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Electrochemical reduction of an imidazolium cation: a convenient preparation of imidazol-2-ylidenes and their observation in an ionic liquid

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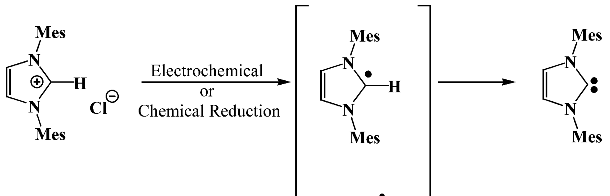
1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride is reduced electrochemically and chemically to produce a nucleophilic carbene, namely 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene. The carbene was also shown to be compatible with and persistent in the ionic liquid tetradecyl(trihexyl)phosphonium chloride.

Ionic liquids have come to the forefront as important components of "Green Chemistry"[1] and they appear ready to replace classical volatile organic solvents in many industrial applications, a move that could have a significant environmental impact. Due to their high thermal stability, low volatility, and variation in co-solvent miscibility,[1] ionic liquids have found applications in organic syntheses[1,2] and recently in bulk chemical syntheses.[3]

The most extensively studied class of ionic liquids is based on imidazolium cations. Perhaps often overlooked is the relationship between an imidazol-2-ylidene (*aka* a nucleophilic carbene), a base, and an imidazolium ion, its conjugate acid.[4] Although several authors have suggested a link (see below), clear evidence for the facile chemical conversion of an imidazolium ion to a nucleophilic carbene through a redox process supported by electrochemical analysis has not been reported. Yet, under certain conditions, this reactivity may dominate the chemistry observed within an ionic liquid. As a part of our ongoing research in the reactivity of imidazol-2-ylidenes, we have recently reported the electrochemical behaviour of imidazol-2-ylidene, the carbene partner of an imidazolium ion.[5] In this communication, we describe how the electrochemical reduction of the 1,3-bis(2,4,6-trimethylphenyl)-imidazolium ion **[1H]** generates its carbene partner[6] and how we took advantage of this observation to develop a large-scale, efficient and economical method to prepare this important carbene (Equation 1). We also show that nucleophilic carbenes are persistent in phosphonium based ionic liquid solutions.



(1)

[1H][Cl] **[1H]•** **1**

The cyclic voltammogram (CV) of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **[1H][Cl]** is illustrated in Fig. 1.† The CV shows that the ion is irreversibly reduced at −2.28 V *versus* a standard calomel electrode (SCE) at 300 mV s^{-1}. Coulometric analysis using ferrocene as an internal standard reveals that the reduction corresponds to a single electron event implying that the species initially produced from the electrochemical reaction is the radical **[1H]**$^\cdot$. Although this radical was not spectroscopically characterised in this study, we recently fully described it using muonium chemistry, a hydrogen atom surrogate.[7]

The CV also shows the presence of a significant peak on the return scan at −0.20 V corresponding to the oxidation of a new chemical species that is generated from the one-electron reduction of **[1H][Cl]**. This peak lies at the same potential as the one we recently measured for the *oxidation* of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **1**[5] (inset in Fig. 1) suggesting that reduction of the imidazolium chloride produces the carbene.

These observations prompted us to test whether the reduction of **[1H][Cl]** can be accomplished on a preparative scale using potassium as a strong reducing agent. We have chosen to use 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **1** to test the method, owing to its stature as arguably the most versatile and extensively used nucleophilic carbene. The optimised procedure uses potassium metal as the reductant and is best carried out as follows.‡ A THF suspension of **[1H][Cl]** is treated with a lump of potassium metal and heated to reflux under a dry nitrogen atmosphere. This results in the production of a pale brown precipitate which separates from a red solution. The filtrate is evaporated and the solid residue is washed with cold hexane. The 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **1** can be isolated as a white solid in 89% yield.[8] When the product of this straightforward procedure is analysed by melting point and ^{1}H and ^{13}C NMR spectroscopy, the data are consistent with those already reported for carbene **1**.[9] Potassium reduction of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, **[2-H][Cl]** was also performed to give the corresponding carbene **2**[10] in 85% yield. This method was also used to prepare ^{13}C labelled carbene **1** in high yield. Note that carbenes are traditionally generated *via* deprotonation of the imidazolium chloride using strong bases, but the reaction involves several purification steps and sometimes produces sticky materials that are often not useful for further reactions. The appeal of our new procedure rests in the fact that it provides a fast, one-step, aprotic method to prepare large quantities of carbenes **1** and **2** without resorting to the use of, for example, liquid ammonia. By

