

Review

# Metal-containing ionic liquids and ionic liquid crystals based on imidazolium moiety

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## Abstract

Ionic liquids and ionic liquid crystals of imidazolium salts composed of various transition and main group metals have been reviewed. Ionic metal complexes of imidazoles and *N*-heterocyclic carbenes possess the similar properties were also included. These types of ILs and ILCs have been realized as potential solvents, catalysts, catalyst precursors and reagents for many organic transformations and provide ecofriendly protocols. They have also been found to play key roles in material science. Many of these IL systems are air- and moisture stable and are considered as alternatives for air- and moisture sensitive chloroaluminate-based ILs. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Metal-containing ionic liquids; Metal-containing ionic liquid crystals; Imidazolium; Imidazole; Carbene

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*Abbreviations:* IL, ionic liquid; MIL, metal-containing ionic liquid; ILC, ionic liquid crystal; MILC, metal-containing ionic liquid crystal; EMIM, 1-ethyl-3-methylimidazolium; BMIM, 1-butyl-3-methylimidazolium; [BDMIM]Cl, 1-butyl-2,3-dimethylimidazolium chloride;  $C_n$ -MIM, 1-alkyl-3-methylimidazolium;  $(C_n)_2$ -IM, 1,3-dialkylimidazolium;  $C_n$ -MBIM, 1-alkyl-3-methylbenzimidazolium;  $(C_n)_2$ -BIM, 1,3-dialkylbenzimidazolium;  $C_n$ -IM, 1-alkylimidazole;  $C_n$ -BIM, 1-alkylbenzimidazole; NHC, *N*-Heterocyclic carbene;  $(C_n)_2$ -IMY, 1,3-dialkylimidazol-2-ylidene;  $(C_n)_2$ -BIMY, 1,3-dialkylbenzimidazol-2-ylidene;  $C_n$ , alkyl chain length of  $C_nH_{2n+1}$ .

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## 1. Introduction

### 1.1. Motivation

In general, compounds composed of ions that exhibit low melting points (usually below 100 °C) have come to be known collectively as ionic liquids (ILs). These salts have extremely low vapor pressures, wide liquid range, good electrolytic properties with large electrochemical window, tunable polarity and are easy to recycle. They therefore have received great attention as potential solvents to replace volatile organic solvents in a wide variety of chemical reaction, separation, and manufacturing processes to provide excellent protocols for clean and green ideology [1]. In recent days the performance of ILs has been extended towards nano- and material sciences [2].

### 1.2. Early breakthroughs

The first IL, [Et<sub>4</sub>N][NO<sub>3</sub>], was reported by Walden in 1914 [3]. Later, Hurely et al. in 1948 [4] developed the first room temperature IL from [EMIM]Cl–AlCl<sub>3</sub> system for the aluminium electroplating. However, these chloroaluminate-based IL systems were brought into more general audience by the groups of Osteryoung and Wilkes only in 1970s and extended by the groups of Hussey and Seddon in 1980s, mainly for the electrochemical and spectroscopic studies [5–7]. Parshall in 1972 [8] employed the ILs of tetraalkylammonium chlorostannate with dissolved PtCl<sub>2</sub> as a reaction medium and catalyst for several homogeneous catalytic reactions of olefins. But the interest in ILs as a reaction medium and catalyst for catalysis was increased after the success of Freidel–Crafts reaction in acidic [EMIM]Cl–AlCl<sub>3</sub> system in 1986 [9]. Wilkes' group again in 1992 got a ma-

ior breakthrough in the IL chemistry by the discovery of air- and moisture stable imidazolium salts with anions such as [BF<sub>4</sub>]<sup>−</sup> and [PF<sub>6</sub>]<sup>−</sup> [10]; this leads to the diversification of ILs with numerous combinations of cations and anions. Today the nitrogen-based ILs of imidazolium, ammonium, and pyridinium cores, and also the phosphonium cores with different anions of simple inorganic or halometallate ions have occupied the central stage in the rapidly expanding literatures (Chart 1).

Ionic liquid crystals (ILCs) are ionic compounds, having liquid crystalline properties are emerged as a sub-class of ILs because many of them have m.p. values below 100 °C. Normally the ILCs can be generated by increasing the alkyl chain length of the organic cations or anions by enhancing the self-organization character [11]. ILCs, which possess orientational order, are potentially useful as ordered media for reactions [11e]. Furthermore, ILCs have also been receiving good reputation in material science [12].

### 1.3. Scopes and Limitation of the present review

In this article, we reviewed metal-containing ionic liquids and ionic liquid crystals based on imidazolium moiety (including closely related other azoliums), that is metal complexes of imidazolium salts with IL and ILC properties. They have been realized as versatile reaction media, catalyst, catalyst precursors and reagents for various chemical processes include nanomaterials [13,14]. Other cores such as pyridinium, ammonium and phosphonium, which have been employed to a lesser extent, will not be included in this review but the representative references were provided [8,15]. Among the metal-containing imidazolium ILs, the chloroaluminate-based ILs were excluded in this review as they were reviewed

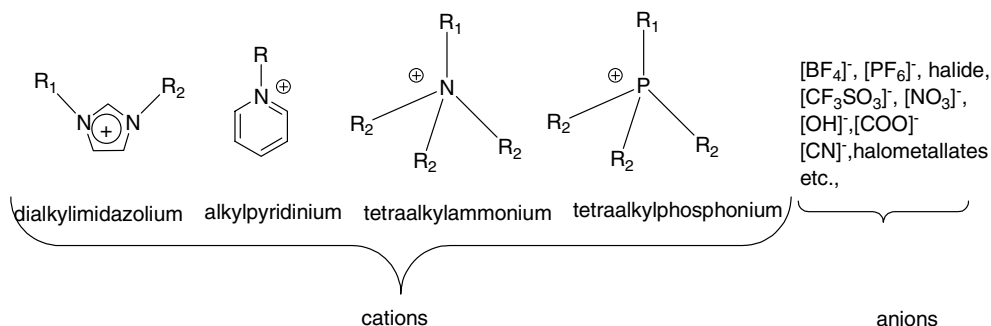


Chart 1.

excellently several times including a recent one in 2004 [1a,1b,1c,1d,1e,1f,16] and that alternative metal systems which have similar properties but are stable toward air and moisture have been developed. In this respect, and based on our research experience [11a,11b,11c,14b,17] we now wish to put together the works reported by several pioneers on ILs of imidazolium salts composed of metal-components other than chloroaluminates. Some times, metal-based imidazolium salts with m.p. values above 100 °C were also included to provide information about solid state ionic interactions and catalytic properties. In a parallel effort, we also like to give exposure to metal containing imidazole or imidazolium-based ILCs, which are ionic metal complexes having liquid crystalline properties [14,17a,17b,17c,17d,17e]. The presence of metal ions provides many additional properties such as color, geometry, and magnetism, which are not achievable by those with simple ILCs [14,17a,17b,17c,17d,17e]. Metal-containing ILCs are also potentially very useful as an ordered media, catalysts and catalyst precursors for chemical transformations. In addition, two new emerging topics, IL supported metal catalysts and IL supported metal nanoparticles, related to the present reviewing will also be discussed.

Based on these facts, we believe that the attempt of this review not only expose the useful role of these metal-containing imidazolium ILs and ILCs in organometallic chemistry and also interlink this topic with catalysis, nano- and material sciences to encourage further efforts.

## 2. Observations and discussion

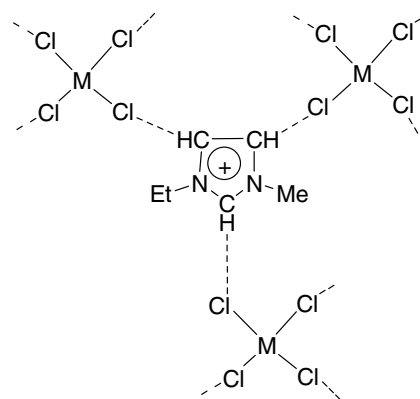
The content has been divided into four classes

1. Metal-containing ILs based on imidazolium salts.
2. Metal-containing ILCs based on
  - (a) Imidazolium salts;
  - (b) Imidazoles;
  - (c) *N*-Heterocyclic carbenes.
3. IL supported metal catalysts.
4. IL supported metal nanoparticles.

