (**5**), 10 (**6**), 12 (**7**)) has been synthesized and characterized (Figure 1). Compounds **1-5** are liquids at room temperature and compounds **6** and **7** show a melting point at 38.3 and 48.3 °C, respectively. The thermogravimetric analysis (TGA) data indicates that all the compounds show negligible volatility and high thermal stability with a decomposition onset temperature near 400 °C.

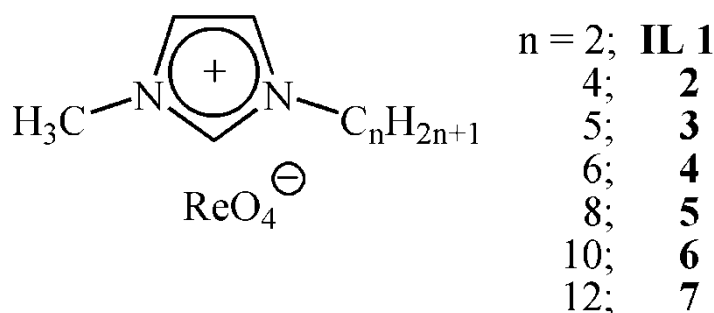


Figure 1. Imidazolium perrhenate ionic liquids.

IPILs **2**, **5** and **7** were found to be very efficient reaction media for the epoxidation of olefins (cyclooctene, 1-octene, styrene) with H_2O_2 as oxidant, thus affording good yields. In all examined epoxidation reaction, H_2O_2 is superior to UHP and TBHP. Furthermore, this system can be recycled at least eight times with constant yields of 98–99 %, which demonstrates the high stability of the IL under oxidative conditions, thus rendering it a good candidate for efficient olefin epoxidation.

Additionally, the IPILs exhibit good catalytic abilities for oxidation of sulfides to sulfones with hydrogen peroxide as oxidant in the normal ionic liquid $[\text{Bmim}][\text{BF}_4]$ at 60 °C. A series of sulfones was obtained with high yields under mild reaction conditions. Furthermore, the functional groups, such as double bonds, hydroxyl groups and esters are tolerated and no epoxidation and aldehyde formation is observed. This was demonstrated that IPILs could be reused at least ten times without considerable loss of activity. The conversion and yield did not decrease on recycling and the products obtained were the desired sulfones.

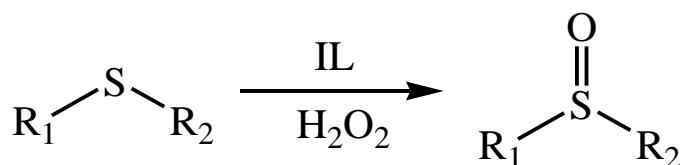
For the mechanism, formation of $\text{O}_3\text{Re-O} \cdots \text{H-O-OH}$ species between the peroxide with IPILs was detected using IR, Raman and DFT calculations techniques. These hydrogen

bridged moieties play a key role in both epoxidation and sulfoxidation reactions. In the IR spectra, the experimentally observed splitting (890–920 cm^{-1}) of the former asymmetric stretching mode of the pure ionic liquid, which was found at about 900 cm^{-1} , was also reflected in the simulated spectra. In the Raman spectra, the asymmetric stretching mode of the pure ionic liquid at about 916 cm^{-1} , was broadened to 885–930 cm^{-1} . Point group analysis showed that this is consistent with a lowering of the local symmetry of $[\text{ReO}_4]^-$ from T_d to C_{2v} . All these changes can be assigned to a distortion of the local symmetry of the anion by weak coordination H-bond, which is supported by DFT calculations as well.

10.2 Oxidation of sulfides to sulfoxides in metal-free ionic liquids

In continuation of the studies described above, new ionic liquids utilizing different cations with a new family of $[\text{B}(\text{Ar}^{\text{F}})_4]$ species have been synthesized and structurally characterized. The synthesis was optimized and is now simple, and the products can be obtained in high yields. All salts have high thermal stability. It has been shown that the $[\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-(CF}_3)_2)_4]^-$ anion salts (**2b**, **3b**, **5b** and **6b**) melting points are reduced by 100 °C compared to the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salts, which lead to opportunities to form ILs materials. The melting points of the salts using tetrabutylammonium and 1,1,3,3-tetramethylguanidium as cation are higher than those of any other salts due to the high symmetry structure. Increasing the size of the salts has been identified as a common and potentially general characteristic of low melting points with large cation. The systematic variation of alkyl substituent on the cation led to usefully predictive trends in melting points. It is important to mention that hydrogen-bonding interactions between $[\text{TMG}]^+$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ has been discovered.

The ionic liquid $[\text{P}_{4,4,4,14}][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ and normal ionic liquid $[\text{C}_4\text{mim}]\text{BF}_4$ can be successfully applied for oxidation of sulfides to sulfoxides without catalyst (Scheme 1). The results show that faster oxidation rate of aliphatic sulfides than aromatic sulfides is due to higher nucleophilicity. Furthermore, these two systems can be recycled for at least four times without loss of activity.



Scheme 1. Oxidation of sulfides to sulfoxides in ILs

The reaction mechanism was examined by IR, Raman and NMR spectroscopy. From these examinations it can be concluded that the crucial step during the oxidation procedure is the

formation of a hydrogen bond between ionic liquid and oxidant.

10.3 Oxidation reactions with polyoxomolybdate salts and MTO Schiff base complexes in ionic liquids

10.3.1 Oxidation reactions catalyzed by polyoxomolybdate salts in ILs

Ionic compounds containing the polyoxomolybdate anion $[\text{Mo}_6\text{O}_{19}]^{2-}$ and a variety of cations were prepared, characterized and investigated with respect to their activity in the epoxidation of several olefins and oxidation of a series of sulfides (Figure 2). Three of the solid state structures were determined by single-crystal X-ray diffraction, exhibiting H...O bond between cation and anion $[\text{Mo}_6\text{O}_{19}]^{2-}$.

These compounds were applied as catalysts for the epoxidation of olefins with urea hydrogen peroxide (UHP) as oxidant in the ionic liquid $[\text{Bmim}]\text{PF}_6$ at 70 °C. The results show that the highest yield was obtained using cyclooctene and cyclohexane as substrates. With regard to some other olefins such as *trans*- β -methylstyrene, limonene, *cis*-stilbene and (+)-camphene, the reactions were rather challenging due to steric hindrance. Moreover, this catalytic procedure was repeated three times with only a minor loss of activity. It was found that the reaction is selective to the desired epoxide in all runs and no diol formation was observed. On the other hand, the oxidation of sulfides to sulfoxides with hydrogen peroxide (H_2O_2) as oxidant and polyoxomolybdate salts as catalysts in MeOH was also investigated. The polyoxomolybdate catalysts show a good performance for oxidation of sulfides to sulfoxides. This system can be reused five times without any loss of activity.

10.3.2 Epoxidation of olefins catalyzed by MTO Schiff base complexes in ILs

A series of different Schiff base methyltrioxorhenium (VII) complexes have been synthesized and investigated with respect to their activity in the epoxidation of several olefins (Figure 3).

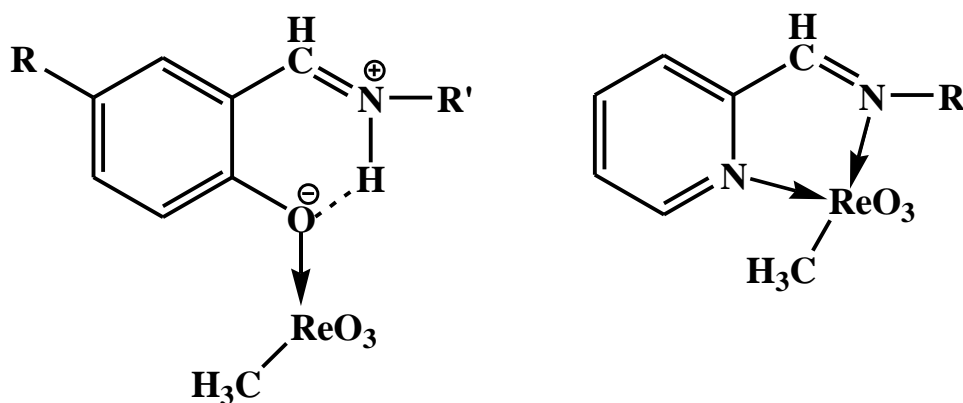


Figure 3.MTO Schiff base complexes

They display good air stability at room temperature. The complexes were applied as catalysts for the epoxidation of cyclooctene in the ionic liquid [Bmim]PF₆ with UHP as oxidant at room temperature. Surprisingly, the MTO complexes are also active when UHP was used as oxidant. It was found that the (N-salicylidene) aniline derived Schiff base complexes of MTO exhibit higher catalytic activity and selectivity than di-nitrogen Schiff bases complexes of MTO. It is noteworthy that this reaction is carried out in non-aqueous media, thus no diol by-product was found during the measurements.

11 Appendix

11.1 This section contains supplementary information to chapter 2: activation of hydrogen peroxide by ionic liquids: mechanistic studies and application in the epoxidation of olefins

11.1.1. Spectroscopic data of the perrhenate-containing ionic liquids

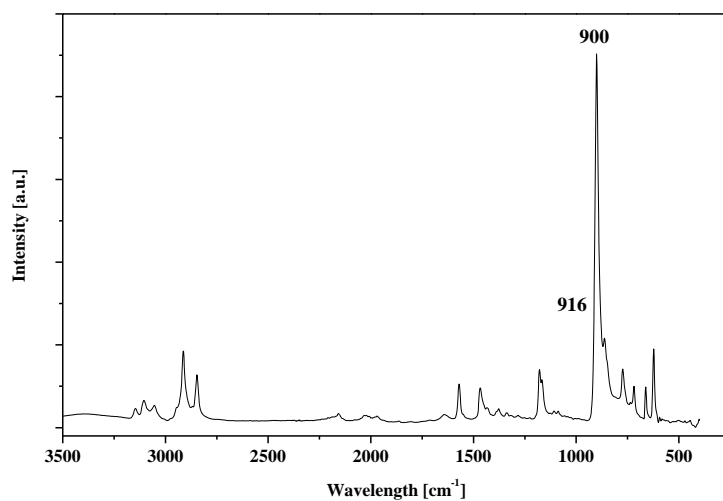


Figure 1. Mid-IR spectrum of [C₈mim][ReO₄].

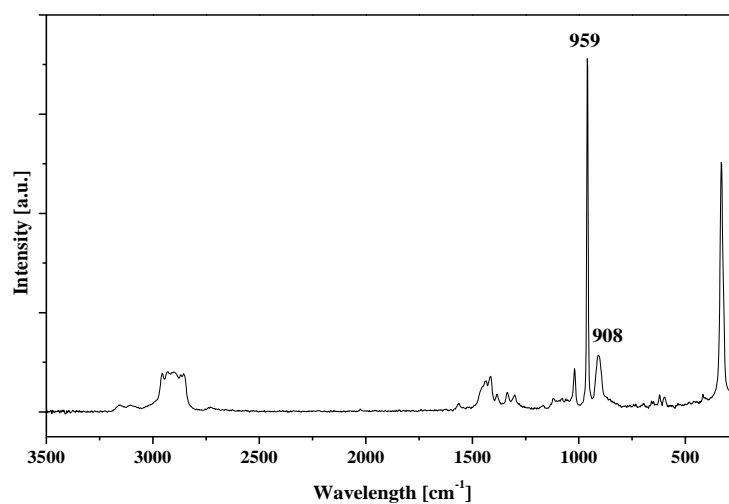


Figure 2. Raman spectrum of [C₈mim][ReO₄].

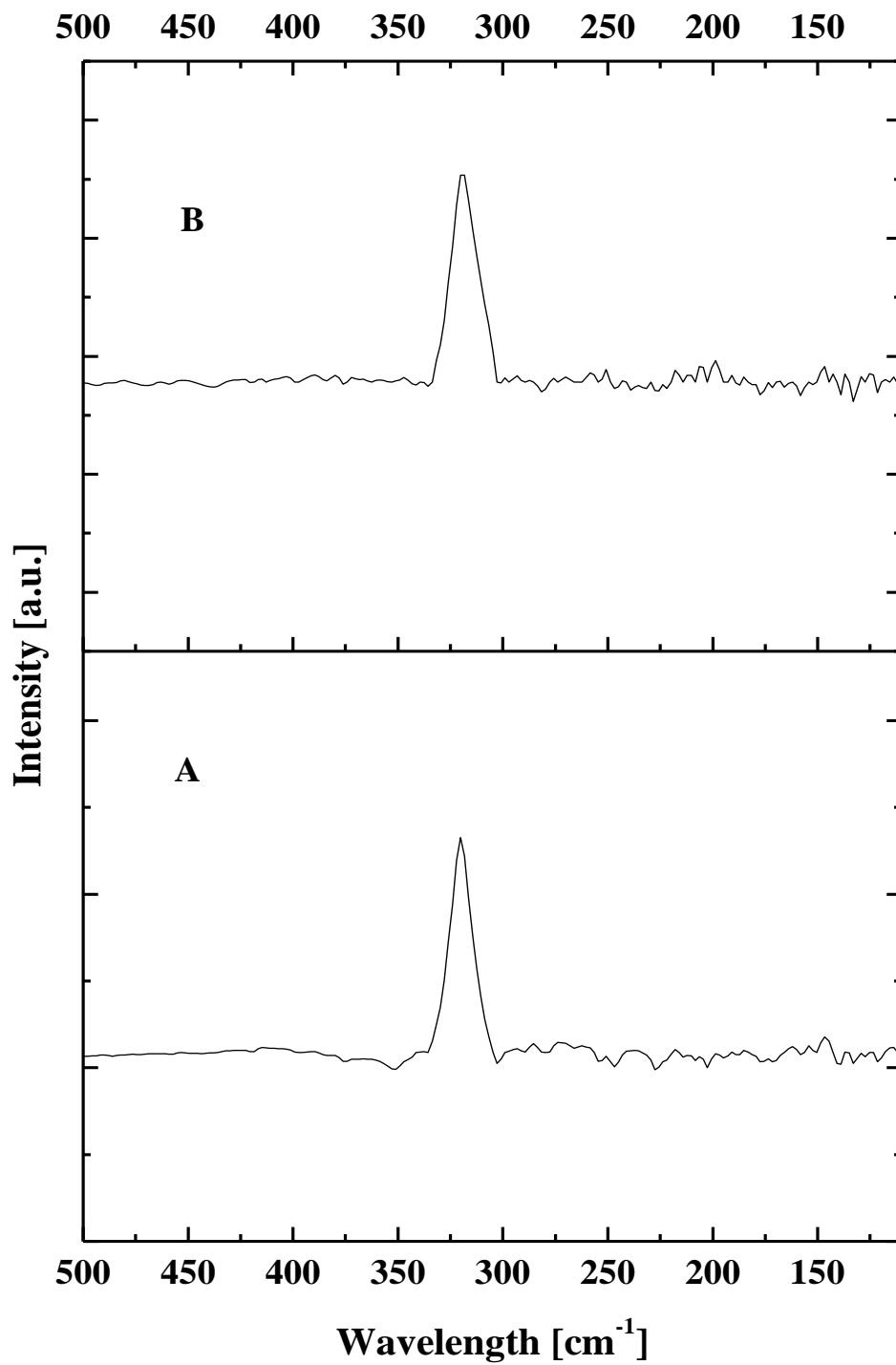


Figure 3. Far-IR spectra of $[\text{C}_8\text{mim}][\text{ReO}_4]$ (Re=O deform.) before (A) and during epoxidation (B).

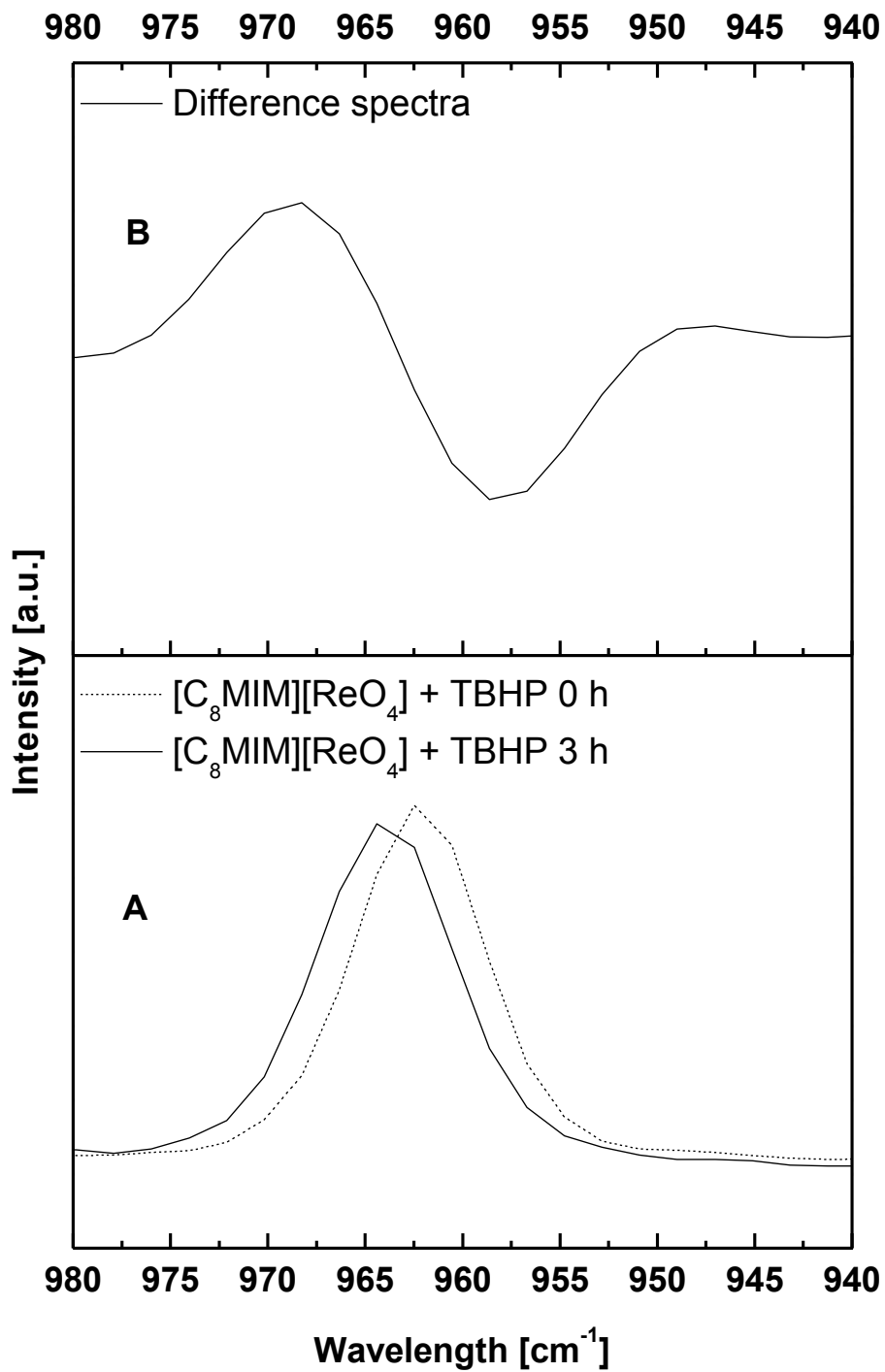


Figure 4. [C₈MIM][ReO₄] with TBHP at 0 h and 3 h (A); Difference spectra (B).

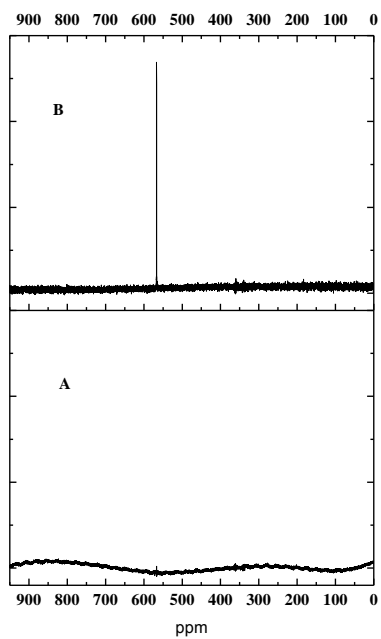
11.1.2 ^{17}O NMR spectra

Figure 5. ^{17}O NMR spectra of (A) cyclooctene oxide in *n*-hexane and (B) $[\text{C}_8\text{mim}][\text{ReO}_4]$.

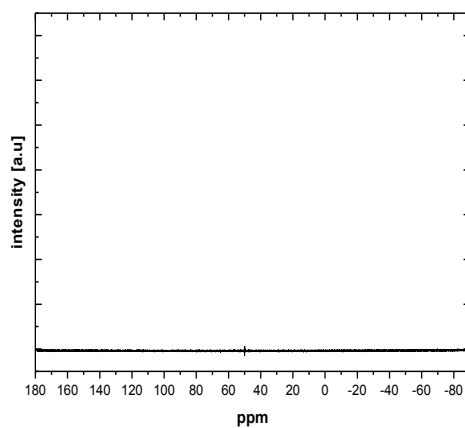


Figure 6. ^{17}O NMR spectra of cyclooctene oxide in *n*-hexane.

11.1.3 Calculated energies

Table 1. Energies E_0 (corrected for the zero-point energy) and Gibbs free energies G .

