New hydrogen carbonate precursors for efficient and byproduct-free syntheses of ionic liquids based on 1,2,3-trimethylimidazolium and *N*,*N*-dimethylpyrrolidinium cores†

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Two new hydrogen carbonate IL precursors, 1,2,3-trimethylimidazolium and *N*,*N*-dimethylpyrrolidinium hydrogen carbonate salts, were synthesized and their structures confirmed by NMR and single-crystal X-ray diffraction. These salts were also evaluated for application in the syntheses of ILs by reacting them with a variety of acids and $[NH_4][ClO_4]$, which resulted in the clean and quantitative formation of a family of 1,2,3-trimethylimidazolium- and *N*,*N*-dimethylpyrrolidinium-based salts. Synthetic protocols for the formation of the hydrogen carbonate salts involved simple alkylation reactions of the chosen neutral amines with dimethyl carbonate, and later conversion of the formed methyl carbonate anion-based salts to hydrogen carbonate salts. The reactions proceed in one step at temperatures close to room temperature using only water. The new organic salts with the chosen anions are formed with only gaseous byproducts (CO_2, H_2O, and in the case of $[NH_4][ClO_4]$, NH_3), thus eliminating further purification steps. This generalized synthetic protocol for the formation of hydrogen carbonate IL precursors may be used as a cleaner, contaminant-free (halides and metal ions) route to many classes of ILs.

Introduction

One of the most challenging problems faced by researchers working with ionic liquids (ILs, defined as salts which melt below 100 °C[1]), is difficulty in the reliable and reproducible preparation of pure compounds. Unfortunately, current methods for preparation of various ILs often involve multi-step synthesis, complex purification, and very often result in formation of undesirable and difficult to remove halide- or metal-containing species, including byproducts from metathesis reactions, incomplete ion exchange, or contamination from clean-up columns.[2–5] Thus, improved techniques for IL synthesis and purification would drive the end product cost down and provide higher purity materials and consistency between batches, even between different suppliers.

Limited examples of imidazolium- or other cation-based halide-free synthesis of ILs are present in the literature; the most commonly known are replacements for haloalkyl alkylating agents like dialkyl sulfates[6,7] and dialkyl carbonates.[8] More recently, the use of alkane sulfonates[9] and alcohols in Mitsunobu alkylation reactions[10] for the synthesis of halide-free alkylated IL materials were reported. These salts, though halide-free, were then typically used as precursors for further ion exchange reactions. Ideally, in order to obtain pure IL salts, the synthesis would have to be carried out directly with routes that are byproduct-free or that allow facile removal of byproducts by their evaporation, rather than by extraction.

The preparation of ILs *via* simple methods that result in formation of the desired salts and easily separated byproducts has been investigated for quite some time. Ohno and coworkers[11] have suggested using an ion exchange column in order to prepare hydroxide derivatives of ILs that later could be reacted with acid, forming the desired product with little but H_2O as a byproduct. In our work we have suggested,[12] along with Tommasi and Sorrentino,[13] the use of dialkylimidazolium-2-carboxylates and decarboxylation reactions in the presence of acids as robust IL precursors for the formation of pure, byproduct-free ILs. Utilizing this methodology, our laboratory successfully prepared the first proof of a stable dialkylimidazolium $[HCO_3]^-$ salt that was then shown to easily react with acids.[14] Parallel to this work, recent patent literature has also proposed the usefulness of a $[HCO_3]^-$-based IL for the halide-free synthesis of many ILs through titration with a Brønsted acid,[15] and these salts have also recently appeared in the Sigma-Aldrich catalog.[16] Moreover, Zheng *et al.* report the formation of carbonate-based tetraalkylammonium salts *via* the reaction of ammonium carbonate with two equivalents of dimethyl carbonate, but with greatly depressed yields in the area of 2–45%.[17]

Although the utilization of zwitterionic carboxylate precursors and their use in halide-free synthesis of ILs as presented in our previous report appears attractive,[18] certain drawbacks of the system suggested that further research was needed toward other "green" IL precursors. While working on the imidazolium carboxylate zwitterionic systems, a few limitations

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were recognized, including: (i) the necessity to use heterocyclic cation cores for formation of zwitterionic carboxylates, (ii) synthesis of the zwitterionic imidazolium carbonate precursor is a two-step reaction, where the second step (carboxylation) is rate-limiting, and often low-yielding, (iii) possible formation of regioisomeric products during the zwitterion synthesis having different reactivities in subsequent reactions, and (iv) need for use of low-volatile polar aprotic solvents such as DMSO for decarboxylation, which is very hygroscopic and hard to remove from the reaction mixture.

In our recent publication,[14] we focused on the synthesis of a hydrogen carbonate IL precursor by using the previously described conditions for the decarboxylation of the 1,3-dimethylimidazolium-2-carboxylate ([1,3-diMeIM-2-COO]) zwitterion. We have utilized the ability of [1,3-diMeIM-2-COO] to react with acids in polar solvents, followed by the zwitterionic decarboxylation, resulting in the formation of a new salt with a counterion from the acid used in the process. Carbonic acid (H_2CO_3) was used to promote the protonation of the 2-carboxylate moiety, initially forming 2-carboxy-1,3-dimethylimidazolium hydrogen carbonate ([2-(COOH)-1,3-diMeIM][HCO_3]), followed by the Krapcho decarboxylation reaction, with the [HCO_3]$^-$ anion serving as the weak nucleophile. This reaction yielded formation of 1,3-dimethylimidazolium hydrogen carbonate ([1,3-diMeIM][HCO_3]).

We have also noted that that when [1,3-diMeIM][HCO_3] is dissolved in pure MeOH, it slowly converts into [1,3-diMeIM][$MeCO_3$] (Fig. 1a). As expected, this methyl carbonate anion in the presence of a strong protic acid could still undergo the decomposition reaction, forming MeOH, H_2O, CO_2, and a new salt. Similarly, Tommasi and Sorrentino[19] described the utilization of 1,3-dialkylimidazolium-2-carboxylates as CO_2 carriers for transcarboxylation reactions; for instance, the zwitterionic carboxylate was reacted with dry methanol and $NaBF_4$ or $NaPF_6$ to form dialkylimidazolium [BF_4]$^-$ or [PF_6]$^-$ salts and sodium methyl carbonate (Fig. 1b).

Both reactions presented in Fig. 1 suggest the possibility of forming the [$MeCO_3$]$^-$ anion directly from both the zwitterionic carboxylate precursor, as well as from the [HCO_3]$^-$ salt in the presence of dry MeOH. On the other hand, even though limited to only two literature examples, studies by Pocker *et al.*[20] and Mori *et al.*[21] helped to clarify the mechanism of the reaction as outlined in Fig. 1c, and showed that the reverse reaction is also possible. In the reverse pathway, the [$MeCO_3$]$^-$ anion reacts with H_2O and acids, with the consecutive formation of either the [HCO_3]$^-$ anion, or alcohol and CO_2, depending on reaction conditions.

Pocker *et al.*[20] investigated the water- and acid-catalyzed decarboxylation of monosubstituted derivatives of carbonic acid (Fig. 1c), and concluded that the alkyl carbonate anions behave similarly to the [HCO_3]$^-$ anion in the presence of an acid and decompose to CO_2 gas and alcohol, as opposed to CO_2 and H_2O as in case of the [HCO_3]$^-$ anion. Another interesting result of this investigation was that the reaction of alkyl carbonate anions with water results in the decomposition of the alkyl carbonate anion with formation of an alcohol and [HCO_3]$^-$ anion. Similar findings have been reported by Mori *et al.*,[21] where the authors describe the conversion of tetraalkylammonium methyl carbonate to the corresponding hydrogen carbonate salt by addition of water. Unfortunately, no experimental data was presented to support this hypothesis in the patent.

The results from the literature on the behavior of alkyl carbonates in water or in acids point to the conclusion that the reactions presented earlier by our group (Fig. 1a) might be reversible, depending on the solvent used. Thus it is anticipated that based on the solvent used for the dissolution of [$MeCO_3$]$^-$- or [HCO_3]$^-$-containing salts, interconversion reactions may be seen between both anions, with both potentially present at the same time in equilibrium.