### 2.1. Metal-containing ILs based on imidazolium salts

The prolific works of Seddon, Welton, Dupont and their co-workers' from the period of 1990s gave a special significance to the ILs and their derivatives composed of transition-metals and main group metals. The information appeared before this period was also covered in the discussion part.

The two isomorphous imidazolium salts [EMIM]<sub>2</sub>-[MCl<sub>4</sub>] (**1–2**) (M = Co (**1**) or Ni (**2**)) with m.p. 90–100 °C were prepared directly by mixing the corresponding



M = Co(II), **1**; Ni(II), **2**

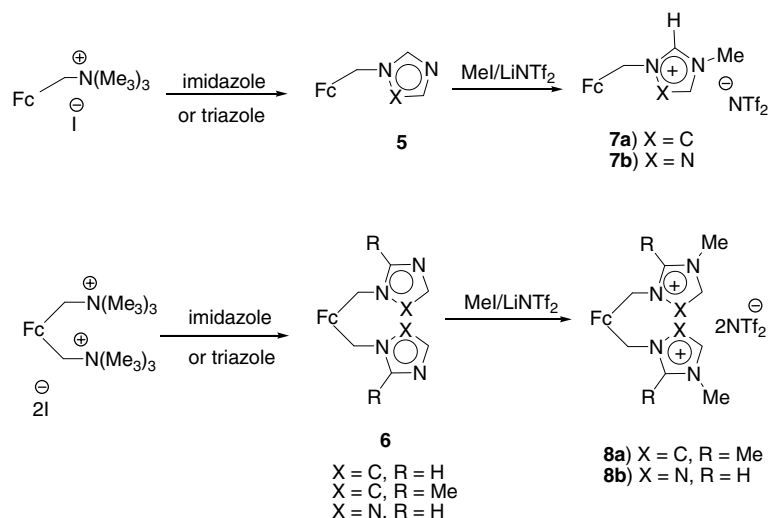
Chart 2.

metal chloride with [EMIM]Cl under dry nitrogen atmosphere [18]. Crystal structure studies showed that extended hydrogen bonding net-works were observed between the [MCl<sub>4</sub>]<sup>−2</sup> chlorides and ring hydrogens (Chart 2).

Vanadium-based salt [EMIM]<sub>2</sub>[VOCl<sub>4</sub>] (**3**) was obtained from the reaction of [EMIM]Cl with VOCl<sub>2</sub>-(CH<sub>3</sub>CN)<sub>x</sub> [19]. Crystal structure results showed that the [VOCl<sub>4</sub>]<sup>−2</sup> anion was approximately square pyramidal. In contrast to the crystal structures of similar compounds **1** and **2**, no hydrogen bonding was detected in **3**. Addition of thionyl chloride to compound **3** produced [EMIM]<sub>2</sub>[VCl<sub>6</sub>] (**4**) [20]. The oxo exchange chemistry of **3** and **4** was investigated in the basic chloroaluminate system.

Shreeve and co-workers [21] reported the preparation of ferrocene containing room temperature ILs (**7**, **8**) (Scheme 1). The reaction of mono or disubstituted(trimethylammonium) ferrocene iodide with azole (imidazole or triazole) gave initially the ferrocene linked azoles **5** and **6**. Quaternization with methyl iodide followed by metathesis with lithium bis(trifluoromethanesulfonyl)amide gave azolium compounds **7a–b** and **8a–b**. Compounds **7a–b** and **8a** having *T<sub>g</sub>* values of −32, −16 and −11 °C respectively are well below room temperature and are thermally stable up to 250–290 °C.

ILs formed from [BMIM]Cl and FeCl<sub>2</sub>/FeCl<sub>3</sub> were reported by Freeman and co-workers [22]. In which [BMIM][FeCl<sub>4</sub>]/[Fe<sub>2</sub>Cl<sub>7</sub>] (**9**) [BMIM]<sub>2</sub>[FeCl<sub>4</sub>] (**10**) and [BMIM]/[Fe(II)/Fe(III)-Cl<sub>n</sub>] (**11**) were studied by Raman spectroscopy and ab initio calculations. Tilve et al. [13i] studied the successful role of [BMIM]Cl–FeCl<sub>3</sub> IL system as a solvent and catalyst in the stereocontrolled glycosidation of 3,4,6-tri-*O*-acetyl-*D*-glucal with different alcohols. Sun et al. [23] demonstrated the use of [BMIM]Cl–FeCl<sub>3</sub> system for the alkylation of deuterated benzene with ethylene. A decrease in the intensity of 2-H of imidazolium ring after the reaction suggested



Scheme 1. Formation of IM-ILs containing ferrocenium.

that the proton for the initiation of the reaction was partly supplied by this 2-H of imidazolium ring. Kollé and Dronskowski [24] prepared the ILs composed of chloroferrate(II, III) and investigated the role of hydrogen bondings on the lattice energies. In that report interaction of [BDMIM]Cl with FeCl<sub>3</sub> and FeCl<sub>2</sub> in a molar ratio of 4:2:1 at 50 °C followed by cooling to ambient temperature gave yellow-green non-hygroscopic [BDMIM]<sub>4</sub>[Fe<sup>II</sup>Cl<sub>4</sub>][Fe<sup>III</sup>Cl<sub>4</sub>]<sub>2</sub> (**12**), which has a m.p. of ~38 °C. Hydrogen bondings between the chloroferrate(II) ions and ring hydrogens of the cations are the dominating force in the determination of packing of ions rather than the contributions from coulombic and dispersive forces. The polycrystalline material obtained upon rapid cooling showed texture reminiscent of liquid crystalline mesophases. This compound may be regarded as a intermediate between liquid (low temperatures [BDMIM][Fe<sup>III</sup>Cl<sub>4</sub>]) and solid (high temperatures [BDMIM]<sub>2</sub>[Fe<sup>II</sup>Cl<sub>4</sub>]) states. The strong hydrogen bonding interactions between the imidazolium hydrogens and chloroferrate(II) ion was also evidenced by the red shifts of the aromatic ν(C–H) stretching bands and down field shifts of ring protons in NMR. The chloroferrate example was claimed to be a method for designing anisotropic materials by combining molecules of tight hydrogen bonding with molecules of weaker coulombic and dispersive interactions. The use of chloroferrate ILs in Biginelli condensation and Friedel–Crafts sulphonylation reaction was briefly mentioned in [13i].

Bolkan and Yoke [25] observed the formation of copper(I)-based room temperature IL system of [EMIM]Cl–CuCl (type-**13**) over the composition range 0.33 < mole fraction CuCl<sub>x</sub> < 0.67 with glass transition temperatures down to about –50 °C. Spectroscopic studies showed that a broad variety such as CuCl<sub>3</sub><sup>2-</sup>, Cu<sub>2</sub>Cl<sub>3</sub><sup>-</sup>, CuCl<sub>4</sub><sup>-</sup> and polynuclear complexes Cu<sub>m</sub>Cl<sub>n</sub><sup>-(n-m)</sup> were formed.

However, these systems were found to be oxygen sensitive [25b]. Very recently Sundermeyer's group reported the copper(II) containing IL formulated as [BMIM]<sub>2</sub>–[Cu<sub>3</sub>Cl<sub>8</sub>] (**14**) [26]. The crystal structure determined at the low temperature of 193 K showed that the Cu(II) center adopted a square-pyramidal geometry with long Cu–Cl bond lengths of ~2.65 Å. When the CuCl<sub>2</sub> catalyzed oxidation of 2,3,6-trimethylphenol was carried out in [BMIM][Cl], generated [BMIM][oxotetracuprate] (**15**) as an active catalyst [27]. Crystal structure of **15** showed that four Cu(II)s formed a tetrahedral core with an oxygen at the center. [(C<sub>n</sub>)<sub>2</sub>-IM]Cl/[CuCl] system (type-**16**) consisting of various chlorocuprates viz., [CuCl<sub>2</sub>]<sup>-</sup>, [Cu<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup> and [Cu<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup> was also prepared [1i].

