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Metal-containing ionic liquids: current paradigm and applications

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Metal-containing ionic liquids have been known for several decades and the scope of their applicability is currently extending. The review briefly considers four key types of these ionic liquids, namely, ionic liquids containing a metal atom in the cation and/or anion; a metal atom or a metal complex coordinated to the cation or anion; a dissolved metal salt or complex; and metal or metal oxide nanoparticles. The use of metal-containing ionic liquids in organic synthesis is considered, including cyclization and isomerization, alkylation, carbonylation, metathesis and C – C coupling reactions. In particular, isobutane alkylation with but-2-ene underlies the production of high-octane fuel. Particular sections are devoted to the use of metal-containing ionic liquids for fuel desulfurization and denitrogenation and for electrodeposition. Promising applications of these materials in biomedicine, biomass refining, CO_2 capture and design of new soft materials are outlined.
The bibliography includes 215 references.

Contents

I.	Introduction	1255
II.	Ionic liquids containing a metal atom as a part of the cation and/or anion	1255
III.	Ionic liquids with a metal atom or a metal complex coordinated to the cation or anion	1255
IV.	Ionic liquids with a dissolved metal salt or a dissolved metal complex	1255
V.	Ionic liquids containing metal or metal oxide nanoparticles	1256
VI.	Application of metal-containing ionic liquids	1256
VII.	Conclusion	1266

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I. Introduction

Ionic liquids (ILs) are ionic compounds with melting points below 100 °C. Metal-containing ionic liquids (M-ILs), also known as metal ion-containing ILs, have a wide application in organic synthesis,[1–5] for desulfurization and denitrogenation of fuels,[6–8] in redox flow batteries[9–14] and so on. Although M-ILs have been known for several decades, there is still no strict definition for this important group of ILs. The following types of M-ILs are considered in this review: (i) ILs containing a metal atom as a part of the cation and/or anion; (ii) ILs with a metal atom or a metal complex coordinated to the cation or anion; (iii) ILs with a dissolved metal salt (or a dissolved metal complex); (iv) ILs containing metal or metal oxide nanoparticles.

II. Ionic liquids containing a metal atom as a part of the cation and/or anion

Ionic liquids and molten salts with a metal atom as a part of the cation and/or anion are charged species the nature of which varies from charged polyatomic molecules in ILs to classical ions in common molten salts. Alkali metal halides with closed-shell halogen atoms and melting points above 800 K provide good examples of molten salts, while most of ionic liquids comprise a polyatomic organic cation and an inorganic or organic anion.

Aluminium chloride ($AlCl_3$) melts at relatively low temperature (192 °C under elevated pressure) (see Chapter 2 in the book [15]) and is highly expanded upon transition to the liquid state ($\Delta V/V_{sol} \sim 80\%$);[16] however, its specific electrical conductivity corresponds to that of a molecular liquid. According to Raman spectroscopy, the melt consists of Al_2Cl_6 molecules.[17] Thus, $AlCl_3$ cannot be considered as an M-IL, although it is often used in IL synthesis.

Special mention should be made of metallomesogens (metal-containing liquid crystals), which form a specific subclass of M-ILs. The metal ion they contain influences the properties of the ionic liquid crystals (LCs), such as magnetism, luminescence and/or redox activity. The ionic LCs endowed with these properties give rise to multifunctional materials. A number of comprehensive studies of neutral (non-charged) metallomesogens are known;[18] however, the publications devoted to ionic metallomesogens are still very few in number.[19, 20]

Metal-containing ionic liquids may contain various transition metals. The structural building block $[MX_4]^{2-}$ (M = Pd, Zn, Co, Cd, Ni, Cu; X = Cl, Br or, more rarely, I) is inherent in numerous M-ILs, which are also called halometallate ionic liquids.[21–23] As the counter-ions, they usually contain quaternary ammonium cations with long alkyl groups[18, 24–26] such as *N*,*N*-dialkylpyrrolidinium, *N*-alkylpyridinium[27–32] or *N*-alkyl-*N*-methylimidazolium.[33, 34] Examples of such M-ILs are $[C_{12}mim]_3[LnBr_6]$ (Ln = Tb, Dy)[35] and $[C_{12}mim]_4[EuBr_6]Br$ ($[C_{12}mim]$ is n-dodecyl-3-methylimidazolium).[36]

Since the acid-base properties of metal-containing ILs can influence their catalytic performance, the acidity characteristics are of great importance.[37–39]

The most promising application of metal-containing ionic LCs is the design light emitting liquid crystals for the application in LC displays.[40, 41] Using lanthanide cations, for example, Eu^{3+} or Sm^{3+} for red, Eu^{2+} or Tm^{3+} for blue, and Tb^{3+} for green, it is possible to obtain the three fundamental colours for LC displays.[42] Furthermore, aligned Ln-containing LCs can emit polarized light.[43] High magnetic anisotropy of the Tm^{3+}, Dy^{3+} and Tb^{3+} ions enables the formation of the mesophase in an external magnetic field.[44] Thus, the application of these compounds in electric and magnetic switchable devices is very promising.

III. Ionic liquids with a metal atom or a metal complex coordinated to the cation or anion

Ionic liquids containing a metal atom or a metal cation act as functional materials that exhibit simultaneously catalytic, magnetic, electric and other properties.[45] Ionic liquids comprising metal complexes are valuable for specific applications, as they offer a wide range of opportunities in molecular design.[46]

The usual metal-containing ILs can be obtained by mere complexation reaction of a neutral compound with an ionic one, for example, $AlCl_3$ with $[C_2mim]Cl$, which affords $[C_2mim]^+[AlCl_4]^-$ ($[C_2mim]$ is 3-ethyl-1-methylimidazolium). These ILs usefully extend the variety of solvents used in synthetic chemistry.[47]

Recently, ionic liquids of the $[M(RNH_2)_4](NTf_2)_2$ type (M = Zn, Ag; R = Me, Et, Pr^n, Bu^t; Tf = CF_3SO_2) have been reported.[48] These ILs have been used for zinc and silver electrodeposition; moreover, their properties can be easily tuned by switching the natures of the central metal ion and the organic group R.

One more interesting example is a study of uranyl cation cordination in ILs.[49] The first coordination sphere of the uranyl cation in room-temperature ionic liquids (RTILs) is formed with the participation of the initial counter-ions, IL anions and other anions and impurities present in the solution. Actinides represent a major constituent of nuclear wastes. Recent studies concerning nuclear fission products (in particular, Sr^{II}) have demonstrated that ILs can be successfully applied for metal ion extraction from aqueous solutions. Visser *et al.*[50] isolated the UO_2^{2+} cation from an acidic aqueous solution by treatment with tributyl phosphate (TBP) and octylphenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), using $[C_4mim][PF_6]$ and $[C_8mim]NTf_2$ ionic liquids (C_4mim and C_8mim are 1-n-butyl-3-methyl- and 1-methyl-3-octylimidazolium, respectively). The degree of uranyl extraction into ionic liquids was found to be higher than that into dodecane. The first reported co-crystals with an ionic liquid were $[C_6mim]_2[\{UO_2(NO_3)_2\}(\mu\text{-}C_2O_4)]$ (C_6mim is 1-n-hexyl-3-methylimidazolium). They contained the $[C_6mim](NO_3)$ IL integrated into the crystal lattice. When long alkyl groups are present in the IL ($[C_{16}mim]^+$), anions associated with the polar groups of the cations form channels between the cationic layers, which are filled with acetonitrile molecules.[51]

IV. Ionic liquids with a dissolved metal salt or a dissolved metal complex

Unlike the previously considered two groups of M-ILs in which metal is a part of the cation or anion or is coordinated to the cation or anion, the two groups of M-ILs considered below contain metals, metal salts or metal oxide nanoparticles dissolved in conventional ILs. The reason why these systems are also classified as M-ILs is that the

ILs significantly influence the thermodynamic properties and stability of metal-containing species.[52]

According to an opinion, charged metal complexes and metal salts have an affinity to ILs as regards the solubility ('like dissolves like'); however, another point of view is that the lack of coordinating groups in both the cation and the anion often results in poor solubility of these ionic species in ILs. It is very important to attain the required solubility for ionic metal compounds (*i.e.*, synthesize task-specific ILs), because the lack of solubility in ILs can interfere in some way with electrodeposition, spectroscopic measurements and the design and application of new metal-containing catalysts. A reasonable way to achieve a high solubility of ionic metal compounds in ILs is introducing functional groups that can surround the metal ion. For gaining deeper understanding and for interpretation of the solubility issues, it is important to have data about the speciation of metal ions in the ILs, which are not always available. The known crystal structures of solid metal complexes may provide useful information that would help to establish a model describing the metal speciation in the solution.[53]

Also, it is necessary to bear in mind that after dissolution, characteristics of both the IL and especially the metal cation fundamentally change. These changes may be crucial for some applications, *e.g.*, electrodeposition. The electrodepositions of a non-modified (bare) atom or a metal chloride complex proceed in totally different ways, require different electrode potentials and produce surface metal layers possessing their own characteristic features.[54]

