1. Introduction

In ancient Greece, a common execution method was to shut the convict in a bathroom with smoldering coals. Although the ancient Greek did not now the cause of death, they assumed that a change in the composition of the air caused the harm when inhaled. Even though it was unknown at that time, this was one of the first applications for carbon monoxide.[1] Additionally, carbon monoxide has been relevant in smelting of ore since the Bronze age. Carbon monoxide is a colorless, odorless, tasteless gas, that, when inhaled, combines with hemoglobin. Consequently, the delivery of oxygen to body tissue is inhibited. Typically, carbon monoxide (CO) is a product of the incomplete combustion of carbon-based substances. CO poisoning is still the most frequently cause of fatal poisonings in many industrialized countries.[2]

Although carbon monoxide is highly toxic, it is commonly used in organic synthesis as a precursor for basic chemicals such as methanol or formic acid. Carbon monoxide is granted an important role in the smelting of ore, for instance, in the production of steel.[3] In addition, organometallic carbonyl compounds are of high interest due to a high structural variety.[3] A carbon monoxide molecule has a dipole moment (0.122 D) with a slight negative partial charge at the carbon atom. Employed as a ligand, the lone pair of carbon can donate electron density to a transition metal, forming a σ-bond. If the transition metal possesses mutable electrons as well, a π-back donation from the metal to the LUMO of CO (antibonding π^* molecular orbital) takes places. The strength of this π-back donation depends on the valence state of the transition metal and the character of other ligands.

Transition metal carbonyls exhibit a wide structural variety. CO is able to form a range of bonding modes. It can either be bound terminally, for instance, in $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ and $Mn_2(CO)_{10}$ or in a bridging mode. In the most common bridging mode, the CO ligand merges a pair of metal centers, e. g., in $Co_2(CO)_8$, $Fe_2(CO)_2$ and $Fe_3(CO)_{12}$.[4] CO bridges between three or even four metals are also known, for instance, in $Rh_6(CO)_{12}(\mu^3\text{-}CO)_4$.[4] In addition to these symmetric bridges, a semi-bridging variation is known (e. g. in (2,2'-bipyridine)$Fe_2(CO)_8$), as well as a side-on coordination, in which CO acts as a four electron or six electron donor, for instance, the $Mn_2(CO)_5$ unit in $(\mu\text{-}Ph_2PCH_2PPh_2)_2Mn_2(CO)_5$ (Ph = phenyl).[4] Less common are bonding modes in which both, carbon and oxygen, bond to different metals as, for instance, in $Cp_2Ti(\mu\text{-}\eta^2\text{-}CO)Mo(CO)_2Cp$ (Cp = cyclopentadienyl).[5] Today, especially clusters containing both, main group and transition metals, are of interest in research not only in view of catalytic applications but also with regard to new structural motifs in bimetallic clusters and the resulting magnetical or optical properties.[6–9]

Conventionally, standard organic solvents (e. g., toluene, ether, tetrahydrofuran, dimethylformamide, etc.) are used for the synthesis of metal carbonyl clusters. Recently, ionic liquids have gained a certain interest due to their variety of tunable properties, such as a wide liquid phase (−20 °C – 400 °C), a high thermal stability (until 400 °C), a polar but often aprotic character, and a high stability toward redox-reactions.[10–14] The term ionic liquid is generally applied to salts with a melting point below 100 °C and was first introduced by Walden with the synthesis of ethylammonium nitrate in 1914.[15] This class of unusual solvents, with properties much different from those of common organic solvents, is typically constituted of large, low charged organic cations and weakly coordinating anions.[10–13] As cations, various derivatives of, for example, alkylammonium, alkylimidazolium, alkylpyridinium, or alkylphosphonium can be found. Tetrafluoroborates, terachloroaluminates, alkyl phosphates, triflates or bistrifylimides represent widely applied anions.