In this work, we have extended our research on the utility of dialkyl carbonates as alkylating agents to form new [HCO_3]$^-$ salt precursors for further halide-free syntheses of other ILs. In order to obtain [$MeCO_3$]$^-$-based salts, we targeted two amines as prototypes: (i) 1,2-dimethylimidazole, since the carboxylation reaction at the C2 carbon during the imidazole alkylation process is prevented due to methyl group substitution (the carboxylation at C4/C5 position requires higher temperatures and should not occur with appropriate reaction conditions), and (ii) *N*-methylpyrrolidine, which due to lack of aromaticity or other conjugation, is less likely to undergo any carboxylation reaction to form a zwitterionic compound.

We report (Fig. 2) the formation of two new examples of [HCO_3]$^-$ IL precursors, 1,2,3-trimethylimidazolium hydrogen carbonate ([1,2,3-triMeIM][HCO_3]) and *N*,*N*-dimethylpyrrolidinium hydrogen carbonate ([*N*,*N*-diMePyr][HCO_3]) where the [HCO_3]$^-$ anion is generated by conversion of the [$MeCO_3$]$^-$ anion in the presence of excess water, and [1,2,3-triMeIM][$MeCO_3$]. The crystallographic characterization of highly deliquescent crystals of [1,2,3-triMeIM][HCO_3]·H_2O and [*N*,*N*-diMePyr][HCO_3] was performed in order to further

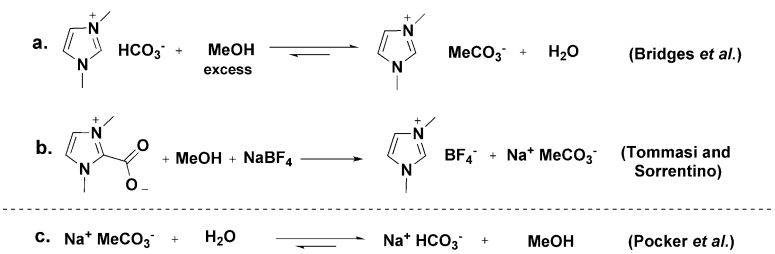


Fig. 1 Literature examples of possible conversions between [HCO_3]$^-$ and [$MeCO_3$]$^-$ anions depending on the reaction conditions and starting materials: a) conversion of [HCO_3]$^-$ anion to [$MeCO_3$]$^-$ in the presence of excess MeOH; b) conversion of dialkylimidazolium-2-carboxylate to dialkylimidazolium [BF_4]$^-$ salt in the presence of MeOH and inorganic salt; c) conversion of [$MeCO_3$]$^-$ anion to [HCO_3]$^-$ anion in the presence of an excess amount of H_2O.

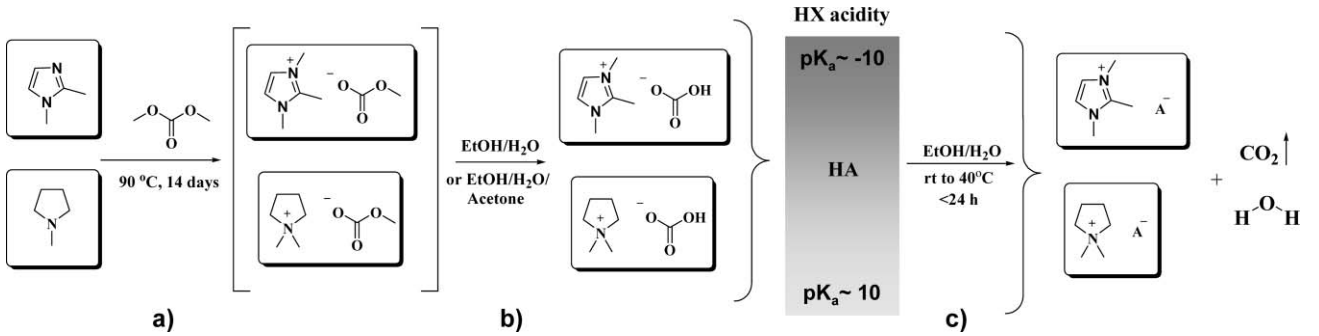


Fig. 2 Efficient, three-step synthesis of halide-free imidazolium- and pyrrolidinium-based organic salts; a) alkylation reaction with formation of $[MeCO_3]^-$ salts; b) conversion of $[MeCO_3]^-$ into $[HCO_3]^-$; c) reaction of $[HCO_3]^-$ salt precursor with acid and formation of final product.

validate product formation of the three new IL precursors. The resulting salts were later used in reactions with several acids to prove their utility as IL precursors for the fast and efficient synthesis of imidazolium- and pyrrolidinium-based organic salts.

Results and discussion

Reactivity of 1,2,3-trimethylimidazolium methyl carbonate ([1,2,3-triMeIM][$MeCO_3$])

The salt 1,2,3-trimethylimidazolium methyl carbonate ([1,2,3-triMeIM][$MeCO_3$]) was synthesized by alkylation of 1,2-dimethylimidazole with dimethyl carbonate, at 70 °C for 10 days in a sealed pressure tube (Fig. 3a).[18] Because of the possible reaction outcomes (*i.e.*, formation of the desired [1,2,3-triMeIM][$MeCO_3$] or the 1,2,3-trimethylimidazolium-4-carboxylate ([1,2,3-triMeIM-4-COO]) byproduct (Fig. 4)), the correct NMR solvent had to be used in order to provide reliable proof for the structure of the final product.

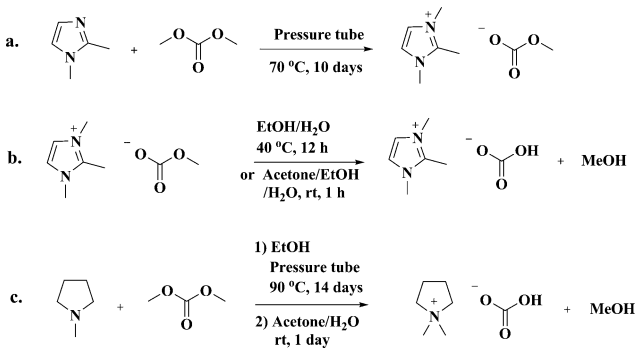


Fig. 3 General protocol for the synthesis of a) 1,2,3-trimethylimidazolium methyl carbonate, b) 1,2,3-trimethylimidazolium hydrogen carbonate, and c) *N*,*N*-dimethylpyrrolidinium hydrogen carbonate.

From our experience, we knew that in the case where the product formed was the [1,2,3-triMeIM-4-COO] zwitterionic salt, the addition of a strongly polar aprotic solvent in the presence of trace amounts of water and atmospheric CO_2 could cause the partial decarboxylation reaction and formation of [1,2,3-triMeIM][HCO_3] (Fig. 4, conditions **a**).[14] On the other hand, the use of pure deuterated MeOD as the NMR solvent could cause a reaction similar to the one reported by Tommasi and Sorrentino,[19] where transcarboxylation from the zwitterion

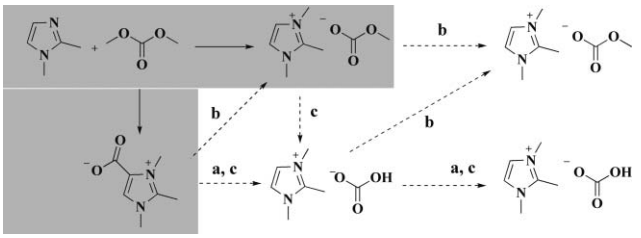


Fig. 4 Possible products from the reaction of 1,2-diMeIM with DMC (highlighted area) and their expected reactivities in the presence of different deuterated solvents: a) polar aprotic solvent, trace H_2O, atmospheric CO_2; b) MeOD; c) D_2O.

and formation of [1,2,3-triMeIM][$MeCO_3$] could occur (Fig. 4, conditions **b**). Such reactions would interfere with the NMR results if the real product of the reaction was actually the anticipated [1,2,3-triMeIM][$MeCO_3$]. Thus, the use of MeOD as the NMR solvent would prove the formation of [1,2,3-triMeIM][$MeCO_3$], but could not rule out the possibility of its formation from the reaction of [1,2,3-triMeIM-4-COO] with the solvent. Also, the use of deuterated H_2O as the NMR solvent could greatly influence the experiment by possible conversion of [1,2,3-triMeIM][$MeCO_3$] into [1,2,3-triMeIM][HCO_3], similar to work by Pocker *et al.*[20] In that case, the existence of the $[HCO_3]^-$ salt could be proven, but the starting material from which it came could not (Fig. 4, conditions **c**). We therefore analyzed our product using ^1H and ^{13}C NMR in deuterated $CHCl_3$ (chosen for its lower polarity than DMSO), relative immiscibility with water, low hygroscopicity, and inert character toward the product.