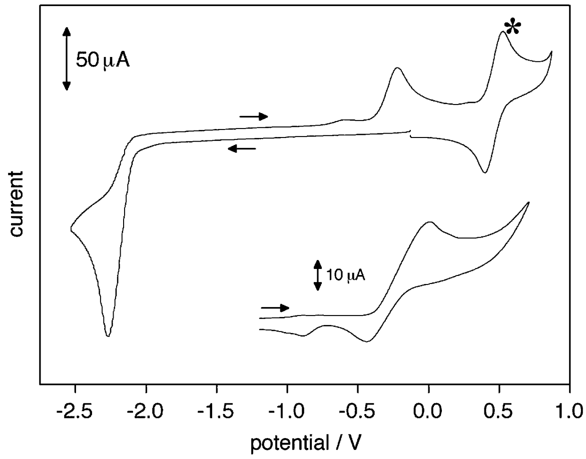


Fig. 1 Cyclic voltammogram of a DMF solution (2 × 10^{-3} M) of **[1H][Cl]** containing tetrabutylammonium hexafluorophosphate (0.1 M) at 300 mV s^{-1} in the presence of ferrocene (1.5 mM). The inset shows the cyclic voltammogram of a THF solution of carbene **1** (4 × 10^{-2} M) at 300 mV s^{-1} containing 0.1 M tetrabutylammonium hexafluorophosphate.[5] Both voltammograms were referenced to SCE using ferrocene (0.475 V *versus* SCE) which is labelled with an asterisk.

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accepting the rational assumption that the electrochemical and chemical reduction generate the same radical intermediate, we can conclude that the oxidation peak at −0.20 V in the CV does correspond to the oxidation of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene in this ECE process.

The fact that carbene **1** can be so conveniently prepared by reducing **[1H][Cl]** is consistent with thermodynamic arguments. As already mentioned we have spectroscopically characterised the radical **[1H]**$^{\cdot}$ after it was *formed* in the exothermic reaction of a hydrogen atom with an imidazol-2-ylidene. It is important to also point out that the *decomposition* of this radical to produce the hydrogen molecule (H_2) and carbene **1** is likewise exothermic, based simply on bond energy considerations alone. Dimerisation of **[1H]**$^{\cdot}$ by forming a C–C bond is an alternative fate of the radical; however, we argue that this reaction is highly unlikely given that the H–H bond (436 kJ mol^{-1}) is much stronger than the C–C bond (348 kJ mol^{-1}) and dimerisation of the **[1H]**$^{\cdot}$ radical is also entropically disfavoured.

We have also confirmed the compatibility of imidazol-2-ylidenes with ionic liquids. Solid **1** is sparingly soluble in tetradecyl(trihexyl)phosphonium chloride (CYPHOS ®IL 101). To increase the solubility for spectroscopic studies, THF-d_8 was added to the suspension until dissolution was complete and the final solution concentration was 0.33 M in 30% CYPHOS ®IL 101/THF solution. ^{1}H and ^{13}C NMR studies on this solution exhibit peaks both for the ionic liquid and **1**. Clearly present in the ^{13}C NMR spectrum is a peak at 216 ppm that we assign to the carbeneic carbon of carbene **1**. This result is exciting since now extremely strong bases, such as **1**, are clearly compatible with ionic liquids, thus opening up chemistry that was perhaps considered not feasible. For example, preliminary NMR studies on solutions of CYPHOS ®IL 101 containing a catalytic amount of **1** show they are capable of performing the benzoin condensation reaction.

