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ARTICLE

Peralkylated imidazolium carbonate ionic liquids: synthesis using dimethyl carbonate, reactivity and structure

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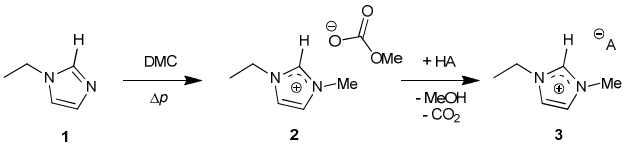
Tri- and tetraalkylimidazoles are quaternised into their corresponding ionic liquids with dimethyl carbonate. Upon metathesis of the obtained methyl carbonate salts, only gaseous by-products are generated. These methyl carbonate salts can be transformed in the hydrogen carbonate by reaction with water. The salts containing a carbonate anion are very alkaline, which results in a hydrogen/deuterium exchange on the anion and some of the cation protons, dependent on the substitution. Moreover, the crystalline 1-ethyl-3,4,5-trimethylimidazolium hydrogen carbonate formed carboxylate species upon dissolution. This particulate carboxylate was able to regenerate the carbene and in the presence of chloroform, this led to the formation of the chloride salt.

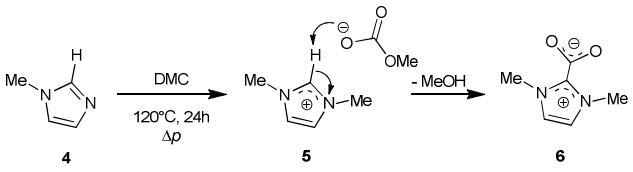
Introduction

The interest in the synthesis of ionic liquids by the quaternisation of organic bases with dimethyl carbonate (DMC) was initiated some 20 years ago by the work of Albert and Mori.[1, 2] This methylating agent is environmently friendly because of both its synthesis and its biodegradability.[3] DMC is synthesised from CO and MeOH over a Cu(I) catalyst, a method developed by Enichem, Italy.[4] Further, the quaternisation of neutral building blocks with DMC leads to methyl carbonate ionic liquids. By addition of the Brønsted acid of an anion of choice, the methyl carbonate anion decomposes into MeOH and CO_2 and the ionic liquid with the conjugate base as anion is obtained (Scheme 1). The quaternisation proceeds via a nucleophilic alkylation reaction ($S_{N,Al}$), which is performed at temperatures above 120 °C. At lower temperatures, a reversible acylation reaction is initiated by a nucleophilic attack on the carbonyl centre of dimethyl carbonate ($S_{N,Ac}$). Therefore, the alkylation reaction is most often performed in an autoclave or a sealed vial, in which the autogenous pressure keeps the DMC in the liquid phase (T_b of DMC: 90 °C).[3]



Scheme 1: Quaternisation of imidazoles with DMC with formation of carbonate salt and metathesis towards a library of imidazolium salts.

The group of Holbrey and Rogers reported on the formation of zwitterionic carboxylates in high yields during reaction of 1-methylimidazole **4** with DMC.[5] The formation is attributed to an $S_{N,Al}$ mechanism and deprotonation of the imidazolium cation **5** by the $[MeCO_3]^-$ anion. The *N*,*N*'-dimethylimidazolium carboxylate **6** is solid and sufficiently stable to precipitate from solution (Scheme 2).



Scheme 2: Formation of the zwitterionic carboxylate (**6**) by reaction of 1-methylimidazole with dimethyl carbonate.[5]

In general, imidazolylidene carbenes have a very high affinity for CO_2 and therefore, 2*H*-imidazolium ionic liquids combined with basic anions (e.g. [C_4mim][OAc]) are excellent for the chemisorption of carbon dioxide.[6-9] The zwitterionic carboxylates themselves are also of particular interest in ionic liquid synthesis, as they have already been applied as such in synthesis,[10] but also as easy to handle pre-catalysts[11] and as CO_2 transfer reagents in carboxylation reactions.[12-14] Furthermore, the carboxylates have been used as intermediates in the synthesis of hydrogen carbonate ionic liquids.[15] Alternatively, these hydrogen carbonate salts can be prepared by oxidation of formate salts over a Pd catalyst.[16] A library of hydrogen carbonate ionic liquids is currently commercially available to be applied in Carbonate Based Ionic Liquid Synthesis (CBILS©).

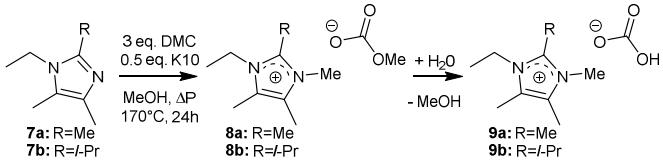
In this research, the application of dimethyl carbonate in the quaternisation of fully substituted imidazoles was investigated. First of all, the reaction conditions, i.e. temperature, reagent stoichiometry and reaction times were optimised to obtain a complete conversion. Subsequently, the composition of the reaction mixtures as well as the structure of the reaction products was analysed. Some of these reaction products showed remarkable reactivity. Finally, the application of the carbonate ionic liquids in metathesis reactions was examined.

Results and Discussion

Quaternisation of 2-alkylimidazoles

High temperatures were required since alkylation demands temperatures above 120 °C (preferably above 160 °C), and alkylated imidazoles are amongst the least reactive organic bases. Therefore, thick wall pressure vials were used, which were submerged in an oil bath. Since the temperature resistance of the screw caps was limited to 180 °C and exceding this temperature led to the rupture and explosion of the pressure vials, the reaction temperature was set at 170 °C (CAUTION).