The results of the NMR analyses in $CDCl_3$ confirmed the anticipated reaction outcome, the symmetric $[1,2,3\text{-triMeIM}]^+$ cation core, by characteristic signals at 2.74 (C2-CH_3), 3.94 (N-CH_3), and 7.74 ppm (C4/C5-H) (Table S1a†). Moreover, the signal at 3.45 ppm has been identified as the CH_3O- group of the $[MeCO_3]^-$ anion, which is highly suggestive of the formation of the desired [1,2,3-triMeIM][$MeCO_3$]. The ^{13}C NMR also confirmed formation of pure [1,2,3-triMeIM][$MeCO_3$], with $[MeCO_3]^-$ anion signals appearing at 52.0 and 158.0 ppm (Table S1b). The other possibility for the assignment of these signals would be formation of [1,2,3-triMeIM][HCO_3] and the presence of MeOH formed during the decomposition of the $[MeCO_3]^-$ anion. However, the signal at 52.0 ppm, due to its position slightly downfield from the expected position for MeOH (49.8 ppm), was assigned to the $[MeCO_3]^-$ anion. A

shift in the position of the CH_3O- signal was expected due to the electron-withdrawing effect of the carbonate group in the $[MeCO_3]^-$ anion. Additionally, in the ^1H NMR of [1,2,3-triMeIM][$MeCO_3$] (Table S1a), a small signal at 3.34 ppm was present. This was assigned to trace amounts of MeOH, possibly formed during the slow conversion process of the $[MeCO_3]^-$ anion into MeOH and $[HCO_3]^-$.

Additional analysis of the same [1,2,3-triMeIM][$MeCO_3$] sample dissolved in $CDCl_3$, 24 h after the initial NMR experiment confirmed the earlier supposition of slow conversion of the $[MeCO_3]^-$ anion into MeOH and $[HCO_3]^-$. In addition to the peaks observed during initial analysis, the signal suspected to be indicative of MeOH at 3.34 ppm appeared to be much more distinct (Table S1c). Additionally, ^{13}C NMR of the same sample (after 24 h) (Table S1d) revealed the appearance of an additional peak at 49.63 ppm, slightly upfield from the signal of the methoxy group on the anion, thus again confirming slow conversion of the $[MeCO_3]^-$ anion into MeOH and $[HCO_3]^-$. 24 h after NMR sample preparation, the ratio of the peak for MeOH (3.35 ppm) to the peak for $[MeCO_3]^-$ (3.45 ppm) was 1 : 4.

A heteronuclear multiple bond correlation (HMBC) NMR experiment was performed to confirm the assumptions about the presence of the $[HCO_3]^-$ anion in the product. The goal of this experiment was to correlate one of the CH_3O- signals (at 3.45 or 3.35 ppm in the ^1H NMR experiment) with the carbon atom of the carbonate group in $[MeCO_3]^-$, since only the $[MeCO_3]^-$ could result in the appearance of the ^3J cross-peak. In contrast, the hydrogen signal of MeOH was anticipated to show no ^3J-coupling correlation with the carbonate signals (Fig. 5).

Of the two analyzed peaks at 3.45 and 3.35 ppm (NMR peaks 4 and 5, Fig. 6) only the peak at 3.45 ppm showed a cross-peak with the carbonate peak on the ^{13}C NMR scale at 158.03 ppm. This directly indicated the presence of the $[MeCO_3]^-$

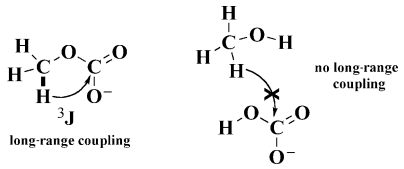


Fig. 5 Expected cross-peak correlation for the $[MeCO_3]^-$ anion utilizing an HMBC NMR experiment.

species in the NMR solution. It was concluded from this NMR experiment that the starting material, before dissolution in $CDCl_3$, was pure [1,2,3-triMeIM][$MeCO_3$], which after 24 h converted approximately 25% of the $[MeCO_3]^-$ anion to $[HCO_3]^-$ and MeOH. This finding is consistent with experimental results from the NMR experiment carried out in deuterated H_2O as solvent, and as discussed below.

To further investigate [1,2,3-triMeIM][$MeCO_3$] and its possible conversion to [1,2,3-triMeIM][HCO_3] in the presence of water, as reported by Mori *et al.*,[21] the NMR spectra of the raw sample, dissolved in deuterated H_2O, was analyzed (Table S1e–g). The first ^1H NMR spectrum was taken ~10 min after dissolution in the NMR solvent and revealed two sets of signals at 3.37 and 3.54 ppm in a 3 : 1 ratio. As previously rationalized, the signal at 3.37 ppm was preliminarily assigned to the MeOH formed from decomposition of the $[MeCO_3]^-$ anion, and a signal at 3.54 ppm was assigned to the remaining $[MeCO_3]^-$ anion. The same sample was analyzed again after 1 h using the same NMR protocol and revealed the disappearance of the signal at 3.54 ppm and only the presence of a signal at 3.37 ppm, corresponding to MeOH being formed during the decomposition of $[MeCO_3]^-$ in the presence of D_2O. A ^{13}C NMR of the sample taken after 1 h (Table S1g) clearly shows (i) all signals present for the imidazolium cation, (ii) a signal at 160.9 ppm assigned to the carbonate group from the anion, and (iii) a signal at 49.6 ppm assigned to the formed MeOD.

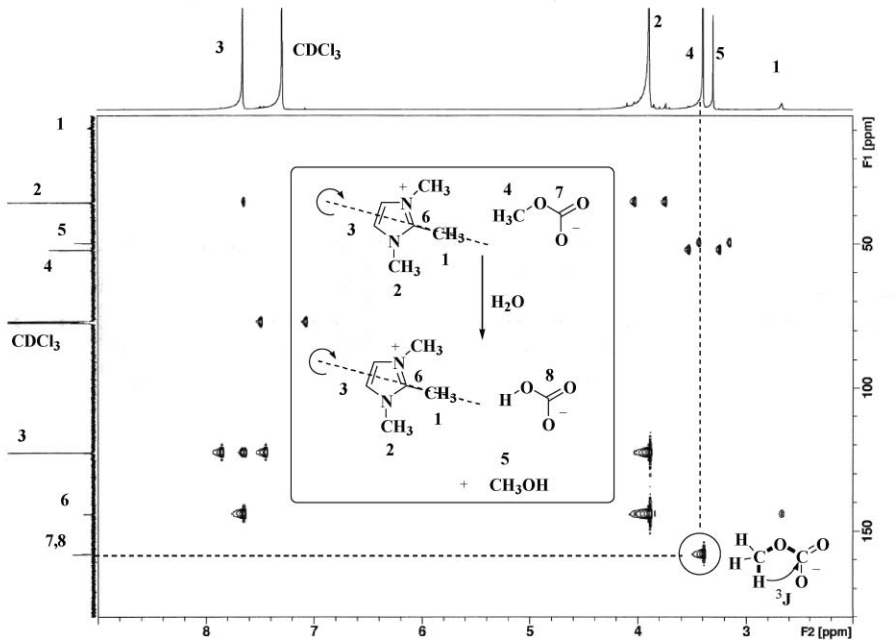


Fig. 6 HMBC NMR (ppm) of [1,2,3-triMeIM][$MeCO_3$] in $CDCl_3$ 24 h after initial sample preparation.