The use of [EMIM]Cl/[ZnCl<sub>2</sub>] ILs system (type-**17**) in the electrodeposition of metals and alloys has been extensively studied by Sun and co-workers [28]. Mixing different ratios of [EMIM]Cl and ZnCl<sub>2</sub> produced Lewis acidic ILs comprising [EMIM] cation with different chlorozincate anions (ZnCl<sub>3</sub><sup>-</sup>, Zn<sub>2</sub>Cl<sub>5</sub><sup>-</sup> and Zn<sub>3</sub>Cl<sub>7</sub><sup>-</sup>). By dissolving other metal ions in [EMIM][ZnCl<sub>2</sub>] and by choosing the proper electrode potentials, metals or alloys can be electrodeposited. Formation of nanoporous platinum by selective anodic dissolution of PtZn surface alloy in this acidic IL system has also been reported [13f]. Various air and moisture stable ILs of [(C<sub>n</sub>)<sub>2</sub>-IM]Cl/ZnCl<sub>2</sub> system (**18**) have been synthesized and promoted as an alternatives for chloroaluminates to be used as an excellent medium and catalyst in the Diels–Alder reactions [29] to give high yields and high endo selectivity.

Kim et al. [13d,30] prepared and used the [RMIM][ZnX<sub>2</sub>Y<sub>2</sub>] IL system (type-**19**) (R = Me, Et, *n*-Bu, benzyl; X = Y = Cl or Br or X = Cl, Y = Br) for the coupling reaction of CO<sub>2</sub> and ethylene or propylene oxide to produce cyclic carbonates. Crystal structure of

[(M)<sub>2</sub>-IM][ZnBr<sub>2</sub>Cl<sub>2</sub>] ((M)<sub>2</sub> = dimethyl) showed that two imidazolium cations were paired with [ZnBr<sub>2</sub>Cl<sub>2</sub>]<sup>−</sup>. The catalytic activities increased with the increasing nucleophilicity of the halide ion. Xia's group have also followed the same reaction by using the [BMIM]Cl/ZnX<sub>2</sub> system [31]. Dupont et al. [32] used the same [BMIM]Cl/[ZnCl<sub>2</sub>] system as a solvent to immobilize RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in the catalytic hydrogenation of 1-hexene. Wilkinson catalyst in [EMIM]Cl/ZnCl<sub>2</sub> IL system catalyzed the regioselective hydroboration of terminal alkynes to vinylboronates within 2 h [33].

IL properties of phosphonium moiety composed of [PdCl<sub>4</sub>]<sup>−2</sup> anion were described [15c], but not with imidazolium moiety. However, they were considered as excellent catalysts or catalyst precursors for various organic transformations. Dupont's group reported the synthesis and catalytic action of [BMIM]<sub>2</sub>[PdCl<sub>4</sub>] (type-20) in the hydrodimerization of 1,3-butadiene in [BMIM][BF<sub>4</sub>] medium [34]. IR spectral data and crystal structure of compound 20 showed the presence of strong hydrogen bonding between the chloride and the hydrogen at the imidazolium cation. During the catalytic process, compound 20 in [BMIM][BF<sub>4</sub>] underwent dealkylation and produced the catalyst precursor *trans*-[PdCl<sub>2</sub>(C<sub>1</sub>-IM)<sub>2</sub>] 21 (Chart 3). Seddon's group also used [BMIM]<sub>2</sub> [PdCl<sub>4</sub>](20) as a catalyst in the Heck reaction conducted in a three-phase [BMIM][PF<sub>6</sub>]/hexane/water system [35]. Generation of metal–NHC in the catalytic cycle was anticipated. Ortwirth et al. [36] characterized the structure of [EMIM]<sub>2</sub> [PdCl<sub>4</sub>] (22), which was prepared by the reaction of Pd(acac)<sub>2</sub> with an acidic [EMIM]Cl–AlCl<sub>3</sub> system.

Shreev and co-workers [13e] highlighted the formation of IL-coordinated compound 23 with the dissolution of PdCl<sub>2</sub> in an IL of monoquaternary bis-2,2'-bimidazole (A) for a Pd(II) catalyzed Heck reaction (Chart 4). This IL-coordinated Pd(II) complex 23 performed well in the Heck reaction at least 10 times without significant loss in its activity. Dyson and co-workers [37] also prepared an IL-coordinated Pd(II) complex [Pd(N≡CC<sub>3</sub>MIM)<sub>2</sub>Cl<sub>2</sub>][BF<sub>4</sub>] 24 (N≡CC<sub>3</sub>MIM = 1-butyl nitrile-2,3-dimethylimidazolium) by using the nitrile functionalized IL (Chart 4). Compound 24 was employed as a solvent and catalyst during the hydrogenation of 1,3-cyclohexadiene. Compound 24 can be retained in the IL upon the extraction of product.

Kozhevnikov's group described the formation of imidazolium salts of tetra- and hexachloroplatinates of the type [C<sub>n</sub>-MIM]<sub>2</sub>[PtCl<sub>n</sub>] (type-25) (C<sub>n</sub> = Et or Bu; n = 4, 6) from the reactions of Pt(II or IV) chlorides with

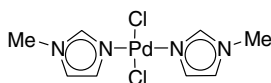


Chart 3.

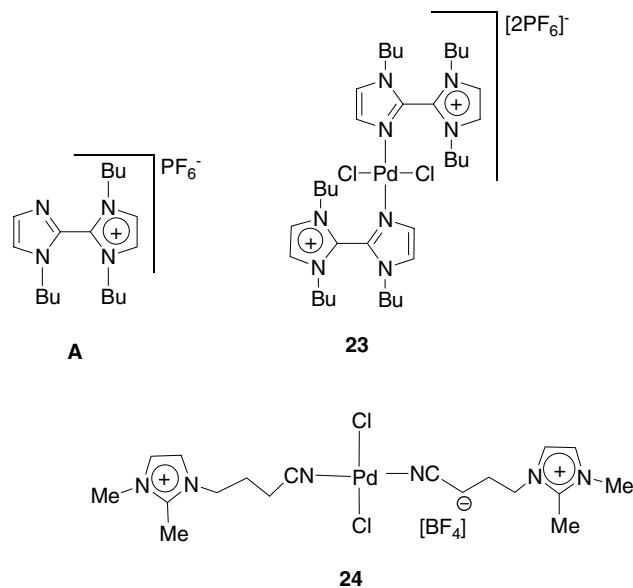


Chart 4.

[C<sub>n</sub>-MIM]Cl/[AlCl<sub>3</sub>] or [C<sub>n</sub>-MIM]Cl [38a]. The [EMIM]<sub>3</sub>[IrCl<sub>6</sub>] (26) was also prepared similarly [38a]. Sun et al. [39] also reported the [EMIM]<sub>3</sub>[IrCl<sub>6</sub>] system for electrochemical studies. The [BMIM]<sub>2</sub>[PtCl<sub>4</sub>] salt exhibited a low m.p. of 68 °C while the other members have relatively high m.p. values (>200 °C). Chen and Matsumoto [40] reported aqua-platinum complex [Mes<sub>2</sub>-IM][PtCl<sub>3</sub>(H<sub>2</sub>O)] (27) (Chart 5) by the reaction of [Mes<sub>2</sub>-IM]Cl with K<sub>2</sub>[PtCl<sub>4</sub>] in aqueous solution. Synthesis and crystal structures of a benzyl bridged bisimidazolium salt of tetra- and hexachloroplatinates [MIM-bz-MIM][PtCl<sub>n</sub>] (28 and 29) (bz = benzyl) were also reported (Chart 5) [40,41]. More notably, ethylene stabilized new *N*-heterocyclic carbene complex (*cis*-[(C<sub>2</sub>H<sub>4</sub>)(EMIM)PtCl<sub>2</sub>]) (30) was isolated from the reaction of ethylene with a mixture of Pt(II and IV) chlorides in a basic [EMIM]Cl/[AlCl<sub>3</sub>] medium (Chart 5) [38a,38b]. Whereas in an acidic medium, mixtures of [EMIM]<sub>2</sub>[PtCl<sub>4</sub>] and [EMIM]<sub>3</sub>[PtCl<sub>6</sub>] were obtained.

Kozhevnikov's group demonstrated also the isolation of [EMIM][AuCl<sub>4</sub>] (31) and [BMIM][AuCl<sub>4</sub>] (32) from the solvent free reaction of [EMIM]Cl or [BMIM]Cl with HAuCl<sub>4</sub> [42]. Exchange reaction between NaAuCl<sub>4</sub> and [EMIM][AlCl<sub>4</sub>] also gave 31. Crystal study showed

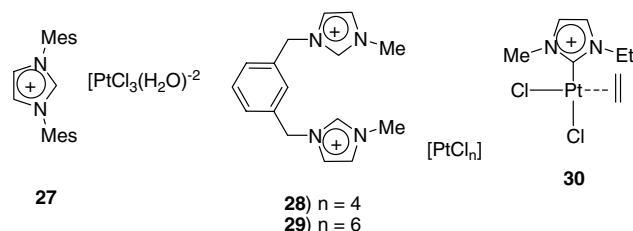


Chart 5.



