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Ionic Liquids

N-Heterocyclic Olefin–Carbon Dioxide and –Sulfur Dioxide Adducts: Structures and Interesting Reactivity Patterns

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Abstract: Depending on the amount of methanol present in solution, CO_2 adducts of N-heterocyclic carbenes (NHCs) and N-heterocyclic olefins (NHOs) have been found to be in fully reversible equilibrium with the corresponding methyl carbonate salts [EMIm][OCO_2Me] and [EMMIm][OCO_2Me]. The reactivity pattern of representative 1-ethyl-3-methyl-NHO–CO_2 adduct **4** has been investigated and compared with the corresponding NHC–CO_2 zwitterion: The protonation of **4** with HX led to the imidazolium salts [NHO–CO_2H][X], which underwent decarboxylation to [EMMIm][X] in the presence of nucleophilic catalysts. NHO–CO_2 zwitterion **4** can act as an efficient carboxylating agent towards CH acids such as acetonitrile. The [EMMIm] cyanoacetate and [EMMIm]$_2$ cyanomalonate salts formed exemplify the first C—C bond-forming carboxylation reactions with NHO-activated CO_2. The reaction of the free NHO with dimethyl carbonate selectively led to methoxycarbonylated NHO, which is a perfect precursor for the synthesis of functionalized ILs [NHO–CO_2Me][X]. The first NHO-SO_2 adduct was synthesized and structurally characterized; it showed a similar reactivity pattern, which allowed the synthesis of imidazolium methyl sulfites upon reaction with methanol.

Introduction

Employing dimethyl carbonate as a mild and non-poisonous methylation agent for nucleophilic cation precursors is by far the most widely applicable way to synthesize ionic liquids (ILs) in a sustainable metal- and halide-free fashion.[1] This route towards methyl-onium methyl carbonates tolerates a vast number of starting nucleophiles, the only requirements being the thermal stability of the reagent towards elevated temperatures of around 130 °C and the stability of the resulting IL cations towards the basic and nucleophilic, potentially weakly solvated methyl carbonate anion and unselective cation carboxylations. In this respect, pentamethylguanidine is one of the few nucleophiles not suitable: A hexamethylguanidinium cation is attacked, whereas the sterically more protected methyl-pentaalkylguanidinium cations are inert towards nucleophilic attack of methyl carbonate at 130 °C.[1g] 1-Alkylimidazoles as nucleophiles are at the borderline of usability, as the ring protons of the resulting N-heterocyclic cations are sufficiently acidic to be engaged in follow-up reactions. This requires careful elucidation of the procedure to find reaction conditions that yield only the desired 1-alkyl-3-methylimidazolium methyl carbonate salts.[1a] If their methyl carbonate anions are not stabilized by solvating hydrogen bridges, for example, in methanol solution, these salts tend to decompose to form imidazolium-carboxylate zwitterions.[1f,j] The latter are formed by the deprotonation of the imidazolium cation and attack of the in situ generated NHC on CO_2, and have proven to be highly versatile reagents themselves. Specifically, the imidazolium-2-carboxylates can be employed as proto-carbenes in the formation of transition-metal complexes,[2] act as CO_2 transfer reagents and organocatalysts,[3] and can still be used as masked carbenes for the synthesis of ILs by reaction with sufficiently acidic reagents.[1f,4] The specific conditions that allow the removal of the CO_2 moiety to generate a reactive carbene or the original imidazolium cation have been thoroughly investigated.[2b,3a,b,5] Owing to their fascinating properties, access to these NHC inner salts has been studied extensively. Considering the sometimes ambiguous results, it has to be noted that the exact dependence of the product on the reaction conditions is still not fully understood. According to literature reports, imidazolium-2-carboxylates can be prepared selectively by feeding gaseous CO_2 into a solution of the corresponding carbene,[6] directly from 1-methylimidazole and dimethyl carbonate,[1f,4c] by continuous flow at 200 °C over an Al_2O_3 catalyst,[7] and even at ambient temperature by introducing CO_2 into imidazolium acetate ILs.[8] Specifically, the first and last approaches allow extension to imidazolium-2-thio- and dithiocarboxylates.[9] The usually undesired 4- and 5-carboxylates, which are associated with the so-called abnormal carbenes,[10] are typically formed at elevated temperatures,[11] but have also been witnessed at temperatures as low as 120 °C.[12] Recent investigations have shown that their formation is also dependent upon the partial pressure of CO_2 and the basicity of the reaction mixture.[13]

The introduction of a methyl group at the 2-position of the imidazolium ring, which is also accompanied by a distinct elevation of the melting point, is typically regarded as a protection