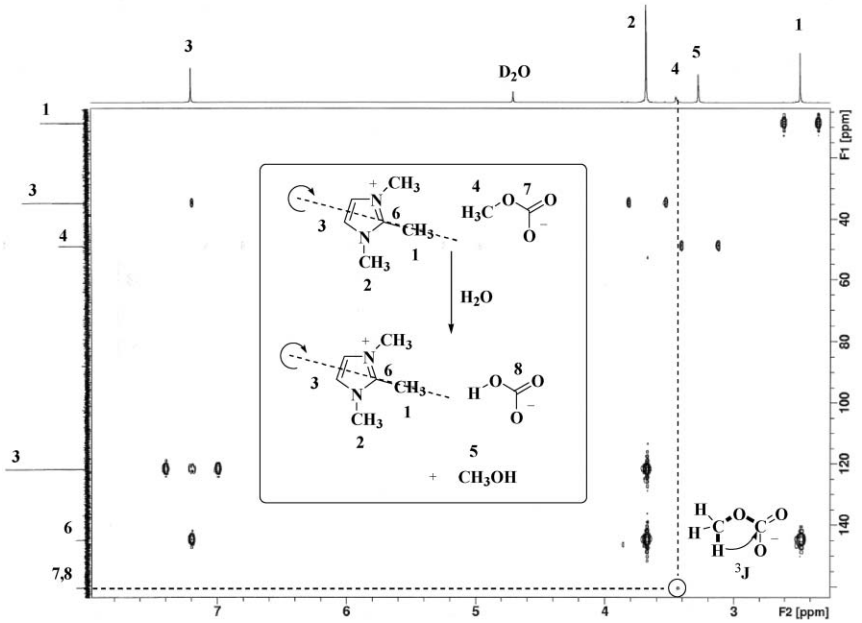


Fig. 7 HMBC NMR (ppm) of [1,2,3-triMeIM][$MeCO_3$] in D_2O 10 min after initial sample preparation.

Lastly, one more HMBC NMR experiment (Fig. 7) was performed to confirm the conversion reaction from $[MeCO_3]^-$ to $[HCO_3]^-$ in the presence of water, and to allow definite assignment of the observed NMR signals in D_2O to the hypothesized products. Even though the HMBC experiment does not require a long time for data collection, it was noticed that over the time of the experiment, the signal at 3.54 ppm almost completely disappeared due to conversion of $[MeCO_3]^-$ to MeOH and $[HCO_3]^-$. Fortunately, enough evidence of the cross-peak was found for this signal, and allowed for its successful correlation with the carbonate peak at 160.9 ppm.

To complete the NMR structural identification of crude [1,2,3-triMeIM][$MeCO_3$], one further experiment was performed using deuterated MeOH to confirm its identity. In the ^1H NMR spectrum, the characteristic peak at 3.24 ppm was assigned to the CH_3O- group of the $[MeCO_3]^-$ anion. Also the ^{13}C NMR showed the peak for CH_3O- at 49.9 ppm adjacent to the septet for MeOD. All chemical shifts for the sample run in MeOD are included in Table S1h–i.

Confirmation of the synthesis of [1,2,3-triMeIM][$MeCO_3$] also came from single-crystal X-ray diffraction analysis (Fig. 8). An examination of the closest contacts suggests six anions surrounding each cation (and *vice versa*) in addition to one cation–cation stacking contact. The closest anion–cation contacts are the asymmetric and bifurcated contacts between the acidic ring hydrogen atoms at C4 and C5 with the carboxylate oxygen atoms of the anions (2.30(2) to 2.40(2) Å). The cation stacking interactions consist of parallel head-to-tail alignment over the N1–C2–N3 bond with a separation of 3.60(4) Å, calculated using centroid-to-centroid distances, where the centroid represents the center of the three atoms. Interestingly, the opposite face of each stacked cation pair is oriented toward the methyl-substituted oxygen in the anions with an O3-to-C2 separation of 2.960(1) Å.

Conversion of [1,2,3-triMeIM][$MeCO_3$] to [1,2,3-triMeIM][HCO_3]

As suggested by the results above, the conversion reaction of $[MeCO_3]^-$ to $[HCO_3]^-$ was attempted using EtOH as a solvent

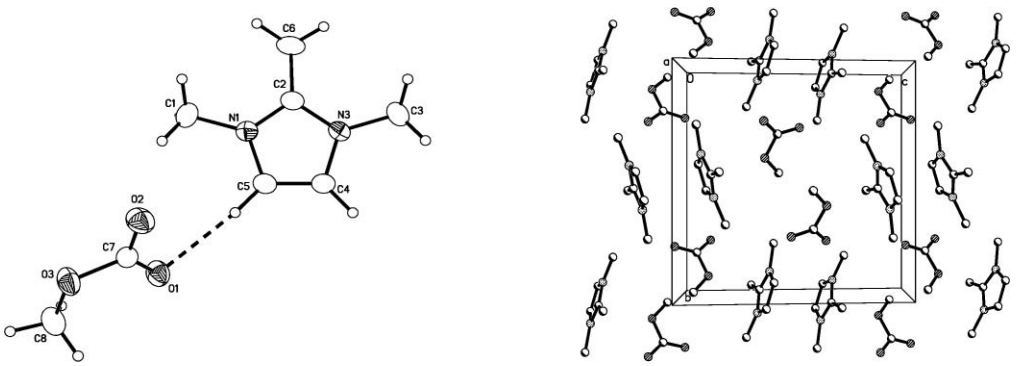


Fig. 8 Asymmetric unit (left, 50% probability thermal ellipsoids; closest anion–cation contact noted) and packing diagram (right, hydrogen atoms omitted for clarity) of [1,2,3-triMeIM][$MeCO_3$].

and H_2O as a reagent (in large excess over any other reactant). The reaction was stirred overnight at 40 °C, after which time the solvent was evaporated using a rotary evaporator and the product isolated (Fig. 3b). The NMR spectra of the product confirmed quantitative conversion to [1,2,3-triMeIM][HCO_3], and the NMR signals were comparable with those for [1,2,3-triMIM][$MeCO_3$] analyzed in D_2O 1 h after initial dissolution, as described above (Table S1f–g).

In an attempt to reduce the reaction steps and streamline the process, the same overall reaction was carried out by addition of wet acetone to [1,2,3-triMeIM][$MeCO_3$] in EtOH resulting in the formation of [1,2,3-triMeIM][HCO_3] directly as a solid precipitating out of solution. The solid was separated by centrifugation, the extract concentrated, and another portion of acetone added to the liquid phase, allowing more of the product to precipitate. (An additional advantage of this route is that colored impurities formed in the raw sample of [1,2,3-triMeIM][$MeCO_3$] are retained in the mother liquor during the precipitation of pure [1,2,3-triMeIM][HCO_3].) The total yield of the process (after drying the product under high vacuum) was calculated to be ~91%.

The NMR of [1,2,3-triMeIM][HCO_3] was performed in D_2O and MeOD separately (Table S1j–m). The NMR analyses in D_2O confirmed the formation of pure [1,2,3-triMeIM][HCO_3], evidenced by the lack of the distinctive peak for the CH_3O-signal of [$MeCO_3$]$^-$ at 59.9 ppm (^{13}C NMR) and 3.2 ppm (^{1}H NMR). A trace signal for the [$MeCO_3$]$^-$ anion at 3.24 ppm was present in the ^{1}H NMR in MeOD after 1 h, indicating that back-conversion of [HCO_3]$^-$ to [$MeCO_3$]$^-$ was occurring,[14] but very slowly.

Slow precipitation of the product from solution produced single-crystals of [1,2,3-triMeIM][HCO_3]·H_2O suitable for X-ray diffraction analysis. In the crystal structure (Fig. 9), one cation, one anion, and one water molecule complete the asymmetric unit. The [HCO_3]$^-$ anions form classic head-to-head hydrogen bonded dimers around crystallographic centers of inversion, with each anion in the dimers accepting additional hydrogen bonds from the cation (the acidic proton on C5) and the water molecule. The strong hydrogen bonds between the water and anions results in a corrugated 2D network with the cations residing between the sheets, similar to the crystal structure of [1,3-diMIM][HCO_3]·H_2O.[14]

Formation of *N*,*N*-dimethylpyrrolidinium hydrogen carbonate ([*N*,*N*-diMePyr][HCO_3])

The pyrrolidinium core was chosen for study to represent non-aromatic amines that would not undergo bonding of the carbonate group to the pyrrolidinium core, and thus not form a zwitterionic species. Another benefit of working with this cation core is its wide electrochemical window, thus having potential for use in electrochemical applications.[22] It was anticipated that in the reaction of *N*-alkylpyrrolidine and dialkyl carbonate, only the *N*,*N*-dialkylpyrrolidinium alkyl carbonate would be formed. This could then undergo an anion conversion process, as described above, with clean formation of the [HCO_3]$^-$-based salt and alcohol as the byproduct.

