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Catalysis with non-precious metals in biphasic systems

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unter der Leitung von

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Table of contents

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Abstract

This work is dedicated to the immobilization of a well-defined iron-based catalyst for the reduction of aldehydes to primary alcohols in ionic liquids.

The immobilized catalyst was successfully employed in liquid-liquid biphasic catalysis, using the reduction of 4-fluorobenzaldehyde as test reaction. By applying the adjustable nature of ionic liquids and their tunable properties, the reaction parameters could be optimized. The reactivity and the phase behavior of the system could be improved by screening of different ionic liquids.

The benefit of liquid-liquid biphasic catalysis was demonstrated in the field of product and catalyst separation. Besides determination of reaction kinetics, recycling of the catalyst was investigated.

The potency of this system was finally explored by studying its scope and limitations for a number of aliphatic and aromatic substrates.

Kurzfassung

Diese Arbeit beschäftigt sich mit der Immobilisierung eines Eisenkatalysators zur katalytischen Reduktion von Aldehyden zu primären Alkoholen in ionischen Flüssigkeiten.

Der immobilisierte Katalysator wurde erfolgreich in der flüssig-flüssig Zweiphasenkatalyse zur Reduktion von 4-Fluorbenzaldehyd eingesetzt. Die Optimierung der Reaktionsparameter konnte durch den Einsatz verschiedener ionischen Flüssigkeiten mit unterschiedlichen Eigenschaften erzielt werden. Sowohl die Reaktivität, als auch das Phasenverhalten konnten verbessert werden.

Die Vorzüge der flüssig-flüssig Zweiphasenkatalyse wurden bei der Trennung von Produkt und Katalysator demonstriert. Neben der Reaktionskinetik wurde auch die Wiederverwertung des Katalysators untersucht.

Abschließend wurde die breite Einsetzbarkeit dieses Systems für verschiedene aliphatische und aromatische Substrate untersucht.

1 Introduction

Catalysis can be considered as the acceleration of a reaction with the help of a catalyst. A catalyst is a substance or a material that increases the reaction rate by lowering the activation energy of the reaction. This is in principle achieved by providing an alternative pathway for the transformation (Figure 1).[1]

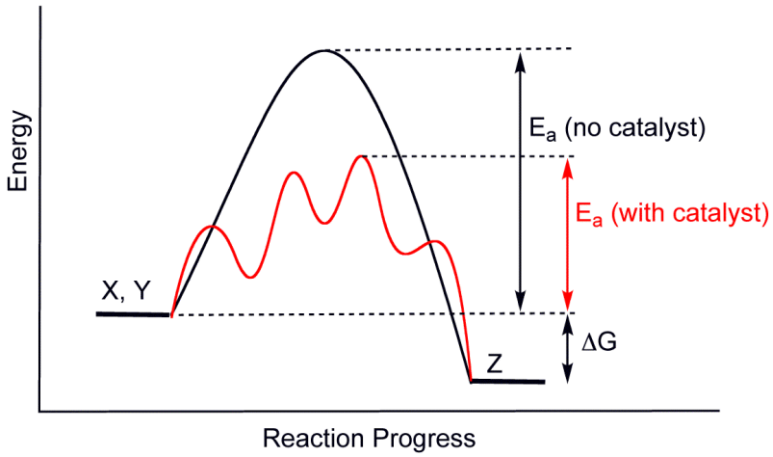


Figure 1. General reaction scheme of a catalyzed reaction[2]

Catalyzed reactions are of great importance in laboratory chemistry as well as in industrial scale. About 90% of all industrialized processes contain at least one catalyzed step.[3] Especially in the production of industrial chemicals and petroleum refinery, catalysis is run in industrial scale. In 1991, chemicals and fuel derived from catalyzed processes exceeded values of 900 billion $ per year.[4]

Catalysis can be classified in two different types: homogeneous and heterogeneous catalysis. In case of homogeneous catalysis, the catalyst is dissolved in the same phase as the substrate. Transition metal catalysts are widely used in the field of homogeneous catalysis, demonstrating high reactivity in a broad variety of transformations.

Besides the reactivity of metal based catalysts in homogeneous systems, several advantages are connected to well-defined metal catalysts. Due to the interaction of the metal center and the ligand system, important properties, such as stability and selectivity of the catalyst can be tuned.[5] Table 1 summarizes the properties of homogeneous systems and opposes them to the attributes of heterogeneous catalysis.

Table 1. Properties of homogeneous and heterogeneous catalysis[6]

	Homogeneous catalysis	***Heterogeneous catalysis***
Activity	high	variable
Selectivity	high	variable
Reaction conditions	mild	harsh
Service life of catalysts	variable	extended
Sensitivity against catalyst poisons	low	high
Diffusion/mass transfer problems	low	important
Catalyst recycling	expensive	not necessary
Variability of electric and steric properties	possible	not possible
Mechanistic understanding	plausible under random conditions	extremely complex

Several types of reactions can be carried with the help of transition metals in homogeneous systems. Table 2 represents a selection of examples employed in industrial processes.

Table 2. Examples of the usage of homogeneous catalysis on industrial scale[7]

Process/Reaction	***Product (Company)***	***Catalyst***	***Production (2009) [1 000 t/a]***
Hydroformylation	e.g. *n*-butyraldehyde,… (e.g. Union Carbide, BASF, Shell,…)	$HRh(CO)_n(PR_3)_n$ $HCo(CO)_n(PR_3)_n$	3 700 2 500
Hydrocyanation	e.g. adiponitrile (DuPont)	$Ni[(P(OR)_3]_4$	~1 000
Acetic acid production	Acetic acid (Eastman Kodak)	$HRhI_2(CO)_2/HI/CH_3I$	1200
Imine-Reduction	Metolachor (Novartis)	[Ir(ferrocenyldiphosphine)]I/ H_2SO_4	10
Isomerization	Citronellal (Takasago)	$[Rh(binap)(COD)]BF_4$	1.5
Sharpless epoxidation	Glycidol (ARCO,SIPSY)	$Ti(^iOPr)_4$/diethyl tartrate	Several tons

However, disadvantages are also connected with homogeneous catalysis. Separation of the catalyst from the reaction mixture and therefore efficient recycling of the catalyst is still challenging. Furthermore, the efficient removal of the catalyst in case of fine chemicals and pharmaceutical products has to be performed, in order to receive pure products without any metal or ligand contaminations.

The second type of catalysis is heterogeneous catalysis. Within this type, the catalyst and the substrate are not dissolved in the same phase. This allows the usage of solid materials, such as metal surfaces, metal oxides or zeolites. The advantage of a heterogeneous system is the easy separation of the catalyst from the product. Therefore processes in continuous flow can be established in which the recycling of the catalyst is not necessary.[6]

Table 3. Examples of the usage of heterogeneous catalysis on industrial scale

Process	***Product***	***Catalyst***	***Production [million t/a]***
Haber-Bosch process	Ammonia	Fe	140 (2013)[8]
Steam reforming	Syngas	Ni/K_2O	500 billion m^3 (1998)[9]
Epoxidation	Ethylene oxide	Ag on Al_2O_3	24 (2009)[10]
Nitric acid production	Nitric acid	Pt	55 (2016)[11]
Fluid catalytic cracking	Ethylene, Propylene	zeolithes	175 (2006)[12]

Besides the advantages, several drawbacks are connected with heterogeneous catalysis. The reaction conditions for this type of catalysis are harsh, compared to the mild parameters of homogeneous catalysis. Mass transport limitation may arise, since the catalyst is not dissolved in the same media as the substrate. Furthermore, heterogeneous catalysts are often sensitive to catalyst poisoning, for example with sulfur or phosphorous traces.

As a consequence, a combination of homogeneous and heterogeneous catalysis, comprising all advantages and eliminating the drawbacks would be desirable for the future.[6]

1.1 Liquid-liquid biphasic catalysis

As described above, homogeneous catalysis is of great importance for the synthesis and manufacturing of bulk and fine chemicals. Nevertheless, recycling of the catalyst is very hard to achieve in homogeneous systems, since product and catalyst are dissolved in the same media. For industrial applications, recovery of the often precious metal and the ligand system (which itself may be very expensive as well) is vital in order to ensure the economic success of the process.[6]

Over the last decades, several multi-phase systems for the efficient separation and recovery of catalysts have been explored. Liquid-liquid biphasic systems seem to be very suitable for these aims, combining the advantages of homogeneous and heterogeneous catalysis.[13]

For this approach, the substrate and the product exist as the organic phase, either in pure form or dissolved in a conventional organic solvent. The catalyst is dissolved in a second, immiscible phase such as water, fluorous solvents or ionic liquids, resulting in a biphasic system. The reaction is carried out under intensive stirring in order to guarantee an efficient interaction of the catalyst and the product. Once the reaction has reached the desired conversion, phase separation can be done by simple decanting.[14] Table 4 represents examples of liquid-liquid biphasic systems and applications in catalysis.

Table 4. Typical examples of liquid-liquid biphasic systems and their application in catalysis

Catalyst containing phase	***Product containing phase***	***Example of application***
Organic solvent	Product (without solvent)	Shell higher olefin process[15]
Water	Organic solvent	Hydroformylation[16]
Fluorous solvent	Organic solvent	Epoxidation[17]
Ionic liquid	Organic solvent	Heck reaction[18]
Ionic liquid	Supercritical CO_2	Hydroformylation[19]

An early industrially applied biphasic system is shown in the Shell higher olefin process (SHOP), which was established in the 1960s. In this process, oligomerization of ethylene to α-olefins under the usage of a Nickel based catalyst is realized (Figure 2).

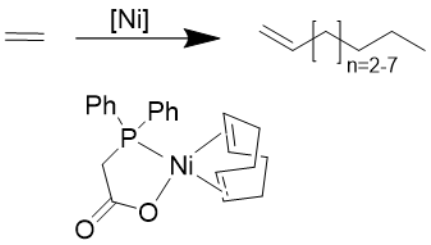


Figure 2. Scheme of Shell higher olefin process

During the development of the process, the problem of recovering the homogeneous catalyst was investigated. This problem was solved by using acetonitrile as solvent instead of toluene, resulting in a biphasic system after the reaction due to its immiscibility with the product fraction. Therefore simple separation of catalyst and product could be achieved.

Further investigation and optimization of the system resulted in a substitution of acetonitrile with 1,4-butanediol (Figure 3).[13,15]

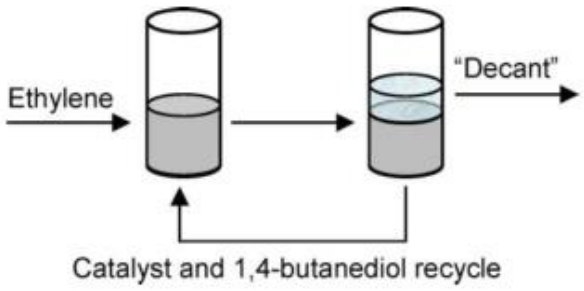


Figure 3. Scheme of Shell higher-olefin process[13]

Although the biphasic system in this process is only built up during the reaction, it demonstrates the idea of biphasic catalysis and is the first known "biphasic catalysis" on industrial scale.[13-19]

1.1.1 Organic-aqueous systems

Several solvent systems can be used in liquid-liquid biphasic catalysis. One option would be water. Choosing water as catalyst carrying phase has several advantages. Water is abundant, non-toxic and also inexpensive. Furthermore, water is immiscible with many organic solvents, forming a broad variety of different biphasic systems.

Besides these advantages, there are several drawbacks connected to aqueous systems. The solubility of many transition metal catalysts is low in water, moreover, many transition metal catalysts show limited stability in water. In order to increase the solubility of complexes, ligand modification has to be done.[20]

One possibility to decrease the hydrophobicity of complexes is the introduction of ion-tagged ligands. In the field of homogeneous catalysis, phosphine ligands are frequently used to increase reactivity and stability of the catalyst, whereas triphenylphosphine (TPP) plays a major role in industrialized processes. By introducing one or more ionic groups on the phenyl-rings of TPP, the solubility in water can be increased for the corresponding complexes. A variety of ion-tagged phosphine ligands can be seen in Figure 4.

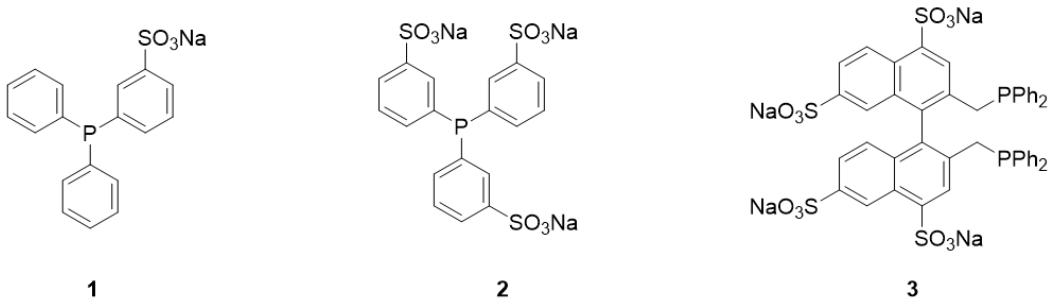


Figure 4. Selection of water soluble ligands[21]

These ligands have a remarkably high water solubility up to 1.1 kg per liter water (ligand **2**, TPPTS), which makes them suitable for industrial processes, for example in biphasic hydroformylations.[21]

The first liquid-liquid biphasic hydroformylation was established by Ruhrchemie/Rhone-Poulenc. In this process terminal, alkenes are converted to linear and branched aldehydes, using carbon monoxide and hydrogen as reagents and a catalyst. The desired products are in principle the linear aldehydes, therefore the selectivity of the catalyst toward the linear product is of importance. Figure 5 demonstrates the rhodium-catalyzed hydroformylation reaction of alkenes.

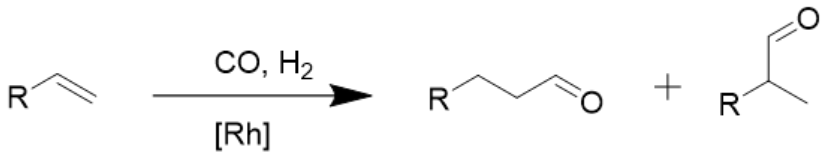


Figure 5. Scheme of hydroformylation

The use of water soluble TPP based ligands in combination with rhodium as coordination center resulted in high selectivity towards the linear product and also showed high reactivity. Propene is the most used alkene for hydroformylation, giving *n*-butyraldehyde and *i*-butyraldehyde as products. Figure 6 demonstrates the biphasic Rhone-Poulenc process.

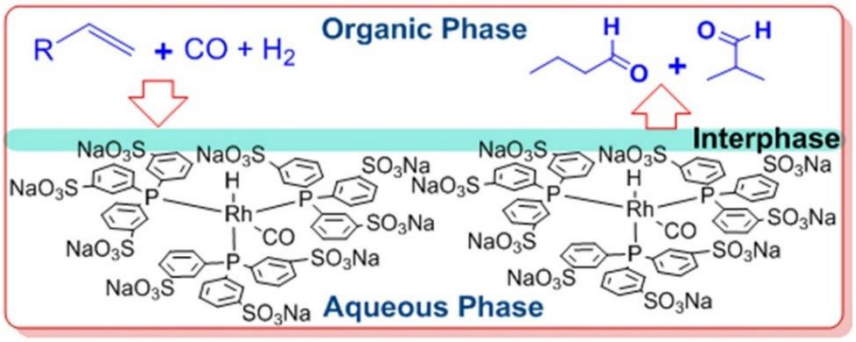


Figure 6. Scheme of Rhone-Poulenc process[22]

There are several advantages of using water-soluble catalysts in hydroformylation reactions. The most obvious one is the recycling of rhodium. Rhodium shows high reactivity and selectivity in this reaction, but it is also one of the most expensive precious metals. In order to keep the process economically successful, an efficient separation and recycling of the catalyst is essential. By having the catalyst dissolved in the aqueous phase, product-separation can be done by simple decanting as it forms a second phase. Therefore recovery of the catalyst can be easily achieved.[16]

Besides all advantages of water as catalyst carrying phase, aqueous systems have drawbacks. One issue is the fact that some organic reagents react with water and hydrolyze. Besides that, not all transition metal catalysts are stable in water, leading to an incompatibility of water and reagents and/or catalysts. Another point is the low solubility of several organic compounds in water. In this case, the reaction only takes place at the interface of the aqueous and the organic phase, which lowers the reactivity of the system.[6]

1.1.2 Fluorous solvents in liquid-liquid biphasic catalysis

Perfluorinated fluids, for instance perfluorinated alkenes or ethers, have unique solvent-properties. Due to the high amount of fluorine atoms in these molecules, they are immiscible with hydrocarbons, but also with water. Therefore perfluorinated substances are usually only miscible with other perfluorinated compounds and show good separation from other solvents. Besides that, fluorous solvents are extremely inert, thermally stable and non-toxic.[23]

The combination of these attributes makes fluorous solvents interesting as reaction media and for separation techniques. One approach is liquid-liquid biphasic catalysis. The concept is quite similar to aqueous/organic solvent systems. The difference is that the ligand has to be modified in a way that it becomes soluble in the hydrophobic and lipophilic fluorous phase. For this purpose, long perfluorinated alkyl chains are often attached to the ligand system.

The reaction itself can be carried out in different ways. One possibility is to start with a biphasic system, where the catalyst is dissolved in the fluorous phase and the starting material is dissolved in the organic phase. After raising the temperature, the two former immiscible phases combine to a homogenous system, resulting in high reactivity. After cooling, the biphasic system is reestablished. This concept and phase behavior is also known as thermomorphic catalysis. The catalyst is dissolved in the fluorous phase while the organic phase contains the product.

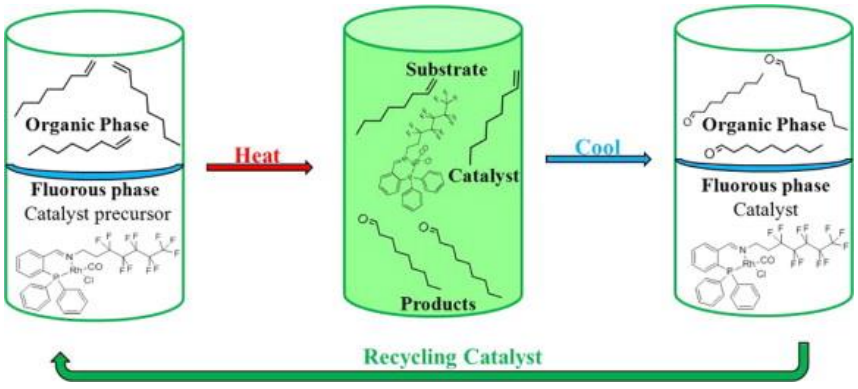


Figure 7. Thermomorphic hydroformylation using fluorous solvent[24]

A second possibility would be to perform the reaction in a biphasic way. This is the case, if the phase transition temperature is too high for the fluorous solvent/organic solvent system.[17]

Several reactions can be performed with fluorous solvents in a biphasic mode. For instance hydroformylation was successfully carried out with fluorous phases. For this purpose, a fluorous-tagged bidentate *P,N*-ligand was used in combination with rhodium (I) (Figure 7). Due to the switch in phase behavior of the system, the low solubility of the alkene in the catalyst carrying phase, which is an issue for the Rhone-Poulenc process, is avoided.[24]

Apart from hydroformylation, epoxidation in biphasic systems, using fluorinated porphyrin systems in combination with cobalt[25] and manganese[26] or cross coupling reactions, for example Negishi type reactions, can be done under the usage of fluorous phases.[27]

1.1.3 Liquid-liquid biphasic catalysis with ionic liquids

Ionic liquids (i.e. salts melting below 100 °C) as reaction media have been studied intensively over the last decades. The possibility of varying the properties of this class of compounds, such as melting point, viscosity and miscibility with various solvents, makes them an interesting alternative to conventional solvents, especially in the field of catalysis.[28] Many different types of reactions, such as catalytic oxidations, acid-base catalyzed reactions and cross coupling reactions have been performed in ionic liquids in the past.[29]

Several advantages are observed when using ionic liquids as reaction media for catalysis:

- No modification of the catalyst is necessary, therefore the efficiency of the catalyst is not changed.
- The careful selection of counterions in the ionic liquid can contribute to the reactivity of the catalyst.
- A large number of different and tunable ionic liquids can be used to fine-tune the activity of the system (nature of cation and anion, alkyl chain length, functional groups,…).
- Compatibility of reagents and catalyst with ionic liquids can be obtained even for water sensitive catalyst systems.
- The ionic liquid may even improve the stability of the catalyst, compared to homogeneous systems.[30]

The fact that the miscibility with other solvents can be modified, makes ionic liquids particularly interesting for biphasic catalysis.

One of the first biphasic, ionic liquid-based systems was reported by Chauvin and coworkers in 1996.[31] In this work, the authors describe a biphasic rhodium catalyzed hydroformylation process with different ionic liquids and phosphine ligands (Figure 8).

The combination of cation, anion and phosphine ligand had a considerable impact on the reactivity of the system. For the hydroformylation of light olefins, 3-butyl-1-methyl-imidazolium hexafluorophosphate ([bmim][PF_6]) has been used in combination with triphenylphosphine or TPPTS as ligand for rhodium. In case of TPP, loss of catalyst could be detected, whereas the catalyst remained in the ionic liquid when employing TPPTS as ligand.[32]

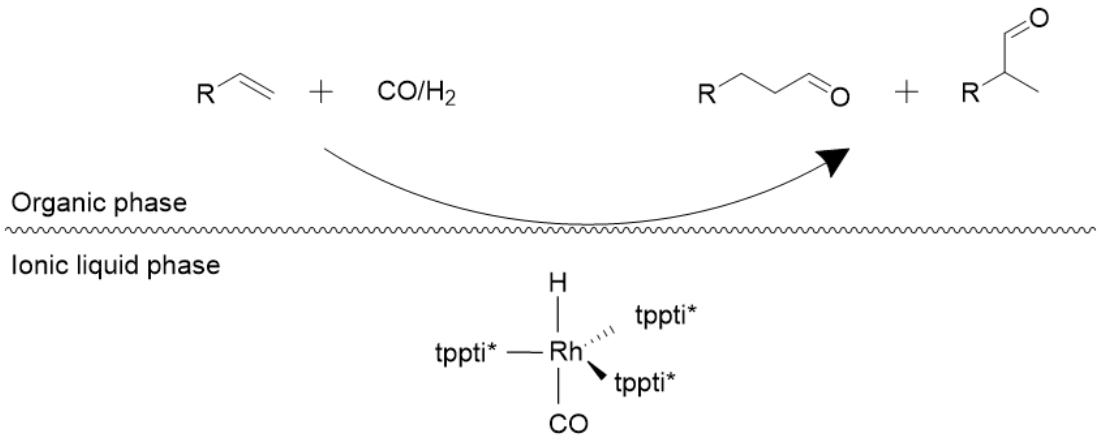


Figure 8. Biphasic hydroformylation using ionic liquids

Another example for the immobilization of a transition metal catalyst is the Heck reaction as reported by Seddon and coworkers. Within this work, the authors describe the coupling of an α,β-unsaturated ester with benzoic acid anhydride or iodobenzene. As solvent they have chosen pyridinium and imidazolium based ionic liquids. These ionic liquids form a biphasic system with the starting material and the resulting product. For work up, the product was extracted with *n*-hexane from the ionic liquid in order to increase the yield.