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against undesired side-reactions due to the acidic proton. Recent investigations have shown that a much more sophisticated substitution pattern is necessary to create imidazolium cations that are stable towards strong nucleophiles and bases such as the hydroxide ion over a period of time, even if they are solvated.[14] It has also been proven that the formation of contact ion pairs in solvents of medium polarity allows hydrogen/deuterium exchange to occur at the apical methyl group.[15] However, starting from methyl carbonate salts, so far carboxylate formation has not been observed at the apical methyl group.[1e] However, it has already been noted that the 2-methyl group shows decreased or diffuse ^{1}H NMR signals in the presence of hydrogen or methyl carbonate anions,[16] which can be attributed to hydrogen/deuterium exchange. These results imply the intermediate formation of an *N*,*N*-ketene diacetal or N-heterocyclic olefin (NHO),[17] for example, **7** in Scheme 1. The selective synthesis of such imidazolium-2-methylenecarboxylates was achieved conveniently from the in situ generated NHOs and CO_2. These compounds have proven to be efficient organocatalysts for the carboxylative cyclization of CO_2 and propargylic alcohols to yield α-alkylidene cyclic carbonates.[18] The procedure can be extended to COS and CS_2 adducts;[19] the effect of the imidazolium substitution pattern on the reactivity was investigated in detailed computational studies.[20] The NHOs, which are generated in situ and most likely the active species in these catalytic cycles, have also been employed as highly basic starting materials for the synthesis of ionic liquids[21] and as polymerization catalysts for propylene oxide,[22] methyl methacrylate,[23] and lactones.[24] They are also versatile organocatalysts for transesterification[25] and base-promoted alkylation reactions.[26] Furthermore, they are interesting ligands in main-group and transition-metal complexes.[27]

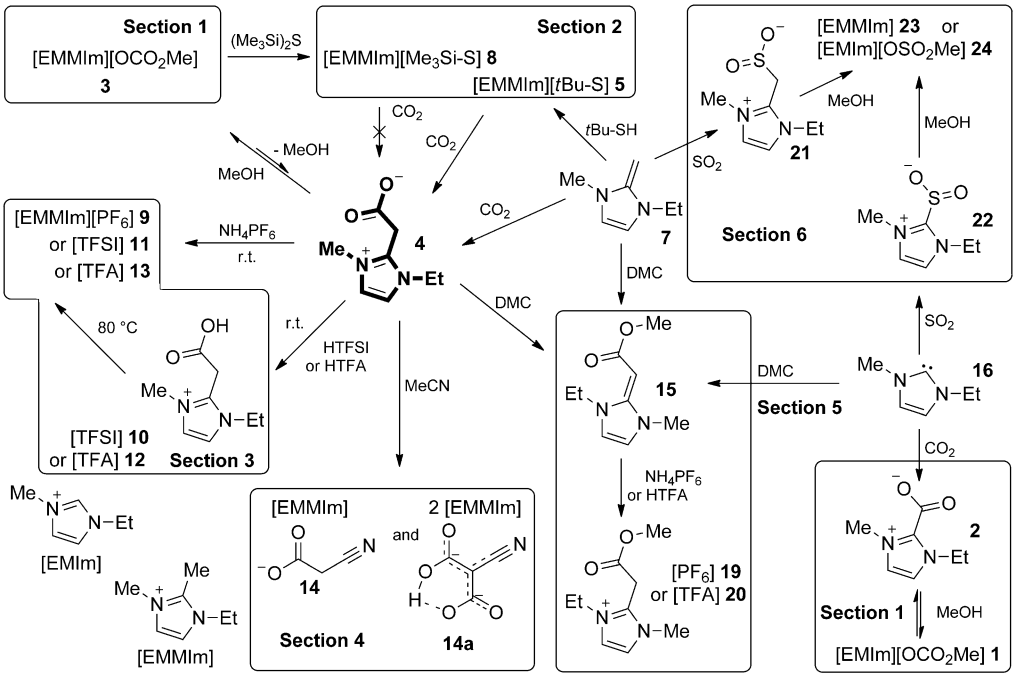
During our investigations, which were primarily concerned with the preparation of organic salts with hydrochalcogenide and trimethylsilylchalcogenolate anions,[1i,j] we noticed a selective and easy access to imidazolium-2-carboxylates and discovered that 1,3-dialkyl-2-methylimidazolium methyl carbonate salts form carboxylate zwitterions as well. As a consequence we investigated whether these zwitterionic imidazolium-2-methylenecarboxylates, formally NHO–CO_2 adducts, to some extent show comparable reactivity to the well-known imidazolium-2-carboxylates, formally NHC–CO_2 adducts, with regard to the preparation of ionic liquids and in C–C coupling reactions.

Results and Discussion

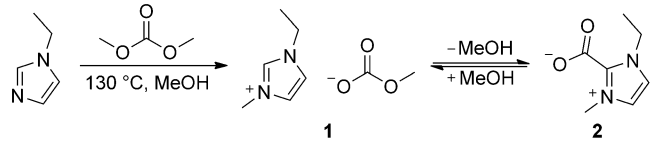
Scheme 1 gives an overview of the results described in this manuscript. Details concerning the particular reactions can be found in the corresponding sections indicated in the scheme.

1. Formation of imidazolium-2-carboxylate and imidazolium-2-methylenecarboxylate

It has proven advantageous to prepare 1-alkyl-3-methylimidazolium methyl carbonate salts from the corresponding alkylimidazole and dimethyl carbonate in the presence of methanol, which not only accelerates the methylation but also prevents the formation of undesired 4-carboxylates.[1a] As the resulting solutions typically contained some excess dimethyl carbonate and small amounts of colored impurities,[1d] we chose to isolate the respective salts by evaporation of the methanol solvent and recrystallization of the solid residue from acetonitrile. During these preparations we noticed that in the case of 1-ethyl-3-methylimidazolium (EMIm) methyl carbonate



Scheme 1. Overview of the results presented in this manuscript. EMIm = 1-ethyl-3-methylimidazolium, EMMIm = 1-ethyl-2,3-dimethylimidazolium, TFA = trifluoroacetate, TFSI = bis(trifluoromethylsulfonyl)imide, DMC = dimethyl carbonate.