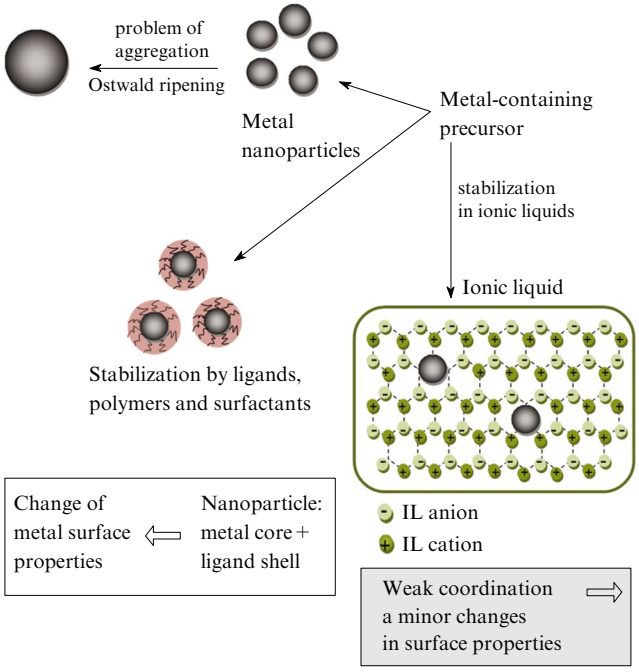


Figure 1. Schematic presentation of the stabilization of metal nanoparticles by stabilizers or in ionic liquids to prevent aggregation.[63]

V. Ionic liquids containing metal or metal oxide nanoparticles

The steric, viscoelastic and electrostatic properties of ILs ensure stabilization of metal nanoparticals (M-NPs) without the need for extra ligands, surfactants or stabilizers. The synthesis of M-NPs in an IL medium can be carried out by thermolysis, chemical or electrochemical reduction, photochemical techniques, including microwave-induced decomposition, or ultrasonication. Nanoparticles in the gas phase can be generated by electron beam or γ irradiation, glow discharge plasma electrolysis, physical vapour deposition and sputtering. The possible M-NP sources include metal carbonyls $M_x(CO)_y$ containing zero-valent metals, with no need for reducing agents. Microwave-assisted thermal decomposition of metal carbonyls is an economic (regarding both time and energy) route to M-NPs, because ILs efficiently absorb MW radiation owing to their high polarity, ionic structure and high dielectric constant. Metal nanoparticle-enhanced ILs can be employed in hydrogenation and C – C coupling reactions.[55]

The nature and properties of nanoparticles with their huge surface area-to-volume ratios are determined by the surface energy.[56] The smaller the nanoparticles, the higher the fraction of exposed surface atoms giving rise to dangling bonds. Metal nanoparticles are studied as 'soluble' analogues of heterogeneous catalysts.[57 – 63] The performance of heterogeneous catalysts is due to their large surface area. However, small nanoparticles are only kinetically stable, being prone to aggregation to thermodynamically more stable bigger particles (Fig. 1).

Metal nanoparticles can be synthesized and stored in ILs for some period of time without any stabilizers added. In this respect ILs can be considered as 'nanosynthetic templates',[64] or as a supramolecular three-dimensional hydrogen-bonded and electrostatically bonded network, which prevents the nanoparticle agglomeration owing to the ionic nature of the ILs,[65] high dielectric constant, high polarity and the supramolecular nature of the system without additional protective ligands.[66 – 71]

VI. Application of metal-containing ionic liquids

Since the beginning of the 1990s, ionic liquids have been widely used in science and technology. Ionic liquids are subjects of a number of books, monographs and chapters in collections;[72 – 79] a chapter devoted to ILs, including M-ILs, appeared even in the third edition of *Industrial Organic Chemicals*. For more targeted application of ILs, it is important to have a comprehension of their structural details. The structural data are beyond the scope of this review; therefore, we give references to some most prominent publications in this field.[80 – 85]

The information on the application of ILs in organic synthesis, for improving characteristics of fuels and in electrodeposition is systematically discussed below and the prospects for the future use of ILs are outlined.

VI.1. Application of metal-containing ionic liquids in organic synthesis

Metal-containing ILs are environmentally friendly alternatives to volatile organic solvents; they exhibit thermal and chemical stability, low (if any) volatility, together with high catalytic activity. Ionic liquids can dissolve metal salts, metal complexes and organometallic compounds (along with metal incorporation into the IL cation and anion), thus providing a polar, weakly coordinating medium for a catalyst. Chauvin *et al.*[86] and Carlin and Wilkes[87] were the

first to show the benefits of using M-ILs in dimerization of alkenes and ethylene polymerization, respectively. Ionic liquids are among the best solvents for simultaneous immobilization and stabilization of nanoparticle matter. A system containing nanoparticles in IL as a solvent was observed in the Heck reaction in which Pd^{II} compounds were used as catalyst precursors.[88]

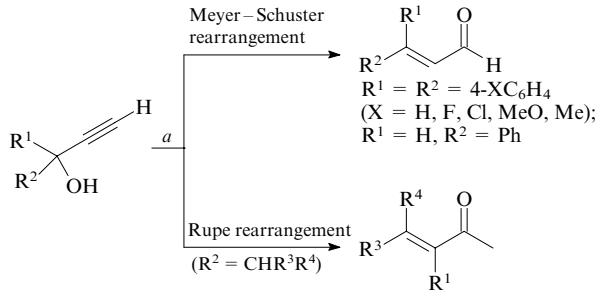
Metal-containing ILs have also found use in industry. Since 2013, PetroChina operates a petrol production process with a capacity of 65000 tons per year based on alkylation of isobutane with isobutene in a medium of IL. Instead of hydrofluoric or sulfuric acid, aluminium chloride-based IL is used in this process as the catalyst.[89]

Previously, attempts have already been made to compile the information on the application of M-ILs in organic synthesis.[90–97] Taking into account these reviews and new results in this field, we would like to present here an up-to-date overview on the use of M-ILs in alkylation, cyclization, isomerization, carbonylation, metathesis and C–C coupling reactions.

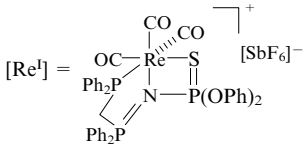
VI.1.a. Cyclization and/or isomerization reactions

Propargylic alcohols are selectively converted, under mild conditions, to aldehydes with double or triple bonds *via* the Meyer–Schuster rearrangement, or to enones or enals *via* the Rupe rearrangement in the presence of the Re^{I}–$[C_4mim][PF_6]$ catalytic system in rhenium-containing ILs (Scheme 1).[98] In the synthesis of enals, the authors were able to attain isolated yields of 91%–94% and gas chromatographic (GC) yields of 97%–99% (in 5–30 min) at 80 °C; the same parameters for the synthesis of enones were 90%–93% and 96%–99% (in 1.5–3 h) at 130 °C.

Scheme 1

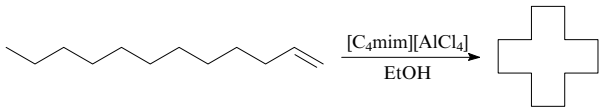


(*a*) $[Re^{I}]$, $[C_4mim][PF_6]$, 80–130 °C (up to 10 cycles);



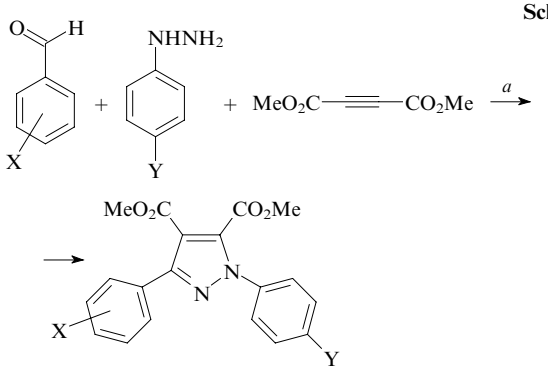
A remarkable cyclization–isomerization of dodec-1-ene to cyclododecane in an ethanol mixture with $[C_4mim]Cl$ and $AlCl_3$ has been reported (Scheme 2).[99] The authors demonstrated an important role of ethanol for homogenization of the IL (1-n-butyl-3-methylimidazolium chloride + $AlCl_3$)–dodec-1-ene two-phase system. The yield of cyclododecane (valuable starting material for Nylon manufacturing) increased from 4.2% (two-phase system) to 23.4% (homogeneous system), with the selectivity increasing from 73.1% to 93.4% (in 12 h).

Scheme 2



Recently, an intriguing example of the synthesis of fully substituted pyrazoles by cyclization–aromatization of hydrazones with dimethyl acetylenedicarboxylate in the presence of $[Bu^{n}_4P][CuBr_3]$ has been reported (Scheme 3).[100] The isolated yields were 66%–92% in 1 h at 100 °C. Other ILs containing the 1-n-butyl-3-methylimidazolium cation and the $[CuBr_3]$, $[CuCl_3]$, $[FeCl_4]$ or $[InCl_4]$ anion were also tested, but they were found to be less active.

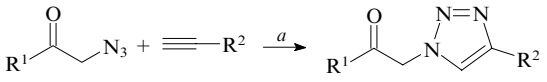
Scheme 3



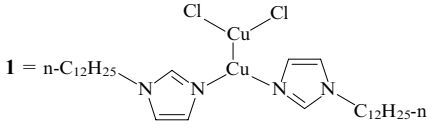
(*a*) $[Bu^{n}_4P][CuBr_3]$ (25 mol.%), 100 °C; X = H, Cl, Br, CN, Me, NO_2 (in different positions); Y = H, Cl, Me

A recent example of cyclization of terminal alkynes with α-azido ketones is also noteworthy (Scheme 4).[101] This process was catalyzed by the copper-containing IL, $[Cu(C_{12}mim)_2][CuCl_2]$ (**1**), while $[C_4mim][BF_4]$ served as the solvent. High product yields were attained (82%–90% at 25 °C in 10–15 min), and it was shown that the catalyst can be recovered and reused for 3–5 runs without a loss of activity.