Ionic liquids have already been noticed as feasible reaction media for the synthesis of nanoparticles, zeolites and metal-organic frameworks and recently for structural chemistry, too.[10–14] There are already a few remarkable compounds available: a new chlatrate type modification of germanium $\square_{24}Ge_{136}$ ($\square$: vacancy), a copper complex $[(\eta^1\text{-}S_8)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})][Al(OR^F)_4]$ with two sulphur rings coordinated to Cu^+, a triangular chromium cluster found in $[CrCl_3]_3$@[BMIm][OMe] or a three-dimensional polybromide network in $[C_4MPyr]_2[Br_{20}]$.[16–19] Due to their high redox stability, ionic liquids are anticipated to be suitable reaction media for metal carbonyls as well as metal halides. Especially imidazolium based ionic liquids, with triflate or bistrifylimide as the anion, seem to be of good use. These ionic liquids show a high stability toward reduction, good solubility of metal halides and metal carbonyls and its cations are large enough to crystallize with large, low-charged cluster compounds. Accordingly, the synthesis and characterization of kinetically stabilized compounds is in the realm of possibilities. In addition, some ionic liquids appear as suitable reaction media for coordination chemistry, since their constituents are weakly coordinating.

The chemistry of metal carbonyls is a long known field. The aim of this thesis is to investigate, if ionic liquids can beneficially contribute to metal carbonyl chemistry. Firstly, the reactivity of metal carbonyls in suitable ionic liquids has been analyzed aiming at the synthesis and characterization of novel metal carbonyl compounds. Additionally, reactions of metal carbonyls with nitrile ligands have been investigated.

A second aspect in this thesis concerns transparent conducting oxides. Semiconducting metal oxides with a band gap throughout the visible range are called transparent conducting oxides (TCOs).[20] With the development and manufacturing of portable and/or flexible electronics, displays, multi-functional windows and solar cells, the interest in transparent conducting oxides has dramatically increased. In recent years, mainly new *n*-type materials have been developed. Furthermore, theoretical methods to understand and predict the properties of TCOs have been applied.[21–24] The main focus of research activities has been directed on materials based on ZnO, In_2O_3 and SnO_2. Currently, these materials are dominating industrial application. The most common used TCO material is still indium oxide doped with tin (ITO), which can exhibit a specific resistivity less than $1 \cdot 10^{-4}\,\Omega\,\mathrm{cm}$.[20,25] On the other hand, a multitude of reasons exist to go for new TCO materials. Most preferably, the synthesis should be easy, cheap and green. The opto-electrical properties should be suitable to flexible, transparent electronics. Ideally, the material shows low toxicity, is stable in air and at high temperature, is chemical resistant and is easy to process (etching, patterning, etc.). Due to their lacking efficiency, *p*-type TCO materials are not used in industrial applications, yet. Thus, for opto-electronic application, it is important to identify a suitable *p*-type conducting material.[20–22,24] Aiming at non toxic, *p*-type conducting materials, a polyol-mediated synthesis of nanoscale doped and co-doped tin oxide shall be developed in this thesis.[26–29]

2. Experimental

2.1. Methods

In this work, two different experimental strategies were applied. Firstly, the synthesis of new inorganic compounds, such as carbonyl clusters or coordination compounds and networks, was carried out in ionic liquids in sealed glass ampules. And secondly, the polyol method was utilized for preparing nanoscaled transparent conducting oxides.

2.1.1. Working under inert gas atmosphere

Working with air sensitive precursors and reaction products requires careful sample handling. For this purpose, standard Schlenk and glovebox techniques were applied. More precisely, a combined evacuation/inert gas device was utilized for this work (Figure 1). The equipment, consisting of an evacuation line and an inert gas line, was used to evacuate and to dry glass apparatus and introduce inert gas, as well as to dehumidify samples by evacuation. The inert gas employed was argon (Argon 4.8, from Air Liquide, Paris, France). By being conveyed through a series of drying towers containing silica gel, potassium hydroxide, molecular sieve (4 Å), and phosphorus pentoxide, and then through titanium sponge at 600 °C (heated in a LOBA tube furnace from HTM Reetz, Berlin, Germany), the argon was purified before use. Vacuum ($p < 10^{-3}$ mbar) was produced by a rotary vane vacuum pump from Vacuubrand (Wertheim, Germany). A cold trap, cooled with liquid nitrogen, was inserted between the vacuum pump and the evacuation line to prevent flow of volatiles into the pump. The pressure was measured with a manometer VAP 5 from Vacuubrand.