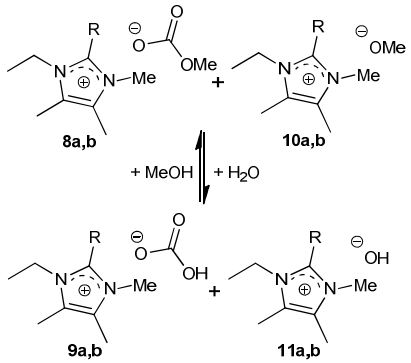
The 2-alkyl-1-ethyl-4,5-dimethylimidazoles (**7a** and **7b**, Scheme 3) were synthesised using a previously reported procedure.[17] They were completely converted into the corresponding ionic liquids upon pressurised heating with 3 equiv. of DMC for 24 hours at 170 °C, although a crude reaction mixture was obtained. Addition of a small amount of MeOH (1.5 equiv.), improved the contact between the neutral imidazole and DMC. Together with the addition of a Lewis acid catalyst, the formation of side products could be suppressed. Thus, K10 Montmorillonite clay was introduced in the reaction mixture as a catalyst without activation. The K10 clay could successfully be recovered by filtration, circumventing contamination of the ionic liquids. After filtration, the catalyst was dried and recycled, and proved equally active as in the first runs.



Scheme 3: Quaternisation of tetraalkylimidazoles.

After reaction, very dark mixtures were obtained and to reduce this colouration lower temperatures and shorter reaction times were investigated. Evaluation of the reaction temperature during quaternisation of **7b** showed that at 150 °C after 3 and 6 hours, 15 and 22% of the endproduct was obtained respectively. At a reaction temperature of 170 °C, after 3 and 6 hours, 65 and 75% of the endproduct **8b** were formed. Hence, to obtain a complete conversion of both 1-ethyl-2,4,5-trimethylimidazole **7a**, and 2-isopropyl-4,5-trimethylimidazole **7b**, the mixtures were heated for 24 hours at 170 °C. The product could then be isolated by filtration and by washing a CH_3CN solution with Et_2O or by aqueous extraction from a EtOAc solution.

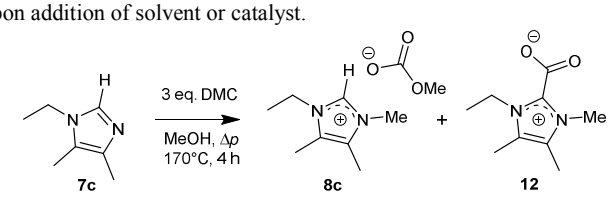
In the ^{13}C NMR spectrum of the filtrated and mildly evaporated reaction mixture, MeOH, $[MeCO_3]^-$ (59, 157 ppm) and $[OMe]^-$ (59 ppm) were observed. The $[MeCO_3]^-$ salts (**8**) were found not to be stable without the presence of methanol for all cations investigated. Upon evaporation, mixtures of methyl carbonate **8** and hydrogen carbonate **9** ($[HCO_3]^-$ signal at 160 ppm) were formed, and eventually completely transformed to the hydrogen carbonate salt over time. Upon addition of water and subsequent evaporation, the equilibrium shifts to the hydrogen carbonate salt **9** or the hydroxide salt **11**, since MeOH has a lower boiling point. After evaporation at 100 °C at 0.5 mbar, none of the former signals were visible in the ^{13}C NMR spectrum. Therefore, it is anticipated that in this case the carbon dioxide is lost and results in the formation of methoxide/hydroxide salts.



Scheme 4: Solvent dependent conversion of the anion in peralkylated imidazolium carbonate ionic liquids. (**8-11a**: R = Me, **8-11b**: R = *i*-Pr).

Quaternisation of 2H-imidazoles

The 1-ethyl-2*H*-4,5-dimehylimidazole (**7c**) was found to be completely converted to different products upon quaternisation with DMC at 170 °C in a thick wall pressure vial. Here, no reaction was observed at 140°C, while at 145°C, 40% was converted after 4 hours and at 170°C, the conversion was completed after 4 hours. In contrast to the 2-alkyl analogues **7a-b**, no improvement on the reaction outcome was observed upon addition of solvent or catalyst.



Scheme 5: Quaternisation of 1-ethyl-2H-4,5-dimethylimidazole **7c** with dimethylcarbonate and formation of the carboxylate zwitterion **12**.

A solid fraction of the residue obtained after solvent evaporation was found to be only soluble in chlorinated solvents, protic solvents, and in hot acetonitrile. Recrystallisation in an CH_3CN:acetone (3:1) mixture led to consecutive crops (up to 4 times, total yield 40-50%). Analysis of the mixture by ^1H NMR in $CDCl_3$ revealed the presence of 2 major compounds, being the hydrogen carbonate salt **9c** and the carboxylate **12**. In CD_3OD, the methyl carbonate **8c** and an amount (< 10%) of the carboxylate were observed, while in D_2O only the hydrogen carbonate salt **9c** was observed.

Upon analysis of the crystals by ^1H NMR in $CDCl_3$, the ratio of the compounds (**9c** and **12**) was always ca. 3:1 respectively and was stable over time (72 hours). Upon mild heating of the $CDCl_3$ solution (60°C, 2 hours), the amount of carboxylate **12** decreased, to eventually disappear. The group of Rogers have observed earlier the presence of two components (the carboxylate and methyl carbonate salt) in DMSO-d_6 NMR spectra of $[C_4mim][MeCO_3]$, and attributed this to the presence of these two compounds in the reaction mixture.[18]

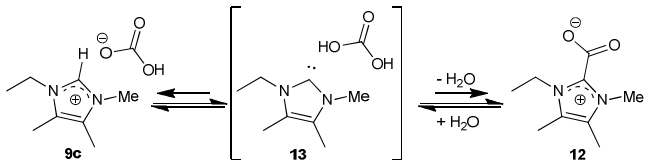
Nonetheless, single crystal X-ray diffraction data showed that the obtained crystals consist entirely of the pure 1-ethyl-3,4,5-trimethylimidazolium hydrogen carbonate salt ($[C_2m_3im][HCO_3]$, **9c**). The compound crystallised in the centro-symmetric space group *P*-1. The asymmetric unit of the structure consists of one $[C_2m_3im]^+$ cation and one $[HCO_3]^-$ anion. The $[HCO_3]^-$ anions form dimers by hydrogen

bonding around crystallographic inversion centers (Figure 2). However, the crystals did not contain the crystal water reported by the group of Rogers.[10, 15] The hydrogen atom bound to O1 does not show an elongated bond (0.95(3) Å) or a disorder, as often noticed for carbonate dimers.[15]