After screening of different combinations of ionic liquids, ligands and bases, the researchers managed to achieve yields up to 99% after one hour of reaction time with the usage of 2 mol% $Pd(OAc)_2$, triphenylphospine as ligand and [bmim][PF_6] as ionic liquid.

Under these conditions, the reaction can be operated in a triphasic system. The idea of the ternary system was to have the palladium catalyst in the ionic liquid layer, the starting material and the product form the organic layer and the salts, which are the side products of this reaction, are dissolved in the aqueous phase. Figure 9 demonstrates the phase behavior of ionic liquid (lower layer), water (middle layer) and cyclohexane (top layer).

Having established this procedure, the reuse of the catalyst and its simple separation from the product was demonstrated in this work. In total, six reaction cycles with the same catalyst/ionic liquid system could be achieved, giving yields between 95% and 99% for each cycle, proving that the catalyst activity is retained.[18]

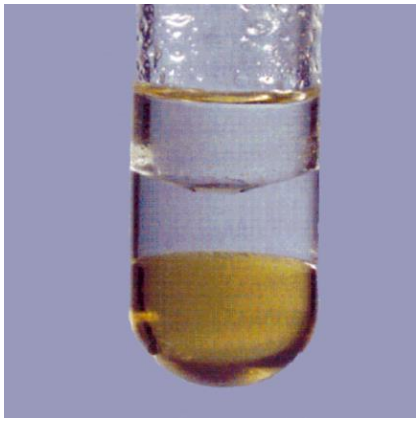


Figure 9. Ternary system employed in the Heck reaction using ionic liquid as catalyst containing phase[18]

An industrially applied biphasic process using ionic liquids is the dimerization of alkenes, such as propene (Dimersol-G) and butenes (Dimersol-X) to higher and branched alkenes. Within the conventional process, homogeneous catalysis is used and a cationic nickel species of the general form $[LNiCH_2R'][AlCl_4]$ ($L=PR_3$) is employed as catalyst. This process is often performed without solvents, although the catalyst shows higher activity in aromatic and halogenated hydrocarbons and problems with separation exist.[33]

Since the Lewis acidity of the active species is of importance for this reaction, the usage of chlorolaluminate containing ionic liquids as solvent was investigated by the Institut Français du Pétrole Énergies nouvelles (IFPEN).

Within this modified process, 1,3-dialkylimidazolium chlorides are combined with $AlCl_3$, Et_2AlCl and a Ni(II) salt. These compounds form a Lewis acidic ionic liquid, which contains an anionic Ni(II)-compound. This Lewis acidic ionic liquid is the catalytically active species for the dimerization process. The process, using this system is called Difasol process.[34,35]

In comparison to the homogeneous process, no addition of ligands is needed. Besides that, the substrates, such as butenes are soluble in the metal containing ionic liquid, but the desired products are not. These properties made it possible to perform the reaction in a liquid-liquid biphasic reactor. A liquid-liquid separator is used to separate the product from the catalyst once the mixture leaves the reactor. The product fraction is then further purified *via* washing and distillation steps, whereas the catalyst is retrieved in the reactor. A simplified process scheme is shown in Figure 10.

Due to this separation technique, the loss of nickel and aluminum could be decreased. Additionally, the reactivity of the catalyst is increased, which makes the process more efficient compared to the conventional Dimersol process. Figure 10 demonstrates the difference between the Dimersol and the Difasol process. In case of the conventional process, four reactors of 120 m^3 each are used. In case of the Difasol process, only one reactor of 50 m^3 is used, giving higher yields of dimers and showing only one tenth of the nickel consumption during the process. A Difasol reactor can be incorporated in a preexisting Dimersol process, which increases the efficiency of the whole process.[35]

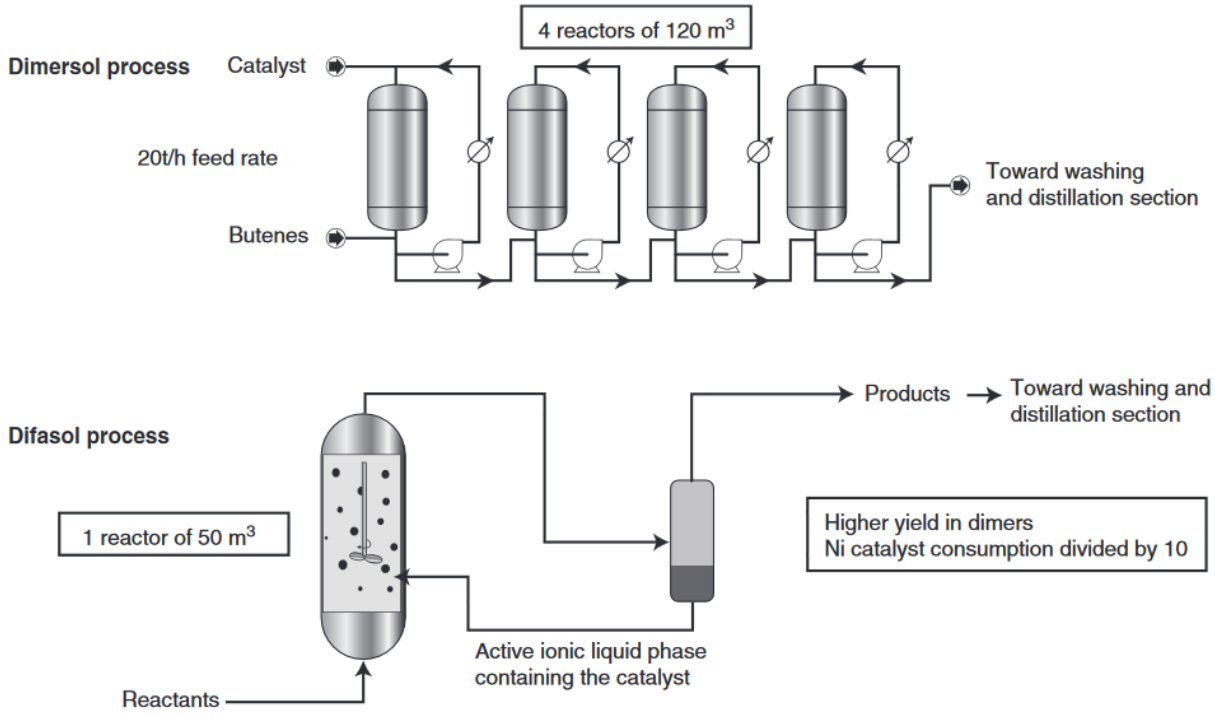


Figure 10. Scheme of the Dimersol and Difasol process[35]

1.1.4 Supported ionic liquid phases (SILPs)

Besides all mentioned advantages, there are some drawbacks connected to liquid-liquid biphasic catalysis using ionic liquids. One issue is the high viscosity of ionic liquids, which may lead to mass transfer limitations. This can be reduced by a high stirring rate. Nevertheless, the interface of catalyst carrying phase and substrate/product containing phase is lower than in heterogeneous systems.

One technique to increase the interface of the ionic liquid and the second, immiscible phase is the so called supported ionic liquid phase (SILP) approach. Within this concept, a solid support material is impregnated with a thin film of ionic liquid. The ionic liquid contains the catalyst or is catalytically active itself (Figure 11).[36] Due to the thin film of ionic liquid, mass transfer limitations are lowered.

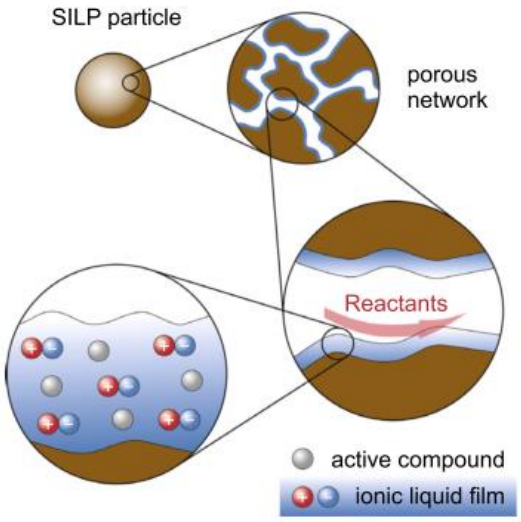


Figure 11. Scheme of a supported ionic liquid phase[37]

However, thanks to the high tunability of ionic liquids, SILPs with catalytically active ionic liquids can be prepared. Brønsted acidic supported ionic liquid phases are known to act as catalysts, for instance in the dehydration of glycerol to acrolein, using silica as support material.[38] Employing Lewis acidic SILPs, Friedel-Crafts type alkylation of aromatic compounds, such as monoalkylated benzenes or naphthalene with dodecene as alkylation agent, can be achieved.[39] Ionic liquids can as well act as organocatalysts. For instance, the reaction of carbon dioxide with epoxides which forms cyclic carbonates, can be catalyzed by halide containing ionic liquids.[40]

If the ionic liquid itself is catalytically inactive, it can be used as media for dissolving and therefore immobilizing an external catalyst. For this purpose, transition metal catalysts, such as rhodium based compounds for hydroformylation reactions can be dissolved in ionic liquid, forming a catalytically active SILP.[36] Besides the use of well-defined catalysts, nanoparticles can also be used as active species within supported ionic liquid phases. For instance Rh(0) nanoparticles can be immobilized with the SILP concept and used for hydrogenation of alkenes with hydrogen gas.[41]

The SILP approach is even run on industrial scale for hydroformylation by Evonik. Within this process, a rhodium based catalyst was successfully immobilized on an oxidic support material using an ionic liquid. The best combination of ligand and ionic liquid was found by using an anthracenetriol derived ligand and an ionic liquid consisting of an imidazolium based cation and an anion containing a diamino motive.

Using this system, it was possible to perform a hydroformylation process of a C_4 fraction in a pilot plant with a fixed bed reactor. Within this process, the long term stability of the established SILP system could be explored, showing a stability of more than 2 000 operating hours, which makes this system interesting for industrial applications. Figure 12 demonstrates the stability of conversion (left axis) and selectivity (right axis) towards the desired product (*n*-pentanal) over operating time.[42]

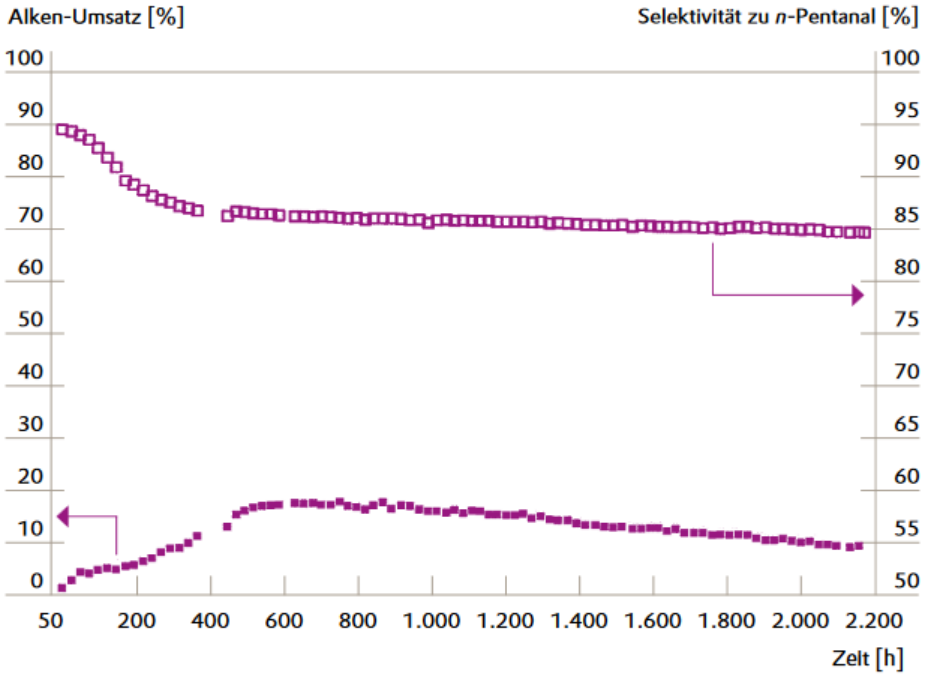


Figure 12. Long term stability of the hydroformylation process with SILP catalysts in the pilot plant by Evonik[42]

1.2 Hydrogenations in ionic liquids

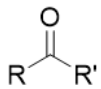
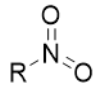
The research field of catalytic reductions in ionic liquids was opened by Chauvin[31] and Dupont independently in 1996.[43] In their publication, Dupont and coworkers describe the catalytic reduction of cyclohexene in imidazolium based ionic liquids using a rhodium catalyst. The reaction can be carried out under moderate hydrogen pressure and at room temperature. Turnover numbers up to 6 000 could be achieved.[43]

Since then, ionic liquids were used as reaction media and as immobilizing media for transition metal catalysts, for carrying out hydrogenation or transfer hydrogenation. Besides that, ionic liquids were also used for the synthesis, stabilization and as reaction media for catalytically active nanoparticles in reduction experiments.[44]

1.2.1 Transition metal catalysis using hydrogen

One important aspect in every hydrogenation reaction is the solubility of hydrogen gas in the reaction media. In case of ionic liquids, the solubility of hydrogen is much lower compared to conventional solvents such as cyclohexane or methanol. This seems to be a problem, but the reactivity of the catalyst does not only depend on the solubility of hydrogen in pure ionic liquid. If the reaction is carried out in a biphasic way, the reaction rate increases since hydrogen is better soluble in the second phase, speeding up the reaction.[45] Besides that, the solubility of hydrogen can be modified by using different anions. For instance, the BF_4^- anion shows lower solubility of hydrogen than the NTf_2^- anion.[46] Table 5 shows several examples of the usage of ionic liquids in hydrogenation reactions.

Table 5. Selected examples of hydrogenations using ionic liquids

Functional group	***Used metal***	***Ionic liquid***	***Reference***
	Pd	[bmim]PF_6 [bmim]OTf	Anderson et al. **2003**[47]
	Pd	[bmim]NTf_2	Hardacre et al. **2006**[48]
	Ru	[P_{4441}]NTf_2 [N_{1114}]NTf_2	Floris et al. **2010**[49]
	Ni Pd Pt	[bmim]BF_4	Xu et al. **2005**[50]

While several hydrogenation reactions are known, the reduction of carbon-carbon double bonds is among the most explored ones. Different types of catalysts can be used for this purpose. Heterogeneous catalysts such as Raney nickel, palladium on carbon or platinum on carbon can be used in combination with ionic liquids.

For the reduction of chloro-nitrobenzenes, 3-butyl-1-methyl-imidazolium tetrafluoroborate ([bmim]BF_4) was successfully used as solvent for the catalyst (Figure 13).

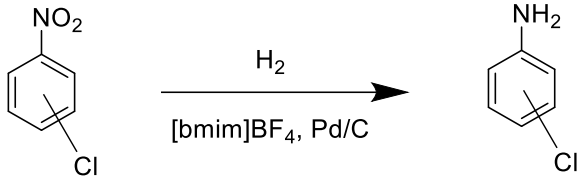


Figure 13. Reduction of nitrobenzenes using ionic liquid as reaction media[44]

Although higher reaction temperatures and pressures were required for the transformation compared to conventional solvents, the usage of [bmim]BF_4 was beneficial to the overall process. Using methanol as solvent resulted in a high degree of undesired dehalogenation reactions, up to 44% in case of *para*-substitution using palladium on carbon. Performing the same reaction in [bmim]BF_4, only a small amount was converted to the undesired dehalogenated byproduct, with the same catalyst system.[50]

Besides using heterogeneous systems, homogeneous catalysts can be applied successfully in combination with ionic liquids. The asymmetric reduction of methyl acetoacetate to the corresponding hydroxyl ester using a well-defined ruthenium based catalyst demonstrates the tunability of ionic liquids as reaction media. Figure 14 demonstrates the reaction scheme of this reduction reaction.

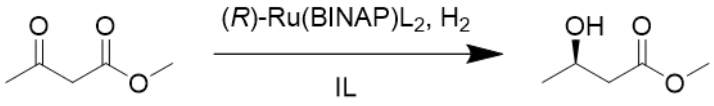


Figure 14. Scheme of reduction of methyl acetoacetate in ionic liquid

The variation of the cation did not lead to a significant change in the reactivity of the system. However, the choice of the anion considerably affects the turnover frequency (TOF). With PF_6^- as counter ion, the TOF reached only half of the value that was obtained with the NTf_2^- anion. Two reasons may contribute to this effect. One issue is the lower solubility of hydrogen in PF_6^- based ionic liquids as described above.

The second reason could be a modification of the catalytically active site of the catalyst by the weakly coordinating NTf_2^- anion, which seems to enhance the reactivity of the system. Plausible interactions of the NTf_2^- ion and the active center are shown in Figure 15.[49]

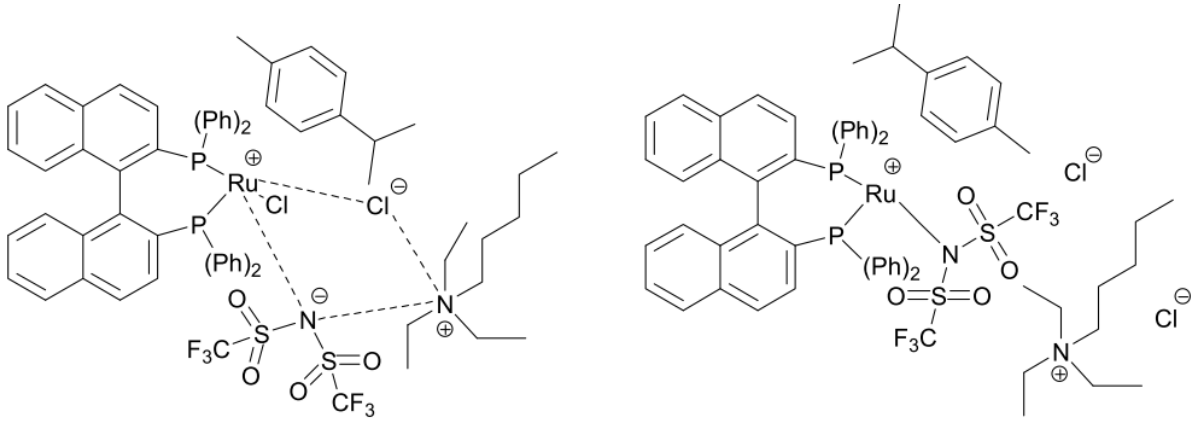


Figure 15. Interaction of the chiral ruthenium complex with NTf_2^-[44]

1.2.2 Transfer hydrogenation

Another possibility of performing catalytic reduction experiments in ionic liquids relies on the concept of transfer hydrogenation. Within this method, hydrogen is transferred from a donor molecule to an acceptor molecule with unsaturated functionalities. Therefore no hydrogen gas is needed to perform this transformation, adding to the overall safety of the process.

Asymmetric transfer hydrogenation in ionic liquids was carried out to reduce acetophenone to 1-phenylethanol, using formic acid/triethylamine as hydrogen donor (Figure 16).

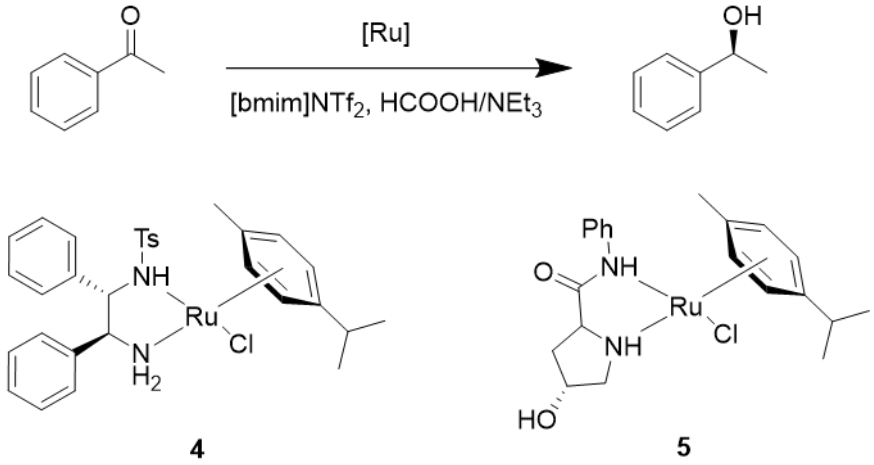


Figure 16. Asymmetric transfer hydrogenation using ionic liquids as reaction media[51]

For this purpose, hydrophilic and hydrophobic ionic liquids were investigated as reaction media. In this context, hydrophilic ionic liquids, such as 3-butyl-1-methyl-imidazolium chloride ([bmim]Cl) showed low efficiency as reaction media. Using hydrophobic ionic liquids, such as tributylmethylphosphonium bis(trifluoromethane)sulfonamide ($[P_{4441}]NTf_2$), increased the reactivity of the system. Conversion up to 99% and ee value up to 97% could be achieved with the usage of $[P_{4441}]NTf_2$ or butyltrimethylammonium bis(trifluoromethane)sulfonamide $[N_{1114}]NTf_2$ together with catalyst **4**. Besides the high reactivity of the system, recycling of the catalyst could be done. Therefore the reaction could be run three times in total with the same catalyst. Separation of the product from the ionic liquid was performed by extraction or by bulb to bulb distillation.

Best results for the usage of catalyst **5** were obtained by using $[bmim]PF_6$ as catalyst carrying phase, reaching 99% conversion and 72 %ee. For this system, five runs with the same catalyst could be done, achieving conversion of 99% for all runs. The enantioselectivity of the system decreased only slightly to 68 %ee after the last run.[51]

1.3 Hydrogenations with iron based catalysts

The use of base metal catalysts, especially iron based, has raised considerable interest in the last decade. Iron is one the most common elements in the earth's crust and therefore inexpensive. Since iron is incorporated in several biological systems, its toxicity can be considered as relatively low. In contrast, platinum group metals, such as ruthenium, rhodium or palladium, which play a major role as catalysts in organic synthesis, have a high price. These noble metals show a high economic importance, but also a large supply risk (Figure 17).