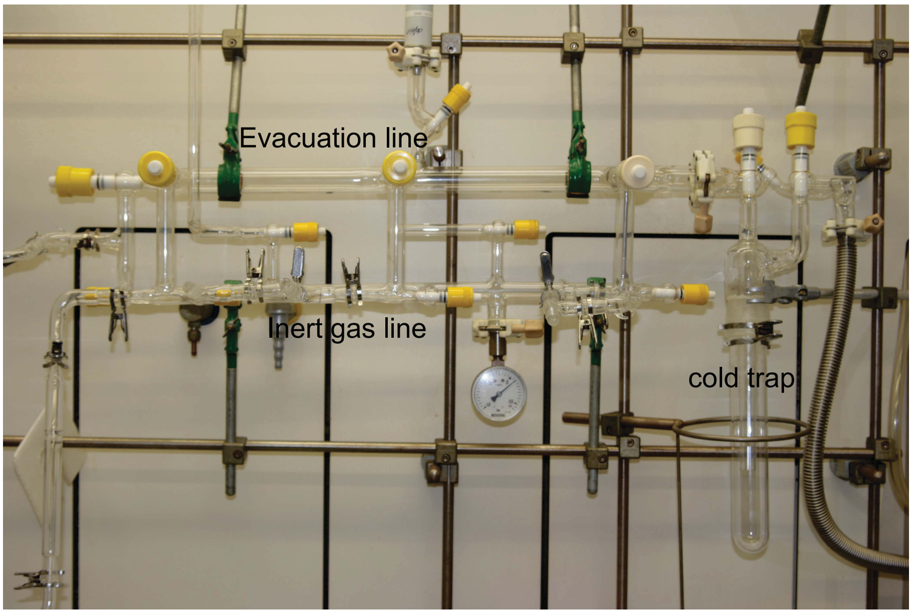

Figure 1: Inert gas device.

Prior to its use, glass devices (e. g., flasks, ampules) were always evacuated to reduced pressure of $1{\cdot}10^{-3}$ mbar, simultaneously dehydrated at 300 °C and subsequently filled with inert gas. This procedure was repeated three times to ensure that residues of water and oxygen had been removed.

Chemicals were weighed in and decanted in gloveboxes from BRAUN (Munich, Germany) (Figure 2). For this purpose, glass devices were brought into the glovebox under vacuum ($p < 10^{-3}$ mbar). If possible, the chemicals were pestled together and funneled into the flasks. These were thoroughly closed and passed out the glovebox. The processing of the experiments was then performed at the evacuation/inert gas device. After reaction the glass devices were opened in a glovebox equipped with a microscope.

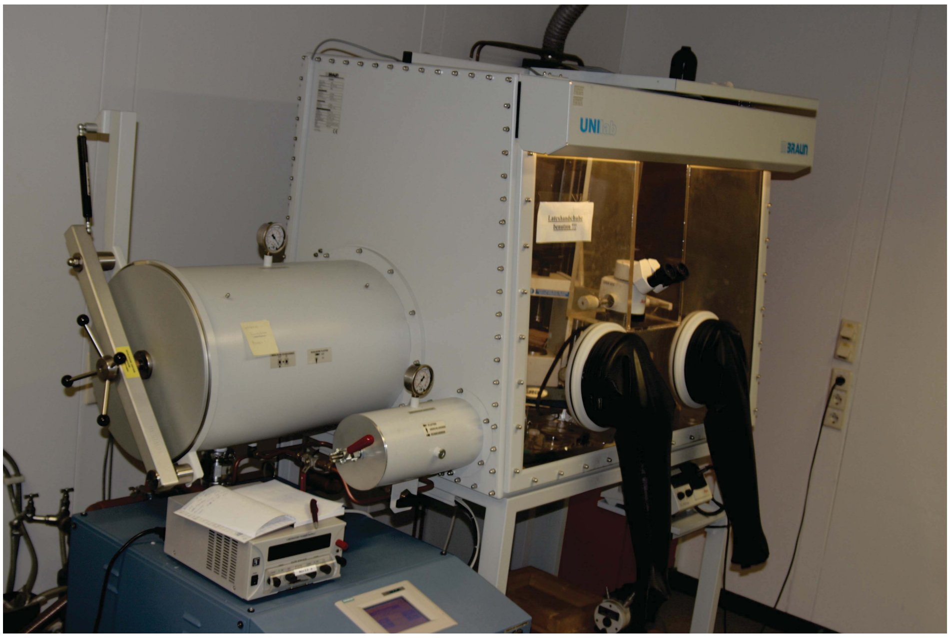

Figure 2: Glovebox with microscope.

2.1.2. Ionic Liquids

The range of synthetic methods and reaction conditions in inorganic chemistry has always been large. Worth to mention are syntheses in liquid ammonia, conventional organic solvents, deposition from the gas phase or reactions in molten salts and solid-state reactions. The latter examples usually need high temperatures up to more than 1000 °C. Ionic liquids, as a novel type of reaction media, offer a new field in inorganic synthesis.