Scheme 2. Known synthesis of EMIm methyl carbonate (**1**) and equilibrium between **1** and NHC–CO_2 adduct **2** at room temperature.

(**1**), even at ambient temperature only the respective 2-carboxylate (**2**) was obtained (Scheme 2). In view of the high basicity of the methyl carbonate anion and the instability of the forming methyl carbonic acid, this has to be expected.

The driving force of this reaction is the removal of methanol under vacuum, which slowly shifts the methyl carbonate/carboxylate equilibrium towards **2**. The reaction proved to be perfectly reversible in NMR experiments. The process can be compared with the removal of acetic acid in the gas stream of CO_2 introduced into imidazolium acetate ILs.[8a]

The NMR spectra in Figure 1 clearly show that the imidazolium-carboxylate (**2**, marked by *) is not primarily formed during the solvothermal synthesis, and that only minimum amounts prevail in the reaction mixture along with the main product imidazolium methyl carbonate (**1**, marked by ^). Spectrum A also shows large amounts of methanol and dimethyl carbonate and minor amounts of ethylimidazole that did not react. Only if the solvent was removed did the carboxylate form to a larger extent (B) until, after thorough drying and recrystallization, the pure carboxylate was obtained (C). If an excess of methanol (eight equivalents in this instance) was added to the NMR sample of C, the carboxylate was very quickly transformed back to the methyl carbonate. Despite the large excess of eight equivalents of methanol, around 10% of the carboxylate zwitterion remained in the NMR sample even after several hours, which allowed us to conclude that equilibrium conditions are reached and only a larger excess will allow the full regeneration of the methyl carbonate. With respect to green IL synthesis protocols, this additional information is important as zwitterion **2** does not show an equally high activity in proton-induced decarboxylation reactions as the methyl carbonate salt **1**.[1f,4a] In our investigation of hydrochalcogenide ILs,[1k] we also noticed that higher concentrated methanol solutions of carboxylate **2** reacted significantly more slowly than dilute solutions containing only the methyl carbonate salt. A mixture of nonseparable products may be the undesirable consequence in these IL syntheses.

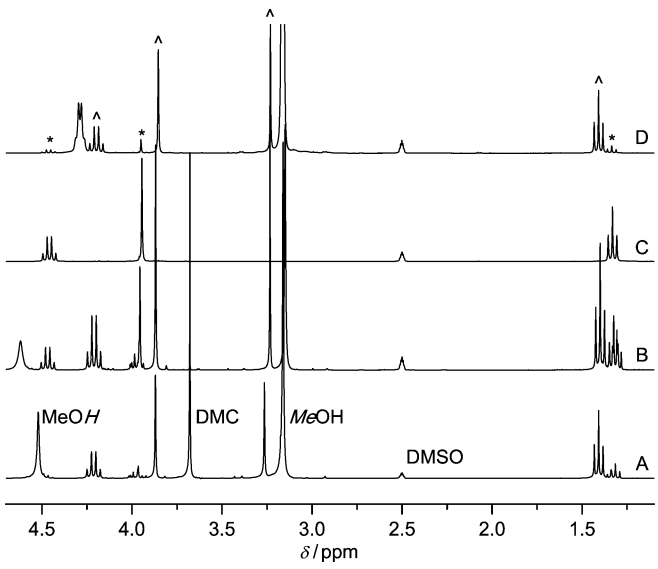
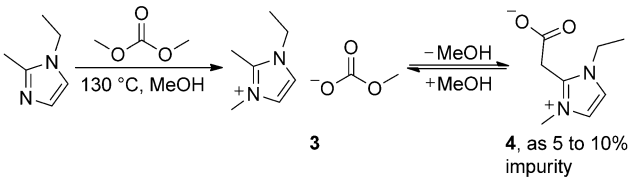


Figure 1. ^{1}H NMR spectra (300.1 MHz, [D_6]DMSO) of A) the reaction mixture of Scheme 2 directly after the solvothermal synthesis, B) the residue of the reaction mixture after removing most of the solvent, C) the isolated adduct NHC–CO_2 **2** after recrystallization, and D) the sample of C with an excess of methanol (**1**).

The 2-methylated 1-ethyl-2,3-dimethylimidazolium (EMMIm) cation in **3** showed an analogous highly selective reaction pattern, although its equilibrium with zwitterion **4** was not as pronounced as in the case of imidazolium cations bearing a proton at the 2-position (Scheme 3). During the preparation



Scheme 3. Preparation of EMMIm methyl carbonate (**3**) and partial equilibrium between **3** and NHO–CO_2 adduct **4** at room temperature.

of **3** we noticed the formation of slightly varying amounts (5–10%) of a side-product after work-up, which we later on identified as the corresponding NHO–CO_2 adduct 1-ethyl-3-methylimidazolium-2-methylenecarboxylate (**4**).

Analogously to the preceding synthesis, this side-product was not present in the crude reaction mixture (Figure 2, A) but was formed at ambient temperature upon evaporating all volatile components and recrystallizing from a acetonitrile/diethyl ether solvent mixture, as indicated by the small additional signals at 3.62 and 3.72 ppm (Figure 2, B). When the recrystallized compound mixture was heated at 80 °C under a CO_2 atmosphere (1 bar) or in a vacuum, a significant increase of the 2-methylenecarboxylate species compared with the original methyl carbonate salt was observed. However, this did not allow convenient synthesis of the pure product. To gain access to a pure reference sample of the carboxylate **4** (Figure 2, C), the procedure of Wang et al.[18a] starting from NHO and CO_2 was employed. Even with this pure standard **4** dissolved in DMSO, immediate back-formation of the methyl carbonate salt was observed upon addition of excess methanol (Figure 2, D).