Name	E_0 [hartree]	G [hartree]
1	-531.094877	-531.131190
1a	-756.386894	-756.438427
1b	-688.281867	-688.327676
2_ts	-531.054635	-531.088383
3	-531.065466	-531.099867
4_ts	-531.035158	-531.067941
5	-531.038108	-531.071743
6	-609.662156	-609.710800
6a	-834.957822	-835.014804
6b	-766.848910	-766.905993
6_cyclooctene	-844.216327	-844.291433
7a_ts	-834.908389	-834.959615
7b_ts	-766.792347	-766.842479
7_ts	-609.601777	-609.644931
7_ts_cyclooctene	-844.167373	-844.237150
8	-609.734717	-609.780142
9_ts	-609.583291	-609.620422
10	-609.633325	-609.676971
11_ts	-609.580826	-609.617127
12	-609.625781	-609.663307
13_ts	-609.554131	-609.59064
14	-609.697547	-609.74182
15_ts	-609.689272	-609.732573
16	-609.734717	-609.780142
17_ts	-609.583308	-609.621484
18_ts	-609.575764	-609.61515
19	-609.608259	-609.651741
20_ts	-609.580208	-609.619535
21_ts	-609.556747	-609.592709
22	-609.597616	-609.633964
HOOH	-151.575626	-151.597939
Perrhenate	-379.495611	-379.525613
TBHP	-308.766887	-308.797878
UHP	-376.875675	-376.909572
epoxide	-153.778917	-153.803005
ethene	-78.564729	-78.586908
cyclooctene	-313.134549	-313.174266
cycloocteneepoxide	-388.360916	-388.401430

11.1.4 Geometries

(Cartesian coordinates in Ångstrom)

1

O	0.51507	-1.11298	-0.89419
Re	-0.52133	0.00002	0.00000
O	0.51592	1.11334	0.89283

Chapter 11

O	-1.53375	0.89189	-1.11378
O	-1.53197	-0.89219	1.11511
O	3.16378	-0.72372	0.07565
O	3.16494	0.72338	-0.07558

1a

C	5.98356	0.12860	-0.03171
O	5.50038	1.24365	0.11956
N	7.20045	-0.05263	-0.68718
N	5.39368	-1.02358	0.42039
O	2.79898	0.13280	0.85868
O	2.14681	-0.39115	-0.33134
O	-0.45022	0.03728	0.03710
Re	-2.22045	0.00931	-0.02684
O	-2.75035	-1.14128	-1.23623
O	-2.86081	-0.45891	1.53437
O	-2.81947	1.60130	-0.44399
H	3.27029	0.90657	0.50608
H	4.41732	-0.89929	0.69853
H	5.59840	-1.87994	-0.07186
H	7.71204	0.80719	-0.81565

1b

O	-0.79735	1.60835	0.09347
Re	-1.55738	0.03101	-0.00092
O	-2.50289	-0.07454	-1.47085
O	-0.30619	-1.22101	0.00036
O	-2.60827	-0.19080	1.38270
O	2.33825	-1.78236	-0.15472
O	2.87324	-0.64686	-0.88100
H	1.37182	-1.56892	-0.13911
C	3.53901	0.25735	0.03135
C	3.99710	1.37673	-0.90934
C	2.56738	0.79263	1.08723
C	4.73706	-0.45231	0.67456
H	5.27184	0.22537	1.34800
H	4.39393	-1.31560	1.24695
H	5.43129	-0.80120	-0.09532
H	4.56231	2.12740	-0.34961
H	4.63706	0.97542	-1.69987
H	3.13427	1.86177	-1.37084
H	3.06542	1.54748	1.70495

2_ts

O	0.41911	-1.51342	-0.49779
Re	-0.36412	-0.02543	0.00629
O	-0.65161	-0.01517	1.71917
O	1.96020	0.52428	0.48375
O	2.89463	-0.33456	-0.23328
O	0.27408	1.60414	-0.69083
O	-1.93428	-0.06629	-0.74603

Chapter 11

3

O	0.70064	-1.50145	-0.39612
Re	-0.27270	-0.07248	0.00683
O	1.62214	0.79940	-0.01150
O	2.78399	-0.06006	-0.03745
O	-0.45106	1.90503	-0.15567
O	-1.63706	-0.27988	-1.06088
O	-0.80765	-0.35933	1.63456

4_ts

O	-0.82001	-1.50025	-0.73548
Re	0.20504	-0.07610	0.03224
O	0.30792	-0.30519	1.74318
O	1.72679	-0.58255	-0.65842
O	-1.40026	0.99738	-0.36222
O	-2.43132	0.19305	0.15685
O	0.89512	1.76139	-0.34424

5

O	1.75983	0.27534	-0.91477
Re	0.01883	-0.10155	0.08641
O	0.54787	1.76195	0.57673
O	0.01058	-0.50205	1.78458
O	-1.87524	0.20376	-0.08307
O	-1.22419	0.68659	-1.32742
O	0.22559	-1.68028	-0.64587

6

C	-5.87127	-0.67204	0.01400
C	-5.86035	0.65797	0.01454
O	-2.39655	0.73789	0.04928
O	-2.40223	-0.70887	-0.10223
O	0.24296	1.12050	-0.89298
Re	1.26980	-0.00136	0.00223
O	2.27489	0.88049	1.12955
O	2.28646	-0.89062	-1.10877
O	0.22021	-1.11528	0.88077
H	-1.59945	0.99254	-0.46188
H	-1.61568	-0.97089	0.42130
H	-6.79887	-1.23864	0.02573
H	-4.93886	-1.22661	0.00152

6a

C	2.21244	3.27193	0.73665
C	1.31307	2.95779	-0.19262
O	-0.47291	-0.10477	-0.13534
Re	-2.24656	-0.12584	-0.04533
O	-2.75938	-0.42461	1.60013
O	-2.86239	1.42743	-0.56925
O	-2.88228	-1.38101	-1.08515
O	2.02402	-0.69842	0.51767

Chapter 11

O	2.31637	-2.12574	0.42519
N	4.40051	0.44351	-0.49077
C	5.36476	-0.46792	-0.19884
N	6.67788	-0.00785	-0.28432
O	5.12829	-1.63187	0.12305
H	3.29103	-2.08673	0.34020
H	3.43945	0.17894	-0.24414
H	4.61386	1.42794	-0.46416
H	7.35466	-0.75577	-0.29644
H	6.86876	0.73979	-0.93488
H	1.07202	-0.64944	0.24250
H	2.74571	4.21886	0.72408
H	2.43540	2.59614	1.55626

6b

C	-0.19156	4.23704	0.18589
C	-1.46708	4.49517	-0.09061
O	-2.37696	1.08613	-0.39647
O	-2.82931	-0.17107	-0.95951
C	-3.44567	-0.98046	0.07005
C	-4.69463	-0.26814	0.60341
C	-3.81766	-2.24834	-0.70541
C	-2.45292	-1.29413	1.19299
O	0.30481	0.79572	-0.18062
Re	1.64742	-0.34924	-0.00509
O	2.71985	0.20169	1.26421
O	1.01287	-1.92845	0.41250
O	2.53645	-0.45679	-1.50842
H	-1.39814	0.94467	-0.35635
H	-5.19806	-0.88240	1.35707
H	-4.41473	0.68316	1.05871
H	-5.39672	-0.06790	-0.21104
H	-4.33953	-2.94917	-0.04766
H	-4.47224	-2.00582	-1.54681
H	-2.91947	-2.73506	-1.09147
H	-2.90233	-1.99261	1.90672
H	-1.53763	-1.74081	0.79770
H	-2.18281	-0.38428	1.73121
H	-1.87310	5.50189	-0.03283
H	-2.14845	3.70242	-0.38343

6_cyclooctene

C	-5.11099	-1.75261	-0.01350
C	-6.49369	-1.40222	-0.58714
C	-7.42007	-0.61481	0.34964
C	-6.83500	0.70519	0.86956
C	-6.28216	1.60668	-0.25526
C	-4.75524	1.75133	-0.26275
C	-3.82993	0.55700	-0.20797
C	-3.95925	-0.77166	-0.09503
O	-0.34515	0.71706	-0.14617
O	-0.35794	-0.72303	0.05794
O	2.29575	0.84544	-1.14519
Re	3.31222	-0.00694	0.01886
O	2.25312	-0.86462	1.13997

Chapter 11

O	4.30171	1.13800	0.89563
O	4.34396	-1.14585	-0.81610
H	0.45286	0.83687	-0.70338
H	0.42159	-0.85111	0.63866
H	-2.78982	0.87977	-0.22964
H	-2.99881	-1.28086	-0.03258
H	-5.22772	-2.06298	1.03697
H	-4.76201	-2.65719	-0.52550
H	-4.46497	2.34784	-1.13856
H	-4.47257	2.37959	0.59553
H	-6.62459	1.23822	-1.22809
H	-6.70195	2.61451	-0.16214
H	-7.00334	-2.33795	-0.84632
H	-6.36165	-0.86533	-1.53209
H	-7.68994	-1.25066	1.20274
H	-8.35728	-0.40456	-0.18319
H	-7.61342	1.23270	1.43174
H	-6.03626	0.49228	1.58776

7a_ts

C	-2.39656	3.12857	-0.08000
C	-1.64190	2.05343	-0.54675
O	-2.11079	1.20763	0.85964
O	-1.99623	-0.49423	1.74411
N	-3.83719	-1.70068	0.28014
C	-4.69676	-0.81544	-0.24774
O	-4.54012	0.41416	-0.18754
N	-5.83321	-1.33143	-0.87898
O	0.77406	-0.90376	0.86625
Re	2.06274	-0.16874	-0.08308
O	1.53160	1.41246	-0.64678
O	3.49834	0.01014	0.90590
O	2.42655	-1.18748	-1.46295
H	-5.74526	-2.24070	-1.30894
H	-6.29519	-0.64724	-1.45940
H	-4.09038	-2.67360	0.33627
H	-3.02960	-1.32150	0.86810
H	-3.03800	0.94854	0.61687
H	-1.05599	-0.60939	1.50807
H	-2.03322	1.45529	-1.36262
H	-0.56009	2.04793	-0.46091

7b_ts

C	1.27357	3.04104	0.54247
C	1.84927	2.54777	-0.64716
O	2.21583	1.11141	-0.04718
O	2.96610	-0.47999	-0.73029
O	-0.32261	0.32189	-0.02240
Re	-2.01552	-0.20578	-0.00509
O	-2.18267	-1.65776	0.95639
O	-3.00078	1.06492	0.69105
O	-2.55719	-0.52290	-1.63871
C	4.10943	-0.75576	0.01839
H	1.32546	0.65536	-0.00445
H	2.82022	2.93203	-0.94759

Chapter 11

H	1.18812	2.35232	-1.48620
H	1.90195	3.44465	1.32649
H	0.23678	2.83300	0.76959
C	4.68074	-2.05149	-0.61165
C	3.77202	-1.01174	1.50122
C	5.15393	0.37391	-0.10678
H	6.08694	0.12230	0.41068
H	5.37709	0.55719	-1.16184
H	4.75632	1.29483	0.32653
H	5.59310	-2.36344	-0.08984
H	3.94321	-2.85433	-0.54586
H	4.91506	-1.88396	-1.66577
H	3.34481	-0.11016	1.94551

7_ts

C	3.78129	-1.62277	-0.26118
C	3.98021	-0.46684	0.52254
O	2.94405	0.44054	-0.29019
O	2.40265	2.22732	-0.01375
Re	-1.01928	-0.06126	0.00763
O	-1.83095	-1.29755	-0.92764
O	-1.92840	0.24479	1.46981
O	0.62164	-0.60683	0.41672
O	-0.90291	1.40636	-0.93928
H	1.59331	2.16971	-0.54626
H	2.05138	0.06354	-0.01993
H	4.90889	0.08324	0.40302
H	3.62023	-0.47394	1.54807

7_ts_cyclooctene

C	3.32378	1.20067	1.21942
C	2.00193	0.64360	0.72820
C	1.74762	-0.45817	-0.10955
C	2.62292	-1.03468	-1.18165
C	3.60176	-2.14335	-0.70595
C	5.00884	-1.65934	-0.33280
C	5.12085	-0.65567	0.82609
C	4.64010	0.79203	0.54377
O	1.53627	1.65840	-0.53438
O	1.37965	3.55364	-1.02131
O	-1.12311	1.12630	0.05235
Re	-2.30951	-0.18352	0.06481
O	-3.21641	-0.14780	1.56231
O	-3.40263	-0.02555	-1.29237
O	-1.43471	-1.70375	-0.05534
H	1.90107	3.39748	-1.81835
H	0.54989	1.66527	-0.45266
H	1.21881	0.80380	1.46467
H	0.75434	-0.89024	-0.03488
H	3.18557	-0.24703	-1.69006
H	1.95704	-1.46790	-1.93271
H	3.39714	0.94329	2.28485
H	3.21801	2.28898	1.17529
H	5.40207	1.48348	0.91920
H	4.58825	0.97823	-0.53233

Chapter 11

H	3.70564	-2.87866	-1.51237
H	3.15820	-2.68164	0.13944
H	5.47984	-1.22020	-1.22301
H	5.61051	-2.54161	-0.07933
H	4.59007	-1.05362	1.70017
H	6.17719	-0.61642	1.11573

8

C	-3.64463	0.03858	-0.59879
C	-3.07235	-1.07445	0.16038
O	-4.43059	-0.64944	0.39228
O	-1.38479	2.71968	0.13796
Re	0.95197	-0.12444	-0.00562
O	0.75701	1.13101	-1.22524
O	0.42750	-1.66678	-0.65145
O	-0.06464	0.31145	1.36756
O	2.62798	-0.22691	0.49106
H	-0.75375	2.47831	-0.55763
H	-1.14614	2.09771	0.84190
H	-3.96308	-0.12811	-1.62575
H	-3.35297	1.05485	-0.34961

9_ts

C	1.03392	1.87840	-0.60396
C	2.13733	1.30601	0.01676
O	1.65859	-0.51826	0.70769
Re	-0.48069	-0.07133	-0.05441
O	-1.19436	-1.40431	0.81604
O	2.37756	-1.48459	-0.09180
O	0.23541	-0.83459	-1.48303
O	-1.78014	0.87836	-0.71185
O	-0.22421	0.93473	1.68618
H	0.46227	2.63340	-0.08062
H	0.95460	1.85297	-1.68449
H	2.92364	0.83289	-0.55997
H	2.40258	1.59520	1.02474

10

C	-4.02136	0.20651	-0.21454
C	-3.92145	-1.12042	-0.19544
O	-0.80804	1.13264	0.64631
O	-0.82132	2.50025	0.17605
Re	0.69110	-0.14648	-0.03747
O	2.10426	-0.07098	0.96908
O	0.90338	1.18989	-1.18570
O	-0.58123	-1.16696	1.11408
O	0.83294	-1.53082	-1.08728
H	-1.17226	-0.56861	1.58954
H	-0.16614	2.43637	-0.55621
H	-4.96982	0.70036	-0.41125
H	-3.15600	0.83784	-0.03619

Chapter 11

11_ts

C	-1.18000	1.83050	0.64446
C	-2.18051	1.26530	-0.14259
O	-1.59594	-0.48729	-0.79533
O	-2.31614	-1.50938	-0.07605
Re	0.50269	-0.01969	-0.05409
O	-0.42886	-0.90197	1.58680
O	1.69847	0.76467	0.94441
O	0.50650	0.93649	-1.51883
O	1.13907	-1.56558	-0.52932
H	-0.59362	-0.26159	2.28252
H	-0.57440	2.63439	0.24600
H	-1.25281	1.77813	1.72547
H	-3.04257	0.77974	0.30114

12

C	1.11343	-0.94649	0.91241
C	2.30175	-1.18820	-0.00563
O	2.73218	-0.05214	-0.75950
O	3.12447	0.99226	0.17074
Re	-0.68514	-0.01965	-0.01961
O	0.55094	1.53648	0.58009
O	-1.81469	-0.38186	1.24772
O	-0.63326	-1.36272	-1.13653
O	-1.31516	1.31537	-1.01283
H	0.18652	2.30684	0.12391
H	0.73161	-1.91924	1.24266
H	1.39494	-0.36485	1.78941
H	3.16280	-1.57658	0.56118

13_ts

C	-1.56634	1.34420	-0.37634
C	-2.63887	0.54364	0.25591
O	-2.87000	-0.70378	-0.19350
O	-1.09595	-1.49232	-0.06278
Re	0.55776	0.02051	-0.03703
O	-0.23128	0.05059	1.83655
O	1.34989	1.56184	0.15286
O	0.38595	-0.16770	-1.78296
O	1.75029	-1.20768	0.37758
H	-0.61480	-0.81174	2.02616
H	-1.57157	1.38568	-1.46278
H	-1.36817	2.29989	0.10420
H	-2.63581	0.64636	1.34979

14

C	3.65424	-0.63395	-0.59859
C	3.57867	0.77719	-0.21660
O	4.50630	-0.11112	0.43790
O	0.40429	-1.30955	-0.34367

Chapter 11

Re	-0.72485	-0.04976	0.10167
O	-1.45250	-0.46726	1.62328
O	0.39429	1.26114	0.51477
O	-1.66071	1.50645	-0.87319
O	-2.07740	-0.84474	-1.14382
H	-1.17362	2.30647	-0.64927
H	2.73279	1.10996	0.37754
H	4.04709	1.52691	-0.85193
H	4.17507	-0.91504	-1.51222

15_ts

C	-3.44707	-0.13817	-0.46324
C	-4.34676	-0.63684	0.57810
O	-4.83636	0.27968	-0.40825
O	-0.78469	1.56565	0.38681
Re	0.96606	-0.10007	-0.00103
O	1.17131	1.55582	-0.87515
O	-0.33572	-1.11582	-0.55735
O	1.07795	-0.10074	1.74195
O	2.42023	-0.88406	-0.54965
H	0.24491	1.94440	-0.40018
H	-0.71272	1.86401	1.29897
H	-3.20641	-0.79111	-1.29690
H	-2.70247	0.61534	-0.21846

16

C	-3.64463	0.03858	-0.59879
C	-3.07235	-1.07445	0.16038
O	-4.43059	-0.64944	0.39228
O	-1.38479	2.71968	0.13796
Re	0.95197	-0.12444	-0.00562
O	0.75701	1.13101	-1.22524
O	0.42750	-1.66678	-0.65145
O	-0.06464	0.31145	1.36756
O	2.62798	-0.22691	0.49106
H	-0.75375	2.47831	-0.55763
H	-1.14614	2.09771	0.84190
H	-3.96308	-0.12811	-1.62575
H	-3.35297	1.05485	-0.34961

17_ts

C	-3.03464	-0.45666	0.67263
C	-3.01095	-0.44224	-0.68001
O	-1.52370	0.89330	-0.05319
Re	0.52958	-0.11552	-0.03632
O	2.24001	-0.26082	0.25334
O	-0.14330	2.02890	-0.14776
O	0.47910	0.15964	-1.78081
O	-0.12417	-1.72746	0.11700
O	0.24965	0.48962	1.85985
H	-0.51184	1.07724	1.90409
H	-3.63737	0.23308	-1.24955

Chapter 11

H	-2.40201	-1.14543	-1.23241
H	-3.66771	0.22089	1.23273

18_ts

C	4.35811	-0.48619	-0.22256
C	3.58321	0.31029	0.63741
O	2.35479	0.54776	-0.40927
O	0.66445	1.25687	-0.26628
Re	-0.74422	-0.11482	0.01076
O	0.65770	-1.23360	-0.18520
O	-1.64956	1.69035	-0.07528
O	-1.85627	-0.76411	-1.16455
O	-1.28551	-0.49118	1.62224
H	-0.98176	2.38539	-0.12621
H	1.86664	-0.35208	-0.41023
H	3.90561	1.32911	0.82827
H	3.12177	-0.16080	1.50161

19

C	-4.12328	0.46495	-0.22680
C	-4.26497	-0.85612	-0.15284
O	1.34571	-1.24615	-1.28568
Re	0.44977	0.02030	0.12859
O	1.37749	1.35736	-1.08864
O	-0.88012	1.47330	-0.16447
O	2.08058	-1.03156	-0.03196
O	0.89029	0.39870	1.77052
O	-0.84486	-1.13340	0.25395
H	2.04049	0.87555	-1.59750
H	-5.24054	-1.33415	-0.20076
H	-3.39607	-1.49638	-0.04067
H	-4.98422	1.12058	-0.33818

20_ts

C	3.19245	0.62672	-0.19756
C	3.10286	-0.72309	-0.23340
O	1.48392	-0.11380	0.90956
Re	-0.53399	-0.09569	-0.01316
O	0.01101	0.69007	-1.75211
O	-0.05713	-0.27403	1.76658
O	-2.26834	-0.07292	0.06646
O	-0.17820	-1.66338	-0.69261
O	-0.30795	1.96283	0.30772
H	0.08182	2.08909	1.17750
H	3.62140	-1.34127	0.48887
H	2.55608	-1.23225	-1.01626
H	3.75940	1.13567	0.57244

21_ts

C	1.70582	-1.45722	0.38273
C	2.60647	-0.61466	-0.27597

Chapter 11

O	1.71389	1.09661	-0.28093
Re	-0.31117	0.07316	-0.06117
O	-2.07849	-0.91398	-0.05992
O	1.10810	1.07368	0.97598
O	-0.08026	-0.78690	-1.59457
O	-0.94190	1.62123	-0.52999
O	-0.71826	-0.36813	1.84895
H	-1.53744	-0.87914	1.83565
H	1.24331	-2.26598	-0.16714
H	1.75300	-1.55535	1.45933
H	3.45074	-0.17862	0.24574

22

C	1.28269	-1.39347	0.26853
Re	-0.37517	0.09640	-0.07452
O	-1.91747	-1.20093	0.20320
C	2.55507	-0.76610	-0.21875
O	2.60823	0.56296	0.29470
O	1.33585	1.18621	0.03891
O	-0.43940	-0.51445	-1.71940
O	-0.95815	1.74982	-0.22690
O	-0.62415	-0.03713	1.89973
H	-1.19779	-0.77874	2.12076
H	-2.12055	-1.60982	-0.64466
H	1.31627	-1.59761	1.33888
H	0.99809	-2.28402	-0.29501

HOOH

O	0.71717	0.11965	-0.05194
O	-0.71717	-0.11965	-0.05194

Perrhenate

O	-0.58605	-0.82875	1.43551
Re	0.00000	0.00001	0.00000
O	1.75815	-0.00018	0.00000

TBHP

C	0.39161	0.00069	0.03577
C	0.40669	1.36998	0.71943
C	0.34386	-1.14402	1.05136
C	1.57229	-0.15665	-0.92638
O	-0.73744	-0.08357	-0.87590
H	0.30123	-2.10938	0.53968
H	1.23767	-1.13012	1.68076
H	-0.52784	-1.05079	1.70151
H	0.43022	2.16734	-0.02694
H	-0.48188	1.50202	1.33835
H	1.28929	1.46488	1.35793
H	1.55937	0.63101	-1.68247
H	2.51063	-0.08917	-0.37061
H	1.53715	-1.12492	-1.43074

UHP

N	2.51364	-0.21759	0.36675
C	1.20833	-0.07418	-0.04443
N	0.77028	1.21462	-0.19854
O	0.49201	-1.05319	-0.25715
H	-1.20610	-0.59336	-0.46722
O	-1.97905	0.00434	-0.61721
H	-0.22860	1.31834	-0.33907
H	1.23878	1.96217	0.28824
H	2.87192	-1.15787	0.30528
H	3.17604	0.52075	0.18716

epoxide

C	-0.73362	-0.37351	0.00000
O	0.00000	0.85564	0.00000
C	0.73362	-0.37351	0.00000
H	-1.27051	-0.59075	0.91981
H	-1.27051	-0.59075	-0.91981

ethene

C	0.00000	0.66439	0.00000
C	0.00000	-0.66441	0.00000
H	-0.92271	1.23529	0.00000
H	0.92274	1.23525	0.00000

cyclooctaepoxide

C	0.40428	-1.49262	-0.63625
C	-0.99620	-1.80404	-0.07768
C	-1.72747	-0.62343	0.59083
C	-1.89059	0.65891	-0.26176
C	-0.91550	1.81707	0.03275
C	0.55218	1.61207	-0.38650
C	1.32719	0.66511	0.50479
O	2.41937	-0.06192	-0.09047
C	1.27719	-0.79918	0.37931
H	-1.22764	-0.36705	1.53150
H	-2.72066	-0.98433	0.87717
H	1.06611	2.57980	-0.37237
H	0.60079	1.25924	-1.41986
H	-1.28687	2.70753	-0.48599
H	-0.96140	2.05669	1.10336
H	-2.90062	1.04961	-0.10044
H	-1.84238	0.40731	-1.32884
H	-1.61381	-2.19226	-0.89556
H	-0.92118	-2.61736	0.65408
H	0.88625	-2.42402	-0.95291
H	0.32857	-0.86945	-1.52958
H	1.48428	-1.37971	1.27983
H	1.56717	1.06603	1.49047

Chapter 11

cyclooctene

C	1.63695	0.89099	-0.37452
C	0.58899	1.69241	-0.16187
C	-0.69666	1.44261	0.59590
C	-1.77172	0.66435	-0.20520
C	-1.72935	-0.86490	-0.07194
C	-0.41786	-1.57415	-0.45004
C	0.74906	-1.39964	0.55518
C	1.91165	-0.52547	0.06252
H	2.69075	-0.50112	0.83780
H	2.38462	-1.03577	-0.78785
H	0.36814	-1.02236	1.50803
H	1.17176	-2.38344	0.78395
H	-0.64154	-2.64185	-0.54162
H	-0.09940	-1.24927	-1.44761
H	-1.98433	-1.13754	0.96099
H	-2.53397	-1.27297	-0.69490
H	-2.76216	0.99552	0.12673
H	-1.69570	0.94382	-1.26250
H	-0.50811	0.93458	1.54530
H	-1.11003	2.41996	0.86166
H	0.64836	2.67728	-0.62186
H	2.44522	1.31600	-0.96831

11.2 This section contains supplementary information to chapter 3: oxidation of sulfides to sulfoxides mediated by ionic liquids

11.2.1 IR spectra comparison

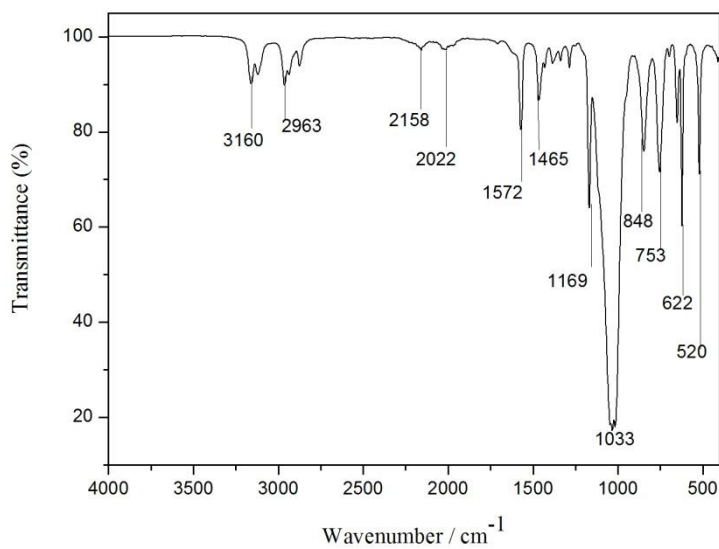


Figure 1. Pure [Bmim]BF₄ ionic liquid.