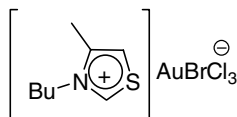


Chart 6.

that both compounds **31** and **32** have similar solid state structure of roughly the CsCl type with weak interionic interactions. The  $[\text{AuCl}_4]^-$  anions oriented perpendicular to each other and formed infinite anionic chains of alternating corner-to-face arranged units. Due to the loose assembly of ions and weak interionic interactions, compounds **31** and **32** showed relatively low melting points ( $\sim 58$  and  $50$  °C respectively) than the corresponding  $[\text{NiCl}_4]^{2-}$  and  $[\text{CoCl}_4]^{2-}$  ( $90$ – $100$  °C) counter parts of compounds **1** and **2**.

Reaction of various ratios of  $[\text{EMIM}]\text{Cl}/\text{AuCl}_3$  has also been described by Freeman's group: a ratio of 2/1 produced room temperature IL; a ratio of 1/1 solid gave  $[\text{EMIM}][\text{AuCl}_4]$  (**33**); higher ratios of  $\text{AuCl}_3$  also gave solid salts [43]. The thermal behavior is different from that of the  $[\text{EMIM}]\text{Cl}/\text{AlCl}_3$  system. Raman spectral data and the computational calculations were consistent with the presence of  $[\text{AuCl}_4]^-$  anion.

Raubenheimer's group prepared the thiazolium-based gold(III) compound  $[\text{BMTz}][\text{AuBrCl}_3]$  (**34**) (Chart 6) from the reaction of 3-butyl-4-methylthiazolium bromide  $[\text{BMTz}]\text{Br}$  with  $\text{HAuCl}_4$  or  $\text{NaAuCl}_4$  [44]. Formation of mixed ion could be due to the substitution of chloride by the softer bromide. Compound **34** was employed both as a solvent and a catalyst in the hydration of phenyl acetylene. However, the conversion rates were found to be low. A neutral monocarbene–Au(III) complex was also isolated from compound **34** by treating it with a base.

Uranium-based salt of the type  $[\text{EMIM}]_2[\text{UCl}_6]$  (**35**) was obtained from the reaction of  $[\text{EMIM}]\text{Cl}$  with  $\text{UCl}_4$  [45]. Controlled aerial oxidation of the methanolic solution of **35** produced  $[\text{EMIM}][\text{UO}_2\text{Cl}_4]$  (**36**). The synthesis of dioxouranium(IV) complexes of  $[\text{C}_n\text{-MIM}][\text{anion}]$  (type-**37**) ( $n = 1, 2, 3, 4, 5, 6, 10, 16$  and  $18$ ); anion =  $\{\text{UO}_2(\text{NO}_3)_2\}_2(\mu_4\text{-C}_2\text{O}_4)$ ,  $[\text{UO}_2(\text{NO}_3)_3]$  and  $[\text{UO}_2(\text{NO}_3)_4]$ , and the subsequent isolation of uranium by electrochemical reduction suggested that the formation of such IL-associated compounds is potentially useful in the recycling process of spent nuclear fuel [46]. Crystal structural work of the laboratory-prepared complexes showed that alkyl chain length of ILs influenced the crystal packing and also the stability of the complex.

Hagiwara's group described the incorporation of fluoroanions of Nb(V) and Ta(V) to the ILs [47]. Reaction of  $[\text{EMIM}]\text{F} \cdot 2.3\text{HF}$  with  $\text{NbF}_5$  and  $\text{TaF}_5$  produced pure  $[\text{EMIM}][\text{NbF}_6]$  (**38**) and  $[\text{EMIM}][\text{TaF}_6]$  (**39**) as pale-yellow liquids. Results from the Raman spectroscopic studies of **38** and **39** were consistent with a

$[\text{EMIM}]$  cation and an octahedral  $[\text{NbF}_6]^-$  or  $[\text{TaF}_6]^-$  anion. Compound **39** has a large electrochemical window of  $\sim 4.5$  V. Hagiwara's group have also reported the crystal structure of  $[\text{EMIM}]_3[\text{LaCl}_6]$  (**40**) to demonstrate the ionic interactions in the imidazolium salts [48] by saturation of  $\text{LaCl}_3$  in basic  $[\text{EMIM}]\text{Cl}-\text{AlCl}_3$ . Crystal structure showed that both the ring and chain hydrogen atoms formed hydrogen bonds with the larger hexachlorolanthanate ion.

Interesting stable room temperature ILs of chloroindates, which possess similar Lewis acidity properties as those of chloroaluminate-based ILs have been reported. Dupont's group prepared  $[\text{BMIM}][\text{InCl}_4]$  (**41**) by mixing equimolar amounts of  $[\text{BMIM}]\text{Cl}$  and  $\text{InCl}_3$  and used it as a medium for tetrahydropyranlation of alcohols [49]. Yang et al. [50] also prepared various room temperature ILs of  $[\text{BMIM}][\text{InCl}_4]$  by varying the mole fraction of  $\text{InCl}_3$  in the mixture. Results from Raman spectral analysis and ab initio calculations suggested that  $\text{InCl}_4^-$  was the primary anion in the IL. In a recent advance Varma's group demonstrated a solvent free microwave-assisted preparation of  $[\text{BMIM}][\text{InCl}_4]$  IL system and its potential catalytic application during the tetrahydropyranlation alcohols to form tetrahydro pyranylethers [13b]. Seddon's team in their continuous contributions to advance the field of ILs, discovered that the  $\text{InCl}_3$ – $[\text{BMIM}]\text{Cl}$  system can be used successfully as a recyclable reaction medium and catalyst for Friedel–Crafts acylation reactions [51]. Although this IL system requires slightly excess of chloroindate(III), however, the workup and recycling of the reaction were found to be more efficient without the leaching of In(III) than the simple  $\text{InCl}_3$  catalyzed reaction. More significantly, aromatic compounds of less reactive than benzene were also effectively acylated in this IL system with high yields. Carpenter and Verbrugge [52] used the  $[\text{EMIM}]\text{Cl}-\text{InCl}_3$  system (**42**) for the electrochemical codeposition of In and Sb.

Chlorostannate-based room temperature ILs were highly recommended in the Pt catalyzed regio-selective hydroformylation reactions [13h]. Reaction of  $[\text{BMIM}]\text{Cl}$  with slightly excess  $\text{SnCl}_2$  produced Lewis acidic  $[\text{BMIM}][\text{SnCl}_3]$  (**43**) and  $[\text{BMIM}][\text{Sn}_2\text{Cl}_5]$  (**44**). The m.p. values of **43** and **44** ( $< 25$  °C) are substantially lower than the tetraethylammonium chlorostannate ILs ( $78$  °C) employed by Parshall in hydroformylation [8]. Fast exchange between anions was observed in the  $^{119}\text{Sn}$  NMR study. The Lewis acidity of the chlorostannate was proposed to play a key role in the generation of catalytically active Pt-complex. The same chlorostannate system was also employed in the ring-opening polymerization of ethylene carbonate [53]. Wrsemann and co-workers [54] demonstrated that by incorporating weakly coordinating and air stable heteroborate anions to imidazolium salts can decrease the m.p. values of ILs. Incorporation of imidazolium cation with alkylated

stannaborate of different chain lengths produced the non-hygroscopic salts  $[(C_n)\text{-MIM}][\text{R-SnB}_{11}\text{H}_{11}]$  (**45**) with m.p. values of 55–105 °C; no short contact was observed between the cation and anion in the solid crystal.