Given the formation of the pure [C_2m_3im][HCO_3] salt (**9c**) as a crystalline solid, the carboxylate zwitterion **12** observed in a $CDCl_3$ solution is formed in situ by thermodynamic stabilisation and water expulsion (Scheme 6). Since no CO_2 liberation occurs upon dissolution of the crystalline [C_2m_3im][HCO_3] and most of the carbonate anions can be regenerated from the carboxylate, it seems that the imidazolylidene carbene immediately forms a carboxylate. As the chances of dissolved CO_2 and a free carbene colliding are very slim, the decomposition of H_2CO_3 might be promoted by the nucleophilic carbene,[19] to form the carboxylate at once (negligible lifetime of compound **13**). This can be supported by the calculated energies of formation for carboxylates from carbenes and CO_2, which show no activation energy barrier at all.[20]

Although the carboxylate is thermodynamically favoured over the hydrogen carbonate[15] and even more stable when the *N*-substituents are not bulky and allow for a planar *p*-orbital overlap,[20] it was not possible to isolate the carboxylate as a solid. This is attributed to the hygroscopicity of the carboxylate, forming the more energetically favoured hydrogen carbonate salt as this is able to lose the lattice energy upon solidification.

In the case of the 2*H*-imidazolium salts, a conversion of the methyl carbonate **8c** into the hydrogen carbonate **9c** salt was found, analogous to the case of the 2-alkylimidazolium salts (Scheme 4). The solid product **9c** is removed from the equilibrium and its formation is dependent on the reaction with air moisture or water present in the reaction or recrystallisation solvents, explaining the successive low yielding crops of crystalline [C_2m_3im][HCO_3]. The $[OH]^-$ and $[OMe]^-$ anions were not experimentally observed in combination with the 2*H*-imidazolium cation. Firstly, the 2*H*-imidazolium hydroxides are unstable (non-existing)[21] and secondly, alkoxide anions are unlikely to be formed in the presence of the imidazolylidene carbene,[20] although [C_4mim][OMe] was earlier reported by Seddon and Earle.[22]

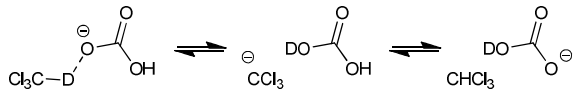


Scheme 6: Acid-base equilibrium between hydrogen carbonate imidazolium salt (**9c**) and the unstable carbene (**13**) which is trapped as the corresponding carboxylate (**12**).

Reactivity of the carbonate salts

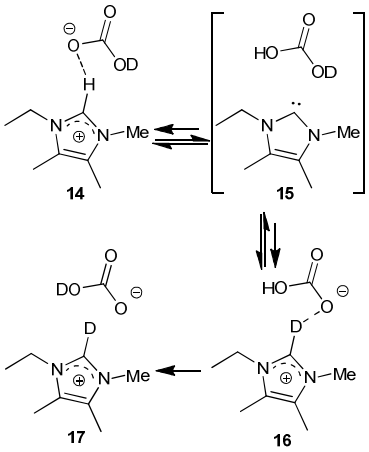
The ^{1}H NMR analysis of any of the tetra- or penta-alkyl-imidazolium $[HCO_3]^-$ salts in deuterated solvents (D_2O, CD_3OD, $CDCl_3$ or CD_3CN) did never reveal the $[HCO_3]^-$ proton due to hydrogen/deuterium (H/D) exchange with the solvent (Scheme 7).

Aromatic ^{1}H NMR signals of the 2*H*-imidazolium carbonate salts (**8c**, **9c**) (indicating a C2 proton) were only found for the entries containing starting imidazole (at 7.30 ppm) and for salts to which a Brønsted acid was added (after metathesis).



Scheme 7: H/D exchange reaction of the hydrogen carbonate anion in deuterated chloroform.

Spectra of freshly prepared or concentrated carbonate ionic liquids in $CDCl_3$ solutions did reveal the aromatic signal (integrating for less than one proton). Therefore, the absence of the aromatic singlets is attributed to hydrogen/deuterium exchange of the C2-H with the deuterated solvent, promoted by the basicity of the anions (Scheme 8). The loss of this singlet is experimentally confirmed in $CDCl_3$ (pK_a: ±15)[23], but also in CD_3CN (pK_a: ±31),[24] although they have been reported in literature at 9.6 ppm in DMSO-d_6 (pK_a: ±35).[15, 24] Remarkably, also the signals of the imidazolium 2-methyl group of compounds **8a** and **9a** were often not visible or reduced in ^{1}H NMR and diffuse in ^{13}C NMR spectra. In the 1-ethyl-2-isopropyl-3,4,5-trimethylimidazolium cation, none of the hydrogens were exchanged.



Scheme 8: Equilibrium of the carbonate ionic liquid with the carbene and fast H/D-exchange in deuterated solvents.

In the case of the solid 2*H*-imidazolium hydrogen carbonate salt (**9c**), mild heating and/or extensive evaporation of the $CDCl_3$ solution lead to the reduction of the carboxylate and the $[HCO_3]^-$ signals in the ^{13}C NMR spectrum. The signals eventually disappear completely, indicating the loss of CO_2. After evaporation of the $CDCl_3$ mixture, the residue was again a solid and could be recrystallised. The crystals obtained were analysed by single crystal X-ray diffraction and are found to consist of the [C_2m_3im][Cl] salt.

The compound **18c** crystallised in the centro-symmetric space group $P2_1/c$. The asymmetric unit of the structure consists of one $[C_2m_3im]^+$ cation and one $[Cl]^-$ anion (Figure 1). The ethyl group is found almost planar with the imidazolium ring (C1-N1-C7-C8 torsion angle of -8.5(2)°).