Scheme 4



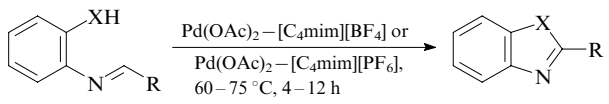
(*a*) $[Cu(C_{12}mim)_2][CuCl_2]$ (**1**), $[C_4mim][BF_4]$, 25 °C, 10–15 min;
R^1 = Ph, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, Me, EtO;
R^2 = Ph, HO(Me)CH, 3-$H_2NC_6H_4$



An intramolecular cyclization of Schiff bases catalyzed by palladium compounds has been reported.[102] Scheme 5 depicts the synthesis of substituted benzothiazoles and

benzoxazoles catalyzed by the $Pd(OAc)_2$ (10%)–$[C_4mim][PF_6]$ (or $[C_4mim][BF_4]$) system. A mechanism involving complexation of palladium to imine nitrogen with subsequent cyclization and elimination was proposed for this reaction.

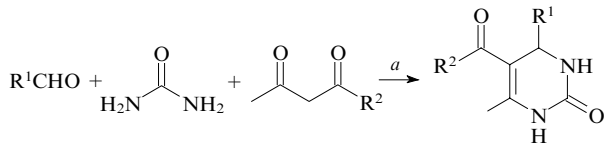
Scheme 5



R = Ar, Het; X = O, S

The application of ILs in the three-component solvent-free Biginelli condensation proceeding in the absence of Lewis acids, described for the first time [103] in 2001, was a breakthrough, but the reaction required relatively harsh conditions (100 °C), the isolated yield being as high as 98% (Scheme 6).

Scheme 6



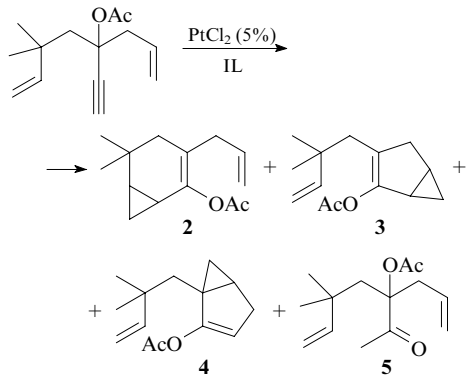
(*a*) IL, 100 °C, 0.5 h; R^1 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$O_2NC_6H_4$, n-C_5H_{11}; R^2 = OEt, Me; IL = $[C_4mim][PF_6]$ or $[C_4mim][BF_4]$

A recent comprehensive mechanistic study of the Biginelli reaction [104] showed that the use of Lewis acid–IL ($CuCl_2$–$[C_4mim][PF_6]$, $CeCl_3 \cdot 7H_2O$–$[C_4mim][BF_4]$) systems allows conducting the reaction under somewhat milder conditions (lowering the temperature to 80 °C) without using an excess of urea. The catalytic cycle was suggested to comprise the formation of an iminium intermediate and evidence for the formation of this intermediate was obtained.

Platinum- and gold-catalyzed cycloisomerization in IL medium has been reported.[105, 106] The Pt-catalyzed migration of the acetate group and cyclization of dienyne proceeded in IL at 80 °C over a period of 1 h (Scheme 7).[105]

In the case of the $PtCl_2$–$[C_4mim]NTf_2$ system, the best reaction selectivity was attained: **2**:**3**:**4**:**5** = 90:10:0:0. The replacement of the IL anion by $[PF_6]$ or $[BF_4]$ resulted in the formation of mixtures of compounds **2**–**5** and other products. Moreover, the highest product yield (99% at

Scheme 7



IL = $[C_4mim]NTf_2$, $[C_4mim][PF_6]$, $[C_4mim][BF_4]$

80 °C in 1 h) was obtained in the presence of $[C_4mim]NTf_2$. For comparison, the $PdCl_2$–toluene system devoid of IL provided a yield of only 90% at 80 °C over a period of 2 h. A thorough investigation of the mechanism of this and other cycloisomerization reactions has been reported.[106]

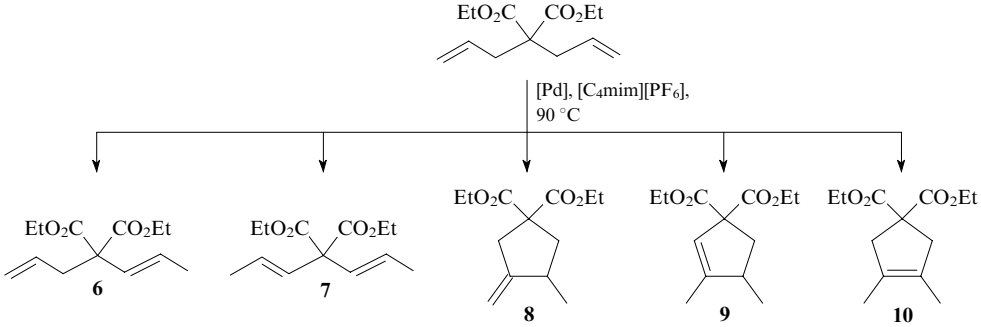
A Pd- and Pd–Ag-catalyzed isomerization–cycloisomerization of 2,2-diallylmalonate to give linear and cyclic isomers **6**–**10** in the $[C_4mim][PF_6]$ medium has been described [107] (Scheme 8). The $PdCl_2 + AgPF_6$ system (corresponding to the bare Pd^{2+} ion) in $[C_4mim][PF_6]$ was found to ensure the highest turnover frequency (TOF) of the catalyst and a 94% selectivity to product **10**. For 50 moles of diallylmalonate to react, 1 mole of palladium is needed. The system containing the Pd precursor in $[C_4mim][PF_6]$ can be used repeatedly with a slightly lower conversion. The reaction with $Pd_2(dba)_3$ (dba is dibenzylideneacetone) affords a product mixture, (**6**+**7**):**9**:**10** = 34:7:53, while in the presence of $AgPF_6$, linear products **6** and **7** are formed predominantly.

VI.1.b. Alkylation reactions

A review [81] addresses the application of halometallate IL-containing systems in alkylation. The most important processes of this type include Friedel–Crafts alkylation of arenes and alkylation of isobutene with but-2-ene for the production of high-octane fuel. According to the data of Chiappe *et al.*,[81] more than 55 patents are devoted to the alkylation with the use of $AlCl_3$-based ILs, and since 2005, M-ILs have been employed as catalysts in a Chinese plant.[108] Below we consider only those papers that are not covered in the cited review [81] for whatever reasons.

A recent series of studies [109–112] addresses the effects of various factors on isobutane alkylation with but-2-ene. Bui

Scheme 8



et al.[109] studied the effects of water, the nature of the cation in exchange resin and a transition metal salt in the $AlCl_3$-based IL medium. A copper(I) chloride-enriched system containing triethylamine hydrochloride and $AlCl_3$ provided trimethylpentane (TMP) yields of up to 72.3% in 15 min at −5 °C, with the research octane number (RON) of the products being up to 99. The role of additives is attributed to the formation of complexes with superacidity or Brønsted acidity.

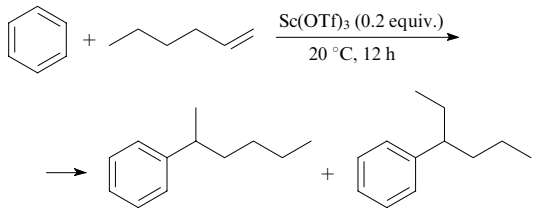
The effect of anhydrous HCl as a co-catalyst has been studied in a batch reactor.[111] Hydrogen chloride was found to increase the reaction rate and the TMP yield.

More stable systems alternative to $AlCl_3$-based ILs have been proposed for alkylation of isobutane with but-2-ene.[112] A selectivity of >70% to octanes and RON > 91 were attained in the presence of $Et_3N \cdot HCl$ and $GaCl_3$–CuCl ($\chi_{GaCl_3} = 0.65$, 5 mol.% CuCl) (χ is the mole fraction of $GaCl_3$ in the $GaCl_3$ + organic salt mixture) at a pressure of 0.5 MPa, stirring rate of 900 rpm and a temperature of 288 K in 15 min using an industrial feed mixture with isobutane to butene ratio of 10. The $Et_3N \cdot HCl$–$GaCl_3$/CuCl catalyst can be reused nine times without a loss of activity.

The Friedel–Crafts addition of alkenes to arenes and coupling of alkynes with arenes are important reactions for both synthetic chemistry and industrial production. Both of these processes have their own shortcomings. A general bottleneck of alkylation, especially in industry, is that traditional catalysts ($AlCl_3$, H_2SO_4, HF) lose activity after water treatment. A serious drawback of the direct Friedel–Crafts alkenylation is polymerization of alkyne, resulting in undesirable side products. A significant breakthrough in solving these issues was made by Song *et al.*[113, 114]

First, they carried out the Friedel–Crafts alkylation of benzene with hex-1-ene in air in the RTIL medium, consisting of moisture-stable dialkylimidazolium cations and $[SbF_6]$, $[BF_4]$ or OTf counter-anions with addition of 1.5 mol.% $Sc(OTf)_3$.[113] This reaction resulted in >99% conversion of hex-1-ene and up to 93% yields of the monoalkylated product (Scheme 9).