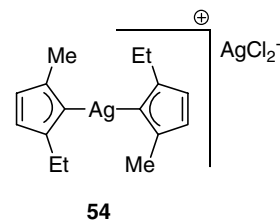
Unexpected isolation of homoleptic pentacoordinate lead(II) ethanoate complex  $[\text{EMIM}]_2[\text{Pb}(\text{O}_2\text{CMe}_4)_4]$  (**46**), by the metathesis of Pb(II)-ethanoate and  $[\text{EMIM}][\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) indicated that ILs could be useful media for the stabilization of unusual metal coordination environments [55]. Attempted synthesis of the  $\text{BiCl}_3$  adduct of 1-methyl-2-imidazoletione and 1,3-dimethyl-2-imidazoletellurone led to the formation of high temperature imidazolium melts with tetrachlorobismuthate(III) anion (**47**) [56]. Crystal structure showed that the polymeric network of  $\text{BiCl}_4^-$  caused a parallel stacking of the imidazolium cation. The difference in the geometries of  $\text{BiCl}_4^-$  was attributed to the extended hydrogen bondings formed with the ring hydrogens.

Efforts were also made to incorporate transition-metal carbonyl-based organometallic species either into the anionic unit or into the cationic unit due to their potential catalytic activity. Welton's group reported the preparation of liquidous  $[\text{BMIM}][\text{Co}(\text{CO})_4]$  (**48**) [13c] by the metathesis reaction between  $[\text{BMIM}][\text{Cl}]$  and  $\text{Na}[\text{Co}(\text{CO})_4]$ . Formation of ILs of  $[\text{BMIM}][\text{HFe}(\text{CO})_4]$  (**49**) and  $[\text{BMIM}][\text{Mn}(\text{CO})_5]$  (**50**) (numbering) type ILs were also mentioned briefly. The electrochemical window of compound **48** was extremely large as were observed for other ILs. In view of the known catalytic activity of cobalt carbonyl species, compound **48** was employed to function both as a solvent and a catalyst in the debromination of 2-bromo-2-naphthophenone and 2-bromoacetophenone to give the corresponding ketones. Dyson et al. [57] prepared the IL  $[\text{BMIM}][\text{Rh}_2(\text{CO})_4\text{I}_2]$  (**51**),

in which the Monsanto catalyst  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  was incorporated as a counter ion.

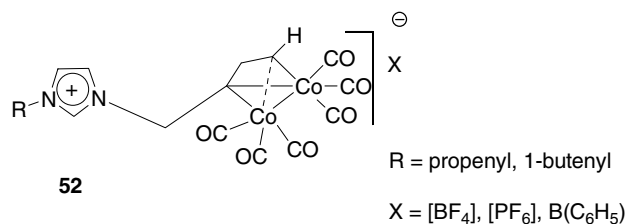
Raubenheimer and co-workers [58] synthesized several cobalt carbonyl derivatives (type-**52**) by using the alkyne functionalized imidazolium salts (Chart 7). Dyson and co-workers [59] also reported the cobalt carbonyl derivatives of the type-**53** (Chart 7) by employing the alkyne functionalized imidazolium salts. Attempts to prepare the metal-carbene complexes by transmetalation were failed.

Finally metal-NHC complexes (NHC = *N*-heterocyclic carbenes) have also been added to the IL family by the interesting contribution from the groups of Waymouth and Hedrick [60]. The silver-NHC complex (**54**) (Chart 8) isolated from the reaction of  $[\text{EMIM}]\text{Cl}$  and  $\text{Ag}_2\text{O}$  was a room temperature IL. Compound **54** was found to be a good precursor of unsaturated NHC as suggested by the DSC study and was employed successfully as catalyst for transesterification reaction. Ring opening polymerization of *l*-lactide was also catalyzed by **54** to produce mono dispersed polylactide of predictable molecular weight.

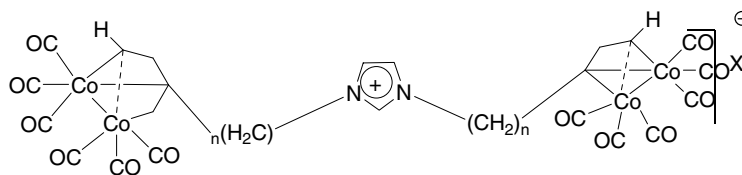


54

Chart 8.



52



53

n = 1, 3; X =  $[\text{BF}_4]$ ,  $[\text{BPh}_4]$ 

Chart 7.

## 2.2. Metal-containing ILCs

Based on the composition these are divided into the following three sections:

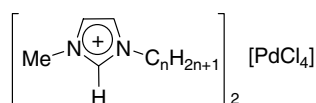
- (a) MILCs based on imidazolium salts;
- (b) MILCs based on imidazoles;
- (c) MILCs based on *N*-heterocyclic carbenes.

### 2.2.1. MILCs based on imidazolium salts

Bruce's and Seddon's groups reported the first liquid crystalline  $[C_n\text{-MIM}][\text{MCl}_4]$  **55** and **56** ( $M = \text{Co}$  (**55**),  $\text{Ni}$  (**56**),  $C_n =$  alkyl chain of  $C_nH_{2n+1}$ ,  $n = 12\text{--}18$ ) [61]. Thermal stability of these compounds was found to depend on the chain length; the longer the chain, the more stable the compound. It was suggested that the use of ordered liquid-crystal as a solvent will certainly influence the selectivity in catalytic reactions. The  $[C_n\text{-MIM}]_2[\text{NiCl}_4]$  systems was also studied by XAFS [62].

The crystal and liquid crystal polymorphism for the compounds of  $[C_n\text{-MIM}][\text{PdCl}_4]$  (type-**57**) was also investigated by Seddon's group as a function of alkyl chain length ( $n = 12, 14, 16, 18$ ) (Chart 9) [14a]. While compounds of  $n = 10$  and 12 are non mesogenic, compounds of  $n = 14, 16, 18$  showed liquid crystal behavior. The m.p. values are higher than the counter parts with inorganic anions like  $\text{Cl}^-$ ,  $\text{BF}_4^-$  and  $\text{PF}_6^-$ , but are comparable with  $[\text{CoCl}_4]^{2-}$  or  $[\text{NiCl}_4]^{2-}$ . The thermotropic mesophase was identified as a fully interdigitated smectic A phase.

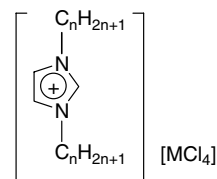
MILCs composed of *N,N'*-dialkylimidazolium salts of Pd(II) and Cu(II) ( $[(C_n)_2\text{-IM}][\text{MCl}_4]$  (**58** and **59**)  $n = 8, 10, 12, 14, 16$ , and 18 for  $M = \text{Pd}^{\text{II}}$  (**58**) and  $n = 10, 12, 14, 16$ , and 18 for  $M = \text{Cu}^{\text{II}}$  (**59**)) were prepared and structurally characterized by Lin's group (Chart 10) [17b]. The crystal structures of  $[(C_{12})_2\text{-IM}]_2[\text{PdCl}_4]$  and  $[(C_{12})_2\text{-IM}]_2[\text{CuCl}_4] \cdot \text{H}_2\text{O}$  were found to be the first example of metal-containing ILCs based on  $[(C_n)_2\text{-IM}]$  salts. In the solid state and liquid crystal phases both series of compounds displayed a well defined lamellar structure. The metal ions were intercalated between the hydrophobic bilayers composed of U-shaped imidazolium cations of highly interdigitated alkyl chains. In addition to the normal H-bonding between the ring C–H protons and anions, an N–CH<sub>2</sub> proton donor was also observed. Both series of compounds exhibited a wide temperature range of SmA mesophase,



$n = 10, 12, 14, 16, 18$

**57**

Chart 9.



**58** M = Pd(II)  
**59** M = Cu(II)

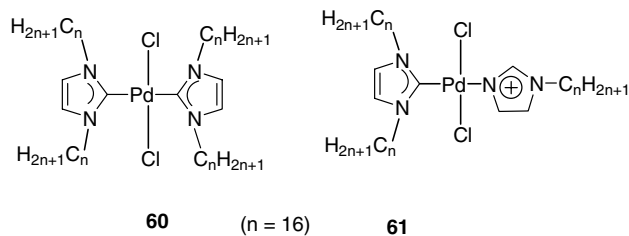


Chart 10.

but thermal decomposition occurred before the clearing temperatures. Palladium dicarbene complex *trans*- $[(C_n)_2\text{-IMY}]_2\text{PdCl}_2$  (**60**) and carbene–imidazole complex *trans*- $[(C_n)_2\text{-IMY}](C_n\text{-IM})\text{PdCl}_2$  (**61**) were identified as the thermal decomposition products (Chart 10).