The formation of the chloride salt is explained by the alkaline action of the salts on (deutero)chloroform residues originating from NMR sampling or recrystallisation (Scheme 9). Upon abstraction of the proton of $CHCl_3$, one chloride is expelled to form dichlorocarbene, which forms consecutively the unstable dichloromethanol and formyl chloride. The latter decomposes rapidly into carbon monoxide (CO) and hydrogen

chloride. Overall, three $[OH]^-$ anions are converted to three $[Cl]^-$ anions, with formation of water and carbon monoxide.[25]

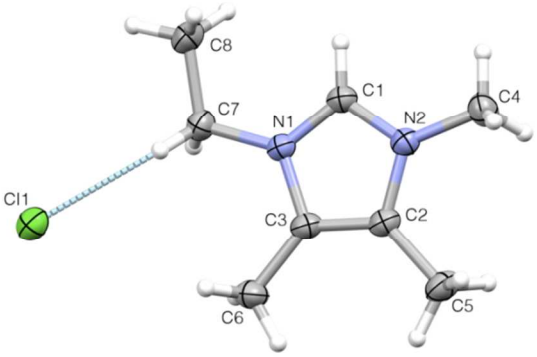
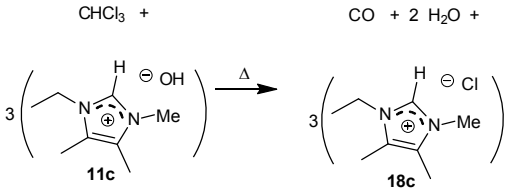


Figure 1: Asymmetric unit in the crystal structure of **18c**, showing thermal displacement ellipsoids at the 30% probability level and atom labeling scheme. The hydrogen bond between the $[C_2m_3im]^+$ cation and the $[Cl]^-$ anion is indicated.

In contrast to the H/D exchange, the formation of the $[Cl]^-$**18c** salt is not readily established, i.e. ^{13}C NMR spectra of carbonate salts can be recorded in $CDCl_3$. On the contrary, it demands evaporation and heating. The proton transfer required during carboxylate formation and H/D exchange in $CDCl_3$ prove that both the imidazolium cation and $CDCl_3$ can be deprotonated.

The 2-methylimidazolium and 2-isopropylimidazolium chloride salts (**18a** and **18b**) could not be retrieved in the same way. Although for the $[C_2C_1m_3im]$ salt, some decomposition of the cation was observed, the $[HCO_3]^-$ signal remained visible by ^{13}C NMR. It seems that the imidazolylidene carbene is necessary to accomplish degradation of chloroform. Therefore it is proposed that during the heating process, the carbonate decomposition is aided by the carboxylate formation, eventually leading to the basic carbene, prior to chloroform decomposition.

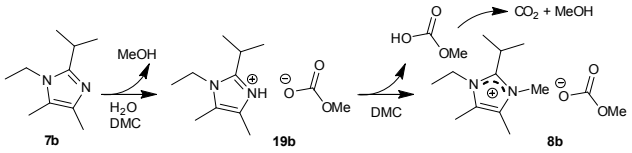
The chloride **18c** and carbonate **8c** salts could be distinguished by their large difference in melting points and by infrared absorption spectra. Furthermore, once the $[Cl]^-$ salt is formed, the aromatic singlet could be emerged in the ^1H NMR spectrum after shaking the $CDCl_3$ solution with a drop of water (Scheme 8). This is not the case for the carbonate salts, as this would lead to $CHCl_3$ formation.



Scheme 9: Formation of the 1-ethyl-2*H*-3,4,5-trimethylimidazolium chloride salt (**18c**).

N-protonated imidazoles

When the reaction of 1-ethyl-2-isopropyl-4,5-dimethylimidazole (**7b**) with dimethyl carbonate was stopped after 3 or 6 hours, 15% to 75% of the end product was observed in the ^1H NMR spectra (*vide supra*). These spectra also revealed the presence of protonated imidazoles (**19**), which are proposed to be formed by neutralisation of $MeOCO_2H$, originating from the hydrolysis of DMC (
Scheme **10**). Formation of $MeOCO_2H$ during work-up could be excluded since the protonated imidazoles were not always found in experiments where unreacted imidazole was still present. This indicates that (i) elevated temperatures are needed for the substitution reaction of DMC by water, (ii) a significant amount of DMC is consumed by water present in the mixture and (iii) protonated imidazoles can react further by the presence of the basic anions in the reaction mixture.[26, 27]



Scheme 10: Formation of imidazolium hydrogen methyl carbonate**19b** via hydrolysis of DMC. The protonated imidazole can be methylated to form the *N*-methyl imidazolium methyl carbonate salt (**8b**).

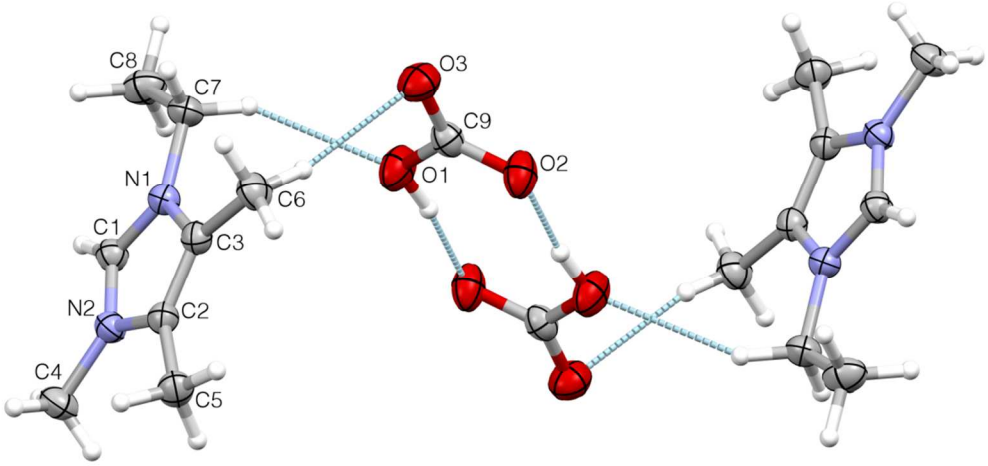


Figure 2: Hydrogen-bonded $[C_2m_3im][HCO_3]$ dimers in the crystal structure of **9c**, showing thermal displacement ellipsoids at the 30% probability level and atom labelling scheme of the asymmetric unit. Hydrogen bonds are indicated.