These observations led to a partial reinterpretation of previous results, in which the formation of carboxylate impurities was traced back solely to the elevated reaction temperatures.[1e] The authors avoided the formation of carboxylate impurities by decreasing the reaction temperature to 70 °C while extending the reaction time to 10 days. This might shift the reaction path from thermodynamic to kinetic control. On at-

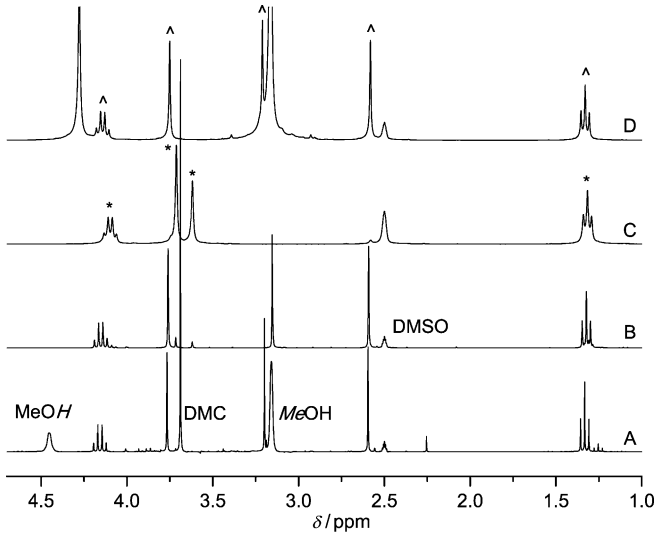
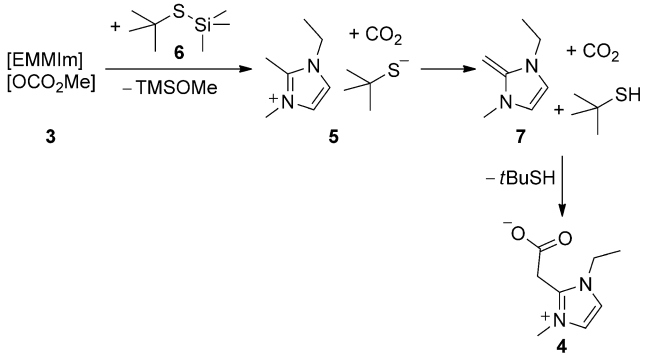


Figure 2. ^{1}H NMR spectra (300.1 MHz, [D_6]DMSO) of A) the reaction mixture of Scheme 3 directly after the solvothermal synthesis in MeOH (130 °C), B) the residue of the reaction mixture after removing most of the solvent, C) the isolated adduct EMMIm-CO_2 **4**, synthesized according to reference [18a] and D) the sample of C with an excess of methanol (**3**).

tempting to reproduce this low-temperature methylation by DMC in a sealed glass ampoule we observed only a low conversion to a variety of unidentified products. None of these was the anticipated methyl carbonate salt. It is known that methoxycarbonylation by DMC is preferred at temperatures of around 90 °C. Only if a reaction mixture is heated to above 120 °C under solvothermal conditions does DMC act as a methylation agent.[28] With the findings presented here, we are convinced that the progressive removal of methanol induces two effects working hand-in-hand: Less well solvated methyl carbonate anions act as a stronger base and the elimination of the reaction product methanol shifts the equilibria of these thermodynamically controlled (reversible) carboxylations quantitatively towards the formation of the adduct NHC–CO_2 or partly towards NHO–CO_2 even at room temperature.

2. Effect of anion basicity on the reactivity of the EMMIm cation towards CO_2

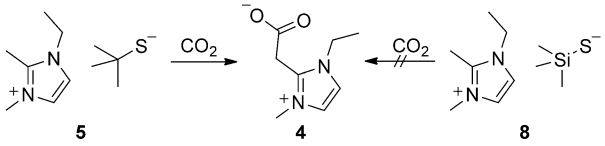
It was anticipated that increased anion basicity would allow the formation of higher amounts of the NHO–CO_2 adduct **4**. This is exemplified by our attempted synthesis of 1-ethyl-2,3-dimethylimidazolium *tert*-butylthiolate (**5**) from the corresponding methyl carbonate precursor. In contrast to H_2S,[1i,k] the weaker acid *t*BuSH was not deprotonated by 1-ethyl-2,3-dimethylimidazolium methyl carbonate in MeOH to any amount detectable by ^{1}H NMR spectroscopy. Apparently, the solvated anion *t*BuS^-(MeOH) is more basic than $MeOCO_2^-$(MeOH). To gain some extra driving force by Si–O bond formation, we employed methyl carbonate as a nucleophilic desilylating agent[1j] of *t*BuS-TMS (**6**) under aprotic conditions. As expected, TMS-OMe was formed in acetonitrile, however, the basic alkylthiolate anion formed initially apparently deprotonated the 2-methylimidazolium cation to form the NHO **7**, which rapidly reacted with the CO_2 released in the previous reaction step to form zwitterionic carboxylate **4** (Scheme 4).