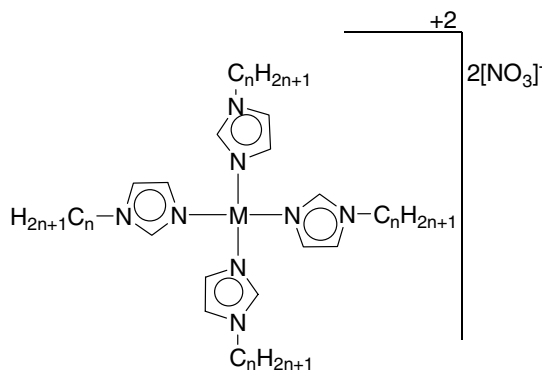
These results were different from that observed for the catalytic system of  $\text{PdCl}_2/[\text{BMIM}] \cdot \text{BF}_4$ , [63] and that using imidazolium salts with bulky substituents [64]. The mixtures with different combinations of the  $\text{PdCl}_4^{2-}$ ,  $\text{CuCl}_4^{2-}$ , and  $\text{Cl}^-$  salts also displayed liquid crystalline properties. Results of these combinations suggested the possibility of providing a partially ordered solvent system for chemical transformations using  $\text{Pd}^{\text{II}}$  and/or  $\text{Cu}^{\text{II}}$  as catalysts.

There is a growing interest in the lanthanide-containing liquid crystalline phases due to their potential photo- and electroluminescent behavior. Bunzli's group showed that the introduction of trivalent Eu(III) salts,  $\text{EuY}_3$  ( $Y = \text{Cl}, \text{NO}_3^-, \text{ClO}_4^-, \text{CF}_3\text{SO}_3^-$ ), into the room temperature ILs of  $[(C_n)_2\text{-MIM}][\text{X}]$  (type-**62**) ( $X = \text{Cl}, \text{NO}_3^-, n = 12, 14, 16, 18$ ) up to 10% produced the luminescent ILC phases [65]. The luminescence properties were tuned by the choice of either the excitation wavelength or of the counter ion. Luminescent studies indicated the presence of single Eu(III) solvated species and the energy transfer from the IL to Eu(III) center. Consequently a  ${}^5\text{D}_0 \leftarrow {}^7\text{F}_0$  was detected. When the Eu(III) center with counter-ions  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ , triflate were used, formation of the polychloro species was observed. On the contrary, the use of  $\text{NO}_3^-$  salt led to stronger anion–Eu(III) interaction and consequently the predominance of meta-centered red transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ).

### 2.2.2. MILCs based on imidazoles

Lin's group synthesized the ionic *N*-alkylimidazole ( $C_n\text{-IM}$ ,  $C_n = C_nH_{2n+2}$ ) complexes (**63–64**) having





$n = 10, 12, 14, 16, 18$

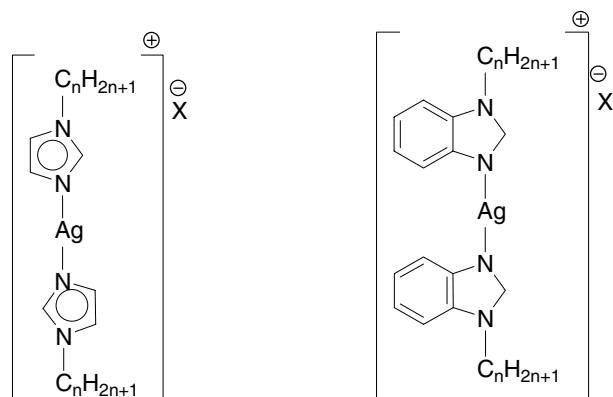
**63** M = Cu(II)

**64** M = Zn(II)

Chart 11.

general formulas of  $[M(C_n\text{-IM})_4][\text{NO}_3]_2$  for M = Cu(II) (**63**) and Zn(II) (**64**) respectively and studied their crystal and liquid crystalline properties (Chart 11) [17c]. The ionic Zn(II) compounds, except that with  $n = 10$ , all exhibited liquid crystal behavior with low melting temperatures. The compound of  $n = 10$  was found to be a room temperature IL and  $n = 12$  a room temperature ILC containing Zn(II) ion. A mesomorphic structure with non-interdigitated tetrahedral monolayer packing, similar to that of tetra-*n*-alkylammonium and phosphonium salts was proposed. In the ionic Cu(II) compounds, except  $n = 10$ , all exhibited mesogenic properties with highly ordered mesophase of the soft crystal G or J. Crystal structure of the compound (**63**) revealed a square planar geometry around the Cu(II) center with alkyl chains arranged in distorted “x” shape.

Lin and co-workers [17d] also reported for the first time the synthesis and mesomorphic properties of a homologous series of  $[\text{Ag}(C_n\text{-IM})_2]^+$  (type-**65**) and  $[\text{Ag}(C_n\text{-BIM})_2]^+$  (type-**66**) cations with different counterions ( $\text{NO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{CF}_3\text{SO}_3^-$ ) (Chart 12). Crystal structure of  $[\text{Ag}(C_{12}\text{-IM})_2][\text{NO}_3]$  showed that the cation adopted a U-shaped conformation with bilayer packing. The molecular cations of  $[\text{Ag}(C_{16}\text{-BIM})_2][\text{NO}_3]$  (BIM = benzimidazole) and  $[\text{Ag}(C_{16}\text{-BIM})_2][\text{BF}_4]$  both adopted a chair conformation. All the  $[\text{Ag}(C_n\text{-IM})_2][\text{NO}_3]$  complexes except for  $n = 10$ , exhibited liquid crystalline properties of SmA mesophase. Free standing films prepared from these ionic liquid crystals can stay for several days at room temperature.  $[\text{Ag}(C_n\text{-BIM})_2][\text{NO}_3]$  and  $[\text{Ag}(C_n\text{-BIM})_2][\text{BF}_4]$  are non-mesogenic; probably due to the larger width to length ratio of the Bimy core.  $[\text{Ag}(C_{16}\text{-IM})_2]^+$  with four different anions,  $[\text{NO}_3]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$  and  $[\text{CF}_3\text{SO}_3]^-$  were also examined. Of the four complexes, only the one with the  $[\text{CF}_3\text{SO}_3]^-$  anion does not show liquid-crystal behavior. The complex with  $[\text{BF}_4]^-$  counter ion exhibited the widest



**65**

$n = 10, 12, 14, 16, 18$

**66**

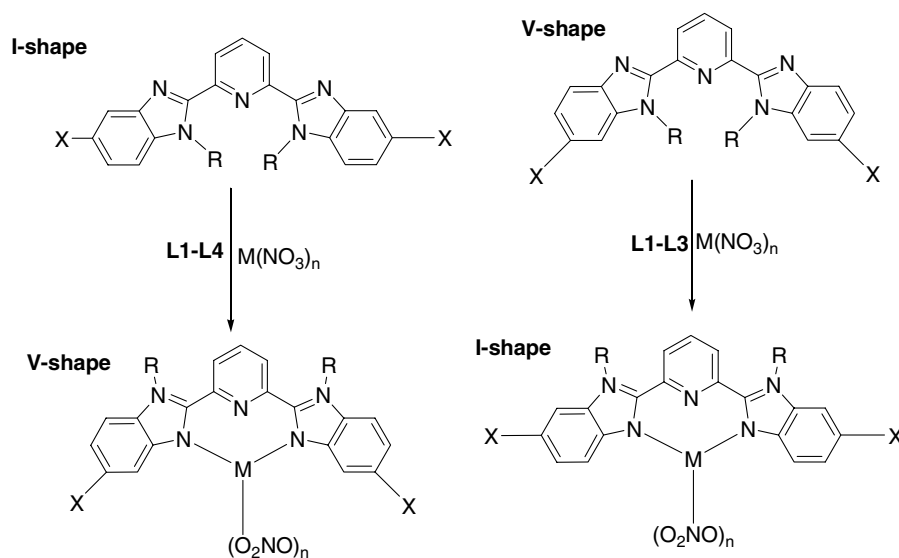
$n = 12, 14, 16, 18$

X =  $[\text{NO}_3]$ ,  $[\text{BF}_4]$ ,  $[\text{PF}_6]$ ,  $[\text{Tf}]$

Chart 12.

temperature range of mesophase and lowest mesophase transition temperature.