Methylpyrrolidine and 200% excess of DMC were reacted at 90 °C for 14 days in a pressure tube. After this time, excess DMC and any possible unreacted *N*-methylpyrrolidine were removed using rotary evaporation; no solid precipitate was observed. Different solvent systems were tried to separate the product, [*N*,*N*-diMePyr][$MeCO_3$], from the colored impurities without success. As in the previous experiments, solvents like DMSO, DMF, trialkylamine, acetone, water, and similar polar solvents had to be generally avoided due to the possible direct conversion of [$MeCO_3$]$^-$ into [HCO_3]$^-$ prior the isolation of [*N*,*N*-diMePyr][$MeCO_3$]. Unfortunately, all the tested solvent systems failed to result in successful isolation of product from the reaction mixture. The only solvent system that successfully separated the product from the decomposition products was found to be acetone. It was also found that the use of acetone in product purification, as previously presented, facilitated the conversion of [$MeCO_3$]$^-$ to [HCO_3]$^-$ and MeOH, thus isolation of a pure [*N*,*N*-diMePyr][$MeCO_3$] salt was not possible, and only a [HCO_3]$^-$-based salt could be isolated.

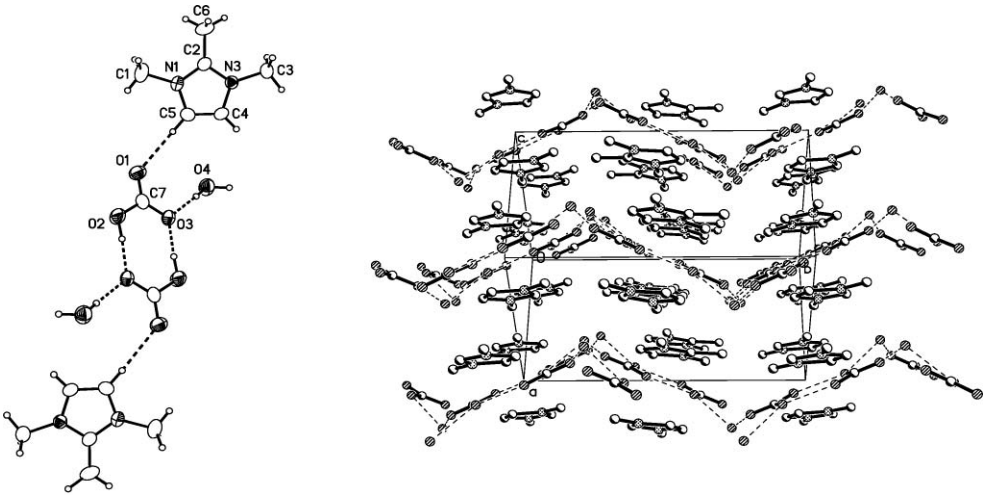


Fig. 9 Crystal structure of [1,2,3-triMeIM][HCO_3]·H_2O (left, 50% probability thermal ellipsoids; depicting the hydrogen bonded anion dimer and closest cation contact) and packing diagram (right, hydrogen atoms removed for clarity) showing the 2D corrugated sheets interpenetrated with stacked [1,2,3-triMeIM]$^+$ cations.

To the oily-red reaction mixture isolated from the rotary evaporation step above, wet acetone was added, resulting in the complete dissolution of the reaction mixture, from which, after 1 h, crystalline product slowly started to appear (Fig. 3c). This white, solid, crystalline, and very hygroscopic material was separated from the liquor by centrifugation, and washed twice with fresh acetone. After drying under high vacuum, NMR and X-ray diffraction analyses were performed.

The NMR spectra in D_2O and DMSO (Table S2) clearly confirmed that the only isolated product was the [*N*,*N*-diMePyr][HCO_3] due to the lack of the CH_3O- singlet signal of the [$MeCO_3$]$^-$ anion expected at ~3.4–3.6 ppm. Additionally, in the NMR spectra in D_2O, no MeOD signal was observed, which proved lack of conversion of [$MeCO_3$]$^-$ to [HCO_3]$^-$ and MeOH during the NMR experiment. Finally, an HMBC NMR experiment in D_2O ruled out any possibility of the presence of [$MeCO_3$]$^-$, showing no cross-peaks between ^{1}H NMR signals and ^{13}C NMR peaks corresponding to the carbonate peak at ~160 ppm; thus it was concluded that the isolated product is pure [*N*,*N*-diMePyr][HCO_3], as confirmed by X-ray diffraction.

The crystal structure of the anhydrous [*N*,*N*-diMePyr][HCO_3] (Fig. 10) consists of hydrogen-bonded hydrogen carbonate dimers and discrete cations. Each anionic dimer is surrounded by eight nearest-neighbor cations, and each cation has four anion and two cation nearest neighbors.

Utilization of new hydrogen carbonate-based IL precursors in the synthesis of ILs and other organic salts

In order to show the possible synthetic applications of [HCO_3]$^-$-based salts as IL precursors, the newly formed [1,2,3-triMeIM][HCO_3] and [*N*,*N*-diMePyr][HCO_3] salts were reacted with a group of organic and inorganic acids (HCl, HNO_3, picric acid), and ammonium perchlorate ([NH_4][ClO_4]; considered here as a very weak acid (pK_a = 9.2)).[23] In all cases but one, [NH_4][ClO_4], the pK_a values of the acids were lower than that of H_2CO_3 (pK_{a1}=6.35),[24] thus complete conversion was expected with the formation of H_2CO_3 as byproduct. H_2CO_3, due to its low stability, was expected to readily decompose to H_2O and gaseous CO_2, thus shifting the reaction equilibrium towards product formation, and after solvent evaporation, to result in byproduct-free salts.

In the case of the reaction of [HCO_3]$^-$-based IL precursors with [NH_4][ClO_4], a different reaction pathway was expected. Instead of relying on a lower pK_a of the acidic reagent in comparison to H_2CO_3, the kinetic equilibrium between [NH_4]$^+$ + [HCO_3]$^-$ and NH_3 + H_2CO_3 was expected to produce volatile products which could be removed from the system, shifting the reaction toward products (Fig. 11, where [X]$^-$ = [ClO_4]$^-$).

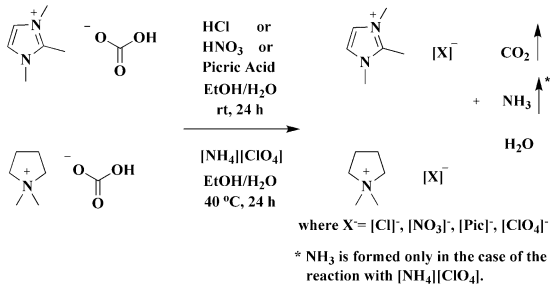


Fig. 11 Reactions of [1,2,3-triMeIM][HCO_3] and [*N*,*N*-diMePyr][HCO_3] with hydrochloric, nitric, and picric acids, as well as ammonium perchlorate.

All eight product salts were confirmed using ^{1}H and ^{13}C NMR. In all cases, no remaining signal for [HCO_3]$^-$ was recorded in the ^{13}C NMR, confirming the anticipated quantitative conversion of [HCO_3]$^-$ IL precursors into new salt products.

Thermal analysis of synthesized salts

All synthesized compounds, along with their [HCO_3]$^-$ IL precursors, were thermally characterized. Melting points and decomposition temperatures were analyzed (Table 1) using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results indicated the thermal stabilities of [$MeCO_3$]$^-$ and [HCO_3]$^-$ salts to be very low, with the lowest thermal stability recorded for [1,2,3-triMeIM][$MeCO_3$] (onset temperature for 5% decomposition, $T_{5\%dec}$, = 104 °C). The [HCO_3]$^-$ salt of this cation exhibited a similar $T_{5\%dec}$ of 112 °C. In comparison, the thermal stability of [*N*,*N*-diMePyr][HCO_3] was substantially higher ($T_{5\%dec}$= 158 °C) than observed for the imidazolium salts.