Scheme 4. Attempted synthesis of 1-ethyl-2,3-dimethylimidazolium *tert*-butylthiolate (**5**) in acetonitrile.

As a result, instead of the anticipated thiolate salt, the 2-methylenecarboxylate **4** was isolated in a yield of 36% as the pure crystallized compound. Compound **5** was later on synthesized by treating the in situ prepared NHO with *tert*-butyl mercaptan. The 2-methylimidazolium cation was stable towards unsolvated *tert*-butylthiolate anion, but only in the absence of CO_2 as the NHO trapping agent. In contrast, the reaction of the imidazolium methyl carbonate **3** with bis(trimethylsilyl) sulfide led to the imidazolium trimethylsilylthiolate **8** in good yield and acceptable purity. The only impurity was unreacted zwitterion **4** (ca. 5%), which was formed as a side-product in the synthesis of the EMMIm methyl carbonate starting material.

Subsequently, we established a competition experiment (Scheme 5). Salt **5** containing the stronger *tert*-butylthiolate



Scheme 5. Different reactivities of **5** and **8** towards CO_2.

base was carboxylated in acetonitrile at 20 °C to the adduct NHO–CO_2 **4**, whereas **8** containing the weaker TMS-thiolate base was not carboxylated: After passing CO_2 over a solution of **5** for 30 min, a conversion to **4** of 32% could be observed by ^{1}H NMR monitoring.

The structures of all three imidazolium compounds in Scheme 5 were elucidated by single-crystal X-ray structure determination. Figure 3 depicts the structure of the *tert*-butylthiolate salt **5**, which is characterized as a hydrogen-bonded dimer. A discussion of the structure of **5** and a comparison with the analogous trimethylsilylthiolate salt **8** is presented in the Supporting Information.

3. Decarboxylation behavior of the adduct NHO–CO_2 4

Imidazolium-2-carboxylates have already proven valuable starting materials for the synthesis of ionic liquids under protic con-

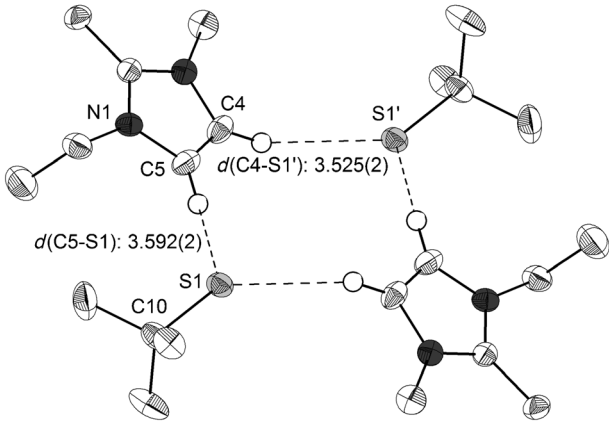
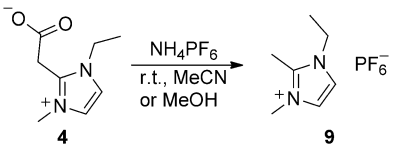


Figure 3. Molecular structure of the hydrogen-bonded dimer of [EMMIm][*t*BuS] (**5**). Hydrogen-bond (donor–acceptor) distances are shown in Å. The disordered position of *t*BuS$^-$ and the THF solvate molecule of **5** are not shown for clarity. Ellipsoids are shown at the 50% probability level. Symmetry operation: I: $-x+1$, $-y+2$, $-z+2$.

ditions.[4a,c] The strong solvent dependence of the decarboxylation was investigated by Denning and Falvey.[5b] For us, the question arose as to whether the 2-methylenecarboxylate **4** can be analogously used for the synthesis of the corresponding organic EMMIm salts upon reaction with Brønsted acids. The observation that the formation of **4** is reversible upon the addition of methanol in DMSO strongly pointed to this possibility. Consequently, we treated **4** with bis(trifluoromethylsulfonyl)imide (HTFSI), trifluoroacetic acid (HTFA), and NH_4PF_6 in methanol and acetonitrile. From the reaction with NH_4PF_6 the expected decarboxylation product [EMMIm][PF_6] (**9**) was isolated in quantitative yield (Scheme 6).



Scheme 6. Synthesis of [EMMIm][PF_6] (**9**) from NHO–CO_2 adduct **4** and NH_4PF_6.

However, the reaction of **4** (Figure 4, spectrum A) and bis(trifluoromethylsulfonyl)imide (HTFSI) at ambient temperature, regardless of the reaction time and the solvent (methanol or acetonitrile), led to only a marginal amount of the anticipated product (Figure 4, spectrum B).

Around 90% of the sample was a hitherto unknown cationic species that shows all the signals of the preceding zwitterion, but at different chemical shifts. In the ^{1}H NMR spectra especially, the resonance signal of the CH_2 group adjacent to the carboxylate moiety is shifted strongly downfield. Furthermore, an additional signal appeared that had to be assigned to a proton with a certain degree of dynamic motion due to its broadened appearance and chemical shift at around 15 ppm. All the findings indicate the formation of the stable carboxylic acid intermediate [NHO–CO_2H][TFSI] (**10**). The small amount of the final product was attributed to the presence of isomeric 4- and 5-carboxylates, which were formed as minor side-products in the preparation of **4** and apparently reacted with the strong acid by immediate decarboxylation. The detection of the intermediate cation of **10** by ESI (+) mass spectrometry was not possible (only the decarboxylated cation was observed), but the IR spectra confirmed the presence of C=O and O–H bonds. Analogous results were obtained from the reaction of **4** with trifluoroacetic acid. Apparently, under specific conditions, the CO_2 elimination is kinetically hindered for the NHO–CO_2 adduct. However, the decarboxylation occurred quickly upon heating the reaction mixture at 60–80 °C (Figure 4, spectrum C). Overall, a temperature-dependent reaction of **4** with strong acids has to be considered (Scheme 7).