Piguet and co-workers [66] made extensive investigations to synthesize liquid crystalline lanthanide(III) complexes by using the mesomorphic ligands of the type **L2–L4** (Scheme 2). Complexation of different lanthanides as  $[\text{Ln}(\text{L}_x)(\text{NO}_3)_3]$  ( $x = 1, 2$  and  $3$  and Ln = Gd, Eu, Lu) (**67–69**) changed the conformation by interconversion of the I-shape and V-shape arrangements. The large  $\text{Ln}(\text{NO}_3)_3$  core prevented mesomorphism in the complexes **67–69**. These results demonstrated that mesogenic ligands do not always lead to metallomesogens upon complexation. Complexation of **L2** with Zn(II) produced five coordinated  $[\text{Zn}(\text{L2})(\text{NO}_3)_2]$  (**70**) and exhibited a monotropic birefringent mesophase. No mesomorphism was exhibited by  $[\text{Zn}(\text{L3})(\text{NO}_3)_2]$  (**71**). In this continuation, a mesomorphic non-planar hexacatenar ligand **L5** was designed by increasing the volume fraction of alkyl chain to study the effect of its increased curvature on the mesomorphism of complexes. Complexation of **L5** with Zn(II) gave a five coordinated complex  $[\text{Zn}(\text{L5})(\text{NO}_3)_2]$  (**72**), which displayed highly viscous bicontinuous cubic mesophase with isotropic texture. When compared to **70** stability of the mesophase in **72** was attributed to the increased curvature of the inter-phase contributed by **L5**. The same effect has also favored the formation of mesogenic nine coordinated complexes  $[\text{Ln}^{\text{III}}(\text{L5})(\text{NO}_3)_3]$  **73a–c** (Ln = Eu, **73a**; Dy, **73b**, Lu, **73c**) complexes. The Eu(III)–**L5** complex **73a** and the Dy(III)–**L5** complex **73b** exhibited bicontinuous cubic mesophase. But, the Lu(III)–**L5** complex **73c** exhibited a hexagonal columnar mesophase. The minor contraction in the lanthanide size from Dy(III) to Lu(III) was proposed to induce a transition from a cubic to a columnar mesophase. These compounds usually have m.p.s higher than  $100^\circ\text{C}$ , and can be considered as high temperature ILs.



M = Ln(III), Zn(II)

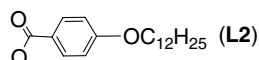
n = 3, Ln(III); 2, Zn(II)

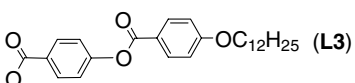
Ln = Eu(III), Dy(III), Lu(III)

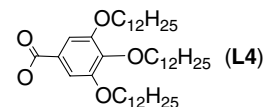
[Ln(Lx)(NO<sub>3</sub>)<sub>3</sub>]: **67** L = 1  
**68** L = 2  
**69** L = 3  
**73** L = 4 [73a, Eu(III); 73b, Dy(III); 73c, Lu(III)]

[Zn(Lx)(NO<sub>3</sub>)<sub>2</sub>]: **70** L = 2  
**71** L = 3  
**72** L = 4

R = Me, X = H: (**L1**)

R = C<sub>2</sub>H<sub>5</sub>, X =  (**L2**)

R = C<sub>2</sub>H<sub>5</sub>, X =  (**L3**)

R = C<sub>2</sub>H<sub>5</sub>, X =  (**L4**)

Scheme 2. Formation of mesogenic Ln(III) and Zn(II) complexes based on benzimidazole.

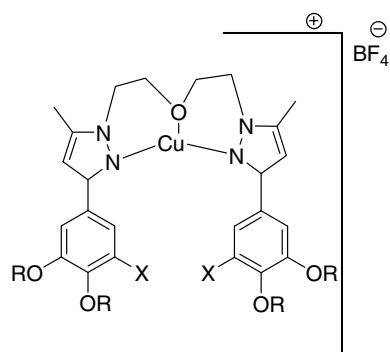
Lin and Lai [67] reported the first time the mesomorphic tricoordinate Cu(I) complexes (**74**) with –N, –O donor of ethoxy bridged pyrazole moieties (Chart 13). Results from DSC, POM and XRD studies indicated the existence of hexagonal columnar phases in these complexes. The relatively low clearing points (94–112 °C) were attributed to the smaller core size.

### 2.2.3. MILCs based on carbene

The Au(I) containing metallomesogens have attracted interests to elucidate the best structure–

mesogenic behavior relationship [68]. In view of the strong sigma coordination properties of NHCs and high thermal stability of their metal complexes, Lin and co-workers [14b] designed the first liquid crystalline compounds of Au(I)–NHCs (**75**) (Chart 14).

In order to avoid the tedious precautions from the usage of strong bases, and to increase the product yields, the PTC technique was used in the reaction of benzimidazolium bromide and Au(SMe<sub>2</sub>)Cl to obtain these Au(I)–NHCs. For the compound with n = 16, the crystal structure revealed a head-to-tail packing with

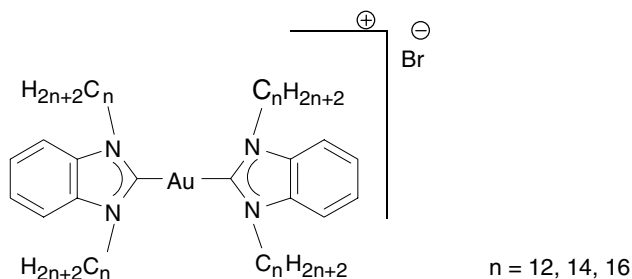


R = (CH<sub>2</sub>)<sub>n</sub>H

**74a**) X = OR

**74b**) X = H

Chart 13.



**75**

Chart 14.

n = 12, 14, 16

interpenetrating long alkyl chains to give a bilayer lamellar structure with Au...Au distances of  $\sim 3.6$  Å. In contrast to the other Au(I) MLCs, these Au(I)–NHCs exhibited relatively low transition temperature, broad mesophase temperature range and higher thermal stability. Based on XRD and POM studies a layered mesophase structure of lamellar  $\beta$  was proposed.

It is noticeable that the interaction of the long alkyl chain imidazolium salts with Ag<sub>2</sub>O followed by

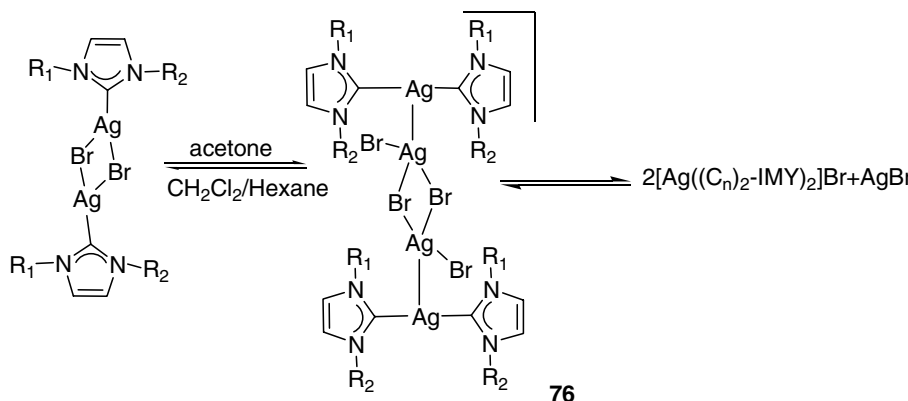
Pd(NCMe)<sub>2</sub>Cl<sub>2</sub> produced the liquid crystalline Pd(II)–NHCs via the in situ generated Ag(I)–NHCs [17a]. On the contrary, the Ag(I)–NHCs isolated from this reaction were non-mesomorphic (Scheme 3). But, the tetranuclear Ag(I)–NHC **76** [17f] isolated has shown liquid crystal properties when (i) mixed with the corresponding imidazolium salts or (ii) partial decomposition occurred to form mixed Br<sup>−</sup>/AgBr<sub>2</sub><sup>−</sup> anions.

### 2.3. IL supported metal catalysts

Although ILs provides high reaction rates and specific selectivities in many catalytic transformations, in certain instances, however, some catalyst has also been extracted from the IL. Hence, it became necessary to modify the metal-complex catalyst to make it more alike to IL solvent medium to avoid the leaching. In this regard, tagging of the IL-functionality (imidazolium cation) to the ligand of metal complex catalysts has been recognized as a useful technique to prevent such catalyst leaching due to the increased ionophilicity towards IL; this approach can improve the catalyst efficiency. Examples of some metal complex catalysts (**77–81**) with imidazolium tags also termed as IL supported catalysts or IL-catalysts were shown in Chart 15 [13g,69]. These catalysts have been reused for several times without the loss of activity in the chemical transformations such as hydrogenation, ring-closing olefin metathesis, Heck and Suzuki cross-coupling reactions.