All of the analyzed salts formed by the reaction of the IL precursors with acids exhibited thermal stabilities >200 °C. This increase in stability was expected, since the new products are composed of stable anions that do not undergo any simple thermal decomposition, as normally found for [HCO_3]$^-$ and [$MeCO_3$]$^-$. The thermal stabilities of the [1,2,3-triMeIM]$^+$-based

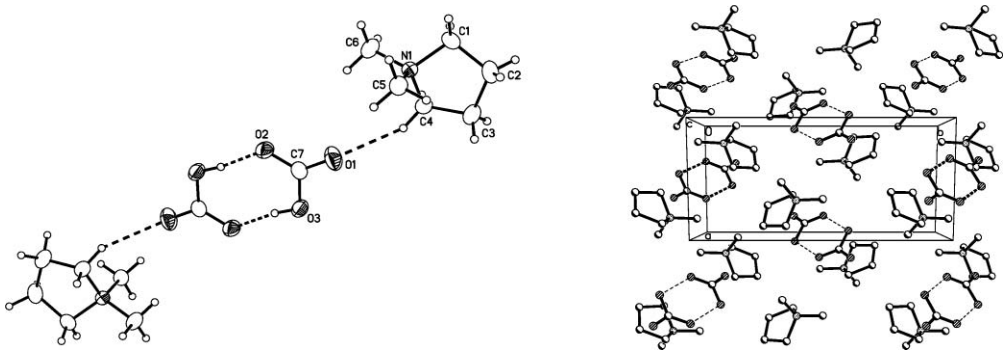
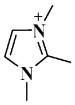
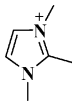


Fig. 10 Crystal structure of [*N*,*N*-diMePyr][HCO_3] (left, 50% probability thermal ellipsoids; depicting the hydrogen-bonded anion dimer and closest cation contact) and packing diagram (right, hydrogen atoms removed for clarity).

Table 1 Melting point transitions and decomposition temperatures of the [1,2,3-triMeIM]$^+$ and [*N*,*N*-diMePyr]$^+$-based salts[a]

Cation				
Anion	m.p./°C	$T_{5\%dec}$/°C	m.p./°C	$T_{5\%dec}$/°C
$[MeCO_3]^-$	**79**	104	n/a	n/a
$[HCO_3]^-$	—[c]	112[d]	—[c]	158
$[Cl]^-$	**71**	205	~260 [a](lit. >350)[25]	231
$[NO_3]^-$	**63**	259	~220[b]	276
$[Pic]^-$	104	224	~280 [b](lit. >310)[26]	269
$[ClO_4]^-$	~220 [b](lit >250)[27]	220	~280 [b](lit. >330)[28]	254

[a] Salts melting below 100 °C are shown in **bold**. [b] Using a standard DSC protocol, the m.p. was not observed; visual m.p. analysis confirmed that the salt remains solid until its decomposition temperature, at which point it melts and decomposes simultaneously, changing to dark brown in color. [c] Due to the extreme hygroscopic nature of the sample, the determination of the m.p. was not possible. [d] Hydrated salt decomposition.

salts ranged from 205 °C for [1,2,3-triMeIM][Cl], to 258 °C for [1,2,3-triMeIM][NO_3]. In the case of the [*N*,*N*-diMePyr]$^+$-based salts, the thermal stabilities ranged between 231 °C for [*N*,*N*-diMePyr][Cl] to 276 °C [*N*,*N*-diMePyr][NO_3].

The melting points of the obtained salts were also analyzed; however, due to the extreme hygroscopic nature of both $[HCO_3]^-$-based salts, the determination of the melting point using DSC did not provide reliable results, and visual melting point determination was attempted. In each of the $[HCO_3]^-$-based samples, placing them directly on a glass slide resulted in fast moisture absorption and deliquescence of the compounds due to the water absorbed from the atmosphere. When the glass slide was placed on the hot-stage apparatus and heated to ~100 °C, the absorbed water appeared to evaporate, leaving a white powder on the slide. Continuous heating of the sample was carried out to the decomposition temperature, at which point the compounds simultaneously melted, evolved gasses, and turned brown in color.

DSC analyses of the [1,2,3-triMeIM]$^+$ salts, except for the $[HCO_3]^-$ and $[ClO_4]^-$ analogs, exhibited a sharp melting transition (on heating) and a sharp crystallization transition (on cooling). The melting points of the [1,2,3-triMeIM]$^+$ salts were surprisingly low, considering the high symmetry of the cation, and were between 64 °C for [1,2,3-triMeIM][NO_3] and 104 °C for [1,2,3-triMeIM][Pic]. The melting transition for [1,2,3-triMeIM][ClO_4] was not detected on the DSC instrument due to the safety limitations set for the DSC experimental protocol. Visual melting point analysis revealed that the sample remained solid until ~220 °C, at which point it melted and decomposed simultaneously. This finding was supported by a literature report where the melting point for [1,2,3-triMeIM][ClO_4] was reported to be >250 °C.[27]

DSC analysis of the melting points for the [*N*,*N*-diMePyr]$^+$-based salts did not result in determination of any melting point transitions within the allowed DSC temperature ranges (up to $T_{DSCmax} = T_{5\%dec} - 50$ °C to avoid decomposition of the analyzed compound in the DCS cell and its contamination). Thus, visual melting point analyses were performed, and revealed that the analyzed salts remain solid until, or very close to, their decomposition temperatures. In all cases the melting points were recorded to be >220 °C, and the melting transition translated directly to the beginning of the decomposition process. Literature reports, although limited, confirm these findings.[25,26,28]

Conclusions

In continuing the search toward novel halide- and metal-free synthetic protocols for the synthesis of ILs, two new $[HCO_3]^-$ IL precursors ([1,2,3-triMeIM][HCO_3] and [*N*,*N*-diMePyr][HCO_3]) were developed and their structures were confirmed by NMR experiments and single-crystal X-ray diffraction. These salts were also evaluated for future possible applications in the syntheses of ILs by reacting them with a variety of acids and [NH_4][ClO_4], which resulted in the clean and quantitative formation of a family of [1,2,3-triMeIM]$^+$- and [*N*,*N*-diMePyr]$^+$-based salts. In the course of development of the synthetic protocols for the formation of $[HCO_3]^-$ salts, the resulting alkylation reactions of the chosen neutral amines (in this case 1,2-dimethylimidazole and *N*-methlypyrrolidine) with DMC, and later conversion of the formed $[MeCO_3]^-$ salts to $[HCO_3]^-$ salts proceeded in one step at temperatures close to room temperature, using only water as reagent.

Previously reported routes to [1,3-diMeIM][HCO_3][14] were limited to the use of zwitterionic [1,3-diMeIM-2-COO], which upon reaction with carbonic acid, or water and CO_2, led to the formation of the desired $[HCO_3]^-$ salt. Here, we have presented a more generalized route to $[HCO_3]^-$ salts which allows for more efficient and faster syntheses of ILs in comparison with the routes through zwitterionic feedstocks.

These new routes are advantageous for at least three reasons. First, the formation of the $[HCO_3]^-$ precursor using the new synthetic protocol does not require prior formation of a zwitterionic salt, thus eliminating the need for a two-step reaction, with the carboxylation step requiring elevated temperatures and extended times. Second, the required formation of the $[MeCO_3]^-$ intermediate *en route* to the $[HCO_3]^-$ salts does not limit the range of cations to heterocycles that can undergo a carboxylation reaction; the only limitation is the ability of the starting amine to undergo alkylation with dialkyl carbonate. Finally, conversion of $[MeCO_3]^-$ to $[HCO_3]^-$, and then consecutive reaction with the acid of choice, is simple in comparison with the requirements of the Krapcho decarboxylation reactions of the zwitterions, which often has to be performed in polar aprotic solvents, like DMSO, and proceeds in two steps.

The new $[HCO_3]^-$-based IL precursors were also used in reactions with several acids and [NH_4][ClO_4] to prove the potential of this family of salts for future applications in halide- and metal-free syntheses of ILs. As shown, it is possible to form virtually any salt from the $[HCO_3]^-$ precursor when the pK_a of the acidic reagent is lower than that of H_2CO_3. Also, the use of ammonium salts results in formation of ammonia gas, which can be evacuated from the system, shifting the equilibrium towards product formation. This reaction can be manipulated to accommodate a wide variety of anions by proper design of the reaction conditions.