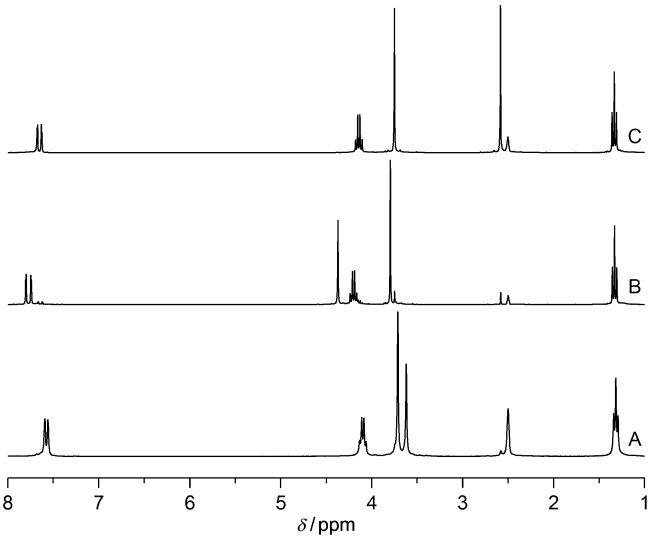
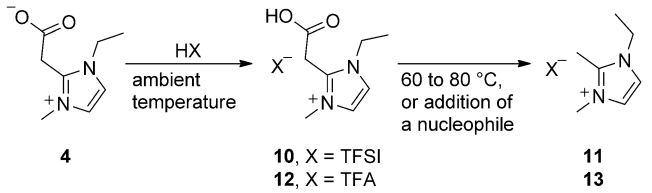


Figure 4. ^{1}H NMR spectra (300.1 MHz, [D_6]DMSO) of A) NHO–CO_2 **4**, B) the reaction mixture between NHO–CO_2 **4** and HTFSI after 4 days at ambient temperature (**10**) and C) the same reaction mixture after a further 3 h at 80 °C (**11**).



Scheme 7. Reactions of NHO–CO_2 adduct **4** with trifluoroacetic acid and bis(trifluoromethylsulfonyl)imide in methanol or acetonitrile.

This result is surprising in view of our previous observation that **4** can be converted into EMMIm methyl carbonate (**3**) by methanol in DMSO at ambient temperature. Weak acids seem to promote a decarboxylation path, which is hampered by a higher activation barrier for strong acids. It is presumed that this reactivity difference can be correlated with the nucleophilicity of the particular conjugate base and that CO_2 elimination does not occur in a spontaneous unimolecular fashion but de-

mands the attack of a nucleophile at the carboxylate carbon atom, similar to the Krapcho decarboxylation.[29] Accordingly, better nucleophiles such as DMSO or NH_3 present in equilibrium with NH_4^+ will allow a faster reaction, whereas weak nucleophiles such as TFA and TFSI anions under acidic conditions lead to a significant increase of the activation barrier. This theory has been substantiated by the observation that the addition of substoichiometric amounts (30 mol%) of nucleophilic catalysts such as 4-dimethylaminopyridine leads to the formation of the anticipated imidazolium salts **11** and **13** at ambient temperature. A related observation was made by Rogers and co-workers, who noticed that 1,3-dimethylimidazolium-2-carboxylate reacted with almost all acids by decarboxylation to form the corresponding 1,3-dimethylimidazolium salts, but that upon reaction with nitric acid a carboxylic acid intermediate was formed as a very stable intermediate. This could be transformed to the desired IL by either heating at 140 °C or by dissolving the substance in DMSO, which allowed the transformation at ambient temperature.[4a]

These observations led us to conclude that under most circumstances the possible formation of the carboxylate will not influence the preparation of ILs with Brønsted acid reagents. However, care has to be taken if the methyl carbonate salt is isolated prior to follow-up reactions and if the anion that is to be introduced shows a low nucleophilicity. With these prerequisites it is mandatory to carry out the reaction at elevated temperatures to avoid contamination of the final product with carboxylate impurities.

