Ionic Liquid (Molten Salt) Phase Organometallic Catalysis

Jairton Dupont,* Roberto F. de Souza, and Paulo A. Z. Suarez

Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre 91501-970, RS, Brazil

Contents

I. Introduction

For economical and ecological reasons, synthetic chemists are confronted with the increasing obligation of optimizing their synthetic methods. Maximizing efficiency and minimizing costs in the production

* Corresponding author. Fax: ++ 55 51 3316 73 04. E-mail: dupont@iq.ufrgs.br.

of molecules and macromolecules constitutes, therefore, one of the most exciting challenges of synthetic chemistry.[1−3] The ideal synthesis should produce the desired product in 100% yield and selectivity, in a safe and environmentally acceptable process.[4] It is now well recognized that organometallic homogeneous catalysis offers one of the most promising approaches for solving this basic problem.[2] Indeed, many of these homogeneous processes occur in high yields and selectivities and under mild reaction conditions. Most importantly, the steric and electronic properties of these catalysts can be tuned by varying the metal center and/or the ligands, thus rendering tailor-made molecular and macromolecular structures accessible.[5,6] Despite the fact that various efficient methods, based on organometallic homogeneous catalysis, have been developed over the last 30 years on the laboratory scale, the industrial use of homogeneous catalytic processes is relatively limited.[7]

The separation of the products from the reaction mixture, the recovery of the catalysts, and the need for organic solvents are the major disadvantages in the homogeneous catalytic process. For these reasons, many homogeneous processes are not used on an industrial scale despite their benefits. Among the various approaches to address these problems, liquid−liquid biphasic catalysis ("biphasic catalysis") has emerged as one of the most important alternatives.[6−11] The concept of this system implies that the *molecular* catalyst is soluble in only one phase whereas the substrates/products remain in the other phase. The reaction can take place in one (or both) of the phases or at the interface. In most cases, the catalyst phase can be reused and the products/substrates are simply removed from the reaction mixture by decantation. Moreover, in these biphasic systems it is possible to extract the primary products during the reaction and thus modulate the product selectivity.[12] For a detailed discussion about this and other concepts of homogeneous catalyst immobilization, the reader is referred elsewhere.[6,7] These biphasic systems might combine the advantages of both homogeneous (greater catalyst efficiency and mild reaction conditions) and heterogeneous (ease of catalyst recycling and separation of the products) catalysis.

The advent of water-soluble organometallic complexes, especially those based on sulfonated phosphorus-containing ligands, has enabled various biphasic catalytic reactions to be conducted on an industrial scale.[13−15] However, the use of water as a
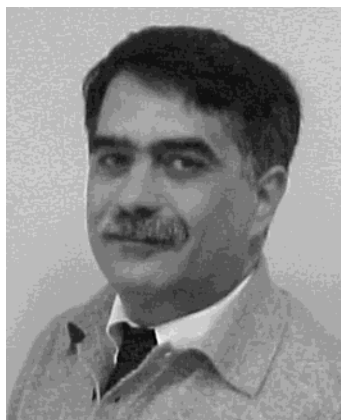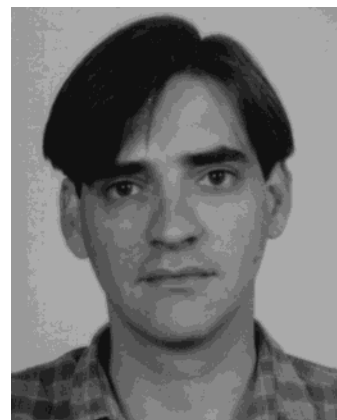
Jairton Dupont was educated in Chemistry at PUCRS (Brazil) and received his Ph.D. in 1988 under the guidance of Dr. M. Pfeffer at the Université Louis Pasteur de Strasbourg (Strasbourg, France). After a Postdoc (1988–1990) with Prof. S. G. Davies at the Dyson Perrins Laboratory, University of Oxford (Oxford, U.K.), he began work as visiting scientist (1990–1992) at the Institute of Chemistry, UFRGS (Porto Alegre, Brazil). In 1992 he became a Professor of Organic Chemistry at the same Institute. He has been invited as Professor at the Faculté de Chimie de Strasbourg, Strasbourg, France (2000). His research interests are centered in synthetic organometallic chemistry with special emphasis in homogeneous in biphasic catalysis. He has authored around 80 scientific publications and 7 patents.

Roberto Fernando de Souza, born in 1958 in Caxias do Sul (Brazil), studied Chemical Engineering at UFRGS (Porto Alegre, Brazil) and received his Ph.D. in 1987 under the guidance of Dr. Igor Tkatchenko at the Université Paul Sabatier (Toulouse, France). He began work as professor in the Institute of Chemistry of UFRGS (Porto Alegre, Brazil) in 1986. In 1994 he studied as Postdoc with Prof. Yves Chauvin at the IFP (France). His research interests are centered in Coordination Catalysis with special emphasis in biphasic catalysis and nickel-catalyzed olefin polymerization. He has authored around 57 scientific publications and 8 patents.

Paulo A. Z. Suarez, born in 1970 in Quarai-RS, studied chemical engineering at UFRGS and received his Ph.D. in 2000 in the group of Professor Dupont at UFRGS with a thesis in ionic liquids. At the present he is Lecturer at UnB (National University of Brasilia). He is the author of 16 publications and 3 patents.

catalyst immobilizing phase has its limitations: (i) It is a highly polar and coordinating protic solvent. (ii) It is reactive toward many organometallic complexes and substrates. (iii) From an environmental perspective, trace amounts of organic compounds in water are notoriously difficult to remove.[16] Moreover, the synthesis of specially designed water-soluble ligands/organometallic complexes is essential for its use. More recently, perfluorocarbons have been used as the nonaqueous phase for various catalytic liquid−liquid biphasic reactions such as the hydroformylation, oxidation, and oligomerization of olefins.[6,17−21] However, the synthesis of specially designed ligands/transition metal compounds to immobilize the catalyst precursors in the fluorinated phase is also indispensable. More recently, supercritical fluids, in particular CO_2, have been investigated as an alternative green solvent for synthesis and catalysis but catalyst recycling apparently remains a problem.[22]

One of the greatest challenges in this field is to devise an immobilizing agent that could act as a simple "solvent" for classical organometallic catalysts. In principle, this might enable the direct transposition of the plethora of known homogeneous catalytic reactions to biphasic systems without ligands/complexes design and synthesis.

Ionic liquids or molten salts, especially those derived from the combination of quaternary ammonium salts and weakly coordinating anions, have been demonstrated to be ideal immobilizing agents for various "classical" transition-metal catalyst precursors in reactions ranging from those of the Ziegler−Natta type to the hydroformylation of olefins.

The synthesis and physical−chemical properties of ionic liquids, in particular haloaluminate derivatives, have been extensively studied, and a series of books[23] on this subject and a review[24] are available. Reviews on the use of ionic liquids as green solvents for chemical reactions and processes are also available.[25,26] The use of room-temperature ionic liquids, in particular haloaluminates, as solvents for organic synthesis and catalysis has been already reviewed.[27−30] More recently, a review describing their synthesis, properties, and potential applications as solvents in transition metal catalysis, with particular emphasis on the type of ionic liquid, has appeared. Impressive overviews of catalytic reactions in ionic liquids have appeared very recently.[31−37] However, in these latter reviews catalytic reactions are catalogued without more in-depth discussion of the catalytic process operating in these media. The aim of our review, however, is focused on the use of ionic liquids as immobilizing agents for organometallic catalysis. The present review concentrates on the catalytic behavior of transition-metal complexes, including catalyst stability, catalytically active species, reaction mechanisms in these media, and catalyst recycling. Moreover, particular attention has been paid to the comparison of the catalytic behavior in ionic liquids

to those observed in homogeneous conditions and/or in aqueous biphasic organometallic catalysis.

II. Ionic Liquids

A. Overview

Ionic liquids or molten salts are in general defined as liquid electrolytes composed entirely of ions. More recently, the melting point criterion has been proposed to distinguish between molten salt ("high-melting, highly viscous, and very corrosive medium") and ionic liquids ("liquid below 100 °C and relatively low viscosity").[31] However, molten salts or ionic liquids are better described as liquid compounds that display ionic−covalent crystalline structures. This definition involves pure inorganic compounds (sodium chloride, mp 801 °C), organic compounds (tetrabutylphosphonium chloride, mp 80 °C), or even eutectic mixtures of inorganic salts (such as lithium chloride/potassium chloride, 6/4, mp 352 °C) or organominerals (triethylammonium chloride/copper chloride, 1/1, mp 25 °C). Among the various known ionic liquids, those based on quaternary ammonium or phosphonium salts exhibit a relatively wide electrochemically stable window, good electrical conductivity, high ionic mobility, a broad range of room-temperature liquid compositions, negligible vapor pressure, and excellent chemical and thermal stabilities.[24,38−43] These properties have been primarily explored for applications in electrochemistry technologies and as solvents in electronic absorption spectroscopy for highly charged complex ions with high- or low-oxidation states. These materials have also been used as media for the clean liquid−liquid extraction processes,[44,45] as recyclable alternatives to aprotic solvents or catalysts for organic[46−48] and organometallic synthesis,[49] catalytic cracking of polyethylene,[50] and radical polymerization,[51] and as media for analytical and physical chemistry,[52] and some of them possess liquid crystal[53] or lubricant properties.[54] Moreover, ionic liquids can be used in biocatalysis with great advantages as compared to those reactions performed in organic solvents.[55]

The ionic liquids can be divided, for the purpose of this review, into two classes: organoaluminates; air- and water-stable ionic liquids. For a short review of the different classes of these materials the reader is invited to refer elsewhere.[56]

B. Organoaluminate Ionic Liquids

Organoaluminate melts are the most investigated class of molten salts.[22−26] These compounds are easily prepared by mixing quaternary ammonium salts, especially *N*-alkylpyridinium and 1,3-dialkylimidazolium halides (Chart 1), with AlCl₃.[40]

Indeed, *N*-ethylpyridinium halides/aluminum halides were among the first ambient-temperature ionic liquids, prepared in 1951.[57] The physical−chemical
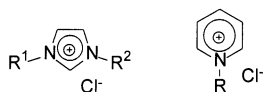
Chart 1

Table 1. Melting Point (Mp) and Viscosity (ν) of 1-Ethyl-3-methylimidazolium Chloride/Aluminum Chloride Ionic Liquid at Different Molar Fractions (*x*) of the Aluminum Compound[58]

x	ν (P)	mp (°C)
0.36	1.59	−60
0.50	0.20	2
0.66	0.16	−80

properties[58] and the structure[59] of these ionic liquids have been investigated in detail.

The combination of 1-ethyl-3-methylimidazolium chloride ((EMI)Cl) or 1-*n*-butyl-3-methylimidazolium chloride ((BMI)Cl) with aluminum chloride produces ionic liquids whose physical−chemical properties depend mainly upon the molar fraction of the aluminum compound (see Table 1).[58]

Thus, ionic liquids with the liquid phase ranging down to −80 °C can be prepared with a relatively small viscosity. Since these organoaluminate ionic liquids have donor and acceptor patterns, the Lewis acidity can also be modulated by the relative amount of the aluminum compound. This Lewis acidity can be expressed by the molar fraction (*x*) of the aluminum compound.[39] Conventionally, when $x = 0.5$ the mixture is called neutral, $x > 0.5$ is acidic, and $x < 0.5$ is basic. The advantage of these controlled Lewis acid ionic liquids is their use in Ziegler−Natta type catalytic reactions. The acidity of these organoaluminate ionic liquids have been investigated in detail by Osteryoung and Wilkes, and reviews about this subject are available.[23] Although these compounds are reactive toward air and water and difficult to handle, they are particularly suitable for several reactions. Indeed, these Lewis acid properties have been extensively explored in organic synthesis (Friedel−Crafts and Diels−Alder reactions)[46,47,60] and for the polymerization[61] of olefins and in Ziegler−Natta type reactions (see later). However, since these melts are extremely air and water unstable and several organic substrates and organometallic compounds are not chemically inert in these media, their application as immobilizing agents for biphasic catalysis is limited.

C. Ambient-Temperature, Air- and Water-Stable Ionic Liquids

Simple quaternary ammonium and phosphonium halides, such as tetrabutylammonium bromide (mp 102−104 °C) and tetrabutylphosphonium bromide (mp 100−103 °C), can be used for the immobilization of transition-metal catalyst precursors. These ionic liquids are particularly suitable for reactions that operate at relatively high temperatures. Moreover, the use of these relatively high melting point ionic liquids allows one to pour off the organic products from the catalyst medium at room temperature. However, since a great number of reactions involving transition metals occur under mild conditions, the use of ambient-temperature, air- and water-stable ionic liquids is indicated.

Ambient-temperature, air- and water-stable ionic liquids can be obtained by the substitution of the halide anion of the 1,3-dialkylimidazolium cation by

Table 2. Physical−Chemical Properties of Room-Temperature Ionic Liquids Based on the 1-Alkyl-3-methylimidazolium Cation
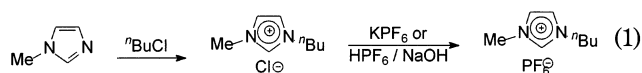
$$R-N^{\oplus}N-Me \quad X^{\ominus}$$

R	X	mp^a (°C)	v_{30}^b (P)	d_{30}^c (g mL^{-1})	K_{60}^d (s cm^{-1} 10^{-2})	EW^e (V)	ref
Et	BF$_4$	15					42
n-Bu	BF$_4$	−81	2.33	1.15	0.864	6.1	63−65
Et	PF$_6$	60					66
n-Bu	PF$_6$	10^g	3.12	1.37	0.656	7.0	63−65
Et	AlCl$_4$	−80				4.8^f	58, 67
n-Bu	AlCl$_4$	−88	2.94	1.23	2.413		58

^{a} Mp = melting point. ^{b} v_{30} = viscosity at 30 °C. ^{c} d_{30} = density at 30 °C. ^{d} K_{60} = electrical conductivity at 60 °C. ^{e} EW = electrochemical window. ^{f} For ionic liquids with x = 0.5. ^{g} Melting point determined by DSC at heating rate of 1 °C/min. However, when the sample was measured at the heating rate of 10 °C/min, only a glass transition at around −72 °C is observed.

other "weakly" coordinating anions (Table 2).[42,62−68] Among the various known ionic liquids, (BMI)BF$_4$ and (BMI)PF$_6$ (Table 2) are most popular and used in biphasic catalysis particularly due to their distinct physical−chemical properties.[65]
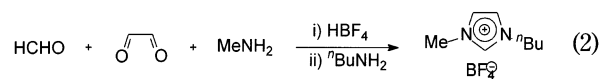
These properties as well as the structure of these ionic liquids have been recently reviewed.[69−71] For example, these ionic liquids have a limited miscibility with various polar and nonpolar organic substrates and solvents, and they dissolve classical organometallic catalyst precursors based on rhodium, ruthenium, palladium, nickel, cobalt, and iron complexes (a more detailed discussion of the solubilities of organic and organometallic compounds in ionic liquids is presented later). Moreover, due to their inherent ionic nature, one might expect that ionic liquids can effectively stabilize cationic transition-metal species that are known to be more active than their neutral analogues.[72] Indeed, it was recently observed that, for example, Ni(I)[73] species or high-valent manganese−oxo compounds (see later) are easily stabilized in these media.

These ionic liquids are easy accessible by the alkylation of commercially available methylimidazole with n-chlorobutane giving the corresponding 1-butyl-3-methylimidazolium chloride followed by anion metathesis, as shown for (BMI)PF$_6$ in eq 1. A simple colorimetric method can be used to monitor the production of the (BMI)Cl intermediate,[74] and a microwave-assisted method can be used for a solventless synthesis of imidazolium ionic liquids.[75] Moreover, most of these ionic liquids are now commercially available and general procedures for their preparation are part of classical organic synthesis.[76,77]

$$Me-N^{\diagup}N \xrightarrow{^nBuCl} Me-N^{\oplus}N^{\,n}Bu \xrightarrow[\text{HPF}_6 / \text{NaOH}]{\text{KPF}_6 \text{ or}} Me-N^{\oplus}N^{\,n}Bu \quad (1)$$
$$ Cl^{\ominus} PF_6^{\ominus}$$

Alternatively, the one-pot reaction of formaldehyde, methylamine, glyoxal, tetrafluoroboric acid, and n-butylamine can be used to obtain a mixture of tetrafluoroborate compounds containing the 1,3-dibutylimidazolium (41%), 1-butyl-3-methylimidazolium (50%), and 1,3-dimethylimidazolium (9%) cat-

ions (eq 2).[78,79] It is important to note that this mixture is liquid at room temperature and can be used as a mobile phase for technological purposes.[79]

$$HCHO + \overset{O}{\diagup}\overset{O}{\diagdown} + MeNH_2 \xrightarrow[\text{ii) } ^nBuNH_2]{\text{i) HBF}_4} Me-N^{\oplus}N^{\,n}Bu \quad (2)$$
$$ BF_4^{\ominus}$$

D. Catalyst Immobilization and Recycling

Organometallic catalysis performed in ionic liquids can lead to various phase systems—as obtained in aqueous biphasic catalysis—where in most of the cases the catalyst resides in the ionic liquid. Before the reaction starts, and where there is no involvement of gas reactants, two systems can usually be formed: a monophase, i.e., the substrates are soluble in the ionic liquid; biphasic systems where the one or all the substrates reside preferentially in an organic phase. If a gas reactant is involved, biphasic and triphasic systems can be formed. At the end of the reaction three systems can be obtained: a monophasic system; a biphasic system where the residual substrates are soluble in the ionic catalytic solution and the products reside preferentially in the organic phase or vice-versa; triphasic systems, formed, for example, by ionic catalytic solutions, with an organic phase containing the desired product and a third phase containing the byproducts (solid phase or water, for example). All of these cases have been reported, and the catalyst recycling and product isolation will be discussed later along with the reactions involved. For an elegant discussion of these types of biphasic catalysis, the reader is referred elsewhere.[6,8]

With regard to biphasic catalysis, the solubility of organic compounds, gases, and transition-metal complexes in these ionic liquids merits further discussion since these factors are usually determinant on catalytic activity and selectivity. Moreover, solubility considerations are extremely relevant for catalyst immobilization, separation processes of the products from the reaction mixture, and catalyst recovery.

The physical−chemical properties of imidazolium-based ionic liquids can be specifically tuned over a wide range by the suitable choice of cations and anions (see Table 2). The physical−chemical properties of ionic liquids, in particular those based on the 1,3-dialkylimidazolium cation, have been recently reviewed.[28,31] The influences of chloride, water, and organic solvents on the physical properties (density, viscosity, etc.) of imidazolium ionic liquids have been systematically investigated.[71,80]

The water concentration in these liquids exceeds 1.0 mol dm^{-3} when exposed to air. The strength of hydrogen bonding between water molecules and anions in 1-n-butyl-3-methylimidazolium ionic liquids increases in the order PF$_6$ < SbF$_6$ < BF$_4$ < (CF$_3$SO$_2$)$_2$N < ClO$_4$ < CF$_3$SO$_3$ < NO$_3$ < CF$_3$CO$_2$.[81] This order is the same as that for the strength of hydrogen bonding between the cation and anion observed in the gas phase.[82] It is also of note that apparently the solvation of organic compounds in imidazolium ionic liquids occurs only with the anion.[81,83]

It is interesting to note that the density of 1-alkyl-3-methylimidazolium ionic liquids decreases fairly

linearly with increasing temperature but at a rate less than that for molecular organic solvents.[84] Several attempts have been made to correlate the electronic and steric properties of the anions and cations with the physical− chemical properties of the ionic liquids, such as the melting point.[62,31] These rationales were not entirely successful since it is almost impossible to correlate the *macroscopic* physical−chemical properties regarding only the cation and anion and their interaction as isolated pairs. It is now well accepted that 1,3-dialkylimidazolium ionic liquids, in the solid and liquid states and even in solution, should be better considered as three-dimensional networks of anions and cations, linked together by weak interactions (such as hydrogen bonds, van der Waals, and Coulombic forces). Ionic liquids, in particular those based on the imidazolium cation, should be thus regarded as supramolecular polymeric structures with weak interactions. Indeed, this supramolecular structure has been evidenced several times in the solid state by X-ray diffraction analysis studies,[42,59,66,85,86] in the gas-phase phase,[87] and also observed even in solution at least in solvents of low dieletric constant.[88−90]

It is well accepted that polarity and polarizability are the simplest indicators of solvent strength and organic solvents are classified on their ability to dissolve and stabilize dipolar or charged species. Solvatochromic probes are commonly used to determine the solvent strength, and several of these probes have been used to determine the "polarity" of imidazolium ionic liquids.[62,91−94] However, in molecular solvents the exact meaning of polarity is complex since various interactions can be involved (hydrogen bonding, van der Waals forces, etc.) and most of the probes allow examination of mainly one interaction with a solvent. In ionic liquids the situation is even more complicated since the cation and the anion have their own distinct interactions. Indeed, the magnitude of the "polarity" of the imidazolium ionic liquids is dependent on the probe used (Reichardt's dye, pyrene, dansylamide, Nile Red, or 1-pyrenecarbaldehyde).[93] Nonetheless, all these studies suggest that the polarity of the imidazolium-based ionic liquids is comparable to that of lower alcohols and it is largely controlled by the nature of the cation.