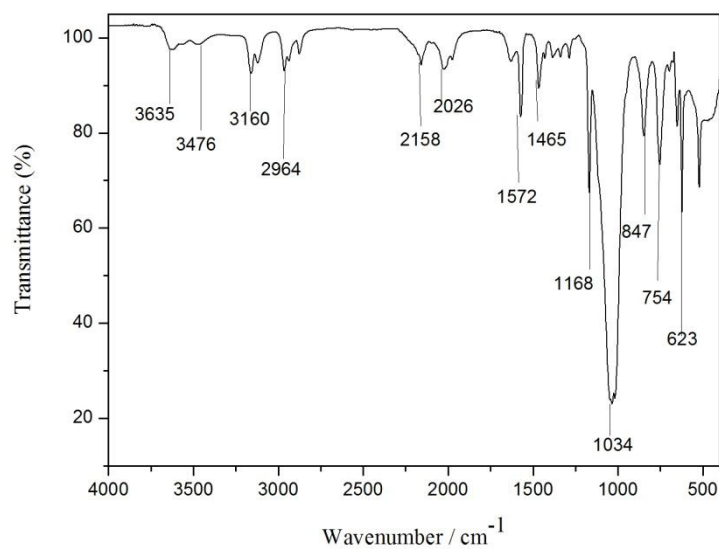


Figure 2. 0.23 mol/L H₂O₂ concentration in ionic liquid.

Chapter 11

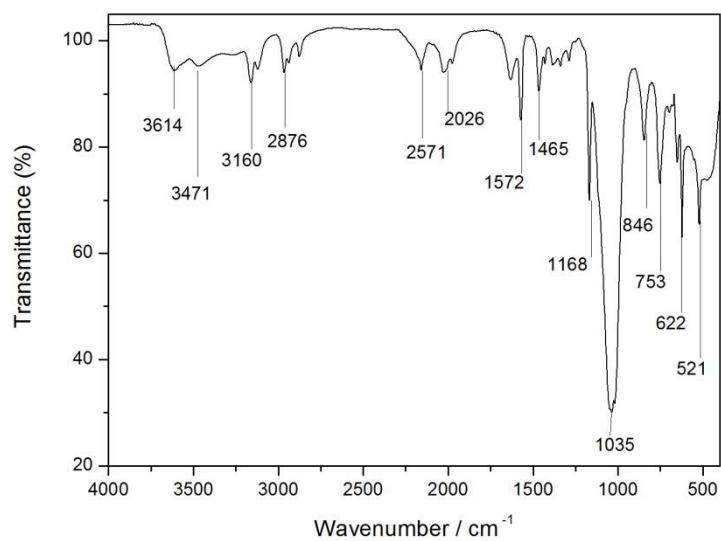


Figure 3. 0.53 mol/L H₂O₂ concentration in ionic liquid.

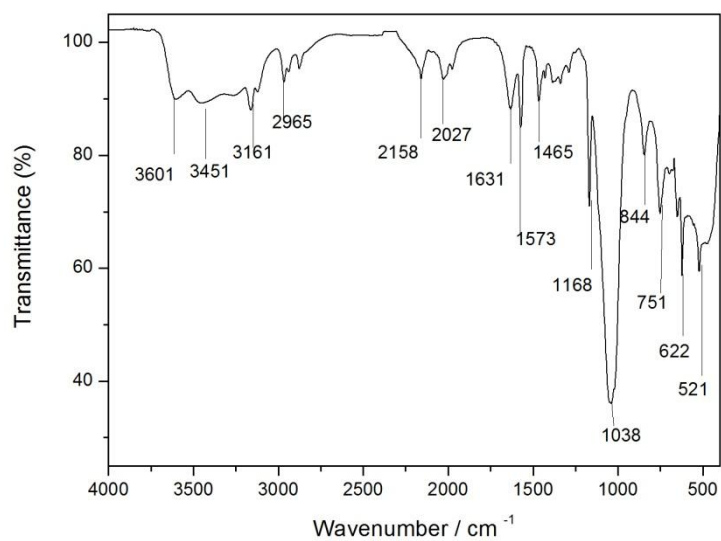


Figure 4. 1.5 mol/L H₂O₂ concentration in ionic liquid.

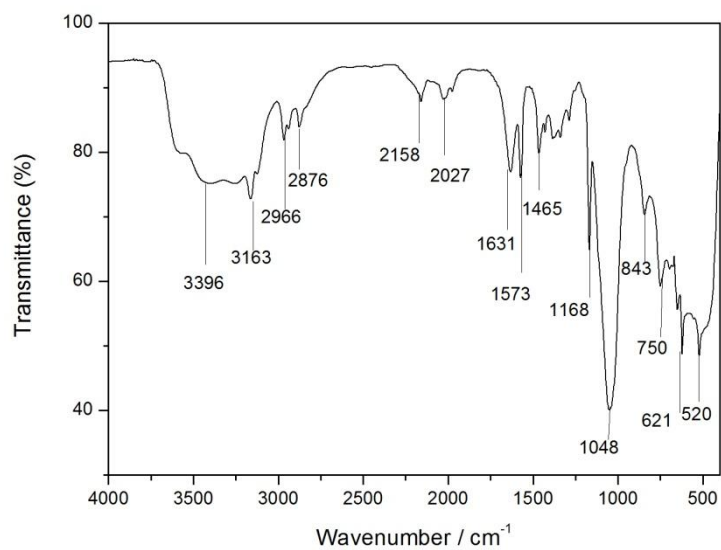


Figure 5. 3.8 mol/L H₂O₂ concentration in ionic liquid.

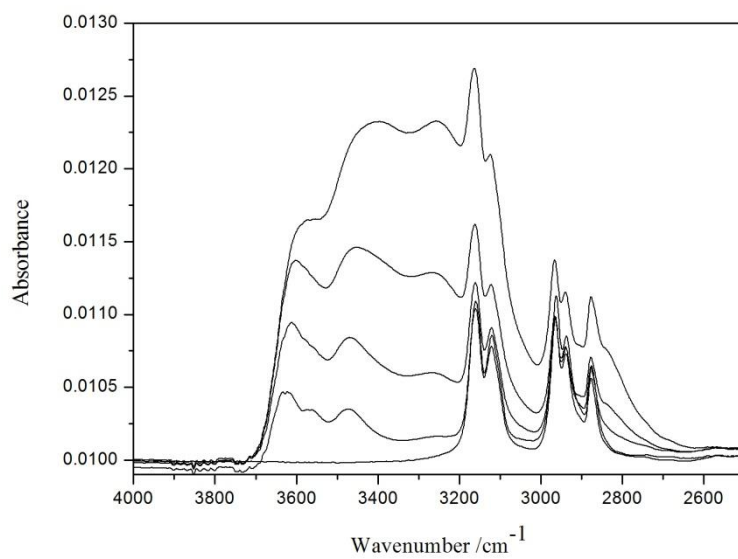


Figure 6. The IR spectra in the range of 3000 to 3500 cm⁻¹ for the treatment of [Bmim]BF₄ with different H₂O₂ concentrations.

11.2.2 Raman spectra comparison

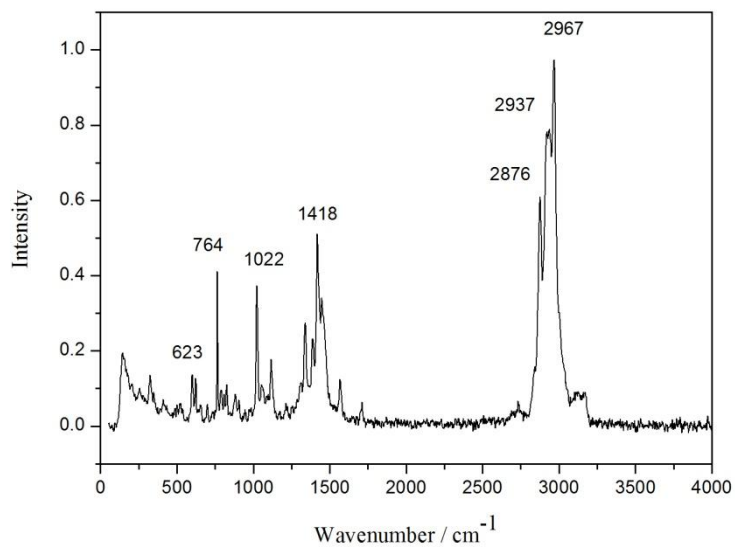


Figure 7. Pure [Bmim]BF₄ ionic liquid.

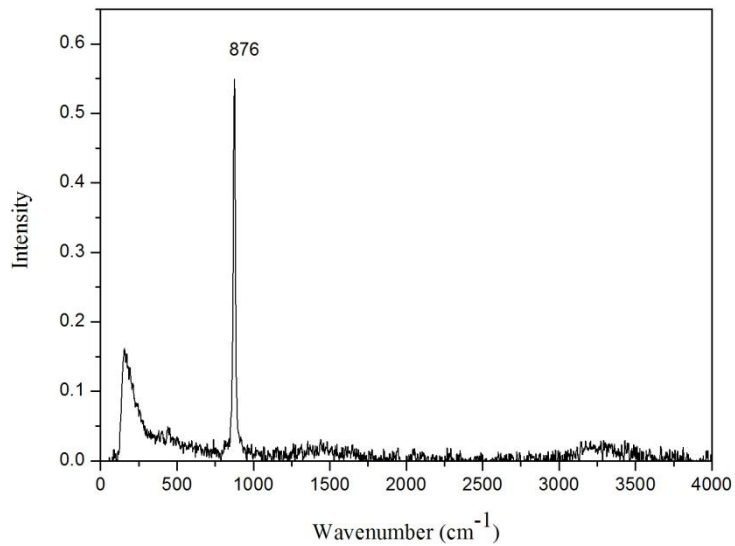


Figure 8. Pure H₂O₂ (35 %).

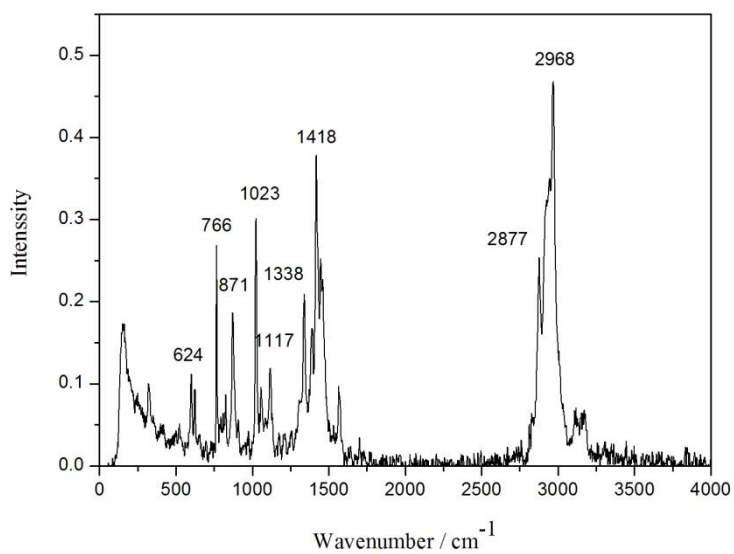


Figure 9. 3.4 mol/L H₂O₂ concentration in ionic liquid.

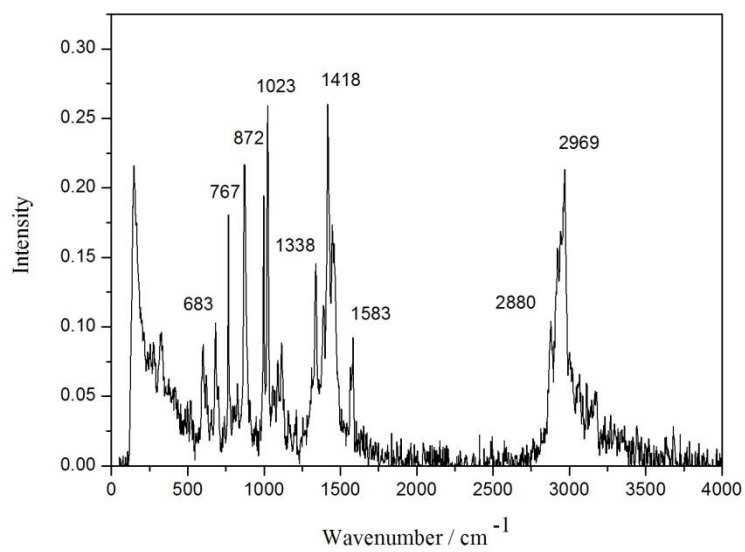


Figure 10. 4.1 mol/L H₂O₂ concentration in ionic liquid.

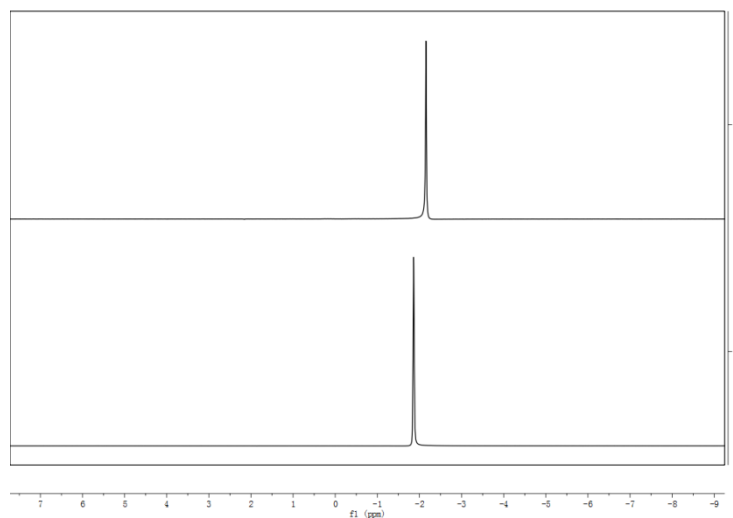
11.2.3 ^{11}B NMR and ^{19}F NMR of IL and IL + H_2O_2 systems

Figure 11. ^{11}B NMR of $[\text{Bmim}]\text{BF}_4$ (1) and $[\text{Bmim}]\text{BF}_4 + \text{H}_2\text{O}_2$ (35 %) (2) system.

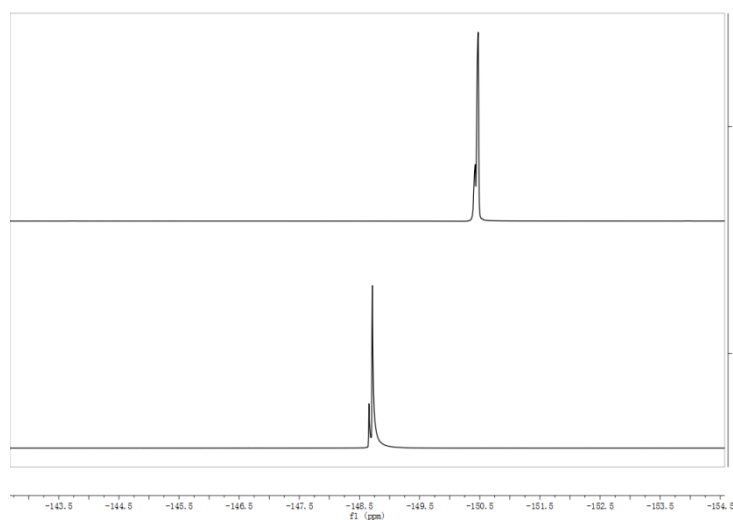


Figure 12. ^{19}F NMR of $[\text{Bmim}]\text{BF}_4$ (1) and $[\text{Bmim}]\text{BF}_4 + \text{H}_2\text{O}_2$ (35 %) (2) system.

11.3 This section contains supplementary information to chapter 5: ionic liquid with the weakly coordinating anions: synthesis, properties and application

11.3.1 Single crystal X-Ray structure determination of compounds 4a, 7a, 2b and 5b

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II, κ -CCD), a rotating anode (Bruker AXS, FR591) with MoK α radiation ($\lambda = 0.71073$ Å), and a graphite monochromator by using the SMART software package.^[1] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.^[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^[2] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX^[7] based on SIR-92.^[3] If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were refined as part of rigid rotating groups, with C–H = 0.98 Å and $U_{\text{iso(H)}} = 1.5U_{\text{eq(C)}}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{\text{iso(H)}} = 1.2U_{\text{eq(C)}}$. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97^[5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.^[4] Images of the crystal structures were generated by PLATON.^[6] CCDC 956711 (**4a**), CCDC 956713 (**7a**), CCDC 956714 (**2b**) and CCDC 956712 (**5b**) contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or [via https://www.ccdc.cam.ac.uk/services/structure_deposit/](https://www.ccdc.cam.ac.uk/services/structure_deposit/)

Chapter 11

Special:

- 4a:** Twin refinement (twin operation: inversion)
- 7a:** Hydrogen atoms could be located in the difference Fourier maps and were allowed to refine freely.
- 2b:** Four CF₃-Groups are disordered over two positions.
The butyl-Group of the cation is disordered over two positions.
Diffractometer: Kappa APEX II (BRUKER AXS); sealed tube
- 5b:** Three CF₃-Groups are disordered over two positions.

Compound 4a

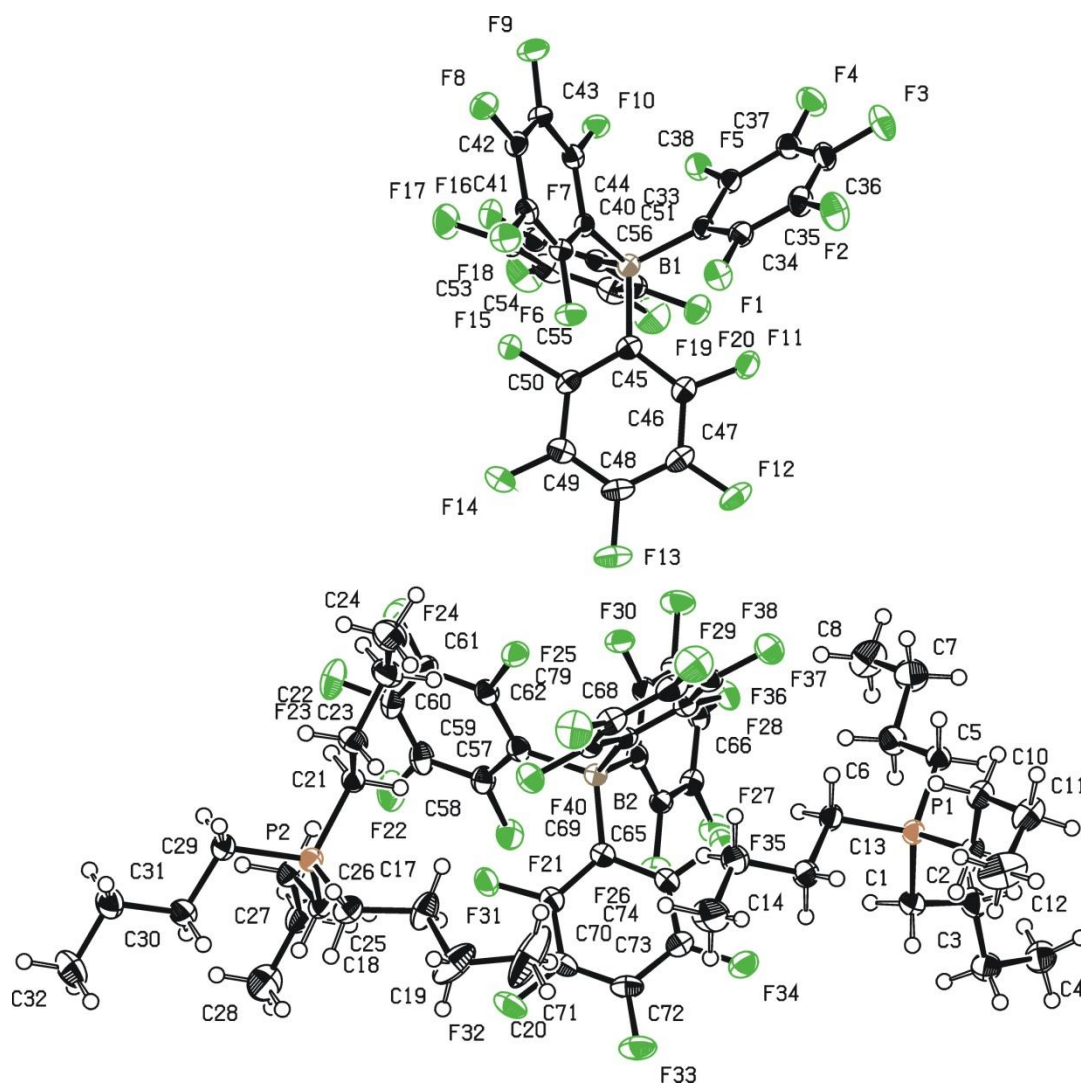


Figure F1 – Ortep drawing drawing of compound **4a** with 50 % ellipsoids. [6]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{40} H_{36} B F_{20} P$ $[(C_{16} H_{36} P)^+], [(C_{24} B F_{20})^-]$
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: $0.48 \times 0.56 \times 0.61$ mm
Molecular Weight:	938.47 a.m.u.
F_{000} :	3808
Systematic Absences:	$0kl: l \neq 2n; h0l: h \neq 2n; 00l: l \neq 2n$
Space Group:	Orthorhombic $Pca2_1$ (I.T.-No.: 29)
Cell Constants:	Least-squares refinement of 9712 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $0.91^\circ < \theta < 25.40^\circ$; $Mo(K\bar{\alpha})$; $\lambda = 71.073$ pm $a = 1895.91(7)$ pm $b = 2229.87(8)$ pm $c = 1924.49(7)$ pm $V = 8136.0(5) \cdot 10^6$ pm ³ ; $Z = 8$; $D_{calc} = 1.532$ g cm ⁻³ ; Mos. = 0.67
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; $\lambda = 71.073$ pm; $Mo(K\bar{\alpha})$

Chapter 11

Temperature:	(-150±1) °C;	(123±1) K
Measurement Range:	0.91 ° < θ < 25.40 °; h: -22/22, k: -26/26, l: -23/23	
Measurement Time:	2 × 5 s per film	
Measurement Mode:	measured: 10 runs; 4833 films / scaled: 10 runs; 4833 films φ - and ω -movement; Increment: $\Delta\varphi/\Delta\omega = 0.50$ °; dx = 50.0 mm	
LP - Correction:	Yes [2]	
Intensity Correction	No/Yes; during scaling [2]	
Absorption Correction:	Multi-scan; during scaling; $\mu = 0.190$ mm ⁻¹ [2]	
Reflection Data:	Correction Factors: $T_{\min} = 0.6499$ $T_{\max} = 0.7452$	
	239019	reflections were integrated and scaled
	7959	reflections systematic absent and rejected
	231060	reflections to be merged
	14933	independent reflections
	0.036	R_{int} : (basis F_o^2)
	14933	independent reflections (all) were used in refinements
	14524	independent reflections with $I_o > 2\sigma(I_o)$
	99.6 %	completeness of the data set
	1126	parameter full-matrix refinement
	13.3	reflections per parameter
Solution:	Direct Methods [3]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	124	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 98, 99$ pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a * P)^2 + b * P$ with a: 0.0402; b: 1.9728; P: [Maximum(0 or F_o^2) + 2 * F_c^2]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	+0.27 e ₀ ⁻ / Å ³ ; -0.22 e ₀ ⁻ / Å ³	
R1:	$\Sigma(F_o - F_c) / \Sigma F_o $	
[$F_o > 4\sigma(F_o)$];	N=14524];	= 0.0245
[all refltns];	N=14933];	= 0.0257
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$];	N=14524];	= 0.0667
[all refltns];	N=14933];	= 0.0682
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO-NV})]^{1/2}$	
Flack's Parameter :	$x = 0.45(5)$	
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$ Twin refinement (twin operation: inversion) The correct enantiomere could not be proved by Flack's Parameter.	