The term ionic liquids is generally applied to salts with a melting point below 100 °C.[10–14] Ionic liquids usually comprise large organic cations, such as imidazolium, alkyl ammonium, piperidinium or pyrolidinium derivates. These cations exhibit a low charge, which is often delocalized by mesomerizm effects. The anions are often large, low charged organic or inorganic anions, such as phosphates, tetrachloroaluminate, halides, nitrates, sulfates or imides. The first known ionic liquid, ethyl ammonium nitrate $[EtH_3N][NO_3]$, showing a melting point of 12 °C, was presented by Walden as early as 1914; hence, ionic liquids have been known for almost a hundred years now.[15] The enormous number of ionic liquids that can be realized by permutation of cations and anions, permits a design of properties that is highly difficult to achieve with conventional solvents. Today, from the multitude of theoretical possible combinations, only a few hundred are commercially available.[30–32]

The properties attributed to ionic liquids, which are rarely found in this combination in conventional organic solvents, provide interesting possibilities for the synthesis of inorganic compounds. A wide range for the liquid phase (for some: $-50\,°C$ to $+400\,°C$), an insignificant low vapor pressure, a stability at high-temperatures (for some, up to 400 °C) and a broad electrochemical window are feasible properties. Furthermore, many ionic liquids exhibit weakly coordinating properties, which enables the synthesis of thermodynamically metastable products. Other ionic liquids do not contain protic functional groups (such as –OH, $–NH_2$, –COOH); these ionic liquids often combine polar, aprotic, and weakly coordinating properties, which have been important for the synthesis presented in this study.

Despite the possibilities ionic liquids provide, it is necessary to carefully choose a suitable ionic liquid for a specific task. Only proper combination of properties lead to a successful result. The stability toward redox-reactions and the synthetic conditions used need as much attention as, for example, the solubility of precursors and products. By using the same cation and only changing the anions slightly from trifluoromethanesulfonate to bis(trifluoromethanesulfonyl)imide, a significant change in the solubility, for instance, of metal iodides can be observed. Moreover, by varying the length of an alkyl group slightly around one or two CH_2-groups, not only the solubility can be modified, but also the resulting product may change due to sterical influences.

Taking the above mentioned issues into consideration, imidazolium derivates in combination with trifluoromethanesulfonate (triflate), bis(trifluoromethanesulfonyl)imide (bistrifylimide) or tetrachloroaluminate as anions are used as reaction media in this work (Figure 3). This group of ionic liquids exhibits a sufficient solubility of the here applied precursors, a thermal stability higher than the expected reaction temperatures (up to 150 °C) and a sufficient stability toward oxidation. In particular, 1-ethylimidazolium, 1-ethyl-3-methylimidazolium, 1-propyl-3-methylimidazolium and 1-butyl-3-methylimidazolium are applied as cations in this work (Figure 3, Table 1).

Table 1: Names of ionic liquids

Ionic Liquid	**Name**
[BMIm][$AlCl_4$]	1-Butyl-3-methylimidazolium tetrachloroaluminate
[BMIm][NTf_2]	1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
[BMIm][OTf]	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
[EHIm][NTf_2]	1-Ethyl-imidazolium bis(trifluoromethanesulfonyl)imide
[EMIm][NTf_2]	1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
[EMIm][OTf]	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate
[PMIm][NTf_2]	1-Propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