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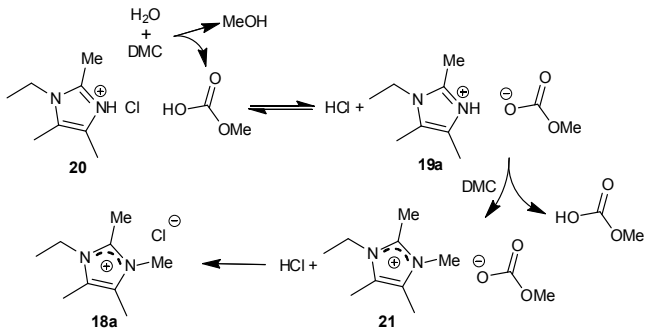
The proposed hypothesis was verified with imidazole **7a** by reacting 1-ethyl-2,4,5-trimethyl imidazolium hydrochloric salt (**20**) with dimethyl carbonate (Scheme 11). Although analogous protonated imidazolium salts could not be quaternised with methyl iodide, these salts could be successfully quaternised using dimethyl carbonate. Here, this is probably due to catalytic amounts of water present, since **19a** can be formed by an anion exchange between **20** and **21**. The reaction to form **18a**, proceeded very clean, quantitatively and was completed in 3 hours, giving an opaque powder, of which single crystal X-ray diffraction data could be recorded. The compound crystallised in the centro-symmetric space group *R*-3. The asymmetric unit of the structure consists of one $[C_2C_1m_3im]^+$ cation and one $[Cl]^-$ anion (Figure 1). The fast formation of this chloride **18a** suggests that other alkylating species might have been formed (e.g. MeCl), or that a strong (auto)catalytic effect of the imidazolium species is present. This catalytic effect of imidazolium salts was earlier demonstrated in the alkylation with dialkylcarbonates of ammonium halide and nitrate salts.[28]



Scheme 11: Quaternisation and *in situ* metathesis of **20** via neutralisation by the methyl carbonate anion.

In contrast to the previous structure of **18c**, the ethyl group is oriented almost perpendicular to the imidazolium ring (C1-N1-C8-C9 torsion angle of 95.8(2)°), due to steric hindrance by the presence of the extra methyl group.

Upon opening of the sealed pressure vial, a substantial amount of CO_2 evolved, independent on the cation type. Since the carbonate anion was found in substantial amounts, the CO_2 does not originate from anion decomposition into CO_2 and $[OMe]^-$, as stated by Tundo.[29] Later, Holbrey *et al*. posed that the anion only decomposes upon protonation,[5] which can be confirmed by the present work, i.e. carbonate anions do not degrade during the reaction or over time.

Metathesis of the CILs

After crystallisation and filtration of 1-ethyl-2*H*-3,4,5-trimethylimidazolium hydrogen carbonate ($[C_2m_3im][HCO_3]$) salts, they could be applied successfully in metathesis reactions with the Brønsted acid aqueous $HNTf_2$ (80%) or the ammonium dicyanamide salt. Hereby, CO_2 gas evolved and the temperature of the mixtures slightly increased. To assure complete reaction, the carbonate salts were stirred with a small excess of the metathesis agent in distilled water and heated to 50°C overnight. ^{1}H NMR analysis of these salts showed that the imidazolium ring proton signals were completely regenerated.

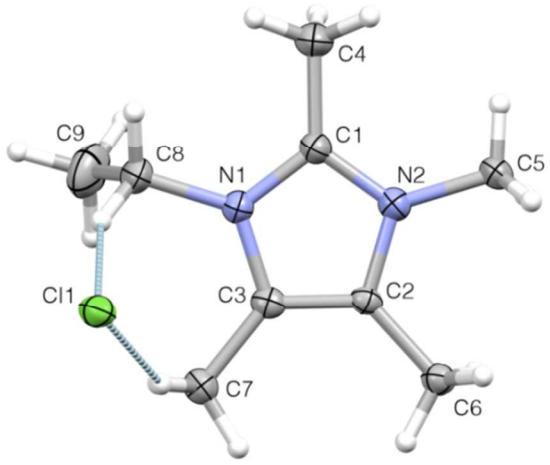
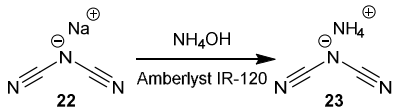


Figure 1: Asymmetric unit in the crystal structure of **18a**, showing thermal displacement ellipsoids at the 50% probability level and atom labelling scheme. Hydrogen bonds between the $[C_2C_1m_3im]^+$ cation and the $[Cl]^-$ anion are indicated.

The most straightforward metathesis reaction is with aqueous $HNTf_2$. The use of $HNTf_2$, which is cheaper with regard to its lithium salt, is also more environmentally benign as carcinogenic quaternisation agents can be substituted by dimethyl carbonate and no stoichiometric amounts of lithium halide salts are formed as a by-product. Here, a small excess of the super acid leads to rapid and complete conversion, while the remainder of the acid can be evaporated.

Dicyanamide salts could not be obtained via the corresponding Brønsted acid. Therefore, ammonium dicyanamide was synthesised by percolating a $NaN(CN)_2$ solution through an acidic ion exchange resin with high sodium affinity, which was neutralised with an ammonium solution prior to the exchange reaction (Scheme 12).[30] After evaporation of the collected aqueous solution, $NH_4N(CN)_2$ was obtained as a white powder in good purity (as analysed by elemental analysis). After metathesis in aqueous medium, the excess ammonium dicyanamide could be precipitated from a solution of the evaporated residue at -18 °C.