The chemistry we describe in this communication has implications for the behaviour of ionic liquids. First, the imidazolium ion is the conjugate acid of a 1,3-bis(alkyl)imidazol-2-ylidene, one of the strongest neutral bases (pK_a = 22–24 in DMSO).[11,12] In the presence of non-spectator anions, such as $[AlCl_4]^-$, generation of an imidazol-2-ylidene through chemical or electrochemical reduction may lead to the formation of *either* free carbenes or acid/base complexes of the carbene, including metal complexes that have clearly shown catalytic activity for many important reactions, amongst which is C–C-bond formation.[13] For example, the electrochemical observations are in accord with studies that show formal oxidative addition of imidazolium ions to low valent metal complexes, for example, those containing Pd^0 or Ni^0.[14,15] Also, recently we observed that chemical reduction of **[1H][Cl]** with $NaBH_4$ produces $\mathbf{1{\cdot}BH_3}$.[16] Secondly, with more innocent anions such as chlorides, phosphonates and triflates, treatment of an ionic liquid with reducing agents should likewise produce *free* imidazol-2-ylidenes, affording highly basic solutions containing imidazol-2-ylidenes. These molecules are active catalysts for reactions requiring a catalytic amount of base, such as the benzoin condensation reaction. Our current work supports the involvement of *free* uncomplexed nucleophilic carbenes in ionic liquids.

In summary, we have shown that imidazol-2-ylidene **1** can be produced electrochemically by reduction of the imidazolium ion. Chemical reduction of imidazolium ions using potassium produces carbenes in a simple one-pot procedure. Free carbenes are persistent in ionic liquids such as CYPHOS ®IL 101.

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Notes and references

† All cyclic voltammetry experiments were performed using a Pine AFCBP1 bipotentiostat with a three-electrode setup using a glassy carbon disk working electrode (5 mm diameter), a platinum wire counter electrode separated from the bulk solution by a frit and a Ag/AgCl (in a saturated NaCl solution) reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, which was purified by recrystallising it three times from ethanol followed by drying it at 110 °C under vacuum for 3 days. All glassware was flame dried and maintained under a positive pressure of nitrogen throughout the entire experiment. The working electrode was polished, sonicated, rinsed with ethanol and dried prior to each experiment. The DMF was of greater than 99% purity and purchased from Aldrich in "sure-sealed" containers packaged under nitrogen. The solvent was further deoxygenated by bubbling dry nitrogen gas through the assembled system. All potentials were referenced to the ferrocene/ferrocenium redox couple taken to have an $E°$ of 0.475 V *versus* SCE. The ferrocene used as the reference was freshly sublimed. The reduction/oxidation potentials for **[1H][Br]** were also obtained: −2.26 V/−0.198 V, values comparable to those obtained for **[1H][Cl]**.

‡ A solution of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (4.00 g, 11.8 mmol) in THF (100 ml) was treated with excess potassium metal (lump, 0.80 g, 20.0 mmol). The resulting slurry was heated at reflux for three hours under nitrogen to produce a red solution and a brown precipitate. The mixture was filtered through Celite, the solvent was evaporated under vacuum and the solid residue was washed with cold hexane to afford 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **1**[9] (3.18 g, 89%) as a white powder: mp 154–155 °C; ^{1}H NMR (400 MHz, THF-d_8) δ 7.01 (s, 2H, NC*H*), 6.90 (s, 4H, Ar*H*), 2.25 (s, 6H, 4-CH_3), 2.02 (s, 12H, 2,6-CH_3); ^{13}C NMR (100.61 MHz, THF-d_8) δ 219.4 (s, N*C*N), 139.8 (s, Ar *C*-1), 137.7 (s, Ar *C*-4), 135.8 (s, Ar *C*-2,6), 129.3 (s, Ar *C*-3,5), 121.4 (s, N*CC*), 21.1 (s, 4-*C*H_3), 18.1 (s, 2,6-*C*H_3).

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