In terms of biphasic organometallic catalysis, ionic liquids are better regarded as "polymeric liquid supports" than "solvents". Therefore, in most of the cases the catalyst precursors are "immobilized" in the ionic liquid rather than "dissolved". Indeed, pure imidazolium-based ionic liquids are highly ordered hydrogen-bonded polymeric liquids.[95−98] However, "wet" ionic liquids may not be regarded as homogeneous structures (solvents) but have to be considered as nanostructures with polar and nonpolar regions,[99] similar to those encountered in some liquid crystalline or concentrated surfactant media.[100] These nanoinhomogeneities can be generated by the addition of controlled amounts of water (up to 12 wt % in (BMI)PF$_6$) or other molecules, which allows neutral molecules to reside in less polar regions and ionic species in the more polar or wet regions. Note that (BMI)PF$_6$ seems to display dual behavior when used

Table 3. Partial Miscibility (wt %) of Organic Compounds in Selected Ionic Liquids

ionic liq	toluene	^{i}PrOH	but-1-ene	butadiene
(BMI)BF$_4$	16^a	22^a	1.0^b	4.4^b
(BMI)PF$_6$	23^a	11^a	1.0^b	2.2^b

^{a} Determined at 26 °C. ^{b} Determined at 25 °C and 771 mmHg.

as a stationary phase for gas chromatography. It acts as a low-polarity stationary phase to nonpolar compounds whereas molecules with proton donor groups are strongly retained.[52p] These properties can be also used in the product separation and catalyst recycling steps by using for example pH-dependent partitioning ionic liquids.[101]

Moreover, gases, organic compounds, and solvents have different miscibilities with ionic liquids. In this context (BMI)PF$_6$ can be viewed as a liquid similar to long alkyl chain alcohols and is suitable for liquid−liquid extraction processes.[44] The partitioning data of various organic solutes (aniline, benzene, phthalic acid, etc.) between (BMI)PF$_6$ and water show a close correlation with partition coefficients of the same solutes between 1-octanol and water. Although the distribution coefficients for the ionic liquid−water system are, in general, 1 order of magnitude lower than those for the 1-octanol−water system, these values are suitable for practical purposes. Traditional extractants such as crown ethers dissolved in ionic liquids can be used in the extraction of Na$^+$, Cs$^+$, and Sr^{2+} cations.[102]

The partial miscibility of some organic compounds in ionic liquids is summarized in Table 3, and the solubility of various organic compounds in (BMI)PF$_6$ has been recently reported.[103]

The data concerning the partial miscibility of gases in these ionic liquids is scarce. It is, however, interesting to note that carbon dioxide is highly soluble in (BMI)PF$_6$, attaining a mole fraction of 0.6 at 8 bar.[104]

Air- and water-stable ionic liquids exhibit different solubilities with water.[65,105] For instance, (BMI)BF$_4$ and water are miscible in all compositions above 6 °C and below this temperature a miscibility gap was observed. This behavior is particularly useful for reactions involving water and water miscible compounds.[106] In opposition, (BMI)PF$_6$ saturated with relatively low quantities of water[107] (12 wt %[71,99] determined by electrochemistry or 2.67 wt %[108] measured by Karl-Fischer) forms, above this composition, a biphasic system.[71,99]

In most of the applications the organic compounds can be easily separated from the ionic solution by decantation or distillation. In some cases until now only liquid−liquid extraction using organic solvents, resulting in cross-contamination, could be used. However, nonvolatile organic compounds, at least some aromatic compounds, can now be removed by using another environmental benign solvent−supercritical carbon dioxide.[104] This process was investigated using (BMI)PF$_6$ as ionic liquid and naphthalene as a low-volatility model solute. Spectroscopic analysis indicated the quantitative recovery of the solute in the supercritical solvent phase without ionic liquid

contamination. This result should provide a new simple way to separate the organic products from the ionic catalytic solution[103] and indeed has been successfully used in a hydroformylation process (see later).

The transition-metal catalyst precursors are usually soluble in imidazolium ionic liquids, and they are prepared by simple mixing of the metal complex with the ionic liquid. When the solubilization of the metal complex is difficult, it can be first dissolved in an organic solvent and added to ionic liquid and then organic solvent removed under reduced pressure. Although, in only a few cases the metal partitioning distributions between the ionic and the organic phases have been systematically investigated, in most of the cases the metal complex is not removed from the ionic liquid solution by nonpolar organic solvents. This is probably one of the greatest advantages of the use of ionic liquids as "solvents" for biphasic catalysis; i.e., classical transition-metal catalyst precursors can be used directly without the use of specially designed ligands. In the case of aqueous or fluorous biphasic catalysis, the ligands need to be modified to ensure catalyst solubility in these media. However, in certain cases transition-metal complexes are removed by polar products (aldehydes, for example) from the ionic liquid catalytic solution. In these cases the catalyst leaching can be avoided by the use of ionic ligands such as sulfonated phosphines (see later).

The stability of transition-metal complexes is strongly dependent upon the nature of the ionic liquid. In organoaluminate imidazolium-based ionic liquids various reactions have been reported to occur, such as alkylation of the transition-metal center in acidic melts, decomposition processes in basic ionic liquids, and generation of N-heterocyclic carbene metal complexes.[49c] Moreover, cationic catalytic side reactions, such as polymerization, are usually observed between unsaturated substrates and basic organoaluminate ionic liquids. Halo-organic ionic liquids, such tetrabutylammonium bromide, undergo facile Hofmann elimination processes in the presence of strong bases whereas deprotonation of halo-1,3-dialkylimidazolium ionic liquids with the formation of imidazole carbenes is also possible. Moreover, the formation of HF was also observed in particular in the case of $(BMI)PF_6$, where decomposition of PF_6 anion is relatively facile in the presence of water (see later in the Oxidation and Hydroformylation sections).

However, in most cases transition-metal catalyst precursors are stable in ionic liquids (in particular $(BMI)BF_4$ and $(BMI)PF_6$) and are not removed by nonpolar organic solvents. The "solvent" properties of haloaluminate ionic liquids in spectroscopy and in the electrochemistry of transition-metal complexes (in particular metal halides) have been well investigated and reviewed.[24,109] The Bronsted superacidity of protons in acidic chloroaluminate ionic liquids have been also investigated in detail.[110,111]

Although some workers have proposed the existence of cationic halide complexes solvated by haloaluminate ionic liquids, it is believed that transition-metal complexes dissolved in these ionic liquids usually do not undergo solvation and solvolysis.[24] However, these phenomena are usually present in molecular solvents such as water and acetonitrile. Further investigation of the behavior of classical transition-metal complexes in air- and water-stable ionic liquids such as $(BMI)BF_4$ and $(BMI)PF_6$ is clearly needed.

E. Brief History of the Use of Ionic Liquids as Immobilizing Agents for Transition-Metal Catalysts Precursors

In 1965 Sundermeyer published the review "Fused Salts and Their Use as Reaction Media" containing more than 200 references. Various aspects of fused salts such as physical properties, structure, solubility of gases, salts and metals, applications in electro-chemical and electrometallurgical processes, and use as reaction media and as catalysts were addressed.[112]

However, initial attempts for the immobilization of transition-metal compounds using quaternary ammonium ionic liquids for biphasic catalysis were reported by Parshall in 1972.[113] He showed that the hydrogenation and alkoxy−carbonylation of C=C bonds could be performed by $PtCl_2$ dissolved in tetraalkylammonium chloride associated with tin dichloride, at temperatures between 60 and 100 °C. "A substantial advantage of the molten salt medium, however, is that the product may be separated by decantation or simple distillation" (compared to reactions run in conventional organic solvents).[113] This statement was made almost 3 decades ago, i.e. many years before the popularization of "biphasic" catalysis.

In 1981 it was reported that ruthenium compounds immobilized in ionic liquids based on the tetrabutylphosphonium cation are able to catalyze the hydrogenation of carbon monoxide to ethylene glycol at 220 °C.[114] The high liquid temperatures associated with these ionic liquids limited their utilization as solvents for biphasic catalysis. This was shortly followed by the investigation of Fischer−Tropsch catalysis promoted by $Ir_4(CO)_{12}$ in molten $AlCl_3/NaCl$ at 175 °C.[115]

At the beginning of the 1990s Chauvin et al. showed that the oligomerization of olefins can be performed by nickel complexes immobilized in organoaluminate ionic liquids.[116−118] This Ziegler−Natta type reaction occurs in a typical biphasic catalytic system where the products are easily separated from the reaction mixture by simple decantation and the recovered ionic catalyst solution can be reused several times without any significant changes in catalytic performance.

The advent of ambient-temperature, air- and water-stable 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids, independently reported by our[63] and Chauvin's group,[119] provided new impetus for the use of these materials as immobilizing agents for transition-metal catalyst precursors.

III. Oligomerization and Polymerization

A. Oligomerization

As we have already pointed out, Lewis acidity can be modulated in 1,3-dialkylimidazolium chloroaluminate ionic liquids with liquid phases below ambient temperature. Moreover, classical nickel complexes such as (η^3-allyl)nickel bromide are soluble in this media, whereas alkenes are not. Chauvin et al. have ingeniously taken advantage of these properties and have developed a biphasic propene catalytic dimerization process.[116−118] The catalytic system was prepared by the dissolution of the nickel catalyst precursor in the ionic liquid composed of (BMI)AlCl$_4$ with different acidities which were controlled by the addition of AlEtCl$_2$. Thus, the complex NiCl$_2$(P^{i}Pr$_3$)$_2$ dissolved in the (BMI)AlCl$_4$/AlEtCl$_2$ ionic liquid (0.54 Al molar fraction) catalyzes the oligomerization of propene with productivities of up to 3300 g of oligomers/g of Ni and 76% selectivity in 2,3-dimethylbutenes, under mild reaction conditions (−15 °C, 1 bar).

The addition of ethylaluminum dichloride is essential to avoid cationic side reactions since AlEtCl$_2$ acts as a proton scavenger in these media. We can note that various nickel catalyst precursors are active in the propene dimerization. In contrast to what was observed in the acidic melts, the catalytic system is not active in basic melts. This behavior is attributed to the displacement of most of the ligands on nickel by the chloride anions present in the medium, forming NiCl$_4^{2-}$ and NiCl$_3$L$^-$ anionic species (detected by UV−spectroscopy), without alkylation of the nickel center. The selectivity in 2,3-dimethylbutene, under homogeneous conditions, is well-known to increase with the increasing steric hindrance of the ligands, and this was also the case in the biphasic reactions. This result demonstrates the effectiveness of the phosphine effect in ionic liquids. In fact, there is no displacement of the trialkylphosphine coordinated to the nickel center by the anionic species present in the ionic liquid.

The selective dimerization of ethene to butenes can also be accomplished by nickel catalyst precursors dissolved in organoaluminate ionic liquids.[120] Thus, the dicationic complex [Ni(MeCN)$_6$][BF$_4$]$_2$ dissolved in the (BMI)AlCl$_4$/AlEtCl$_2$ ionic liquid (0.54 Al molar fraction) catalyzes the oligomerization of ethene with turnover frequencies (TOF) of 5954 h^{-1} and 56% selectivity in butenes, under mild reaction conditions (25 °C, 8 bar). The selectivity in butenes could be raised to 100% (TOF = 1731 h^{-1}) by increasing the ethylene pressure (18 bar) and reducing the reaction temperature to −10 °C. In these reactions, the use of aromatic cosolvents is essential for the selectivity in butenes, since other hydrocarbons induce the formation of higher ethylene oligomers. The effect of aromatic cosolvents in these systems can be ascribed to the modulation ("buffering") of the acidity of the melt due to the aromatic ring being able to coordinate to aluminum chloride centers.

The catalytic system [Ni(MeCN)$_6$][BF$_4$]$_2$ dissolved in the (BMI)AlCl$_4$/AlEtCl$_2$ ionic liquid (0.54 Al molar fraction), used for ethylene dimerization, catalyzes also the oligomerization of butenes under mild reaction conditions (10 °C and atmospheric pressure) when associated with 1 equiv of PCy$_3$CS$_2$.[121,122] The main products formed in these reactions are butene dimers with TOF up to 1.9 s^{-1} corresponding to a productivity of 6 kg of oligomers/g of Ni in 1 h! These activities are higher than those usually obtained using homogeneous catalytic systems. It is worthwhile noting that, in these cases, branched butene dimers are formed preferentially (up to 94%).[121]

Linear 1-butene dimers can be selectively obtained from Ni(cod)(hfacac) catalyst precursor immobilized in 1-butyl-4-methylpyridinum chloride/AlCl$_3$ ionic liquid (Chart 2).[123]

Chart 2
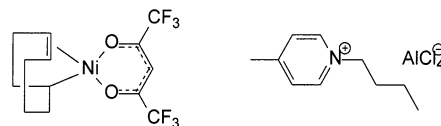

To avoid cationic side reactions, the ionic liquid, in this case, was buffered by the addition of weak organic bases (such as N-methylpyrrole, quinoline, or pyridines). It is interesting to note that the addition of AlClEt$_2$ causes rapid catalyst decomposition. Selectivities up to 68% in linear 1-butene dimers and TOF of 0.68 s^{-1} were reported. These selectivities, in biphasic conditions, are similar to those obtained under homogeneous conditions (typically 75%). However, the catalytic activity is significantly enhanced compared with those observed in organic solvents (TOF of 0.14 s^{-1}). Moreover, this catalytic system can be used for the dimerization of butenes with higher selectivities and activities then those observed in toluene.[124] Catalytic oligomerization process by non-nickel catalyst precursors in ionic liquids has been also described in a recent patent application.[125]

The catalytic oligomerization of alkenes by nickel catalyst precursors dissolved in ionic liquids has been performed in batch and semicontinuous reactors. Experimentally, in semicontinuous reactors, as the reaction proceeds, the amount of the liquid hydrocarbon phase (upper phase) increases until the reactor is filled. The organic phase is simply removed by decantation, and the reaction can be carried out again several times.

The catalytically active species involved in the oligomerization reactions are probably nickel−hydride complexes as indicated by their activity in carbon−carbon bond formations (oligomerization) and carbon−carbon double-bond shifts (isomerization). The proposed mechanism of these biphasic reactions is analogous to the reactions occurring under one-phase conditions, and it is exemplified for the dimerization of butenes in Scheme 1.[121]

More recently, a new catalytic system containing a tungsten complex (Cl$_2$W^{IV}=NPh(PMe$_3$)$_3$) dissolved in (BMI)Cl/AlCl$_3$ mixture was described as being able to catalyze ethene oligomerization without using any cocatalyst.[126] Indeed, at 60 °C and 40 bar, an oligomeric mixture containing butenes (81%), hexenes (18%), and heavier olefins (1%) was obtained.

Scheme 1
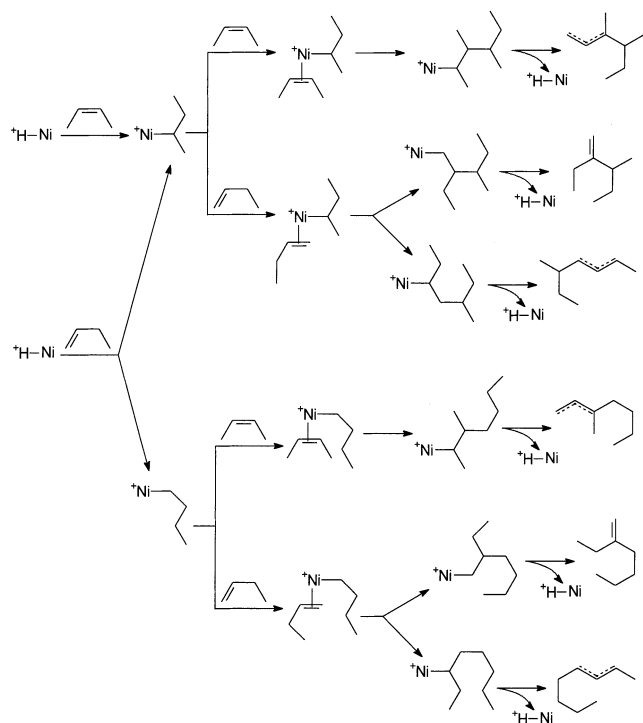
It is well-known that the homogeneous hydrovinylation of styrenes is catalyzed by various Ni(II)/phophine compounds under mild reaction conditions.[127] Wilke's complex (Scheme 2) is by far the most

Scheme 2

EMI.BARF

Wilke's catalyst
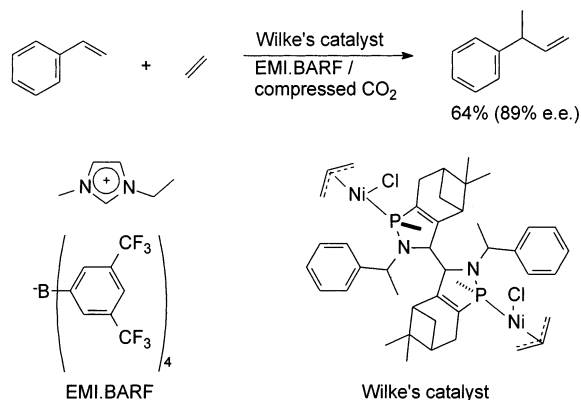
active and selective catalyst precursor for performing the enantioselective hydrovinylation of styrene.[128] However, this nickel complex is only active when associated with alkylaluminum compounds, which act as chlorine abstractors and akylating agents.

An impressive optimization process was disclosed by the combination of imidazolium ionic liquids such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BARF) and compressed CO_2. This biphasic system allows one to activate, tune, and immobilize the Ni catalyst in a continuous flow system.[129] The activation of the catalyst is probably aided by the formation and stabilization of ionic catalytically active species involved in the process by the ionic liquid. The use of compressed CO_2 greatly decreases the ionic liquid's viscosity and facilitates the mass transfer. Moreover, the product separation is performed without exposing

the catalytic system to variations of pressure, temperature, or substrate concentration. This protocol opens the possibility of using a reactor design very similar to that of classical fixed-bed reactors.

A simple and a continuos flow biphasic Pd-catalyzed dimerization of methylacrylate to dihydrodimethylmuconate has been recently described.[130] The catalytic system was obtained by the combination of Pd(acac)$_2$ with N,N-dimethyl-2-ethenyl-di-n-butylphosphine and tetrafluoroboric acid in (BMI)-BF$_4$.

B. Polymerization

As described for oligomerization, Ziegler–Natta type polymerizations can also be carried out in dialkylimidazolium halides/aluminum halide ionic liquids using AlCl$_{3-x}$R$_x$ as cocatalysts.

Thus, ethylene was polymerized using (η^5-Cp)$_2$TiCl$_2$ dissolved in acidic 1-ethyl-3-methylimidazolium chloride/AlCl$_3$ (EMIC) using AlCl$_{3-x}$R$_x$ (R = Me, Et) as cocatalysts.[131] The reaction was performed by bubbling ethylene (1 bar) into the (η^5Cp)$_2$MCl$_2$ solution. At the end, the reaction was quenched with THF, and the polymer was extracted by this solvent. It was observed that all metallocenes are inactive in basic EMIC/AlCl$_3$ mixtures. However, in acid media, the (η^5-Cp)$_2$MCl$_2$ catalyst precursor was able to promote polymerization with a catalytic activity up to 0.023 g of ethylene min^{-1}. Nevertheless, no recycling experiments have been apparently performed.