Scheme 12: Metathesis with ammonia to form ammonium dicyanamide ($NH_4N(CN)_2$) via an ion exchange resin.

Conclusion

Completely substituted imidazoles can successfully be methylated in a green way using dimethyl carbonate. Although K10 Montmorillonite is found to be an excellent catalyst, which allows complete conversion without formation of side products. Still, very high temperature are needed, which lead to very intense colouration. Purification is straightforward in the case of the 2*H*-imidazolium salts, this product is solid and can be recrystallised to obtain a colourless compound. In the case of the liquid 2-substituted imidazolium salts, the product can be washed with Et_2O in CH_3CN or with EtOAc in demineralised water.

The carbonate anions are stable and do not readily decompose under ambient conditions. The formation of anions by loss of carbon dioxide was observed (for 2-alkyl-imidazolium salts), unless a carboxylate can be formed (for $[C_2m_3im][HCO_3]$). This carboxylate is formed from a carbene, which reacts immediately with the mutually formed H_2CO_3. The carbene derived from $[C_2m_3im][HCO_3]$ has a very high affinity for CO_2 and the resulting carboxylate is thermodynamically favoured, although unstable in contact with air or nucleophilic and protic solvents. The presence of the carboxylate in the reaction mixture was confirmed by ^{1}H NMR analysis in CD_3OD, while the amount is strongly dependent on the solvent. Most likely, the carbonate salts are stabilised by H-bonding. Thus, the formation of the carboxylate is more pronounced in chloroform and is anticipated to be the crucial step in chloroform decomposition to form the chloride anion. The formation of chloride salts with chloroform is only found for $[C_2m_3im][HCO_3]$. Nonetheless, it was found that the 2-alkyl-imidazolium hydrogen salts can be methylated, leading to methylated salts combined with the right anion at once.

The carbonate salts are reactive species, which will transform when dissolved in different solvents or left open at ambient air. Thus, [imidazolium][$MeCO_3$] forms the [imidazolium][HCO_3] when in contact with air moisture or water present in the solvents. Since this conversion is possible with all of the imidazolium cation types, the carboxylate is not necessary. The conversion of the $[MeCO_3]^-$ to the $[HCO_3]^-$ anion is observed in water, while in the presence of methanol, the methyl carbonate anion is stable. In the case of the extracted 2-alkyl-imidazolium salts, also $[OH]^-$ of $[OMe]^-$ can be present, which make NMR based quantification difficult during metathesis.

Experimental Section

Procedure for the synthesis of ammonium dicyanamide (23): A glass column was packed with 2.74 g of Amberlite IR120 in distilled water (column height: 3.5 cm). The resin was slowly percolated with a 1 M NH_4Cl solution (200 mL) until the effluent stream pH, monitored by pH indicator paper, had raised to that of the influent. Subsequently, the column was rinsed with aq. dest. (75 mL) until the effluent samples did no longer show precipitation upon addition of $AgNO_3$. Sodium dicyanamide (2 mmol, 178 mg) was dissolved in aq. dest. (40 mL) and MeOH (20 mL), and this solution was percolated very slowly over the column. The percolated solution and the rinsing water (aq. dest., 20 mL) were subjected to lyophilisation to yield the ammonium dicyanamide. Elemental analysis calcd (%) for $C_2H_4N_4$: C 28.57, H 4.80, N 66.64; found: C 27.83, H 4.49, N 64.82; yield: 95%; white powder. At elevated temperatures, decomposition rather than fusion occurs.

Procedure for the synthesis of 1-ethyl-2-isopropyl-3,4,5-trimethylimidazolium hydrogen carbonate $[C_2C_{i3}m_3im][HCO_3]$ (9a): A flame-dried glass 14 mL pressure vial was filled with MeOH (5 mmol, 160 mg), dimethyl carbonate (30 mmol, 2.7 g), 1-ethyl-2-isopropyl-4,5-dimethylimidazole (10 mmol, 1.67 g), Montmorillonite K10 (0.83 g) and a PTFE stirring bar. The pressure vial was flushed with nitrogen, closed and submerged in a preheated oil bath at 170 °C. After 24 hours, the vial was allowed to cool and opened, the mixture was diluted in methanol and filtrated over a filter paper (Euro Scientific, 90 mm) on a sintered glass filter. The solvents were removed by rotary evaporation at room temperature. The resulting oil was brought into 10 mL of demineralised water and stirred at **50** °C. After 3 hours, the mixture was cooled and the water and methanol were removed via lyophilisation or rotary evaporation. The different spectral data sets of the 1-ethyl-2-isopropyl-3,4,5-trimethylimidazolium carbonate salts were obtained by dissolving these crystals in different solvents. As the liquid analogues are extremely hygroscopic, density and viscosity were not measured.

1-Ethyl-3,4,5-trimethylimidazolium hydrogen carbonate $[C_2m_3im][HCO_3]$ (9c+12): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = (maj.): δ = 1.49 (t, ^3J(H,H) = 7.2 Hz, 3H; CH_2CH_3), 2.23 (s, 3H; $CH_3C^{4/5}$), 2.24 (s, 3H; $CH_3C^{4/5}$), 3.87 (s, 3H; NCH_3), 4.19 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2CH_3), 10.07 ppm (s; C^2H), (min.): δ = 1.42 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_2CH_3), 2.24 (s, 3H; $CH_3C^{4/5}$), 2.26 (s, 3H; $CH_3C^{4/5}$), 3.97 (s, 3H; NCH_3), 4.51 ppm (q, ^3J(H,H) = 7.1 Hz, 2H; CH_2CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): (maj.): δ = 8.29 ($CH_3C^{4/5}$), 8.38 ($CH_3C^{4/5}$), 15.31 (CH_2CH_3), 33.53 (NCH_3), 42.22 (CH_2), 125.90 ($C^{4/5}$), 127.03 ($C^{4/5}$), 136.30-136.59 (m, C^2), 160.86 ppm ($[HCO_3]^-$), (min.): δ = 8.52 ($CH_3C^{4/5}$), 8.73 ($CH_3C^{4/5}$), 15.76 (CH_2CH_3), 33.24 (NCH_3), 41.65 (NCH_2), 124.44 ($C^{4/5}$), 125.79 ($C^{4/5}$), 141.58 (C^2), 156.04 ppm (CO_2); **IR** (ATR): δ = 625, 985, 1203, 1342, 1377, 1570, 1617, 2341, 2360, 3386 (broad) cm^{-1}; **MW** (g mol^{-1}): 200.24; yield: 52%, colourless crystals, **T_m** (°): 41.