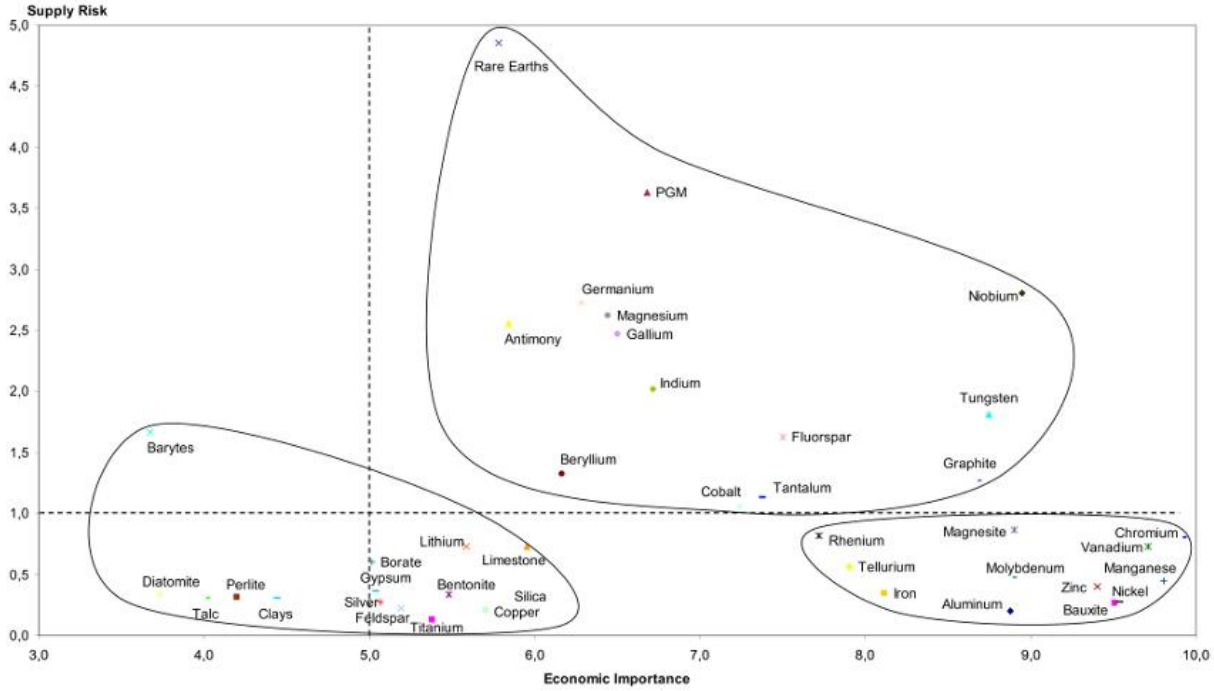
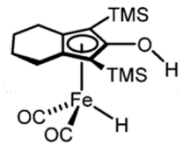
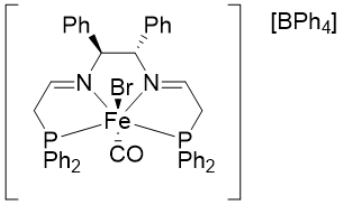
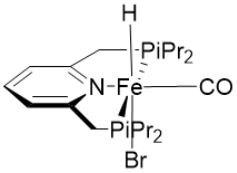
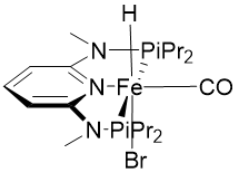
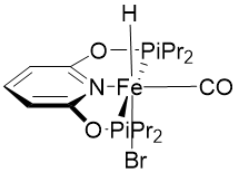


Figure 17. Graph of supply risk and economic importance for several raw materials[52]

Besides these advantages, iron has the drawback of rather low reactivity in catalytic transformations compared to several noble metals. Therefore, fine-tuned ligand systems have to be employed in order to boost the reactivity and stability of iron based catalysts. Nevertheless, the rapidly expanding research field in iron catalysis demonstrates its potential.[53,54]

A broad variety of transformations can be achieved with iron catalysts. Apart from addition, substitution and oxidation reactions, reduction of polarized double bonds, such as carbonyl functionalities, are of great interest in organic chemistry.[53] Table 6 demonstrates a selection of different iron based catalysts for the reduction of the carbonyl motive.

Table 6. Selection of iron catalysts for the reduction of carbonyls

Catalyst	*Reference*
	Knölker et al. **2007**[55]
	Morris et al. **2008**[56]
	Milstein et al. **2011**[57]
	Kirchner et al. **2014**[58]
	Hu et al. **2015**[59]

Knölker's complex is one of the first examples of a well-defined iron(II)hydride-catalyst, which is able to reduce aldehydes, ketones and imines under moderate hydrogen pressure in a chemoselective way at room temperature. Isolated carbon-carbon double bonds, nitro groups and esters are not affected. Even the reactive epoxide functionality is not opened to the corresponding alcohol. Although only moderate turnover numbers (TON) were reached (maximum TON = 50), the concept of reducing carbonyl groups with the usage of a well-defined iron complex was proven.[55]

After an intense study of this system, including stoichiometric experiments and computational calculation, Casey et al. came up with a proposed mechanism (Figure 18).[60]

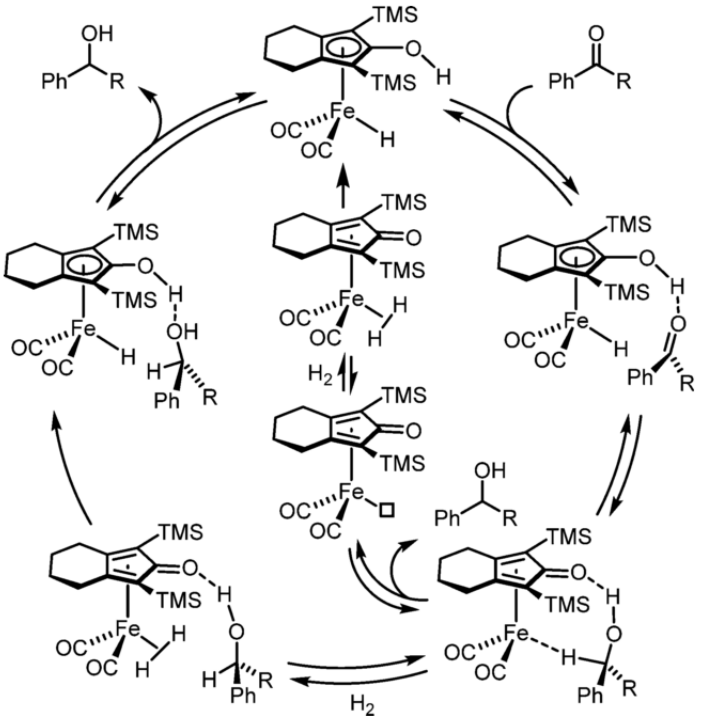


Figure 18. Proposed mechanistic cycle of the reduction of ketones using Knölker's complex[53]

Morris and coworkers published several dicationic iron complexes for the reduction of the carbonyl motive in 2008. The complexes were based on four-dentate P_2N_2 ligands, showing excellent yields for benzophenone as substrate under 25 bar H_2 pressure at 50 °C. With the usage of a chiral diimine-diphosphine ligand system, it was possible to carry out an enantioselective reaction for the first time in the field of iron catalyzed reduction of carbonyl groups. The results were moderate (40% yield, 27% ee), but opened a future perspective in the field of iron catalysis.[56]

Another milestone in this research field was established by Milstein and coworkers, since they established the usage of pincer ligands in 2011. This hydride complex bearing a PNP pincer ligand with a CH_2 linker between the pyridine ring and the phosphine moiety is up to now the most efficient catalyst for the reduction of ketones at moderate reaction conditions. Turnover numbers up to 1 880 under 4 bar H_2 pressure at room temperature can be achieved in ethanol with the addition of a base.[57]

In 2014 Kirchner and coworkers came up with a different pincer based complex, using NH or NMe as linkers. The reactivity of the NH linker complex towards ketones is among the best iron based catalysts by now. The pre-catalyst with the NMe-linker did not show any reactivity towards ketones at all, but is highly reactive for the reduction of aldehydes.[58]

Investigation of the NMe-system revealed remarkable reactivity and chemoselectivity towards aldehydes. Double bonds, whether in conjugation with carbonyl group or not, esters, nitro compounds or epoxides were not affected and ketones were not reduced. Turnover numbers up to 80 000 and turnover frequencies up to 20 000 h^{-1} using 4-fluorobenzaldehyde as substrate could be achieved. A broad variety of substrates was tested, showing high reactivity for aromatic as well as for aliphatic aldehydes. This makes this catalyst one of the most reactive and at the same time chemoselective catalyst for the reduction of aldehydes with hydrogen.

Considering the mechanism of this reaction, Kirchner and coworkers came up with a proposed mechanistic cycle, supported by DFT calculations and stoichiometric experiments (Figure 19). The pre-catalyst is activated with hydrogen with the usage of a base. One hydride ligand attacks the aldehyde, which then coordinates to the iron center. The alcoholate ligand is then replaced by a solvent molecule. After a split of hydrogen gas and protonation of the alcoholate, the dihydride complex is regenerated and can undergo another catalytic cycle.[61]

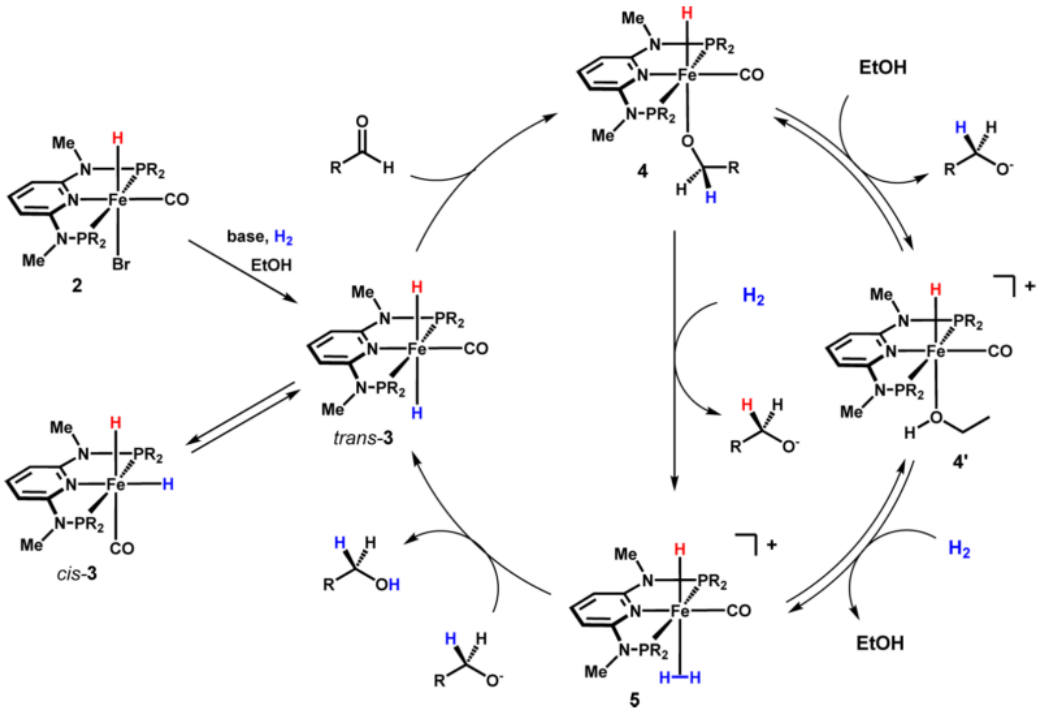


Figure 19. Proposed mechanism of the reduction of aldehydes using Kirchner's complex[61]

2 Aim of the thesis

The reduction of aldehydes is an important transformation in organic chemistry. This transformation can be achieved with the usage of reagents, or, in a more atom economic way by catalytic hydrogenation. Among all hydrogen sources, hydrogen gas is the cheapest. Several catalysts are known to literature to catalyze this reaction, however Kirchner's catalyst shows remarkable chemoselectivity towards aldehyde reductions and high reactivity. However, efficient product separation from the catalyst and possible recycling is difficult to achieve, since reactions are typically run in a homogeneous process relying on ethanol as solvent.

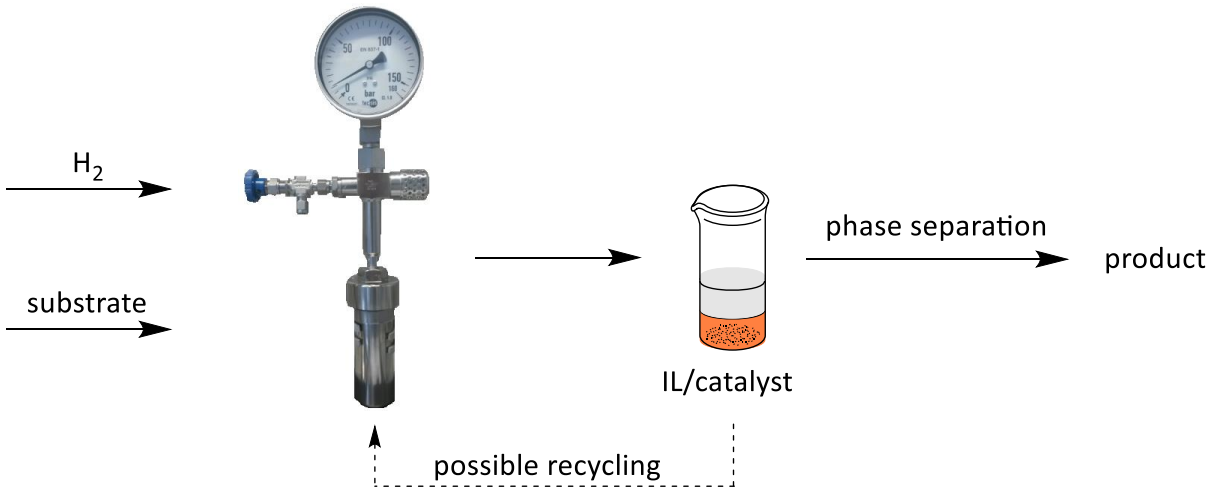


Figure 20. Scheme of work flow for the reduction of aldehydes in biphasic systems

The aim of this thesis was to immobilize Kirchner's catalyst in ionic liquid media and investigate its potential in liquid-liquid biphasic catalysis. After optimization of the reaction parameters, recycling of this iron-based catalyst should be explored. Moreover, scope and limitation of the biphasic system should be examined.

3 Results and discussion

3.1 Selection and synthesis of ionic liquids

In order to carry out catalysis using Kirchner's catalyst in a liquid-liquid biphasic system, a variety of ionic liquids as catalyst containing phase had to be chosen. Several properties for the selection of ionic liquids are of importance:

- High solubility and stability of the pre-catalyst in the ionic liquid
- Very low miscibility of ionic liquid and organic solvent
- No leaching of catalyst and ionic liquid into the organic phase
- High solubility of the substrate in the ionic liquid
- High solubility of hydrogen in the ionic liquid
- Stability and reactivity of the active catalyst in the ionic liquid

By choosing different cations and anions, the properties of ionic liquids can be adjusted. In Figure 21, a small variety of commonly used cations and anions are shown. Besides density and viscosity, the hydrophobicity of ionic liquids can be adjusted *via* the combination of different ions.

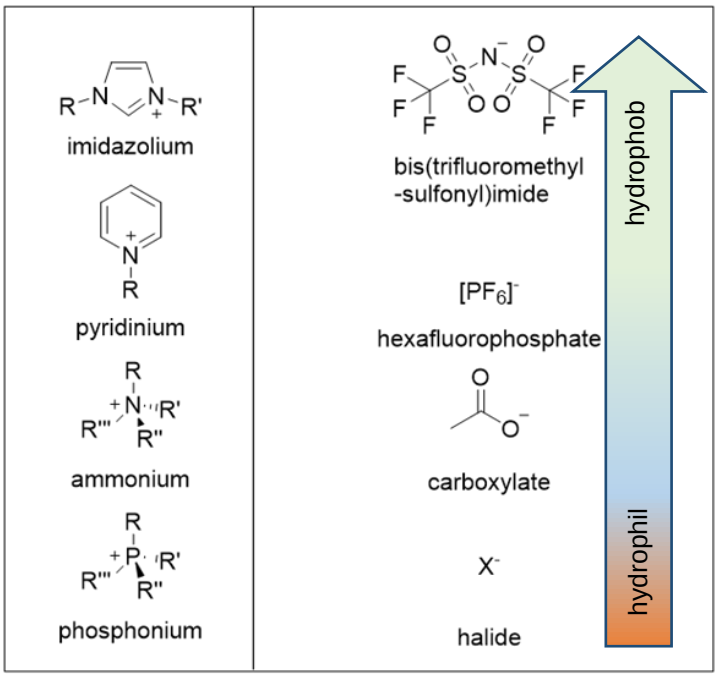


Figure 21. Frequently used cations and anions for the design of ionic liquids

Preliminary work showed that the pre-catalyst is soluble in hydrophobic ionic liquids, based on NTf_2^- anion. Apart from simple preparation and hydrophobicity of the NTf_2^- ion, it has several additional advantages. Ionic liquids containing the NTf_2^- motive tend to have lower viscosity compared to other hydrophobic ions.[62] Another benefit of the NTf_2^- ion is its weakly coordinating nature.[63] This should avoid ligand substitution reactions on the (pre-)catalyst. Besides that, ionic liquids containing the NTf_2^- ion show higher hydrogen gas solubility than ionic liquids with other anions, such as PF_6^- or BF_4^-.[49]

3.1.1 Brønsted basic ionic liquids

Due to the necessity of a base such as DBU during iron-catalyzed hydrogenation with Kirchner's catalyst, special attention in this thesis is dedicated to Brønsted basic ionic liquids. In general, Brønsted basic ionic liquids are ionic liquids that contain at least one Brønsted basic group either on the cation or on the anion. Sterically hindered amines are often used on the cation side, whereas carboxylates are commonly used as anions. Figure 22 represents a selection of basic cations and anions.[64]

The scope of functionalized ionic liquids such as Brønsted basic derivatives is often beyond the role of a solvent. Such ionic liquids often have an influence on the reactivity and/or stability of the investigated system and can be considered as so called "task specific" ionic liquids (TSIL). Due to the more or less infinite amount of different cation-anion combinations, the properties of TSIL can be adjusted to tune the efficiency of the entire system.[65]

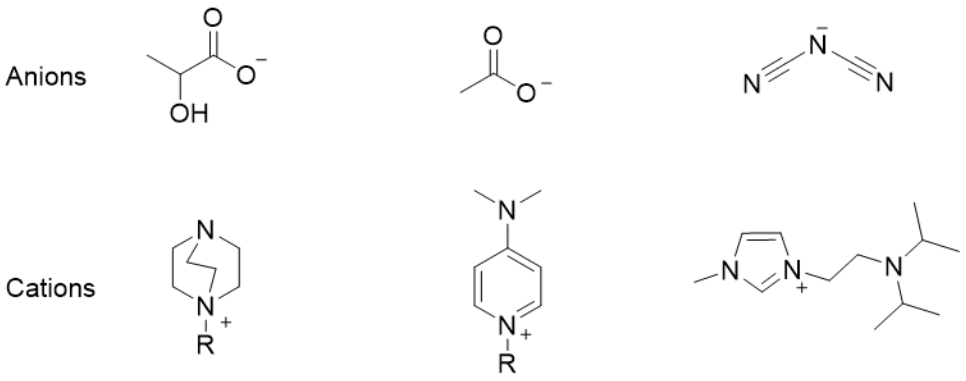


Figure 22. Selection of basic ions as building blocks of ionic liquids[64]

Basic ionic liquids can be used as an alternative to commonly used (in)organic bases, such as $NaHCO_3$ or DBU. Several applications, such as Knoevenagl condensation[66], Michael type reaction[67] or as base in the Heck reaction[68] are known to literature. Besides the use in synthesis, basic ionic liquids can be used for gas storage[69] or in the field of electrochemistry.[70]

Based on these considerations, a set of conventional and Brønsted basic ionic liquids based on the NTf_2^- anion was selected and prepared. Figure 23 gives an overview of all ionic liquids used within this work.

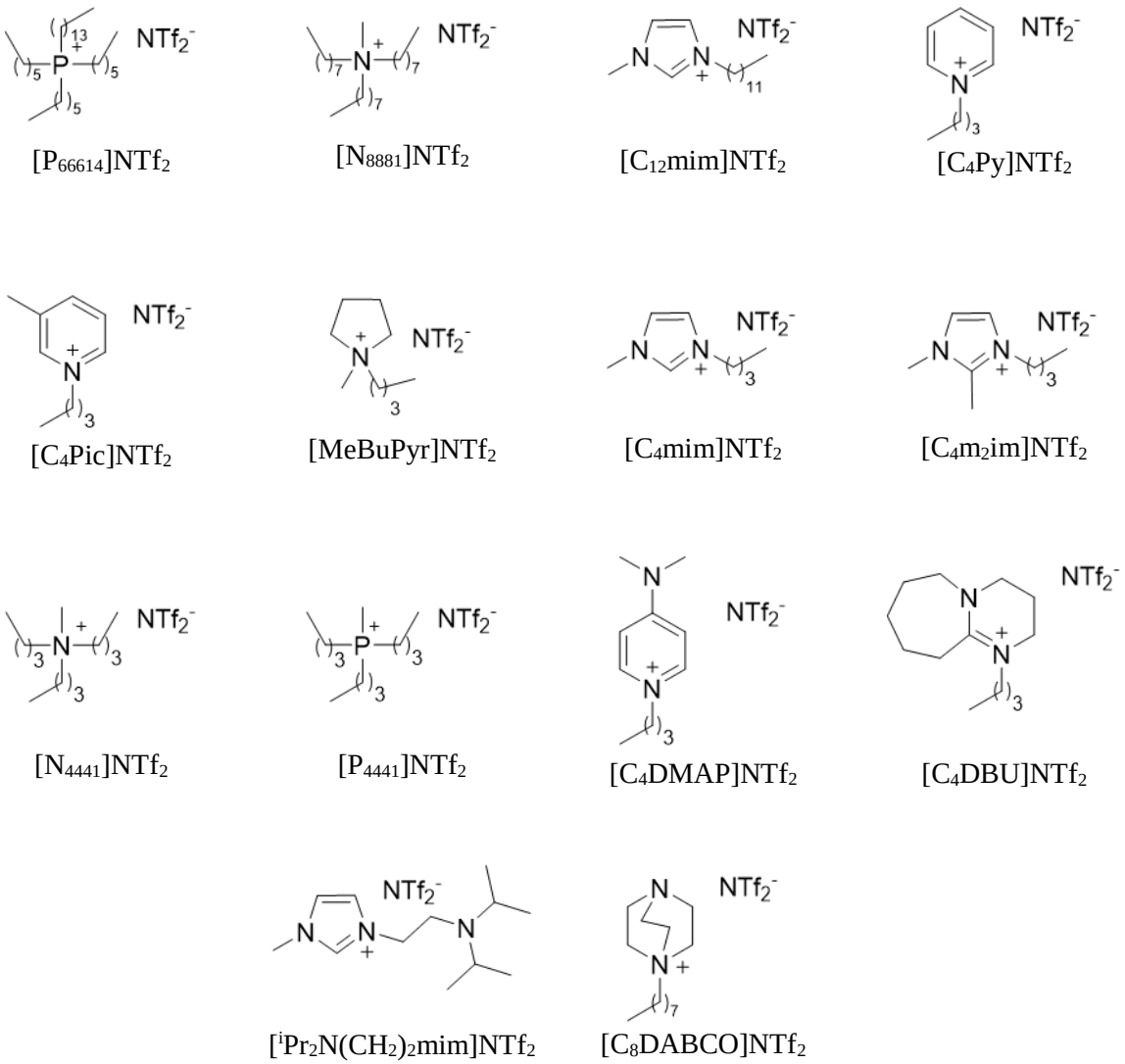


Figure 23. Overview of ionic liquids, which were used as reaction media in this work

In general, hydrophobic ionic liquids containing the NTf_2^- moiety were synthesized in a two-step protocol, starting with an alkylation reaction, to obtain a halide salt. A consecutive ion exchange step with $LiNTf_2$ gave the desired ionic liquid. The synthesis of NTf_2^- containing ionic liquids is shown below on the example of $[C_4mim]NTf_2$ (Figure 24).