It is known that the complex [NbO(C$_{16}$H$_{11}$O$_6$)-(C$_2$O$_4$)] is able to polymerize 1,3-butadiene to a polybutadiene with a high 1,4-cis units content under homogeneous conditions using AlClEt$_2$ as cocatalyst.[132] Surprisingly, when this reaction was carried out in 1-n-butyl-3-methylimidazolium chloride/AlCl$_3$ using AlEt$_2$Cl as cocatalyst, an unusual inversion on the selectivity was observed; i.e., polybutadiene with a high 1,4-trans units content was obtained.

Polyethylenes with bimodal molecular weight distribution have been obtained from the polymerization of ethylene by (1,4-bis(2,6-diisopropylphenyl)acenaphthenediimine)dichloronickel(II) (Chart 3) dissolved in

Chart 3

Ar= 2,6-^{i}Pr$_2$(C$_6$H$_3$)
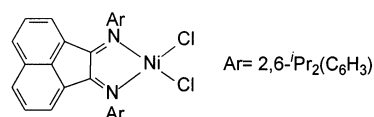
1-n-butyl-3-methylimidazolium organochloroaluminate ionic liquid under mild reaction conditions (1050 mbar and temperatures ranging from −10 to 10 °C).

The reaction proceeds as a typical biphasic system where the nickel catalyst is immobilized in the ionic liquid and the products in the organic phase (toluene). The ionic catalyst solution could be reused in successive polymerization cycles upon addition of alkylaluminum cocatalyst.[133] The recycled ionic liquid catalyst solution showed enhanced activity as compared to those reactions performed in organic solvents. This suggests the predominance of dissociated cationic nickel centers in the ionic phase (allowing easier monomer access to the catalytic active species)

Table 4. Hydrogenation C=C Bonds by Transition-Metal Complexes Dissolved in 1-Butyl-3-methylimidazolium-Based Ionic Liquids

entry	olefin	ionic liq	catal	[olefin]/[catal]	time (h)	$p(H_2)$ (bar)	T (°C)	conv (%)	select (%) alkenes	select (%) alkane	TOF (h^{-1})	ref
1	cyclohexene	(BMI)BF$_4$	Rh[a]	15000	120	10	25	40			56	63
2	cyclohexene	(BMI)PF$_6$	Rh[a]	15000	120	10	25	40			50	63
3	cyclohexene	(BMI)BF$_4$	Ru[b]	15000	4.5	25	30	30			170	139
4	cyclohexene	(BMI)BF$_4$	Ru[b]	15000	20	25	60	100			73	139
5	hex-1-ene	(BMI)BF$_4$	Ru[b]	15000	6	25	30	100			328	139
6	hex-1-ene	(BMI)BF$_4$	Ru[b]	15000	3	25	30	84			537	139
7	butadiene	(BMI)BF$_4$	Ru[b]	5000	4.5	25	30	68	71	29	493	139
8	butadiene	(BMI)BF$_4$	Ru[b]	5000	8	40	30	100	87	13	377	139
9	butadiene	(BMI)BF$_4$	Co[c]	5000	72	25	25	100	100		72	139
10	butadiene	(BMI)BF$_4$	Co[c]	5000	72	25	60	22	100		15	139
11	butadiene	(BMI)BF$_4$	Co[d]	5000	22	25	50	18	93	7	10	138
12	butadiene	(BMI)PF$_6$	Co[d]	5000	22	25	50	23	72	28	13	138
13	cyclohexa-1,3-diene	(BMI)SbF$_6$	Rh[e]	370	2	10	30	96	98	2	192	119

[a] RhCl(PPh$_3$)$_3$. [b] RuCl$_2$(PPh$_3$)$_2$. [c] Na$_3$Co(CN)$_5$. [d] Co(acac)$_2$. [e] [Rh(nbd)(PPh$_3$)$_2$][PF$_6$].

over the contact ion pair usually observed in nonpolar organic media. The polyethylenes obtained present typical bimodal molecular weight distribution indicating the formation of nonuniform nickel catalytic active centers in the ionic liquid phase. In opposition, the polyethylenes obtained under homogeneous conditions present only slightly bimodal molecular weight distribution.[134]

Rh(nbd)(acac) (nbd = norbornadiene) catalyst precursor immobilized in (BMI)BF$_4$ in the presence of triethylamine catalyzes the polymerization of phenylacetylene producing poly(phenylacetylene) with molecular weights between 55 000 and 200 000 Da. The polymer precipitates as a yellow solid which is extrated with toluene, and the recovered ionic catalytic solution could be reused without loss in activity.[135]

Copper(I) *N*-propyl-2-pyridylmethanimine immobilized in (BMI)PF$_6$ ionic liquid promote methyl methacrylate living radical polymerization.[136] The reaction rate is enhanced as compared to the polymerization performed in polar organic solvents, and narrow polydispersity polymers are obtained. The poly(methyl methacrylates) are easily isolated from the catalyst ionic solution and are recovered essentially copper-free by a simple solvent wash. However, the recycling of the recovered ionic liquid catalyst mixture has not yet been possible.

IV. Hydrogenation

A. Hydrogenation of Simple Alkene and Dienes

The classical catalyst precursors RhCl(PPh$_3$)$_3$,[137] RuCl$_2$(PPh$_3$)$_2$, and Co(CN)$_5$$^{3-}$ that activate the hydrogen molecule by oxidative addition and heterolytic and homolytic cleavage, respectively, when dissolved in the ionic liquid (BMI)BF$_4$, reduce the C=C bond of olefins (Table 4).[63,119,138,139] These reactions are typically performed in liquid−liquid biphasic systems where the substrates and products (upper phase) are not miscible with the ionic catalyst solution. The products are removed from the reaction mixture by simple decanting, and the recovered ionic catalyst solution can be reused several times without any significant change in catalytic performance (activity and selectivity).
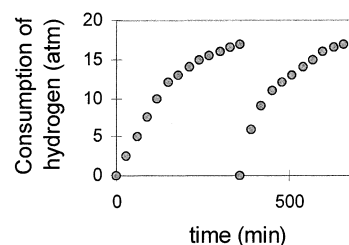

Figure 1. Consumption of hydrogen in the two first recharges of hex-1-ene.[138]

The reuse of the catalytic system is best visualized by Figure 1, where the consumption of hydrogen is plotted against the reaction time for the catalyst recharge in the hydrogenation (25 bar) of 1-hexene by RuCl$_2$(PPh$_3$)$_3$ dissolved in (BMI)BF$_4$ at 30 °C. A total of seven recharges were performed leading to a productivity of 12 kg of hexane/g of Ru.[138]

It is important to note that the metal content in the ionic phase was always greater than 99.5% (confirmed by atomic absorption analysis). Moreover, in comparison to what was described for the aqueous biphasic catalytic systems, there was no formation of stable emulsions in all the cases involving ionic liquids.[140]

The observed reaction rates are generally higher than those obtained with classical water-soluble phosphine transition-metal complexes, which give generally lower TOFs and require the use of more drastic conditions (temperature and hydrogen pressure). For example, a TOF of 19 h^{-1} with 50% conversion was attained in the biphasic catalytic hydrogenation of hex-1-ene with RuHCl(dpm)$_3$·2H$_2$O [dpm = PPh$_2$(*m*-C$_6$H$_4$SO$_3$Na)] at 80 °C under 3 bar of H$_2$ for 24 h.[141] Moreover, alkene isomerization products are formed in these reactions. It is worth noting that using ionic liquids, no alkene isomerization products were detected. However, Chauvin et al. observed isomerization products in the hydrogenation of pent-1-ene by [Rh(nbd)(PPh$_3$)$_2$]PF$_6$ (nbd = norbornadiene) dissolved in (BMI)BF$_4$, (BMI)PF$_6$, or (BMI)-SbF$_6$.[119] Notwithstanding it was observed that alkene isomerization might occur, when the ionic liquids contain trace amounts of the strongly coordinating chlorine anions. However, when chlorine-free ionic liquids were used, the isomerization reaction was not

detectable.[139,140] It is interesting to note that olefin hydrogenations by Wilkinson's catalyst immobilized in (BMI)PF$_6$ and supercritical CO$_2$ gave similar results to those obtained in the absence of a cosolvent or when using hexane as cosolvent.[142] However, the use of supercritical CO$_2$/(BMI)PF$_6$ for the reduction of CO$_2$ by RuCl$_2$(dppe)$_2$ (dppe = diphenylphosphin-ethane) in the presence of secondary amines gave excellent results for the generation of formamides.

A temperature-controlled reversible (BMI)BF$_4$ ionic liquid−water portioning system for the catalytic hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol by [Rh(η^4-C$_7$H$_8$)(PPh$_3$)$_2$][BF$_4$] catalyst precursor has been recently reported.[143] The reaction was conducted in one-phase conditions at 80 °C, and the product separation was performed at 20 °C whereby a biphasic system ((BMI)BF$_4$/water) is formed. This process is similar to the one reported earlier for the hydrodimerization of butadiene (see later) by palladium compounds immobilized in (BMI)BF$_4$.

The cobalt catalyst precursor Na$_3$Co(CN)$_5$ dissolved in (BMI)BF$_4$ has been shown to be extremely selective in the reduction of one double bond of 1,3-butadiene producing 1-butene with 100% selectivity. However, in this particular case the ionic catalyst solution cannot be reused. The cobalt complex is transformed into (BMI)$_3$Co(CN)$_5$ in this medium, and this new compound is inactive for the hydrogenation reaction.[139] This limitation can be overcome by the use of Pd(acac)$_2$ (acac = acetylacetonate) as the catalyst precursor dissolved in (BMI)BF$_4$ or (BMI)PF$_6$ ionic liquids, which is able to hydrogenate up to 95% of butadiene into butenes before starting the butane formation.[144] Indeed, the ionic phase containing the palladium compound was recycled at least 15 times without any loss in its catalytic activity. This catalytic system is also able to hydrogenate hexadienes, cyclohexadienes, and cyclooctadiene giving excellent selectivities in monoenes. The catalyst precursors Co-(acac)$_2$, Ni(acac)$_2$, Co(acac)$_3$, and Fe(acac)$_3$ are also active in the selective hydrogenation of butadiene to butenes without deactivation, and it is possible to reuse the recovered ionic solution.[145] It is interesting to note that the selectivity in butenes is greater in (BMI)BF$_4$ than in the hexafluorophosphate analogue and that the butenes are twice as soluble in this latter ionic liquid. The same trend was reported for the hydrogenation of cyclohexadiene to cyclohexene by [Rh(nbd)(PPh$_3$)$_2$]PF$_6$ (nbd = norbornadiene) dissolved in (BMI)SbF$_6$.[119] These results are strong indications that the hydrogenation reaction occurs preferentially in the ionic phase. The reaction activity (TOF) achieved in the hydrogenation reactions are presented in Table 4 and are comparable to those observed for the same catalyst precursors dissolved in organic solvents.

The hydrogenation of cyclohexene, styrene, and 1-octene by Ru$_3$(CO)$_{12-x}$(TPPTS)$_x$ (x = 1−3, TPPTS = triphenylphosphine trisulfonate, sodium salt) clusters immobilized in (BMI)BF$_4$ gave extremely low catalytic activity.[146] It is interesting to note that these Ru clusters are only sparingly soluble in the ionic liquid. The authors also mentioned that these transition-metal carbonyl clusters react with chloroalumi-
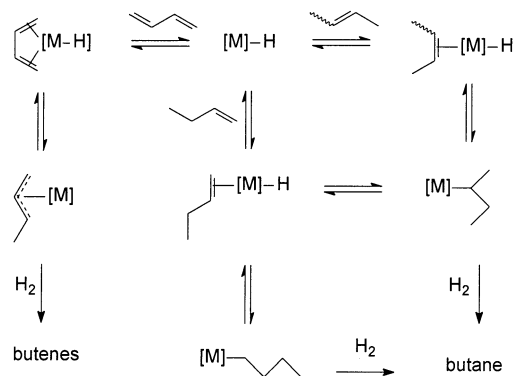
nate ionic liquids but the products were not characterized.

RuCl$_2$(PPh$_3$)$_3$ immobilized in organozincate ionic liquids prepared by mixing (BMI)Cl with ZnCl$_2$ are also interesting catalytic systems for the hydrogenation of olefins.[147] These low-melting zincate salts (60 °C), containing Ru compounds, promote the hydrogenation of 1-hexene (TOF up to 44 min^{-1}), and the recovered solid catalyst phase has been reused several times.

Catalytic solutions of PtCl$_2$ immobilized in [Et$_4$N]$^+$-[SnCl$_3$]$^-$ ionic liquid are also able to hydrogenate olefins and polyenes.[113] In particular, this catalyst promotes the selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene (87% selectivity) at 160 °C and 100 bar. For other polyenes, such as 1,5-cyclooctadiene, the isomerization reaction to give the 1,3-diene is more rapid than the reduction process. The isolation, from the catalytic ionic solid, of the complex [HPt(SnCl$_3$)$_4$]$^{3-}$ suggests that the hydrogenation in this media proceeds by a classical olefin insertion mechanism.

The high selectivity in the hydrogenation of polyenes when monoenes are present is generally assumed to originate from the exceptional stability of the η^3-allyl intermediate complexes, formed by M−H addition to the conjugated diene. In a homogeneous hydrogenation mixture there is a competition between the diene and the monoene for the catalytically active site (Scheme 3). The reaction pathway involv-

Scheme 3

ing the η^3-allyl intermediate is thermodynamically favored. Consequently, the diene in the reaction medium is almost completely hydrogenated before the concentration of the monoene increases to the point that it gains access to the metal center.[113] In the case of biphasic catalysis in ionic liquids a similar pathway can explain the observed results. Moreover, in these cases, the high selectivity in monoenes can also be attributed to the higher concentration of the diene in the ionic phase, where the reaction is presumably taking place, since in most of the cases the dienes are much more soluble in the ionic phase than the monoenes (see Table 3).

The selective hydrogenation of functionalized dienes into their monoenes has found technological applications since starting materials for fine chemicals can be obtained. In this respect, two successful trends using biphasic catalysis have recently appeared.[144,148] Thus, sorbic acid dissolved in methyl-*tert*-butyl ether

(MTBE) could be selectively hydrogenated to 3-hexenoic acids using Cp*Ru(sorbic acid) complex dissolved in (BMI)PF$_6$. The formation of hexanoic acid has been observed only after almost complete consumption of sorbic acid.[148] Moreover, Pd(acac)$_2$ dissolved in (BMI)BF$_4$ was shown to be active for methyl sorbate, sorbic acid, and 1-nitro-buta-1,3-diene hydrogenations.[144] Methyl sorbate and nitrobutadiene hydrogenations produce almost exclusively the conjugated trans monoene, whereas sorbic acid was completely hydrogenated into hexanoic acid. It is important to note that both ruthenium and palladium containing ionic solutions could be recovered after the catalytic reactions and recycled. However, during the hydrogenation of sorbic acid using Pd-(acac)$_2$, the formation of metallic palladium was observed which rendered its reuse impractical.

B. Hydrogenation of Polymers

The technological applicability of the ionic liquids in the immobilization of organometallic catalysts precursors has been recently reported on the selective biphasic hydrogenation for NBR (acrylonitrile−butadiene rubber) dissolved in toluene by RuHCl(CO)-(PCy$_3$)$_2$ dissolved in (BMI)BF$_4$ under mild conditions.[149] The selective hydrogenation of the C=C bond of NBR is usually performed by homogeneous or heterogeneous catalysts under severe reaction conditions. However, these catalytic systems are inhibited by the presence of the nitrile group in the polymer and only low catalytic activities are generally achieved.[150] It has been found that RuHCl(CO)(PCy$_3$)$_2$ dissolved in (BMI)BF$_4$ is able to reduce selectively NBR to HNBR (hydrogenated acrylonitrile−butadiene rubber) under hydrogen pressures between 10 and 40 bar at 100−160 °C with rate constants up to 1.65 mmol Ru^{-1} min^{-1} (higher than the 0.30 mmol Ru^{-1} min^{-1} observed under homogeneous conditions). The reaction rate increases with increasing ionic liquid volume indicating that the reaction occurs preferentially in the ionic phase. At the end of the reaction the hydrogenated polymer solution was recovered by decantation and, again, the ionic catalytic system could be reused several times without any loss in catalytic performance.

C. Hydrogenation of Arenes

The catalytic hydrogenation of arenes (benzene, toluene, cumene) to cycloalkanes can be performed by the ruthenium cluster catalyst precursor [H$_4$Ru$_4$-(η^6-C$_6$H$_6$)$_4$][BF$_4$]$_2$ immobilized in (BMI)BF$_4$ ionic liquid.[151] The reaction occurs under relatively mild reaction conditions (60 bar H$_2$, 60 °C), and TOF values ranging from 136 h^{-1} for cumene to 364 h^{-1} for benzene hydrogenation have been achieved. These TOF values obtained in the ionic liquid are similar to those obtained with the same catalyst precursor dissolved in water or by the known homogeneous catalytic systems such as [(η^6-C$_6$Me$_6$)Ru$_2$(μ-Cl)]Cl$_2$.[152] The products were separated from the catalyst ionic solution by distillation under high vacuum, thus eliminating the environmental problems associated with the related aqueous−organic biphasic regimes.

Table 5. Asymmetric Hydrogenation of C=C Bonds by Transition-Metal Complexes Dissolved in Ionic Liquids

entry	catal	ionic liq	substrate	[subs]/[catal]	P (bar)	% ee^a	ref
1	(−)-Rh	(MBI)SbF$_6$	**1**	100	10	64 (S)	119
2	(S)-Ru	(MBI)BF$_4$	**2**	20	50	78 (S)	154
3	(S)-Ru	(MBI)BF$_4$	**2**	400	25	72 (S)	154
4	(R)-Ru	(MBI)BF$_4$	**2**	40	25	86 (R)	154
5	(S)-Ru	(MBI)BF$_4$	**3**	200	75	80 (S)	154

^{a} At 100% conversion.

It is interesting to note that colloidal Rh catalysts dissolved in (BMI)BF$_4$ are not active for the hydrogenation of arenes whereas they are active in aqueous/supercritical fluid biphasic media.[153]

D. Asymmetric Hydrogenation and Transfer Hydrogenation Reactions

Asymmetric hydrogenation reactions can also be performed with classical Ru and Rh complexes dissolved in ionic liquids. However, in these cases the substrates should be dissolved in an appropriate solvent. 2-Propanol was shown to be the best cosolvent for these reactions. The substrates are soluble in this alcohol, whereas the reaction mixture is only partially miscible with the ionic liquids.[119,154] Moreover, the catalyst precursors are not removed from the ionic catalytic solution by 2-propanol. Nonracemic cationic [Rh(cod)((−)-DIOP)]PF$_6$ (cod = cycloocta-1,5-diene) dissolved in (BMI)SbF$_6$ catalyzes the asymmetric hydrogenation of α-acetamidocinnamic acid (**1**) to (S)-phenylalanine in 64% ee (Table 5).[119] Similarly, the optically active [RuCl$_2$BINAP]$_2$·NEt$_3$ (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) catalyst precursor immobilized in (BMI)BF$_4$ catalyzes the asymmetric hydrogenation of 2-phenylacrylic acid (**2**) and 6-methoxy-2-naphthylacrylic acid (**3**) (Table 5).[154]

The ee's obtained in these asymmetric hydrogenations are similar to those obtained under homogeneous conditions.[155] In these cases, again, the catalytic ionic solution could be reused several times without any loss in catalytic activity or selectivity.