1-Ethyl-3,4,5-trimethylimidazolium hydrogen carbonate $[C_2m_3im][HCO_3]$ (9c):^{1}H NMR (300 MHz, D_2O, 25 °C, ACN): δ = 1.43 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_2CH_3) , 2.21 (s, 3H; $CH_3C^{4/5}$), 2.23 (s, 3H; $CH_3C^{4/5}$), 3.71 (s, 3H; NCH_3), 4.08 ppm (q, ^3J(H,H) = 7.3 Hz, 2H; NCH_2); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.78 ($CH_3C^{4/5}$), 7.92 ($CH_3C^{4/5}$), 14.65 (CH_2CH_3), 33.46 (NCH_3), 42.41 (NCH_2), 127.16 ($C^{4/5}$), 128.06 ($C^{4/5}$), 132.92 (C^2), 161.61 ppm (HCO_3).

1-Ethyl-3,4,5-trimethylimidazolium methyl carbonate $[C_2m_3im][CH_3CO_3]$ (8c): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.52 (t, ^3J(H,H) = 7.4 Hz, 3H; CH_2CH_3), 2.24 (s, 3H; $CH_3C^{4/5}$), 2.26 (s, 3H; $CH_3C^{4/5}$), 3.55 (s, 3H; CH_3CO_3), 3.88 (s, 3H; NCH_3), 4.20 (q, ^3J(H,H) = 7.4 Hz, 2H; CH_2CH_3), 10.43 ppm (s; C_2H); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.23 ($CH_3C^{4/5}$), 15.19 (CH_2CH_3), 33.44 (NCH_3), 42.19 (NCH_2), 52.28 (CH_3O), 126.05 ($C^{4/5}$), 127.11 ($C^{4/5}$), 136.28 (C^2), 158.76 ppm (C=O).

1-Ethyl-2,3,4,5-tetramethylimidazolium hydrogen carbonate $[C_2C_1m_3im][HCO_3]$ (9a): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.31 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_2CH_3) , 2.23 (s, 3H; $CH_3C^{4/5}$), 2.24 (s, 3H; $CH_3C^{4/5}$), 2.70 (s, 3H, C^2CH_3), 3.71 (s, 3H; NCH_3), 4.15 ppm (q, ^3J(H,H) = 7.3 Hz, 2H; CH_2CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.50 ($CH_3C^{4/5}$), 8.75 ($CH_3C^{4/5}$), 10.23 (C^2CH_3), 14.93 (CH_2CH_3), 32.15 (NCH_3), 40.55 (NCH_2), 124.69 ($C^{4/5}$), 126.08 ($C^{4/5}$), 142.07 (C^2), 160.27 ppm (HCO_3); **IR** (ATR): δ = 740, 1372, 1626, 2928, 3390 cm^{-1}; **MW** (g mol^{-1}): 214.26; yield: 47%, transparent crystals, **T_m** (°): 37.

1-Ethyl-2-isopropyl-3,4,5-trimethylimidazolium hydrogen carbonate $[C_2C_{i3}m_3im][HCO_3]$ (9b): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.36 (t, ^3J(H,H) = 7.4 Hz, 3H; CH_2CH_3), 1.51 (t, ^3J(H,H) = 7.1 Hz, 6H; $CH(CH_3)_2$), 2.27 (s, 6H; $CH_3C^{4/5}$), 3.58-3.72 (m, 1H; $CH(CH_3)_2$), 3.83 (s, 3H; NCH_3), 4.24 ppm (q, ^3J(H,H) = 7.4 Hz, 2H; CH_2CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.69 ($CH_3C^{4/5}$), 8.86 ($CH_3C^{4/5}$), 15.73 (CH_2CH_3), 19.30 ($CH(CH_3)_2$), 25.16 ($CH(CH_3)_2$), 32.98 (NCH_3),

40.87 (NCH_2), 125.15 ($C^{4/5}$), 127.15 ($C^{4/5}$), 147.43 (C^2), 160.41 ppm (HCO_3); **IR** (ATR): δ= 1334, 1385, 1522, 1649, 3388 cm^{-1}; **MW** (g mol^{-1}): 242.32; yield: 89%, brown oil.

1-Ethyl-3,4,5-trimethylimidazolium chloride [C_2m_3im][Cl] (18c): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ= 1.55 (t, J^3(H,H) = 7.3 Hz, 3H; CH_2CH_3) , 2.26 (s, 3H; $CH_3C^{4/5}$), 2.27 (s, 3H; $CH_3C^{4/5}$), 3.95 (s, 3H; NCH_3), 4.24 (q, J^3(H,H) = 7.3 Hz, 2H; CH_2CH_3) 10.74 ppm (s, 1H; C^2H); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ= 8.47 ($CH_3C^{4/5}$), 8.55 ($CH_3C^{4/5}$), 15.42 (CH_2CH_3), 33.85 (NCH_3), 42.45 (NCH_2), 125.98 ($C^{4/5}$), 127.08 ($C^{4/5}$), 136.27 ppm (C^2); IR (ATR): δ= 1200, 1252, 1457, 1572, 1637, 2342, 2362, 2953, 3390 cm^{-1}; **MW** (g mol^{-1}): 174.67; **elemental analysis** calcd (%) for $C_8H_{15}ClN_2$: C 55.01, H 8.66, N 16.04; found: C 54.32, H 8.75, N 15.79; yield: 81%, opaque powder, **T_m** (°): 54.