Experimental

Chemicals

All reagents were purchased from Sigma-Aldrich (St. Louis, MO) and were used as received.

Synthesis of 1,2,3-trimethylimidazolium methyl carbonate ([1,2,3-triMeIM][$MeCO_3$])

The synthesis of [1,2,3-triMeIM][$MeCO_3$] followed a previously published method for the synthesis of [1,3-diMeIM-2-COO] *via* an alkylation reaction of 1-methylimidazole with DMC.[18] 4.8 g (50 mmol) of 1,2-dimethylimidazole and 9 g (100 mmol) of DMC were placed in a 20 mL thick-walled glass pressure tube. The tube was sealed, placed in an oven, and heated to 70 °C for 10 days (Fig. 3a). The resulting yellow liquor was cooled to room temperature and unreacted substrates removed under high vacuum, at which time the product (7.44 g) crystallized in the form of slightly colored crystals.

1,2,3-Trimethylimidazolium methyl carbonate ([1,2,3-triMeIM][$MeCO_3$]). White solid, very hygroscopic, 80% yield, m.p. 79 °C, $T_{5\%dec}$= 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.74 (s, 3H, C2-CH_3), 3.45 (s, 3H, CH_3CO_3), 3.94 (s, 6H, N-CH_3), 7.74 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 9.52 (C2-CH_3), 35.16 (N-CH_3), 52.02 (CH_3CO_3), 122.69 (C4/C5), 143.99 (C2), 157.98 (CH_3CO_3); ^{1}H NMR (500 MHz, [D_4]MeOH) δ = 2.50 (s, 3H; C2-CH_3), 3.23 (s, 3H; CH_3CO_3), 3.71 (s, 6H, N-CH_3), 7.35 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz, [D_4]MeOH) δ = 9.34 (C2-CH_3), 35.42 (N-CH_3), 49.90 (CH_3CO_3), 123.35 (C4/C5), 146.52 (C2), 161.37 (CH_3CO_3). Single-crystal X-ray diffraction analysis: colorless plates; $C_8H_{14}N_2O_3$; MW 186.21; T = 173 K; Monoclinic; $P2_1/n$; a = 6.8805(6) Å; b = 11.6254(10) Å; c = 11.9614(11) Å; β = 96.229(2)°; V = 951.13(15) Å^3; Z = 4; D_c = 1.300 g cm^{-3}; R_1, wR_2 [$I > 2\sigma(I)$] = 0.0428, 0.1044; R_1, wR_2 (all data) = 0.0510, 0.1087.

Synthesis of 1,2,3-trimethylimidazolium hydrogen carbonate ([1,2,3-triMeIM][HCO_3])

By reaction in EtOH–H_2O. 0.5 g (2.7 mmol) of [1,2,3-triMIM][$MeCO_3$] was dissolved in 3 mL of EtOH and 1.5 mL (83 mmol) DI H_2O was added (Fig. 3b). The reaction was stirred overnight at 40 °C, after which time the solvent was evaporated on the rotary evaporator, and the sample was analyzed by NMR. The NMR spectra confirmed the quantitative conversion to [1,2,3-triMeIM][HCO_3]. The slightly colored solid product (0.46 g) was obtained in 99% yield.

By reaction in EtOH–acetone. 1.5 g (8.1 mmol) of [1,2,3-triMeIM][$MeCO_3$] was dissolved in a minimum amount of EtOH (2 mL) and heated to 40 °C to allow complete dissolution of the starting material. 10 mL of acetone, spiked with 0.3 mL (16.7 mmol) DI H_2O, was then added dropwise to the EtOH solution, producing a precipitate which was separated by centrifugation. The remaining solution was concentrated by partial evaporation of the solvent on a rotary evaporator at 40 °C, and another portion of acetone (10 mL) was added allowing for more precipitation. The process was repeated 2 more times until no precipitate was noticed. The combined solid was dried under high vacuum at 40 °C for 12 h. A white, hygroscopic solid (1.39 g), with a melting point at the decomposition temperature was obtained with a total yield of 91%.

1,2,3-Trimethylimidazolium hydrogen carbonate monohydrate ([1,2,3-triMeIM][HCO_3]·H_2O). White solid, very hygroscopic, 91% yield, m.p. at $T_{5\%dec}$, $T_{5\%dec}$ = 112 °C; ^{1}H NMR (500 MHz, D_2O) δ = 2.57 (s, 3H; C2-CH_3), 3.78 (s, 6H, N-CH_3), 7.30 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz, D_2O) δ = 9.41 (C2-CH_3), 35.32 (N-CH_3), 122.55 (C4/C5), 145.50 (C2), 161.03 (HCO_3); ^{1}H NMR (500 MHz, [D_4]MeOH) δ = 2.51 (s, 3H; C2-CH_3), 3.72 (s, 6H, N-CH_3), 7.36 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz, [D_4]MeOH) δ = 9.37 (C2-CH_3), 35.44 (N-CH_3), 123.35 (C4/C5), 146.48 (C2), 161.32 (CH_3CO_3). Single-crystal X-ray diffraction analysis of [1,2,3-triMeIM][HCO_3]·H_2O: colorless needles; $C_7H_{14}N_2O_4$; MW 190.20; T = 173 K; monoclinic; $P2_1/n$; a = 7.479(2) Å; b = 13.289(4) Å; c = 9.636(3) Å; β = 90.011(5)°; V = 954.0(5) Å^3; Z = 4; D_c = 1.324 g cm^{-3}; R_1, wR_2 [$I > 2\sigma(I)$] = 0.0719, 0.1097; R_1, wR_2 (all data) = 0.1822, 0.1407.

Synthesis of *N*,*N*-dimethylpyrrolidinium hydrogen carbonate ([*N*,*N*-diMePyr][HCO_3])

4.0 g (50 mmol) of *N*-methypyrrolidine was initially dissolved in 5 mL of EtOH and transferred into a 20 mL thick-walled pressure tube. Next, 9 g (100 mmol) of DMC was added to the solution at room temperature. The tube was sealed, stirred vigorously, placed in the oven, and heated to 90 °C. The reaction mixture was kept under those conditions for 14 days, and then cooled to room temperature (Fig. 3c), giving a dark red liquor. Excess unreacted substrates were removed using a rotary evaporator at 90 °C, and later high vacuum at 70 °C. No product crystallized from the mother liquor.

Due to problems with isolating the product from the red liquor, the intermediate was converted *in situ* into *N*,*N*-dimethylpyrrolidinium hydrogen carbonate. To the oily-red concentrated reaction mixture 10 mL of wet acetone was added, resulting in the complete dissolution of reaction mixture. After 1 h a crystalline product slowly started to appear. After 24 h at room temperature, the vessel was placed in the refrigerator and kept at this temperature for an additional 72 h. A white, solid, very hygroscopic product was separated from the red liquor by centrifugation, and washed twice with cold acetone. The remaining extract was concentrated, more solid product precipitated, and later was separated by centrifugation. After combining the two precipitation batches, the product was dried under high vacuum for 12 h at room temperature, resulting in a white, hygroscopic solid (5.80 g; 72% total yield and 98% purity), with a melting point at the decomposition temperature.

***N*,*N*-Dimethylpyrrolidinium hydrogen carbonate ([*N*,*N*-diMePry][HCO_3]).** White solid, very hygroscopic, 72% yield, m.p. at $T_{5\%dec}$, $T_{5\%dec}$ = 158 °C; ^{1}H NMR (500 MHz, D_2O) δ = 2.23 (t, 4H; CH_2), 3.14 (s, 6H, N-CH_3), 3.51 (t, 4H, N-CH_2); ^{13}C NMR (125 MHz, D_2O) δ = 21.65 (CH_2), 51.67 (N-CH_3), 65.82 (N-CH_2), 160.17 (HCO_3); ^{1}H NMR (500 MHz, [D_6]DMSO) δ = 2.08 (t, 4H; CH_2), 3.05 (s, 6H, N-CH_3), 3.42 (t, 4H, N-CH_2); ^{13}C NMR (125 MHz, [D_6]DMSO) δ = 21.76 (CH_2), 51.50 (N-CH_3), 65.33 (N-CH_2), 158.93 (HCO_3). Single-crystal X-ray diffraction

analysis: colorless plates; $C_7H_{15}NO_3$; MW 161.20; monoclinic; $P2_1/n$; $a = 6.6199(6)$ Å; $b = 13.9451(12)$ Å; $c = 9.2587(8)$ Å; $\beta = 101.760(2)°$; $V = 836.8(1)$ Å^3; $Z = 4$; $D_c = 1.280$ g cm^{-3}; R_1, wR_2 [$I > 2\sigma(I)$] = 0.0356, 0.0890; R_1, wR_2 (all data) = 0.0445, 0.0937.