Compound 7a

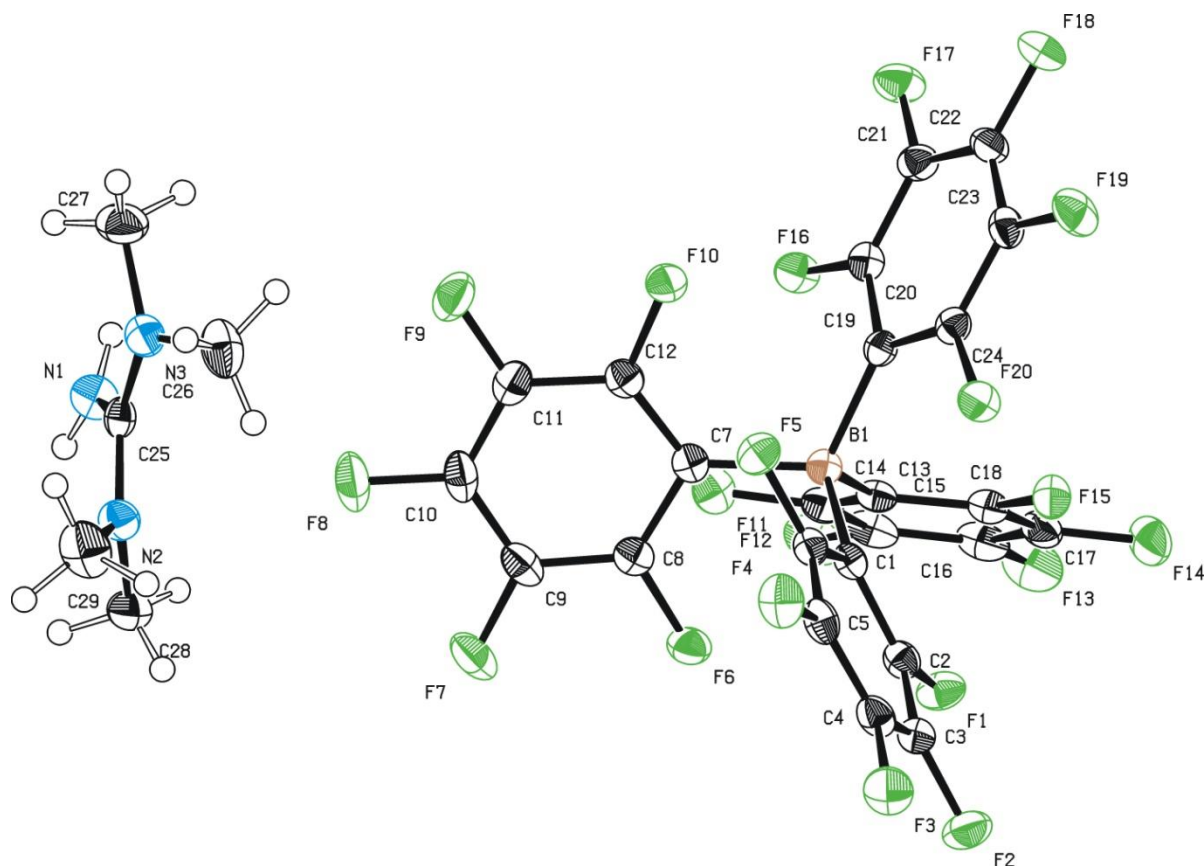


Figure F2 – Ortep drawing drawing of compound **7a** with 50 % ellipsoids. [6]

Operator:	*** Herdtweck ***		
Molecular Formula:	$C_{29} H_{14} B F_{20} N_3$ [[$C_{24} B F_{20}$]], [($C_5 H_{14} N_3$) ⁺]		
Crystal Color / Shape	Colorless fragment		
Crystal Size	Approximate size of crystal fragment used for data collection: 0.10 × 0.25 × 0.36 mm		
Molecular Weight:	795.24 a.m.u.		
F_{000} :	788		
Systematic Absences:	none		
Space Group:	Triclinic	$P\bar{1}$	(I.T.-No.: 2)
Cell Constants:	Least-squares refinement of 9961 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.41^\circ < \theta < 25.43^\circ$; Mo($K\alpha$); $\lambda = 71.073$ pm		
	$a =$	815.71(2) pm	$\alpha =$ 89.4091(12)°
	$b =$	1271.09(4) pm	$\beta =$ 83.9006(12)°
	$c =$	1455.97(4) pm	$\gamma =$ 81.7908(12)°
	$V = 1485.66(7) \cdot 10^6$ pm ³ ; $Z = 2$; $D_{\text{calc}} = 1.778$ g cm ⁻³ ; Mos. = 0.72		
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; $\lambda = 71.073$ pm; Mo($K\alpha$)		
Temperature:	(-150 ± 1) °C; (123 ± 1) K		
Measurement Range:	$1.41^\circ < \theta < 25.43^\circ$; h: -9/9, k: -15/15, l: -17/17		
Measurement Time:	2 × 5 s per film		
Measurement Mode:	measured: 7 runs; 3291 films / scaled: 7 runs; 3291 films		
	φ - and ω -movement; Increment: $\Delta\varphi/\Delta\omega = 0.50^\circ$; dx = 35.0 mm		
LP - Correction:	Yes [2]		
Intensity Correction	No/Yes; during scaling [2]		

Chapter 11

Absorption Correction:	Multi-scan; during scaling; $\mu = 0.194 \text{ mm}^{-1}$ [2]	
Correction Factors:	$T_{\min} = 0.6491$	$T_{\max} = 0.7452$
Reflection Data:	51233 reflections were integrated and scaled	
	51233 reflections to be merged	
	5423 independent reflections	
	0.039 R_{int} : (basis F_o^2)	
	5423 independent reflections (all) were used in refinements	
	5014 independent reflections with $I_o > 2\sigma(I_o)$	
	98.9 % completeness of the data set	
	534 parameter full-matrix refinement	
	10.2 reflections per parameter	
Solution:	Direct Methods [3]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	53 Non-hydrogen atoms with anisotropic displacement parameters	
	14 Hydrogen atoms with isotropic displacement parameters	
Hydrogen Atoms:	All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a * P)^2 + b * P$	
	with a: 0.0426; b: 0.6762; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2 * F_c^2] / 3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	$+0.29 \text{ e}_0^- / \text{\AA}^3$; $-0.19 \text{ e}_0^- / \text{\AA}^3$	
R1:	$\Sigma (F_o - F_c) / \Sigma F_o $	
$[F_o > 4\sigma(F_o)$;	N=5014]:	= 0.0296
[all refltns;	N=5423]:	= 0.0322
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
$[F_o > 4\sigma(F_o)$;	N=5014]:	= 0.0778
[all refltns;	N=5423]:	= 0.0808
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO-NV})]^{1/2}$	= 1.031
Remarks:	Refinement expression	$\Sigma w(F_o^2 - F_c^2)^2$

Compound 2b

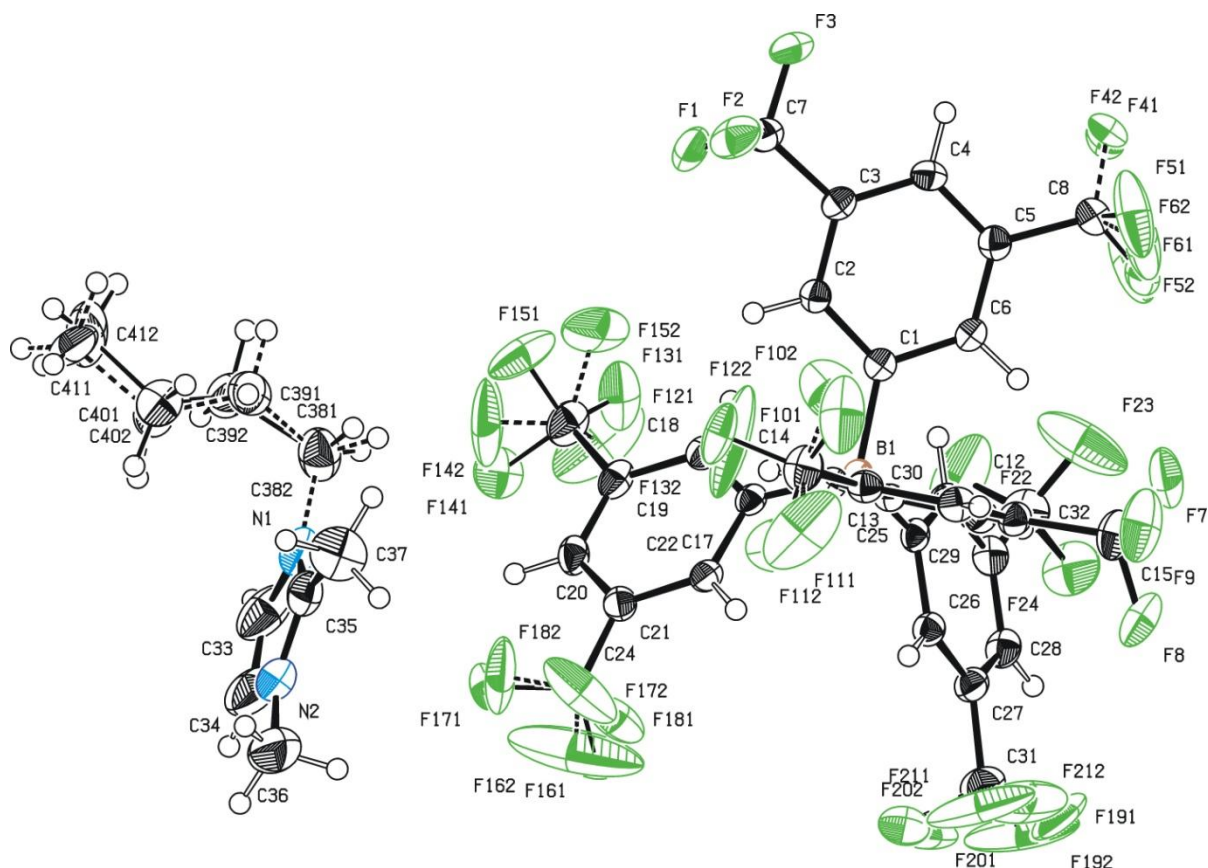


Figure F4 – Ortep drawing drawing of compound **2b** with 50 % ellipsoids. [6]

Operator:	*** Herdtweck ***		
Molecular Formula:	$C_{41} H_{29} B F_{24} N_2$ [[$C_{32} H_{12} B F_{24}$], [$C_9 H_{17} N_2$] ⁺]		
Crystal Color / Shape	Colorless block		
Crystal Size	Approximate size of crystal fragment used for data collection: 0.38 × 0.51 × 0.51 mm		
Molecular Weight:	1016.47 a.m.u.		
F_{000} :	2040		
Systematic Absences:	h0l: $l \neq 2n$; 0k0: $k \neq 2n$		
Space Group:	Monoclinic $P 2_1/c$ (I.T.-No.: 14)		
Cell Constants:	Least-squares refinement of 9688 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.82^\circ < \theta < 25.50^\circ$, Mo($K\alpha$); $\lambda = 71.073$ pm		
	$a =$	2013.91(5) pm	
	$b =$	1393.55(3) pm	$\beta = 111.2143(9)^\circ$
	$c =$	1625.59(4) pm	
	$V = 4253.03(18) \cdot 10^6$ pm ³ ; $Z = 4$; $D_{\text{calc}} = 1.587$ g cm ⁻³ ; Mos. = 0.67		
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 50 kV; 30 mA; $\lambda = 71.073$ pm; Mo($K\alpha$)		
Temperature:	(-150 ± 1) °C; (123 ± 1) K		
Measurement Range:	$1.82^\circ < \theta < 25.50^\circ$; h: -24/24, k: -16/16, l: -19/19		
Measurement Time:	2 × 10 s per film		
Measurement Mode:	measured: 9 runs; 4878 films / scaled: 9 runs; 4878 films ϕ - and ω -movement; Increment: $\Delta\phi/\Delta\omega = 0.50^\circ$; dx = 45.0 mm		
LP - Correction:	Yes [2]		
Intensity Correction	No/Yes; during scaling [2]		

Chapter 11

Absorption Correction:	Multi-scan; during scaling; $\mu = 0.167 \text{ mm}^{-1}$ [2]	
Correction Factors:	$T_{\min} = 0.6736$	$T_{\max} = 0.7452$
Reflection Data:	137576	reflections were integrated and scaled
	4050	reflections systematic absent and rejected
	2	obvious wrong intensity and rejected
	133524	reflections to be merged
	7872	independent reflections
	0.019	R_{int} : (basis F_o^2)
	7872	independent reflections (all) were used in refinements
	6806	independent reflections with $I_o > 2\sigma(I_o)$
	99.4 %	completeness of the data set
	785	parameter full-matrix refinement
	10.0	reflections per parameter
Solution:	Direct Methods [3, 7]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	68+18	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 95, 98, 99 \text{ pm}$). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4, 5, 7]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$	
	with a: 0.0401; b: 3.0998; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2*F_c^2]/3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	$+0.47 \text{ e}^-/\text{\AA}^3$; $-0.43 \text{ e}^-/\text{\AA}^3$	
R1:	$\Sigma(F_o - F_c) / \Sigma F_o$	
$[F_o > 4\sigma(F_o)$;	N=6806]:	= 0.0396
[all reflectns;	N=7872]:	= 0.0472
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
$[F_o > 4\sigma(F_o)$;	N=6806]:	= 0.0937
[all reflectns;	N=7872]:	= 0.1006
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO-NV})]^{1/2}$	
Remarks:	Refinement expression	$\Sigma w(F_o^2 - F_c^2)^2$

Compound 5b

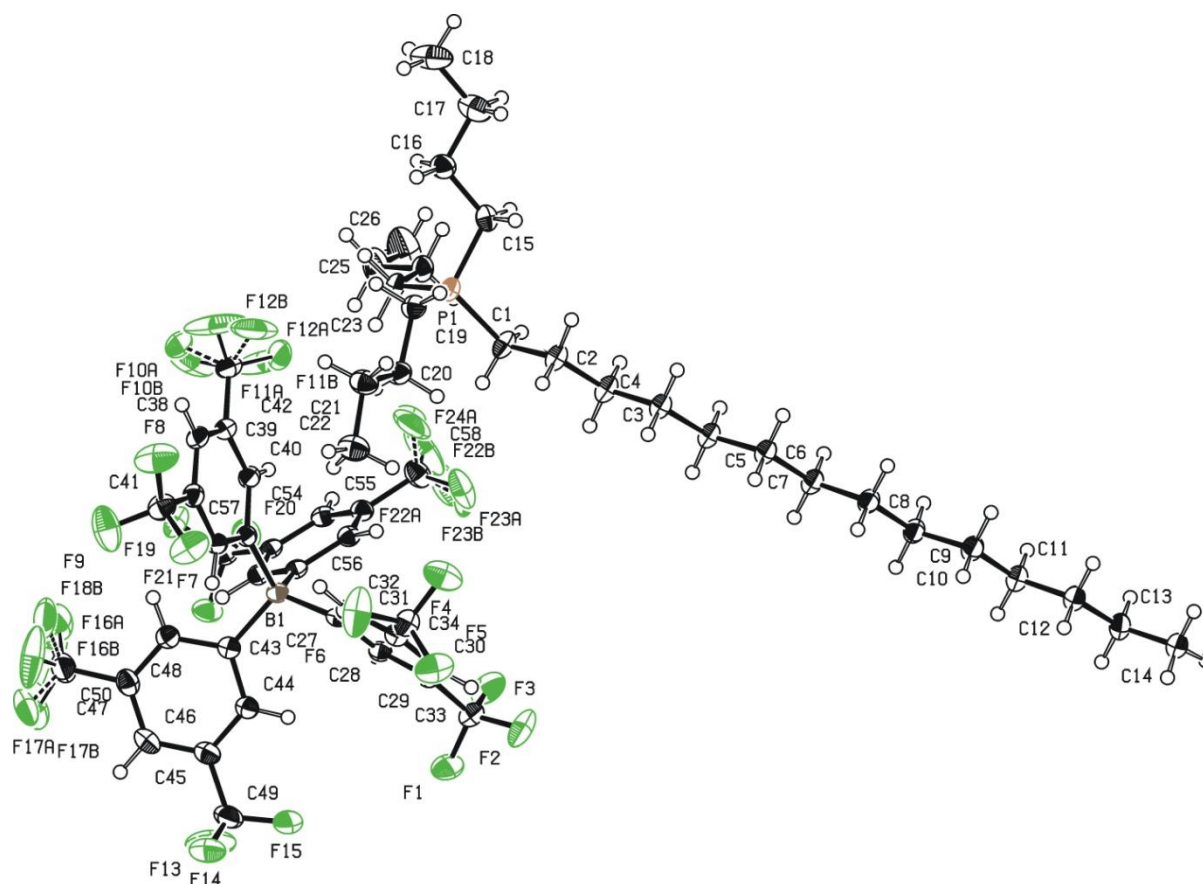


Figure F5 – Ortep drawing drawing of compound **5b** with 50 % ellipsoids. [6]

Operator:	*** Herdtweck ***		
Molecular Formula:	$C_{58} H_{68} B F_{24} P$ [[$C_{32} H_{12} B F_{24}$], [($C_{26} H_{56} P$) ⁺]]		
Crystal Color / Shape	Colorless fragment		
Crystal Size	Approximate size of crystal fragment used for data collection: 0.56 × 0.59 × 0.59 mm		
Molecular Weight:	1262.90 a.m.u.		
F_{000} :	1304		
Systematic Absences:	none		
Space Group:	Triclinic	$P\bar{1}$	(I.T.-No.: 2)
ell Constants:	Least-squares refinement of 9093 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.19^\circ < \theta < 25.43^\circ$; Mo($K\alpha$): $\lambda = 71.073$ pm		
	$a =$	1297.32(4) pm	$\alpha =$ 105.4144(14)°
	$b =$	1404.01(4) pm	$\beta =$ 97.8526(13)°
	$c =$	1803.89(5) pm	$\gamma =$ 97.5892(13)°
	$V = 3088.64(16) \cdot 10^6$ pm ³ ; $Z = 2$; $D_{\text{calc}} = 1.358$ g cm ⁻³ ; Mos. = 0.67		
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; $\lambda = 71.073$ pm; Mo($K\alpha$)		
Temperature:	(-150 ± 1) °C; (123 ± 1) K		
Measurement Range:	$1.19^\circ < \theta < 25.43^\circ$; h: -15/15, k: -16/16, l: -21/21		
Measurement Time:	2 × 5 s per film		
Measurement Mode:	measured: 9 runs; 5070 films / scaled: 9 runs; 5070 films ϕ - and ω -movement; Increment: $\Delta\phi/\Delta\omega = 0.50^\circ$; dx = 45.0 mm		
LP - Correction:	Yes [2]		

Chapter 11

Intensity Correction	No/Yes; during scaling [2]	
Absorption Correction:	Multi-scan; during scaling; $\mu = 0.153 \text{ mm}^{-1}$ [2]	
	Correction Factors:	$T_{\min} = 0.6784$ $T_{\max} = 0.7452$
Reflection Data:	95414	reflections were integrated and scaled
	95414	reflections to be merged
	11372	independent reflections
	0.030	R_{int} : (basis F_o^2)
	11372	independent reflections (all) were used in refinements
	10444	independent reflections with $I_o > 2\sigma(I_o)$
	99.6 %	completeness of the data set
	845	parameter full-matrix refinement
	13.5	reflections per parameter
Solution:	Direct Methods [3]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	93	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{\text{C-H}} = 95, 98, 99 \text{ pm}$). Isotropic displacement parameters were calculated from the parent carbon atom ($U_{\text{H}} = 1.2/1.5 U_{\text{C}}$). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a * P)^2 + b * P$	
	with a: 0.0394; b: 1.6926; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2 * F_c^2] / 3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	$+0.53 \text{ e}^- / \text{\AA}^3$; $-0.50 \text{ e}^- / \text{\AA}^3$	
R1:	$\Sigma(F_o - F_c) / \Sigma F_o$	
$[F_o > 4\sigma(F_o)$;	N=10444]:	= 0.0363
[all reflctns;	N=11372]:	= 0.0399
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
$[F_o > 4\sigma(F_o)$;	N=10444]:	= 0.0889
[all reflctns;	N=11372]:	= 0.0929
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO-NV})]^{1/2}$	
Remarks:	Refinement expression	$\Sigma w(F_o^2 - F_c^2)^2$

11.3.2 Bond distances (Angstrom) and bond angles (Degrees) for 4a, 7a, 2b and 5b**Bond distances (Angstrom) and bond angles (Degrees) for 4a****Table 1.** Bond Distances (Angstrom) for **4a**

P1	C1	1.8076(18)	P2	C21	1.8004(16)
P1	C5	1.8023(16)	P2	C25	1.7977(17)
P1	C9	1.8068(16)	P2	C17	1.7975(18)
P1	C13	1.8040(16)	P2	C29	1.8077(16)
C1	C2	1.543(3)	C17	C18	1.529(3)
C2	C3	1.508(3)	C18	C19	1.519(3)
C3	C4	1.520(3)	C19	C20	1.515(4)
C5	C6	1.539(2)	C20	C22	1.531(3)
C6	C7	1.507(3)	C22	C23	1.513(3)
C7	C8	1.518(3)	C23	C24	1.528(3)
C9	C10	1.535(2)	C25	C26	1.531(2)
C10	C11	1.532(3)	C26	C27	1.534(3)
C11	C12	1.513(3)	C27	C28	1.510(3)
C13	C14	1.531(2)	C29	C30	1.535(3)
C14	C15	1.528(2)	C30	C31	1.518(3)
C15	C16	1.531(3)	C31	C32	1.532(3)
F1	C34	1.355(2)	F21	C58	1.354(2)
F2	C35	1.345(2)	F22	C59	1.348(2)
F3	C36	1.347(2)	F23	C60	1.342(2)
F4	C37	1.352(2)	F24	C61	1.348(2)
F5	C38	1.3514(19)	F25	C62	1.354(2)
F6	C40	1.3538(18)	F26	C64	1.3487(18)
F7	C41	1.3432(18)	F27	C65	1.3474(18)
F8	C42	1.3482(18)	F28	C66	1.3465(19)
F9	C43	1.3499(18)	F29	C67	1.3497(18)
F10	C44	1.3507(19)	F30	C68	1.3548(19)
F11	C46	1.3591(18)	F31	C70	1.3561(18)
F12	C47	1.343(2)	F32	C71	1.353(2)

Chapter 11

F14	C49	1.349(2)	F34	C73	1.351(2)
F15	C50	1.3672(18)	F35	C74	1.3577(18)
F16	C52	1.3572(18)	F36	C76	1.352(2)
F17	C53	1.349(2)	F37	C77	1.351(2)
F18	C54	1.348(2)	F38	C78	1.342(2)
F19	C55	1.349(2)	F39	C79	1.345(2)
F20	C56	1.358(2)	F40	C80	1.360(2)
C33	C38	1.393(2)	C57	C58	1.392(2)
C33	B1	1.664(2)	C57	C62	1.390(2)
C33	C34	1.394(2)	C57	B2	1.664(2)
C34	C35	1.382(3)	C58	C59	1.386(3)
C35	C36	1.380(2)	C59	C60	1.376(3)
C36	C37	1.377(2)	C60	C61	1.375(3)
C37	C38	1.387(2)	C61	C62	1.392(2)
C39	C40	1.394(2)	C63	C64	1.390(2)
C39	B1	1.656(2)	C63	C68	1.390(2)
C39	C44	1.391(2)	C63	B2	1.661(2)
C40	C41	1.389(2)	C64	C65	1.392(2)
C41	C42	1.377(2)	C65	C66	1.373(2)
C42	C43	1.374(2)	C66	C67	1.379(2)
C43	C44	1.381(2)	C67	C68	1.376(2)
C45	B1	1.657(2)	C69	C70	1.390(2)
C45	C46	1.389(2)	C69	C74	1.399(2)
C45	C50	1.389(2)	C69	B2	1.654(2)
C46	C47	1.383(2)	C70	C71	1.387(2)
C47	C48	1.380(3)	C71	C72	1.374(2)
C48	C49	1.380(3)	C72	C73	1.380(2)
C49	C50	1.381(2)	C73	C74	1.380(2)
C51	C56	1.396(2)	C75	C76	1.387(2)
C51	B1	1.659(2)	C75	C80	1.390(2)
C51	C52	1.385(2)	C75	B2	1.662(2)
C4	H43	0.98	C20	H203	0.98
C4	H41	0.98	C20	H201	0.98
C5	H52	0.99	C21	H211	0.99
C5	H51	0.99	C21	H212	0.99