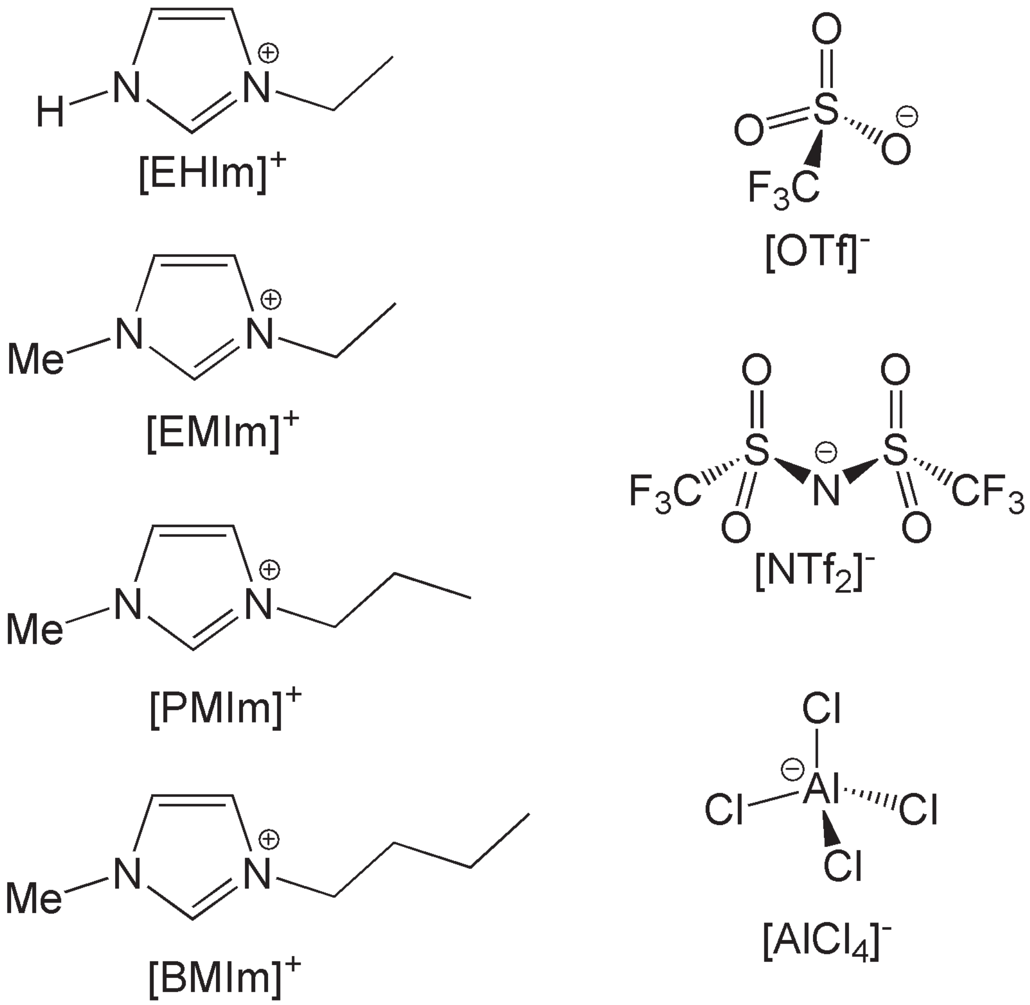

Figure 3: Cations and anions of the here applied ionic liquids.

The separation of the obtained compounds from the ionic liquid and residues of precursors turned out to be difficult in many cases. Long filtration times (12–24 hours) were standard, caused not only by the high viscosity of the ionic liquid itself, but also by the sensitivity toward reduced pressure of many obtained compounds. By reason of the sensitivity of the obtained compounds, the products were often washed with the pure ionic liquid, which was used in the synthesis, to remove residues of non-reacted precursors. Due to their similar solubility behavior, it was often impossible to find a solvent, which dissolves the ionic liquid and not the product. In some cases tetrahydrofuran could successfully be applied. As a result, sample processing and analytical characterization proved to be time-consuming and sometimes difficult. On that account, the crystals for X-ray analysis, FT-IR and UV-Vis spectroscopy were usually separated manually under a microscope. For methods, such as Mössbauer spectroscopy, residues of the ionic liquid do not influence the outcome.

Working in Ampules

Ionic liquids exhibit a very low volatility, which predestine them to work in closed reaction systems at higher temperature. The solid state reactions in this study were carried out in sealed glass ampules under argon at a temperature between 100 and 130 °C. For this purpose, the glass ampules were filled with solid precursors inside a glovebox, followed by adding the ionic liquid and liquid precursors (e. g. $Fe(CO)_5$) under argon stream at the inert gas device. Afterward, the glass ampules were sealed under argon and heated in ovens (LOBA tube furnace from HTM Reetz, Berlin, Germany) for 4–8 days at the given temperature. The cooling rate was $1\,K\,h^{-1}$ to ensure sufficient time for crystallization. After reaction, the ampules were opened inside a glovebox with integrated microscope to investigate the outcome.