4. NHO–CO_2 adduct 4 as carboxylation agent for acetonitrile

During a preliminary exploration of the reaction of the CO_2-masked NHO **4** with CH acidic reaction partners, we noticed an interesting C–C coupling of CO_2 and MeCN. Heating the weakly soluble zwitterion **4** in acetonitrile yielded a readily soluble orange oil that slowly solidifies upon thorough drying at 5×10^{-3} mbar. The substance was identified as 1-ethyl-2,3-dimethylimidazolium cyanoacetate (**14**) from its NMR and MS spectra. Furthermore, a small amount of the cyanomalonate salt **14a**, which results from a second deprotonation and attack at CO_2, was present (Scheme 8). The cyanomalonate salt **14a** appears to be formed in equilibrium with the main product cyanoacetate **14** and the NHO–CO_2 adduct **4**, as it was found in almost identical percentages (ca. 10%), regardless of the reaction temperature, reaction time, and initial NHO–CO_2 concentration in acetonitrile. If **14a** was the final product and not in equilibrium with **14**, the amount formed should vary significantly for different reactant dilutions (the concentration of **4** in acetonitrile was varied from 0.034 to 1.68 mol L^{-1}). This equilibrium was also formed in DMSO solution. When pure **14a** was dissolved in [D_6]DMSO, the compound immediately started to dissociate into **14** and the NHO–CO_2 adduct **4**. When equimolar amounts of pure NHO–CO_2 adduct **4** and isolated cyanoacetate **14** were combined in [D_6]DMSO, an analogous product mixture was formed consisting of **4**, **14**, and **14a** in the approximate percentages 35, 48, and 17%, respectively (see the Supporting Information for details).

To conveniently separate the two salts the raw product was triturated with dichloromethane, which selectively dissolved **14** but not the dianion-based salt **14a**. The isolated yields were 64% for **14** and 10% for **14a**. The structure of salt **14a** was characterized by single-crystal X-ray diffraction; its molecular structure is depicted in Figure 5 and discussed in the Supporting Information.

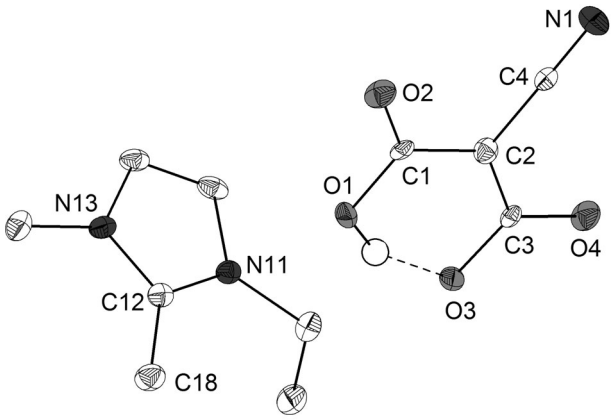
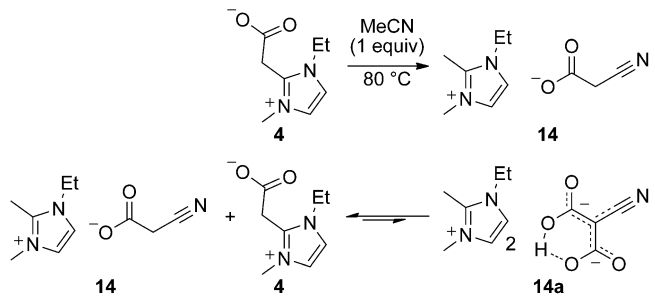


Figure 5. Molecular structure of [EMMIm]$_2$[NC-C(CO$_2$)$_2$H] (**14a**). The second cation molecule, the cation hydrogen atoms, and a disordered position of the anion have been omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances [Å] and angles [°]: C1–O1 1.327(3), C1–O2 1.247(3), C1–C2 1.427(3), C2–C3 1.443(3), C2–C4 1.433(3), C4–N1 1.154(4), C3–O3 1.309(3), C3–O4 1.253(3), O1-H1···O3 2.432(2), O1-C1-O2 119.9(2), C1-C2-C3 124.1(2), O3-C3-O4 122.0(2), C2-C4-N1 179.2(2).



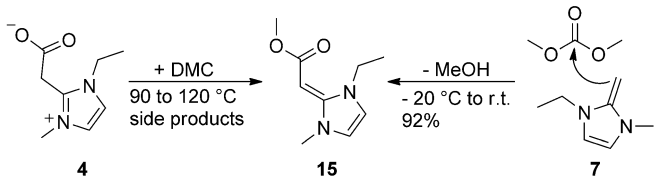
Scheme 8. Formation of the imidazolium cyanoacetate **14** and cyanomalonate **14a** from **4** and acetonitrile.

These reactions serve as the first examples of an N-heterocyclic olefin (NHO) acting as an organic mediator for C–C bond-coupling *C*-carboxylations of CH-acidic positions by NHO-activated CO_2. A related C–O bond formation has been described by Wang and co-workers who employed NHO–CO_2 adducts as catalysts for the *O*-carboxylation of propargylic alcohols and propylene oxides to obtain cyclic α-alkylidene and propylene carbonates, respectively.[18a,19] The carboxylation of acetonitrile was also observed with a 1,3-di-*tert*-butylimidazolium-2-carboxylate.[30] In contrast to the NHO–CO_2 adduct **4**, the NHC–CO_2 adduct **2** did not lead to such a selective carboxylation of acetonitrile, even under solvothermal conditions at 120 °C. These observations are in accord with the interpretation that the *tert*-

butyl-substituted carbene (van Ausdall)[30] and NHO (this work) are sufficiently basic to assist the deprotonation of the CH acid whereas NHC **16** is not basic enough. The same appears to be true for the corresponding EMMIm methyl carbonate salt **3**, which did not lead to the carboxylation of acetonitrile at 80 °C. The preliminary results presented here require a more detailed investigation of NHO mediated—in the presence of strong inorganic bases maybe even NHO catalyzed—carboxylations of CH acidic compounds.