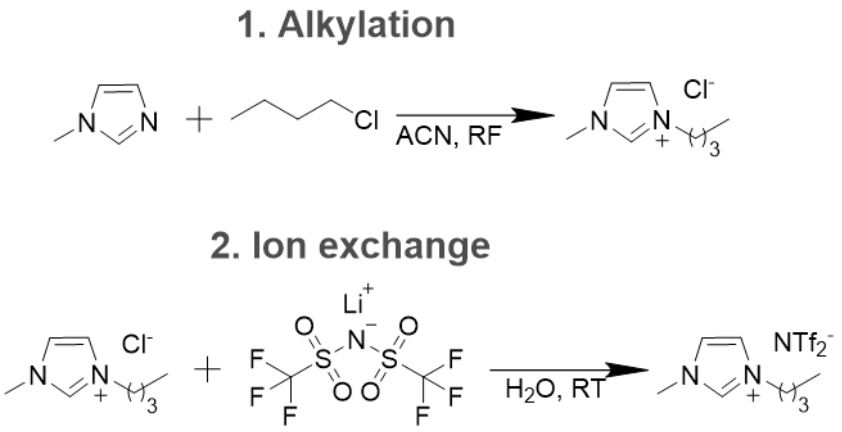


Figure 24. Synthesis of NTf_2^- based ionic liquids on the example of $[C_4mim]NTf_2$

3.1.2 Synthesis of ionic liquids and precursors *via* alkylation

As described above, the ionic liquids, which were used as catalyst carrying phase, were synthesized in two steps, starting with a salt formation step. This transformation is achieved *via* a nucleophilic substitution reaction, whereas alkylhalides are often chosen as alkylation agents. The reactivity of these alkylation reagents depends on the nature of the leaving group. Iodine typically represents the most reactive halide, followed by bromide and chloride, which is also reflected in the required reaction times to reach full conversion.

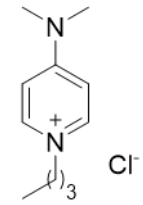
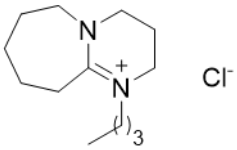
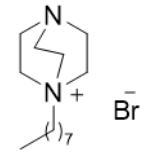
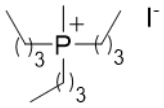
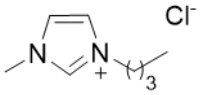
Yet typically chlorides are chosen for the synthesis of ionic liquids, since they are commercially available and comparingly cheap. The alkylation reactions using alkyl chlorides are usually done by refluxing (e.g. in ACN or EE) the nucleophile with the alkylation agent for several days, in order to achieve full conversion. Heating to higher temperatures would increase the reaction rate, but would also lead to a change in color of the product, which indicates the presence of impurities. Reaction monitoring can be done *via* ^{1}H-NMR spectroscopy.

In case of $[C_8DABCO]Br$, a bromide containing alkylation agent was used, due to its availability in the research group. In case of $[P_{4441}]I$, idomethane was used for methylation based on its favorable boiling point. It is available as a liquid at room temperature, whereas methylchloride and methylbromide are gases and therefore not easy to handle and dose.

Another option, especially for methylation reactions, would be the usage of dialkylsulfates (e.g. dimethylsulfate). These reagents however have, the drawback that they are highly toxic and consequently, they were not used in here.

The yields and reaction conditions for the alkylation reactions are shown below (Table 7).

Table 7. Yields for the alkylation step in the synthesis of ionic liquids

Entry	*Ionic liquid/precursor*	*Alkylation agent*	*Reaction time*	*Solvent*	*Yield [%]*
1	 [C_4DMAP]Cl	butylchloride	4 d	ACN	96
2	 [C_4DBU]Cl	butylchloride	4 d	ACN	56
3	 [C_8DABCO]Br	octylbromide	3 d	EE	39
4	 [P_{4441}]I	iodomethane	1 h	CH_2Cl_2	94
5	 [C_4mim]Cl	butylchloride	5 d	ACN	85

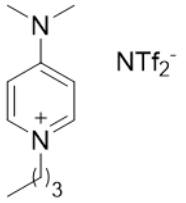
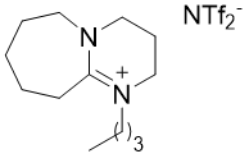
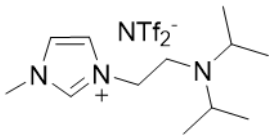
The alkylation of DMAP and tributylphosphine to the corresponding salts gave high isolated yields, since a pure product without the need of further purification was obtained after work up. In case of [C_4mim]Cl, the yield is lower, since three crystallization steps had to be performed in order to receive a pure product. The alkylation of DBU and DABCO was rather low yielded, since the products were washed several times with fresh solvents to increase their purity.

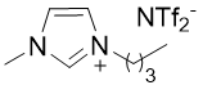
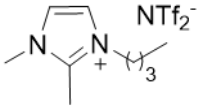
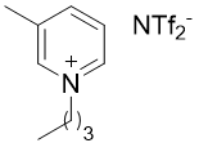
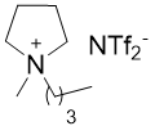
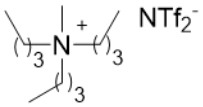
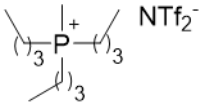
3.1.3 Synthesis of ionic liquids *via* ion exchange

The last step to receive NTf_2^- based ionic liquids was the ion exchange. The halide ion was replaced by NTf_2^- *via* an ion metathesis reaction. Part of the driving force of this reaction is the formation of lithium halide, which is preferentially dissolved in water. The obtained ionic liquids were then washed several times with water in order to remove traces of lithium chloride, which would have had great impact on the properties of the ionic liquid. After the washing step, intensive drying is necessary, since the water content is a factor of equal importance which affects the properties of ionic liquids. In order to facilate drying and to decrease the viscosity of the system, this is usually done *in vacuo* under intensive stirring at 50 °C for several hours.

The results of these exchange reactions are shown in Table 8.

Table 8. Yields for the ion exchange step in the synthesis of ionic liquids

Entry	***Ionic liquid***	***Yield [%]***
1	 [C_4DMAP]NTf_2	86
2	 [C_4DBU]NTf_2	85
3	 [^{i}Pr$_2$N(CH$_2$)$_2$mim]NTf_2	88

Entry	*Ionic liquid*	*Yield [%]*
4	 [C_4mim]NTf_2	91
5	 [C_4m_2im]NTf_2	88
6	 [C_4Pic]NTf_2	73
7	 [MeBuPyr]NTf_2	86
8	 [N_{4441}]NTf_2	84
9	 [P_{4441}]NTf_2	89

The resulting yields for all NTf_2^- based ionic liquids are good to excellent, since this ion exchange procedure is well established. Besides several washing steps with water in order to remove the halide salt, no further purification of the products had to be done.

3.2 Synthesis of the pre-catalyst

3.2.1 Synthesis of the ligand

The first steps towards Kirchner's catalyst involve the synthesis of the PNP-ligand. A microwave assisted reaction was done to substitute the two bromine atoms of 2,6-dibromo-pyridine with amino functionalities (Figure 25).

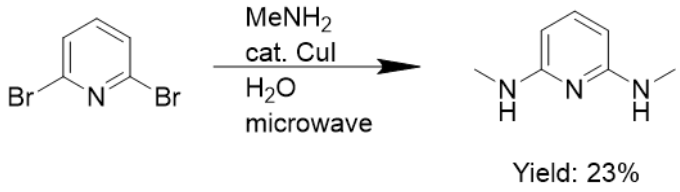


Figure 25. Synthesis of N,N'- dimethyl-2,6-diaminopyridine

Since enough product was obtained from this reaction for the next step and since this reaction is already known to literature in higher yield, the comparingly low yield was not further investigated.

Next, a two-step protocol was employed to transfer *N,N'*-dimethyl-2,6-diaminopyridine *via* lithiation technique into the phosphorylated derivative (Figure 26).

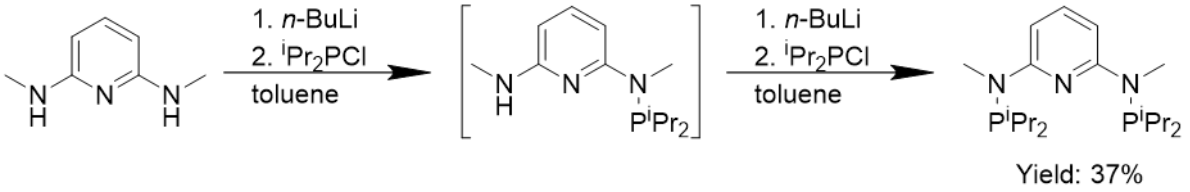


Figure 26. Synthesis of N,N'(diisopropylphosphino)-N,N'-2,6-diaminopyridine

The monophosphorylated intermediate was not isolated and directly used, after a short work up for the second phosphorylation step, giving the final PNP-pincer ligand in moderate yield.

This reaction is known to literature in higher yields. No further investigation on the optimization of this reaction was performed, since enough product was gained for the following synthetic steps.

3.2.2 Synthesis of the pre-catalyst

Initially, $FeBr_2$ was reacted with the synthesized PNP ligand in anhydrous THF giving [(^{i}Pr-PNPMe)Fe(Br)$_2$] in good yield (Figure 27).

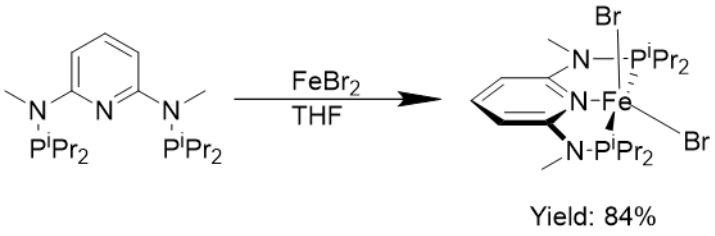


Figure 27. Synthesis of [(^{i}Pr-PNPMe)Fe(Br)$_2$]

This complex was further reacted with carbon monoxide. A consecutive ligand substitution to change the bromine substituent to a hydride ligand was done using a Na[$HBEt_3$] solution (Figure 28). The result of this reaction is a mixture of two isomers. For one isomer, the hydride ligand is in *cis* position to the bromine atom, whereas a second isomer with *trans* configuration is also obtained.

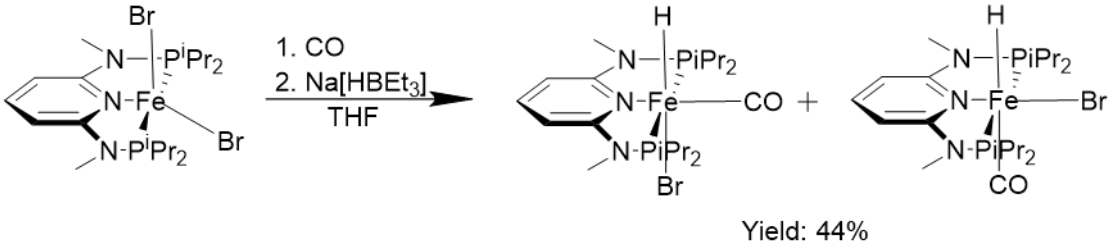


Figure 28. Synthesis of [Fe(^{i}Pr-PNPMe)(H)(CO)(Br)]

For catalytic applications, the *trans*-isomer serves as pre-catalyst, whereas the *cis*-isomer cannot be transformed to a catalytic active species.

Due to the preferential solubility of the *cis*-isomer in Et_2O, the resulting mixture of isomers can be enriched in the *trans*-isomer by washing the mixture with Et_2O. A ratio of *cis*:*trans* of roughly 1:3 was achieved after all purification steps.

3.3 Hydrogenation experiments

In order to investigate Kirchner's catalyst for the reduction of aldehydes in a liquid-liquid biphasic system with ionic liquids as catalyst containing phase, the reduction of 4-fluorobenzaldehyde was chosen as test reaction (Figure 29).

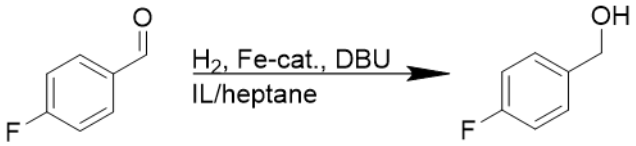


Figure 29. Reduction of 4-fluorobenzaldehyde using Kirchner's catalyst in ionic liquid/organic biphasic system

Using 4-fluorobenzaldehyde as substrate has several advantages. With this substrate the highest turnover numbers (TON) were achieved in the homogeneous system, since the catalyst seems to be very active for this aldehyde.

Moreover, two different approaches are available for the analysis of the reaction including HPLC-analysis and ^{19}F-NMR spectroscopy.

In case of HPLC analysis, a method was developed for the separation and quantification of the reaction mixture. The entire reaction mixture was diluted after the reaction with MeOH and a sample was taken for analysis. The analysis performed done on a reversed phase column, using ACN/H_2O as mobile phase. This has the advantage that a distribution of the starting material or substrate between the ionic liquid and organic phase does not influence the quantification. On the other hand, this is also a drawback of performing analysis *via* HPLC. Since the entire sample had to be dissolved in methanol, a loss of information, for instance leaching of ionic liquid into the organic phase, had to be taken into consideration.

Since this HPLC analysis has been performed in a reversed phase mode, the retention time of polar compounds is shorter than the retention time of non-polar compounds.

A typical analysis is shown in Figure 30. The product peak has a retention time of approx. 8 minutes, the peak at approx. 13 minutes retention time represents the starting material, and methylbenzoate which was used as internal standard can be seen at approx. 20 minutes. In order to quantify the substances, a calibration of the starting material and the product was performed.

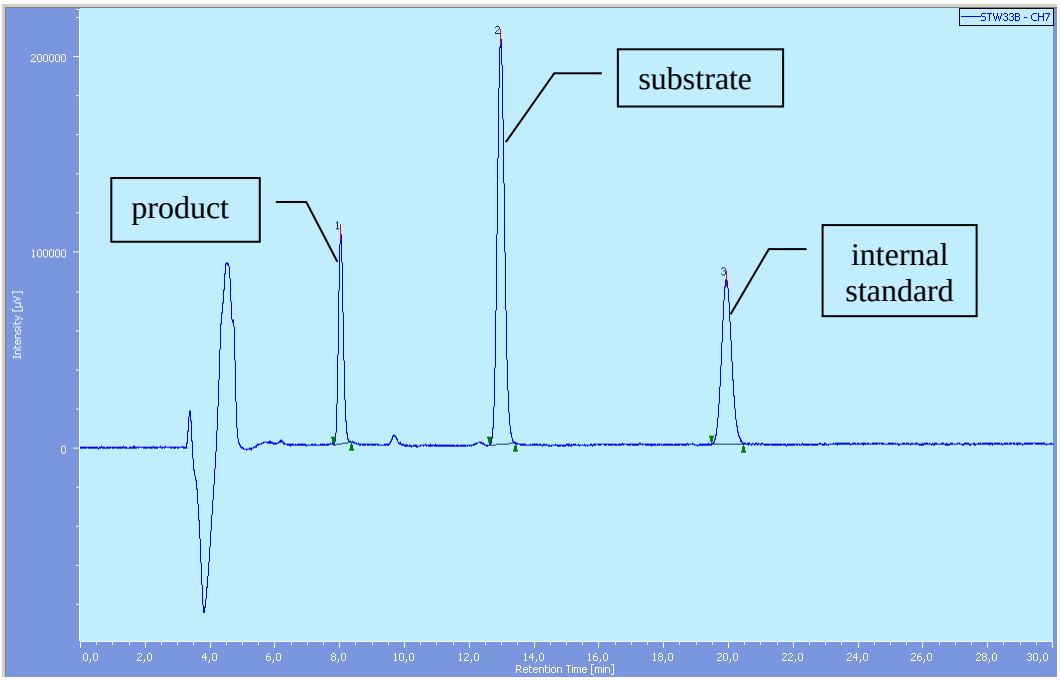


Figure 30. Typical example of HPLC analysis; the peak at approx. 8 minutes represents the product, the signal at approx. 13 minutes represents the substrate and the internal standard gives a signal at approx. 20 minutes

As alternative, the reaction could be monitored *via* ^{19}F-NMR spectroscopy. A typical example of a ^{19}F-NMR analysis can be seen in Figure 31.

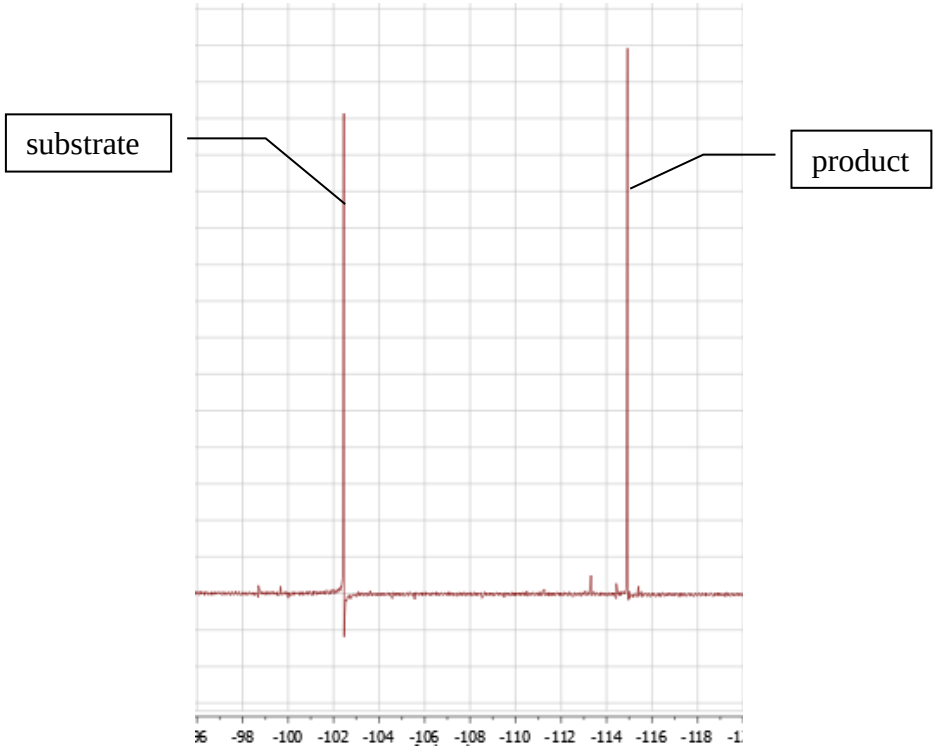


Figure 31. Typical example for a ^{19}F-NMR analysis of the organic phase after the reaction; the product can be detected at approx. -115 ppm, whereas the substrate gives a signal at approx. -103 ppm

Using ^{19}F-NMR technique, no calibration was done, since the area for the product and the substrate signal were compared to determine the yield, as followed:

$$Y = \frac{A_p}{(A_p + A_s)} \cdot 100$$

Y … yield [%]

A_p… area product peak []

A_s… area substrate peak []

Equation 1. Determination of yield via ^{19}F-NMR

Apart from this, the measurement only required one to two minutes as the ^{19}F-nucleus is very sensitive for NMR analysis. An additional advantage of analysis with ^{19}F-NMR spectroscopy is the fact that samples of both phases can be taken after the reaction. Therefore separate analysis of the organic phase may reveal important information, such as leaching problems.

After performing both types of analysis, ^{19}F-NMR spectroscopy was chosen as standard method.

3.3.1 Optimization of reaction parameters *via* screening of ionic liquids

The investigation of the hydrogenation of 4-fluorobenzaldehyde in a biphasic system initially required a screening of different ionic liquids as catalyst containing phase. For the first experiments, hydrophobic ionic liquids with long alkyl chain were used to dissolve the pre-catalyst (Figure 32).

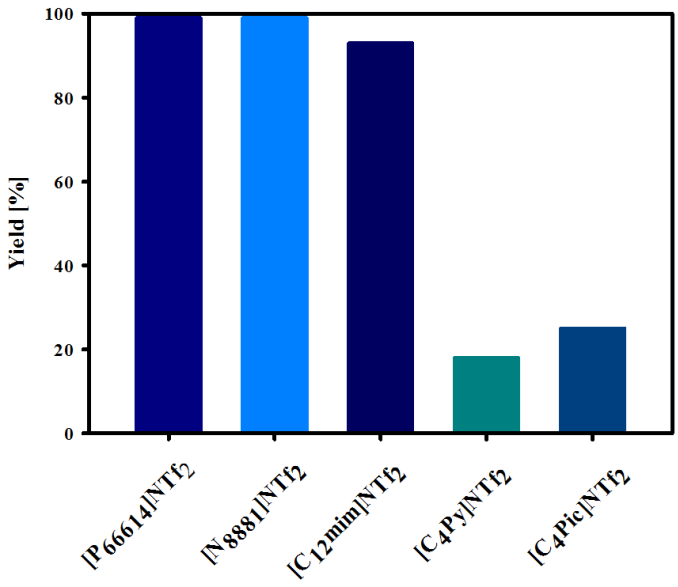


Figure 32. Ionic liquid screening using long chained or pyridinium based cations

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

Although these candidates had a high viscosity due to the long alkyl chain of the cation, they showed excellent yield for $[C_{12}mim]NTf_2$ and quantitative yield in case of $[P_{66614}]NTf_2$ and $[N_{8881}]NTf_2$. However, ^{19}F-NMR analysis of the organic phase revealed leaching of the ionic liquid for all these candidates. Since the NTf_2^- ion contains fluorous atoms, it can be detected using ^{19}F-NMR. Figure 33 demonstrates a sample with leaching of ionic liquid. The product can be seen at about -115 ppm. The NTf_2^-anion gives an additional signal at approx. -78 ppm.