The Rh−EtDuPHOS and Rh−MeDuPHOS[156] complexes, when immobilized in (BMI)PF$_6$/^{i}PrOH or (BMI)BF$_4$/^{i}PrOH, catalyze the asymmetric hydrogenation of enamides (Scheme 4) with enantioselectivities similar to those obtained by the same catalyst dissolved in organic solvents.[157,158] Moreover, this process of immobilization provides extra stability for
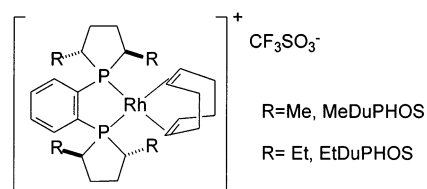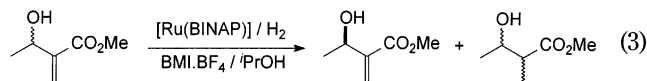
Scheme 4

Table 6. Cyclodimerization of 1,3-Butadiene with [Fe$_2$(NO)$_4$Cl$_2$] Dissolved in (BMI)PF$_6$ and (BMI)BF$_4$ Ionic Liquids under Various Reaction Conditions[162]

entry	ionic liq	reducing agent (mmol)	T (°C)	butadiene (mmol)	[Fe] (mmol)	select (%)[a]	TOF (h^{-1})
1	(BMI)BF$_4$	Zn (2.5)	50	466	0.26	100	1440
2	(BMI)BF$_4$	Zn (3.3)	30	296	0.33	100	480
3	(BMI)BF$_4$	Zn (3.3)	10	220	0.32	100	60
4	(BMI)PF$_6$	Zn (3.5)	50	364	0.36	100	420
5	(BMI)PF$_6$	Zn (3.5)	10	263	0.36	100	240
6	b	Zn (2.0)	50	295	0.35	100	240

[a] At 100% conversion. [b] In toluene.

the otherwise air-sensitive rhodium complex and the ionic catalytic solution could be reused for further reactions. Remarkable effects on the enantioselectivity of these reactions were observed as a function of the molecular hydrogen concentration in the ionic phase. It was demonstrated, in these cases, that the hydrogen concentration, rather than hydrogen pressure in the gas phase, is the important kinetic parameter to be considered under different gas–liquid mass transfer conditions. This is particularly true for the imidazolium ionic liquids, where the hydrogen solubility is almost four times greater in (BMI)BF$_4$ than in (BMI)PF$_6$.[157]

Classical Ru–BINAP complexes immobilized in (BMI)PF$_6$/^{i}PrOH promote the kinetic resolution of methyl-3-hydroxy-2-methylenebutanoate[157] (eq 3) with the same degree of enantiomer selection as those obtained under homogeneous conditions (methanol).[159]

(3)

The asymmetric hydrogenation of tiglic acid by the Ru–BINAP catalyst precursors proceeds readily in wet (BMI)PF$_6$, and the product was extracted from the ionic liquid catalytic solution by using supercritical CO$_2$.[160] The enantioselectivity was hydrogen "pressure" dependent as usually observed under "homogeneous conditions". The use of supercritical CO$_2$ for product extraction allows the recovered ionic liquid catalytic solution to be reused for up to four times without any significant changes in the conversion and enantioselectivity of the system.
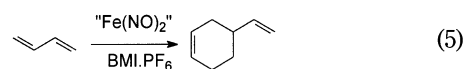
Tetralkyl- and tetraarylphosphonium tosylates have been used in rhodium-catalyzed transfer hydrogenation reactions. For example, the reduction of acetophenone by Rh$_2$(OAc)$_4$/2(−)-DIOP immobilized in ethyl-tri-n-octylphosphonium tosylate salt (mp = 90 °C) in the presence of KOH/^{i}PrOH at 120 °C affords 1-phenethylethanol (92% ee, L = DIOP) in 50% yield (eq 4).[161] These tosylate salts are liquid at the reaction temperature and solid at room temperature, thereby facilitating catalyst recovery ("pouring off" the organic products).
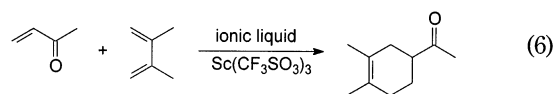

(4)

V. Dimerization and Telomerization of Dienes

A. Cyclodimerization of 1,3-Dienes

The 1,3-butadiene cyclodimerization reaction can be performed by iron complexes, prepared in situ by the reduction of [Fe$_2$(NO)$_4$Cl$_2$] with metallic zinc, dissolved in (BMI)BF$_4$ or (BMI)PF$_6$ ionic liquids (eq 5 and Table 6). In the reactions performed with (BMI)BF$_4$, at 50 °C, 4-vinylcyclohexene was obtained in 100% conversion and selectivity with TOFs up to 1440 h^{-1}.[162]
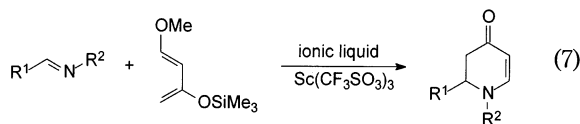

(5)

It is interesting to note that the conversion increases with the solubility of the diene in the ionic liquid (1,3-butadiene is two times more soluble in the BF$_4$-based ionic liquid than in the PF$_6$ salt) and with increasing reaction temperature. All these results indicate that the catalytic reaction occurs preferentially in the ionic phase and that the reaction follows analogous mechanisms proposed for the reactions occurring in homogeneous media. Again, the achieved TOFs are comparable or even higher to those observed in organic solvents. Such a rate acceleration effect of ionic liquids has been observed in related Diels–Alder reactions catalyzed by scandium triflate immobilized in imidazolium ionic liquids such as (BMI)BF$_4$ and (BMI)PF$_6$ (eq 6).[163]

(6)

This ionic catalytic system gave much higher reaction rates and selectivities than those performed in classical organic solvents and allowed easy catalyst recycling. This immobilized Diels–Alder catalytic system has been reused up to 10 times without any changes in catalytic activity or selectivity. Moreover, in these reactions the ionic liquid can be used in stoichiometric amounts. The rate acceleration effect of ionic liquids has been observed in several other condensation reactions such as the Baylis–Hillman reaction, and an internal pressure effect has been postulated.[164] Here again, more in-depth studies are clearly needed.
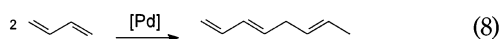
The scandium triflate catalyst precursor immobilized in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate or 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium trifluoromethanesulfonate ionic liquids form a

recyclable catalytic system for aza-Diels−Alder reactions to produce 5,6-dihydro-4-pyridone derivatives (eq 7).[165]

$$R^1 \diagup N \diagdown R^2 \;+\; \text{(diene with OMe, OSiMe}_3\text{)} \xrightarrow[\text{Sc(CF}_3\text{SO}_3)_3]{\text{ionic liquid}} \text{(product)} \qquad (7)$$
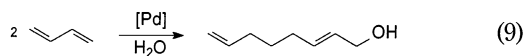
B. Linear Dimerization of 1,3-Butadiene

The linear dimerization of 1,3-butadiene can also be performed with transition-metal complexes immobilized in ionic liquids (eq 8).[166] Thus, Pd(II) salt (chloride or acetate for example)/PPh$_3$ catalyst precursors dissolved in (BMI)F$_4$ or (BMI)PF$_6$ catalyze the linear dimerization of 1,3-butadiene to 1,3,6-octatriene that was isolated by extraction with toluene. For example, when the catalyst precursor derived from PdCl$_2$ with 2 equiv of PPh$_3$ was used as the catalyst precursor, dissolved in (BMI)BF$_4$ ionic liquid, octatriene was formed with 100% selectivity after 13% conversion. The TOF of 49 h^{-1} is significantly higher than in homogeneous conditions (THF, TOF 6 h^{-1}) under the same reaction conditions (70 °C, 3 h, butadiene/Pd = 1250).

$$2 \diagdown\diagup \xrightarrow{\text{[Pd]}} \diagdown\diagup\diagdown\diagup \qquad (8)$$

C. Hydrodimerization of 1,3-Butadiene

Palladium catalyst precursors dissolved in (BMI)-BF$_4$ are also able to promote the hydrodimerization of 1,3-butadiene (eq 9).[106] 1,3-Butadiene conversions of up to 28%, TOF of 118 h^{-1}, and a selectivity of 94% in octa-2,7-dien-1-ol were achieved with (BMI)$_2$PdCl$_4$ (BMI = 1-n-butyl-3-methylimidazolium) dissolved in (BMI)BF$_4$.

$$2 \diagdown\diagup \xrightarrow[\text{H}_2\text{O}]{\text{[Pd]}} \diagdown\diagup\diagdown\diagup \text{OH} \qquad (9)$$

The 1,3-butadiene conversion and TOF were significantly increased to 49% and 204 h^{-1}, respectively, by employing a 5 bar pressure of carbon dioxide. These reactions were performed under homogeneous conditions at 70 °C. However, at temperatures below 5 °C, a biphasic system is formed and the products are easily removed from the reaction mixture by simple decanting. As already pointed out earlier for the other reactions, the recovered ionic catalytic solution could be reused several times without any significant changes in the catalytic performance. The achieved TOFs are similar to those observed in the aqueous systems.[167]

The direct characterization of the active catalytic species in these ionic media is not easy. It was, however, found that the catalyst precursor (BMI)$_2$-PdCl$_4$ dissolved in (BMI)BF$_4$ and in the presence of water is almost quantitatively transformed into PdCl$_2$(MI)$_2$ (MI = methylimidazole) with evolution of 1-butene and an increase in the medium acidity (pH from 7 to 3). PdCl$_2$(MI)$_2$ was shown to be the effective catalyst precursor in these hydrodimerization reactions. This result indicates that the ionic liquids

cannot be considered as simple solvents, but that they can induce reactions that do not occur in organic solvents.

VI. Carbonylation

A. Hydroformylation

The hydroformylation of olefins has been employed industrially since the 1940s, and it is one of the most important catalytic industrial chemical processes. The oxo process is usually performed in industry using cobalt and rhodium complexes in homogeneous conditions or by aqueous rhodium complexes under biphasic conditions.[6] Although hydroformylation is one of the most investigated catalytic reactions, in view of its importance it is still attracting continuous and increasing academic and industrial interest. In this respect several homogeneous catalytic systems including supercritical CO$_2$[22] and biphasic aqueous[6,8,14] or fluorous[15,17−21] systems based mainly on modified rhodium catalyst precursors are currently being investigated.
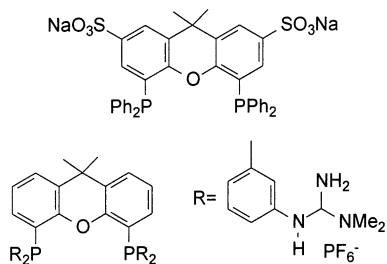
Not surprisingly, this reaction was one of the first to be investigated using molten sats as immobilizing agents but employing Ru catalyst precursors.[168,169] The catalyst precursor was prepared by the dispersion of RuO$_2$ hydrate, Ru(acac)$_2$, and Ru$_3$(CO)$_{12}$ cluster in low-melting phosphonium salts such as tetrabutylphosphonium bromide (melting point 100−103 °C). Hydroformylation of terminal or internal olefins with this catalytic system under moderate syngas pressures are facile, and the major products are linear alcohols. Aldehydes may also be predominant under certain reaction conditions, and internal olefins can be converted into oxo products. Spectroscopic investigation indicated that the major species in solution is the [H(Ru$_3$(CO)$_{11}$]$^-$ polynuclear anion. The modification of the catalytic system by the combination of bidentate ligands such as 2,2′-bipyridine and 1,2-bis(diphenylphosphino)ethane allows the regioselective hydroformylation of internal olefins to linear alcohols and aldehydes with selectivities greater than 99%. The species involved in this modified catalytic system is probably the anion cluster [HRu$_3$(CO)$_9$(L−L)]$^-$ (L−L = bidentate ligand) that is known to catalyze this reaction under one-phase conditions with selectivities in linear products of up to 95%.[170] The anionic ruthenium catalytically active species in the tetrabutylphosphonium ionic liquid are high stable, probably due to the formation of ion pairs of the type [P(Bu)$_4$]$^+$[Ru]$^-$. This property allows the easy separation of the products (even employing thermal separation techniques) and reuse of the ionic catalytic solution. The mechanism suggested for this process is similar to that proposed for homogeneous conditions.

Although these highly promising results were published more than a decade ago, this study was not followed up. However, the hydroformylation of 1-hexene to heptanals using Rh$_2$(OAc)$_4$ and PPh$_3$ as catalyst precursors and new high-melting phosphonium tosylates salts, such as n-butyltriphenylphosphonium tosylate (mp 116−117 °C), was recently described.[171] Upon cooling of the reaction mixture,
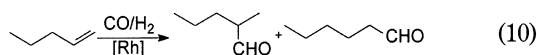
these salts solidify and the organic products are separated by filtration. This system affords, in 100% yield, *n*-heptanal and 2-methylhexanal ($n/i = 2$) under 40 bar for 4 h at 120 °C. The recovered ionic phase, where the catalyst precursor is retained, could be reused several times, without changes in its catalytic performance.

Inasmuch as hexanals are poorly soluble in the ionic liquids, a biphasic hydroformylation of 1-pentene can be performed by classical rhodium catalyst precursors.[119] Chauvin et al. have shown that Rh-(CO)$_2$(acac) associated with PPh$_3$ dissolved in (BMI)-PF$_6$ catalyzes the hydroformylation of 1-pentene into hexanals (eq 10) with a 99% yield (n/i (*n*-hexanal/*i*-hexanal) = 3) and a TOF of 333 h^{-1} under relatively mild reaction conditions (p(H$_2$/CO, 1/1) = 20 bar, 2 h at 80 °C). However, in this particular case, a small part of the rhodium catalyst is extracted into the organic phase. The extraction of the catalyst can be suppressed by the use of polar ligands such as the sodium salts of monosulfonated (tppms) and trisulfonated (tppts) phosphine ligands. Thus, the Rh(CO)$_2$-(acac)/tppms system dissolved in (BMI)PF$_6$ produces hexanals ($n/i = 3.9$) in 16% yield with TOF of 59 h^{-1} under the same conditions as described above. In this case, the extraction of the rhodium catalyst from the ionic solution was completely avoided. It is now clear that the use of modified phosphine ligands with polar groups such sulfonates or quaternary ammonium salts associated with the rhodium precursors is essential to avoid metal leaching in the hydroformylation reactions. Thus, classical water-soluble ligands such as sulfonated triphenylphosphine and xantphos (Chart 4) have been successfully applied in the

Chart 4

hydroformylation of long-chain olefins with significant advantages over the classical biphasic aqueous-phase systems.[172,173]

Moreover a series of modified imidazolium[174] and pyridinium ionic phosphines have been recently prepared (Chart 5) by the P-nucleophilic addition to 1-vinylimidazole[175] or 4-vinylpyridine.[176]

The corresponding Rh complexes immobilized in various imidazolium and pyridinium ionic liquids
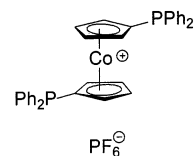
Chart 5

have been employed in the hydroformylation of various olefins.

Electron-poor ionic phosphine ligands with cobaltocenium backbones can be also used to effectively immobilize the rhodium catalyst in the ionic liquid phase.[177] Thus, Rh−1,1′-bis(diphenylphosphino)cobaltocenium hexafluorophosphate (Chart 6) dissolved in (BMI)PF$_6$ is an effective catalytic system for the biphasic hydroformylation of 1-octene.

Chart 6

For example, catalytic activities (TOF) up to 810 h^{-1}, 94% selectivity in *n*-nonanal ($n/i = 16.2$), and no detectable catalyst leaching were observed at 100 °C and 10 bar of syngas pressure. The 1-octene solubility (around 2.5 mol % at 25 °C) in the (BMI)PF$_6$ ionic liquid, although limited, allows higher reaction rates than the biphasic reactions performed in water.

Using PtCl$_2$(PPh$_3$)$_2$ dissolved in the ambient-temperature liquid (BMI)Cl/SnCl$_2$ (x(SnCl$_2$) = 0.51) mixture, a remarkable n/i selectivity appears to be achieved in the hydroformylation of 1-octene.[178] Indeed, at 120 °C and 90 bar CO/H$_2$, nonanals (n/i = 19/1) were obtained with TOF up to 126 h^{-1}.

It is now apparent that the (BMI)PF$_6$ ionic liquid is the ionic liquid of choice for the biphasic hydroformylation of olefins in particular for product isolation and catalyst recycling steps. (BMI)PF$_6$ has been, indeed, essential for the stabilization of the Rh catalyst under thermal stress during product distillation. Moreover, since this ionic liquid is almost nonmiscible with water as well as with nonpolar solvents such as hexanes, extraction methods can be used for the separation and catalyst regeneration steps and thus circumvent the problems associated with distillation cycles. It is, however, interesting to note that the presence of water in (BMI)PF$_6$ or the use of organic cosolvents causes a dramatic change in the selectivity of the hydroformylation of long-chain olefins.[172] Although this effect can be attributable to the changes in the polymeric structure of this well-organized nanostructured ionic liquid, more in-depth studies in this area are needed.

Rh(CO)$_2$(acac) associated with 2,2′-bis((((4-methoxy-6-*tert*-butyl)phenoxy)phosphino)oxy)-1,1′-binaphthyl (Chart 7) dissolved in (BMI)PF$_6$ has also been successfully used in the homogeneous hydroformylation of methyl-3-pentanoate (eq 11). Indeed, re-
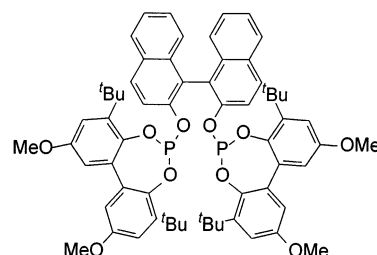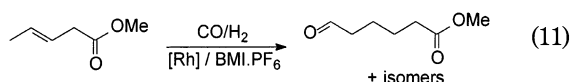
Chart 7

Table 7. Hydroesterification of Styrene Derivatives by PdCl$_2$(PhCN)$_2$/(+)-(NMDPP) Dissolved in (BMI)BF$_4$[182]

	R group				
	H	4-Me	4-Cl	2-Cl	4-MeO
yield (%)	89	76	71	60	22

cycling the same ionic catalyst solution 10 times yields a total turnover number (TON) of 6640.[179] This TON is almost 7-fold greater than those obtained in reactions performed in organic solvents (CH$_2$Cl$_2$ or toluene). In this case, the product, which is of significant importance for an alternative synthesis of adipic acid, has been separated from the ionic catalyst solution by distillation at 110 °C under reduced pressure (0.2 mbar).
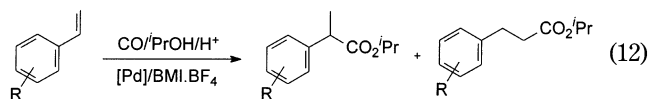
$$\text{(11)}$$

A significant breakthrough for catalyst recycling and product separation for the hydroformylation of olefins has been disclosed by the use of a continuous-flow process in supercritical carbon dioxide–ionic liquid mixtures.[180] In this case again the rhodium complexes are associated with sulfonated triphenyl-phosphine and immobilized in (BMI)PF$_6$. The hydro-formylation of 1-octene was performed at a constant rate in a continuous-flow process in which the olefin, syngas, and products were transported in and out of the reactor dissolved in supercritical CO$_2$. Catalyst leaching in this case was less than 1 ppm. The catalyst ionic solution was reused up to 11 times.

Rh-catalyzed hydroformylations of olefins have been also performed in 1,2,3-trimethylimidazolium triflate and 1-ethyl-2,3-dimethylimidazolium triflate ionic liquids that are easily prepared by alkylation of 1,2-dimethylimidazole with the corresponding tri-flates. High conversions were obtained in the reactions performed in these ionic liquids but with a higher tendency toward olefin isomerization and hydrogenation byproducts as compared to those performed in toluene.[181]

B. Alkoxy Carbonylation

Palladium compounds dissolved in (BMI)BF$_4$ cata-lyze the hydroesterification of styrene derivatives to produce 2-arylpropionic esters in very good yields and regioselectivities (eq 12).[182]
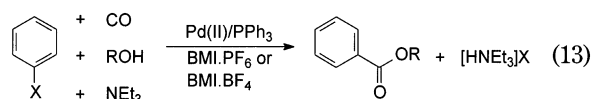
$$\text{(12)}$$

The best catalyst precursor was found to be PdCl$_2$-(PhCN)$_2$ associated with (+)-neomenthyldiphenylphos-phine (NMDPP) and p-toluenesulfonic acid (TsOH) dissolved in (BMI)BF$_4$. The reaction was performed under relatively mild reaction conditions (10 bar of CO at 70 °C for 20 h). In all the cases described in Table 7 the regioselectivity was >99.5% for the branched ester (eq 12). The phosphine ligand was selected to achieve high regioselectivities. The use of
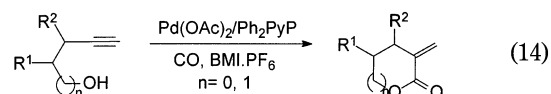
triphenylphosphine or cyclohexyldiphenylphosphine (sterically less hindered than NMDPP) reduces the regioselectivity to 80%. On the other hand, the use of the highly hindered tri-o-tolylphosphine inhibited the hydroesterification reaction. It is interesting to note that although (+)-NMDPP is optically active, the observed degree of asymmetric induction was very low (<5%) similar to those observed in organic solvents (under the same reaction conditions). The 2-arylpropionic esters formed in these reactions are easily separated from the ionic solution by simple decanting. However, the recovered ionic catalytic solution could not be recycled. The palladium catalyst was partially or totally decomposed after the catalytic reaction. Nevertheless, the formed esters are free of metal. The simple separation of the products and the use of lower CO pressures are the major advantages of the use of ionic liquids in the hydroesterification of styrene derivatives as compared with the reactions performed under homogeneous conditions.[183]

Palladium–benzothiazole carbene catalyst precur-sor immobilized in molten N(n-Bu)$_4$Br promotes the alkoxy carbonylation of various aryl halides.[184] The beneficial effect exerted by N(n-Bu)$_4$Br on the cata-lytic activity as compared to the reactions performed in organic solvents and other ionic liquids was attributed to the formation and stabilization of [L$_2$-PdBr]$^-$[N(n-Bu)$_4$]$^+$ (L = benzothiazole carbene) as the catalytic active species. It is interesting to note that the formation of the large [L$_2$PdBr]$^-$[N(n-Bu)$_4$]$^+$ complex should impede of palladium clusters by imposing a Coulombic barrier.