General procedure for the preparation of 1,2,3-trimethylimidazolium and *N*,*N*-dimethylpyrrolidinium chloride [Cl]$^-$, nitrate [NO_3]$^-$, picrate [Pic]$^-$, and perchlorate [ClO_4]$^-$ salts

All reactions were performed using the same procedure: 0.01 mol of the appropriate acid (HPF_6, HCl, H_2SO_4, picric acid) or salt ([NH_4][ClO_4]) was dissolved in 10 mL of H_2O (ethanol in the case of picric acid) and added dropwise, at room temperature (40 °C in case of [NH_4][ClO_4]), to a stirred solution of 0.01 mol of [1,2,3-triMeIM][HCO_3] or [*N*,*N*-diMePyr][HCO_3] in 50% aqueous ethanol (v/v, 20 mL). The mixture was stirred for an additional 24 h in a closed flask (to avoid inorganic acid evaporation) and the solvent and gaseous byproducts were evaporated on a rotary evaporator under vacuum. All samples were then dried under high vacuum at room temperature. All salts obtained were checked for the presence of starting material using ^{1}H and ^{13}C NMR, and none of the spectra revealed any residual peaks for the [HCO_3]$^-$ anion.

1,2,3-Trimethylimidazolium chloride ([1,2,3-triMeIM][Cl]). White solid, very hygroscopic, 99% yield, m.p. 71 °C, $T_{5\%dec}$= 205 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.62$ (s, 3H, C2-CH_3), 3.83 (s, 6H, N-CH_3), 7.46 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 10.38$ (C2-CH_3), 35.57 (N-CH_3), 123.26 (C4/C5), 146.45 (C2).

1,2,3-Trimethylimidazolium nitrate ([1,2,3-triMeIM][NO_3]). White crystalline solid, 98% yield, m.p. 63 °C, $T_{5\%dec}$= 259 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.60$ (s, 3H, C2-CH_3), 3.84 (s, 6H, N-CH_3), 7.43 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 10.01$ (C2-CH_3), 35.34 (N-CH_3), 123.26 (C4/C5), 146.40 (C2).

1,2,3-Trimethylimidazolium picrate ([1,2,3-triMeIM][Pic]). Yellow crystalline solid, 98% yield, m.p. 104 °C, $T_{5\%dec}$= 224 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.56$ (s, 3H, C2-CH_3), 3.76 (s, 6H, N-CH_3), 7.58 (s, 2H, C4/C5-H), 8.59 (s, 2H, picrate); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 9.48$ (C2-CH_3), 34.54 (N-CH_3), 121.82 (C4/C5), 124.03 (picrate), 125.07 (picrate), 141.73 (picrate), 144.59 (C2), 160.68 (picrate).

1,2,3-Trimethylimidazolium perchlorate ([1,2,3-triMeIM][ClO_4]). White crystalline solid, 98% yield, m.p. at $T_{5\%dec}$ (hot-stage apparatus) ~220 °C, $T_{5\%dec}$= 220 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.57$ (s, 3H, C2-CH_3), 3.77 (s, 6H, N-CH_3), 7.50 (s, 2H, C4/C5-H); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 10.00$ (C2-CH_3), 35.81 (N-CH_3), 123.36 (C4/C5), 146.35 (C2).

***N*,*N*-Dimethylpyrrolidinium chloride ([*N*,*N*-diMePyr][Cl]):.** White solid, very hygroscopic, 99% yield, m.p. at $T_{5\%dec}$ (hot-stage apparatus) ~260 °C, $T_{5\%dec}$= 231 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.26$ (t, 4H, -CH_2-), 3.20 (s, 6H, N-CH_3), 3.58 (t, 4H, N-CH_2); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 22.99$ (-CH_2-), 52.55 (t, N-CH_3), 66.95 (t, N-CH_2).

***N*,*N*-Dimethylpyrrolidinium nitrate ([*N*,*N*-diMePyr][NO_3]).** White solid, 98% yield, m.p. at $T_{5\%dec}$ (hot-stage apparatus) ~220 °C, $T_{5\%dec}$= 276 °C;^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.26$ (t, 4H, -CH_2-), 3.18 (s, 6H, N-CH_3), 3.55 (t, 4H, N-CH_2); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 22.97$ (-CH_2-), 52.45 (t, N-CH_3), 66.93 (t, N-CH_2).

***N*,*N*-Dimethylpyrrolidinium picrate ([*N*,*N*-diMePyr][Pic]).** Yellow crystalline solid, 98% yield, m.p. at $T_{5\%dec}$ (hot-stage apparatus) ~280 °C, $T_{5\%dec}$= 269 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.28$ (t, 4H, -CH_2-), 3.19 (s, 6H, N-CH_3), 3.56 (t, 4H, N-CH_2), 8.87 (s, 2H, picrate); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 22.79$ (-CH_2-), 52.69 (N-CH_3), 66.96 (N-CH_2), 127.54 (picrate), 128.52 (picrate), 142.76 (picrate), 163.52 (picrate).

***N*,*N*-Dimethylpyrrolidinium perchlorate ([*N*,*N*-diMePyr][ClO_4]).** White solid, 97% yield, m.p. at $T_{5\%dec}$ (hot-stage apparatus) ~280 °C, $T_{5\%dec}$= 254 °C; ^{1}H NMR (500 MHz, [D_4]MeOH) $\delta = 2.26$ (t, 4H, -CH_2-), 3.17 (s, 6H, N-CH_3), 3.55 (t, 4H, N-CH_2); ^{13}C NMR (125 MHz [D_4]MeOH) $\delta = 22.97$ (-CH_2-), 52.50 (N-CH_3), 66.97 (N-CH_2).

X-Ray crystallographic studies

Solid [1,2,3-triMeIM][$MeCO_3$] was crystallized out of the reaction mixture after the excess of DMC was evaporated. The crystals of [1,2,3-triMeIM][HCO_3]·H_2O and [*N*,*N*-diMePyr][HCO_3] were recrystallized from acetone, by dissolution of small amount of the sample in warm acetone, and slow cooling of the solution to room temperature.

Single crystals suitable for analysis were isolated in air, mounted on fibers, and transferred to the goniometer. The crystals were cooled to −100 °C with a stream of nitrogen gas and data were collected on a Seimens SMART diffractometer equipped with a CCD area detector, using graphite-monochromated MoKα radiation. The SHELXTL software package was used for each solution and refinement.[29] Absorption corrections were made with SADABS.[30] Each structure was refined by using full-matrix least-squares methods on F^2. All non-hydrogen atoms were readily located and their positions refined anisotropically, while all hydrogen atoms were located from difference Fourier maps and isotropically refined without restraint.

Thermal analysis

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA 2950 TA Instrument under dried air atmosphere. Samples between 5–15 mg were heated from 40–500 °C with an isocratic heating rate of 5 °C min^{-1} under air atmosphere. Decomposition temperatures ($T_{5\%dec}$) were determined from the onset to 5 wt% mass loss in an isocratic TGA experiment, which provides a more realistic representation of thermal stability at elevated temperatures.

Melting points were determined by differential scanning calorimetry (DSC) TA Instruments model 2920 Modulated DSC (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter was calibrated for temperature and cell constants using indium (mp 156.61 °C, ΔH 28.71 J g^{-1}). Data were collected at constant atmospheric pressure, using samples between

10–40 mg in aluminium sample pans. Experiments were performed with heating at a rate of 5 °C min^{-1} to the temperature 50 °C below the decomposition temperature ($T_{5\%dec}$) and then cooled down to –100 °C. This heating and cooling cycle was repeated twice for each sample. The DSC instrument was adjusted so that zero heat flow was between 0 and –0.5 mW, and the baseline drift was less than 0.1 mW over the temperature range 0–180 °C. An empty sample pan was used as reference.

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