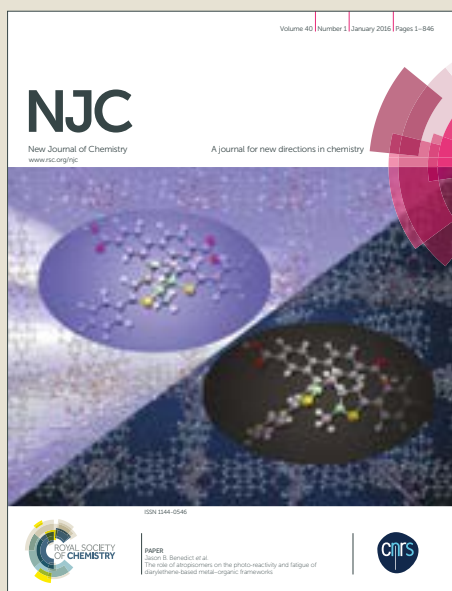


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COMMUNICATION

First direct evidence of N-heterocyclic carbene in BMIm acetate ionic liquid. An electrochemical and chemical study on the role of temperature

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Cyclic voltammetry provides the first direct evidence of N-heterocyclic carbene (NHC) presence in neat 1-butyl-3-methylimidazolium acetate ionic liquid (BMImAcO) at 120°C. The NHC existence, proved by its oxidation current in cyclic voltammetry, was confirmed by the formation of a PhCHO-NHC adduct in pure ionic liquid. The role of the temperature was considered.

In the past few decades, N-heterocyclic carbenes (NHCs) have emerged not only as powerful ligands for transition metals¹ but also as organocatalysts² for various molecular reactions and as catalysts in metal-free polymer synthesis.³ The ability of NHCs to induce the inversion of the polarity (umpolung) of a specific group plays a considerable role in modern organic synthesis.² Owing to the acidity of the C2-H group of imidazolium salts, NHCs could be prepared by deprotonation of these structures with suitable bases. Also the electrochemical methodology allows obtaining NHCs by cathodic reduction of azolium salts, thus avoiding the utilization of bases.⁴

Nevertheless, some NHC-catalysed reactions, or anyhow requiring the presence of NHC, were carried out using imidazolium based acetate or chloride (BMImX; X: AcO, Cl) in the absence of any base or reducing agent purposely added to the reaction mixture. As regards this question, some results related to the Claisen rearrangement,⁵ the benzoin condensation⁶ and the synthesis of 1-ethyl-3-methylimidazole-2-thione⁷ are significant and suggest that the formation of NHC could be due to the counter ion acetate or chloride (thus basic enough). This question spurred some authors to search for the presence of NHC in neat BMImX salts via different experimental procedures (spectroscopic analyses: photoelectron spectroscopy, mass spectra etc.).⁸ In recent

studies, quantum chemical calculations ruled out the presence of NHC in BMImAcO and suggested a concerted mechanism that, by-passing the carbene formation, provides an alternative explanation for its reactivity.⁹

However, despite the direct observation of NHC in this ionic liquid is still not obtained, some reactions (benzoin condensation, Claisen rearrangement, etc.) can be activated by the presence of BMImAcO or BMImCl. The electrochemical methodology can give a decisive contribution on this issue. In fact, the actual presence of NHC in neat BMImX can be ascertained by a simple voltammetric analysis because NHC is an electro-active species and it is oxidable via a one-electron exchange with the anodic surface.¹⁰⁻¹⁶

As the literature reports the possible presence of NHC in BMImCl **1** and BMImAcO **2** (Figure 1), we studied these two ionic liquids by cyclic voltammetry, in order to verify the actual NHC presence in these pure salts. Moreover, the effect of temperature on NHC concentration was considered.

Evidence of endogenous NHC presence in neat ionic liquid by cyclic voltammetry and chemical reactivity.

Cyclic voltammetry experiments. In the voltammetric curves of **1** and **2**, recorded at different temperatures, on vitreous carbon electrode, the cathodic limit is determined by the reduction of the imidazolium cation to yield the corresponding NHC (and molecular hydrogen), as attested by the increase of the voltammetric current (Figure 2, blue curves). In this way NHC is electrogenerated during the negative scan and, being electro-active, it is oxidised when the potential reaches enough positive values.