Palladium(II)/PPh$_3$ compounds dissolved in (BMI)-BF$_4$ or (BMI)PF$_6$ catalyze the alkoxy carbonylation of aryl halides under relatively mild reaction condi-tions (eq 13) to afford the corresponding benzoates[185] The carbonylation reaction performed by the Pd compounds immobilized in the ionic liquids is greatly accelerated compared to those effected in alcohols.[186] The benzoates were separated by distillation or extraction with diethyl ether, and the ionic catalytic mixture could be recycled.

$$\text{(13)}$$

Similarly, the intramolecular alkoxy carbonylation of alkynols has been successfully performed by Pd-(II)/PyPh$_2$P complexes immobilized in (BMI)BF$_4$ or (BMI)PF$_6$ to afford selectively exo-methylene five- and six-membered lactones in high yields (eq 14).[187] Product isolation and catalyst recycling was the same as described above for the carbonylation of aryl halides.

$$\text{(14)}$$
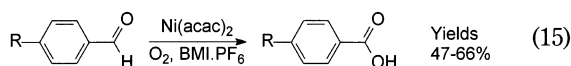
VII. Oxidation and Radical Reactions

Ionic liquids have been used as media and catalysts for oxidation reactions since the 1950s.[112] More recently, it has been reported that the bis(acetyl-

acetonato)nickel(II)/tetra-*n*-butylammonium tetra-fluoroborate salt system can be used in the liquid phase oxidation of ethyl benzene in air yielding ethylbenzene hydroperoxide at atmospheric pressure.[188] Moreover, bis(acetylacetonato)nickel(II)/(BMI)-PF$_6$ promotes also the oxidation of ethylbenzene at atmospheric pressure, showing that this catalytic system is an important industrial alternative to the heterogeneous catalysts presently used for this oxidation process.[189]

Low-melting imidazolium and pyridinium ionic liquids are stable toward strong chemical oxidizing agents, such as fuming sulfuric acid, have a large stable electrochemical window (up to 7 V),[64,67] and are, therefore, suitable media for oxidation reactions. However, it should be pointed out that (BMI)PF$_6$ in the presence of ruthenium compounds decomposes in the presence of molecular oxygen and at higher temperatures (100 °C).

Nonetheless, it is surprising that only recently typical transition-metal-catalyzed oxidation reactions have been performed in these media. The results obtained so far demonstrated the advantage of ionic liquids over other immobilizing agents.
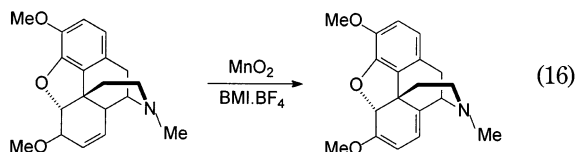
Various aromatic aldehydes can be oxidized to the corresponding carboxylic acids using bis(acetylacetonato)nickel(II) immobilized in (BMI)PF$_6$ and dioxygen at atmospheric pressure as the oxidant (eq 15).[190]

$$R\text{—}C_6H_4\text{—CHO} \xrightarrow[\text{O}_2, \text{ BMI.PF}_6]{\text{Ni(acac)}_2} R\text{—}C_6H_4\text{—COOH} \qquad \begin{matrix}\text{Yields}\\ \text{47-66\%}\end{matrix} \qquad (15)$$

It is interesting to note that a similar catalytic system based on nickel complexes dissolved in perfluorinated solvents gave similar results for the oxidation of aromatic aldehydes. However, in this case modification of the 1,3-diketone nickel ligand (incorporating perfluorinated chains) was necessary to ensure the solubility of the catalyst in the perfluorinated phase and reduce leaching.[19]
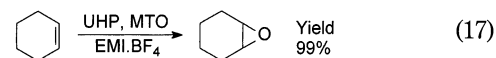
More recently, classical oxidations of alcohols promoted by tetra-*N*-propylammonium perruthenate[191] have been performed in tetraethylammonium bromide or 1-ethyl-3-methylimidazolium hexafluorophosphate ionic liquid.[192] The use of this catalytic system in oxidation reactions with oxygen or *N*-methylmorpholine *N*-oxide allows the facile recovery and reuse of the ionic solution (the products are simply extracted with organic solvents).

Ionic liquids can be also used in classical organic oxidation reactions with great advantages (yield and selectivity) compared to those performed in organic solvents. For example, (BMI)BF$_4$ has been used to remove or extract excess of MnO$_2$ and associated impurities from the oxidation reaction of codeine methyl ether to thebaine (eq 16).[193]

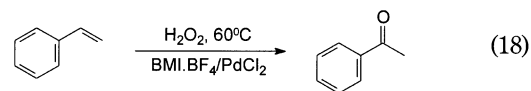$$\xrightarrow[\text{BMI.BF}_4]{\text{MnO}_2} \qquad (16)$$

Alkenes and allylic alcohols can be epoxidized using methyltrioxorhenium (MTO) immobilized in (EMI)-

BF$_4$ and urea hydrogen peroxide as the oxidizing agent (eq 17).[194] Urea hydrogen peroxyde (UHP) and MTO are completely soluble in the ionic liquid, thus forming a homogeneous solution (note, the mixture UHP−MTO is heterogeneous in organic media). Conversion falls with decreasing alkene solubility in the ionic liquid, and the epoxidation reaction rates are comparable to those obtained in classical solvents.
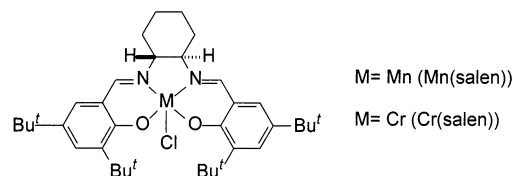
$$\xrightarrow[\text{EMI.BF}_4]{\text{UHP, MTO}} \qquad \begin{matrix}\text{Yield}\\ 99\%\end{matrix} \qquad (17)$$

Wacker-type oxidation reactions have been also performed with great advantages (compared to the reactions performed in water) by PdCl$_2$ immobilized in (BMI)BF$_4$ and (BMI)PF$_6$ using hydrogen peroxide as the oxidant (eq 18).[195]

$$\xrightarrow[\text{BMI.BF}_4/\text{PdCl}_2]{\text{H}_2\text{O}_2, 60°C} \qquad (18)$$
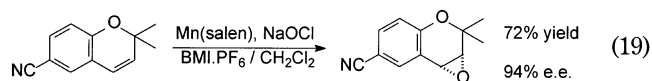
Jacobsen's chiral Mn(III) salen ([*N,N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride)[196] (Chart 8) immobilized in

Chart 8
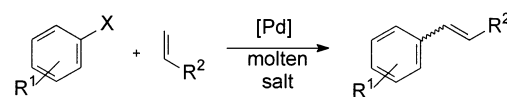
M= Mn (Mn(salen))

M= Cr (Cr(salen))

(BMI)PF$_6$ ionic liquid constitutes one the most efficient and recyclable catalytic systems for the asymmetric epoxidation of alkenes using aqueous NaOCl as the oxidizing agent and CH$_2$Cl$_2$ as the cosolvent (eq 19).[197] The electrochemical investigation of the activation of molecular oxygen by Jacobsen's epoxidation catalyst immobilized in (BMI)PF$_6$ ionic liquid showed the formation of the postulated high-valent manganese−oxo active intermediate, which was otherwise undetectable in organic solvents.[198]

$$\xrightarrow[\text{BMI.PF}_6 / \text{CH}_2\text{Cl}_2]{\text{Mn(salen), NaOCl}} \qquad \begin{matrix}72\% \text{ yield}\\ 94\% \text{ e.e.}\end{matrix} \qquad (19)$$

The conversion of alkenes to epoxides and enantioselectivities were comparable to those obtained without an ionic liquid. Moreover, these oxidation reactions proceeded faster than those performed without (BMI)PF$_6$.
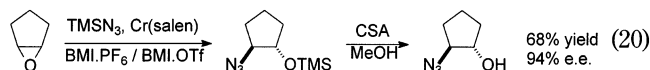
The same group has disclosed an impressive new and highly practical recycling procedure of Cr−salen-catalyzed asymmetric ring-opening reactions of *meso*-epoxides in RTILs.[199] The procedure consists of running the reaction of trimethylsilyl azide (TMSN$_3$) with *meso*-epoxides (cyclopentene oxide, mainly) in the presence of catalytic amounts of *N,N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]chromium(III) chloride dissolved in 1-*n*-butyl-3-methylimidazolium ionic liquids (eq 20). The yield and enantioselectivity are strongly dependent upon the nature of counteranion; while the reaction performed

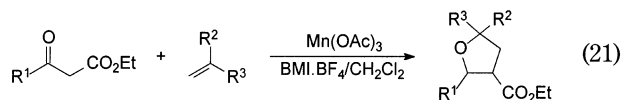**Table 8. Heck Reaction by Palladium Compounds Immobilized in Ionic Liquids**

entry	catal precursor	ionic liq	X	R^1	R^2	conv (%)	TON[a]	ref
1	$PdCl_2(PPh_3)_2$	$(C_{16}H_{34})(Bu)_3PBr$	Br	H	CO_2Bu	99	90	204
2	$PdCl_2(PPh_3)_2$	$(C_{16}H_{34})(Bu)_3PBr$	Br	4-OMe	CO_2Bu	99	51	204
3	$PdCl_2(PPh_3)_2$	Bu_4NBr	Br	H	CO_2Bu	86	51	204
4	palladacycle	Bu_4NBr	Br	$4-COCH_3$	Ph	99	106	213
5	palladacycle	Ph_4PCl	Cl	$4-NO_2$	Ph	99	100	213
6	palladacycle	Ph_4PCl	Cl	H	Ph	39	390	213

[a] TON = mol of product/mol of Pd.

in hydrophobic $(BMI)PF_6$ ionic liquid gave high yields and degrees of enantioselectivity (similar to those obtained in organic solvents), the system is almost inactive when performed in hydrophilic $(BMI)BF_4$. The best recyclable catalytic system was obtained by immobilizing the catalyst precursor in a mixture (5/1 v/v) of hydrophobic $(BMI)PF_6$ and the hydrophilic $(BMI)OTf$ ionic liquids (eq 20).

Transition-metal-mediated C−C bond-forming radical reactions have also been performed with significant advantages compared with those performed in organic solvents. For example, the yields in cyclic ethers (eq 21) obtained from $Mn(OAc)_3$-mediated radical cyclization reactions in $(BMI)BF_4/CH_2Cl_2$[200] are similar or higher than those performed in acetic acid or by alternative cyclization methods.[201]
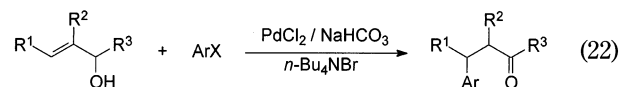

VIII. Heck, Suzuki, Stille, Sonogashira Negishi, and Ullmann Coupling Reactions

The homogeneous palladium-catalyzed C−C coupling reactions of aromatic and vinylic systems ("Heck" reaction)[202,203] have received increasing attention due to their synthetic versatility.[204] The need for high amounts of palladium catalyst is one of the technical limitations for the applicability of this reaction. However, this limitation can be overcome by immobilizing the catalyst. Inasmuch as the Heck reaction is usually performed in polar solvents and that salt additives[205−209] such as $N(n-Bu)_4Br$ can activate and stabilize the catalytically active palladium species, ionic liquids appear to be the ideal immobilizing agents. Indeed, Kaufmann[204] has demonstrated that the vinylation of aryl halides can be performed by simple palladium catalyst precursors such as palladium chloride, palladium acetate, and $PdCl_2(PPh_3)_2$ dissolved in hexadecyltributylphosphonium bromide and tetrabutylammonium chloride ionic liquids, without the addition of phosphine ligands. The conversion of bromoarenes and reaction yields up to 99% have been reported (see Table 8). The product was separated by distillation, and the

remaining catalyst showed catalytic activity in the melt in two following runs. However, the reaction failed with chlorobenzene.
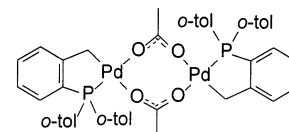
The Heck coupling of aryl iodides and bromides with allylic alcohols catalyzed by $PdCl_2$ in molten n-Bu_4NBr furnishes the corresponding β-arylated carbonyl compounds (eq 22) that are extracted with diethyl ether, and the recovered ionic liquid/palladium mixture could be reused.[210] Substituted acrylates also undergo[211] Heck couplings catalyzed by palladium−benzothiazole carbene complex in molten n-Bu_4NBr.

The use of molten n-Bu_4NBr for the immobilization of palladium-containing dipyridyl or pyridylquinoyl ligands was essential for the promotion of the Heck coupling of aryl chlorides or for the amination of aryl bromides.[212]

Herrmann[213,214] has also reported that chloro- and bromoarenes can be vinylated (styrene) by different palladium compounds, such as a phosphapalladacycle[215] catalyst precursor (Chart 9), $Pd(OAc)_2$ and

Chart 9

$PdCl_2$, immobilized in tetrabutylammonium bromide ionic liquid. Conversions up to 99% with TON of 1 000 000 have been reported on the reaction of styrene with 4-bromoacetophenone (see Table 8).[213] These systems are suitable for catalyst recycling depending on the stability of the catalyst precursors. Whereas, for the reaction of bromobenzene with styrene using $PdCl_2$ as catalyst precursor, the reaction yield in stilbene decreases after 4 runs, when using the phosphapalladacycle compound, at least 12 runs could be performed without loss in the reaction yield.[214] Most importantly, the reactions performed in ionic liquids have various advantages as compared to all previously described molecular solvents, such as catalytic efficiency for the vinylation of chloroarenes[216] and improved thermal catalyst stability and lifetime during the reaction. The mechanism of the
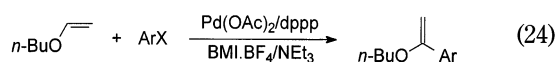
Heck reaction in ionic liquids still remains unclear, and more research in this area is necessary.

Heck type reactions can be also performed by palladium-containing benzothiazole carbene ligands immobilized in tetrabutylammonium bromide ionic liquid.[217] The reaction of bromobenzene with n-butyl acrylate is extremely fast, 94% yield in 10 min at 130 °C using 1% of Pd. In these reactions the use of sodium bicarbonate as base is crucial to avoid ionic liquid decomposition since other bases such as NaOAc and Na_2CO_3 promote the Hofmann elimination. N-heterocyclic carbene complexes of palladium can also be formed in situ under the Heck reaction conditions using imidazolium melts as the immobilizing agents.[218] Palladium−carbene complexes were formed from the deprotonation of the imidazolium cation of (BMI)Br in the presence of the catalyst precursor (eq 23).

$$\text{Me-N} \overset{+}{\underset{\text{Br}}{N}} {}^{n}\text{Bu} \ + \ \text{Pd(OAc)}_2 \ \xrightarrow[\text{ionic liquid}]{\text{NaOAc}} \ \text{complex} \quad (23)$$

Palladium−carbene complexes[219] were also formed when the reactions were performed in (BMI)BF_4 ionic liquid, clearly indicating the noninnocent nature of these media in palladium-catalyzed coupling reactions (in particular in the presence of strong bases).[220] The Heck reaction of iodobenzene or bromoarenes substituted with electron-withdrawing groups with acrylates or styrene are markedly more efficient in (BMI)Br than in (BMI)BF_4 and this was attributable to the formation of more active palladium carbene catalytic active species in the imidazolium bromide salt. Interestingly, iodo arenes are efficiently coupled with alkenes and alkynes, by Pd(II) compounds dissolved in 1,3-n-butylimidazolium ionic liquids at room temperature and ultrasonic irradiation.[221] In this case, the presence of monodispersed grains with nearly spherical shape was observed by transmission electron microscopy (TEM). These clusters of Pd(0) nanoparticles in ionic liquids were found to be stable even after 1 week. A heterogeneous version for the Heck reaction has been performed by Pd/C in (BMI)-PF_6, but only highly activated aryl iodides were tested.[222] It is however interesting to note that even reaction vessel ultratrace amounts of palladium catalyze the Heck reaction involving aryl iodides.[223] Moreover, it highly recommendable the use of the *three-phase test* in these cases, to verify if the reaction is promoted by metal particles (bulk) or single metal compounds dissolved during the process.[224]
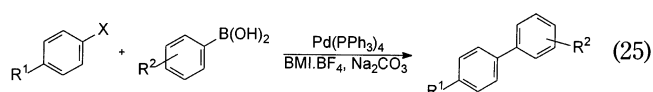
Palladium complexes associated with 1,3-bis-(diphenylphosphino)propane (dppp) immobilized in (BMI)BF_4 promote the regioselective arylation of butyl vinyl ether, affording almost exclusively the α-isomer (eq 24). In opposition the reactions performed in organic solvents afford variable mixtures of the α- and β-isomers.[225]

$$n\text{-BuO} \diagup\diagdown \ + \ \text{ArX} \ \xrightarrow[\text{BMI.BF}_4/\text{NEt}_3]{\text{Pd(OAc)}_2/\text{dppp}} \ n\text{-BuO} \diagup\diagdown \text{Ar} \quad (24)$$

The Heck reaction can also be performed in room-temperature ionic liquids such as (BMI)PF_6 and N-hexylpyridinium hexafluorophosphate.[226,227] The
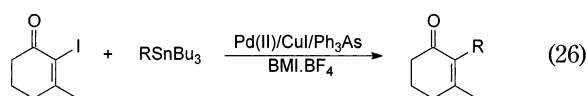
main difference of these media over the others is the workup procedure for the catalyst recycling. The vinylated products can be simply distilled off under reduced pressure or extracted with hexanes. The use of the hydrophobic (BMI)PF_6 allows the generation of a three-phase system ((BMI)PF_6/water/hexane). The palladium catalyst remains in the ionic liquid, the organic products remain in the hexane phase, and the salt byproducts remain in the aqueous phase. The greater catalytic activity observed in the reactions performed in the imidazolium ionic liquids compared to those in the pyridinium analogues was attributed to the formation of palladium−carbene complexes (by base abstraction of the 2H imidazolium proton) in the former melt.