Chapter 11

C6	H61	0.99	C22	H221	0.99
C6	H62	0.99	C22	H222	0.99
C7	H72	0.99	C23	H231	0.99
C7	H71	0.99	C23	H232	0.99
C8	H82	0.98	C24	H241	0.98
C8	H83	0.98	C24	H242	0.98
C8	H81	0.98	C24	H243	0.98
C9	H92	0.99	C25	H252	0.99
C9	H91	0.99	C25	H251	0.99
C10	H102	0.99	C26	H261	0.99
C10	H101	0.99	C26	H262	0.99
C11	H111	0.99	C27	H271	0.99
C11	H112	0.99	C27	H272	0.99
C12	H122	0.98	C28	H281	0.98
C12	H121	0.98	C28	H282	0.98
C12	H123	0.98	C28	H283	0.98
C13	H132	0.99	C29	H292	0.99
C13	H131	0.99	C29	H291	0.99
C14	H142	0.99	C30	H302	0.99
C14	H141	0.99	C30	H301	0.99
C15	H152	0.99	C31	H312	0.99
C15	H151	0.99	C31	H311	0.99
C16	H161	0.98	C32	H323	0.98
C16	H163	0.98	C32	H322	0.98

Table 2. Bond Angles (Degrees) for **4a**

C1	P1	C5	110.24(8)	C25	P2	C29	110.47(8)
C1	P1	C9	107.39(8)	C17	P2	C29	108.67(8)
C1	P1	C13	110.56(8)	C17	P2	C21	110.20(8)
C5	P1	C9	110.92(8)	C17	P2	C25	107.00(8)
C5	P1	C13	107.98(8)	C21	P2	C25	110.49(8)
C9	P1	C13	109.76(8)	C21	P2	C29	109.96(8)
P1	C1	C2	110.99(12)	P2	C17	C18	113.23(13)
C1	C2	C3	115.47(15)	C17	C18	C19	112.35(17)
C2	C3	C4	110.85(16)	C18	19	C20	111.4(2)
P1	C5	C6	113.70(11)	P2	C21	C22	113.71(12)

Chapter 11

C5	C6	C7	112.80(16)	C21	C22	C23	112.93(16)
C6	C7	C8	113.35(18)	C22	C23	C24	111.79(18)
P1	C9	C10	114.68(12)	P2	C25	C26	115.80(12)
C9	C10	C11	112.48(15)	C25	C26	C27	111.61(14)
C10	C11	C12	113.62(18)	C26	C27	C28	113.63(16)
P1	C13	C14	114.00(11)	P2	C29	C30	112.67(12)
C13	C14	C15	111.43(14)	C29	C30	C31	112.99(15)
C14	C15	C16	110.98(16)	C30	C31	C32	110.99(17)
C34	C33	C38	113.20(15)	C58	C57	B2	119.65(14)
C34	C33	B1	119.94(14)	C62	C57	B2	126.33(15)
C38	C33	B1	126.29(14)	C58	C57	C62	113.43(15)
F1	C34	C33	119.22(15)	F21	C58	C57	119.30(15)
F1	C34	C35	116.01(15)	C57	C58	C59	124.41(16)
C33	C34	C35	124.77(16)	F21	C58	C59	116.28(15)
F2	C35	C34	121.25(16)	F22	C58	C59	120.49(16)
F2	C35	C36	119.49(16)	C58	C60	C59	119.49(16)
C34	C35	C36	119.25(16)	F22	C60	C59	120.02(16)
F3	C36	C35	120.90(15)	F23	C61	C60	120.02(16)
F3	C36	C37	120.22(15)	C59	C61	C60	118.94(17)
C35	C36	C37	118.89(15)	F23	C59	C60	121.04(17)
F4	C37	C36	119.43(15)	C60	C62	C61	119.78(16)
F4	C37	C38	120.66(15)	F24	C60	C61	119.76(16)
C36	C37	C38	119.90(15)	F24	C62	C61	120.46(16)
F5	C38	C33	121.41(14)	F25	C61	C62	114.43(15)
F5	C38	C37	114.66(14)	C57	C61	C62	123.94(16)
C33	C38	C37	123.93(16)	F25	C57	C62	121.62(15)
C40	C39	C44	113.26(14)	C64	C68	C63	113.82(14)
C40	C39	B1	127.75(13)	C68	B2	C63	119.21(13)
C44	C39	B1	118.68(13)	C64	B2	C63	126.60(13)
F6	C40	C39	121.00(14)	F26	C63	C64	121.44(14)
F6	C40	C41	115.11(14)	C63	C65	C64	123.38(14)
C39	C40	C41	123.89(14)	F26	C65	C64	115.18(13)
F7	C41	C40	121.10(13)	C64	C66	C65	119.76(14)
F7	C41	C42	119.33(14)	F27	C64	C65	120.79(13)
C40	C41	C42	119.56(14)	F27	C66	C65	119.45(14)

Chapter 11

F8	C42	C41	120.18(14)	F28	C65	C66	120.39(14)
F8	C42	C43	120.63(15)	F28	C67	C66	120.39(15)
C41	C42	C43	119.18(15)	C65	C67	C66	119.20(15)
F9	C43	C42	119.86(14)	F29	C66	C67	119.23(15)
F9	C43	C44	120.78(14)	C66	C68	C67	119.22(15)
C42	C43	C44	119.33(15)	F29	C68	C67	121.54(15)
F10	C44	C39	118.80(14)	F30	C63	C68	119.04(14)
F10	C44	C43	116.49(14)	F30	C67	C68	116.40(14)
C39	C44	C43	124.71(15)	C63	C67	C68	124.56(15)
C46	C45	C50	112.61(14)	C70	C74	C69	113.24(14)
C46	C45	B1	128.17(14)	C70	B2	C69	127.80(14)
C50	C45	B1	118.98(13)	C74	B2	C69	118.52(13)
F11	C46	C45	120.56(14)	C69	C71	C70	123.63(15)
F11	C46	C47	114.91(14)	F31	C71	C70	115.78(14)
C45	C46	C47	124.51(15)	F31	C69	C70	120.57(14)
F12	C47	C46	120.71(15)	F32	C70	C71	120.00(15)
F12	C47	C48	119.53(15)	F32	C72	C71	119.36(15)
C46	C47	C48	119.72(16)	C70	C72	C71	120.64(16)
F13	C48	C47	120.72(17)	F33	C71	C72	120.71(16)
F13	C48	C49	120.49(17)	C71	C73	C72	118.28(16)
C47	C48	C49	118.79(16)	F33	C73	C72	121.01(16)
F14	C49	C48	120.24(15)	F34	C72	C73	120.03(15)
F14	C49	C50	120.93(15)	F34	C74	C73	120.32(15)
C48	C49	C50	118.83(16)	C72	C74	C73	119.64(16)
F15	C50	C45	119.38(13)	F35	C69	C74	119.54(13)
F15	C50	C49	115.09(14)	F35	C73	C74	115.89(14)
C45	C50	C49	125.54(15)	C69	C73	C74	124.57(15)
C52	C51	C56	112.89(15)	C76	B2	C75	127.37(14)
C52	C51	B1	127.69(14)	C80	B2	C75	118.91(14)
C56	C51	B1	119.09(14)	C76	C80	C75	113.40(15)
F16	C52	C51	120.87(15)	C75	C77	C76	123.86(16)
F16	C52	C53	114.90(14)	F36	C77	C76	114.91(15)
C51	C52	C53	124.23(15)	F36	C75	C76	121.22(15)
F17	C53	C52	120.09(15)	F37	C78	C77	119.85(15)
F17	C53	C54	120.12(15)	C76	C78	C77	120.22(17)

Chapter 11

C52	C53	C54	119.80(16)	F37	C76	C77	119.93(16)
F18	C54	C53	120.72(17)	F38	C79	C78	120.56(17)
F18	C54	C55	120.21(17)	C77	C79	C78	118.53(16)
C53	C54	C55	119.07(16)	F38	C78	C77	120.91(17)
F19	C55	C54	120.08(15)	F39	C79	C78	119.55(15)
F19	C55	C56	120.93(16)	C78	C79	C80	119.08(17)
C54	C55	C56	118.99(17)	F39	C79	C80	121.37(17)
F20	C56	C51	118.79(14)	F40	C80	C75	119.48(15)
F20	C56	C55	116.19(15)	C75	C80	C79	124.89(17)
C51	C56	C55	125.03(16)	F40	C80	C79	115.63(15)
C33	B1	C45	115.59(13)	C57	B2	C63	101.86(12)
C33	B1	C51	112.21(13)	C57	B2	C69	115.73(13)
C39	B1	C51	114.18(13)	C57	B2	C75	112.01(13)
C45	B1	C51	101.39(12)	C63	B2	C69	112.11(13)
C39	B1	C45	112.12(13)	C63	B2	C75	114.64(13)
C33	B1	C39	101.89(12)	C69	B2	C75	101.08(12)
P1	C1	H12	109.00	P2	C17	H171	109.00
P1	C1	H11	109.00	P2	C17	H172	109.00
H11	C1	H12	108.00	C18	C17	H171	109.00
C2	C1	H11	109.00	C18	C17	H172	109.00
C2	C1	H12	109.00	H171	C17	H172	108.00
C1	C2	H21	108.00	C17	C18	H181	109.00
C3	C2	H21	108.00	C17	C18	H182	109.00
C3	C2	H22	108.00	C19	C18	H181	109.00
C1	C2	H22	108.00	C19	C18	H182	109.00
H21	C2	H22	107.00	H181	C18	H182	108.00
C4	C3	H31	109.00	C18	C19	H191	109.00
C4	C3	H32	109.00	C18	C19	H192	109.00
C2	C3	H31	109.00	C20	C19	H191	109.00
C2	C3	H32	109.00	C20	C19	H192	109.00
H31	C3	H32	108.00	H191	C19	H192	108.00
H42	C4	H43	109.00	C19	C20	H201	109.00
C3	C4	H41	109.00	C19	C20	H202	110.00
C3	C4	H42	110.00	C19	C20	H203	110.00
C3	C4	H43	109.00	H201	C20	H202	109.00

Chapter 11

H41	C4	H42	110.00	H201	C20	H203	110.00
H41	C4	H43	109.00	H202	C20	H203	109.00
H51	C5	H52	108.00	P2	C21	H211	109.00
P1	C5	H51	109.00	P2	C21	H212	109.00
P1	C5	H52	109.00	C22	C21	H211	109.00
C6	C5	H51	109.00	C22	C21	H212	109.00
C6	C5	H52	109.00	H211	C21	H212	108.00
C7	C6	H62	109.00	C21	C22	H221	109.00
H61	C6	H62	108.00	C21	C22	H222	109.00
C7	C6	H61	109.00	C23	C22	H221	109.00
C5	C6	H62	109.00	C23	C22	H222	109.00
C5	C6	H61	109.00	H221	C22	H222	108.00
C8	C7	H71	109.00	C22	C23	H231	109.00
C6	C7	H71	109.00	C22	C23	H232	109.00
C6	C7	H72	109.00	C24	C23	H231	109.00
C8	C7	H72	109.00	C24	C23	H232	109.00
H71	C7	H72	108.00	H231	C23	H232	108.00
C7	C8	H82	109.00	C23	C24	H241	109.00
C7	C8	H81	109.00	C23	C24	H242	109.00
H81	C8	H82	110.00	C23	C24	H243	109.00
H81	C8	H83	109.00	H241	C24	H242	110.00
C7	C8	H83	109.00	H241	C24	H243	109.00
H82	C8	H83	109.00	H242	C24	H243	109.00
C10	C9	H91	109.00	P2	C25	H251	108.00
C10	C9	H92	109.00	P2	C25	H252	108.00
P1	C9	H91	109.00	C26	C25	H251	108.00
P1	C9	H92	109.00	C26	C25	H252	108.00
H91	C9	H92	108.00	H251	C25	H252	108.00
C9	C10	H101	109.00	C25	C26	H261	109.00
H101	C10	H102	108.00	C27	C26	H261	109.00
C11	C10	H101	109.00	C27	C26	H262	109.00
C11	C10	H102	109.00	H261	C26	H262	108.00
C10	C11	H111	109.00	C26	-C27	H271	109.00
C10	C11	H112	109.00	C26	C27	H272	109.00
C12	C11	H111	109.00	C28	C27	H271	109.00

Chapter 11

C12	C11	H112	109.00	C28	C27	H272	109.00
H111	C11	H112	108.00	H271	C27	H272	108.00
H121	C12	H122	109.00	C27	C28	H281	109.00
H121	C12	H123	110.00	C27	C28	H282	110.00
C11	C12	H123	109.00	C27	C28	H283	110.00
C11	C12	H121	109.00	H281	C28	H282	109.00
C11	C12	H122	109.00	H281	C28	H283	109.00
H122	C12	H123	110.00	H282	C28	H283	109.00
P1	C13	H132	109.00	P2	C29	H291	109.00
P1	C13	H131	109.00	P2	C29	H292	109.00
H131	-C13	H132	108.00	C30	C29	H291	109.00
C14	C13	H131	109.00	C30	C29	H292	109.00
C14	C13	H132	109.00	H291	C29	H292	108.00
C13	C14	H141	109.00	C29	C30	H301	109.00
C15	C14	H141	109.00	C29	C30	H302	109.00
C15	C14	H142	109.00	C31	C30	H301	109.00
C13	C14	H142	109.00	C31	C30	H302	109.00
H141	C14	H142	108.00	H301	C30	H302	108.00
C16	C15	H151	109.00	C30	C31	H311	110.00
C16	C15	H152	109.00	C30	C31	H312	109.00
C14	C15	H151	109.00	C32	C31	H311	109.00
C14	C15	H152	109.00	C32	C31	H312	109.00
H151	C15	H152	108.00	H311	C31	H312	108.00
H162	C16	H163	109.00	C31	C32	H321	109.00
C15	C16	H161	110.00	C31	C32	H322	109.00
C15	C16	H162	110.00	C31	C32	H323	109.00
C15	C16	H163	110.00	H321	C32	H322	109.00
H161	C16	H162	109.00	H321	C32	H323	110.00
H161	C16	H163	109.00	H322	C32	H323	109.00

Bond distances (Angstrom) and bond angles (Degrees) for 7a**Table 3.** Bond distances (Angstrom) for 7a

F1	C2	1.3568(15)	C1	C6	1.4005(19)
F2	C3	1.3459(17)	C1	B1	1.6605(19)
F3	C4	1.3491(17)	C2	C3	1.3866(19)
F4	C5	1.3458(16)	C3	C4	1.374(2)

Chapter 11

F5	C6	1.3529(15)	C4	C5	1.374(2)
F6	C8	1.3546(16)	C5	C6	1.3796(19)
F7	C9	1.3432(18)	C7	C12	1.3838(19)
F8	C10	1.3437(17)	C7	B1	1.6544(19)
F9	C11	1.3428(17)	C7	C8	1.3925(19)
F10	C12	1.3557(15)	C8	C9	1.381(2)
F11	C14	1.3547(16)	C9	C10	1.376(2)
F12	C15	1.3454(17)	C10	C11	1.374(2)
F13	C16	1.3448(17)	C11	C12	1.387(2)
F14	C17	1.3465(18)	C13	C18	1.3916(19)
F15	C18	1.3574(15)	C13	B1	1.659(2)
F16	C20	1.3566(15)	C13	C14	1.3904(19)
F17	C21	1.3435(17)	C14	C15	1.3867(19)
F18	C22	1.3421(16)	C15	C16	1.373(2)
F19	C23	1.3407(16)	C16	C17	1.375(2)
F20	C24	1.3525(15)	C17	C18	1.381(2)
N1	C25	1.3304(19)	C19	B1	1.658(2)
N2	C28	1.464(2)	C19	C24	1.3839(18)
N2	C29	1.462(2)	C19	C20	1.3956(19)
N2	C25	1.3370(18)	C20	C21	1.3840(19)
N3	C26	1.465(2)	C21	C22	1.379(2)
N3	C25	1.3357(17)	C22	C23	1.376(2)
N3	C27	1.466(2)	C23	C24	1.3879(19)
C1	C2	1.3868(19)			
N1	H1	0.89(2)	C27	H273	0.97(2)
N1	H2	0.86(2)	C28	H281	0.964(18)
C26	H261	0.99(2)	C28	H282	0.96(2)
C26	H262	0.97(2)	C28	H283	0.99(2)
C26	H263	0.99(2)	C29	H291	0.98(2)
C27	H271	1.00(2)	C29	H292	0.99(2)
C27	H272	0.93(2)	C29	H293	0.98(2)

Table 4. Bond angles (degrees) for **7a**

C25	N2	C28	120.86(12)	C14	C13	C18	113.19(12)
C25	N2	C29	122.21(13)	F11	C14	C13	121.41(12)
C28	N2	C29	115.72(13)	F11	C14	C15	114.63(12)

Chapter 11

C25	N3	C26	121.67(12)	C13	C14	C15	123.96(13)
C25	N3	C27	120.34(13)	F12	C15	C16	119.92(13)
C26	N3	C27	115.52(13)	C14	C15	C16	119.73(13)
C2	C1	B1	127.96(12)	F12	C15	C14	120.36(13)
C25	N2	C28	120.86(12)	C14	C13	C18	113.19(12)
C25	N2	C29	122.21(13)	F11	C14	C13	121.41(12)
C28	N2	C29	115.72(13)	F11	C14	C15	114.63(12)
C25	N3	C26	121.67(12)	C13	C14	C15	123.96(13)
C25	N3	C27	120.34(13)	F12	C15	C16	119.92(13)
C26	N3	C27	115.52(13)	C14	C15	C16	119.73(13)
C2	C1	B1	127.96(12)	F12	C15	C14	120.36(13)
C25	N2	C28	120.86(12)	C14	C13	C18	113.19(12)
C25	N2	C29	122.21(13)	F11	C14	C13	121.41(12)
C28	N2	C29	115.72(13)	F11	C14	C15	114.63(12)
C25	N3	C26	121.67(12)	C13	C14	C15	123.96(13)
C25	N3	C27	120.34(13)	F12	C15	C16	119.92(13)
C2	C1	C6	113.01(12)	F13	C16	C17	120.61(14)
C6	C1	B1	118.82(11)	F13	C16	C15	120.26(14)
C1	C2	C3	124.10(12)	C15	C16	C17	119.13(13)
F1	C2	C3	114.21(12)	C16	C17	C18	119.19(14)
F1	C2	C1	121.69(12)	F14	C17	C16	120.20(13)
F2	C3	C4	119.63(12)	F14	C17	C18	120.60(13)
F2	C3	C2	120.49(12)	F15	C18	C17	115.72(12)
C2	C3	C4	119.85(13)	C13	C18	C17	124.71(13)
C3	C4	C5	119.03(13)	F15	C18	C13	119.55(12)
F3	C4	C3	120.10(13)	C20	C19	B1	119.50(11)
F3	C4	C5	120.86(13)	C20	C19	C24	113.12(12)
C4	C5	C6	119.29(13)	C24	C19	B1	126.96(11)
F4	C5	C6	120.94(12)	F16	C20	C21	116.04(12)
F4	C5	C4	119.76(12)	C19	C20	C21	124.65(13)
C1	C6	C5	124.67(13)	F16	C20	C19	119.30(11)
F5	C6	C1	119.23(12)	C20	C21	C22	119.25(13)
F5	C6	C5	116.09(12)	F17	C21	C22	119.86(13)
C8	C7	B1	118.75(11)	F17	C21	C20	120.89(12)
C8	C7	C12	113.52(12)	F18	C22	C23	120.32(12)

Chapter 11

C12	C7	B1	127.54(12)	F18	C22	C21	120.81(13)
C7	C8	C9	124.50(13)	C21	C22	C23	118.87(13)
F6	C8	C9	116.11(12)	C22	C23	C24	119.72(12)
F6	C8	C7	119.37(12)	F19	C23	C24	120.45(12)
C8	C9	C10	119.10(13)	F19	C23	C22	119.82(12)
F7	C9	C10	120.08(13)	F20	C24	C23	114.43(11)
F7	C9	C8	120.81(13)	F20	C24	C19	121.19(11)
F8	C10	C9	120.53(14)	C19	C24	C23	124.38(12)
C9	C10	C11	119.18(13)	N1	C25	N2	118.82(12)
F8	C10	C11	120.29(13)	N1	C25	N3	119.66(13)
F9	C11	C12	120.50(12)	N2	C25	N3	121.52(12)
F9	C11	C10	119.86(12)	C7	B1	C19	113.30(10)
C10	C11	C12	119.64(13)	C13	B1	C19	102.29(10)
C7	C12	C11	123.98(13)	C1	B1	C7	102.82(10)
F10	C12	C7	121.34(12)	C1	B1	C13	112.87(10)
F10	C12	C11	114.68(12)	C1	B1	C19	113.14(10)
C18	C13	B1	119.09(11)	C7	B1	C13	112.85(10)
C14	C13	B1	127.60(12)				
C25	N1	H1	122.1(13)	H271	C27	H273	111.8(18)
C25	N1	H2	119.4(12)	N2	C28	H283	110.7(11)
H1	N1	H2	118.4(18)	H281	C28	H282	109.7(18)
N3	C26	H263	110.6(12)	H282	C28	H283	108.8(18)
N3	C26	H261	110.4(12)	N2	C28	H281	110.8(11)
C7	C12	C11	123.98(13)	C1	B1	C7	102.82(10)
N3	C26	H262	107.8(12)	H281	C28	H283	110.2(15)
H261	C26	H263	106.4(16)	N2	C28	H282	106.7(12)
H262	C26	H263	113.6(16)	N2	C29	H291	108.8(11)
H261	C26	H262	108.1(18)	N2	C29	H293	107.8(13)
N3	C26	H262	107.8(12)	H281	C28	H283	110.2(15)
N3	C27	H271	111.2(11)	H291	C29	H292	114.6(17)
N3	C27	H273	108.3(14)	H291	C29	H293	104.1(16)
H271	C27	H272	106.2(19)	H292	C29	H293	110.7(18)
N3	C27	H272	108.1(14)	N2	C29	H292	110.4(14)

Bond distances (Angstrom) and bond angles (Degrees) for 2b**Table 5.** Bond distances (angstrom) for **2b**

F1	C7	1.338(2)	N2	C36	1.460(3)
F2	C7	1.337(2)	C1	C2	1.398(2)
F3	C7	1.344(2)	C1	B1	1.640(2)
F7	C15	1.337(2)	C1	C6	1.403(2)
F8	C15	1.343(2)	C2	C3	1.396(2)
F9	C15	1.339(2)	C3	C7	1.497(3)
F22	C32	1.315(3)	C3	C4	1.386(2)
F23	C32	1.322(2)	C4	C5	1.393(2)
F24	C32	1.325(2)	C5	C8	1.493(2)
F41	C8	1.312(8)	C5	C6	1.385(2)
F42	C8	1.28(3)	C9	C14	1.402(2)
F51	C8	1.316(7)	C9	B1	1.637(2)
F52	C8	1.30(2)	C9	C10	1.399(2)
F61	C8	1.327(6)	C10	C11	1.391(2)
F62	C8	1.28(2)	C11	C12	1.381(2)
F101	C16	1.316(6)	C11	C15	1.497(3)
F102	C16	1.36(2)	C12	C13	1.390(2)
F111	C16	1.333(8)	C13	C14	1.391(2)
F112	C16	1.25(2)	C13	C16	1.495(2)
F121	C16	1.370(6)	C17	B1	1.635(2)
F122	C16	1.156(18)	C17	C18	1.400(2)
F131	C23	1.253(3)	C17	C22	1.402(2)
F132	C23	1.393(11)	C18	C19	1.390(2)
F141	C23	1.369(3)	C19	C20	1.382(2)
F142	C23	1.177(8)	C19	C23	1.496(3)
F151	C23	1.329(4)	C20	C21	1.388(3)
F152	C23	1.424(7)	C21	C24	1.492(3)
F161	C24	1.393(3)	C21	C22	1.393(2)
F162	C24	1.042(15)	C25	C30	1.397(2)
F171	C24	1.356(6)	C25	B1	1.640(2)
F172	C24	1.215(14)	C25	C26	1.403(2)
F172	F182	1.33(3)	C26	C27	1.390(2)
F181	C24	1.347(5)	C27	C28	1.388(2)