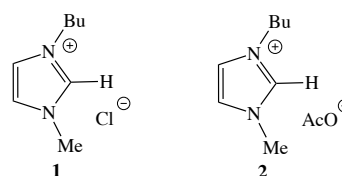


Fig.1 Ionic liquids used in this paper

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NHC Oxidation is attested by the positive current at a potential between 0.3 and +1.0 V. The more negative is the potential reached in the cathodic scan of the cyclic voltammetry, the larger the amount of NHC electrogenerated, the higher the positive peak current in the anodic scan (see Figures S1 and S2 in Supplementary Information). Therefore, the presence of NHC (endogenous or cathodically generated) can be verified by the presence of the oxidation peak in the cyclic voltammograms.

In order to verify the presence of endogenous NHC in the two ionic liquids, it is thus necessary to avoid the cathodic reduction of the imidazolium cation, reverting the potential scan before it happens (at a less negative potential than the one for NHC electrogeneration). In Figure 2, red lines, the cyclic voltammograms of BMImCl and BMImAcO are recorded at two different temperatures, according to a reversed potential higher than -1.0 V, thus avoiding NHC electroreduction. The voltammetric analysis of ionic liquid **1** rules out the presence of NHC (at a concentration detectable by this methodology) for both values of temperature studied. In fact, the NHC anodic peak is absent (Figure 2, top, red lines). Contrary, the voltammetric behaviour of **2** is affected by the temperature. Up to 100°C the voltammetric curves of **2** do not show the oxidation peak (Figure 2, red line). However, if the temperature is higher than 100°C (120-150°C) the cyclic voltammetry shows the presence of an oxidation peak at a potential corresponding to the NHC oxidation. This result points out the presence of endogenous NHC in the ionic liquid **2** at 120°C and higher (Figure 2, bottom, right, red line).

The different behaviour of BMImCl and BMImAcO is highlighted also in Figure 3, where cyclic voltammograms of these two salts at 100, 120 and 150°C are reported, with a potential scan range which excludes the electrogeneration of NHC (-0.7 to +1.0 V).

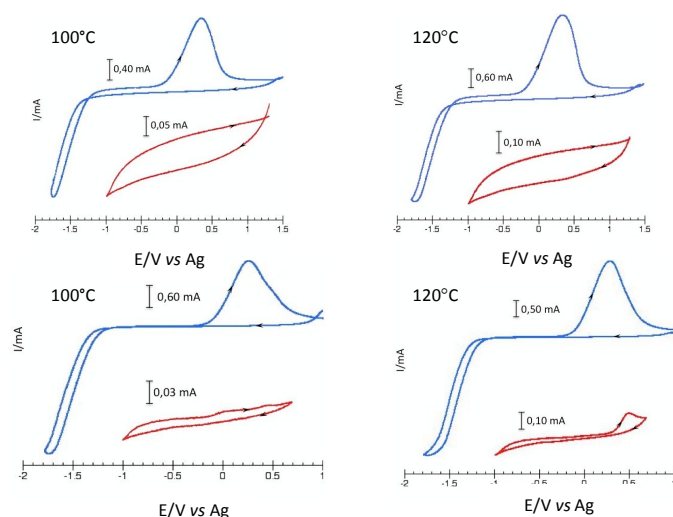


Fig. 2 Voltammetric analysis of, top: ionic liquid BMImCl at 100°C (left) and 120°C (right); bottom: ionic liquid BMImAcO at 100°C (left) and 120°C (right). A492/GC/3 Amel microelectrode was employed, using a Pt wire counter electrode and an Ag wire pseudoreference electrode. The scanning rate was $\nu = 0.2 \text{ V s}^{-1}$.