Suzuki cross-coupling reactions catalyzed by palladium compounds have been also successfully performed in room-temperature ionic liquids (eq 25).[228]

$$R^1 \diagdown\diagup X \ + \ R^2 \diagdown\diagup B(OH)_2 \ \xrightarrow[\text{BMI.BF}_4, \text{Na}_2\text{CO}_3]{\text{Pd(PPh}_3)_4} \ R^1 \diagdown\diagup\diagdown\diagup R^2 \quad (25)$$

The reactions of phenyl boronic acids with haloarenes have been conducted by Pd(PPh$_3$)$_4$ immobilized in (BMI)BF_4 ionic liquid with several advantages over reactions performed in classical organic solvents. The reactions show a significant increase in reactivity, the homocoupling aryl byproducts can be eliminated, the reaction can be performed in air, and the catalyst can be reused several times without loss of catalyst activity. In these cases the products were extracted with diethyl ether and the byproducts (NaHCO$_3$ and Na[XB(OH)$_2$]) washed out with water affording the clean ionic liquid catalytic solution. The use of ultrasound in palladium−bis(carbene) complex dissolved in (BMI)BF_4 allows the Suzuzki coupling of various aryl halides with phenylboronic acid to be conducted at 30 °C.[229] However, the performance of these catalytic systems involving aryl bromides and activated aryl chlorides should be taken with caution since almost any palladium complex promotes the Suzuki coupling even at room temperature.[230,231]

The use of palladium complexes immobilized in (BMI)BF_4 also offers great advantages over classical organic solvents for Stille-[232] and Negishi-type[233] coupling reactions. For example, Pd(II) or Pd(0) catalyst precursors associated with Ph$_3$As, dissolved in (BMI)BF_4 and the in the presence of CuI, promote the reaction of vinyl and aryl stannanes with α-iodoenones (eq 26) and aryl halides under mild reaction conditions; the Pd/(BMI)BF_4 catalytic mixture has been reused up to five times with minimal loss of activity.
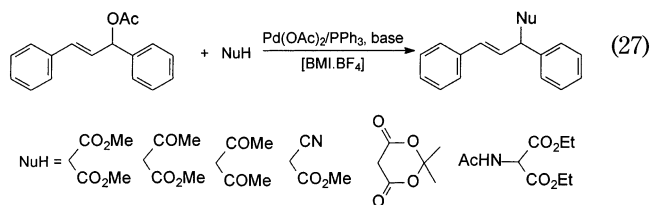
$$\text{enone-I} \ + \ \text{RSnBu}_3 \ \xrightarrow[\text{BMI.BF}_4]{\text{Pd(II)/CuI/Ph}_3\text{As}} \ \text{enone-R} \quad (26)$$

Nickel-catalyzed homocouplings of various aryl halides have been conducted in (BMI)PF_6.[234] The homocoupling reaction of iodo- and bromoarenes was performed by a catalytic system composed of NiCl$_2$-(PPh$_3$)$_2$/Zn/PPh$_3$ mixture under reaction conditions similar to those employed in homogeneous condi-

tions.[235] The yields obtained in (BMI)PF$_6$ as solvent for the reaction were comparable to those observed in DMF, the usual solvent for this reaction.

The Sonogashira[236] coupling of iodoarenes with 1-alkynes can be performed in absence of CuI (necessary when the reaction is performed in organic solvents) when the palladium catalyst, PdCl$_2$(PPh$_3$)$_2$, is immobilized in (BMI)PF$_6$.[237] This recyclable catalytic solution could be applied in a microflow system in conjunction with an IMM micromixer. Moreover, the combination of Pd(OAc)$_2$ with mesytilene imidazolium salt in the presence of Cs$_2$CO$_3$ as base efficiently promotes the coupling of aryl bromides with alkynylsilanes.[238]

IX. Allylation Reactions

Palladium(0)-catalyzed allylic alkylations of soft carbon nucleophiles represent a very useful tool for organic synthesis, and several efficient homogeneous systems have been developed. More recently, it has been reported that palladium acetate, with PPh$_3$ dissolved in (BMI)BF$_4$, catalyzes the alkylation of 3-acetoxy-1,3-diphenylprop-1-ene by dimethyl malonate and other active methylene compounds (eq 27).[239] The reactions were performed at 80 °C, and quantitative yields were achieved.

$$\text{(27)}$$

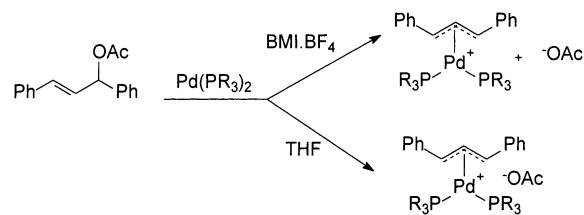When using PPh$_3$, separation or solvent extraction of the products from the ionic phase is not feasible. However, when the hydrophilic phosphine P(m-C$_6$H$_4$-SO$_3$Na)$_3$ was used, the ionic liquid could be recovered and recycled three times without losing activity in the alkylation by dimethyl malonate.
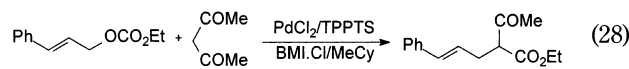
The asymmetric version of this reaction is also feasible by using palladium complexes associated with nonracemic ferrocenylphosphine ligands immobilized in (BMI)PF$_6$.[240] The degree of asymmetric induction obtained in the allylic substitution of rac-E-1,3-diphenyl-3-acetoxyprop-1-ene with dimethyl malonate is of the same order of magnitude as those obtained in reactions performed in organic solvents. However, a continuous drop in the reaction yield using recycled ionic catalyst solution was observed as a result of catalyst leaching during the product extraction step.

The palladium-catalyzed allylic alkylation is slower in THF than in (BMI)BF$_4$, and these observations were rationalized in terms of different allylpalladium intermediates arising from the oxidative addition of the acetato substrates to active Pd(0) species. These allylpalladium intermediates may exist as free cations in the ionic liquid but contact ion pairs in the organic solvent (Scheme 5).[241] In these reactions the phosphine ligands exert a profound effect on the catalytically active species, with more electron-donating phosphines affording faster reaction rates.
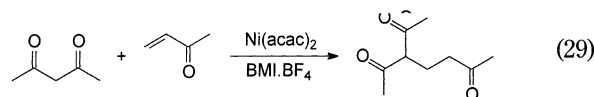
Scheme 5

Yields of up to 90% with TOF of 23 h^{-1} have been achieved in the Trost−Tsuji C−C coupling of cinnamyl carbonate and ethyl acetoacetate with a water-soluble Pd/TPPTS catalyst (TPPTS = triphenylphosphine trisulfonate, sodium salt) immobilized in (BMI)Cl ionic liquid (eq 28).[242]

$$\text{(28)}$$

The ionic liquid catalytic system has definite advantages over aqueous catalytic analogues such as faster reaction rates and selectivity (the formation of cinnamyl alcohol byproduct is suppressed in the reactions performed in (BMI)Cl), and common organic layers can be used for product extraction without catalyst deactivation. This advantages were also significant in related Ni(acac)$_2$-catalyzed Michael additions in (BMI)BF$_4$ (eq 29).[243]
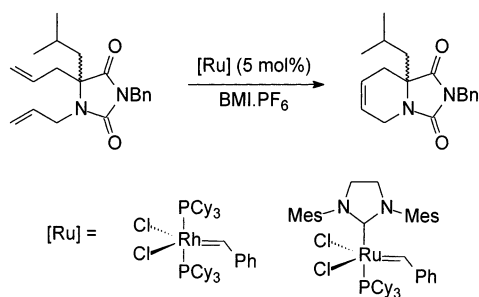

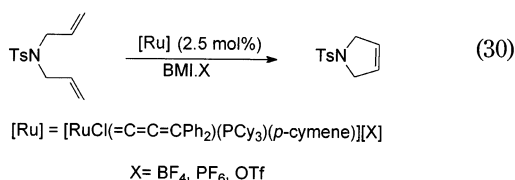$$\text{(29)}$$

X. Olefin Metathesis

Homogeneous transition-metal-catalyzed olefin metathesis—encompassing reactions such as ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET), ring-closing metathesis (RCM), and metathesis of acyclic olefins—is a focal issue in both organic synthesis and polymer chemistry.[244]

Initial attempts to immobilize Ru[245,246] and Mo−carbene[247] homogeneous catalyst precursors in (BMI)-BF$_4$ and (BMI)PF$_6$ have failed.[248] However, the ring-closing metathesis of dienes such as 1,7-octadiene was achieved with the Grubbs Ru catalyst precursor[245] initially "dissolved" in (BMI)PF$_6$. The reaction in fact takes place in the organic phase where the Ru species are leached from the ionic liquid phase.[248] However, it has been recently reported that the Grubbs Ru catalyst precursor in (BMI)PF$_6$ promoted the RCM of various dienes and the Ru catalyst were recycled (after extraction of the product with diethyl ether) for at least three cycles (Scheme 6). The diene conversion drops from 97% on the first run to 61% on the second recycling.[249]

RCM of dienes has recently been performed by ruthenium allenylidene salts immobilized in imidazolium ionic liquids such as in eq 30.[250] In these cases the N-tosyldihydropyrrole product was isolated by extraction with toluene and the ionic catalytic solution could be efficiently reused only once. The catalytic activity is strongly dependent on both anions, X = OTf being the the anion of choice. The
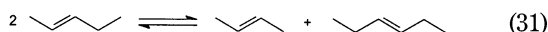
Scheme 6

same trend was observed in RCM by the same Ru catalyst precursors dissolved in toluene.[251]

Moreover, transition-metal-catalyzed RCM and ROMP in ionic liquids such as (EMI)PF$_6$ has been also described in a recent patent application.[252]

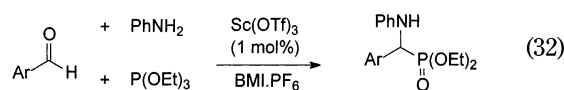Olefin disproportionation can also be performed by transition-metal metathesis catalysts based on W(VI) and Mo(V) compounds immobilized in (BMI)AlCl$_4$ ionic liquid.[253] This is a practical method for the conversion of terminal or internal linear olefins into a thermodynamic mixture of olefins. For example, 2-pentene can be converted into the thermodynamic 50/25/25 mixture of 2-pentene/2-butene/3-hexene at room temperature in the presence of (2,6-Ph$_2$C$_3$H$_3$O)$_2$-WCl$_4$ dissolved in (BMI)AlCl$_4$, activated by AlCl$_2$Et (eq 31).
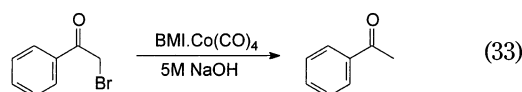

The authors claimed that related hindered aryloxy W(VI) and Mo(V) compounds were effective and that various quaternary ammonium and phosphonium ionic liquids are also useful as immobilizing agents.
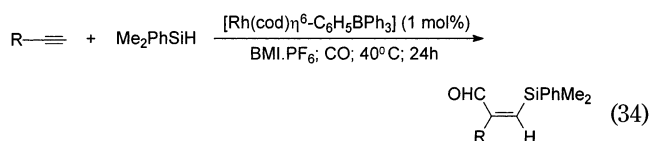
XI. Miscellaneous Reactions

The lanthanide triflate (such as Sc(OTf)$_3$, Yb(OTf)$_3$, and Sm(OTf)$_3$) catalyzed three component synthesis of α-amino phosphonates has been investigated in various imidazolium ionic liquids ((BMI)PF$_6$, (BMI)-SbF$_6$, (BMI)BF$_4$, and (BMI)OTf). The catalytic activities were very dependent on the imidazolium counterion as well as on the phosphorus nucleophile. It was found that anhydrous Sc(OTf)$_3$ dissolved in the hydrophobic (BMI)PF$_6$ ionic liquid was the best system for the three component reactions of aldehydes, amines, and P(OEt)$_3$ (eq 32).[254] α-Amino phosphonates—an important class of compounds in pharmaceutical chemistry[255]—were obtained in high yields (>90%) by extraction with benzene, and the immobilized catalyst could be reused several times without any loss of activity.
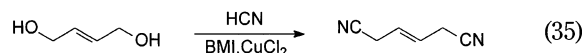

Imidazolium ionic liquids containing organometallic anions such as Co(CO)$_4$ have been recently prepared and were shown to be active for the catalytic debromination of 2-bromoketones in the presence of NaOH.[256] Thus, NaOH[257] dissolved in (BMI)Co(CO)$_4$ catalyzes the debromination of 2-bromoacetophenone (eq 33) and the organometallic containing ionic liquid could be recovered unchanged after catalysis.
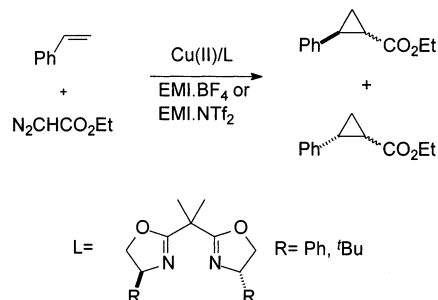

The silylformylation of 1-alkynes has been performed by the zwitterionic [Rh(cod)][η^6-C$_6$H$_5$)BPh$_3$] catalyst precursor immobilized in (BMI)PF$_6$ in a typical biphasic system. Once again, the ionic catalytic solution could be reused (eq 34).[258]

1,4-Dicyano-2-butene can be produced from the reaction of 3-butene-1,2-diol or 2-butene-1,2-diol with hydrogen cyanide in the presence of a molten catalyst comprising cuprous chloride or bromide and ammonium chloride or bromide salts (eq 35).[259]

A recyclable bis(oxazoline)copper catalytic system immobilized in ionic liquids such as (EMI)BF$_4$ for the enantioselective cyclopropanation of styrene with ethyl diazoacetate has been recently reported (Scheme 7).[260] Cyclopalladated compounds have been also

Scheme 7

effectively immobilized in 1-n-octyl-3-methylimidazolium tetrafluoroborate ionic liquid and used as recyclable catalyst for the cyclopropanation of styrene with ethyl diazoacetate.[261]

Moreover, a catalytic hydroamino methylation process in ionic liquids such as (EMI)PF$_6$ has been also described in a recent patent application.[262] A continuous hydroamination method has been devel-

oped using $Zn(CF_3SO_3)_2$ immobilized in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (eq 36).[263]

$$\text{(36)}$$

A significant breakthrough in the preparation and stabilization of transition-metal nanoparticles for biphasic catalysis has been very recently reported. In this context (BMI)PF$_6$ ionic liquid is not only a suitable medium for the preparation and stabilization of iridium nanoparticles but also ideal for the generation of recyclable biphasic catalytic systems for hydrogenation reactions. Ir(0) nanoparticles with a mean diameter of 2 nm have been prepared by reduction of Ir(I) dissolved in the ionic liquid with H$_2$, and this catalytic solution can be reused several times for the biphasic hydrogenation of olefins under mild reaction conditions (room temperature, 4 atm).[264]

XII. Mechanistic Aspects of the Reactions in Ionic Liquids

Although is difficult to know exactly in which phase the catalytic reaction is occurring (ionic phase, organic phase, both phases, or at the interface), in most of the cases investigated so far it is most likely that the reaction occurs preferentially in the ionic phase and that it follows a similar mechanism assumed to occur in one-phase reactions. In this context it is important to note that, in most of the cases, the metal complexes are not removed by organic solvents from the ionic solution. In the cases where extraction of the complexes did occur, this leaching process could be suppressed by the use of sulfonated phosphine ligands. Moreover, it is believed that transition-metal complexes are not solvated by ionic liquids.[24] Therefore, it can be anticipated that the catalytic species formed in ionic liquids (especially cationic species) are more electronically unsaturated than those present in polar organic solvents. Indeed, this effect was nicely put into evidence by Chauvin when investigating the species involved in the hydrogenation of C=C bonds by rhodium−phosphine complexes dissolved in BMI-based ionic liquids.[119] In homogeneous catalysis it is assumed that the formation of a cationic Rh−dihydrido complex (responsible for the hydrogenation path) is in equilibrium with a neutral Rh−monohydrido complex (responsible for both hydrogenation and C=C bond isomerization paths, eq 37).

$$[Rh(H)_2(PPh_3)_2(Solv)_n]^+ \underset{}{\overset{-H^+}{\rightleftharpoons}} [RhH(PPh_3)_2(Solv)_n]$$
$$\text{(37)}$$
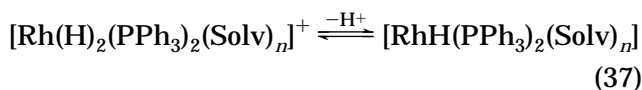
The ^{31}P NMR spectrum of the rhodium phosphine complex dissolved in (BMI)SbF$_6$ activated by molecular hydrogen indicates the formation of a symmetrical Rh−hydrido complex. The results also suggest the formation of a single catalytic species, namely a cationic nonsolvated Rh−dihydrido complex with two free coordinating sites.

Another interesting parallel between the reactions in ionic liquids with those occurring in homogeneous

conditions is that ligand effects are still operative in biphasic conditions (see for example the oligomerization and asymmetric hydrogenation of C=C bonds). At the present time there is no evidence indicating that the ligands are replaced by the (BMI)BF$_4$ and (BMI)PF$_6$ ionic liquids, except in the case of strong bases where carbene complexes are formed. Moreover, with the exception of organoaluminate ionic liquids, where cationic side reactions can occur, the organic reactants and products are the same as those obtained by transition-metal catalysts dissolved in organic solvents.

Although the kinetics of the catalytic reactions in ionic liquids have been investigated in only a few cases, it is interesting to note that the observed reaction order in the catalyst is very similar to those determined for one-phase reactions.[149] The use of deuterium NMR spectroscopy is a potential tool for monitoring the reaction kinetics in ionic liquids, as for example in oxidation reactions.[265] However, these observations should be taken with caution since mass transfer aspects in these biphasic systems are extremely important[266] and they have not been investigated in detail so far.

XII. Conclusions and Perspectives

Although the exploration of 1,3-dialkylimidazolium-based ionic liquids in organometallic biphasic catalysis is in its early days, these salts have already been shown to be the immobilizing agents of choice for various classical transition-metal complexes. The achieved catalytic performance in this medium is similar and in some cases superior to reactions performed in organic solvents or aqueous systems. Moreover, the unique physical−chemical properties of ionic liquids should boost clean technology development, especially in industrial catalytic processes. Indeed, IFP (Rueil-Malmaison, France) has just launched a commercial process for the dimerization of butenes to isooctenes (Difasol process).[267] This new process provides significant benefits over the existing homogeneous Dimersol X process, which is currently in operation in five industrial plants, producing nearly 200 000 tons/year of isooctenes.[268]

It is now evident that various one-phase transition-metal-catalyzed reactions can be transposed directly to biphasic systems using ionic liquids as the mobile phase. Organoaluminate ionic liquids derived from the combination of alkylaluminum compounds and 1-alkyl-3-methylimidazolium chloride are the immobilizing agents of choice for Ziegler−Natta type organometallic catalytic reactions. (BMI)BF$_4$ ("hydrophilic") and (BMI)PF$_6$ ("hydrophobic"), or their combination, are the most suitable media for other transition-metal catalyst precursors for processes operating under biphasic or homogeneous conditions.

In the cases of imidazolium and pyridinium cations, by simply varying the anion and the alkyl chain on the aromatic ring, one can increase the number of different ionic liquids. Thus, a further knowledge of the synthesis and physical−chemical properties of ionic liquids should enable one to access tailor-made ionic liquids for organometallic catalysis.