Chapter 11

F182	C24	1.300(13)	C27	C31	1.498(3)
F191	C31	1.293(7)	C28	C29	1.385(3)
F192	C31	1.249(13)	C29	C32	1.493(3)
F201	C31	1.312(9)	C29	C30	1.396(2)
F202	C31	1.325(9)	C33	C34	1.326(4)
F211	C31	1.252(9)	C35	C37	1.478(3)
F212	C31	1.305(8)	C381	C391	1.423(7)
N1	C382	1.472(3)	C382	C392	1.602(7)
N1	C33	1.381(3)	C391	C401	1.523(8)
N1	C381	1.472(3)	C392	C402	1.487(7)
N1	C35	1.332(3)	C401	C411	1.63(2)
N2	C35	1.335(3)	C402	C412	1.55(2)
N2	C34	1.370(3)			
C2	H21	0.95	C37	H373	0.98
C4	H41	0.95	C381	H382	0.99
C6	H61	0.95	C381	H381	0.99
C10	H101	0.95	C382	H384	0.99
C12	H121	0.95	C382	H383	0.99
C14	H141	0.95	C391	H391	0.99
C18	H181	0.95	C391	H392	0.99
C20	H201	0.95	C392	H393	0.99
C22	H221	0.95	C392	H394	0.99
C26	H261	0.95	C401	H401	0.99
C28	H281	0.95	C401	H402	0.99
C30	H301	0.95	C402	H403	0.99
C33	H331	0.95	C402	H404	0.99
C34	H341	0.95	C411	H411	0.98
C36	H361	0.98	C411	H412	0.98
C36	H362	0.98	C411	H413	0.98
C36	H363	0.98	C412	H416	0.98
C37	H371	0.98	C412	H414	0.98
C37	H372	0.98	C412	H415	0.98

Chapter 11

Table 6. Bond angles (degrees) for **2b**

F182	F172	C24	61.2(11)	C19	C20	C21	118.19(15)
F172	F182	C24	55.0(8)	C20	C21	C22	120.83(15)
C33	N1	C382	124.6(2)	C22	C21	C24	120.00(16)
C33	N1	C35	108.48(19)	C20	C21	C24	119.13(15)
C35	N1	C381	126.80(17)	C17	C22	C21	121.97(15)
C33	N1	C381	124.6(2)	F141	C23	F151	101.4(2)
C35	N1	C382	126.80(17)	F141	C23	C19	110.6(2)
C35	N2	C36	125.5(2)	F131	C23	C19	113.4(2)
C34	N2	C36	125.5(2)	F132	C23	C19	112.7(4)
C34	N2	C35	109.0(2)	F142	C23	C19	121.7(4)
C2	C1	C6	115.76(14)	F151	C23	C19	110.8(2)
C2	C1	B1	123.64(13)	F131	C23	F151	111.9(3)
C6	C1	B1	120.07(14)	F132	C23	F142	105.3(7)
C1	C2	C3	122.13(14)	F132	C23	F152	95.4(5)
C2	C3	C4	121.00(15)	F142	C23	F152	105.3(5)
C4	C3	C7	120.66(14)	F152	C23	C19	113.0(2)
C2	C3	C7	118.34(14)	F131	C23	F141	108.0(3)
C3	C4	C5	117.78(15)	F162	C24	F182	109.6(15)
C4	C5	C6	120.96(14)	F182	C24	C21	114.1(7)
C6	C5	C8	119.30(15)	F162	C24	F172	118.0(13)
C4	C5	C8	119.68(14)	F162	C24	C21	123.8(10)
C1	C6	C5	122.36(15)	F172	C24	C21	112.2(7)
F1	C7	F2	105.98(14)	F181	C24	C21	114.9(3)
F1	C7	F3	106.27(15)	F161	C24	F181	99.8(3)
F1	C7	C3	112.36(14)	F161	C24	C21	109.98(18)
F2	C7	F3	106.48(14)	F161	C24	F171	100.1(3)
F3	C7	C3	112.94(14)	F171	C24	C21	111.5(3)
F2	C7	C3	112.29(15)	F171	C24	F181	118.4(3)
F42	C8	F52	102.4(19)	F172	C24	F182	63.8(13)
F62	C8	C5	112.5(8)	C26	C25	C30	116.14(14)
F51	C8	C5	111.5(3)	C26	C25	B1	120.08(13)
F42	C8	F62	109.8(18)	C30	C25	B1	123.60(14)
F52	C8	F62	103.6(17)	C25	C26	C27	122.06(15)
F41	C8	F51	107.6(6)	C26	C27	C31	119.63(15)

Chapter 11

F41	C8	F61	104.9(4)	C28	C27	C31	119.47(16)
F41	C8	C5	113.5(4)	C26	C27	C28	120.91(17)
F51	C8	F61	105.4(5)	C27	C28	C29	117.94(16)
F42	C8	C5	114.7(13)	C28	C29	C30	121.15(15)
F61	C8	C5	113.4(3)	C30	C29	C32	118.22(16)
F52	C8	C5	112.9(7)	C28	C29	C32	120.61(16)
C10	C9	C14	116.10(13)	C25	C30	C29	121.80(16)
C10	C9	B1	120.41(12)	F191	C31	F201	103.2(7)
C14	C9	B1	22.48(13)	F201	C31	F211	110.0(7)
C9	C10	C11	122.19(14)	F191	C31	F211	105.9(5)
C12	C11	C15	121.15(15)	F211	C31	C27	114.9(4)
C10	C11	C12	120.78(15)	F192	C31	C27	117.5(5)
C10	C11	C15	118.06(14)	F191	C31	C27	112.2(3)
C11	C12	C13	118.21(15)	F212	C31	C27	113.2(4)
C12	C13	C14	120.97(14)	F192	C31	F202	107.2(8)
C12	C13	C16	117.98(15)	F202	C31	C27	112.7(4)
C14	C13	C16	121.03(15)	F201	C31	C27	110.0(4)
C9	C14	C13	121.74(15)	F202	C31	F212	97.0(8)
F7	C15	C11	112.12(17)	F192	C31	F212	107.2(7)
F8	C15	F9	106.15(17)	F22	C32	C29	113.11(16)
F9	C15	C11	112.83(16)	F23	C32	F24	105.45(16)
F8	C15	C11	112.31(16)	F24	C32	C29	114.00(18)
F7	C15	F9	107.07(16)	F23	C32	C29	112.72(16)
F7	C15	F8	105.89(16)	F22	C32	F24	105.21(17)

Bond distances (Angstrom) and bond angles (Degrees) for 5b**Table 7.** Bond distances (Angstrom) for **5b**

P1	C1	1.8003(15)	C45	C46	1.389(2)
P1	C15	1.8009(15)	C46	C47	1.386(2)
P1	C19	1.8067(16)	C47	C50	1.499(2)
P1	C23	1.8039(14)	C47	C48	1.399(2)
C1	C2	1.534(2)	C51	C52	1.4008(18)
C2	C3	1.529(2)	C51	B1	1.6525(19)
C3	C4	1.524(2)	C51	C56	1.405(2)
C4	C5	1.528(2)	C52	C53	1.3946(19)

Chapter 11

C5	C6	1.524(2)	C53	C57	1.4978(19)
C6	C7	1.526(2)	C53	C54	1.386(2)
C7	C8	1.522(2)	C54	C55	1.390(2)
C8	C9	1.526(2)	C55	C58	1.498(2)
C9	C10	1.525(2)	C55	C56	1.393(2)
C10	C11	1.524(2)	C7	H72	0.99
C11	C12	1.522(2)	C1	H12	0.99
C12	C13	1.523(2)	C1	H11	0.99
C13	C14	1.522(2)	C2	H21	0.99
C15	C16	1.533(2)	C2	H22	0.99
C16	C17	1.518(2)	C3	H31	0.99
C17	C18	1.520(3)	C3	H32	0.99
C19	C20	1.533(2)	C4	H42	0.99
C20	C21	1.524(2)	C4	H41	0.99
C21	C22	1.524(2)	C5	H52	0.99
C23	C24	1.532(2)	C5	H51	0.99
C24	C25	1.518(2)	C6	H61	0.99
C25	C26	1.523(3)	C6	H62	0.99
F1	C33	1.3386(18)	C7	H71	0.99
F2	C33	1.3380(19)	C8	H81	0.99
F3	C33	1.3371(19)	C8	H82	0.99
F4	C34	1.3418(19)	C9	H91	0.99
F5	C34	1.3405(17)	C9	H92	0.99
F6	C34	1.324(2)	C10	H102	0.99
F7	C41	1.3326(19)	C10	H101	0.99
F8	C41	1.3291(19)	C11	H112	0.99
F9	C41	1.343(2)	C11	H111	0.99
F10A	C42	1.251(6)	C12	H122	0.99
F10B	C42	1.372(4)	C12	H121	0.99
F11A	C42	1.290(8)	C13	H131	0.99
F11B	C42	1.270(5)	C13	H132	0.99
F12A	C42	1.355(6)	C14	H141	0.98
F12B	C42	1.293(4)	C14	H142	0.98
F13	C49	1.334(2)	C14	H143	0.98
F14	C49	1.330(2)	C15	H151	0.99

Chapter 11

F15	C49	1.335(2)	C15	H152	0.99
F16A	C50	1.339(4)	C16	H161	0.99
F16B	C50	1.199(6)	C16	H162	0.99
F17A	C50	1.377(4)	C17	H172	0.99
F17B	C50	1.320(7)	C17	H171	0.99
F18A	C50	1.243(5)	C18	H182	0.98
F18B	C50	1.452(6)	C18	H181	0.98
F19	C57	1.3529(17)	C18	H183	0.98
F20	C57	1.3376(17)	C19	H192	0.99
F21	C57	1.3366(17)	C19	H191	0.99
F22A	C58	1.358(7)	C20	H202	0.99
F22B	C58	1.293(6)	C20	H201	0.99
F23A	C58	1.328(6)	C21	H212	0.99
F23B	C58	1.267(16)	C21	H211	0.99
F24A	C58	1.301(10)	C22	H223	0.98
F24B	C58	1.385(8)	C22	H222	0.98
C27	C32	1.4061(18)	C22	H221	0.98
C27	C28	1.4048(19)	C23	H232	0.99
C27	B1	1.6497(19)	C23	H231	0.99
C28	C29	1.3956(19)	C24	H242	0.99
C29	C30	1.3879(19)	C24	H241	0.99
C29	C33	1.496(2)	C25	H252	0.99
C30	C31	1.389(2)	C25	H251	0.99
C31	C32	1.395(2)	C26	H263	0.98
C31	C34	1.498(2)	C26	H262	0.98
C35	C36	1.4052(19)	C26	H261	0.98
C35	C40	re1.4035(19)			
C35	-B1	1.649(2)	C28	-H281	0.95
C36	-C37	1.3988(19)	C30	-H301	0.95
C37	-C38	1.387(2)	C32	-H321	0.95
C37	-C41	1.497(2)	C36	-H361	0.95
C38	-C39	1.385(2)	C38	-H381	0.95
C39	-C42	1.502(2)	C40	-H401	0.95
C39	-C40	1.394(2)	C44	-H441	0.95
C43	-B1	1.650(2)	C46	-H461	0.95

Chapter 11

C43	-C44	1.4033(19)	C48	-H481	0.95
C43	-C48	1.3998(19)	C52	-H521	0.95
C44	-C45	1.391(2)	C54	-H541	0.95
C45	-C49	1.501(2)	C56	-H561	0.95

Table 8. Bond angles (Degrees) for **5b**

C1	P1	C15	109.46(7)	F11B	C42	C39	113.6(3)
C1	P1	C19	112.94(7)	F12B	C42	C39	115.2(4)
C1	P1	C23	106.47(7)	F10A	C42	C39	113.4(3)
C15	P1	C19	107.88(7)	F11A	C42	C39	115.1(3)
C15	P1	C23	109.91(7)	F12A	C42	C39	110.5(2)
C19	P1	C23	110.17(7)	F10A	C42	F11A	111.6(5)
P1	C1	C2	117.95(10)	F10A	C42	F12A	103.4(4)
C1	C2	C3	109.24(11)	F11A	C42	F12A	101.6(5)
C2	C3	C4	114.81(12)	C44	C43	C48	115.61(12)
C3	C4	C5	111.27(11)	C44	C43	B1	122.09(12)
C4	C5	C6	114.09(12)	C48	C43	B1	121.91(12)
C5	C6	C7	112.44(12)	C43	C44	C45	122.44(13)
C6	C7	C8	114.35(12)	C44	C45	C46	120.78(14)
C7	C8	C9	112.46(11)	C44	C45	C49	120.48(13)
C8	C9	C10	113.91(12)	C46	C45	C49	118.73(14)
C9	C10	C11	113.03(12)	C45	C46	C47	118.15(14)
C10	C11	C12	113.60(13)	C46	C47	C48	120.71(14)
C11	C12	C13	113.84(13)	C46	C47	C50	119.50(15)
C12	C13	C14	112.63(13)	C48	C47	C50	119.76(14)
P1	C15	C16	113.21(10)	C43	C48	C47	122.25(13)
C15	C16	C17	112.27(13)	F13	C49	F14	105.30(14)
C16	C17	C18	112.18(16)	F13	C49	F15	107.45(14)
P1	C19	C20	115.78(10)	F13	C49	C45	112.38(14)
C19	C20	C21	111.35(12)	F14	C49	F15	105.25(14)
C20	C21	C22	112.68(13)	F14	C49	C45	112.36(13)
P1	C23	C24	113.54(10)	F15	C49	C45	113.49(14)
C23	C24	C25	112.68(13)	F16A	C50	F17A	100.2(3)
C24	C25	C26	111.40(15)	F16A	C50	F18A	109.2(3)
F16A	C50	C47	111.4(2)				
C28	C27	C32	115.22(12)	F17A	C50	F18A	107.5(3)

Chapter 11

C28	C27	B1	120.07(11)	F17A	C50	C47	111.9(2)
C32	C27	B1	124.63(12)	F18A	C50	C47	115.5(2)
C27	C28	C29	122.63(12)	F16B	C50	C47	117.7(5)
C28	C29	C30	120.93(13)	F17B	C50	C47	113.2(4)
C28	C29	C33	118.68(12)	F18B	C50	C47	109.8(3)
C30	C29	C33	120.39(13)	F16B	C50	F17B	115.4(7)
C29	C30	C31	117.67(13)	F16B	C50	F18B	100.8(6)
C30	C31	C32	121.28(13)	F17B	C50	F18B	96.7(5)
C30	C31	C34	118.82(13)	C52	C51	C56	115.53(12)
C32	C31	C34	119.84(13)	C52	C51	B1	122.49(12)
C27	C32	C31	122.25(13)	C56	C51	B1	121.62(11)
F1	C33	F2	105.92(12)	C51	C52	C53	122.34(13)
F1	C33	F3	105.50(12)	C52	C53	C54	121.11(12)
F1	C33	C29	112.38(13)	C52	C53	C57	118.55(13)
F2	C33	F3	106.50(13)	C54	C53	C57	120.29(12)
F2	C33	C29	113.48(12)	C53	C54	C55	117.72(13)
F3	C33	F5	112.47(12)	C54	C55	C56	121.04(13)
F4	C34	F6	104.61(12)	C54	C55	C58	119.03(13)
F4	C34	C31	106.51(13)	C56	C55	C58	119.89(13)
F4	C34	C31	112.25(12)	C51	C56	C55	122.26(12)
F5	C34	F6	106.46(12)	F19	C57	F20	105.65(11)
F5	C34	C31	112.98(13)	F19	C57	F21	105.59(11)
F6	C34	C31	113.38(12)	F19	C57	C53	111.73(11)
C36	C35	C40	115.55(12)	F20	C57	F21	106.97(11)
C36	C35	B1	121.66(11)	F20	C57	C53	113.19(12)
C40	C35	B1	122.79(12)	F21	C57	C53	113.12(11)
C35	C36	C37	122.12(13)	F22A	C58	F23A	101.6(5)
C36	C37	C38	120.91(13)	F22A	C58	F24A	106.5(6)
C36	C37	C41	119.27(13)	F22A	C58	C55	112.0(3)
C38	C37	C41	119.79(13)	F23A	C58	F24A	106.2(6)
C37	C38	C39	118.02(13)	F23A	C58	C55	114.6(3)
C38	C39	C40	121.04(13)	F24A	C58	C55	114.8(4)
C38	C39	C42	119.37(13)	F22B	C58	C55	114.4(4)
C40	C39	C42	119.58(13)	F23B	C58	C55	113.7(7)
C35	C40	C39	122.31(13)	F24B	C58	C55	107.3(5)

Chapter 11

F7	C41	F8	106.29(13)	F22B	C58	F23B	114.9(9)
F7	C41	F9	104.96(13)	F22B	C58	F24B	102.2(11)
F7	C41	C37	113.12(13)	F23B	C58	F24B	102.5(10)
F8	C41	F9	107.02(14)	C27	B1	C43	109.43(10)
F8	C41	C37	113.07(14)	C27	B1	C51	110.29(11)
F9	C41	C37	111.82(13)	C35	B1	C51	107.53(10)
F10B	C42	F11B	102.0(5)	C43	B1	C51	107.75(10)
F10B	C42	F12B	105.6(5)	C35	B1	C43	110.71(11)
F10B	C42	C39	112.1(4)	C27	B1	C35	111.06(10)
F11B	C42	F12B	107.4(4)				
P1	C1	H11	108.00	H161	C16	H162	108.00
P1	C1	H12	108.00	C16	C17	H171	109.00
C2	C1	H11	108.00	C16	C17	H172	109.00
C2	C1	H12	108.00	C18	C17	H171	109.00
H11	C1	H12	107.00	C18	C17	H172	109.00
C1	C2	H21	110.00	H171	C17	H172	108.00
C1	C2	H22	110.00	C17	C18	H181	109.00
C3	C2	H21	110.00	C17	C18	H182	109.00
C3	C2	H22	110.00	C17	C18	H183	109.00
H21	C2	H22	108.00	H181	C18	H182	109.00
C2	C3	H31	109.00	H181	C18	H183	110.00
C2	C3	H32	109.00	H182	C18	H183	109.00
C4	C3	H31	109.00	P1	C19	H191	108.00
C4	C3	H32	109.00	P1	C19	H192	108.00
H31	C3	H32	108.00	C20	C19	H191	108.00
C3	C4	H41	109.00	C20	C19	H192	108.00
C3	C4	H42	109.00	H191	C19	H192	107.00
C5	C4	H41	109.00	C19	C20	H201	109.00
C5	C4	H42	109.00	C19	C20	H202	109.00
H41	C4	H42	108.00	C21	C20	H201	109.00
C4	C5	H51	109.00	C21	C20	H202	109.00
C4	C5	H52	109.00	H201	C20	H202	108.00
C6	C5	H51	109.00	C20	C21	H211	109.00
C6	C5	H52	109.00	C20	C21	H212	109.00
H51	C5	H52	108.00	C22	C21	H211	109.00

Chapter 11

C5	C6	H61	109.00	C22	C21	H212	109.00
C5	C6	H62	109.00	H211	C21	H212	108.00
C7	C6	H61	109.00	C21	C22	H221	109.00
H71	C7	H72	108.00	P1	C23	H232	109.00
C7	C8	H81	109.00	C24	C23	H231	109.00
C7	C8	H82	109.00	C24	C23	H232	109.00
C9	C8	H81	109.00	H231	C23	H232	108.00
C9	C8	H82	109.00	C23	C24	H241	109.00
H81	C8	H82	108.00	C23	C24	H242	109.00
C8	C9	H91	109.00	C25	C24	H241	109.00
C8	C9	H92	109.00	C25	C24	H242	109.00
C10	C9	H91	109.00	H241	C24	H242	108.00
C10	C9	H92	109.00	C24	C25	H251	109.00
C7	C6	H62	109.00	C21	C22	H222	110.00
H61	C6	H62	108.00	C21	C22	H223	109.00
C6	C7	H71	109.00	H221	C22	H222	110.00
C6	C7	H72	109.00	H221	C22	H223	109.00
C8	C7	H71	109.00	H222	C22	H223	109.00
H91	C9	H92	108.00	C24	C25	H252	109.00
C9	C10	H101	109.00	C26	C25	H251	109.00
C9	C10	H102	109.00	C26	C25	H252	109.00
C11	C10	H101	109.00	H251	C25	H252	108.00
C11	C10	H102	109.00	C25	C26	H261	109.00
H101	C10	H102	108.00	C25	C26	H262	109.00
C10	C11	H111	109.00	C25	C26	H263	109.00
C10	C11	H112	109.00	H261	C26	H262	109.00
C12	C11	H111	109.00	H261	C26	H263	109.00
C12	C11	H112	109.00	H262	C26	H263	109.00
H111	C11	H112	108.00	C17	C16	H162	109.00
C11	C12	H121	109.00	C29	C28	H281	119.00
C11	C12	H122	109.00	C27	C28	H281	119.00
C13	C12	H121	109.00	C29	C30	H301	121.00
C13	C12	H122	109.00	C31	C30	H301	121.00
H121	C12	H122	108.00	C31	C32	H321	119.00
C12	C13	H131	109.00	C27	C32	H321	119.00

C12	C13	H132	109.00	C35	C36	H361	119.00
C14	C13	H131	109.00	C37	C36	H361	119.00
C14	C13	H132	109.00	C37	C38	H381	121.00
H131	C13	H132	108.00	C39	C38	H381	121.00
C13	C14	H141	109.00	C39	C40	H401	119.00
C13	C14	H142	109.00	C35	C40	H401	119.00
C13	C14	H143	110.00	C43	C44	H441	119.00
H141	C14	H142	109.00	C45	C44	H441	119.00
H141	C14	H143	109.00	C45	C46	H461	121.00
H142	C14	H143	109.00	C47	C46	H461	121.00
P1	C15	H151	109.00	C47	C48	H481	119.00
P1	C15	H152	109.00	C43	C48	H481	119.00
C16	C15	H151	109.00	C51	C52	H521	119.00
C16	C15	H152	109.00	C53	C52	H521	119.00
H151	C15	H152	108.00	C53	C54	H541	121.00
C15	C16	H161	109.00	C55	C54	H541	121.00
C15	C16	H162	109.00	C55	C56	H561	119.00
C17	C16	H161	109.00	C51	C56	H561	119.00

11.3.3. IR spectra comparison

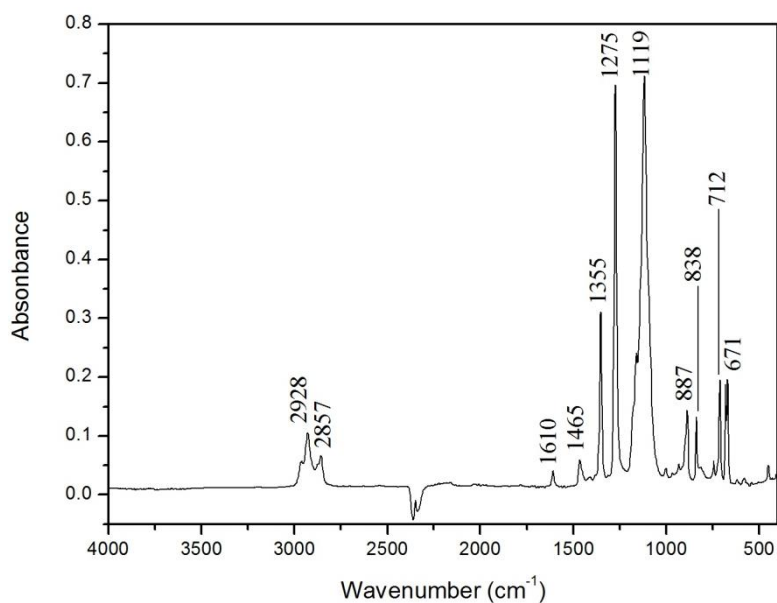


Figure 1. Pure $[P_{4,4,4,14}][B(C_6H_3-3,5-(CF_3)_2)_4]$ ionic liquid.