2.1.3. Polyol Method

Polyols are multivalent, high boiling alcohols, usually with a high viscosity that are able to coordinate multidentately. Due to their comparably high dielectric constant (e. g. diethylenglycol: $32\,As(Vm)^{-1}$),[33] these solvents are able to dissolve many metal halides, whereas metal oxides and elemental metals are insoluble. Hence, they are predestined for liquid phase synthesis of metal oxide nanoparticles. The polyol method allows not only to synthesize metal oxides but also elemental metals, sulfides, hydroxides and selenides.[34–39]

In this work, diethylen glycol (DEG) was chosen as a solvent (Figure 4), since it has proved to be an excellent synthesize media for nanoscaled oxides.[37,38] Due to its three oxygen atoms, DEG is able to coordinate to a nanoparticle's surface, and acts as both, surfactant and solvent. As a result, the nanoparticles are stabilized directly after nucleation; this prevents agglomeration, and stable suspensions can be obtained without using an additional stabilizer. Moreover, with a boiling point of 246 °C, high reaction temperatures (180 – 200 °C) can be applied, which supports highly crystalline products.[33]

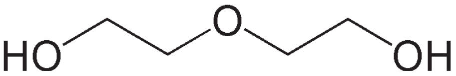

Figure 4: Diethylenglycol.

In order to synthesize nanoparticles with a narrow size distribution, the nucleation process must be separated from the growth of the particles. To realize this, precipitation has to occur within a homogeneous solution. For this purpose, the solution must be stirred continuously and all precursors have to be dissolved well prior to the intended precipitation point.

For doped materials, it is imperative to minimize the amount of impurities. To achieve this, highly pure tin *tert*-butoxide was used as a precursor and water as precipitation reagent. The employed DEG was purified over magnesium and distilled off prior to reaction, to remove residues of water that could induce an unrequested precipitation. As by-product *tert*-butanol is generated, which is well soluble in DEG and was distilled off together with unreacted water during the reaction.

2.2. Chemicals

The following chemicals were used in the syntheses presented in this work (Table 2). The ionic liquids used are presented separately (Table 3). Tin(IV) iodide (SnI_4) and tin(II) iodide (SnI_2) were synthesized according to Brauer by reaction of tin and iodine in toluene or in hydrochloric acid, respectively.[40]

Table 2: Chemicals used.

Chemicals	**Empirical Formula**	**Purity**	**Distributor**
[BMIm]Cl	$N_2C_8H_{15}Cl$	99 %	Iolitec
Dicobalt octacarbonyl	$Co_2(CO)_8$	≥ 90 % moistened with hexane	Sigma Aldrich
1,3-dicyanobenzene	$C_8N_2H_4$	98 %	Sigma Aldrich
1,4-dicyanobenzene	$C_8N_2H_4$	98 %	Sigma Aldrich

Continued on next page

Chemicals	**Empirical formula**	**Purity**	**Distributor**
Diethyleneglycol	$C_4H_{10}O_3$	99 %	Acros Organics
Dimanganese decacarbonyl	$Mn_2(CO)_{10}$	98 %	Sigma Aldrich
[EHIm]Cl	$N_2C_5H_9Cl$	99 %	Iolitec
[EMIm]Cl	$N_2C_6H_{11}Cl$	99 %	Iolitec
Ethanol	C_2H_5OH	98 %	Seulberger
Germanium(IV) iodide	GeI_4	99.99 %	Sigma Aldrich
Li[NTf$_2$]	$LiN(SO_2CF_3)_2$	pure	3M
Li[OTf]	$LiSO_3CF_3$	99.995 %	Sigma Aldrich
Iodine	I_2	99.5 %	VWR
Iron pentacarbonyl	$Fe(CO)_5$	99.99 %	Sigma Aldrich
Isopropanol	C_3H_7OH	98 %	Seulberger
Methylenchloride (Dichlormethane)	CH_2Cl_2	pure	Seulberger
[PMIm]Cl	$N_2C_7H_{13}Cl$	99 %	Iolitec
Scandium nitrate	$Sc(NO_3)_3 \cdot H_2O$	99.9 %	Sigma Aldrich
Tellurium(IV) iodide	TeI_4	99.9 %	ABCR
Tetrahydrofuran (THF)	C_4H_8O	pure	Seulberger
Tetramethylammonium-fluoride	$N(CH_3)_4F \cdot 4\,H_2O$	98 %	Sigma Aldrich
Tin	Sn	99.999 %	Sigma Aldrich
Tin(II) iodide	SnI_2	-	self-synthesized
Tin(IV) iodide	SnI_4	-	self-synthesized
Tin(IV) *tert*-butoxide	$Sn(OC_4H_9)_4$	99.999 %	Sigma Aldrich
Toluene	C_7H_8	pure	Seulberger
Yttrium nitrate	$Y(NO_3)_3 \cdot 6\,H_2O$	99.9 %	Sigma Aldrich