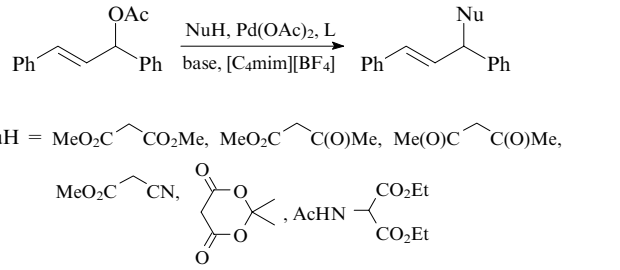
Scheme 9



Subsequently, the same authors reported impressive results on metal triflate-catalyzed Friedel–Crafts alkenylation of aromatics.[114] High product yields (up to 96% at 85 °C, usually in 2–6 h) were attained with the use of the $[C_4mim][SbF_6]$–$Sc(OTf)_3$ system for a broad range of aromatic substrates, containing either electron-donating or electron-withdrawing substituents.

The $Pd(OAc)_2$–phosphine system serves as a good catalyst for the alkylation with allyl derivatives in $[C_4mim][BF_4]$ (Scheme 10).[115] An influence of phosphine ligands on the Pd catalyst activity was noted. The PCy_3 ligand (Cy is cyclohexyl) and other electron-donating phosphines accelerate the reaction, whereas the phosphite $P(OPh)_3$ and other strong electron acceptors induce a sharp decrease in the conversion. The authors state that ILs affect the electronic and steric properties of the ionic reaction medium.

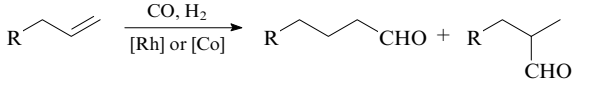
Scheme 10



VI.1.c. Carbonylation reactions

The conduction of hydroformylation, a highly important carbonylation reaction, in RTILs has been surveyed in a review.[116] Therefore, in the present review, we consider only the most recent publications that have not been covered in the mentioned review,[116] such as the Co-catalyzed hydroformylation in a two-phase system using ILs[117] and highly promising prospects of using functionalized Rh-containing ILs (Scheme 11).[118]

Scheme 11



Application of the design of experiment (DoE) strategy and high-throughput systems (HTS) for upgrading the hydroformylation of alkenes in the presence of the $Co(CO)_8$–2-methoxypyridine system in M-ILs has been reported.[117] Among the parameters determining the yield of the reaction product, most significant are the temperature and the ratio of the organic phase and the IL.

Unlike the researcher cited above,[117] who dissolved the Co catalyst in ILs, Jiang *et al.*[119] evaluated the catalytic properties of some ILs containing the imidazolium cation and the $[Co(CO)_4]^-$ anion towards carbonylation of methyl chloroacetate. The conversion of the latter reached 94.3% at a CO pressure of 2 MPa and at 85 °C in 3 h. For the $[C_4mim][Co(CO)_4]$ catalyst, which was reused four times, the selectivity to the malonic ester reached 99% with an average yield of dimethyl malonate of 93%. This catalyst demonstrated high activity and good reusability in comparison with the known $Na[Co(CO)_4]$ catalyst. The $[Co(CO)_4]^-$ anion present as a part of the IL was found to be highly stable in air.

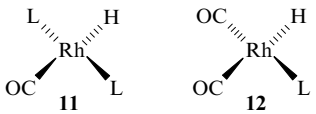
Rhodium-catalyzed hydroformylation in ILs also attracts chemists' attention.[120–124] Recently, ethylene hydroformylation in imidazolium-based ILs has been described.[120] The stability and activity of the Rh catalyst is influenced by the structure of the IL. The use of ILs with large side chains in the cation was found to be unfavourable. The $[C_4mim][BF_4]$ ionic liquid as a solvent provides a TOF of 10 627 h^{-1} for the Rh catalyst. Ionic liquids were

more efficient in the Rh-catalyzed hydroformylation than toluene. According to electrospray ionization mass spectrometry (ESI-MS) data, $[C_4mim]^+$ acts as a ligand of the Rh catalyst to give a renewable dynamic complex, $[Rh(CO)(PPh_3)_2(C_4mim)(BF_4)]^+$, in which the Rh atom is attached to the C(2) atom of the imidazole ring (the peak at m/z = 793.1969 in the ESI-MS spectrum). The role of the IL in the prevention of formation of low-activity Rh clusters was emphasized.

Kolbeck *et al.*[121] studied the effect of the ligand on the interface composition in IL solutions containing Rh with the hydrophilic tris(3-sodium sulfonatophenyl)phosphine (TSSPP) ligand, which is used in hydroformylation catalysis. The nature of the ligand affects the catalyst location in the multiphase catalytic system, in particular, either at the interface or in the bulk phase. In the case of Rh-TSSPP in $[C_2mim][EtOSO_3]$, a relatively high surface concentration of rhodium was detected, whereas a similar complex, $[Rh(acac)(CO)_2]$ (acac is acetylacetonate) in the absence of TSSPP was largely removed from the interface. Understanding of the rhodium behaviour at the interface in IL medium is expected to initiate new researchers' attempts to affect the surface activity of transition metal complexes in multiphase catalytic systems.

Phosphine-functionalized phosphonium ionic liquids (PFILs) have been used [122] as constituents of Rh complexes in the hydroformylation of long-chain alkenes. A relatively high conversion of oct-1-ene (91% – 100% in 3 h) was attained only at temperatures of 75 – 100 °C using the $[Rh(acac)(CO)_2]$ – IL system based on tri-n-butylphosphonium; the reaction selectivity was moderate (linear : branched aldehyde ratio was 1.8 to 4.1). The nature of PFIL had an effect on the stability, catalytic activity and regeneration ability of the Rh system and on the reaction selectivity. The long-chain alkyl substituents in the phosphonium group are favourable for the product formation, as they increase the solubility of higher alkenes, while shorter substituents are beneficial for the reaction selectivity as they increase the concentration of the Rh^I complex in the reaction medium. Compounds **11** and **12** are formed as active intermediates of hydroformylation, the former being responsible for the formation of linear aldehydes and the latter giving rise to a mixture of linear and branched aldehydes.

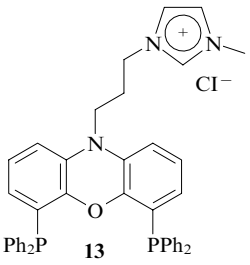
Structures 11, 12



$L = R_3\overset{+}{P}(CH_2)_{11}PPh_2\overset{-}{N}Tf_2$ (R = Me, Bu^n, n-C_8H_{17})

The Rh-catalyzed hydroformylation of higher alkenes was gradually improved,[123] as regards the selectivity to the required aldehydes (up to 90%) and decrease in the rhodium loss. This was achieved by using a supercritical fluid – IL system, with the nixantphos ligand being attached to the imidazolium cation (structure **13**). The use of rhodium complexes with this ligand dissolved in $[C_8mim]NTf_2$ in a continuous flow reactor with supercritical CO_2 as the carrier resulted in the first cost-effective process of higher alkene hydroformylation.

Structure 13



13

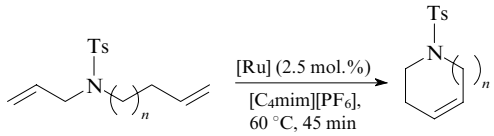
Hintermair *et al.*[124] demonstrated the applicability of compressed CO_2 for the transfer of reacting gases, substrates and products over a supported IL, which served as the catalyst, in hydroformylation of oct-1-ene. Since the $[C_8mim]NTf_2$ ionic liquid was chosen with the aim to dissolve oct-1-ene, the thickness of the IL layer did not affect the reaction rate. As the substrate flow was increased, the reaction rate increased, but the conversion somewhat decreased.

Apart from hydroformylation, mention should be made of the oxidative carbonylation of amines catalyzed by Pd-containing IL supported on mesoporous SiO_2 of the SBA-15 type (ImmPd-IL@SBA-15), resulting in the formation of oxamates and urea.[125] The reaction was carried out under the following conditions: 1 mmol of the amine, 15 ml of alcohol, 0.1 mmol of NaI, 1 mol.% of ImmPd-IL@SBA-15, 60 °C, 4 h. The amount of the metal extracted by the ionic liquid was 4.6 mass %.

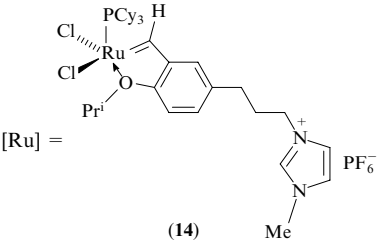
VI.1.d. Metathesis reactions

The metathesis of alkenes in ILs has been thoroughly considered in a review.[126] An exhaustive study of the use of imidazolium-tagged Ru catalysts (for example, compound **14**) in the metathesis of alkenes with product yields of up to 98% has been reported [127] (Scheme 12).

Scheme 12



n = 1, 2; Ts = 4-$MeC_6H_4SO_2$



(14)

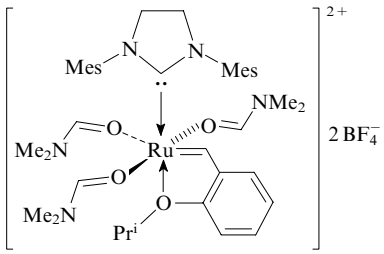
An N-heterocyclic carbene rhodium complex containing an imidazolium moiety has been synthesized.[127] This complex was successfully employed in the metathesis of substrates with low reactivity. The use of $[C_4mim][PF_6]$ – toluene two-phase system substantially increased the catalyst recyclability; in this case, the Rh content in the product was very low (according to inductively coupled plasma mass spectrometry).