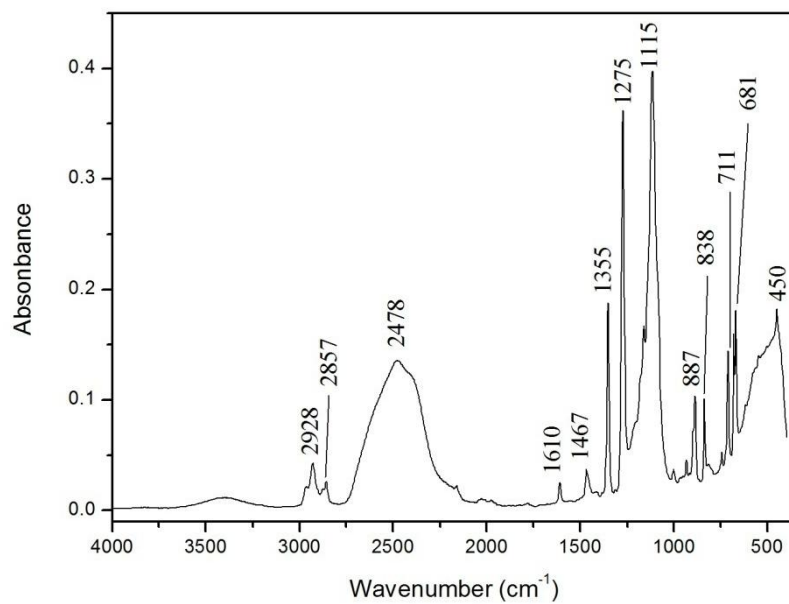


Figure 2. Ionic liquid with D₂O mixture.

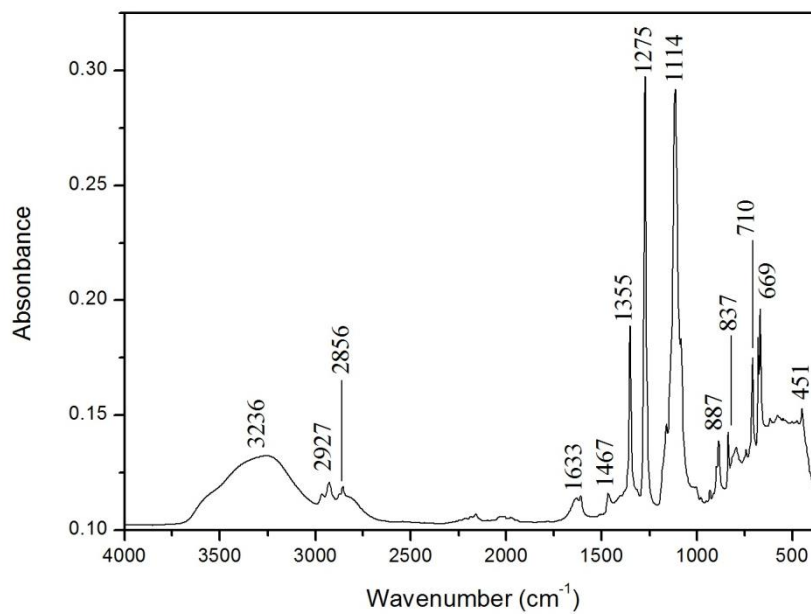


Figure 3. Ionic liquid with H₂O₂ mixture

11.3.4 NMR spectra comparison

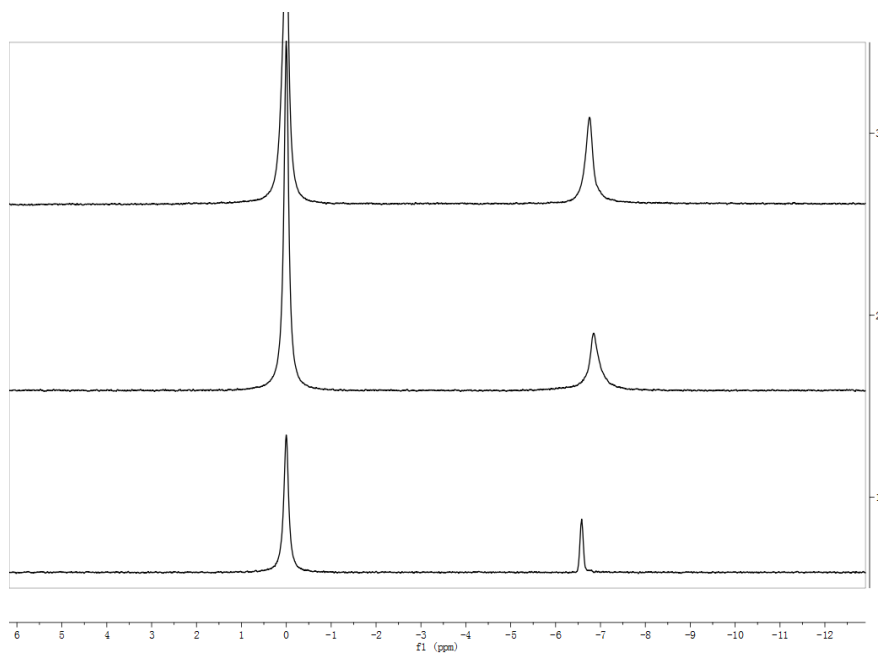


Figure 4. ^{11}B NMR of pure ionic liquid (1), ionic liquid with H_2O mixture (2) and ionic liquid H_2O_2 (30 %) (3).

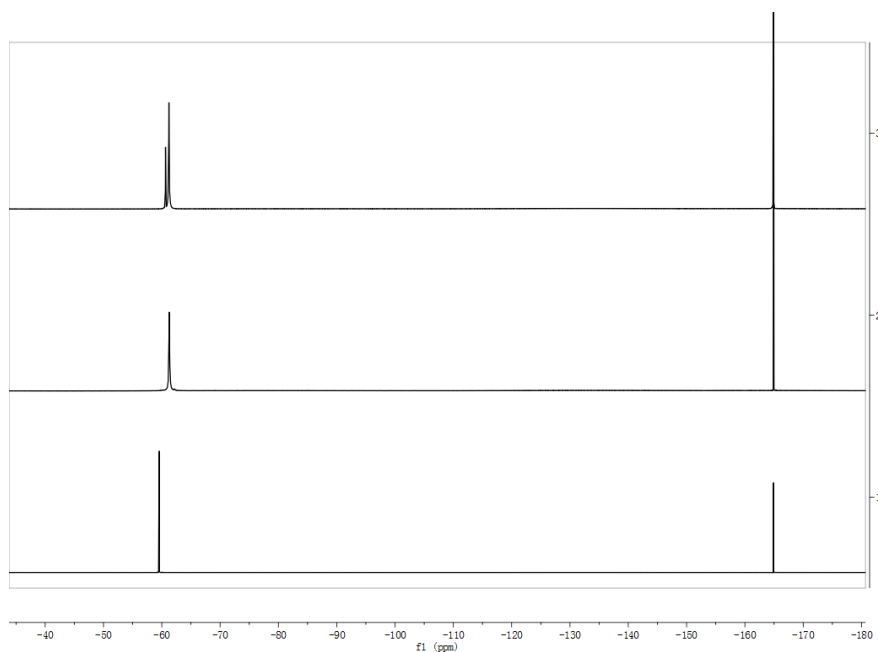
 ^{19}F NMR spectra comparison

Figure 5. ^{19}F NMR of pure ionic liquid (1), ionic liquid with H_2O mixture (2) and ionic liquid H_2O_2 (30 %) (3).

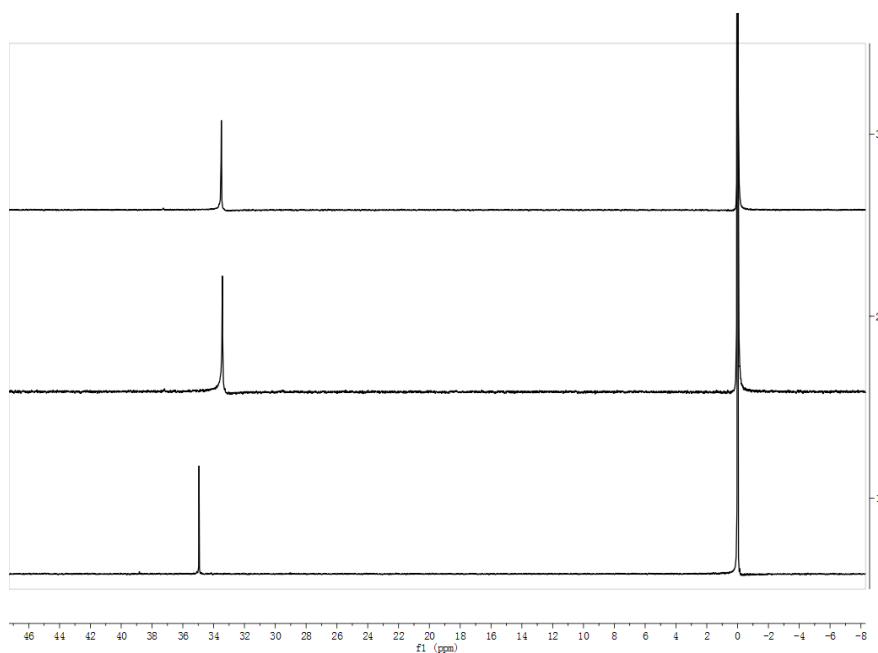


Figure 6. ^{31}P NMR of pure ionic liquid (1), ionic liquid with H_2O mixture (2) and ionic liquid H_2O_2 (30 %) (3).

10.3.5 References:

- [1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "SIR92", *J. Appl. Cryst.* **1994**, *27*, 435-436.
- [4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**.
- [5] Sheldrick, G. M. "SHELXL-97", University of Göttingen, Göttingen, Germany (1998).
- [6] Spek, A. L. "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (2010).
- [7] L. J. Farrugia, "WinGX (Version 1.70.01 January 2005)", *J. Appl. Cryst.* **1999**, *32*, 837-838.

11.4 This section contains supplementary information to section 6: oxidation reactions catalyzed by polyoxomolybdate salts

11.4.1 Crystallographic details of compounds 1, 3 and 4

Table 1. Crystallographic details of 1, 3 and 4.

	1	3	4
Formula	C ₃₂ H ₇₂ PO ₁₉ Mo ₆	C ₁₆ H ₃₀ N ₄ O ₁₉ Mo ₆	C ₁₈ H ₃₄ N ₄ O ₁₉ Mo ₆
M_r	1398.48	1158.08	1186.13
Cryst. Size, mm ³	0.25×0.26×0.47	0.10×0.20×0.22	0.24×0.41×0.46
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> , Å	16.0547(3)	8.5458(16)	11.0074(2)
<i>b</i> , Å	16.0680(3)	17.085(3)	10.7827(2)
<i>c</i> , Å	19.7281(4)	11.075(2)	13.5900(3)
α , deg	90	90	90
β , deg	106.2476(7)	108.937(8)	91.045(1)
γ , deg	90	90	90
<i>V</i> , Å ³	4885.94(16)	1529.5(5)	1612.72(5)
<i>Z</i>	4	2	2
D_{calcd} , g cm ⁻³	1.901	2.515	2.443
$\mu(\text{MoK}\alpha)$, mm ⁻¹	1.625	2.471	2.347
<i>F</i> (000), e	2792	1116	1148
<i>hkl</i> range	-19 ≤ <i>h</i> ≤ +19 -19 ≤ <i>k</i> ≤ +19 -21 ≤ <i>l</i> ≤ +23	-10 ≤ <i>h</i> ≤ +10 -20 ≤ <i>k</i> ≤ +20 -13 ≤ <i>l</i> ≤ +13	-13 ≤ <i>h</i> ≤ +13 -13 ≤ <i>k</i> ≤ +13 -16 ≤ <i>l</i> ≤ +16
$\theta_{\text{min/max}}$, deg	1.8, 25.4	2.4, 25.6	2.4, 25.5
Refl. Measured	15516	48445	40353
Refl. Unique	4475	2836	2928
R_{int}	0.017	0.048	0.82
Param. Refined	414	208	218
$R(F)/wR(F^2)^a$ (all reflexions)	0.0177, 0.0370	0.0196, 0.0395	0.0264, 0.0660
GoF (F^2) ^b	1.05	1.06	1.16
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.34, -0.34	0.34, -0.27	1.36, -0.58

^a $R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$, $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^b GoF = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$

11.4.2 Bond distances and angles of compounds 1, 3 and 4

Bond distances and angles of 1

C₃₂H₇₂PMo₆O₁₉ (**1**): a clear pale yellow fragment-like specimen of C₃₂H₇₂Mo₆O₁₉P₂, approximate dimensions 0.252 mm x 0.260 mm x 0.469 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2592 frames were collected. The total exposure time was 7.20 h. The frames were integrated with the

Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 42081 reflections to a maximum θ angle of 25.35° (0.83 Å resolution). The final cell constants of $a = 16.0547(3)$ Å, $b = 16.0680(3)$ Å, $c = 19.7281(4)$ Å, $\beta = 106.2476(7)^\circ$, volume = $4885.94(16)$ Å³, are based upon the refinement of the XYZ-centroids of 216 reflections above $20 \sigma(I)$ with $3.605^\circ < 2\theta < 66.77^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.909. Bond distances and angles of **1** are shown in Table S2 and Table S3.

Table 2. Bond distances (Å) in compound **1**.

Mo1	-O2	1.6779(18)	C14	-C15	1.518(3)
Mo1	-O7	1.9284(13)	C15	-C16	1.520(3)
Mo1	-O9	1.9298(13)	C1	-H1B	0.93(2)
Mo1	-O7_a	1.9284(13)	C1	-H1A	0.94(2)
Mo1	-O9_a	1.9298(13)	C2	-H2A	0.95(3)
Mo1	-O1	2.3177(16)	C1	-H2B	0.90(3)
Mo2	-O1	2.3135(16)	C3	-H3A	0.99(3)
Mo2	-O11_a	1.9308(13)	C3	-H3B	0.91(2)
Mo2	-O8_a	1.9269(13)	C4	-H4A	0.97(3)
Mo2	-O11	1.9308(13)	C4	-H4B	0.95(3)
Mo2	-O3	1.6800(19)	C4	-H4C	0.93(3)
Mo2	-O8	1.9269(13)	C5	-H5A	0.95(2)
Mo3	-O4	1.6833(13)	C5	-H5B	0.92(2)
Mo3	-O9	1.9287(13)	C6	-H6A	0.96(2)
Mo3	-O10	2.0020(13)	C6	-H6B	0.94(2)
Mo3	-O11	1.9227(13)	C7	-H7B	0.98(2)
Mo3	-O1	2.3188(2)	C7	-H7A	0.94(2)
Mo3	-O6_a	1.8610(13)	C8	-H8A	0.99(3)
Mo4	-O6	1.9902(13)	C8	-H8B	0.92(3)
Mo4	-O8	1.9193(13)	C8	-H8C	0.94(3)
Mo4	-O10	1.8681(14)	C9	-H9A	0.92(2)
Mo4	-O7	1.9282(13)	C9	-H9B	0.89(2)
Mo4	-O1	2.3177(2)	C10	-H10A	0.91(2)
Mo4	-O5	1.6879(14)	C10	-H10B	0.92(2)
P1	-C1	1.804(2)	C11	-H11A	0.95(2)

Chapter 11

P1	-C5	1.801(2)	C11	-H11B	0.93(2)
P1	-C9	1.803(2)	C12	-H12A	0.96(2)
P1	-C13	1.800(2)	C12	-H12B	0.92(2)
C1	-C2	1.528(3)	C12	-H12C	0.90(3)
C2	-C3	1.517(3)	C13	-H13B	0.92(2)
C3	-C4	1.514(4)	C13	-H13A	0.92(2)
C5	-C6	1.528(3)	C14	-H14A	0.94(2)
C6	-C7	1.524(3)	C14	-H14B	0.94(2)
C7	-C8	1.518(3)	C15	-H15B	0.96(2)
C9	-C10	1.527(3)	C15	-H15A	0.93(2)
C10	-C11	1.518(3)	C16	-H16C	0.92(3)
C11	-C12	1.519(3)	C16	-H16A	0.94(2)
C13	-C14	1.528(3)	C16	-H16B	0.95(3)

Table 3. Bond angles (°) in compound **1**.

O2	-Mo1	-O7_a	103.17(4)	O5	-Mo4	-O6	102.04(6)
O2	-Mo1	-O9_a	103.42(4)	O7	-Mo4	-O8	152.87(6)
O7	-Mo1	-O9	86.94(6)	O6	-Mo4	-O8	84.47(5)
O7	-Mo1	-O7_a	153.67(6)	O6	-Mo4	-O10	153.85(6)
O7	-Mo1	-O9_a	87.00(6)	C1	-P1	-C13	105.02(10)
O7_a	-Mo1	-O9	87.00(6)	C5	-P1	-C9	110.02(10)
O9	-Mo1	-O9_a	153.16(6)	C5	-P1	-C13	112.35(10)
O7_a	-Mo1	-O9_a	86.94(6)	C9	-P1	-C13	108.48(9)
O1	-Mo1	-O2	180.00(1)	C1	-P1	-C5	108.37(9)
O1	-Mo1	-O7	76.83(4)	C1	-P1	-C9	112.55(9)
O1	-Mo1	-O9	76.58(4)	Mo1	-O1	-Mo2	180.00(1)
O1	-Mo1	-O7_a	76.83(4)	Mo1	-O1	-Mo3	90.13(4)
O1	-Mo1	-O9_a	76.58(4)	Mo1	-O1	-Mo4	89.92(4)
O2	-Mo1	-O7	103.17(4)	Mo1	-O1	-Mo3_a	90.13(4)
O2	-Mo1	-O9	103.42(4)	Mo3	-O1	-Mo3_a	179.74(8)
O8	-Mo2	-O8_a	152.87(6)	Mo1	-O1	-Mo4_a	89.92(4)
O8	-Mo2	-O11_a	87.00(6)	Mo2	-O1	-Mo3	89.87(4)
O8_a	-Mo2	-O11	87.00(6)	Mo2	-O1	-Mo4	90.08(4)
O11	-Mo2	-O11_a	153.71(6)	Mo2	-O1	-Mo3_a	89.87(4)
O8_a	-Mo2	-O11_a	86.89(6)	Mo2	-O1	-Mo4_a	90.08(4)
O1	-Mo2	-O11_a	76.86(4)	Mo3	-O1	-Mo4	90.20(1)

Chapter 11

O3	-Mo2	-O8	103.56(4)	Mo4	-O1	-Mo4_a	179.85(8)
O3	-Mo2	-O11	103.14(4)	Mo3	-O1	-Mo4_a	89.81(1)
O1	-Mo2	-O3	180.00(1)	Mo3_a	-O1	-Mo4	89.81(1)
O1	-Mo2	-O8	76.44(4)	Mo3_a	-O1	-Mo4_a	90.20(1)
O1	-Mo2	-O11	76.86(4)	Mo3_a	-O6	-Mo4	116.35(7)
O1	-Mo2	-O8_a	76.44(4)	Mo1	-O7	-Mo4	116.28(7)
O3	-Mo2	-O8_a	103.56(4)	Mo2	-O8	-Mo4	116.86(7)
O3	-Mo2	-O11_a	103.14(4)	Mo1	-O9	-Mo3	116.57(7)
O8	-Mo2	-O11	86.89(6)	Mo3	-O10	-Mo4	116.07(7)
O1	-Mo3	-O4	176.62(5)	Mo2	-O11	-Mo3	116.22(7)
O1	-Mo3	-O9	76.57(6)	P1	-C1	-C2	118.17(15)
O1	-Mo3	-O10	75.61(4)	C1	-C2	-C3	111.72(19)
O10	-Mo3	-O11	84.58(5)	C2	-C3	-C4	113.6(2)
O6_a	-Mo3	-O10	153.70(6)	P1	-C5	-C6	115.66(14)
O6_a	-Mo3	-O11	90.42(6)	C5	-C6	-C7	111.66(17)
O4	-Mo3	-O11	102.94(6)	C6	-C7	-C8	111.34(18)
O4	-Mo3	-O6_a	105.28(6)	P1	-C9	-C10	116.21(14)
O9	-Mo3	-O10	83.81(5)	C9	-C10	-C11	111.75(17)
O1	-Mo3	-O11	76.88(6)	C10	-C11	-C12	112.81(17)
O1	-Mo3	-O6_a	78.10(4)	P1	-C13	-C14	118.12(15)
O4	-Mo3	-O9	103.25(6)	C13	-C14	-C15	110.66(17)
O4	-Mo3	-O10	101.00(6)	C14	-C15	-C16	112.63(19)
O9	-Mo3	-O11	152.92(6)	P1	-C1	-H1A	105.0(13)
O6_a	-Mo3	-O9	89.26(6)	C2	-C1	-H1A	108.7(14)
O1	-Mo4	-O7	76.84(6)	C2	-C1	-H1B	110.7(14)
O1	-Mo4	-O5	177.38(5)	P1	-C1	-H1B	108.1(14)
O1	-Mo4	-O6	75.74(4)	H1A	-C1	-H1B	105(2)
O7	-Mo4	-O10	89.21(6)	C3	-C2	-H2A	111.4(15)
O8	-Mo4	-O10	89.99(6)	C3	-C2	-H2B	109.4(17)
O5	-Mo4	-O7	101.66(6)	H2A	-C2	-H2B	106(2)
O5	-Mo4	-O8	104.82(6)	C1	-C2	-H2B	109.0(17)
O5	-Mo4	-O10	104.09(6)	C1	-C2	-H2A	108.9(16)
O6	-Mo4	-O7	84.40(5)	C4	-C3	-H3A	109.3(16)
O1	-Mo4	-O8	76.47(6)	C2	-C3	-H3A	107.6(15)
O1	-Mo4	-O10	78.11(4)	C2	-C3	-H3B	112.2(15)

Chapter 11

H3A	-C3	-H3B	104(2)	C9	-C10	-H10B	110.3(16)
C4	-C3	-H3B	109.4(16)	C11	-C10	-H10B	111.0(15)
C3	-C4	-H4B	109.7(19)	C9	-C10	-H10A	109.7(16)
C3	-C4	-H4A	110.2(17)	C10	-C11	-H11A	106.9(15)
H4A	-C4	-H4C	111(3)	C12	-C11	-H11B	108.2(15)
C3	-C4	-H4C	108.8(19)	H11A	-C11	-H11B	110(2)
H4A	-C4	-H4B	110(2)	C10	-C11	-H11B	108.1(14)
H4B	-C4	-H4C	108(3)	C12	-C11	-H11A	110.7(15)
P1	-C5	-H5A	108.3(13)	C11	-C12	-H12A	109.8(14)
P1	-C5	-H5B	106.7(14)	H12A	-C12	-H12B	105(2)
C6	-C5	-H5A	109.0(13)	C11	-C12	-H12B	112.1(15)
C6	-C5	-H5B	111.3(13)	C11	-C12	-H12C	111.9(17)
H5A	-C5	-H5B	105.4(19)	H12B	-C12	-H12C	108(2)
C5	-C6	-H6A	108.6(13)	H12A	-C12	-H12C	110(2)
C5	-C6	-H6B	111.3(13)	P1	-C13	-H13B	104.7(14)
C7	-C6	-H6A	109.7(13)	P1	-C13	-H13A	103.5(15)
C7	-C6	-H6B	108.6(13)	H13A	-C13	-H13B	107.3(19)
H6A	-C6	-H6B	106.9(19)	C14	-C13	-H13A	110.4(13)
C6	-C7	-H7A	108.3(13)	C14	-C13	-H13B	112.0(13)
C6	-C7	-H7B	109.4(12)	C15	-C14	-H14B	109.7(15)
C8	-C7	-H7A	111.0(13)	H14A	-C14	-H14B	108(2)
C8	-C7	-H7B	110.4(11)	C15	-C14	-H14A	108.6(14)
H7A	-C7	-H7B	106.4(18)	C13	-C14	-H14A	111.1(13)
H8A	-C8	-H8B	109(2)	C13	-C14	-H14B	108.9(14)
H8A	-C8	-H8C	107(2)	C14	-C15	-H15A	110.9(14)
H8B	-C8	-H8C	105(2)	C14	-C15	-H15B	109.6(13)
C7	-C8	-H8B	111.0(17)	C16	-C15	-H15A	109.5(13)
C7	-C8	-H8C	113.1(15)	C16	-C15	-H15B	109.0(13)
C7	-C8	-H8A	112.1(15)	H15A	-C15	-H15B	104.9(18)
P1	-C9	-H9A	106.1(15)	C15	-C16	-H16C	111.9(15)
P1	-C9	-H9B	104.9(16)	H16A	-C16	-H16C	108(2)
C10	-C9	-H9A	110.5(16)	H16B	-C16	-H16C	107(2)
C10	-C9	-H9B	112.0(16)	H16A	-C16	-H16B	107(2)
H9A	-C9	-H9B	107(2)	C15	-C16	-H16A	111.2(14)
C11	-C10	-H10A	110.6(16)	C15	-C16	-H16B	111.4(14)

Bond distances and angles of 3

$C_{16}H_{30}N_4Mo_6O_{19}$ (**3**): a clear light yellow fragment-like specimen of Mo_6O_{19} , $2(C_8H_{15}N_2)$, approximate dimensions 0.104 x 0.196 x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 3967 frames were collected. The total exposure time was 5.51 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 48484 reflections to a maximum θ angle of 25.62° (0.82 Å resolution), of which 2838 were independent (average redundancy 17.084, completeness = 98.2 %, $R_{int} = 4.83$ %, $R_{sig} = 1.79$ %) and 2586 (91.12 %) were greater than $2\sigma(F_2)$. The final cell constants of $a = 8.5458(16)$ Å, $b = 17.085(3)$ Å, $c = 11.075(2)$ Å, $\beta = 108.937(8)^\circ$, volume = $1529.5(5)$ Å³, are based upon the refinement of the XYZ-centroids of 61 reflections above $20\sigma(I)$ with $4.568^\circ < 2\theta < 56.01^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.894. Bond distances and angles of **3** are shown in Table S4 and Table S5.