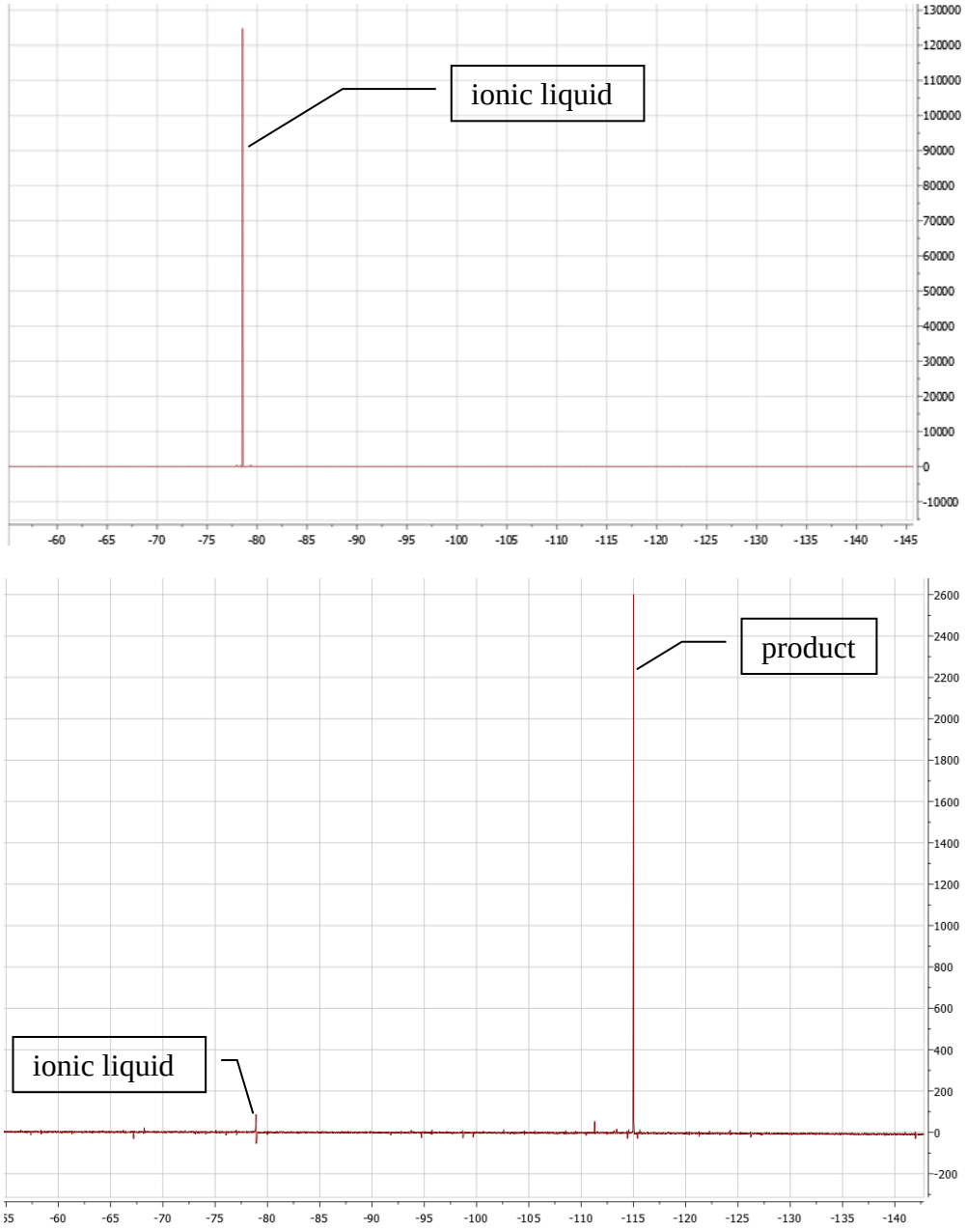


Figure 33.^{19}F-NMR analysis of a sample with leaching of ionic liquid (bottom) and pure ionic liquid (top)

Due to the leaching problems of the cations with a long alkyl chain, different ionic liquids were investigated. Since shorter alkyl chains should reduce the solubility in the organic phase, the alkyl chain length was decreased. Pyridinium based ionic liquids with a short alkyl chain seemed to be very interesting, because they tend to have comparingly low viscosity. Unfortunately, the yields for using this type of media led to a drastic drop in reactivity of the catalyst and only gave poor yields for the investigated transformation.

One reason for that might be an interference of the pyridinium based head group with the catalyst, forming an inactive species. Using pyridinium based ionic liquids led to a dark, almost black color of the ionic liquid phase after the reaction. In contrast, the colors for all other ionic liquids were orange to slightly red after the reaction. This might indicate an undesired interaction between the catalyst and the pyridinium ion.

The screening was continued with hydrophobic ionic liquids with cationic head groups other than pyridinium. Structures containing the pyrrolidinium, imidazolium, ammonium or phosphonium head group structural motive were selected in combination with a *n*-butyl group as alkyl chain. With this shorter alkyl chain, the leaching into the organic phase should be less problematic. The results are shown in Figure 34.

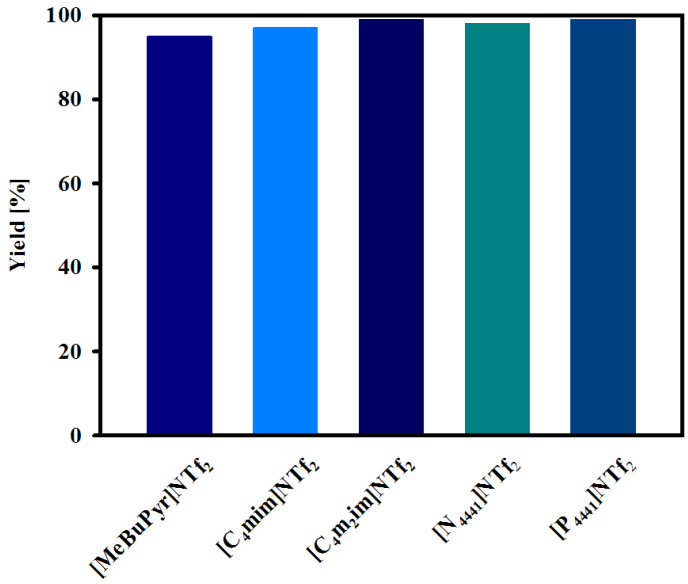


Figure 34. Ionic liquid screening using cations with short alkyl chain

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

The yields are excellent for [MeBuPyr]NTf_2 and [C_4mim]NTf_2. Almost full conversion could be determined for [N_{4441}]NTf_2, [C_4m_2im]NTf_2 and [P_{4441}]NTf_2, which suggests that these ionic liquids are the most promising candidates for further investigations. In addition, no leaching of the immobilizing phase into the organic phase for these ionic liquids could be detected.

When comparing [C_4mim]NTf_2 with [C_4m_2im]NTf_2 no significant difference in the reaction performance or yield was observed. [C_4mim]NTf_2 contains a C-H acidic proton on the carbon between the two nitrogens in the imidazole ring. This proton can in principle be abstracted by a base, forming a carbene with a metal center. This type of ligand is electron donating, which can improve the reactivity of a catalyst.[71] In case of [C_4m_2im]NTf_2, the C-H acidic proton is substituted by a methyl group. Therefore this C-H position is replaced and no possible carbene formation can occur.

Within this work, no substantial difference between [C_4m_2im]NTf_2 and [C_4mim]NTf_2 as reaction media could be determined, indicating that the formation of a carbene is not relevant for the reactivity of the system.

In case of using [C_4m_2im]NTf_2 as catalyst carrying phase, an ICP-MS analysis was performed to determine possible leaching of iron into the organic phase after the reaction. According to the analysis, the iron content of the sample was below the detection limit (< 10 ng iron) of this analysis technique. This indicates that the catalyst is successfully immobilized in the ionic liquid without any losses in the organic phase.*

* ICP-MS analysis was performed in the group of Prof. Limbeck by Dr. Winfried Nischkauer on the Institute of Chemical Technologies and Analytics at the TU Wien.

KINETICS OF THE REACTION

Kinetic data of the reaction was determined for $[C_4m_2im]NTf_2$ and $[P_{4441}]NTf_2$ since they were the most promising candidates for further investigations. The results of this evaluation are shown below (Figure 35).

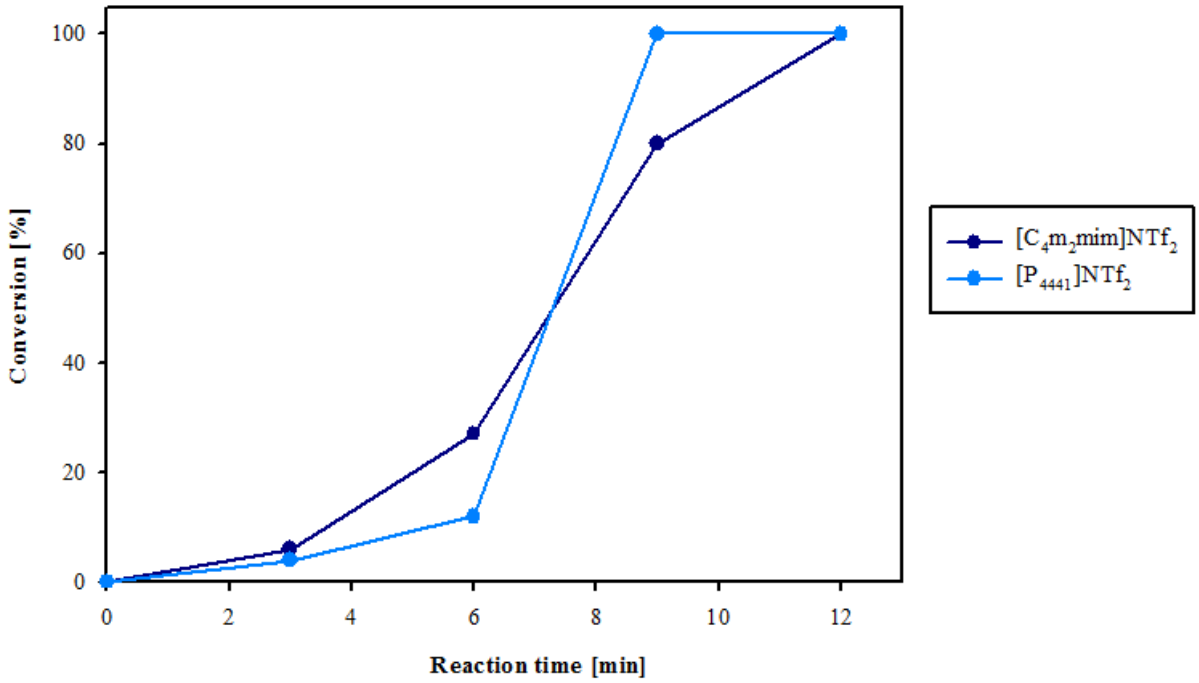


Figure 35. Kinetic data of the reduction experiments using $[C_4m_2im]NTf_2$ and $[P_{4441}]Ntf_2$

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

As it can be seen from the figure above, the reaction is quite slow at the beginning. This is a result of the initial activation of the pre-catalyst that has to be activated by a base and H_2.

Once the catalytically active species (Figure 36) is quantitatively formed, the reduction of aldehyde is performed very fast.

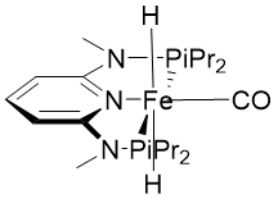


Figure 36. Catalytically active species

Comparing $[C_4m_2im]NTf_2$ with $[P_{4441}]NTf_2$, the reaction seems to be faster at the beginning using $[C_4m_2im]NTf_2$. This indicates that the active species is formed faster than in the case of $[P_{4441}]NTf_2$. However, once the catalytically active species is formed in the phosphonium based ionic liquid, the reactivity seems to be higher, showing full conversion after only 9 minutes. In case of using $[C_4m_2im]NTf_2$, full conversion could be detected after 12 minutes.

From these kinetic measurements, the turnover frequency can be calculated according to Equation 2.

$$TOF = \frac{n_s}{n_c \cdot t_r}$$

TOF … turnover frequency [s^{-1}]

n_s… amount of substrate [mmol]

n_c… amount of catalyst [mmol]

t_r… reaction time for full conversion [s]

Equation 2. Calculation of the turnover frequency

In general, the turnover frequency describes how many molecules are converted by one catalyst molecule per time unit, therefore indicating how fast the reaction is performed. The results for the determination of the TOFs are shown in Table 9. The ionic liquid $[P_{4441}]NTf_2$ gave a higher turnover frequency than $[C_4m_2im]NTf_2$, which was expected according to the kinetic measurements.

Table 9. Turnover frequency of reduction using $[C_4m_2im]NTf_2$ and $[P_{4441}]NTf_2$

Ionic liquid	***Turnover frequency [s^{-1}]***
$[C_4m_2im]NTf_2$	0.28
$[P_{4441}]NTf_2$	0.37

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

TURNOVER NUMBERS

Beside the turnover frequency, which gives information about the rate of the reaction, the turnover number is often used to describe the stability of the catalyst. This means that the catalyst is reacted with a large excess of substrate until no conversion can be achieved anymore, resulting in the "exhaustive turnover number". Therefore it can be calculated how much substrate can be converted by the catalyst in the investigated system.

$$TON = \frac{n_p}{n_c}$$

TON … turnover number []

n_p… amount product [mmol]

n_c… amount catalyst [mmol]

Equation 3. Calculation of turnover number

Exhaustive turnover numbers were determined for $[C_4m_2im]NTf_2$ and $[P_{4441}]NTf_2$ and are shown in Table 10.

Table 10. Exhaustive turnover numbers for reduction using $[C_4m_2im]NTf_2$ and $[P_{4441}]Ntf_2$

Ionic liquid	***Turnover number***
$[C_4m_2im]NTf_2$	1258
$[P_{4441}]NTf_2$	793

Performed with 20 mmol aldehyde, 0.05 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

In contrast to the TOF, the turnover number in the case of the imidazolium based ionic liquid is higher compared to the phosphonium based one.

3.3.2 Isolation of the product

After the successful screening of different ionic liquids, isolation of the product was done in case of using $[C_4m_2im]NTf_2$, $[N_{4441}]NTf_2$. and $[P_{4441}]NTf_2$. Figure 28 demonstrates the work-flow of the isolation procedure.

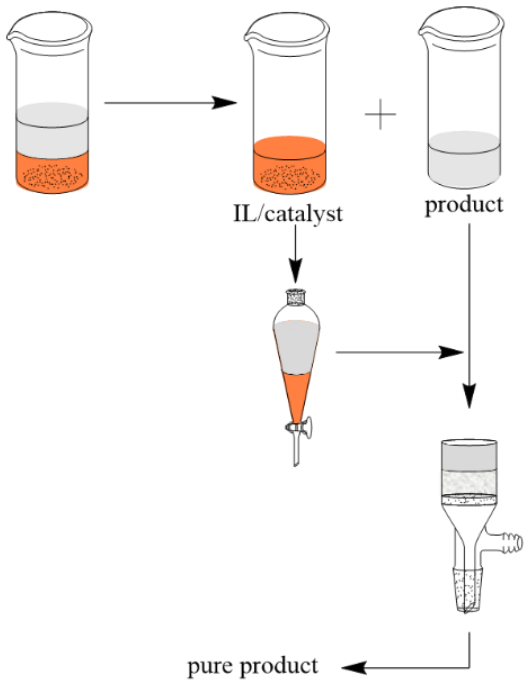


Figure 28. Work flow for the isolation of the product after the reaction

Once the reaction was completed, the catalyst phase was separated from the product phase. The ionic liquid was extracted several times using Et_2O in order to extract the entire product. After filtration of the combined organic phases over silica and evaporation of the solvent, the product was obtained in high purity according to NMR data. The results of the isolation experiments are shown in Table 11.

Table 11. Isolated yields for the reduction of 4-fluorobenzaldehyde to 4-fluorobenzyl alcohol

Ionic liquid	***Isolated yield [%]***
$[C_4m_2im]NTf_2$	95
$[N_{4441}]NTf_2$	92
$[P_{4441}]NTf_2$	93

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

Excellent yields could be achieved for all three ionic liquids, with the best result obtained with $[C_4m_2im]NTf_2$.

3.3.3 Investigations towards catalyst recycling

Apart from the benefit of having an easy way to separate the catalyst from the product phase without any metal contamination of the product, possible recycling of the catalyst is an advantage in liquid-liquid biphasic catalysis.

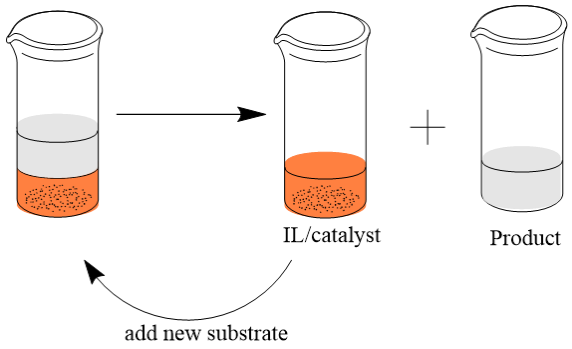


Figure 29. Scheme for possible recycling of the catalyst

Figure 29 demonstrates the concept of catalyst recycling. In general, the concept is based on the phase separation after complete reaction and product extraction. The remaining catalyst should then be available for a second run after addition of new substrate materials.

The results from the recycling experiments can be seen in Table 12. The yields for the first run were, as expected, excellent. Using Et_2O for extraction, no conversion could be detected for the second run, using $[C_4m_2im]NTf_2$ as catalyst carrying phase. With the usage of Et_2O/*n*-heptane 1:1, the same results were obtained. Changing to $[P_{4441}]NTf_2$ as ionic liquid did not lead to any improvement for the recycling studies.

Table 12. Data on recycling experiments

Solvent for extraction	***Yield 1st run using $[C_4m_2im]NTf_2$ [%]***	***Yield 2nd run using $[C_4m_2im]NTf_2$ [%]***	***Yield 1st run using $[P_{4441}]NTf_2$ [%]***	***Yield 2nd run using $[P_{4441}]NTf_2$ [%]***
Et_2O	>99	-	>99	-
Et_2O/ *n*-heptane 1:1	>99	-	>99	-

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

These results indicate a total loss of activity of the catalyst. A ^{31}P-NMR analysis of the catalyst directly after the reaction with $[C_4m_2im]NTf_2$ as immobilizing phase supports a decomposition of the catalyst, since several signals can be detected in regions where uncoordinated phosphorous compounds are usually found. Only a small signal can be detected which would fit to the signal of the (pre-)catalyst. A ^{31}P-NMR spectra of the dissolved pre-catalyst in $[C_4m_2im]NTf_2$ and a ^{31}P-NMR spectra of the ionic liquid phase after the reaction are shown in Figure 37.

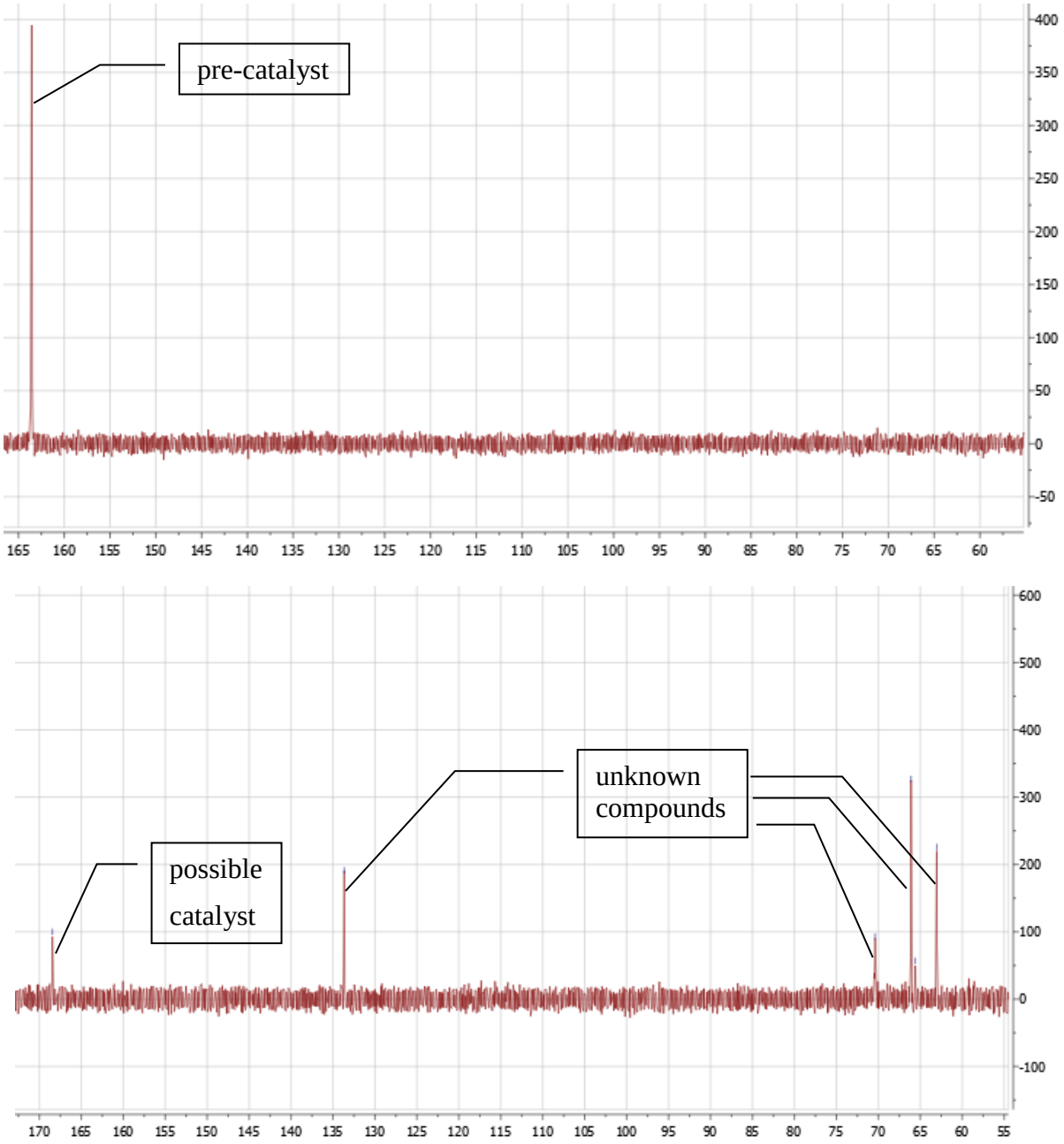


Figure 37. ^{31}P-NMR spectra of pre-catalyst dissolved in [C_4m_2im]NTf_2 (top) and ^{31}P-NMR spectra of [C_4m_2im]NTf2 phase after the reaction (bottom)

ALTERNATIVE PATHWAY FOR RECYCLING

Since the stability of the catalyst after full conversion of the substrate was a problem, a different approach had to be found. One strategy relied on a continuous addition of fresh substrate to the system before all of the starting material is used in order to keep the catalyst in a "working state" and avoid deactivation or decomposition. For this concept of continuous addition, kinetic data was of great importance to know when to add new substrate. This must be done before the catalyst converts all of the starting material.

For this purpose, a sample of the organic phase was taken every five minutes and substrate was added three times every five minutes. After the last addition (after 15 minutes), the reaction was run for further 75 minutes, taking samples of the organic phase after 20, 25 and 30 minutes. The results of this experiment are shown in Figure 38.