The metathesis of methyl ricinoleate and methyl oleate has been reported.[128] The experiments were carried out in the presence of alkylidene ruthenium complex (substrate : Ru = 100) in the medium of ionic liquids [Cat][An] ([Cat] = [C4mim], [C4dmim]; [An] = [PF_6], [BF_4], NTf_2; C4dmim is 1-n-butyl-2,3-dimethylimidazolium) at 40–60 °C for 4 h. High conversions (up to 92%) and selectivities (up to 99%) were attained, with the catalyst recyclability being moderate (the loss of activity was 25% by the third cycle). In this paper, the mechanism of the process was not discussed; however, in another publication,[129] the same authors considered the role of traditional solvents and ILs in the metathesis of alkenes using density functional theory (DFT). The obtained results suggest that alkenes and catalysts are better stabilized by ILs than by conventional solvents. In addition, ILs decrease the activation energy of the reaction to a higher extent than conventional solvents.

Stark *et al.*[130] studied the effects of the substrate solubility in the IL, the solvent polarity and the presence of impurities in the IL on the reaction outcome in relation to the homometathesis of substrates ranging from oct-1-ene to tetradec-7-ene in the presence of a first generation Grubbs catalyst — benzyidenebis(tricyclohexylphosphine)-dichlororuthenium (0.02 mol.%). Three major impurities in 1-methylimidazole (water, halides and imines) were found to influence the catalytic activity of M-ILs.

The dicationic alkylidene ruthenium complex **15** proved to be an efficient catalyst in continuous metathesis processes in the presence of supported ILs.[131]

Structure 15



Mes = 2,4,6-$Me_3C_6H_2$

15

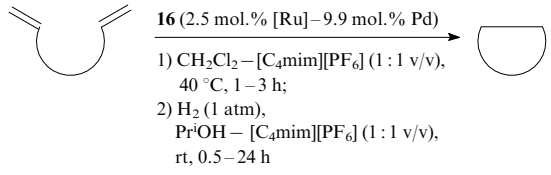
Recently[132] it has been found that Ru-containing ILs can serve as environmentally benign green solvents for metathesis reactions in petrochemical industry.

Monolithic supports for conducting homometathesis and ring closing metathesis (RCM) in two-phase systems were prepared by ring opening polymerization; these supports were used for immobilizing the [C_4dmim][BF_4]–catalyst system. Highly promising turnover numbers (TON) for the catalyst were attained and leaching of the catalyst was found to be negligibly low (0.1%).

The Grubbs catalysts are efficient in the synthesis of macrocyclic tetralactones *via* RCM in the IL medium.[133] Under mild reaction conditions (60 °C, 8–24 h), ten ILs and five Grubbs catalysts were tested and high product yields were obtained (76%–93%).

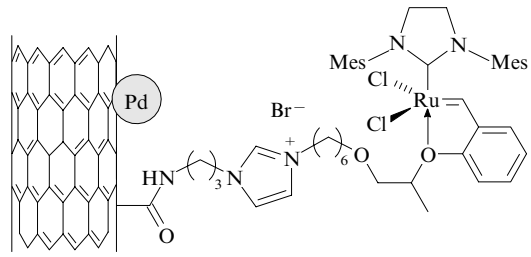
The most impressive examples of tandem metathesis–hydrogenation reactions in ILs have been reported by Lee *et al.*[134] The authors immobilized both Pd nanoparticles and a Ru carbene complex on carbon nanotubes functionalized by imidazole moieties *via* amide spacers (structure **16**) to carry out the process with catalyst recycling. The bifunctional immobilized catalyst demonstrated a very high activity in the metathesis–hydrogenation process in ILs (Scheme 13). The catalyst was recovered and reused up to four times.

Scheme 13



substrates: $(CH_2{=}CHCH_2)_2NTs$, $(CH_2{=}CHCH_2)_2C(CO_2Et)_2$, $[CH_2{=}CH(CH_2)_2](CH_2{=}CHCH_2)NTs$, *etc.*

16 =

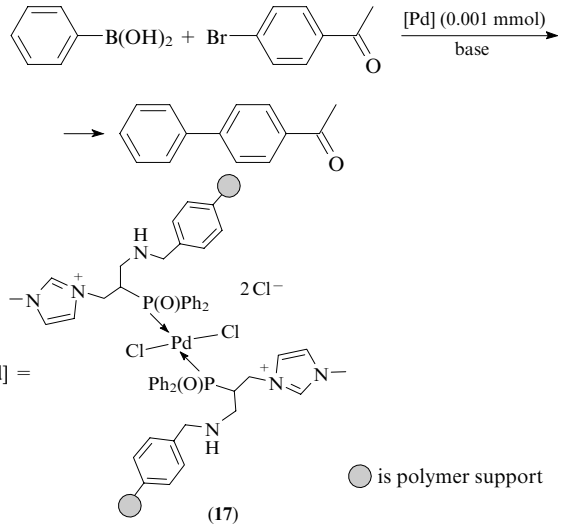


VI.1.e. Coupling reactions

Palladium-catalyzed C–C coupling reactions have been considered in detail in reviews.[135, 136] Below we discuss the papers that are not covered by these reviews and the use of M-ILs with other metals in C–C coupling reactions.

The recently reported new phosphorus-containing ILs[137] were used for the synthesis of polymer supported Pd^{II} complexes with ILs (**17**),[138] which proved to be excellent catalysts for the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid in an aqueous medium. The polymer-supported Pd^{II} complex containied imidazole-based IL (Scheme 14).[139]

Scheme 14



[Pd] =

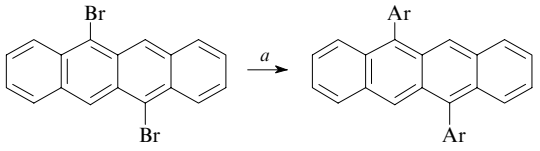
is polymer support

(17)

The Suzuki–Miyaura reaction under homogeneous conditions has been reported.[140] 5,11-Diaryltetracene deriva-

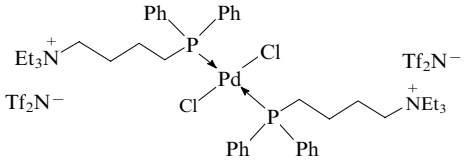
tives can be synthesized in good to quantitative yields in pyrrolidinium-based ILs by the reaction of 5,11-dibromotetracene and arylboronic acids in the presence of complex **18** as the catalyst (Scheme 15).

Scheme 15



(*a*) $ArB(OH)_2$, K_3PO_4, **18**, $[bmpyr]NTf_2-H_2O$ (2 : 1 v/v); bmpyr is 1-n-butyl-1-methylpyrrolidinium

18 =

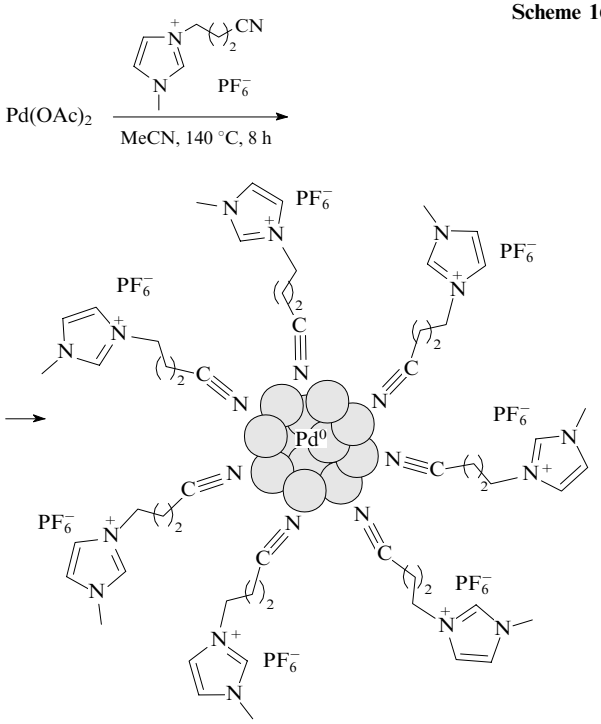


The use of both ILs and ionic ligands is more favourable for obtaining products in excellent chemical yields under mild reaction conditions.

The microwave-assisted controlled Heck reaction in the IL medium proceeding at a high rate has been described.[141] The reaction was conducted in sealed glass tubes on heating for 5 – 45 min. A solution of the catalyst [$PdCl_2$ in the presence or in the absence of P(*o*-Tol)$_3$; *o*-Tol = 2-MeC_6H_4] could be reused without a considerable decrease in the product yield.

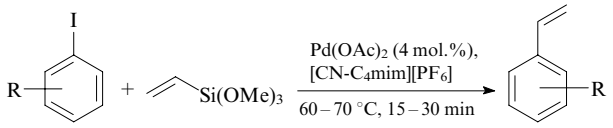
The Hiyama reaction of heteroaryl halides and aryl halides without a phosphine, catalyzed by functionalized Pd nanoparticles (Pd-NP) in ILs has been reported.[142] The Pd nanoparticles (of 2 – 5 nm size) were synthesized by thermal decomposition of $Pd(OAc)_2$ in the presence of 3-(3-cyanopropyl)-1-methyl-1*H*-imidazolium hexafluorophosphate ([CN-C_4mim][PF_6]) (Scheme 16).