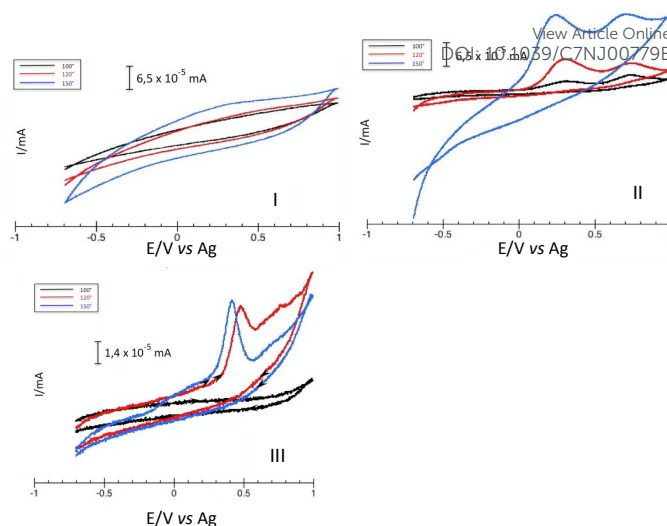


Fig. 3 Cyclic voltammograms performed on ionic liquid at the scan rate of 0.2 V s^{-1} and at different temperatures (100, 120, 150 °C). A492/GC/3 Amel microelectrode ($d = 3 \text{ mm}$) was employed, using a Pt wire counter electrode and an Ag wire pseudoreference electrode. (I) Anodic scan on neat ionic liquids BMImCl (II) BMImCl (2.5 mL) after electrolyses under galvanostatic control and the consumption of 10 Coulombs in a divided cell (Pt catode and anode, $J = 15 \text{ mA cm}^{-2}$). (III) Anodic scan on neat ionic liquids BMImAcO

The anodic scan on neat ionic liquid **1** recorded at 100, 120 and 150°C does not show any oxidation peak, according to the absence of endogenous NHC in this ionic liquid (Figure 3-I). Whereas, the voltammetric curves of ionic liquid **1** after electrolysis, show the anodic peak, according to the presence of electrogenerated NHC in the electrolyzed ionic liquids (Fig. 3-II). On the contrary, the voltammograms of BMImAcO show the anodic peak, according to the presence of endogenous NHC at 120 and 150°C, (Figure 3-III, red and blue lines), but not at $T = 100^\circ\text{C}$ (black line).

The overall voltammetric investigation suggests that the presence of endogenous NHC in ionic liquids BMImX is affected by the nature of X as well as by the temperature and that an equilibrium reaction, involving NHC and AcO^- , is operative in ionic liquid **2** at 120°C or higher:



This equilibrium is able to regenerate NHC removed by the oxidation process at the electrode surface. The values of oxidation peak current are affected by the equilibrium constant as well as by the kinetics of the related processes. According, the ionic liquid **2** could be regarded as a reservoir for NHC oxidized at the vitreous carbon surface (vide infra). **Chemical reactivity.** Spurred by the results of the voltammetric analysis, we investigated the ability of ionic liquids **1** and **2** to promote the reaction of NHC with benzaldehyde.

The aim was to confirm the results obtained by voltammetric analysis, *i.e.* that endogenous NHC is present in the BMImAcO, but not in the BMImCl (in appreciable amount). The reaction was carried out mixing 0.5 mmol of ionic liquid and 3.0 mmol of benzaldehyde (freshly distilled) at 60°C for 1 hour.

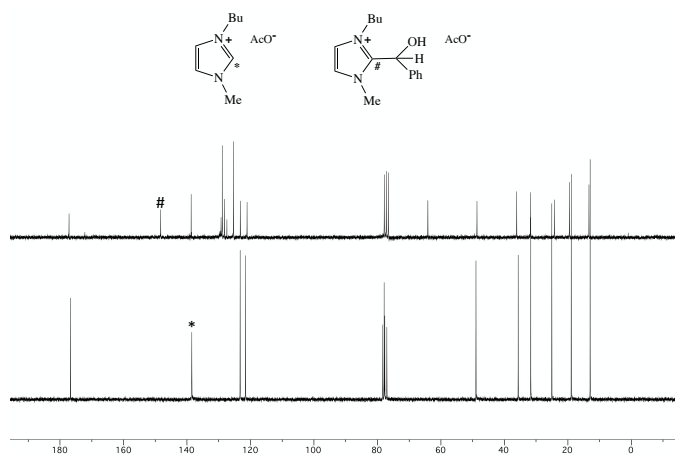
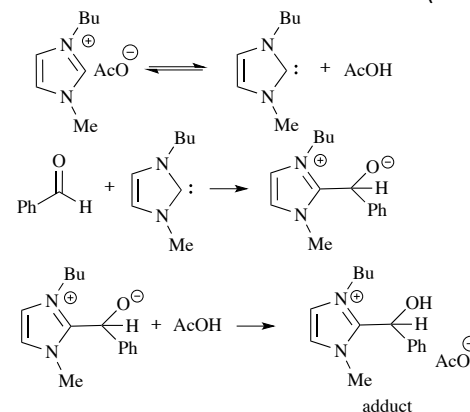