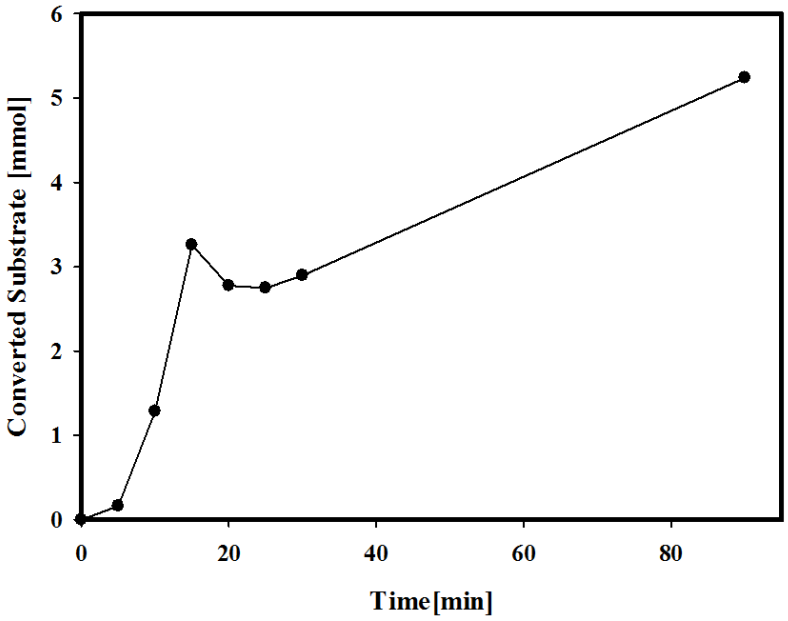


Figure 38. Data on continuous addition experiment using $[P_{4441}]NTf_2$

As it can be seen in the figure, substrate is continuously converted until it reaches a conversion maximum at 15 minutes reaction time. After that, the converted amount of substrate seems to decrease. An explanation for that would be a distribution of product over the two immiscible phases. Since the product is an alcohol, it is equally well soluble in ionic liquid and in *n*-heptane. However, in these experiments only the organic phase was analyzed, as taking a sample of the ionic liquid would have led to a loss of catalyst.

In order to quantify the entire amount of product in the biphasic system, the mixture was diluted with CH_2Cl_2 after 90 minutes, giving a homogeneous system. This revealed that 5.24 mmol of substrate was converted in total. That is about 66% of all substrate that was added, which is comparable to two and a half runs. This data suggests that the catalyst reactivity can be in principle retained by continuous addition of starting material.

The autoclave had to be depressurized and opened to take a sample and to add substrate. This might also have a negative influence on the reactivity of the air-sensitive catalyst. A possibility to avoid both problems would be the use of a liquid-liquid continuous flow system.

In this case, the product would be continuously extracted by a flow of organic solvent. Besides that, simplified analysis of the product outcome would be possible. However, due to the considerable effort of developing a continuous process, this set up was beyond the scope of this master thesis and will be addressed in future projects.

3.3.4 Catalysis without the addition of an external base

In order to simplify the work-flow, DBU, which is needed to activate the catalyst, as external base should be replaced. Two different approaches seem to be promising to achieve this simplification. One option is the use of the dihydride complex (Figure 39, right). If the catalytically active species is used instead of the pre-catalyst, no base would be required.

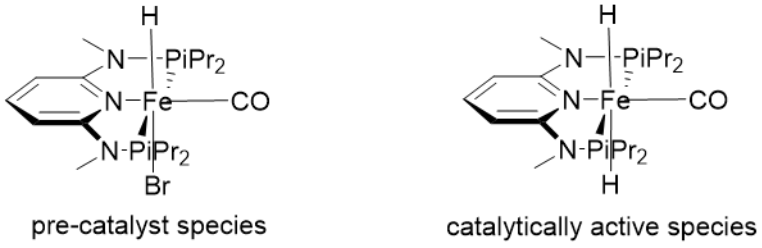


Figure 39. Pre-catalyst and catalytically active species

$[P_{4441}]NTf_2$ was chosen as reaction media for the base-free transformation using the dihydride complex. Using the same amount of ionic liquid, the dihydride complex was not completely dissolved, resulting in a cloudy solution. This can be considered as a drawback, compared to the pre-catalyst, which is dissolved in $[P_{4441}]NTf_2$ after a few minutes.

Table 13. Data on reduction using dihydride complex and $[P_{4441}]NTf_2$

Ionic liquid	***Yield [%]***
$[P_{4441}]NTf_2$	98

Performed with 2 mmol aldehyde, 0.5 mol% catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

Besides the solubility issue, the yield (Table 13) is slightly lower than in the case of the pre-catalyst. Additionally the stability of the active species seems to be an issue, which also limits its applicability for recycling studies. ^{1}H- and ^{31}P-NMR of the dihydride complex revealed that the compound already started to decompose after two hours in the ionic liquid.

The ^{31}P-NMR spectra of the dihydride complex in $[P_{4441}]NTf_2$ is shown in Figure 40. This is a considerable drawback compared to the pre-catalyst, which is stable in $[P_{4441}]NTf_2$ even over one week according to ^{1}H- and ^{31}P-NMR.

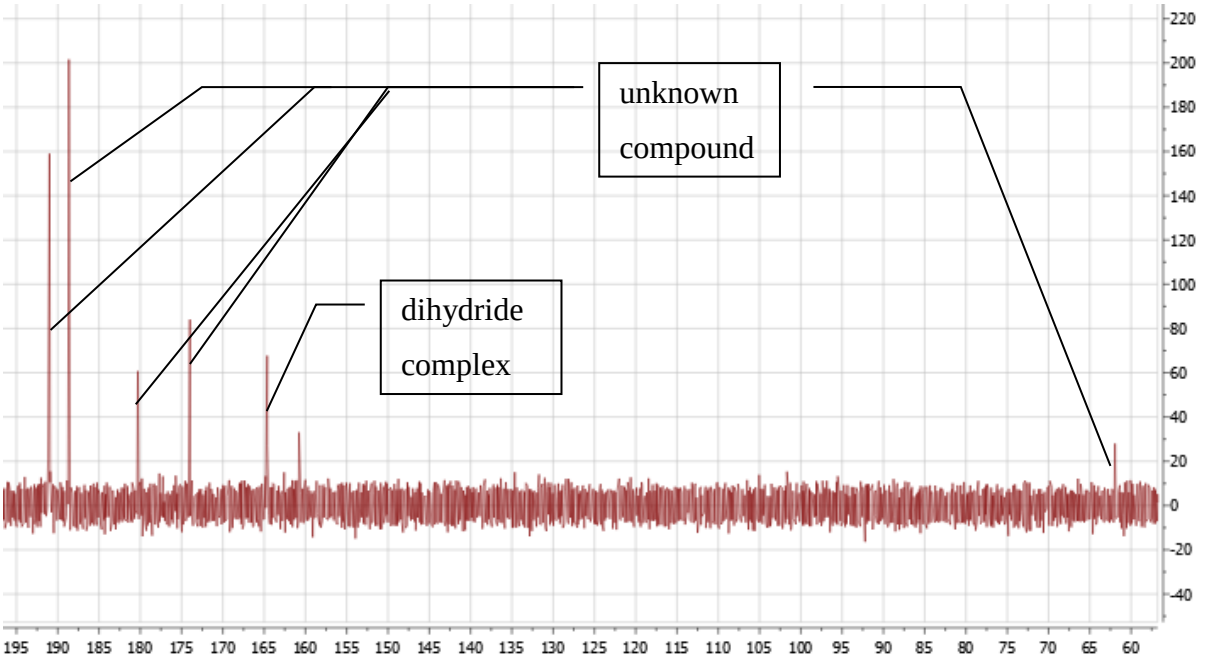


Figure 40. ^{31}P-NMR of the dihydride complex in $[P_{4441}\ NTf_2]$ after being dissolved for two hours

The second option was to use basic ionic liquids as solvent and as a base for the activation step. Since Brønsted basic ionic liquids were successfully used as substituent for external bases in previous papers[72], several basic ionic liquids were used as catalyst carrying phase. The results of these experiments can be seen in Figure 41.

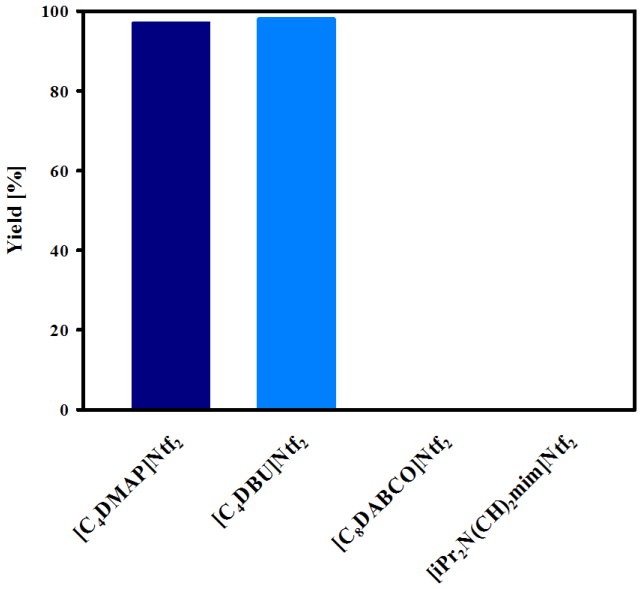


Figure 41. Ionic liquid screening using basic ionic liquids

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, in 255 mg ionic liquid/1.5 ml n-heptane
Yield determined via ^{19}F-NMR

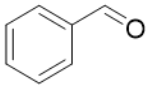
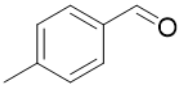
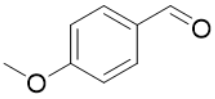
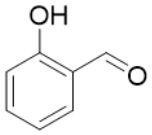
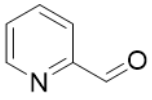
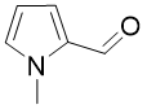
A considerable difference in the performance of the investigated basic ionic liquids could be observed. Using [C_4DMAP]NTf_2 and [C_4DBU]NTf_2 resulted in high yields without addition of an external base. Furthermore, no leaching of ionic liquid into the organic phase could be detected using ^{19}F-NMR analysis. Therefore, these ionic liquids were suitable as catalyst carrying phase and efficient reagents for the activation of the pre-catalyst at the same time.

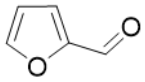
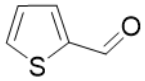
The DABCO based and the bulky basic imidazolium based ionic liquids showed no reactivity for catalysis, suggesting that the pre-catalyst could not be activated. Several properties seem to be important for the activation. Basicity of the ionic liquids may play a role in the activation step. Another possibility for the different reactivity might be steric effects. The investigated DMAP and DBU based ionic liquids tend to be sterically less hindered than the other two candidates.

3.3.5 Scope and limitation

After optimization and investigation of catalyst recycling, scope and limitation of the established biphasic system had to be explored. For that reason, a broad variety of aldehydes were used as substrates. Table 14 demonstrates the reactivity towards aromatic and hetero aromatic systems, using $[P_{4441}]NTf_2$ as ionic liquid.

Table 14. Scope and limitation for aromatic substrates

Entry	***Substrate***	***Yield detected by GC/MS [%]***	***Isolated yield [%]***
1		-	90
2		99	93
3		>99	89
4		88	79
5		98	87
6		0	-

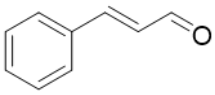
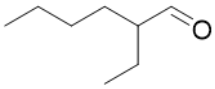
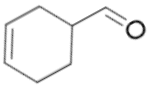
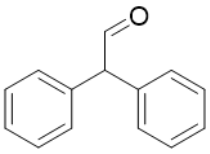
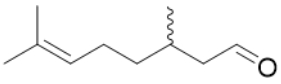
Entry	*Substrate*	*Yield detected by GC/MS [%]*	*Isolated yield [%]*
7		0	-
8		>99	89

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane

As it can be seen from the table above, good to excellent yields could be achieved for aromatic systems, even in the presence of coordinating groups. For example high yields were obtained for 4-methoxybenzaldehyde and 2-hydroxybenzaldehyde (entry **3** and **4)**, demonstrating the high reactivity of the established system towards aromatic aldehydes. In the case of heterocyclic systems, excellent yields could be obtained for pyridine and thiophene based substrates. However, in the case of furan and pyrrol based heterocycles, no conversion could be determined *via* GC/MS. This might be linked to strong coordination of the heterocycle itself to the (pre-)catalyst, leading to an inactivation of the complex.

Besides aromatic systems, aliphatic substrates were investigated as well. Table 15 shows the results for aliphatic systems.

Table 15. Scope and limitation for aliphatic substrates

Entry	*Substrate*	*Yield detected by GC/MS [%]*	*Isolated yield [%]*
1		99	88
2		8	-
3		2	-
4		0	-
5		25	21
6		59	45

Performed with 2 mmol aldehyde, 0.5 mol% pre-catalyst, 5 mol% DBU, in 255 mg ionic liquid/1.5 ml n-heptane

An excellent yield was obtained using cinnamon aldehyde as substrate (entry **1**). For long chain aldehydes (entry **2**and **3**), the system gave poor yield and no conversion at all in case of 4-cyclohexenecarbaldehyde (entry **4)**. The presence of aromatic groups in the molecule slightly increased the reactivity (entry **5**). Citronellal (entry **6**) showed a moderate yield according to GC/MS analysis. The isolated yield is slightly lower, since the purification of the product *via* column chromatography gave several mixed fractions with an unknown compound.

These results suggest, that the reactivity of the iron catalyst for aliphatic systems is much lower than in the case of the homogeneous system, using ethanol as solvent.

In general, it is difficult to compare the performance of catalysis in liquid-liquid biphasic systems with homogeneous catalysis relying on ethanol as solvent. If the reaction is done in the homogeneous system, almost full conversion with a substrate to catalyst ratio of 10 000 or more was achieved for all investigated substrates, including a variety of aliphatic compounds.

However, these reactions were performed at 40 °C and 30 bar H_2 pressure for 16 hours, using ethanol as solvent. Due to the substantial differences of the reaction conditions (room temperature, 10 bar H_2 pressure, one hour *vs.* 40 °C, 30 bar H_2 pressure, 16 hours), a comparison between the Kirchner catalyst in homogeneous and biphasic system is hard to make.

A comparison to another iron based catalyst, containing a PONOP ligand established by Hu and coworkers[59] can be made, since this catalyst was operated at 8 bar H_2 pressure for 24 hours at room temperature, using methanol as solvent. The catalysis was performed with 10 mol% catalyst, which is twenty times the amount compared to the reactions reported in this work.

Kirchner etal. **2014**[58] (used in this work) Hu et al. **2015**[59]

Figure 42. Kirchner's and Hu's catalyst for the reduction of aldehydes

In the case of aromatic systems, the established biphasic system gave higher yields for the same substrates than the PONOP based system. In contrast, the system established by Hu *et al.* gave yields between 55% and 74% for aliphatic systems.

Comparing the established biphasic system with Hu's catalyst for substrate 4-cyclohexenecarbaldehyde (Table 15, entry **4**), a yield of 60% could be achieved with Hu's catalyst in homogeneous phase, whereas no conversion could be determined the in case of the biphasic system.

Within this context, lower reactivity for aliphatic systems can be observed for both systems in comparison to aromatic substrates.

4 Conclusion

In this work, several ionic liquids were synthesized *via* alkylation and ion exchange. These ionic liquids were used as catalyst carrying phase in liquid-liquid biphasic reduction of aldehydes to the corresponding primary alcohols, using Kirchner's catalyst and hydrogen gas as hydrogen source.

As a test reaction for this system, 4-fluorbenzaldehyd was reduced to 4-fluorobenzyl alcohol. Optimization of the reaction was done with different hydrophobic ionic liquids. The use of $[C_4m_2im]NTf_2$, $[N_{4441}]NTf_2$ and $[P_{4441}]NTf_2$ showed the highest yields and no losses of catalyst or ionic liquid in the product phase could be detected. Excellent isolated yields, fast reaction times and a simple work up strategy could be developed and highlighted the positive impact of the liquid-liquid biphasic system for this reaction. Further studies on scope and limitations of the system revealed high reactivity for aromatic substrates, whereas aliphatic substances are only poorly converted. Interestingly the catalyst showed much higher reactivity towards citronellal than for other aliphatic substrates.

Studies on the catalyst recovery and reuse were not successful, as the catalyst seems to decompose during workup after the reaction. However, it could be demonstrated that a continuous addition of the substrate is possible while maintaining catalyst activity.

Additional improvement of the system could be achieved by substitution of the required base DBU with a Brønsted basic ionic liquid. Further studies will address the use of these basic ionic liquids as reaction media in a continuous-flow approach.

5 Experimental part

5.1 Materials and methods

All used reagents and solvents were purchased from commercial suppliers and directly used without further purification, if not stated otherwise. Anhydrous CH_2Cl_2, Et_2O, *n*-heptane, MeOH, THF and toluene were dried over molecular sieve and/or *via* Na/K alloy and degassed *via* pump freezing.

Hydrogenation reactions were carried out in a Roth steel autoclave using a Tecsis manometer.

^{1}H-, ^{19}F- and ^{31}P-NMR were recorded in acetonitrile-d_6, chloroform-*d*, methylene chloride-d_2, dimethylsulfoxide-d_6 or methanol-d_4 solution on a Bruker Avance 200 (200 MHz) or Bruker Avance 250 (250 MHz). All chemical shifts (δ) are reported in ppm, using tetramethylsilane for ^{1}H-, trichlorofluoromethane for ^{19}F- and triphenylphosphine for ^{31}P-NMR spectra. All coupling constants (J) are reported in Hertz (Hz). The following abbreviations are used to describe multiplets: s = singlet, bs = broad singlet, d = duplet, t = triplet, q = quintet, m = multiplet.

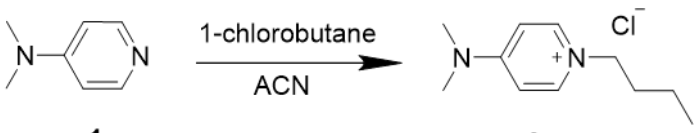
GC–MS analysis was conducted on a ISQ LT Single quadrupole MS (Thermo Fisher) directly interfaced to a TRACE 1300 Gas Chromatographic systems (Thermo Fisher), using a Rxi-5Sil MS (30 m, 0.25mm ID) cross-bonded dimethyl polysiloxane capillary column. The oven program temperature was 60 °C (2 min)//20 °C/min//300 °C (5 min).

HPLC analysis was performed on a Jasco HPLC unit equipped with a PDA detector, which was used for detection of 4-fluorobenzaldehyde and 4-fluorobenzyl alcohol. A Maisch ReproSil 100 C18 250 × 4.6, 5 µm was used with ACN:H_2O (0.1% TFA) 65:35 as solvent and a flow of 1 ml/min; detection was done at 210 nm, at 30 °C column oven temperature, 25 °C tray temperature. Retention times were 8.4 min for 4-fluorobenzyl alcohol, 13.3 min for 4-fluorobenzaldehyde and 20.2 min for methylbenzoate as internal standard.

5.2 Synthesis of ionic liquids

5.2.1 Synthesis of ionic liquids and precursors *via* alkylation

*5.2.1.1 Synthesis of 1-butyl-4-(dimethylamino)pyridine-1-ium chloride (**2**)*



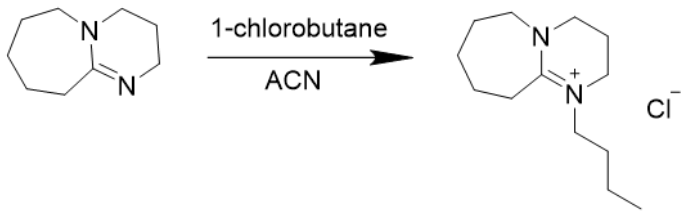
1 **2**

N,*N*-Dimethylpyridine-4-amine **1** (1.0 equiv., 93 mmol, 11.4 g) was dissolved in HPLC-grade ACN under Ar atmosphere. Freshly distilled 1-chlorobutane (1.95 equiv., 180 mmol, 16.9 g) was added in one batch. The reaction mixture was refluxed for four days. During the reaction, the product precipitated from the reaction mixture as colorless solid. After reaching full conversion as detected by ^{1}H-NMR, the reaction mixture was cooled to room temperature. The solid was separated from the solution *via* filtration. The solid was washed three times with Et_2O and dried *in vacuo* to yield **2** as colorless solid (19.2 g, 96%)

^{1}H-NMR (200 MHz, methylene chloride-d_2) δ = 8.44 (d, *J* = 7.8 Hz, 2H, *H*-pyridine), 6.92 (d, *J* = 7.8 Hz, 2H, *H*-pyridine), 4.27 (t, *J* = 7.3 Hz, 2H, N-$\underline{CH_2}$-CH_2), 3.16 (s, 6H, N-$\underline{CH_3}$), 1.77 (q, *J* = 7.5 Hz, 2H, -CH_2-$\underline{CH_2}$-CH_2), 1.39 – 1.18 (m, 2H, -CH_2-$\underline{CH_2}$-CH_3), 0.88 ppm (t, *J* = 7.3 Hz, 3H, -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[73]

*5.2.1.2 Synthesis of 1-butyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium chloride (**4**)*



3 **4**

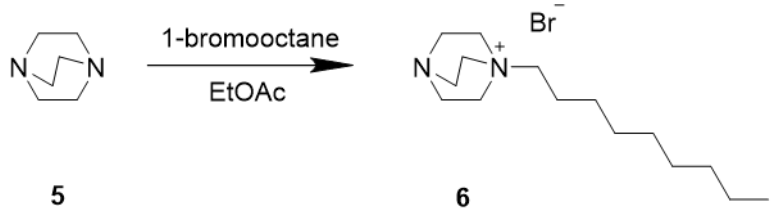
Freshly distilled 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine **3** (1.0 equiv., 82.0 mmol, 12.4 g) was dissolved in HPLC-grade ACN under Ar atmosphere. Freshly distilled 1-chlorobutane (1.9 equiv., 152.0 mmol, 13.8 g) was added in one batch.

The reaction mixture was refluxed for four days to reach full conversion as detected by ^{1}H-NMR. The solvent was removed giving an orange oil. The product was washed several times with Et_2O and EE and dried *in vacuo* to yield **4** as orange oil (11.1 g, 56%).*

^{1}H-NMR (250 MHz, chloroform-*d*) δ = 3.71 – 3.37 (m, 8H), 2.88 – 2.75 (m, 2H), 2.13 (p, *J* = 5.9 Hz, 2H, N-$\underline{CH_2}$-CH_2), 1.91 – 1.69 (m, 8H), 1.62 (quint, *J* = 15.5, 7.5 Hz, 2H, CH_2-$\underline{CH_2}$-CH_2-), 1.37 (sext, *J* = 7.3 Hz, 2H, CH_2-$\underline{CH_2}$-CH_3)), 0.98 ppm (t, *J* = 7.2 Hz, 3H; -CH_2-$\underline{CH_3}$)

Compound **4** was used directly without further purification for the synthesis of 5.2.1.2.