Most of the chemicals were used as received. DEG was purified by heating for 6 hours with magnesium and iodine at 200 °C. Subsequently, it was distilled off under reduced pressure ($\approx 10^{-2}$ mbar). Toluene and THF were dried with sodium and benzophenone as indicator under reflux, and then distilled off. Iron pentacarbonyl was distilled off under reduced pressure ($\approx 10^{-2}$ mbar) on a regular basis to remove decomposition products (especially $Fe_2(CO)_9$). 1,3- and 1,4-dicyanobenzene were dehumidified under reduced pressure (10^{-3} mbar) at 100 °C for 24 hours, followed by recrystallization in toluene and again dried under reduced pressure (10^{-3} mbar) at 100 °C for 24 hours. Iodine was sublimated once, prior to use.

In this work, different ionic liquids have been applied as reaction media. The commercially available ionic liquids often contain small amounts of water, and were therefore dried under reduced pressure ($1 \cdot 10^{-3}$ mbar) at 100 °C for 48 hours prior to use. The purity was ensured by FT-IR and NMR spectroscopy. As some ionic liquids were ordered by different suppliers and sometimes self-synthesized, an overview is given in Table 3.

Table 3: Ionic Liquids used.

Ionic Liquid	Sum formula	Purity	Distributer
[BMIm][$AlCl_4$]	$C_8H_{15}N_2AlCl_4$	99 %	Sigma Aldrich
[BMIm][NTf_2]	$C_{10}H_{15}N_3S_2F_6O_4$	-	self-synthesized
[BMIm][OTf]	$C_9H_{15}N_2SF_3O_3$	99 %	IoLitec
		99.9 %	Merck
		-	self-synthesized
[EHIm][NTf_2]	$C_7H_9N_3S_2F_6O_4$	-	self-synthesized
[EMIm][NTf_2]	$C_8H_{11}N_3S_2F_6O_4$	-	self-synthesized
[EMIm][OTf]	$C_7H_{11}N_2SF_3O_3$	-	self-synthesized
		99 %	Iolitec
[PMIm][NTf_2]	$C_9H_{13}N_3S_2F_6O_4$	-	self-synthesized

Some ionic liquids were synthesized via metathesis. The cation chloride was reacted with the anion's lithium salt, giving the ionic liquid and lithium chloride as byproduct.

Synthesis of [Im][NTf_2] [41]

[Im]Cl (1.05 eq) and Li[NTf_2] (1 eq) were dissolved separately, each with 50 ml of water. The solution of [Im]Cl was added to Li[NTf_2], followed by stirring for 30 min. The ionic liquid was extracted with CH_2Cl_2 and washed with deionised water to remove LiCl. Afterward, CH_2Cl_2 was distilled off under reduced pressure (10^{-1} mbar). The resulting

product was obtained as a yellowish, highly viscous liquid that was dried under vacuum (10^{-3} mbar) at 100 °C for 48 hours and analyzed by FT-IR and NMR spectroscopy to ensure purity.
$[\mathrm{Im}]^+$ = $[\mathrm{BMIm}]^+$, $[\mathrm{EHIm}]^+$, $[\mathrm{EMIm}]^+$, $[\mathrm{PMIm}]^+$

Synthesis of [Im][OTf]
[Im]Cl (1.05 eq) and Li[OTf] (1 eq) were dissolved separately, each in 50 ml of CH_2Cl_2. Subsequently, the solution of [Im]Cl was added to Li[OTf]. After some seconds, a white precipitation of LiCl occurred, which was filtered off after stirring for 30 min. The resulting solution was washed one time with deionised water to remove residues of LiCl. In the following, CH_2Cl_2 was distilled off the ionic liquid under reduced pressure (10^{-1} mbar). The resulting product is a yellowish, highly viscous liquid that was dried under vacuum (10^{-3} mbar) at 100 °C for 48 hours and analyzed by FT-IR and NMR spectroscopy to ensure purity.
$[\mathrm{Im}]^+$ = $[\mathrm{BMIm}]^+$, $[\mathrm{EMIm}]^+$