"Ionic liquids, which still represent a wide territory, will take their place alongside nonpolar and water-like solvents, and, like these, will frequently be the best solvents for given preparations."[112]

XIII. Acknowledgments

XIV. References

(1) Trost, B. M. *Science* **1991**, *254*, 1471−1477.
(2) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281.
(3) Hall, H. K., Jr. *Chemtech* **1997**, *27* (6), 20−25.
(4) For a recent review of solventless reactions, see: Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159−2169.
(5) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1049−1067.
(6) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 1996.
(7) Driessen-Höllscher, B. *Adv. Catal.* **1998**, *42*, 473−505.
(8) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544.
(9) Chaudhari, R. V.; Bhattacharya, A.; Bhanage, B. M. *Catal. Today* **1995**, *24*, 123−133.
(10) Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 853−860.
(11) (a) Anastas, P. T.; Barlett, L. B.; Kirchhoff, M. M.; Williamson, T. C. *Catal. Today* **2000**, *55*, 11−22. (b) Keim, W.; Behr, A.; Limbacker, B.; Kroger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (c) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235−244.
(12) Prinz, T.; Keim, W.; Driessen-Höllscher, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1708−1710.
(13) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1575−1577.
(14) *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 1996.
(15) Horvath, I. T. *J. Mol. Catal. A: Chem.* **1997**, *116*, 1−2.
(16) Cusack, R. W. *Chem. Eng. Prog.* **1996**, *92*, 56−63.
(17) Horváth, I. T.; Rabai, J. *Science* **1994**, *266*, 72−75.
(18) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rabai, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133−3143.
(19) Klement, I.; Lütjens, H.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1454−1456.
(20) Keim, W.; Vogt, M.; Wasserscheid, P.; Driessen-Hölscher, B. *J. Mol. Catal. A: Chem.* **1999**, *139*, 171−175.
(21) Fish, R. H. *Chem.—Eur. J.* **1999**, *5*, 1677−1680.
(22) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475−493.
(23) *Advances in Molten Salt Chemistry*; Mamantov, G., Mamantov, C., Eds.; Elsevier: New York, 1983; Vols. 5 and 6.
(24) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763−1772.
(25) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Process.* **1999**, *1*, 223−1346.
(26) Dupont, J.; Consorti, C.; Spencer, J. *J. Braz. Chem. Soc.* **2000**, *11*, 337−344.
(27) Olivier, H. *J. Mol. Catal. A: Chem.* **1999**, *146*, 285−289.
(28) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2084.
(29) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159−2169.
(30) Zhang, S. B.; Ding, M. X.; Gao, L. X. *Chin. J. Org. Chem.* **2002**, *22*, 159−163.
(31) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773−3789.
(32) Sheldon, R. *Chem. Commun.* **2001**, 2399−2407.
(33) Gordon, C. M. *Appl. Catal., A* **2001**, *222*, 101−117.
(34) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal. A.: Chem.* **2002**, *182–183*, 419−437.
(35) Deetlefs, M.; Raubenheimer, H. G.; Esterhuysen, M. W. *Catal. Today* **2002**, *72*, 29−41.
(36) Zhao, D.; Wu, M.; Kou, Y.; Min, E. *Catal. Today* **2002**, *74*, 157−189.
(37) Dyson, P. J. *Transition Met. Chem.* **2002**, *27*, 353−358.
(38) Seddon, K. R. In *Molten Salt Chemistry*; Mamantov, G., Marassi, R., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1987; p 365.
(39) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263−1264.
(40) Hussey, C. L. In *Advances in Molten Salts Chemistry*; Mamantov, G., Mamantov, C., Eds.; Elsevier: New York, 1983; Vol. 5, pp 185−230.
(41) Dieter, M. K.; Dymek, C. J., Jr.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722.
(42) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965−967.
(43) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim. Acta* **2000**, *357–358*, 97−102.
(44) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers R. D. *Chem. Commun.* **1998**, 1765−1766.
(45) (a) Bosmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. *Chem. Commun.* **2001**, 2494−2495. (b) Shyu, L.; Zhang, Q.; Zhang, Z. WO200140150-A1, 2000.
(46) See for example: (a) Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Chem. Commun.* **1998**, 2245−2246. (b) Chauvin, Y.; Hirschauer, A.; Olivier, H. *J. Mol. Catal. A: Chem.* **1994**, *92*, 155−165. (c) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097−2098. (d) Song, C. E.; Shim, W. H.; Roh, E. J.; Choi, J. H *Chem. Commun.* **2000**, 1695−1696. (e) Qiao, K.; Deng, Y. Q. *J. Mol. Catal. A: Chem.* **2001**, *171*, 81−84. (f) deCastro, C.; Sauvage, E.; Valkenberg, M. H.; Holderich, W. F. *J. Catal.* **2000**, *196*, 86−94. (g) Rebeiro, G. L.; Khadilkar, B. M. *Synth. Commun.* **2000**, *30*, 1605−1608. (h) Ludley, P.; Karodia, N. *Tetrahedron Lett.* **2001**, *42*, 2011−2014. (i) Green, L.; Hemeon, I.; Singer, R. D. *Tetrahedron Lett.* **2000**, *41*, 1343−1346. (j) Laali, K. K.; Gettwert, V. J. *J. Org. Chem.* **2001**, *66*, 35−40. (k) Laali, K.; Gettwert, V. J. *J. Fluorine Chem.* **2001**, *107*, 31−34. (l) Dubreuil, J. F.; Bazureau, J. P. *Tetrahedron Lett.* **2000**, *41*, 7351−7355. (m) Adams, C. J.; Earle, M. J.; Seddon, K. R. *Chem. Commun.* **1999**, 1043−1044. (n) Howarth, J.; James, P.; Ryan, R. *Synth. Commun.* **2001**, *31*, 2935−2938. (o) Branco, L. C.; Afonso, C. A. M. *Tetrahedron* **2001**, *57*, 4405−4410. (p) Peng, J. J.; Deng, Y. Q. *New J. Chem.* **2001**, *25*, 639−641. (q) Kitazume, T.; Zulfiqar, F.; Tanaka, G. *Green Chem.* **2000**, *2*, 133−136. (r) Smietana, M.; Mioskowski, C. *Org. Lett.* **2001**, *3*, 1037−1039. (s) Calo, V.; Nacci, A.; Lopez, L.; Lerario, V. L. *Tetrahedron Lett.* **2000**, *41*, 8977−8980. (t) McCluskey, A.; Garner, J.; Young, D. J.; Caballero, S. *Tetrahedron Lett.* **2000**, *41*, 8147−8151. (u) Scott, J. L.; MacFarlane, D. R.; Raston, C. L.; Teoh, C. M. *Green Chem.* **2000**, *2*, 123−126. (v) Morrison, D. W.; Forbes, D. C.; Davis, J. H. *Tetrahedron Lett.* **2001**, *42*, 6053−6055. (w) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. H.; Tambyrajah, V. *Green Chem.* **2002**, *4*, 24−26. (x) Qiao, K.; Deng, Y. Q. *Acta Chim. Sin.* **2002**, *60*, 528−531. (y) Leadbeater, N. E.; Torenius, H. M. *J. Org. Chem.* **2002**, *67*, 3145−3148.
(47) See for example: (a) Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Green Chem.* **2000**, *2*, 261−262. (b) Le Boulaire, V.; Gree, R. *Chem. Commun.* **2000**, 2195−2196. (c) Peng, J. J.; Deng, Y. Q. *Tetrahedron Lett.* **2001**, *42*, 5917−5919. (d) Peng, J. J.; Deng, Y. Q. *Tetrahedron Lett.* **2001**, *42*, 403−405. (e) Rebeiro, G. L.; Khadilkar, B. M. *Synthesis* **2001**, 370−372. (f) Kitazume, T.; Tanaka, G. *J. Fluorine Chem.* **2000**, *106*, 211−215. (g) Harjani, J. R.; Nara, S. J.; Salunkhe, M. M. *Tetrahedron Lett.* **2001**, *42*, 1979−1981. (h) Fraga-Dubreuil, J.; Bazureau, J. P. *Tetrahedron Lett.* **2001**, *42*, 6097−6100. (i) Harjani, J. R.; Nara, S. J.; Salunkhe, M. M. *Tetrahedron Lett.* **2002**, *43*, in press. (j) Deng, Y. Q.; Shi, F.; Beng, J. J.; Qiao, K. *J. Mol. Catal. A: Chem.* **2001**, *165*, 33−36. (k) Lee, C. W. *Tetrahedron Lett.* **1999**, *40*, 2461−2464. (l) Badri, M.; Brunet, J. J. *Tetrahedron Lett.* **1992**, *33*, 4435−4438. (m) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097−2098. (n) Dubreuil, J. F.; Bazureau, J. P. *Tetrahedron Lett.* **2000**, *41*, 7351−7355. (o) Ren, R. X.; Wu, J. X. *Org. Lett.* **2001**, *3*, 3727−3728. (p) Chiappe, C.; Capraro, D.; Conte, V.; Pieraccini, D. *Org. Lett.* **2001**, *3*, 1061−1063. (q) Laali, K.; Gettwert, V. *J. Org. Chem.* **2001**, *66*, 35−40. (r) Rosa, J. N.; Afonso, C. A. M.; Santos, A. G. *Tetrahedron* **2001**, *57*, 4189−4193. (s) Potdar, M. K.; Mohile, S. S.; Salunkhe, M. M. *Tetrahedron Lett.* **2001**, *42*, 9285−9287. (t) Ren, R. X.; Zueva, L. D.; Ou, W. *Tetrahedron Lett.* **2001**, *42*, 8441−8443. (u) Ren, R. X.; Ou, W. *Tetrahedron Lett.* **2001**, *42*, 8445−8446. (v) Forsyth, S. A.; MacFarlane, D. R.; Thomson, R. J.; von Itzstein, M. *Chem. Commun.* **2002**, 714−715. (w) Kabalka, G. W.; Venkataiah, B. *Tetrahedron Lett.* **2002**, in press. (x) Ohara, H.; Kiyokane, H.; Itoh, T. *Tetrahedron Lett.* **2002**, *43*, 3041−3044.
(48) See for example: (a) Laali, K. K.; Borodkin, G. I. *J. Chem. Soc., Perkin Trans. 2* **2002**, 953−957. (b) Gordon, C. M.; Ritchie, C. *Green Chem.* **2002**, 124−128. (c) Law, M. C.; Wong, K.-Y.; Chan, T. H. *Green Chem.* **2002**, 161−164. (d) Ross, J.; Xiao, J. *Green Chem.* **2002**, 129−133. (e) Imrie, C.; Elago, E. R. T.; McCleland, C. W.; Williams, N. *Green Chem.* **2002**, 159−160. (f) Qiao, K.; Deng, Y. Q. *New J. Chem.* **2002**, *26*, 667−670.
(49) See for example: (a) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Femoni, C.; Steiner, A.; Winterton, N. *Inorg. Chem.* **2001**, *40*, 795−800. (b) Dyson, P. J.; Grossel, M. C.; Srinivasan, N.; Vine, T.; Welton, T.; Williams, D. J.; White, A. P.; Zigras, T. *J. Chem. Soc., Dalton Trans.* **1997**, 3465−3469. (c) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Steiner, A.; Winterton,

N. *J. Chem. Res.* **2000**, *8*, 392−393. (d) Crofts, D.; Dyson, P. J.; Sanderson, K. M.; Srinivasan, N.; Welton, T. *J. Organomet. Chem.* **1999**, *573*, 292−298.

(50) Adams, J. A.; Earle, M. J.; Seddon, K. R. *Green Chem.* **2000**, *2*, 21−23.

(51) (a) Biedron, T.; Kubisa, P. *Macromol. Rapid Commun.* **2001**, *22*, 1237−1242. (b) Zhang, H.; Hong, K.; Mays, J. W. *Polym. Prepr.* **2001**, *42*, 583−585. (c) Noda, A.; Watanabe, M. *Electrochim. Acta* **2000**, *45*, 1265−1270.

(52) See for example: (a) Berthod, A.; He, L.; Armstrong, D. W. *Chromatographia* **2001**, *53*, 63−68. (b) Armstrong, D. W.; Zhang, L.-K.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679−3686. (c) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001**, *73*, 3737−3741. (d) Yanes, E. G.; Gratz, S. R.; Baldwin, M. J.; Robison, S. E.; Stalcup, A. M. *Anal. Chem.* **2001**, *73*, 3838−3844. (e) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529. (f) Marcinek, A.; Zielonka, J.; Gebicki, J.; Gordon, C. M.; Dunkin, I. R. *J. Phys. Chem. A* **2001**, *105*, 9305−9309. (g) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607−7614. (h) Fletcher, K. A.; Pandey, S.; Storey, I. K.; Hendricks, A. E.; Pandey, S. *Anal. Chim. Acta* **2001**, in press. (i) Forsyth, S.; Golding, J.; MacFarlane, D. R.; Forsyth, M. *Electrochim. Acta* **2001**, *46*, 1753−1757. (j) Wasserscheid, P.; Bosmann, A.; Bolm, C. *Chem. Commun.* **2002**, 200−201. (k) Quinn, B. M.; Ding, Z. F.; Moulton, R.; Bard, A. J. *Langmuir* **2002**, *18*, 1734−1742. (l) Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J.; Goncalves, R. S. *J. Braz. Chem. Soc.* **2002**, *13*, 106−109. (m) Fletcher, K. A.; Pandey, S.; Storey, I. K.; Hendricks, A. E.; Pandey, S. *Anal. Chim. Acta* **2002**, *453*, 89−96. (n) Endres, F.; El Abedin, S. Z. *Chem. Commun.* **2002**, 892−893. (o) Armstrong, D. W.; He, L.; Liu, Y.-S. *Anal. Chem.* **1999**, *71*, 3873−3876.

(53) (a) Bowlas, C. J.; Bruce, D. W.; Seddon, K. R. *Chem. Commun.* **1996**, 1625−1626. (b) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627−2636. (c) Davies, J. H., Jr.; Forrester, K. J.; Merrigan, T. *Tetrahedron Lett.* **1998**, *39*, 8955−8958. (d) Hardacre, C.; Holbrey, J. D.; McCormac, P. B.; McMath, S. E. J.; Nieuwenhuyzen, M.; Seddon, K. R. *J. Mater. Chem.* **2001**, *11*, 346−350. (e) Compton, D. L.; Laszlo, J. A. *J. Electroanal. Chem.* **2002**, *520*, 71−78. (f) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447−4452.

(54) Ye, C. F.; Liu, W. M.; Chen, Y. X.; Yu, L. G. *Chem. Commun.* **2001**, 2244−2245.

(55) (a) Lau, M. R.; van Rantwijk, F.; Seddon, K. R.; Sheldon, R. A. *Org. Lett.* **2000**, *2*, 4189. (b) Cull, S. G.; Holbrey, J. D.; Vargas-Mora, V.; Seddon, K. R.; Lye, G. J. *Biotechnol. Bioeng.* **2000**, *69*, 227−233. (c) Schofer, S. H.; Kaftzik, Wasserscheid, P.; Kragl, U. *Chem. Commun.* **2001**, 425−426. (d) Itoh, T.; Akasaki, E.; Kudo, K.; Shirakami, S. *Chem. Lett.* **2001**, 262−263. (e) Kim, K. W.; Song, B.; Choi, M. Y.; Kim, M. J. *Org. Lett.* **2001**, *3*, 1507−1509. (f) Lozano, P.; De Diego, T.; Carrie, D.; Vaultier, M.; Iborra, J. L. *Biotechnol. Lett.* **2001**, *23*, 1529−1533. (g) Howarth, J.; James, P.; Dai, J. *Tetrahedron Lett.* **2001**, *42*, 7517−7519. (h) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, *66*, 8395−8401. (i) Lozano, P.; de Diego, T.; Guegan, J. P.; Vaultier, M.; Iborra, J. L. *Biotechnol. Bioeng.* **2001**, *75*, 563−569. (j) Lozano, P.; de Diego, T.; Carrie, D.; Vaultier, M.; Iborra, J. L. *Chem. Commun.* **2002**, 692−693. (k) Nara, S. J.; Harjani, J. R.; Salunkhe, M. M. *Tetrahedron Lett.* **2002**, *43*, 2979−2982. (l) Reetz, M. T.; Wiesenhofer, W.; Francio, G.; Leitner, W. *Chem. Commun.* **2002**, 992−993. (m) Sheldon, R. A.; Lau, R. M.; Sorgedrager, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002**, 147−151.

(56) Cooper, E. I.; M. O'Sullivan, E. J. In *Proceedings of the 8th International Symposium on Molten Salts*; The Electrochemical Society: Pennington, NJ, 1992; Vol. 92-16, p 386 and references therein.

(57) Hurley, F. H.; Wier, T. P. *J. Electrochem. Soc.* **1951**, *98*, 203.

(58) Fannin, A. A., Jr.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, *88*, 2614−2621.

(59) Dymek, C. J., Jr.; Grossie, D. A.; Fratini, A. V.; Adams, W. W. *J. Mol. Struct.* **1989**, *213*, 25−34.

(60) Goledzinowski, M.; Birss, V. I.; Galuszka, J. *Ind. Eng. Chem. Res.* **1993**, *32*, 1795−1797.

(61) Ambler, P. W.; Hodgson, P. K. G.; Stewart, N. J. Eur. Pat. Appl. 0558187, 1993; *Chem. Abstr.* **1994**, *120*, 77937q.

(62) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Graitzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(63) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217−1219 (received 26 June 1995).

(64) Suarez, P. A. Z.; Selbach, V. M.; Dullius, J. E. L.; Einloft, S.; Piatnicki, C. M.; Azambuja, S. D. S.; de Souza, R. F.; Dupont, J. *Electrochim. Acta* **1997**, *42*, 2533−2535.

(65) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *J. Chim. Phys.* **1998**, *95*, 1626−1639.

(66) Fuller, J.; Carlin, R. T.; De Long, H. C.; Haworth, D. *J. Chem. Soc., Chem. Commun.* **1994**, 299−300.

(67) Lipsztajn, M.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1968−1969.

(68) (a) Pernak, J.; Czepukowicz, A.; Pozniak, R. *Ind. Eng. Chem. Res.* **2001**, 2379−2383. (b) Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105*, 4603−4610.

(69) Hagiwara, R.; Ito, T. *J. Fluorine Chem.* **2000**, *105*, 221−227.

(70) Consorti, C. S.; Souza, R. F.; Dupont, J.; Suarez, P. A. Z. *Quim. Nova* **2001**, *24*, 830−837.

(71) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(72) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089−3091.

(73) Sweeny, B. K.; Peters, D. G. *Electrochem. Commun.* **2001**, *3*, 712−715.

(74) Holbrey, J. D.; Seddon, K. R.; Wareing, R. *Green Chem.* **2001**, *3*, 33−36.

(75) (a) Varma, R. S.; Namboodiri, V. V. *Chem. Commun.* **2001**, 643−644. (b) Westam, J. WO200072956-A1, 2000. (c) Varma, R. S.; Namboodiri, V. V. *Pure Appl. Chem.* **2001**, *73*, 1309−1313.

(76) Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F. *Org. Synth.* **2002**, *79*, 236−243.

(77) For a recent series of quaternary ammonium ionic liquids see: Golding, J.; Forsyth, S.; McFarlane, D. R.; Forsyth, M.; Deacon, G. B. *Green Chem.* **2002**, *4*, 223−229.

(78) Arduengo, A. J., III. U.S. Patent 5077414, 1991; *Chem. Abstr.* **1992**, *116*, 106289e.

(79) (a) Dupont, J.; Souza, R. F.; Muller, L. L.; Suarez, P. A. Z. Braz. Patent PI BR 9802101, 1997. (b) de Souza, R. F.; Rech, V.; Dupont, J. *Adv. Synth. Catal.* **2002**, *344*, 153−155.

(80) Baker, S. N.; Baker, G. A.; Bright, F. V. *Green Chem.* **2002**, 165−169.

(81) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192−5200.

(82) (a) Gozzo, F. C.; Consorti, C. S.; Dupont, J.; Eberlin, M. N. Submitted for publication.

(83) Hanke, C. G.; Atamas, N. A.; Lynden-Bell, M. R. *Green Chem.* **2002**, *4*, 107−111.

(84) Gu, Z.; Brennecke, J. F. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(85) Takahashi, S.; Suzuya, K.; Kohara, S.; Koura, N.; Curtiss, L. A.; Sabougni, M.-L. *Z. Phys. Chem.* **1999**, *209*, 209−221.

(86) Larsen, A. S.; Holbrey, J. D.; Thams, F. S. Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264−7272.

(87) See for example: (a) Reference 82. (b) AbdulSada, A. K.; Elaiwi, A. E.; Greenway, A. M.; Seddon, K. R. *Eur. Mass Spectrom.* **1997**, *3*, 245−247. (c) de Andrade, J.; Boes, E. S.; Stassen, H. *J. Phys. Chem. B* **2002**, *106*, 3546−3548.

(88) Dupont, J.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Kintzinger, J.-P. *Chem.−Eur. J.* **2000**, *6*, 2377−2381.

(89) Huang, J. F.; Chen, P. Y.; Sun, I. W.; Wang, S. P. *Spectrosc. Lett.* **2001**, *34*, 591−603.

(90) Huang, J. F.; Chen, P. Y.; Sun, I. W.; Wang, S. P. *Inorg. Chim. Acta* **2001**, *320*, 7−11.

(91) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591−595.

(92) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commun.* **2001**, 413−414.

(93) Fletcher, K. A.; Storey, I. A.; Hendricks, A. E.; Pandey, S.; Pandey, S. *Green Chem.* **2001**, *3*, 210−215.

(94) Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 433−435.

(95) Gannon, T. J.; Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. *Langmuir* **1999**, *15*, 8429−8434.

(96) Carmichael, A. J.; Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Seddon, K. R. *Mol. Phys.* **2001**, *99*, 795−800.

(97) Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2879−2885.

(98) Carmichael, A. J.; Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Seddon, K. R. *Anal. Chem.* **1999**, *71*, 4572−4574.

(99) Schröeder, U.; Wadhnawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *New J. Chem.* **2000**, *12*, 1009−1015.

(100) Elliot, J. M.; Attard, G. S.; Barlett, P. N.; Owen, J. R.; Ryann, N.; Singh, G. J. *New Mater. Electrochem. Syst.* **1999**, *2*, 239.

(101) Visser, A. E.; Swatloski, R. P.; Rogers, R. D. *Green Chem.* **2000**, *2*, 1−4.

(102) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596−3604.

(103) Blanchard, L. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, *40*, 287−292.

(104) (a) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28−29. (b) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.

(105) Wadhawan, J. D.; Schroder, U.; Neudeck, A.; Wilkins, S. J.; Compton, R.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *J. Eletroanal. Chem.* **2000**, *493*, 75−83.