Table 4. Bond distances (Å) in compound **3**.

Mo1	-O2	2.3206(5)	N2	-C3	1.373(4)
Mo1	-O5	1.8507(18)	N2	-C8	1.470(4)
Mo1	-O8	1.9738(17)	C2	-C3	1.343(4)
Mo1	-O9	1.6815(18)	C4	-C5	1.509(3)
Mo1	-O1_a	2.0149(18)	C5	-C6	1.532(4)
Mo1	-O6_a	1.8877(17)	C6	-C7	1.504(5)
Mo2	-O1	1.8620(18)	C1	-H1	0.9500
Mo2	-O2	2.3286(5)	C2	-H2	0.9500
Mo2	-O3	1.9229(17)	C3	-H3	0.9500
Mo2	-O5	2.0052(18)	C4	-H4A	0.9900
Mo2	-O10	1.6784(18)	C4	-H4B	0.9900
Mo2	-O4_a	1.9333(18)	C5	-H5A	0.9900
Mo3	-O2	2.3178(5)	C5	-H5B	0.9900
Mo3	-O3	1.9318(18)	C6	-H6A	0.9900
Mo3	-O4	1.9356(18)	C6	-H6B	0.9900
Mo3	-O6	1.9661(18)	C7	-H7A	0.9800
Mo3	-O7	1.6812(19)	C7	-H7B	0.9800
Mo3	-O8	1.8835(17)	C7	-H7C	0.9800

Chapter 11

N1	-C1	1.330(3)	C8	-H8A	0.9800
N1	-C2	1.373(3)	C8	-H8B	0.9800
N1	-C4	1.476(3)	C8	-H8C	0.9800
N2	-C1	1.333(3)			

Table 5. Bond angles (°) in compound **3**.

O2	-Mo1	-O5	78.25(6)	Mo2_a	-O2	-Mo3	89.94(1)
O2	-Mo1	-O8	75.66(5)	Mo3	-O2	-Mo3_a	180.00
O2	-Mo1	-O9	175.56(6)	Mo1_a	-O2	-Mo2_a	89.82(1)
O1_a	-Mo1	-O2	75.48(5)	Mo1_a	-O2	-Mo3_a	90.10(1)
O2	-Mo1	-O6_a	77.38(5)	Mo2_a	-O2	-Mo3_a	90.06(1)
O5	-Mo1	-O8	88.26(7)	Mo2	-O3	-Mo3	117.03(9)
O5	-Mo1	-O9	105.62(8)	Mo2_a	-O4	-Mo3	116.16(9)
O1_a	-Mo1	-O5	153.54(7)	Mo1	-O5	-Mo2	116.64(9)
O5	-Mo1	-O6_a	92.29(7)	Mo1_a	-O6	-Mo3	116.48(8)
O8	-Mo1	-O9	102.06(8)	Mo1	-O8	-Mo3	116.64(8)
O1_a	-Mo1	-O8	82.32(7)	C1	-N1	-C2	108.4(2)
O6_a	-Mo1	-O8	152.33(7)	C1	-N1	-C4	127.2(2)
O1_a	-Mo1	-O9	100.53(8)	C2	-N1	-C4	124.41(19)
O6_a	-Mo1	-O9	104.41(8)	C1	-N2	-C3	108.2(2)
O1_a	-Mo1	-O6_a	85.06(7)	C1	-N2	-C8	125.1(2)
O1	-Mo2	-O2	78.09(5)	C3	-N2	-C8	126.7(2)
O1	-Mo2	-O3	89.57(7)	N1	-C1	-N2	108.7(2)
O1	-Mo2	-O5	153.31(7)	N1	-C2	-C3	107.3(2)
O1	-Mo2	-O10	103.93(8)	N2	-C3	-C2	107.5(2)
O1	-Mo2	-O4_a	90.31(7)	N1	-C4	-C5	112.8(2)
O2	-Mo2	-O3	76.39(5)	C4	-C5	-C6	111.1(2)
O2	-Mo2	-O5	75.22(5)	C5	-C6	-C7	113.0(3)
O2	-Mo2	-O10	177.82(6)	N1	-C1	-H1	126.00
O2	-Mo2	-O4_a	76.60(5)	N2	-C1	-H1	126.00
O3	-Mo2	-O5	83.89(7)	N1	-C2	-H2	126.00
O3	-Mo2	-O10	104.34(8)	C3	-C2	-H2	126.00
O3	-Mo2	-O4_a	152.41(7)	N2	-C3	-H3	126.00
O5	-Mo2	-O10	102.77(8)	C2	-C3	-H3	126.00
O4_a	-Mo2	-O5	83.92(7)	N1	-C4	-H4A	109.00
O4_a	-Mo2	-O10	102.45(8)	N1	-C4	-H4B	109.00
O2	-Mo3	-O3	76.50(5)	C5	-C4	-H4A	109.00

Chapter 11

O2	-Mo3	-O4	76.83(5)	C5	-C4	-H4B	109.00
O2	-Mo3	-O6	76.01(5)	H4A	-C4	-H4B	108.00
O2	-Mo3	-O7	177.35(7)	C4	-C5	-H5A	109.00
O2	-Mo3	-O8	77.38(5)	C4	-C5	-H5B	109.00
O3	-Mo3	-O4	153.12(7)	C6	-C5	-H5A	109.00
O3	-Mo3	-O6	85.08(7)	C6	-C5	-H5B	109.00
O3	-Mo3	-O7	102.21(8)	H5A	-C5	-H5B	108.00
O3	-Mo3	-O8	88.76(7)	C5	-C6	-H6A	109.00
O4	-Mo3	-O6	85.40(7)	C5	-C6	-H6B	109.00
O4	-Mo3	-O7	104.31(8)	C7	-C6	-H6A	109.00
O4	-Mo3	-O8	88.59(7)	C7	-C6	-H6B	109.00
O6	-Mo3	-O7	101.63(8)	H6A	-C6	-H6B	108.00
O6	-Mo3	-O8	153.39(7)	C6	-C7	-H7A	109.00
O7	-Mo3	-O8	104.97(8)	C6	-C7	-H7B	109.00
Mo1_a	-O1	-Mo2	116.21(8)	C6	-C7	-H7C	109.00
Mo1	-O2	-Mo2	89.82(1)	H7A	-C7	-H7B	109.00
Mo1	-O2	-Mo3	90.10(1)	H7A	-C7	-H7C	110.00
Mo1	-O2	-Mo1_a	180.00	H7B	-C7	-H7C	109.00
Mo1	-O2	-Mo2_a	90.18(1)	N2	-C8	-H8A	109.00
Mo1	-O2	-Mo3_a	89.90(1)	N2	-C8	-H8B	110.00
Mo2	-O2	-Mo3	90.06(1)	N2	-C8	-H8C	109.00
Mo1_a	-O2	-Mo2	90.18(1)	H8A	-C8	-H8B	109.00
Mo2	-O2	-Mo2_a	180.00	H8A	-C8	-H8C	109.00
Mo2	-O2	-Mo3_a	89.94(1)	H8B	-C8	-H8C	109.00
Mo1_a	-O2	-Mo3	89.90(1)				

Bond distances and angles of 4

$C_{18}H_{34}N_4 Mo_6O_{19}$ (**4**): a clear light yellow fragment-like specimen of $2(C_9 H_{17} N_2)$, $Mo_6 O_{19}$, approximate dimensions 0.240 mm x 0.410 mm x 0.460 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 3797 frames were collected. The total exposure time was 5.28 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40353 reflections to a maximum θ angle of 25.47° (0.83 Å resolution), of which 2989 were independent (average redundancy 13.501, completeness = 99.9 %, $R_{int} = 8.15$ %, $R_{sig} = 2.24$ %) and 2902 (97.09 %) were greater than

Chapter 11

$2\sigma(F_2)$. The final cell constants of $a = 11.0074(2)$ Å, $b = 10.7827(2)$ Å, $c = 13.5900(3)$ Å, $\beta = 91.0450(10)^\circ$, volume = $1612.72(5)$ Å³, are based upon the refinement of the XYZ-centroids of 179 reflections above $20 \sigma(I)$ with $3.027^\circ < 2\theta < 65.42^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.788. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4091 and 0.5983. Bond distances and angles of **4** are shown in Table S6 and Table S7.

Table 6. Bond distances (Å) in compound **4**.

Mo1	-O5	1.967(2)	N2	-C8	1.434(6)
Mo1	-O9	1.937(3)	C1	-C9	1.451(6)
Mo1	-O10	1.681(3)	C2	-C3	1.305(6)
Mo1	-O1	1.903(2)	C4	-C5	1.527(5)
Mo1	-O2	2.3162(3)	C5	-C6	1.519(6)
Mo1	-O4	1.891(2)	C6	-C7	1.524(6)
Mo2	-O1	1.944(3)	C2	-H2	0.9500
Mo2	-O2	2.3157(3)	C3	-H3	0.9500
Mo2	-O6	1.898(2)	C4	-H4A	0.9900
Mo2	-O9_a	1.906(3)	C4	-H4B	0.9900
Mo2	-O8	1.678(3)	C5	-H5A	0.9900
Mo2	-O7_a	1.969(2)	C5	-H5B	0.9900
Mo3	-O2	2.3243(3)	C6	-H6A	0.9900
Mo3	-O3	1.686(2)	C6	-H6B	0.9900
Mo3	-O4	1.971(2)	C7	-H7A	0.9800
Mo3	-O6	1.971(2)	C7	-H7B	0.9800
Mo3	-O5_a	1.888(2)	C7	-H7C	0.9800
Mo3	-O7	1.874(2)	C8	-H8C	0.9800
N1	-C2	1.425(6)	C8	-H8A	0.9800
N1	-C1	1.327(5)	C8	-H8B	0.9800
N1	-C4	1.476(6)	C9	-H9A	0.9800
N2	-C3	1.421(6)	C9	-H9B	0.9800
N2	-C1	1.308(6)	C9	-H9C	0.9800

Chapter 11

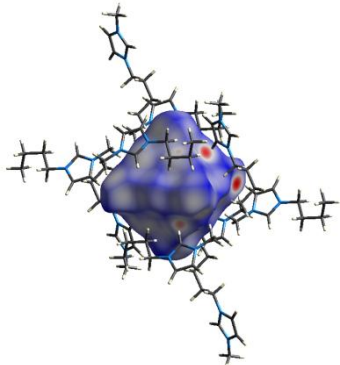
Table 7. Bond angles (°) in compound **4**.

O5	-Mo1	-O9	84.56(11)	Mo2_a	-O2	-Mo3	89.98(1)
O5	-Mo1	-O10	101.76(13)	Mo3	-O2	-Mo3_a	180.00
O9	-Mo1	-O10	102.61(13)	Mo1_a	-O2	-Mo3	89.94(1)
O2	-Mo1	-O4	77.59(7)	Mo1_a	-O2	-Mo3_a	90.06(1)
O2	-Mo1	-O5	76.03(7)	Mo1_a	-O2	-Mo2_a	89.84(1)
O1	-Mo1	-O2	77.13(7)	Mo1	-O4	-Mo3	116.40(12)
O1	-Mo1	-O4	89.00(10)	Mo1	-O5	-Mo3_a	116.59(12)
O1	-Mo1	-O5	86.48(10)	Mo2	-O6	-Mo3	116.01(11)
O1	-Mo1	-O9	153.05(10)	Mo2_a	-O7	-Mo3	117.15(12)
O1	-Mo1	-O10	104.09(13)	Mo1	-O9	-Mo2_a	117.18(13)
O2	-Mo1	-O10	177.46(11)	C1	-N1	-C4	127.4(4)
O4	-Mo1	-O5	153.59(10)	C1	-N1	-C2	107.7(4)
O2	-Mo1	-O9	76.05(7)	C2	-N1	-C4	124.5(3)
O4	-Mo1	-O10	104.59(13)	C1	-N2	-C3	107.9(3)
O4	-Mo1	-O9	87.84(11)	C1	-N2	-C8	131.4(4)
O1	-Mo2	-O6	87.73(10)	C3	-N2	-C8	120.5(4)
O1	-Mo2	-O2	76.39(7)	N2	-C1	-C9	124.7(4)
O7_a	-Mo2	-O9_a	85.71(11)	N1	-C1	-C9	125.5(4)
O2	-Mo2	-O7_a	75.67(7)	N1	-C1	-N2	109.7(4)
O2	-Mo2	-O9_a	76.62(8)	N1	-C2	-C3	106.9(4)
O1	-Mo2	-O8	104.08(12)	N2	-C3	-C2	107.8(4)
O1	-Mo2	-O7_a	84.68(10)	N1	-C4	-C5	109.3(3)
O1	-Mo2	-O9_a	152.83(10)	C4	-C5	-C6	111.5(3)
O2	-Mo2	-O6	77.70(7)	C5	-C6	-C7	111.5(3)
O2	-Mo2	-O8	178.73(10)	C3	-C2	-H2	126.00
O6	-Mo2	-O7_a	153.33(10)	N1	-C2	-H2	127.00
O6	-Mo2	-O9_a	89.57(11)	N2	-C3	-H3	126.00
O6	-Mo2	-O8	103.48(12)	C2	-C3	-H3	126.00
O8	-Mo2	-O9_a	102.84(12)	N1	-C4	-H4A	110.00
O7_a	-Mo2	-O8	103.17(12)	N1	-C4	-H4B	110.00
O2	-Mo3	-O4	75.92(6)	H4A	-C4	-H4B	108.00
O2	-Mo3	-O3	177.79(8)	C5	-C4	-H4B	110.00
O5_a	-Mo3	-O7	90.38(11)	C5	-C4	-H4A	110.00
O3	-Mo3	-O6	102.12(10)	C6	-C5	-H5A	109.00

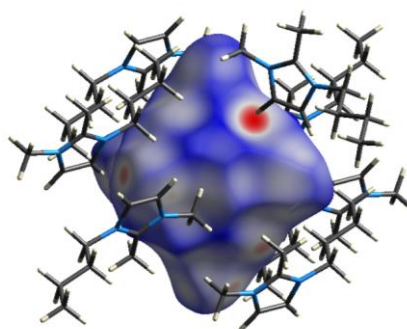
Chapter 11

O3	-Mo3	-O7	104.46(11)	C4	-C5	-H5B	109.00
O3	-Mo3	-O5_a	104.08(11)	C4	-C5	-H5A	109.00
O2	-Mo3	-O6	76.15(6)	C6	-C5	-H5B	109.00
O2	-Mo3	-O7	77.19(7)	H5A	-C5	-H5B	108.00
O2	-Mo3	-O5_a	77.29(7)	C5	-C6	-H6A	109.00
O3	-Mo3	-O4	102.59(11)	H6A	-C6	-H6B	108.00
O5_a	-Mo3	-O6	86.79(10)	C5	-C6	-H6B	109.00
O4	-Mo3	-O7	87.25(10)	C7	-C6	-H6A	109.00
O4	-Mo3	-O5_a	152.96(9)	C7	-C6	-H6B	109.00
O4	-Mo3	-O6	83.35(10)	C6	-C7	-H7A	109.00
O6	-Mo3	-O7	153.15(9)	C6	-C7	-H7B	110.00
Mo1	-O1	-Mo2	116.44(11)	C6	-C7	-H7C	110.00
Mo1	-O2	-Mo3	90.06(1)	H7B	-C7	-H7C	109.00
Mo1	-O2	-Mo2	89.84(1)	H7A	-C7	-H7B	109.00
Mo2_a	-O2	-Mo3_a	90.03(1)	H7A	-C7	-H7C	109.00
Mo2	-O2	-Mo2_a	180.00	N2	-C8	-H8B	109.00
Mo2	-O2	-Mo3_a	89.98(1)	H8A	-C8	-H8C	109.00
Mo1	-O2	-Mo1_a	180.00	N2	-C8	-H8C	110.00
Mo1	-O2	-Mo2_a	90.16(1)	H8A	-C8	-H8B	109.00
Mo1	-O2	-Mo3_a	89.94(1)	N2	-C8	-H8A	109.00
Mo2	-O2	-Mo3	90.03(1)	H8B	-C8	-H8C	110.00
Mo1_a	-O2	-Mo2	90.16(1)	C1	-C9	-H9C	109.00
H9A	-C9	-H9C	109.00	C1	-C9	-H9A	109.00
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H9A	-C9	-H9B	110.00				

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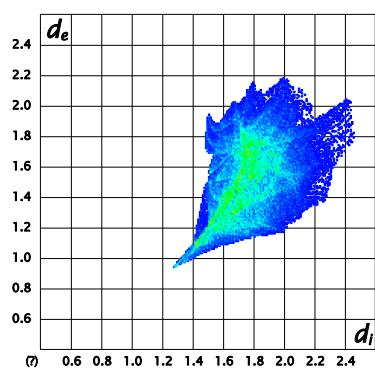
[Bmim]₂[Mo₆O₁₉] (3) d_{norm} :

Min	-0.2863
Max	10.435
Mean	0.3811
Mean+	0.3951
Mean-	-0.0860

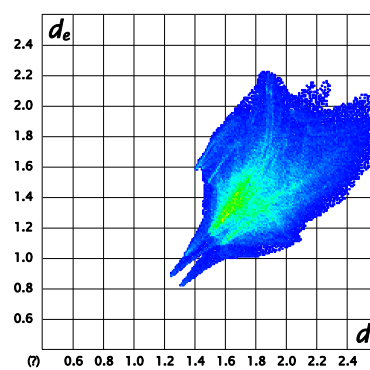
Dmbim]₂[Mo₆O₁₉] (4) d_{norm} :

Min	-0.3784
Max	11.577
Mean	0.4164
Mean+	0.4333
Mean-	-0.1021

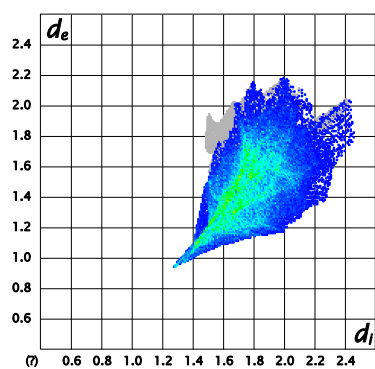
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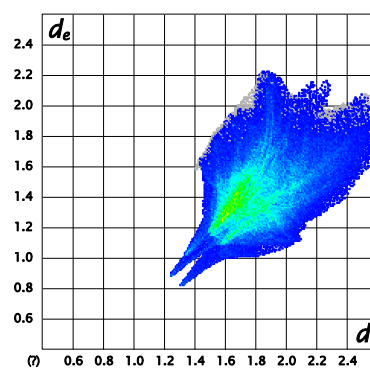
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Chapter 12

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Scientific contributions

List of Publications

- [1] **B. Zhang**, M. D. Zhou, M. Cokoja, J. Mink, S. L. Zang, F. E. Kühn, "Oxidation of sulfides to sulfoxides mediated by ionic liquids", *RSC advances* **2012**, 2, 8416-8420.
- [2] **B. Zhang**, S. Li, S. Yue, M. Cokoja, M.-D. Zhou, S. L. Zang, F. E. Kühn, "Imidazolium perrhenate ionic liquids as efficient catalysts for the selective oxidation of sulfides to sulfones", *J. Organomet. Chem.* **2013**, 744, 108-112.
- [3] **B. Zhang**, S. Li, E. Herdtweck, F. E. Kühn, "Schiff base complexes of methyltrioxorhenium (VII): synthesis and catalytic application", *J. Organomet. Chem.* **2013**, 739, 63-68.
- [4] I. I. E. Markovits, W. A. Eger, S. Yue, M. Cokoja, C. J. Münchmeyer, **B. Zhang**, M. D. Zhou, A. Genest, J. Mink, S. L. Zang, N. Rösch, F. E. Kühn, "Activation of hydrogen peroxide by ionic liquids: mechanistic studies and application in the epoxidation of olefins", *Chem. Eur. J.* **2013**, 19, 5972-5979.
- [5] S. Li, **B. Zhang**, F. E. Kühn, "Benzimidazolic complexes of methyltrioxorhenium (VII): Synthesis and application in catalytic olefin epoxidation", *J. Organomet. Chem.* **2013**, 730, 132-136.
- [6] **B. Zhang**, M. Köberl, A. Pöthig, M. Cokoja, W. A. Herrmann, F. E. Kühn, "Synthesis and characterization of imidazolium salts with the weakly coordinating $[B(C_6F_5)_4]^-$ anion", *Z. Naturforsch., B: J. Chem. Sci.* **2012**, 67(10), 1030-1036.
- [7] **B. Zhang**, S. Li, A. Pöthig, M. Cokoja, S. L. Zang, W. A. Herrmann, F. E. Kühn, "Oxidation reactions catalyzed by polyoxomolybdate salts", *Z. Naturforsch., B: J. Chem. Sci.* **2013**, 68 (5/6), 587-597.
- [8] S. Yue, D. Fang, J. Li, S.-L. Zang, M.-D. Zhou, **B. Zhang**, I. I. E. Markovits, M. Cokoja, F. E. Kühn, "Synthesis and characterization of Imidazolium perrhenate ionic liquids", *Z. Naturforsch., B: J. Chem. Sci.* **2013**, 68 (5/6), 598-604.
- [9] **Bo Zhang**, Su Li, Mirza Cokoja, Eberhardt Herdtweck, János Mink, Shu-Liang Zang and Fritz E. Kühn, "Ionic liquids with the weakly coordinating anions: synthesis, properties

and application”, in preparation.

[10] Su Li, **Bo Zhang**, Mirza Cokoja, Eberhardt Herdtweck, Alexander Pöthig, János Mink and Fritz E. Kühn, “New (σ -Aryl) trioxorhenium (VII) Complexes: Synthesis, Structure Characterization, Properties and Application”, in preparation.

Oral presentation

Ionic liquids with the weakly coordinating anions: synthesis, properties and application

Bo Zhang, Su Li, Mirza Cokoja, Eberhardt Herdtweck, János Mink, Shu-Liang Zang and Fritz E. Kühn

The 16th National Conference on Catalysis of China, 15-19 October 2012, Shenyang, China.

Poster

Oxidation of sulfides to sulfoxides mediated by ionic liquids

Bo. Zhang, Ming-Dong Zhou, Mirza. Cokoja, János Mink, Shu-Liang Zang and Fritz E. Kühn

The 15th International Congress on Catalysis (ICC), 01-06 July 2012, Munich, Germany.

Oxidation reactions catalyzed by polyoxomolybdate salts

Bo Zhang, Su Li, Alexander Pöthig, Mirza Cokoja, Shu-Liang Zang and Fritz E. Kühn

The 16th National Conference on Catalysis of China, 15-19 October 2012, Shenyang, China.

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