Fig. 4. Top: ^{13}C NMR spectrum of reaction mixture; bottom: ^{13}C NMR spectrum of **2**

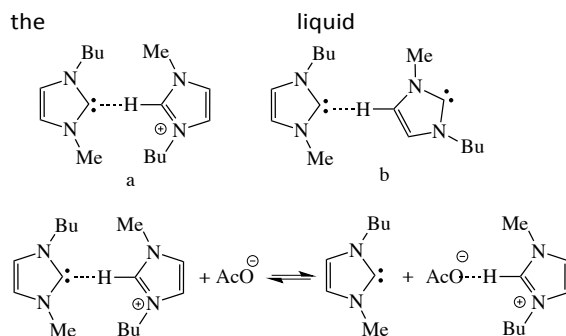
In the case of BMImAcO, we ascertained in the final mixture the presence of the NHC-PhCHO adduct in >90 % yield (Figure 4). The absence of the electrode during this reaction rules out any chemical role of the electrode material on NHC formation. As previously stated, the equilibrium between BMIm⁺ and AcO⁻ can act as a NHC reservoir, shifting toward right as NHC is subtracted and transformed into adduct (Scheme 1). Contrary, in the case of BMImCl, no NHC-PhCHO adduct was evidenced by NMR analysis and unchanged ionic liquid and benzaldehyde were the only products present in the reaction mixture. A question arises about the temperature of the chemical reaction to yield adduct. The voltammetric analysis of BMImAcO at 60°C does not show the presence of NHC, present only at 120°C or higher. On the other hand the chemical synthesis of NHC-PhCHO adduct is carried out at 60°C. Keeping in mind the fast voltammetric times, the equilibrium system is unable, in our opinion, to supply, at the interface electrode/ionic liquid, the NHC previously oxidized. The appearance of the oxidation peak only above 120 °C is related to a significant effect of temperature on the thermodynamic and kinetic of the equilibrium involving NHC and AcO⁻. Contrary, during the longer reaction time (1h at 60°C) the equilibrium is able to supply NHC in the bulk of the mixture, allowing a quantitative yield of the adduct product. Kim and co-workers recently reported that ab initio calculations and molecular dynamics simulations predict that "N-heterocyclic carbene formation from an EMImAcO ion pair is strongly suppressed in polar environments" (i.e., in ionic liquid) and that NHC reaction with carbon dioxide to yield the adduct is concerted (deprotonation and nucleophilic attack).⁹ Therefore we cannot exclude that at temperatures below 120°C the NHC-PhCHO adduct from BMImAcO is formed in a concerted way, while at 120°C or higher in a stepwise manner. In the case of BMImCl, no adduct is formed at 60°C and no carbene is present in the cyclic voltammetry at 120°C or higher. We can thus conclude that chloride ion is not basic enough to generate the corresponding carbene, nor to induce a concerted formation of NHC-PhCHO adduct.¹⁸ Therefore, the ionic liquid **2** behaves as an efficient source of free NHC in the total absence of any exogenous base purposely added to the

reaction mixture giving adduct in >90% yield. The reactivity of NHC could be strongly reduced by the presence of dimeric structures due to hydrogen bond between NHC and the parent BMIm⁺ or between two NHC molecules (Scheme 2; a, b).¹⁷



Scheme 1. Synthesis of adduct

The AcO⁻ anion (for its high ability to establish hydrogen bond) can bind the H-donors and release NHC from the NHC-BMIm⁺ or/and NHC-NHC dimers, increasing its reactivity. The increase of NHC reactivity can be due to an AcO⁻ double role: as a base, with continuous generation of consumed NHC by BMIm⁺ deprotonation (equilibrium reaction in Scheme 2) and as an H bond acceptor, freeing NHC from H-bond.¹⁹ In conclusion, a simple voltammetric analysis of BMImAcO allows detecting the presence of endogenous NHC. The electrochemical investigation of imidazolium based ionic liquid BMImX carried out at different values of temperature (T = 60-150°C) allows to differentiate the chemistry of BMImCl and of BMImAcO as regards the presence of the endogenous free NHC. The presence of the endogenous free NHC in BMImX is strongly affected by the basicity of the anion (AcO⁻ or Cl⁻) as well as by the temperature. Owing to the presence an acid-base equilibrium able to regenerate NHC, ionic liquid **2** (but not **1**) can give stoichiometric NHC reactions as demonstrated by the formation of the adduct with benzaldehyde. The significant reactivity of NHC in BMImAcO is also consistent with the singular ability of the AcO⁻ anion to establish hydrogen bond with BMIm⁺, thus releasing NHC from the NHC-BMIm⁺ H-bonded dimer. To the best of our knowledge, this is the first direct evidence of NHC presence in BMImAcO in the