Scheme 16



The Pd-NP – [CN-C_4mim][PF_6] system acts as a catalyst formed *in situ* for C – C coupling reactions of vinyl- and aryltrimethoxysilanes with heterocyclic and aromatic halides. A number of aromatic heterocycles, substituted biphenyls and styrene derivatives have been studied, the product yields being 76% – 97% in all cases (Scheme 17).[142]

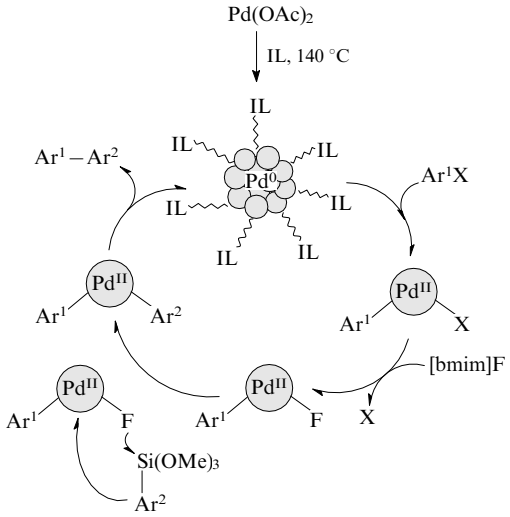
Scheme 17



R = H, Me, OMe, NO_2, CF_3, CN, F (in different positions)

The mechanism proposed for this reaction includes the oxidative addition of aryl halide to Pd^0 to give the Pd aryl complex. The aggregation of 'naked' Pd^0 species is avoided as a result of stabilizing effect of [CN-C_4mim][PF_6]. This is followed by transmetallation to give a Pd^{II} diaryl complex *via* the [C_4mim]F-activated nucleophile transfer to Pd, resulting in the intermediate complex. The Pd^0 regeneration occurs *via* reductive elimination (Scheme 18).

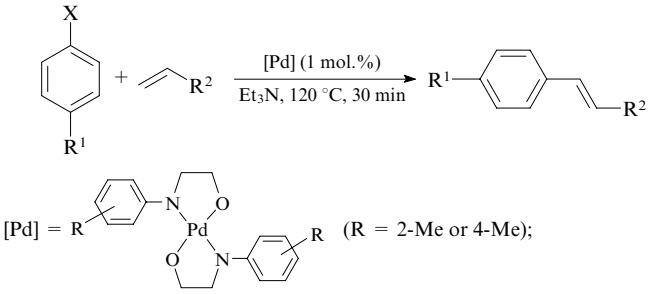
Scheme 18



IL = [CN-C_4mim][PF_6]

High product yields (99% according to GC data) and moderate to high TON values were attained in the Heck reaction (catalyst loading of 1%) and Suzuki reaction (catalyst loading of 5%) within 30 min at 120 °C using easy-to-synthesize Pd^{II} complexes $[Bu^n_4N]_2[Pd(2\text{-Mepma})_2]\cdot 4H_2O$ and $[Bu^n_4N]_2[Pd(4\text{-Mepma})_2]\cdot 2H_2O\cdot MeCN$ (2-Mepma and 4-Mepma are *N*-2-methylphenyl- and *N*-4-methylphenyloxamates, respectively).[143] The Heck reaction of alkenes and aryl halides catalyzed by the bis(oxamato)palladate(II) – $[Bu^n_4N]Br$ system results in product yields of up to 99% (Scheme 19).

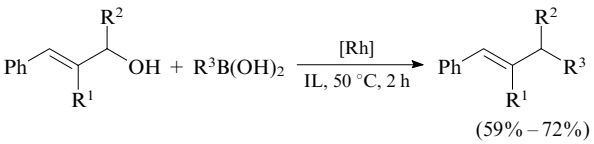
Scheme 19



R^1 = H, Me, OMe, Ac, CN, CO_2Me; X = Br, I;
R^2 = CO_2Et, CN, Ph

A catalytic system based on the Rh precursor and IL was used for coupling of vinyl- and arylboronic acids with allylic alcohols (Scheme 20).[144]

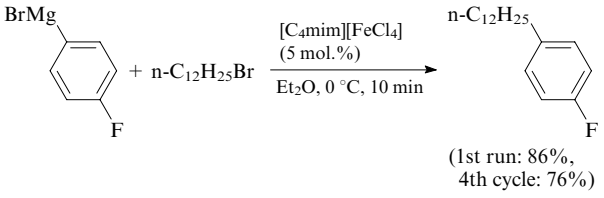
Scheme 20



R^1 = H, Me; R^2 = H, Ph; R^3 = Ar, Het, Alkenyl;
[Rh] = $RhCl_3 \cdot x\,H_2O$, Rh(acac)(cod)Cl or $Rh(PPh_3)_3Cl$;
cod is cycloocta-1,5-diene; IL = $[C_4mim][PF_6]$

An air-stable catalytic system based on $[C_4mim][FeCl_4]$ has been reported to efficiently catalyze the coupling of Grignard reagents with alkyl halides in a two-phase system under mild conditions (Scheme 21).[145] It is worth noting that secondary alkyl halides such as bromocyclohexane and 2-bromooctane selectively form the coupling products without reductive elimination or α-elimination.

Scheme 21



VI.2. Application of metal-containing ionic liquids in desulfurization and denitrogenation of fuels

Currently, denitrogenation and desulfurization of fuels attract considerable attention of researchers because of the new stringent regulations on the atmospheric pollution caused by NO_x and SO_x oxides.[146] A 10 ppm limit for the permitted atmospheric content of sulfur has been established in developed countries and regions, such as Japan (since 2007), Australia, New Zealand and Europe (since 2009), in order to prevent the environmental pollution.[147] The state of the art in the field of IL-mediated diesel fuel desulfurization has been considered in reviews;[148, 149] below we discuss only the publications that are not included in those reviews.

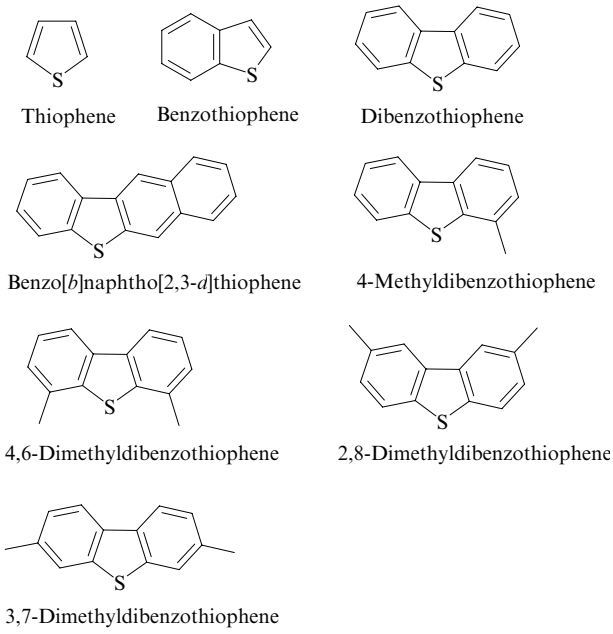


Figure 2. Structures of sulfur compounds that are difficult to remove from crude oil.[148]

The major sulfur-containing components of crude oil are [149] elemental sulfur, sulfides (RSR′), thiols (RSH), H_2S, disulfides (RSSR′), polysulfides (RS_nR'), thiophenes, dibenzothiophene (dbt), benzothiophene (bt) and their derivatives. Dibenzothiophene is most difficult to remove. The most typical thiophene derivatives occurring in crude oil are shown in Fig. 2. In conformity with the modern stringent standards, complete removal of these substances is highly important.[148]

The key methods for desulfurization of fuels include hydrodesulfurization (HDS), biodesulfurization (BDS), adsorptive desulfurization (ADS) with special solid adsorbents, oxidative desulfurization (ODS)[149] and extractive desulfurization (EDS). The two last-mentioned processes refer to the major application areas of M-ILs. Several patents address the use of M-ILs in desulfurization processes.[150–153] The most interesting results were obtained using $AlCl_3$- or $[AlCl_4]^-$-based ILs, but their sensitivity to water (HCl generation) and low stability restrict their practical application.

Several metal-containing ILs have been used to remove dbt *via* extractive desulfurization of model oils. Ren *et al.*[154] studied the dependence of the efficiency of dbt removal on the nature of the ions (organic and metal ions), ionic liquid to metal molar ratio, ionic liquid to oil volume ratio and the time of extraction. The best results were obtained for the $[C_4mim]HSO_4-FeCl_3$ system.