*5.2.1.3 Synthesis of 1-octyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (**6**)*



5 **6**

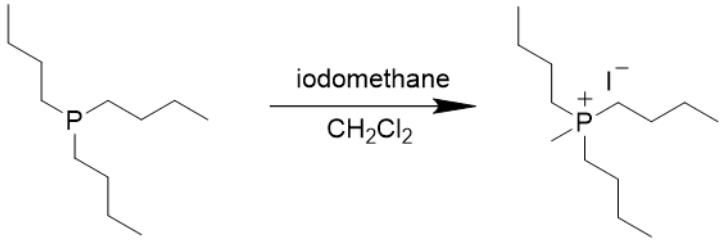
1,4-Diazabicyclo[2.2.2]octane **5** was dried for one hour *in vacuo* before use. Compound **5** (1.0 equiv., 49.1 mmol, 5.5 g) was dissolved in EE under Ar atmosphere. 1-Bromooctane (1.0 equiv., 49.1 mmol, 9.5 g) was dissolved in EE and added to the solution containing **5** dropwise. The reaction mixture was refluxed for three days, showing full conversion *via* ^{1}H-NMR. During the reaction, the product precipitated from the reaction mixture as light yellow solid. The reaction mixture was cooled to room temperature and the solid was separated from the solution *via* filtration. The solid was washed several times with EE and anhydrous THF. The product was dried *in vacuo*, giving **6** as light yellow solid (5.9 g, 39%)

^{1}H-NMR (250 MHz, methylene chloride-d_2) δ = 3.36 – 3.09 (m, 14H), 1.8-1.68 (m, 2H), 1.46 – 1.20 (m, 13H), 0.98 ppm (t, J = 7.1 Hz, 3H)

Analytical data is in accordance with literature.[74]

* Even after several attempts of purification, impurities of 10-20% of an unknown compound according to ^{1}H-NMR (signals at approx. 2.4 ppm and approx. 2 ppm) could not be removed.

*5.2.1.4 Synthesis of tributyl(methyl)phosphonium iodide (**8**)*



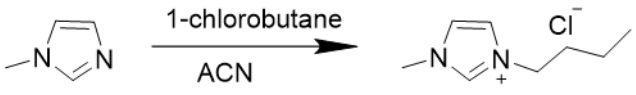
7 **8**

Freshly distilled tributylphosphine **7** (1.0 equiv., 96.3 mmol, 19.5 g) was dissolved in anhydrous CH_2Cl_2 under Ar atmosphere. The solution was cooled to 0 °C and iodomethane (1.1 equiv., 105.9 mmol, 15.0 g) was added dropwise. The reaction was allowed to warm to room temperature and then refluxed for one hour. After cooling to room temperature, the solvent was removed, giving a colorless solid. The product was dried *in vacuo* to give **8** as colorless solid (31.3 g, 94%)

^{1}H-NMR (250 MHz, chloroform-*d*) δ = 2.52 – 2.32 (m, 6H, P-$\underline{CH_2}$-CH_2-), 2.07 (d, *J* = 13.3 Hz, 3H, P-$\underline{CH_3}$), 1.52 – 1.49 (m, 12H, -CH_2-$\underline{CH_2}$- $\underline{CH_2}$-), 0.93 ppm (t, 9H, *J* = 7.3 Hz, -CH_2-$\underline{CH_3}$)

^{31}P-NMR (250 MHz, chloroform-*d*) δ = 43.4 ppm (s)

*5.2.1.5 Synthesis of 3-butyl-1-methyl-imidazolium chloride (**10**)*



9 **10**

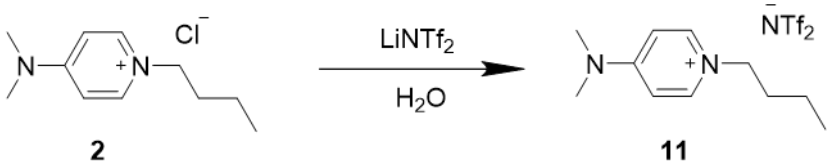
Freshly distilled **9** (1.0 equiv., 2.12 mol, 173.8 g) was dissolved in HPLC grade ACN under Ar atmosphere. Freshly distilled 1-chlorobutane (1.3 equiv., 2.8 mol, 92.6 g) was added in one batch. The reaction was mechanically stirred and refluxed. The conversion of the reaction was monitored *via* ^{1}H-NMR, showing unconverted **9** after two days of refluxing. 1-Chlorobutane (0.2 equiv., 551 mmol, 51.0 g) was added. After three additional days, full conversion was detected *via* ^{1}H-NMR. Unreacted 1-chlorobutane and solvent was removed *via* distillation from the reaction mixture, giving a brown oil. The product was dissolved in ACN and crystallized in EE, giving an off-white solid. This procedure was done twice. The product was finally recrystallized from ACN/EE, giving **10** (369.2 g, 85%) as colorless solid.

^{1}H-NMR (200 MHz, chloroform-*d*) δ= 10.61 (s, 1H, *H*-imidazol), 7.54 (s, 1H, *H*-imidazol), 7.39 (s, 1H, *H*-imidazol), 4.27 (t, *J* = 7.4 Hz, 2H, N-$\underline{CH_2}$-CH_2-), 4.06 (s, 3H, N-$\underline{CH_3}$), 2.02 – 1.71 (m, 2H, N-CH_2-$\underline{CH_2}$-), 1.45 – 1.14 (m, 2H, -CH_2-$\underline{CH_2}$-CH_3), 0.89 ppm (t, *J* = 7.3 Hz, 3H, -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[75]

5.2.2 Synthesis of ionic liquids *via* ion exchange

*5.2.2.1 Synthesis of 1-butyl-4-(dimethylamino)pyridinium bis(trifluoromethane)sulfonamide (**11**)*

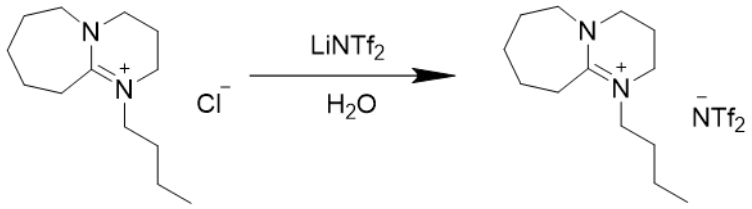


Compound **2** (1.0 equiv., 32.7 mmol, 7.0 g) was dissolved in H_2O. Lithium bis(trifluoromethane)sulfonamide ($LiNTf_2$) (1.1 equiv., 35.9 mmol, 10.3 g) was dissolved in H_2O and added dropwise to the solution containing **2**. The mixture was stirred for one hour at room temperature. A formation of a second phase was observed during the reaction. After the reaction, the phases were separated. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with MilliQ-grade H_2O until the chloride test using an $AgNO_3$ solution was negative. The organic phase was dried over Na_2SO_4, filtrated and the solvent was removed. After drying *in vacuo* overnight, **11** (12.9 g, 86%) was obtained as colorless liquid.

^{1}H-NMR (200 MHz, methylene chloride-d_2) δ = 8.44 (d, *J* = 7.8 Hz, 2H, *H*-pyridine), 6.92 (d, *J* = 7.8 Hz, 2H, *H*-pyridine), 4.27 (t, *J* = 7.3 Hz, 2H, N-$\underline{CH_2}$-CH_2), 3.16 (s, 6H, N-$\underline{CH_3}$), 1.77 (q, *J* = 7.5 Hz, 2H, -CH_2-$\underline{CH_2}$-CH_2), 1.39 – 1.18 (m, 2H, -CH_2-$\underline{CH_2}$-CH_3), 0.88 ppm (t, *J* = 7.3 Hz, 3H, -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[76]

*5.2.2.2 Synthesis of 1-butyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium bis(trifluoromethane)sulfonamide (**12**)*



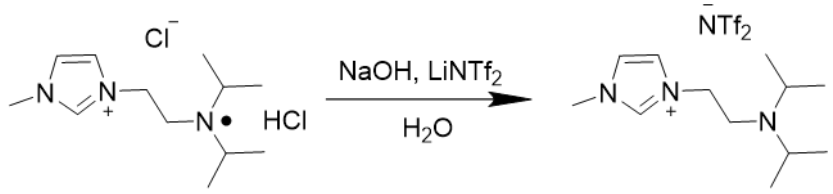
4 **12**

Compound **12** was prepared according to procedure 5.2.2.1 using **4** (1.0 equiv., 45.3 mmol, 11.1 g) and $LiNTf_2$ (1.1 equiv., 49.9 mmol, 14.3 g). The product was washed several times with Et_2O and dried *in vacuo*. Compound **10** (18.8 g, 85%) was yielded as orange liquid.

^{1}H-NMR (250 MHz, chloroform-*d*) δ = 3.71 – 3.37 (m, 8H), 2.88 – 2.75 (m, 2H), 2.13 (p, *J* = 5.9 Hz, 2H, N-$\underline{CH_2}$-CH_2), 1.91 – 1.69 (m, 8H), 1.62 (quint, *J* = 15.5, 7.5 Hz, 2H, CH_2-$\underline{CH_2}$-CH_2-), 1.37 (sext, *J* = 7.3 Hz, 2H, CH_2-$\underline{CH_2}$-CH_3)), 0.98 ppm (t, *J* = 7.2 Hz, 3H; -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[72]

*5.2.2.3 Synthesis of 3-(2-(diisopropylamino)ethyl)-1-methyl-imidazol-3-ium bis(trifluoromethane)sulfonamide (**14**)*



13 **14**

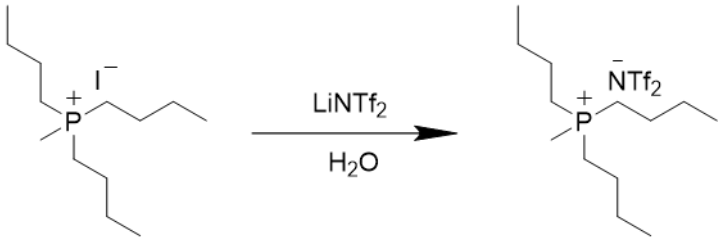
Compound **13** (1.0 equiv., 17.2 mmol, 5.0 g) was dissolved in dichloromethane. Sodium hydroxide (1.0 equiv., 17.2 mmol, 0.7 g) was dissolved in water and added to the solution containing **13**. The biphasic system was stirred for ten minutes at room temperature. Lithium bis(trifluoromethane)sulfonamide (1.1 equiv., 18.6 mmol, 5.3 g) was dissolved in water and added in one batch. The mixture was stirred for one hour at room temperature. After the reaction, the phases were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with MilliQ-grade water until no chloride could be detected using an $AgNO_3$ solution. The solution was dried over Na_2SO_4,

filtrated and the solvent was removed. The product was dried *in vacuo* overnight, giving **14** (7.65 g, 88%) as colorless liquid.

^{1}H-NMR (250 MHz, methylene chloride-d_2) δ = 8.49 (s, 1H, *H*-imidazol), 7.25 (t, *J* = 1.8 Hz, 1H, *H*-imidazol), 7.15 (t, *J* = 1.8 Hz, 1H, *H*-imidazol), 4.04 (d, *J* = 6.1 Hz, 2H,N-$\underline{CH_2}$-CH_2-), 3.84 (s, 3H, N-$\underline{CH_3}$), 2.92 (hept, *J* = 6.6 Hz, 2H, CH_2-$\underline{CH_2}$-N), 2.72 (t, *J* = 5.5 Hz, 2H, N-$\underline{CH}$-*i*Pr_2), 0.81 ppm (d, *J* = 6.6 Hz, 12H, CH-$\underline{^{i}Pr_2}$)

Analytical data is in accordance with literature.[68]

*5.2.2.4 Synthesis of tributyl(methyl)phosphonium bis(trifluoromethane)sulfonamide (**15**)*



8 **15**

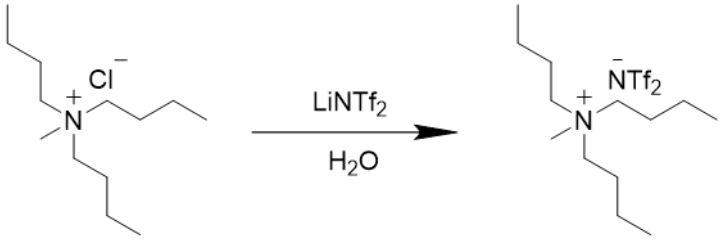
Compound **8** (1.0 equiv., 55.8 mmol, 20.0 g) was dissolved in a mixture of H_2O and acetone 4:1. Lithium bis(trifluoromethane)sulfonamide (1.1 equiv., 53.6 mmol, 18.2 g) was dissolved in H_2O and added in one batch. The reaction was stirred overnight at room temperature. Formation of a second phase was observed. After the reaction, acetone is removed under reduced pressure. The phases were separated. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with MilliQ-grade H_2O until the chloride test using an $AgNO_3$ solution was negative. The organic phase was dried over Na_2SO_4, filtrated and the solvent was removed. After drying *in vacuo* overnight, compound **15** (25.8 g, 89%) was obtained as colorless liquid.

^{1}H-NMR (250 MHz, chloroform-*d*) δ = 2.52 – 2.32 (m, 6H, P-$\underline{CH_2}$-CH_2-), 2.07 (d, *J* = 13.3 Hz, 3H, P-$\underline{CH_3}$), 1.52 – 1.49 (m, 12H, -CH_2-$\underline{CH_2}$- $\underline{CH_2}$-), 0.93 ppm (t, 9H, *J* = 7.3 Hz, -CH_2-$\underline{CH_3}$).

^{31}P-NMR (250 MHz, $CDCl_3$) δ = 43.4 ppm (s)

Analytical data is in accordance with literature.[77]

*5.2.2.5 Synthesis of tributyl(methyl)ammonium bis(trifluoromethane)sulfonamide (**17**)*

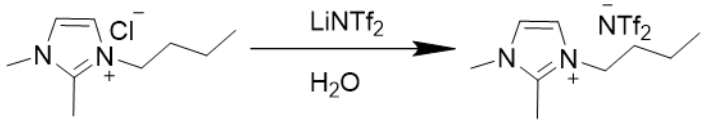


16 **17**

According to procedure 5.2.2.1 compound **17** was prepared from **16** (1.0 equiv., 20.8 mmol, 4.9 g) and $LiNTf_2$ (1.1 equiv., 22.1 mmol, 6.6 g). Ionic liquid **17** (8.4 g, 84%) was obtained as colorless liquid.

^{1}H-NMR (200 MHz, methylene chloride-d_2) δ = 3.18 (d, *J* = 8.2 Hz, 6H, N-$\underline{CH_2}$-$\underline{CH_2}$-), 2.97 (s, 3H, N-$\underline{CH_3}$), 1.79 – 1.47 (m, 6H, - CH_2-$\underline{CH_2}$-CH_2-), 1.47 – 1.23 (m, 6H, CH_2-$\underline{CH_2}$-CH_3), 1.00 ppm (t, *J* = 7.2 Hz, 9H, -CH_2-$\underline{CH_3}$)

*5.2.2.6 Synthesis of 3-butyl-1,2-dimethyl-imidazolium bis(trifluoromethane)sulfonamide (**19**)*



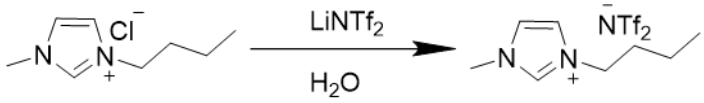
18 **19**

According to procedure 5.2.2.1 compound **19** was prepared from **18** (1.0 equiv., 34.6 mmol, 6.5 g) and $LiNTf_2$ (1.1 equiv., 38 1 mmol, 10.9 g). Ionic liquid **19** (13.3 g, 88%) was obtained as colorless liquid.

^{1}H-NMR (250 MHz, methylene chloride-d_2) δ = 7.24 (q, *J* = 2.2 Hz, 2H, *H*-imidazol), 4.08 (t, *J* = 7.5 Hz, 2H, -N-$\underline{CH_2}$-CH_2-), 3.82 (s, 3H,-N-$\underline{CH_3}$), 2.62 (s, 3H C-$\underline{CH_3}$), 1.92 – 1.72 (m, 2H, CH_2-$\underline{CH_2}$-CH_2), 1.41 (dq, *J* = 14.6, 7.3 Hz, 2H, -CH_2-$\underline{CH_2}$-CH_3), 1.00 ppm (t, *J* = 7.3 Hz, 3H, -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[78]

*5.2.2.7 Synthesis of 3-butyl-1-methyl-imidazolium bis(trifluoromethane)sulfonamide (**20**)*



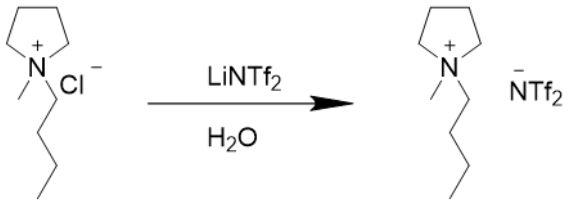
10 **20**

According to procedure 5.2.2.1 compound **20** was prepared from **10** (1.0 equiv., 107.3 mmol, 18.7 g) and $LiNTf_2$ (1.1 equiv., 112.6 mmol, 32.3 g). Ionic liquid **20** (41.1 g, 91%) was obtained a colorless liquid.

^{1}H-NMR (200 MHz, chloroform-*d*) δ = 10.61 (s, 1H, *H*-imidazol), 7.54 (s, 1H, *H*-imidazol), 7.39 (s, 1H, *H*-imidazol), 4.27 (t, *J* = 7.4 Hz, 2H, N-$\underline{CH_2}$-CH_2-), 4.06 (s, 3H, N-$\underline{CH_3}$), 2.02 – 1.71 (m, 2H, N-CH_2-$\underline{CH_2}$-), 1.45 – 1.14 (m, 2H, -CH_2-$\underline{CH_2}$-CH_3), 0.89 ppm (t, *J* = 7.3 Hz, 3H, -CH_2-$\underline{CH_3}$).

Analytical data is in accordance with literature.[79]

*5.2.2.8 Synthesis of 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonamide (**22**)*



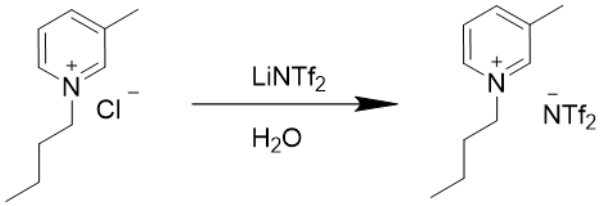
21 **22**

According to procedure 5.2.2.1 compound **22** was prepared from **21** (1.0 equiv., 56.3 mmol, 10.0 g) and $LiNTf_2$ (1.05 equiv., 59.1 mmol, 17 g) Ionic liquid **22** (20.4 g, 86%) was obtained as orange liquid.

^{1}H-NMR (250 MHz, methylene Chloride-d_2) δ = 3.61 – 3.37 (m, 4H, pyrrolidin N-$\underline{CH_2}$-CH_2-CH_2-), 3.37 – 3.22 (m, 2H, N-$\underline{CH_2}$-CH_2), 3.03 (s, 4H N-$\underline{CH_3}$), 2.36 – 2.16 (m, 4H, pyrrolidin N-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-), 1.76 (m, 8.2, 6.0 Hz, 2H, -CH_2-$\underline{CH_2}$-CH_2-), 1.55 – 1.32 (m, 2H, -CH_2-$\underline{CH_2}$-CH_3), 1.08 – 0.93 ppm (t, J= 7.1 Hz, 3H, -CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[80]

*5.2.2.9 Synthesis of 1-butyl-3-methylpyridinium bis(trifluoromethane)sulfonamide (**24**)*



23 **24**

According to procedure 5.2.2.1 compound **24** was prepared from **23** (1.0 equiv., 80.8 mmol, 15 g) and $LiNTf_2$ (1.05 equiv., 84.8 mmol, 24.4 g). Ionic liquid **24** (20.4 g, 86%) was obtained as colorless liquid.

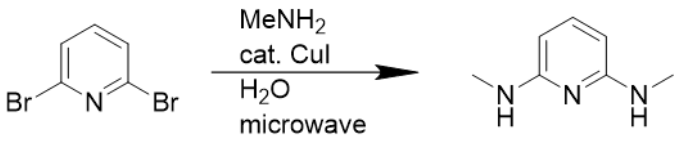
^{1}H-NMR (250 MHz, methylene chloride-d_2) δ = 8.49 – 8.30 (m, 2H, *H*-pyridine), 8.11 (t, J = 9.0 Hz, 1H, *H*-pyridine), 7.77 (t, J = 7.3 Hz, 1H, *H*-pyridine), 4.49 – 4.25 (m, 2H, N-$\underline{CH_2}$-CH_2), 2.48 – 2.34 (m, 3H, pyridine-$\underline{CH_3}$), 1.93 – 1.67 (m, 2H, CH_2- $\underline{CH_2}$-CH_2), 1.37 – 1.08 (m, 2H, CH_2- $\underline{CH_2}$-CH_3), 0.93 – 0.70 ppm (m, 3H, - CH_2-$\underline{CH_3}$)

Analytical data is in accordance with literature.[81]

5.3 Synthesis of ligand and iron complexes

5.3.1 Synthesis of the ligand

*5.3.1.1 Synthesis of N,N'-dimethyl-2,6-diaminopyridine (**26**)*



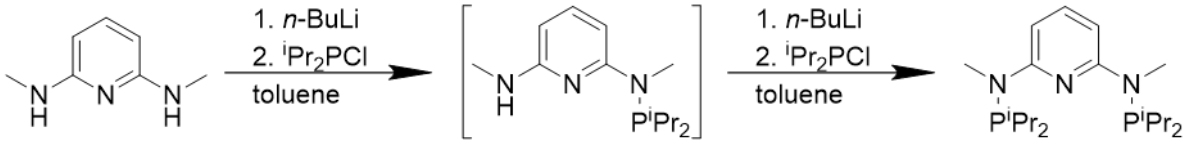
25 **26**

Four 20 ml microwave vials were charged with compound **25** (1.0 equiv., 25 mmol, 6.0 g), CuI (10 mg) and an aqueous solution of methylamine (6.0 equiv.,150 mmol, 12 ml, 41 wt%) each. The vials were sealed and the reaction mixture was heated to 180 °C for 2 hours in the microwave. After cooling to room temperature, K_2CO_3 (12.2 equiv., 304 mmol, 42 mg) was added and the solvent was removed under reduced pressure. The residue was taken up in anhydrous CH_2Cl_2, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation (high vacuum, 180-205 °C). Compound **26** (3.1 g, 23%) was obtained as a light brown solid.