Scheme 2. Dimeric structures due to hydrogen bond between NHC and the parent BMIm⁺ (a) or between two NHC molecules (b). The equilibrium reaction between dimeric structure (a) and AcO⁻ anion

Experimental

All the ionic liquids were purchased from Iolitec and used after being kept at reduced pressure at room temperature for 24 h. Electrolyses under galvanostatic control were carried out at 80 °C (using an Amel 552 potentiostat equipped with an Amel 771 integrator) in a two compartment home made glass cell. The electrode surface area (flat Pt spirals, 99.9%) was ca. 1.0 cm² for the cathode and 0.8 cm² for the anode. ¹H-NMR and ¹³C-NMR spectra were acquired at room temperature on a Bruker AC 200 using CDCl₃ as internal standard.

Cyclic voltammetries and electrochemical procedure

Cyclic voltammetries were performed on ionic liquids kept at controlled temperature under nitrogen atmosphere, after a few minutes of vigorous stirring. A 492/GC/3 Amel microelectrode was employed, using a Pt wire counter electrode and an Ag pseudo-reference electrode. The scanning rate was $n = 0.2 \text{ V s}^{-1}$.

Catholyte (2.5 mL of ionic liquid) and anolyte (1.0 mL of same ionic liquid) were separated through a porous glass frit (porosity 3). The electrolysis was carried out, under N₂ atmosphere, at controlled temperature and constant current ($J = 15 \text{ mA cm}^{-2}$). After the consumption of 10 C, the current was switched off, the anodic compartment removed and the catholyte analyzed by cyclic voltammetry at different temperatures.

Addition of NHC to benzaldehyde

Benzaldehyde (3.0 mmol), freshly distilled, was added to BMImAcO (0.5 mmol) or BMImCl (0.5 mmol), and the mixture stirred in an open vessel at 60 °C for 1.0 h. The reaction mixture was washed with ethyl ether to remove excess of aldehyde and the residue was analysed by ¹H-NMR ¹³C-NMR. Only 1-butyl-3-methylimidazol-3-ium-2-yl)-phenylmethanol acetate adduct was obtained.

¹H NMR (CDCl₃, 200 MHz), δ : 10.1 (br s, 1H), 7.14-7.34 (m, 8H), 6.68 (s, 1H), 4.03-4.24 (m, 2H), 3.83 (s, 3H), 1.89 (s, 1H), 1.58-1.34 (m, 2H), 1.15 (q, , 2H, J = 7.3 Hz), 0.73 (t, 3H, J = 7.3 Hz). ¹³C NMR (CDCl₃, 50.3 MHz), δ : 177.1, 172.2, 148.3, 138.7, 129.1, 128.9, 128.2, 127.4, 125.3, 121.0, 64.1, 48.6, 36.1, 31.7, 19.5, 13.3. ESI-MS m/z : Calcd for C₁₅H₂₁N₂O⁺ [M+H]⁺: 245.2; Found 245.1.

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Graphical abstract

View Article Online
DOI: 10.1039/C7NJ00779E**First direct evidence of N-heterocyclic carbene in BMIm acetate ionic liquid. An electrochemical and chemical study on the role of temperature**I. Chiarotto,^{*a} M. Feroci,^a A. Inesi^b^a Dept. Scienze di Base e Applicate per l'Ingegneria Sapienza Università di Roma via Castro Laurenziano,7 - 00161 Roma Italy ^b via Antelao, 9 - 00141 Roma, Italy

Cyclic voltammetry measurements provide the first direct evidence of N-heterocyclic carbene in neat 1-butyl-3-methylimidazolium acetate ionic liquid at temperature over 120°C.