### 2.4. IL supported nanoparticles

In recent years, as a consequence of the nanotechnology boom, the research work in the area of metal nanoparticles synthesis and their application is of significant importance in the scientific world. It is worth noting that imidazolium-based ILs have been shown tremendous promise in the field of nanoscience and technology. They can stabilize and facilitate the formation of several precious metal-nanoparticles like Au, Pt, Pd, Rh, Ir, etc.



Scheme 3. Tetranuclear Ag(I)–NHC complex and the equilibrium.

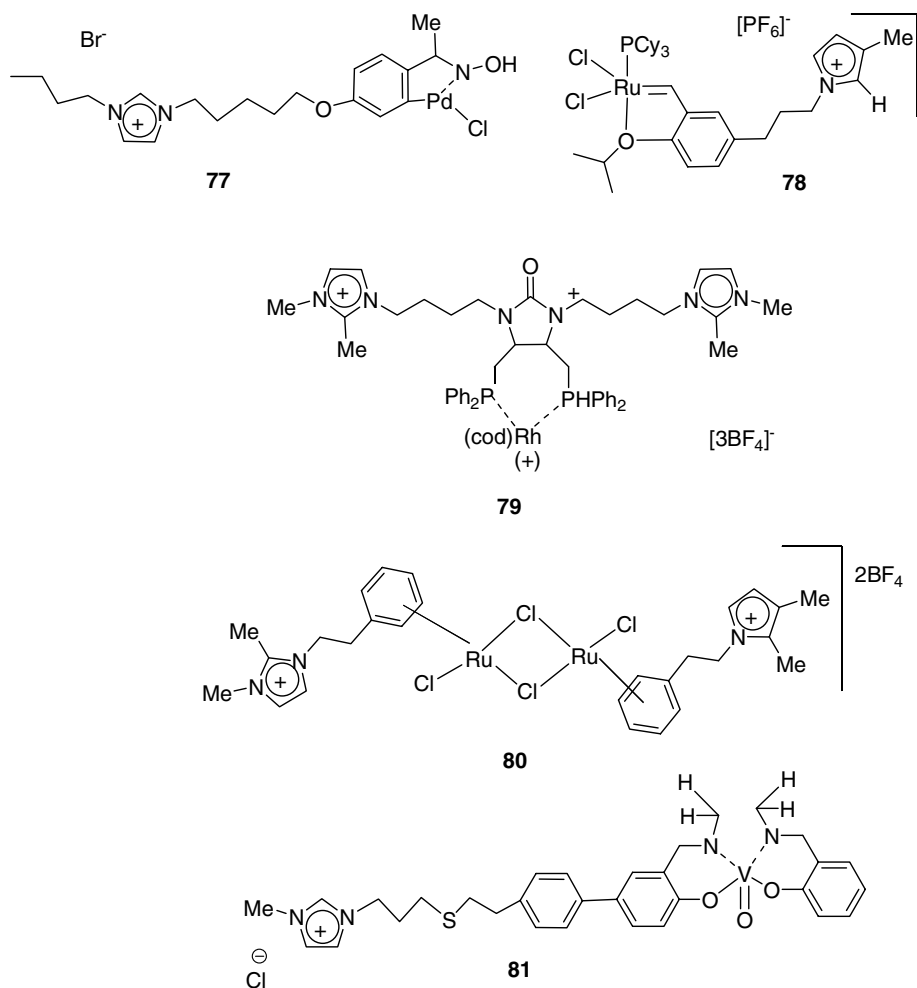


Chart 15.

[70] with narrow size distributions from their organometallic or simple metal salt precursors via decomposition or reduction. The formation of nanoparticles has been attributed to the ability of ILs to form extended hydrogen bonding interaction of self-structured species in the solid and liquid states. The electronic and steric effects provided by these ILs during the stabilization of the nanoparticles were proposed to be similar to the model for the stabilization of nanoclusters by polyoxo-anions or by tetralkylammonium salts. When the metal-nanoparticles have been stabilized and capped by IL, it is quite meaningful to define them as metal-doped or metal-containing ILs. Since the vapor pressure of the ILs was expressed to be zero, Dupont's group monitored the TEM experiments and gave evidence for the interaction between the nanoparticles and IL [70b]. Itoh et al. [70c] showed when the surface of the gold nanoparticle was bound to IL, the hydrophobic and hydrophilic properties of gold nanoparticles can be tuned by exchanging the anions of the IL moiety. Imidazolium-based zwitterionic liquid functionalized (zwitter-Au) Gold nanoparticle stable in both organic and inorganic

electrolytes have also been appeared recently [70h]. These nanoparticles stabilized in ILs are efficient catalysts for many chemical reactions such as hydrogenation, C–C bond formation and Heck reaction, etc. [70].

### 3. Summary and conclusion

ILs of imidazolium salts composed of various transition metal components have been reviewed; notable examples include halides of V, Fe, Co, Ni, Cu, Zn, Sn, In, Pt, Pd and Au and carbonyls of Co and Rh. Many of these metal-containing ILs are air and moisture stable and have tunable Lewis acidity. These systems are capable to mediate wide variety of synthetic reactions and exhibit great potential in organometallic chemistry and catalysis. The success of chlorozincate systems applied in the Diels–Alder and hydrogenation reactions and chloroindate-based systems applied in the Friedel–Crafts acylation, reveals the bright scope of many of these systems as alternatives for chloroaluminates in several other transformations in the coming years. In

addition, ILs of metal–NHCs with their recent advances in catalytic reactions will certainly enrich their potential applications. When a metal-containing IL serves as both a solvent and a catalyst, the problem of catalyst leaching is negligible and therefore a very neat way of conducting the reactions can be achieved. Tagging of IL-functionality (imidazolium cation) to the ligand of metal complex catalyst has also been suggested as an effective technique to minimize the catalyst leaching problem.

Imidazolium salts with long alkyl chains formed thermotropic ILCs. Introduction of metal ions to these systems provides additional properties like color, geometry and magnetism, etc., which can not be obtained from ordinary ILCs. Metal-containing ILCs based on 1,3-dialkyl-imidazolium, 1-alkylimidazole and NHCs, designed with metal ions such as Co, Ni, Cu, Zn, Pd, Ag and Au, have exhibited interesting and some what unusual structural motifs. Due to the ordered structures and wide mesophase range, these metal-containing ILCs can be used as catalysts and also as ordered media for chemical transformations. It is especially interesting to note that certain metal–carbenes can be formed readily in the metal-containing imidazolium ILCs. The luminescence properties of Eu(III) doped ILC suggests that lanthanide containing ILCs are good candidates for the development of liquid crystal displays.

The preparation and stabilization of IL protected metal nanoparticulates (Au, Pt, Pd, Rh, Ir, Cu, etc.), have a profound impact on the nanoscience and organometallic chemistry. Decomposition of metal complexes in ILs generates stable metal nanoparticles with narrow size distributions. These IL protected nanoparticles were realized as efficient catalysts for many chemical reactions and also provide recyclable nanoparticle catalytic systems. It is interesting to note that Pd-nanoparticles have been observed during the Pd(II)–carbene catalyzed Heck reaction in IL medium [71]. Nanoporous materials with high surface area can also be obtained from the IL mediated electrochemical reactions.

Although the use of metal-containing ILCs to prepare nanomaterials has less been studied, the use of copper-containing pyridinium ILC to synthesize CuCl nanoplatelets as desulfurization and denitration catalyst has appeared [72]. The ordered environment and the unique structure properties possessed by metal-containing ILCs of imidazole, imidazolium, and NHC moieties can benefit the formation of nanomaterials with specific structure. The metal nanoparticles stabilized in ILCs can also serve as catalytic systems with partially ordered reaction environment. Metal-containing ILCs will certainly become an important emerging field in the nanotechnology.

Finally, we comment that metal-containing ILs and ILCs based on imidazolium moiety can interlink all branches of chemistry and make them more prosperous due to their multifunctional applications via ‘green chemistry’ protocols.

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