1-Ethyl-2,3,4,5-Tetramethylimidazoliumchloride [$C_2C_1m_3im$][Cl] (18a): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ= 1.40 (d, ^3J(H,H) = 7.4 Hz, 3H; CH_2CH_3), 2.26 (s, 6H; $CH_3C^{4/5}$), 2.94 (s, 3H; C^2CH_3), 3.87 (s, 3H; NCH_3), 4.23 ppm (q, J^3(H,H) = 7.4 Hz, 2H; CH_2CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C, TMS): δ= 8.70 ($CH_3C^{4/5}$), 8.99 ($CH_3C^{4/5}$), 11.18 (C^2CH_3), 15.12 (CH_2CH_3), 32.89 (NCH_2), 41.07 (NCH_3), 124.69 ($C^{4/5}$), 126.16 ($C^{4/5}$), 142.45 ppm (C^2); IR (ATR): δ= 1091, 1346, 1446, 1649, 2978, 3393 cm^{-1}; **MW** (g mol^{-1}): 188.70; yield: 99%, white powder, **T_m** (°): 59.

Procedure for the synthesis of 1-ethyl-2-isopropyl-3,4,5-trimethylimidazolium bis(trifluorosulfonyl)amide [$C_2C_{i3}m_3im$][NTf_2]: An excess (1.1 equiv., for full conversion) of hydrogen bis(trifluorosulfonyl)imide ($HNTf_2$) was added to a vigorously stirred aqueous solution (cont. 20% CH_3CN) of freshly prepared [$C_2C_{i3}m_3im$][HCO_3], taking the weight into account of completely converted imidazole. The acid was added dropwise to prevent acid evaporation induced by the exothermic reaction. During addition, gas (CO_2) evolution was visible. The mixture was allowed to stir for 30 minutes at room temperature after which the solvents were evaporated. Slow crystallisation of the liquor occurred in a sealed flask at room temperature. Spectral data of the compound was consistent with the data to be found in the experimental part of reference [17].

Procedure for the synthesis of 1-ethyl-2-isopropyl-3,4,5-trimethylimidazolium dicyanamide [$C_2C_{i3}m_3im$][$N(CN)_2$]: To an aqueous solution (cont. 20% CH_3CN) of freshly prepared [$C_2C_{i3}m_3im$][HCO_3] (taking the weight into account of completely converted imidazole), was added an excess (1.1 equiv., for full conversion) of $NH_4N(CN)_2$. The reaction was stirred at room temperature for 24h. After metathesis, the mixture was evaporated, consecutively dissolved in methanol and again evaporated. The excess ammonium dicyanamide could be precipitated from an $CHCl_3$ solution of the evaporated residue at -18 °C. Spectral data of the compound was consistent with the data to be found in the experimental part of reference [17].

Single crystal X-ray diffraction

For the structures of compounds **9c**, **18c** and **18a**, X-ray intensity data were collected on a Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using CuK α radiation (λ = 1.54178 Å) and ω scans. The images were interpreted and integrated with the program CrysAlisPro (CrysAlisPro, Agilent Technologies, Version 1.171.36.28, Agilent Technologies). Using Olex2,[31] the structure was solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on F^2 using the ShelXL program package.[32] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U (eq.) of the parent atoms (1.5 times for methyl groups and the hydroxyl group), with the C/O-H distances free to refine. All hydrogen atoms could be unambiguously located from a difference Fourier electron density map. CCDC 967637-967639 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystal data for compound 9:. $C_9H_{16}N_2O_3$, M = 200.24, triclinic, space group P-1 (No. 2), a = 6.9516(3) Å, b = 8.1294(3) Å, c = 9.6234(4) Å, α = 74.586(4)°, β = 80.157(4)°, γ = 83.657(3)°, V = 515.35(4) $Å^3$, Z = 2, T = 293(2) K, ρ_{calc} = 1.290 g cm^{-3}, μ(Cu-Kα) = 0.806 mm^{-1}, F(000) = 216, 8198 reflections measured, 2005 unique (R_{int} = 0.0187) which were used in all calculations. The final R1 was 0.0387 ($I>2\sigma(I)$) and wR2 was 0.1125 (all data).

Crystal data for compound 18c: $C_8H_{15}ClN_2$, M = 174.67, monoclinic, space group $P2_1/c$ (No. 14), a = 6.77997(17) Å, b = 14.4971(4) Å, c = 9.8785(3) Å, β = 100.572(3)°, V = 954.48(5) $Å^3$, Z = 4, T = 293(2) K, ρ_{calc} = 1.215 g cm^{-3}, μ(Cu-Kα) = 3.066 mm^{-1}, F(000) = 376, 4198 reflections measured, 1807 unique (R_{int} = 0.0261) which were used in all calculations. The final R1 was 0.0366 ($I>2\sigma(I)$) and wR2 was 0.1064 (all data).

Crystal data for compound 18a: $C_9H_{17}ClN_2$, M = 188.70, trigonal, space group R-3 (No. 148), $a = b$ = 19.8873(6) Å, c = 14.4048(4) Å, V = 4933.9(4) $Å^3$, Z = 18, T = 100(2) K, ρ_{calc} = 1.143 g cm^{-3}, μ(Cu-Kα) = 2.702 mm^{-1}, F(000) = 1836, 10529 reflections measured, 2230 unique (R_{int} = 0.0529) which were used in all calculations. The final R1 was 0.0399 ($I>2\sigma(I)$) and wR2 was 0.0981 (all data). Disordered solvent peaks (probably from aceton or diethylether) were omitted from the refinement model with the Squeeze procedure in Platon.[33]

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Notes and references

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