(106) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; de Cian, A. *Organometallics* **1998**, *17*, 815−819.

(107) For solution thermodynamics of IL and water see: Anthony, J. F.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.

(108) Wong, D. S. H.; Chen, J. P.; Chang, J. M.; Chou, C. H. *Fluid Phase Equilib.* **2002**, *194−197*, 1089−1095.

(109) Tortorelli, L. J.; Flowers, P. A.; Harward, B. L.; Mamantov, G.; Klatt, L. N. *J. Organomet. Chem.* **1992**, *429*, 119−134.

(110) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 525−530.

(111) Campbell, J. L. E.; Johnson, K. E. *J. Am. Chem. Soc.* **1995**, *117*, 7791−7800.

(112) Sundermeyer, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 222−238.

(113) Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 8716−8719.

(114) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959−3961.

(115) Collman, J. P.; Brauman, J. I.; Tustin, G.; Wann, G. S. *J. Am. Chem. Soc.* **1983**, *105*, 3913−3922.

(116) Chauvin, Y.; Gilbert, B.; Guibard, I. *J. Chem. Soc., Chem. Commun.* **1990**, 1715−1716.

(117) Chauvin, Y.; Olivier-Bourbigou, H. *Chemtech* **1995**, *25*, 26−30.

(118) Chauvin, Y.; Einloft, S.; Olivier, H. *Ind. Eng. Chem. Res.* **1995**, *34*, 1149−1155.

(119) Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2698−2700 (received 18 August 1995). This paper was erroneously indexed in the SCI (ISI) database with 1996 as the year.

(120) Einloft, S.; Dietrich, F. K.; de Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *19*, 3257−3259.

(121) Chauvin, Y.; Olivier, H.; Wyrvalski, C. N.; Simon, L. C.; de Souza, R. F. *J. Catal.* **1997**, *165*, 275−278.

(122) Simon, L. C.; Dupont, J.; de Souza, R. F. *Appl. Catal., A* **1998**, *175*, 215−220.

(123) Elllis, B.; Keim, W.; Wassercheid, P. *Chem. Commun.* **1999**, 337−338.

(124) Wasserscheid, P.; Eichmann, M. *Catal. Today* **2001**, *66*, 309−316.

(125) Dixon, J. T.; Grove, J. J. C.; Ranwell, A. WO200138270-A1, 2000.

(126) Olivier, H.; Laurent-Gérot, P. *J. Mol. Catal. A: Chem.* **1999**, *148*, 43−48.

(127) See for example: (a) RajanBabu, T. V.; Nomura, N.; Jin, J.; Radetich, B.; Park, H.; Nandi, M. *Chem.−Eur. J.* **1999**, *5*, 1963−1968. (b) Monteiro, A. L.; Seferin, M.; Dupont, J.; de Souza, R. F. *Tetrahedron Lett.* **1996**, *37*, 1157−1160.

(128) Wilke, G.; Monkkiewicz, J.; Kunh, H. U.S. Patent 4,912,274, 1990; *Chem. Abstr.* **1991,** *109*, 6735j.

(129) Bosmann, A.; Francio, G.; Janssen, E.; Solinas, M.; Leitner, W.; Wasserscheid, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2697−2699.

(130) Zimmermann, J.; Wasserscheid, P.; Tkatchenko, I.; Stutzmann, S. *Chem. Commun.* **2002**, 760−761.

(131) Carlin, R. T.; Wilkes, J. S. *J. Mol. Catal. A: Chem.* **1990**, *63*, 125−129.

(132) Suarez, P. A. Z.; Rosa, N. T.; Einloft, S.; de Souza, R. F.; Dick, Y. P. *Polym. Bull.* **1998**, *41*, 175−182.

(133) Pinheiro, M. F.; Mauler, R.; de Souza, R. F. *Macromol. Rapid Commun.* **2001**, *22*, 425−428.

(134) De Souza, R. F.; Mauler, R. S.; Escher, F. F. N. *J. Braz. Chem. Soc.* **2001**, *12*, 47−51.

(135) Mastrorilli, P.; Nobile, C. F.; Gallo, V.; Suranna, G. P.; Farinola, G. *J. Mol. Catal. A: Chem.* **2002**, in press.

(136) Carmichael, A. J.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237−1238.

(137) For the behaviour of RhCl(PPh₃)₃ in (EMI)AlCl₄, see: Mann, B. E.; Guzman, M. H. *Inorg. Chim. Acta* **2002**, *330*, 143−148.

(138) Suarez, P. A. Z. M.S. Dissertation, Institute of Chemistry, Federal University of Rio Grande do Sul, Porto Alegre, Brazil), 1996.

(139) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *J. Inorg. Chim. Acta* **1997**, *255*, 207−209.

(140) Renaud, E.; Russell, R. B.; Fortier, S.; Brown, S. J.; Baird, M. C. *J. Organomet. Chem.* **1991**, *419*, 403−415.

(141) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1978**, *2*, 137−144.

(142) Liu, F. C.; Abrams, M. B.; Baker, R. T.; Tumas, W. *Chem. Commun.* **2001**, 433−434.

(143) Dyson, P. J.; Ellis, D. J.; Welton, T. *Can. J. Chem.* **2001**, *79*, 705−708.

(144) Dupont, J.; Suarez, P. A. Z.; Umpierre, A. P.; de Souza, R. F. *J. Braz. Chem. Soc.* **2000**, *11*, 293−297.

(145) Suarez, P. A. Z.; de Souza, R. F.; Dupont, J. Manuscript in preparation.

(146) Ellis, D. J.; Dyson, P. J.; Parker, D. G.; Welton, T. *J. Mol. Catal. A: Chem.* **1999**, *150*, 71−75.

(147) Dupont, J.; Suarez, P. A. Z.; Umpierre, A. P.; de Souza, R. F. *Catal. Lett.* **2001**, *73*, 211−213.

(148) Steines, S.; Wassercheid, P.; Driessen-Hölscher, B. *J. Prakt. Chem.* **2000**, *342*, 348−354.

(149) Müller, L. A.; Dupont, J.; de Souza, R. F. *Macromol. Rapid Commun.* **1998**, *19*, 409−411.

(150) McManus, N. T.; Rempel, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1995**, *C35*, 239−285.

(151) Dyson, P. J.; Ellis, D. J.; Parker, D. G.; Welton, T. *Chem. Commun.* **1999**, 25−26.

(152) Bennet, M. A.; Huang, T. N.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 312−314.

(153) Bonilla R. J.; James, B. R.; Jessop, P. G. *Chem. Commun.* **2000**, 941−942.

(154) Monteiro, A. L.; Zinn, F. K.; de Souza, R. F.; Dupont, J. *Tetrahedron: Asymmetry* **1997**, *8*, 177−179.

(155) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley: New York, 1994; pp 16−94.

(156) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138.

(157) Berger, A.; de Souza, R. F.; Delgado, M. R.; Dupont, J. *Tetrahedron: Asymmetry* **2001**, *12*, 1825−1828.

(158) Guernik, S.; Wolfson, A.; Herskowitz, M.; Greenspoon, N.; Geresh, S. *Chem. Commun.* **2001**, 2314−2315.

(159) Kitamura, M.; Kasahara, I.; Manabe, K.; Noyori, R.; Takaya, H. *J. Org. Chem.* **1988**, *53*, 708−710.

(160) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254−1255.

(161) Comyns, C.; Karodia, N.; Zeler, S. Andersen, J. A. *Catal. Lett.* **2000**, *67*, 113−115.

(162) Ligabue, R. A.; de Souza, R. F.; Dupont, J. *J. Mol. Catal. A: Chem.* **2001**, *169*, 11−17.

(163) Song, C. E.; Shim, W. H.; Roh, E. J.; Lee, S.; Choi, J. H. *Chem. Commun.* **2001**, 1122−1123.

(164) See for example: Kumar, A. *Chem. Rev.* **2001**, *101*, 1−19.

(165) Zulfiqar, F.; Kitazume, T. *Green Chem.* **2000**, *2*, 137−139.

(166) Silva, S. M.; Suarez, P. A. Z.; de Souza, R. F.; Dupont, J. *Polym. Bull.* **1998**, *40*, 401−405.

(167) Monflier, E.; Bourdauducq, P.; Couturier, J.; Kervennal, J.; Mortreux, A. *Appl. Catal., A* **1995**, *131*, 167−178.

(168) Knifton, J. F. *J. Mol. Catal.* **1987**, *43*, 65−77.

(169) Knifton, J. F. *J. Mol. Catal.* **1988**, *47*, 99−116.

(170) Mitsudo, T.; Suzuki, N.; Kondo, T.; Watanabe, Y. *J. Mol. Catal. A: Chem.* **1996**, *109*, 219−225.

(171) Karodia, N.; Guise, S.; Newlands, C.; Andersen, J.-A. *Chem. Commun.* **1998**, 2341−2342.

(172) Dupont, J.; Silva, S. M.; de Souza, R. F. *Catal. Lett.* **2001**, *77*, 131−133.

(173) Wasserscheid, P.; Waffenschmidt, H.; Machnitzki, P.; Kottsieper, K. W.; Stelzer, O. *Chem. Commun.* **2001**, 451−452.

(174) Brauer, D. J.; Kottsieper, K. W.; Liek, C.; Stelzer, O.; Waffenschmidt, H.; Wasserscheid, P. *J. Organomet. Chem.* **2001**, *630*, 177−184.

(175) Kottsieper, K. W.; Stelzer, O.; Wasserscheid, P. *J. Mol. Catal. A: Chem.* **2001**, *175*, 285−288.

(176) Favre, F.; Olivier-Bourbigou, H.; Commereuc, D.; Saussine, L. *Chem. Commun.* **2001**, 1360−1361.

(177) Brasse, C. C.; Englert, U.; Salzer, A.; Waffenschmidt, H.; Wasserscheid, P. *Organometallics* **2000**, *19*, 3818−3823.

(178) Waffenschmidt, H.; Wasserscheid, P. *J. Mol. Catal. A: Chem.* **2000**, *164*, 61−67.

(179) Keim, W.; Vogt, D.; Waffenschmidt, H.; Wasserscheid, P. *J. Catal.* **1999**, *186*, 481−484.

(180) Sellin, M. F.; Webb, P. B.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 781−782.

(181) Stenzel, O.; Raubenheimer, H. G.; Esterhuysen, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1132−1138.

(182) Zim, de Souza, R. F.; Dupont, J.; Monteiro, A. L. *Tetrahedron Lett.* **1998**, *39*, 7071−7074.

(183) Zhou, H.; Hou, J.; Cheng, J.; Lu, S.; Fu, H.; Wang, H. *J. Organomet. Chem.* **1997**, *543*, 227−228.

(184) Calo, V.; Giannoccaro, P.; Nacci, A.; Monopoli, A. *J. Organomet. Chem.* **2002**, *645*, 152−157.

(185) Mizushima, E.; Hayashi, T.; Tanaka, M. *Green Chem.* **2001**, *3*, 76−79.

(186) For a recent example in "homogeneous" conditions see: Magerlein, W.; Indolese, A. F.; Beller, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2856−2859.

(187) Consorti, C. S.; Ebeling, G.; Dupont, J. *Tetrahedron Lett.* **2002**, *43*, 753−755.

(188) Alcántara, R.; Canoira, L.; Guilhermo-Joao, P.; Santos, J.-M.; Vazquez, I. *Appl. Catal., A* **2000**, *203*, 259−268.

(189) Alcantara, R.; Canoira, L.; Guilhermo-Joao, P.; Perez-Mendo, J. P. *Appl. Catal., A* **2001**, *218*, 269−279.

(190) Howarth, J. *Tetrahedron Lett.* **2000**, *41*, 6627.

(191) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639−666.

(192) Ley, S. V.; Ramarao, C.; Smith, M. D. *Chem. Commun.* **2001**, 2278−2279.

(193) Singer, R. D.; Scammells, P. J. *Tetrahedron Lett.* **2001**, *42*, 6831−6833.

(194) Owens, G. S.; Abu-Omar, M. M. *Chem. Commun.* **2000**, 1165−1166.

(195) Varma, R. S.; Sahle-Demessie, E.; Pillai, U. R. *Green Chem.* **2002**, 170−173.

(196) For general review in asymmetric epoxidation see, for example: Katsuki, H. In *Comprehensive Asymmetric Catalysis*; Springer-Verlag: Berlin, Heidelberg, 1999; Vol. 2, pp 621−677.
(197) Song, C. E.; Roh, E. J. *Chem. Commun.* **2000**, 837−838.
(198) Gaillon, L.; Bedioui, F. *Chem. Commun.* **2001**, 1458−1459.
(199) Song, C. E.; Oh, C. R.; Roh, E. J.; Choo, D. J. *Chem. Commun.* **2000**, 1743.
(200) Bar, G.; Parsons, A. F.; Thomas, C. B. *Chem. Commun.* **2001**, 1350−1351.
(201) See for example: Asouti, A.; Hadjiarapoglou, L. P. *Tetrahedron Lett.* **1998**, *39*, 9073−9076.
(202) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1996.
(203) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.
(204) Kaufmann, D. E.; Nouroozian, M.; Henze, H. *Synlett* **1996**, 1091−1092.
(205) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667−2670.
(206) Herrmann, W. A.; Elison, M.; Fisher, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371−2374.
(207) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481−483.
(208) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165−168.
(209) Gürtler, C.; Buchwald, S. L. *Chem.—Eur. J.* **1999**, *5*, 3107−3112.
(210) Bouquillon, S.; Ganchegui, B.; Estrine, B.; Henin, F.; Muzart, J. *J. Organomet. Chem.* **2001**, *634*, 153−156.
(211) (a) Calo, V.; Nacci, A.; Monopoli, A.; Lopez, L.; di Cosmo, A. *Tetrahedron* **2001**, *57*, 6071−6077. (b) Calo, V.; Nacci, A. *Z. Naturforsch., A: Phys. Sci.* **2001**, *56*, 702−706.
(212) Silberg, J.; Schareina, T.; Kempe, R.; Wurst, K.; Buchmeiser, M. R. *J. Organomet. Chem.* **2001**, *622*, 6−18.
(213) Herrmann, W. A.; Böhm, V. P. W. *J. Organomet. Chem.* **1999**, *572*, 141−145.
(214) Böhm, V. P.; Herrmann, W. A. *Chem.—Eur. J.* **2000**, *6*, 1017−1025.
(215) For a recent review on the use of palladacycles in organometallic catalysis, see: Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917−1927.
(216) Efficient catalyst precursors for the Heck reaction of chloroarenes at room temperature have been recently reported: Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989−7000.
(217) Calló, V.; Nacci, A.; Lopez, L.; Mannarini, N. *Tetrahedron Lett.* **2000**, *41*, 8973−8976.
(218) Xu, L.; Chen, W.; Xiao, J. *Organometallics* **2000**, *19*, 1123−1127.
(219) For the synthesis and use of palladium carbene complexes in C−C bond formation reactions, see for example: Yang, C.; Nolan, S. P. *Synlett* **2001**, 1539−1542.
(220) Mathews, C. J.; Smith, P. J.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **2001**, *20*, 3848−3850.
(221) Deshmukh, R. R.; Rajagopal, R.; Srinivasan, K. V. *Chem. Commun.* **2001**, 1544−1545.
(222) Hagiwara, H.; Shimizu, Y.; Hoshi, T., Suzuki, T.; Ando, M.; Ohkubo, K.; Yokoyama, C. *Tetrahedron Lett.* **2001**, *42*, 4349−4351.
(223) Gruber, A. S.; Pozebon, D.; Monteiro A. L.; Dupont, J. *Tetrahedron Lett.* **2001**, *42*, 7345−7348.
(224) Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139−10140.
(225) Xu, L. J.; Chen, W. R.; Ross, J.; Xiao, J. L. *Org. Lett.* **2001**, *3*, 295−297.
(226) Howarth, J.; Dallas, A. *Molecules* **2000**, *5*, 851−855.
(227) Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, *1*, 997−1000.
(228) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, 1249−1250.
(229) Rajagopal, R.; Jarikote, D. V.; Sribivasan, K. V. *Chem. Commun.* **2002**, 616−617.
(230) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550−9561.
(231) Zim, D.; Monteiro, A. L.; Dupont, J. *Tetrahedron Lett.* **2000**, *41*, 8199−8202.
(232) Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, *3*, 233−236.
(233) Sirieix, J.; Ossberger, M.; Betzemeier, B.; Knochel, P. *Synlett* **2000**, 1613−1615.
(234) Howarth, J.; James, Dai, J. *Tetrahedron Lett.* **2000**, *41*, 10319−10321.
(235) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, *39*, 3375−3378.
(236) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467−4470.
(237) Fukuyama, T.; Shinmen, M.; Nishitani, S.; Sato, M.; Ryu, I. *Org. Lett.* **2002**, in press.
(238) Yang, C. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 1020−1022.
(239) Chen, W. P.; Xu, L. J.; Chatterton, C.; Xiao, J. L. *Chem. Commun.* **1999**, 1247−1248.
(240) Toma, S.; Gotov, B.; Kmentov'a, I.; Solcaniov'a, E. *Green Chem.* **2000**, *2*, 149−151. (b) Kmentová, I.; Gotov, B.; Solcaniova, E.; Toma S. *Green Chem.* **2002**, *4*, 103−106.
(241) Ross, J.; Chen, W.; Xu, L.; Xiao, J. *Organometallics* **2001**, *20*, 138−142.
(242) De Bellefon, C.; Pollet, E.; Grenouillet, P. *J. Mol. Catal. A: Chem.* **1999**, *145*, 121−126.
(243) Dell'Anna, M. M.; Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. *Chem. Commun.* **2002**, 434−435.
(244) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037−2056.
(245) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975.
(246) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490−2493.
(247) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041−4042.
(248) Dullius, J. E. L.; de Souza, R. F.; Dupont, J. Unpublished results.
(249) Buijsman, R. C.; van Vuuren, E.; Sterrenburg, J. G. *Org. Lett.* **2001**, *3*, 3785−3787.
(250) Semeril, D.; Olivier-Bourbigou, H.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **2002**, 146−147.
(251) Picquet, M.; Touchard, D.; Dixneuf, P. H. *New J. Chem.* **1999**, 141−143.
(252) Guertler, C.; Jautelat, M. EP1035093-A2, 2000.
(253) Chauvin, Y.; Di Marco van Tiggelen, F. U.S. Patent 5,675,051, 1996; *Chem. Abstr.* **1996**, *123*, 344115j.
(254) Lee, S.; Park, J. H.; Kang, J.; Lee, J. K. *Chem. Commun.* **2001**, 1698−1699.
(255) See for example: Kafarski, P.; Lejczak B. *Phosphorus Sulfur Silicon* **1991**, *63*, 193−215.
(256) Brown, R. J. C.; Dyson, P. J.; Ellis, D. J.; Welton, T. *Chem. Commun.* **2001**, 1862−1863.
(257) For examples of Co(CO)₄ anion catalyzed dehalogenation and coupling reactions see: Alper, H.; Logbo, K. D.; des Abbayes, H. *Tetrahedron Lett.* **1977**, 2861−2864.
(258) Okazaki, H.; Kawanami, Y.; Yamamoto, K. *Chem. Lett.* **2001**, 650−651.
(259) Imi, K.; Wake, S. U.S. 5637751-A, 1997; EP 563859-A2, 1993.
(260) Fraile, J. M.; Garcia, J. I.; Herrerias, C. I.; Mayoral, J. A.; Carrie, D.; Vaultier, M. *Tetrahedron: Asymmetry* **2001**, *12*, 1891−1894.
(261) Yang, F.; Zhang, Y. M.; Qiu, W. W.; Tang, J.; He, M. Y. *Chin. J. Chem.* **2002**, *20*, 114−116.
(262) Eilbracht, P.; Greiving, H.; Mersch, C. DE 10010046-A1, 2001.
(263) Neff, V.; Müller, T. E.; Lercher, J. A. *Chem. Commun.* **2002**, 906−907.
(264) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228−4229.
(265) Durazo, A.; Abu-Omar, M. M. *Chem. Commun.* **2002**, 66−67.
(266) Sun, Y.; Landau, R. N.; Wang, J.; LeBlond, C.; Blackmond, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 1348−1353 and references therein.
(267) (a) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: New York, 1996; Vol. 1, p 245. (b) Chauvin, Y.; de Souza, R. F.; Olivier, H. U.S. Patent 5,723,712, 1996; *Chem. Abstr.* **1999**, *126*, 173356u.
(268) Freemantle, M. *Chem. Eng. News* **1998**, *76*, 32−37.