The effect of ILs on the removal of sulfur has been examined.[155] A high efficiency towards the removal of dbt (up to 99.4%) was found for the $[C_8mim]Cl-2\,FeCl_3$ system. In the presence of other metal salts, the results were much more modest: $BiCl_3$, 17.8%; $MnCl_2$, 46.7%; $CoCl_2$, 46.7%; $NiCl_2$, 48%; and $ZnCl_2$, 60.8% (Fig. 3). The $[C_8mim]Cl-2\,FeCl_3$ system was suitable for removal of 99.4% of dbt from model oils at room temperature (oil : IL = 20 : 1). Over a short period of time (30 min), the efficient removal of 4,6-dimethyldibenzothiophene

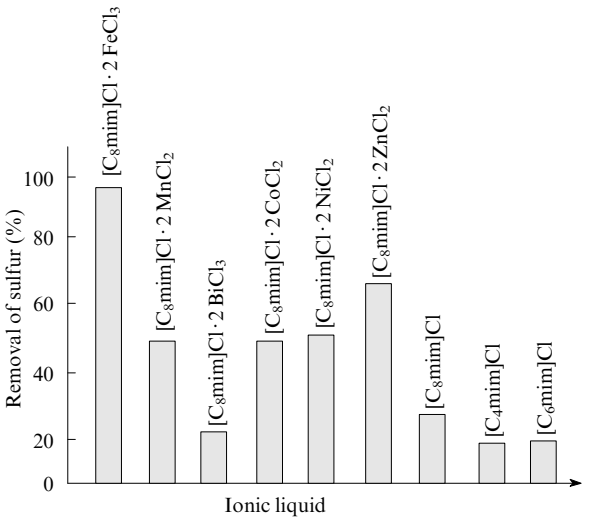


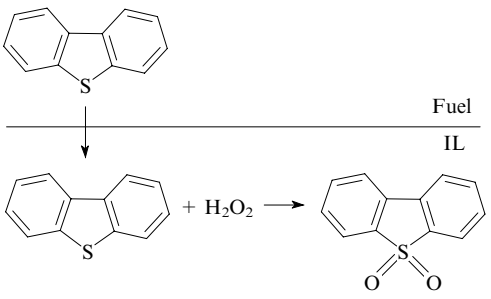
Figure 3. Removal of dibenzothiophene using metal-containing ionic liquids at 25 °C in 10 min.[155]
Model fuel: a solution of dibenzothiophene in n-octane, 2 ml of the fuel and 1 ml of IL.

(4,6-Me_2dbt) (99.3%) and benzothiophene (96.2%) was also accomplished. The efficiency of extraction increased in the series bt < 4,6-Me_2dbt < dbt. It is important to emphasize that the IL retained the extractive efficiency for 5 cycles.

In a similar study [156] of $FeCl_3$-based ILs for desulfurization of model fuel (dbt in n-dodecane, fuel : IL = 5 : 1 by mass, 30 °C, minimum extraction time of 30 min, sulfur content of 50 ppm), [C_4mim][$FeCl_4$] was found to be the IL of choice, while [C_8mim][$FeCl_4$] proved to be the least efficient.

The removal of sulfur by H_2O_2 oxidation in the fuel – IL system [156] was used to facilitate the formation of the corresponding sulfur oxides (Scheme 22). In this case, desulfurization includes the following stages: addition of hydrogen peroxide to model fuel, the formation of sulfone and its removal.

Scheme 22

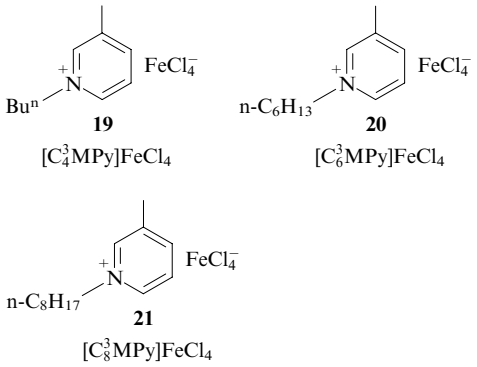


Surfactant-type metal-containing ILs, namely, methyl-tri(n-octyl)ammonium peroxotungstate and peroxomolybdate, [Me(n-$C_8H_{17})_3$N]W_2O_{11} and [Me(n-$C_8H_{17})_3$N]Mo_2O_{11}, proved to be active catalysts for dbt oxidation with H_2O_2.[7] The amphiphilic nature of these liquid catalysts is important both for the formation of an emulsion and for repeated dbt oxidation cycles. The highest efficiency of dbt removal (96.2%) was achieved at 30 °C and a fuel : M-ILs ratio of 40 : 1.

Fast oxidative desulfurization with dialkylpyridinium tetrachloroferrates **19** – **21** and an H_2O_2 solution (30 mass %) as the oxidant has also been reported.[157] Desulfurization of the model fuel (up to 100% dbt removal) was attained in 10 min at 298 K. Moreover, these ILs can be used twice without the loss of activity. The oxidative desulfurization in [C_8^3MPy][$FeCl_4$] was also accomplished for a real fuel and resulted in 44% desulfurization at the IL : fuel mass ratio of 1 : 3. The advantages of the above-described ODS experiments include mild reaction conditions (room temperature) and short time needed to reach equilibrium.

Although currently there are no stringent restrictions on the contents of nitrogen compounds in the motor fuel, the probability that these restrictions will appear in the future is very high. The significance of fuel denitrogenation processes is also due to the fact that nitrogen compounds are responsible for the evolution of nitrogen oxides, which poison the catalyst during desulfurization.[158]

Structures 19 – 21



Hansmeier *et al.*[159] tested imidazolium- and pyridinium-based ILs in desulfurization and denitrogenation of heteroaromatic compounds present in crude oil. All of the studied ILs showed degrees of extraction of nitrogen compounds above 99%. The extraction of pyrrole from refinery feed such as light catalytically cracked spirit (LCCS) reached 45%.

Zinc-containing imidazolium alkyl sulfonates, alkyl phosphites and dialkyl phosphates were tested [146] in denitrogenation of model oils containing quinoline, acridine and indole. The degree of extraction was 93.9% for quinoline, 86.5% for acridine and 100% for indole (for the oil : IL ratio of 5 : 1 by mass). Then quinoline was extracted with diethyl ether, and [C_2mim]$EtOSO_3$ – $ZnCl_2$ was thus regenerated. With this regeneration, the system could be reused up to eight times.

VI.3. Application of metal-containing ionic liquids in electrodeposition

A number of valuable properties of M-ILs such as high electrical conductivity (up to 100 mS cm^{-1}), wide electrochemical window (up to 5.8 V) and broad region of existence in the liquid state (~173 – 523 K) make it possible to develop new and improve existing technologies relying on these materials.[160] Electroplating (electrodeposition) is used in the fabrication of decorative and corrosion-resistant

coatings and in other branches of industry. By using ILs, one can overcome drawbacks of the existing water-based processes such as low current efficiency and toxicity of chemicals.[161] There are several books[162,163] and reviews[160,161] devoted to electrodeposition; therefore, we discuss only the papers that are not surveyed in the mentioned sources.

A recent study[164] describes an industrially applicable method for the synthesis of photonic crystals, characterized by a high dielectric constant, by direct electrodeposition at room temperature with the use of templates made of polystyrene (PS) colloid crystals, from a $GeCl_4$ solution in ionic liquids [C_6mim]fap [1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate] and [C_2mim]NTf_2.

Usually, germanium is difficult to recover from aqueous solutions, because the electric current is rather spent for water decomposition with hydrogen evolution than for germanium deposition. In polyethelene glycol and some other organic solvents, the problems of low current efficiency and hydrogen formation are retained. However, electrodeposition of germanium from ILs is a very promising technique. Polystyrene is suitable as a template because it can be easily eliminated by treatment with THF, with the structure of macroporous germanium being unaffected. The authors used scanning electron microscopy (SEM) to confirm a three-dimensionally ordering of the 1.5 mm thick germanium layer (electrode potential of -1.9 V *versus* Ag electrode; room temperature, 3 h).

The deposited germanium was shown to possess a well-ordered macroporous architecture with uniform close-packed spherical pores. Electrodeposition did not cause any shrinkage (the average distance between the pores was about 555 nm). The authors confirmed a smooth surface morphology and clearly demonstrated a steady growth of germanium in the voids of the polystyrene template and good ordering of the framework on the 4×4 μm scale.

A novel non-enzymatic, highly sensitive glucose sensor based on multi-walled carbon nanotubes and nickel (Ni-MWNT) has been fabricated by one-step co-electrodeposition in ILs.[165] An advantage of the proposed system is the very sensitive response to glucose. The sensor has a short response time (<2 s), substantial sensitivity (67.2 μA litre $mmol^{-1}$ cm^{-2}) and a low detection limit (0.89 μmol $litre^{-1}$; signal-to-noise ratio of 3). A comparison with other currently used non-enzymatic glucose sensors shows a wide range of linearity (up to 17.5 mmol $litre^{-1}$) and fast response of the new system.

Seddon *et al.*[166] prepared a number of 1-methyl-3-n-octylimidazolium chlorogallates(III) ($GaCl_3$ mole fraction: $0.33 < \chi_{GaCl3} < 0.75$) with sodium chloride as a buffer. Gallium deposition from these systems was studied by energy-dispersive X-ray spectroscopy (EDX) and SEM. The sample deposited from the buffered solution had a more uniform morphology than the sample obtained from the unbuffered solution. The authors attributed this result to more stable anionic composition of the buffered systems.

Liu *et al.*[167] studied the electrodeposition of zinc films from solutions of $Zn(OTf)_2$ in two moisture- and air-stable ionic liquids — 1-n-butyl-1-methylpyrrolidinium and 3-ethyl-1-methylimidazolium trifluoromethanesulfonates ([$Pyr_{1,4}$]OTf and [C_2mim]OTf). Samples with different surface morphology were obtained from different ILs: uniform thick films with good adhesion were formed in the case of [C_2mim]OTf, while grey zinc films with a poorer adhesion were fabricated from [$Pyr_{1,4}$]OTf. A SEM examination showed a hexagonal structure of zinc grains for the deposits obtained from [C_2mim]OTf and a flower-like structure in the case of [$Pyr_{1,4}$]OTf.[167]

The electrochemical window of ILs and the morphology of zinc films depend, first of all, on the presence of water and on the temperature. In water, pure zinc films were obtained, whereas in ILs, both Zn–Au alloys and zinc were formed. It was found that the grain size and predominant grain orientation of the metal can be controlled by varying the temperature; in addition, nanocrystalline films were preferably formed in the pyrrolidinium IL.