^{1}H-NMR (250 MHz, dimethylsulfoxide-d_6) δ = 7.1 (t, J = 7.8 Hz, 1H,*H*-pyridine), 5.86 (d , J = 4.8 Hz, 2H,-NH-CH_3), 5.6 (d, J = 7.9 Hz, 2H,*H*-pyridine), 2.71 ppm (t, J = 4.9 Hz, 6 H, -NH-CH_3)

Analytical data is in accordance with literature.[82]

*5.3.1.2 Synthesis of N,N'(diisopropylphosphino)-N,N'-2,6-diaminopyridine (**27**)*



26 **27**

Compound **26** (1.0 equiv., 51 mmol, 7.0 g) was dissolved in anhydrous toluene and cooled to -20 °C . *n*-BuLi (2.5 M solution in hexane, 1.15 equiv., 58.7 mmol, 23.3 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 additional hours. The mixture was cooled to -60 °C and diisopropylchlorophosphine

(1.0 equiv., 51 mmol, 8.3 ml) was added dropwise. The solution was allowed to warm to room temperature, stirred for additional 2 hours and then stirred overnight at 80 °C.

After cooling to room temperature, a degassed, saturated $NaHCO_3$ solution (24.4 ml) was added. The phases were separated, the organic phase was dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. The obtained brown oil was then dissolved in toluene and the procedure above was carried out for a second time. The crude product was purified by crystallization from anhydrous MeOH at -30 °C. Compound **27** (7.0 g, 37%) was obtained as a white solid.

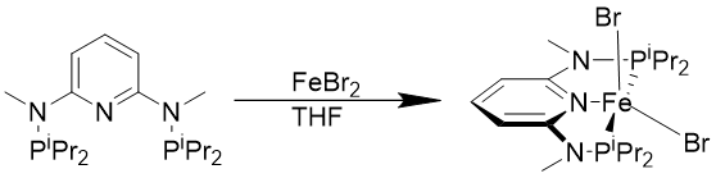
^{1}H-NMR (250 MHz, dimethylsulfoxide-*d_6*) δ = 7.3 (t, J= 7.5 Hz, 1H, *H*-pyridine), 6.6 (s, 2H, *H*-pyridine), 3.03 (s, 3H, -N-$\underline{CH_3}$), 1.17 – 0.87 ppm (m, 28H, -P-$^{i}\underline{Pr_2}$).

^{31}P-NMR (250 MHz, dimethylsulfoxide-*d_6*) δ = 68.8 ppm (bs)

Analytical data is in accordance with literature.[83]

5.3.2 Synthesis of the iron complexes

*5.3.2.1 Synthesis of [(^{i}Pr-PNPMe)Fe(Br)$_2$] (**28**)*



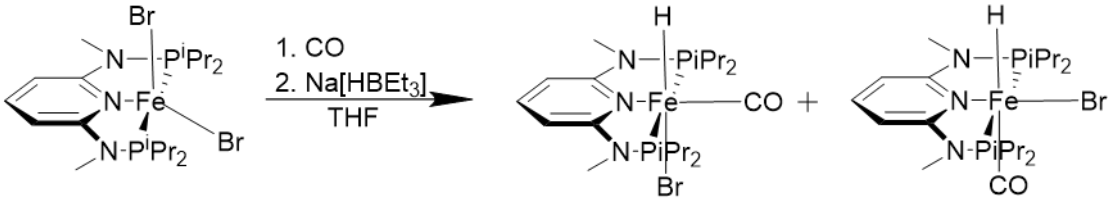
27 **28**

Compound **27** (1.0 equiv., 8.2 mmol, 1.8 g) was dissolved in anhydrous THF. $FeBr_2$ (1.05 equiv., 8.6 mmol, 2.5 g) was added and the resulting suspension was stirred for 3 days. The amount of solvent was reduced to approximately 1/10. Anhydrous Et_2O was added to complete the precipitation. The supernatant solution was removed, the residue was washed with anhydrous Et_2O and dried *in vacuo*. Compound **28** (3.5 g, 84%) was obtained as yellow solid.

^{1}H-NMR (250 MHz, acetonitrile-*d_6*/methanol-*d_4*) δ = 8.91 (s, 1H, *H*-pyridine), 7.63 (s, 2H, *H*-pyridine), 4.36 (s, 6H, -N-$\underline{CH_3}$), 2.79 ppm (m, 28H, -P-$^{i}\underline{Pr_2}$).

^{31}P-NMR (250 MHz, acetonitrile-*d_6*/methanol-*d_4*) δ = 134.1 ppm (s)

*5.3.2.2 Synthesis of [Fe(iPr-PNPMe)(H)(CO)(Br)] (**29**)*



28 **29** **30**

Compound **28** (1.0 equiv., 1 mmol, 0.5 g) was dissolved in anhydrous THF. Carbon monoxide was bubbled through the mixture for 5 minutes, giving a dark blue solution. The reaction mixture was cooled to 0 °C, a solution of $Na[HBEt_3]$ in toluene (1 M, 1.1 equiv., 1 08 mmol, 1.08 ml) was added dropwise and the mixture was stirred for 1 hour at room temperature. The solution was filtrated and the solvent was removed. The residue was dissolved in anhydrous THF and precipitated by adding anhydrous pentane. The supernatant solution was removed and the solid was washed several times with anhydrous Et_2O. A mixture of **29** and **30** (**29**+**30**: 200 mg, 44%) was obtained as an orange powder.

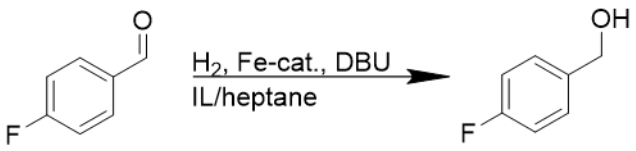
^{1}H-NMR (250 MHz, methylene chloride-d_2) δ = 7.31 (1H, t, J=7.4 Hz, *H*-pyridine), 5.81 (d, *J* = 8.2 Hz, 2H, *H*-pyridine), 3.01 (s, 3H, -N-$\underline{CH_3}$), 1.79 – 1.35 (m, 28H), -21.9 ppm (1H, t, J= 58 Hz Fe-$\underline{H}$),

^{31}P-NMR (250 MHz, methylene chloride-d_2) δ = 164, 161 ppm

Analytical data is in accordance with literature.[58]

5.4 Hydrogenation experiments

5.4.1 General procedure for the reduction of 4-fluorobenzaldehyde



OPERATIONS INSIDE THE GLOVEBOX

Compound **29** (0.05 equiv., 0.01 mmol, 5 mg) was dissolved in ionic liquid (255 mg) inside the glass tube of the steel autoclave. 4-Fluorobenzaldehyde (1.0 equiv., 2 mmol, 248 mg) was mixed with anhydrous *n*-heptane (1.5 ml) and DBU (0.05 equiv., 0.1 mmol, 15 µg) and taken up with a syringe.

OPERATIONS OUTSIDE THE GLOVEBOX

The steel autoclave was evacuated and flushed with Ar. The glass tube was transferred inside the autoclave. After sealing the autoclave, it was evacuated and flushed again with Ar. The autoclave was connected to the hydrogen supply. The substrate was quickly added. The autoclave was flushed with hydrogen. The reaction was carried out under 10 bar H_2 pressure at room temperature for one hour. After the reaction, the pressure was released and the glass tube was removed from the autoclave.

For screening studies one drop of the organic phase was taken as sample for ^{19}F-NMR analysis.

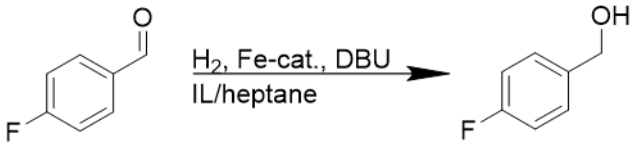
ISOLATION OF THE PRODUCT

The organic phase was separated from the ionic liquid. The ionic liquid was extracted four times with 2 ml Et_2O. The combined organic phases were filtrated over silica. The solvent was removed *in vacuo*, giving 4-fluorobenzyl alcohol as colorless liquid (233 - 238.4 mg, 92-95%)

^{1}H-NMR (200 MHz, chloroform-*d*) δ = 7.37 – 7.15 (m, 2H), 7.06 – 6.86 (m, 2H), 4.58 (s, 2H), 1.76 ppm (s, 1H)

Analytical data is in accordance with literature.[84]

5.4.2 Determination of turnover numbers



The determination of turnover numbers was performed according to procedure 5.4.1 using $[P_{4441}]NTf_2$ or $[C_4m_2im]NTf_2$ as ionic liquid and 4-fluorobenzaldehyde as substrate (10.0 equiv., 10 mmol), compound **29**, (0.005 equiv., 0.1 mmol, 5 mg) and DBU (0.05 equiv., 0.1 mmol, 15 µg).

The reaction was carried out under 10 bar H_2 pressure at room temperature for approx. 80 hours.

After the reaction, the mixture was diluted with CH_2Cl_2 to give a homogenous solution. One drop of this solution was taken as sample for ^{19}F-NMR analysis.

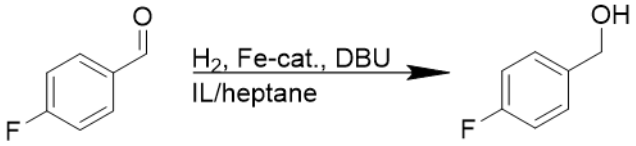
$$TON = \frac{n_p}{n_c}$$

TON … turnover number []

n_p… amount product [mmol]

n_c… amount catalyst [mmol]

5.4.3 Determination of turnover frequencies



For the determination of turn over frequencies, a sample was prepared as described in 5.4.1. After starting the reaction, samples are taken every three minutes by releasing the pressure from the autoclave, taking one drop of the organic phase and pressurizing the autoclave again.

$$TOF = \frac{n_s}{n_c \cdot t_r}$$

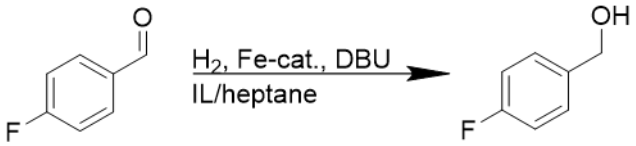
TOF … turnover frequency [s^{-1}]

n_s… amount of substrate [mmol]

n_c… amount of catalyst [mmol]

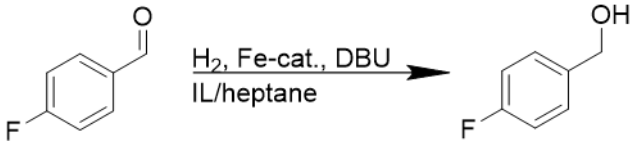
t_r… reaction time for full conversion [s]

5.4.4 Recycling experiments



The reaction was carried out as described in 5.4.1. After the reaction, the phases were separated under Ar atmosphere. The ionic liquid was extracted four times with 2 ml Et_2O or Et_2O/*n*-heptane (1:1). Traces of solvents were removed *in vacuo*. New substrate was added according to 5.4.1. After the reaction, one drop of the organic phase was taken as sample for ^{19}F-NMR analysis.

5.4.5 Recycling experiments with continuous addition of substrate



The reaction was carried out as described in 5.4.1 for 5 min. The pressure was released from the autoclave and one drop of the organic phase was taken as sample for analysis. Fresh 4-fluorobenzaldehyde (1.0 equiv., 2 mmol, 248 mg) was added in 0.5 ml *n*-heptane and the autoclave was pressurized again. This procedure described above was repeated several times. In total 8 mmol substrate were used in this experiment.

$$S_c = \frac{A_{p(t)}}{(A_{p(t)}+A_{s(t)})} \cdot n_{s(t)}$$

S_c … converted substrate at certain reaction time [mmol]

$A_{p(t)}$… area product peak at certain reaction time []

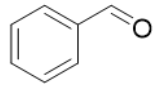
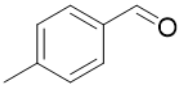
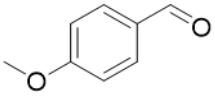
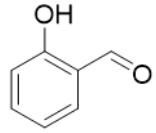
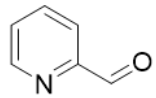
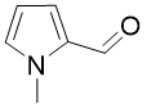
$A_{s(t)}$… area substrate peak at certain reaction time []

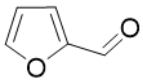
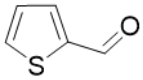
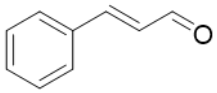
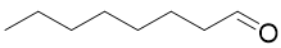
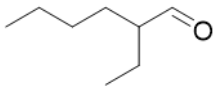
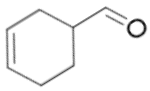
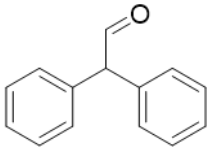
$n_{s(t)}$… amount of substrate added until certain reaction time [mmol]

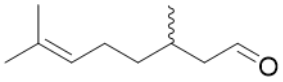
5.4.6 Scope and limitations

Scope and limitations of the system were determined according to the general procedure 5.4.1 using $[P_{4441}]NTf_2$ as ionic liquid and different substrates (1.0 equiv., 2 mmol).

After the extraction with Et_2O, 20-40 µl of the combined phases were taken as sample for GC-MS analysis. Isolation is done as described in 5.4.1.

Entry	***Substrate***	***GC-MS***	***^{1}H-NMR***	***Isolated yield [%]***
1		-	**^{1}H-NMR** (200 MHz, chloroform-*d*) δ = 7.40 – 7.14 (m, 5H), 4.63 (s, 2H), 1.6 ppm (s, 1H)[85]	90
2		RT (GC): 6.00 min MS: 122.06 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ =7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 4.66 (s, 2H), 2.38 (s, 3H), 1.80 ppm (s, 1H)[86]	93
3		RT (GC): 7.43 min MS: 138.08 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 7.32 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 4.64 (s, 2H), 3.85 (s, 3H), 1.62 ppm (s, 1H)[84]	89
4		RT (GC): 5.22 min MS: 123.08 $(M-H)^+$	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 7.23 – 6.88 (m, 3H), 6.78 (td, *J* = 7.8, 1.0 Hz, 2H), 4.76 ppm (s, 2H)[87]	79
5		RT (GC): 6.00 min MS: 109.07 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 8.48 (d, *J* = 4.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.28 – 7.05 (m, 2H), 4.70 (s, 2H), 4.02 ppm (s, 1H)[88]	87
6		RT substrate (GC): 4.78 min MS: 110.09 $(M-H)^+$	-	-

Entry	*Substrate*	*GC-MS*	*^{1}H-NMR*	*Isolated yield [%]*
7		RT substrate (GC): 3.15 min MS: 98 M^+	-	-
8		RT (GC): 5.07 min MS: 114.083 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 7.37 – 7.27 (m, 1H), 7.02 (ddd, *J* = 8.4, 4.7, 3.4 Hz, 2H), 4.87 (s, 2H), 1.74 ppm (s, 1H)[89]	89
9		RT (GC): 7.38 min MS: 134.11 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 7.67 – 7.08 (m, 5H), 6.76 – 6.48 (m, 1H), 6.47 – 6.19 (m, 1H), 4.41 – 4.16 (m, 2H), 1.80 ppm (s, 1H)[84]	88
10		RT substrate (GC): 5.41 min MS: 97.09 $(M\text{-}X)^+$	-	-
11		RT substrate (GC): 4.39 min MS: 98.07 $(M\text{-}X)^+$	-	-
12		RT substrate (GC): 4.2 min MS: 110.04 M^+	-	-
13		RT (GC): 9.77 min MS: 196 M^+	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 7.45 – 7.19 (m, 10H), 4.33 – 4.14 (m, 3H), 1.6 ppm (s, 1H)[90]	21

Entry	*Substrate*	*GC-MS*	*^{1}H-NMR*	*Isolated yield [%]*
14		RT (GC): 6.83 min MS: 152.15 $(M\text{-}X)^+$	**^{1}H-NMR** (250 MHz, chloroform-*d*) δ = 5.15-5.05 (m, 1H), 3.75 – 3.59 (m, 2H), 2.14 – 1.84 (m, 2H), 1.79 – 1.58 (m, 6H), 1.58 – 1.36 (m, 2H), 1.36 – 1.07 (m, 2H), 0.91 ppm (d, *J* = 6.6 Hz, 3H)[91]	45

Additional column chromatography was done to receive a pure product in cases of entry **4** (PE/EE 3:1), **13** (PE then EE) and **14** (1st column PE/EE 15:1, 2nd column PE/EE 3:1).

Analytical data is in accordance with literature.[59-91]

5.5 HPLC analysis

CALIBRATION CURVES

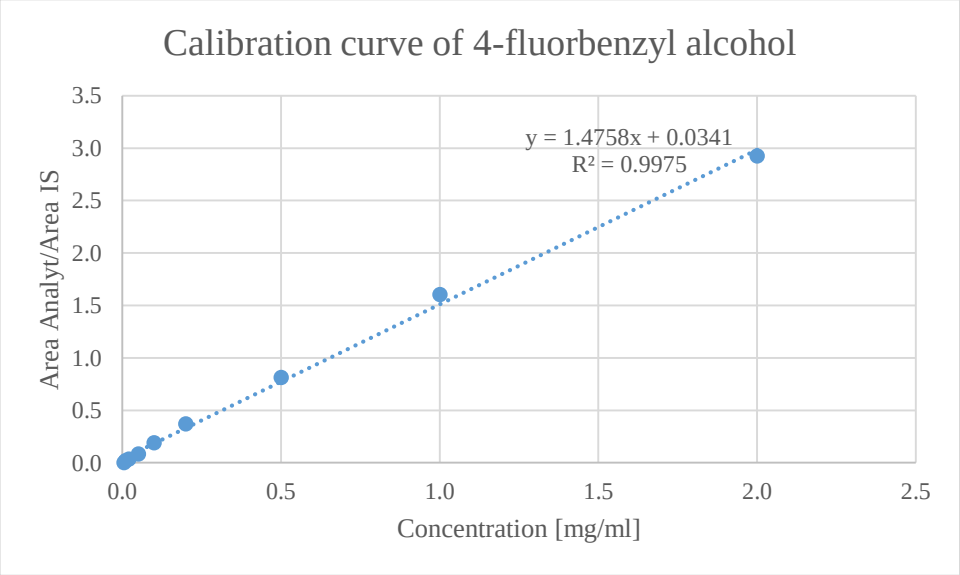
4-FLUOROBENZYL ALCOHOL

A stock solution of 100 mg 4-fluorobenzyl alcohol in 10 ml MeOH was prepared. A dilution series, using this stock solution, was prepared (Table 16).

1 ml of each solution was transferred into a HPLC vial and 200 µl of methylbenzoate (50.1 mg/ 100 ml in MeOH) as internal standard (IS) was added. For the analysis, the area of the analyte was divided by the area of the IS.

Table 16. Concentration of solutions of 4-fluorobenzyl alcohol for the measurement of the calibration curve

Solution	***Concentration [mg/ml]***
A	2
B	1
C	0.5
D	0.2
E	0.1
F	0.05
G	0.02
H	0.01
I	0.005



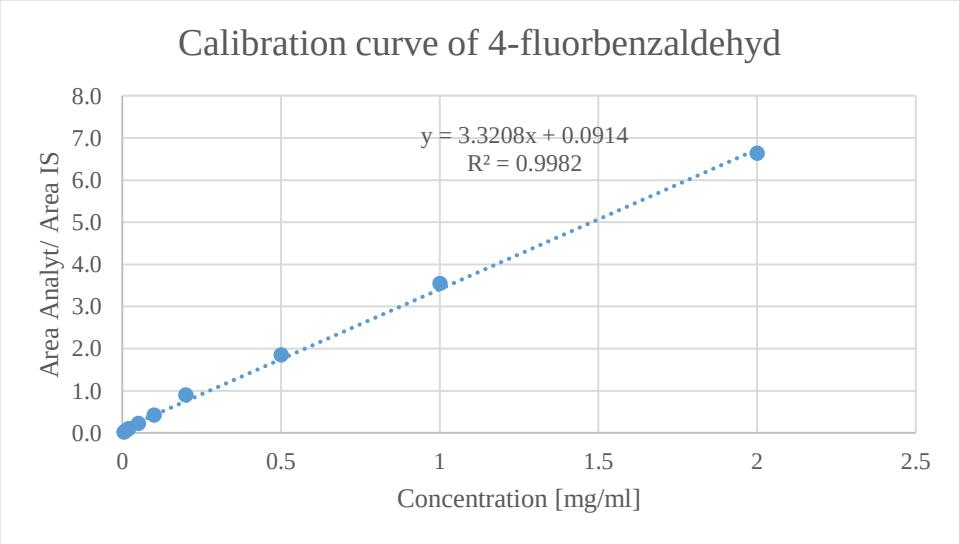
4-FLUOROBENZALDEHYDE

A stock solution of 100 mg4-fluorobenzaldehyde in 10 ml MeOH was prepared. A dilution series, using this stock solution, was prepared (see Table 17).

1 ml of each solution was transferred into a HPLC vial and 200 µl of methylbenzoat (50.1 mg/ 100 ml in MeOH) as internal standard (IS) were added. For the analysis, the area of the analyte was divided through by area of the IS.

Table 17. Concentration of solutions of 4-fluorbenzaldehyd for the measurement of the calibration curve

Solution	***Concentration [mg/ml]***
A	2
B	1
C	0.5
D	0.2
E	0.1
F	0.05
G	0.02
H	0.01
I	0.005



6 Appendix

6.1 List of abbreviations

ACN ..... acetonitrile
Ar ..... argon
$AgNO_3$ ..... silver nitrate
BF_4^- ..... tetrafluoroborate
[bmim]BF_4 ..... 3-butyl-1-methyl-imidazolium tetrafluoroborate
[bmim]PF_6 ..... 3-butyl-1-methyl-imidazolium hexafluorophosphate
[bmim]NTf_2 ..... 3-butyl-1-methyl-imidazolium bis(trifluoromethane)sulfonamide
CH_2Cl_2 ..... dichlormethane
CuI ..... copper (I) iodine
DABCO ..... 1,4-diazabicyclo[2.2.2]octane
DBU ..... 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine
DMAP *N*,*N*-dimethylpyridine-4-amine
DMSO ..... dimethylsulfoxide
EE ..... ethylacetate
Et_2O ..... diethylether
$FeBr_2$ ..... iron (II) bromide
GC ..... gaschromatography
H_2 ..... hydrogen
H_2O ..... water
HPLC ..... high performance liquid chromatography
IL ..... ionic liquid
IS ..... internal standard
K_2CO_3 ..... potassium carbonate
MS ..... mass spectroscopy
MeOH ..... methanol
Na_2SO_4 ..... sodium sulfate
Na[HEt_3] ..... sodium triethylborohydride
n-BuLi ..... butyllithium
NTf_2^- ..... bis(trifluoromethane)sulfonamide
PF_6^- ..... hexafluorophosphate
Rh ..... rhodium
SILP ..... supported ionic liquid phase
THF ..... tetrahydrofuran
TOF ..... turnover frequency
TON ..... turnover number
TPP ..... triphenylphosphine
TPPTS ..... triphenylphosphinetrisulfonate

6.2 List of figures

6.3 List of tables

7 References

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