Kurachi *et al.*[168] investigated dysprosium electrodeposition and electrochemical behaviour in a phosphonium IL. The authors used a two-electrode cell with a copper plate cathode and a dysprosium metal anode. EDS examination of the films showed narrow peaks corresponding to characteristic dysprosium lines. In addition, the metallic electronic state of dysprosium, except for the surface layer, was confirmed by X-ray photoelectron spectroscopy (XPS).

Electrodeposition of copper on tantalum from ILs in a high vacuum has been reported.[169] The ionic liquid [C_2mim]Cl–$Cu(NTf_2)_2$ used as the source of copper is less viscous than [C_2mim]Cl–$CuCl_2$. Furthermore, the same group of authors[170] reported that liquid metal salts, $[Cu(MeCN)_4]NTf_2$, $[Ag(MeCN)_4][Ag(NTf_2)_3]$ and [$Ag(C_2mim)(C_4mim)$]NTf_2, do not undergo cathodic decomposition. Even at high current densities (25 A dm^{-2}) no signs of ligand or counter-ion (anion) elimination were observed. All earlier efforts to perform direct deposition of copper on tantalum resulted in the formation of an oxide layer at the Cu–Ta interface (because of the presence of water and oxygen traces). The attempts to completely remove oxygen and water from [C_2mim]Cl in a high vacuum were unsuccessful. The complete removal of water was accomplished by heating (to 150 °C), and deoxygenation required the use of hydroquinone as a trap. After this type of treatment of [C_2mim]Cl, direct deposition of copper on tantalum without formation of an oxide layer was possible. The proposed approach can be considered as a significant progress in the design of copper-plated microelectronic devices.

Krischok *et al.*[171] used 0.5 M solutions of TaF_5 and NbF_5 in 1-methyl-3-n-propylimidazolium and 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amides for tantalum and niobium electrodeposition. The layers thus formed were usually rough and had cracks. Moreover, they contained residual amounts of ILs; therefore, according to XPS data, the metal layers were substantially oxidized (more likely, this is caused by contact with the environment).

The multilayer $Fe_{50}Pt_{50}/Fe_2Pt_{98}$ coatings were successfully electrodeposited[172] from [C_2mim]Cl at 353 K with the pulse potential control. As the platinum source, $(NH_4)_2[PtCl_6]$ was used, and $FeCl_2$ served as the source of iron. The cross-sectional images of the multilayers show distinct layers with a columnar structure. The magnetic hysteresis curves indicate that the coercive force increased from 153 to 800 Oe as the Fe_{50}/Pt_{50} layer thickness in the four-bilayer structure (FBS) increased from 118 to 300 nm.

VI.4. Prospects of application of ionic liquids

The potential of ILs for biomedical applications is enormous, ranging from new pharmaceuticals[173] (an example is

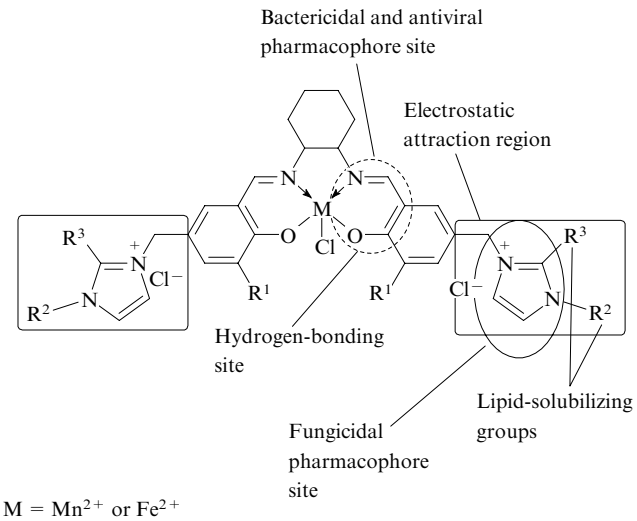


Figure 4. Structure of the metal-containing ionic liquid in which the imidazolium moiety is attached to the *N*,*N*′-bis(salicylidene)-(±)-*trans*-1,2-diaminocyclohexane core with indication of pharmacaphore sites.[176]

ranitidine docusate, where docusate is used to transfer ranitidine to the liquid phase[174]) to antibacterial coatings.[175] Although the potential of M-ILs in this field was underrated for a long period of time, a recent study[176] reports the antibacterial activity against *Staphylococcus aureus* and *Bacillus subtilis* for Mn^{III}- and Fe^{III}-containing ILs that incorporate an imidazolium moiety attached to the *N*,*N*′-bis(salicylidene)-(±)-*trans*-1,2-diaminocyclohexane (saldach) core (Fig. 4). The anti-*Escherichia coli* and anti-*Candida albicans* activities of these ILs were lower and an activity against *Aspergillus flavus* was totally absent.

There are great prospects for the design of new M-IL-based coatings for medical implants and biomaterials.

The application of ILs for biomass processing appeared to be exceptionally successful.[177] In recent years, M-ILs have also proved to be efficient for this application.[178–182] Yi *et al.*[178] employed Zr-containing ILs for microwave-assisted cellulose conversion to 5-hydroxymethylfuran (HMF). Among the tested metal chloride catalysts, the $ZrOCl_2$–$CrCl_3$ system in combination with the [C4mim]Cl ionic liquid was most efficient (the yield of HMF from cellulose fibre reached 57%). Microwave-assisted conversion of cellulose to glucose in Li-containing ILs has been reported:[181] the product yield reached 51% in 15 min at 100 °C. In the future, M-ILs would be used for the production of these and other organic products (such as carboxylic acids, ethers and esters) in high yields.

The use of ILs in energy devices[183] is not limited to Li-ion[184–187] or lithium–air, magnesium–air and zinc–air batteries.[188–191] Of considerable interest is the application of TiO_2-containing ILs in dye-sensitized solar cells.[192]

The separation of alkenes and alkanes with Cu- and Ag-containing ILs[193–196] is an alternative to the traditional cryogenic distillation (separation of propylene and propane), which consumes a lot of energy. This new separation method can be combined with a membrane technique and can be applied to the separation of some other mixtures.

The easily tunable functionality makes M-ILs excellent candidates to be used as CO_2 absorbents for post-combustion CO_2 capture.[197–200] The significance of M-ILs for this process and other similar processes aimed at the environmental protection (*e.g.*, treatment of high-level nuclear wastes) will only increase in the future.

We have already discussed the desulfurization and denitrogenation of fuels. Further research in this area may deal with the dearomatization of fuels (to prevent the formation of particulate matter) by either extraction[201] or hydrogenation[202] in M-ILs.

The application of M-ILs in the design of novel soft materials is also a growing area.[203, 204] These materials are used in optics as flexible displays;[203] in the manufacture of commodity polymers, conductive materials with desired shapes (cables and thin films),[205] structural and packaging materials, foams and adhesives, detergents and cosmetics, paints, food additives, lubricants, fuel additives and tyres; in nanotechnologies[206] and so on. The fascinating luminescence characteristics of these materials, in particular, long luminescence lifetime and exceptional colour purity, in combination with the coating properties and high content of ILs account for their optical applications, including the manufacture of flexible displays.

The use of the [C4mim][PF_6]–tri-n-butyl phosphate system for lithium extraction from brines has been reported.[207]

Along with practical application, fundamental studies addressing the M-IL structure and interactions in them are highly important. A recent publication[208] presents a thorough DFT study of the energetic and geometric characteristics of M-ILs, which elucidated the effect of the transition metal incorporated in the cation or the anion on the intermolecular interactions. The studies of M-ILs with a metal chelate serving as the cation seem especially promising.[209] These M-ILs could be efficient for CO_2 capture and find use in lithium ion batteries.

Although data on the toxicity of ILs are available,[210, 211] the enormous potential of the biological activity of ILs, including M-ILs, is beyond doubt.[212]

VII. Conclusion

Metal-containing ionic liquids, incorporating weakly basic anions, are attracting considerable attention as functional materials combining the specific characteristics of ILs with catalytic, magnetic and emission properties of metals and their compounds. The unique properties of M-ILs are caused by a balance of acidic and basic characteristics that can be tuned by varying the natures of the metal and the IL. For instance, chlorometallate ILs are, as a rule, more acidic than usual ILs, while the ILs containing a coordinated transition metal atom in the cation usually show higher basicity. Unfortunately, the M-IL acidity (basicity) issues have been considered only in few papers.[39, 213]

More than a half of papers of the last 10 years dealing with M-ILs address their applications in organic synthesis. However, it is impossible to cover the whole range of reactions involving M-ILs as catalysts and/or reaction media within one review. Therefore, we considered only the most important processes (alkylation, isomerization, hydroformylation, metathesis and C–C coupling), although the enormous potential of M-ILs in other processes, for example, in CO_2 fixation is also obvious.[96] In addition, we also considered some issues of fuel desulfurization and denitrogenation and electrodeposition from

M-ILs. One more promising trend for the development of this area is the use of polymerized M-ILs for gas separation membranes,[214] coordination of small protic molecules, solid-state ion conductors and the development of chiral M-ILs for enantioselective synthesis.[215]

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