5. Further C–C coupling reactions of the NHO–CO_2 adduct 4

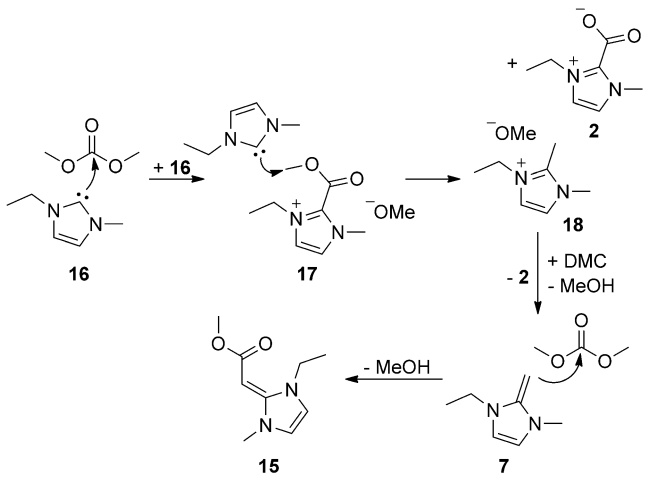
We also treated the NHO–CO_2 adduct **4** with dimethyl carbonate hoping for either a selective *O*-methylation or, after decarboxylation, a *C*-methoxycarbonylation or *C*-methylation of the NHO. The latter reaction would be related to known NHC chemistry, precisely a methylation/deprotonation/methylation at the 2-position of an NHC–CO_2 adduct, which was observed by Annese et al. and in sum led to a 2-ethylation by dimethyl carbonate at high temperatures.[31] However, at temperatures of 190 or 150 °C, the reaction of **4** with dimethyl carbonate led to a rather unselective decomposition of the reactants. Neither by NMR spectroscopy nor by ESI mass spectrometry did we find evidence for a *C*-methylation leading to a 2-ethylimidazolium derivative. Upon further decreasing the reaction temperature a partly selective reaction could be achieved. The reaction of **4** with dimethyl carbonate at 90 °C resulted in a mixture of only three compounds. One of the major components of the mixture was identified as the methoxycarbonylated NHO **15** (Scheme 9).



Scheme 9. Reactivity of NHO **7** and its CO_2 adduct **4** with dimethyl carbonate (DMC).

The relative amount of this component **15** and also the number of side-reactions increased when the reaction temperature was set to 120 °C. Compound **15** may be formed in two ways, for example, by methylation of the carboxylate moiety and consequent deprotonation of the cation by the formed methyl carbonate anion. However, as pointed out before, dimethyl carbonate does not typically act as a methylation agent below 120 °C. The alternative is a temperature-induced decarboxylation of the NHO–CO_2 zwitterion, the in situ formation of the NHO, and consequent attack of this nucleophile at the central carbon atom of DMC. During a nucleophilic substitution reaction at the carbonyl group and in the presence of available protons, methanolate may act as a leaving group deprotonating the imidazolium moiety to form **15**. This scenario is supported by the observation that the corresponding unsubstituted NHO **7**, generated in situ from [EMMIm]Br and KH, very selectively reacted with dimethyl carbonate between −20 °C and ambient temperature to form the methoxycarbonylated NHO **15** (Scheme 9).

Surprisingly, NHC **16**, generated in situ from [EMIm]Br and KH, was also transformed into C–C coupling product **15** upon reaction with dimethyl carbonate under analogous conditions. Compound **15** was found as a mixture with the NHC–CO_2 adduct **2** in a ratio of 4:6 (Scheme 10).



Scheme 10. Reactivity of NHC **16** with dimethyl carbonate (DMC) and a proposed mechanism for the formation of **15** from NHC **16** and dimethyl carbonate.

To explain the formation of these two species, it was assumed that the carbene attacks dimethyl carbonate preferentially at the carbonyl carbon atom leading to the cationic 2-methoxycarbonyl species **17** and a solvated methoxide anion. Cationic species such as **17**, which is an *O*-methylated NHC–CO_2 adduct, have been synthesized previously by treating a lithiated alkylimidazole with methyl chloroformate and subsequent methylation of the imidazole ring with methyl triflate.[32] Type **17** cations have also been obtained by methanolysis of a 2-chlorocarbonyl-substituted imidazolium cation.[6a] Such a cationic methyl ester **17** would certainly be a better methylating agent than neutral DMC. An S_N2-type dimethylation would lead to **2** as the major product, which precipitates from the reaction mixture (Scheme 10). The more nucleophilic NHC **16** was methylated at the 2-position first by a C–C coupling reaction and the more basic methoxide anion formed was then available to act as a sufficiently strong base to deprotonate the generated 2-methylimidazolium cation **18** to yield NHO **7**. The methoxycarbonylation of **7** to **15** by DMC has independently been proven with isolated **7** to be a highly selective second C–C coupling reaction (Scheme 9). If an alternative mechanism involving methylation of NHC **16** by DMC occurred, a product ratio different to 4:6 (of **15**:**2**) would have been expected. Nevertheless, it should be pointed out that in principle NHCs can also be methylated, for example, by MeI (instead of DMC).[18a] With an excess of strong base a second

methylation or benzylation of the intermediate NHO with the formation of 2-ethyl- or 2-ethylphenylimidazoles has also been observed.[33] The NHO methoxycarbonylation product **15** described here is thermally stable. It sublimes at 120 °C/5 × 10^{-3} mbar to yield colorless single crystals suitable for a molecular X-ray structure determination (Figure 6).

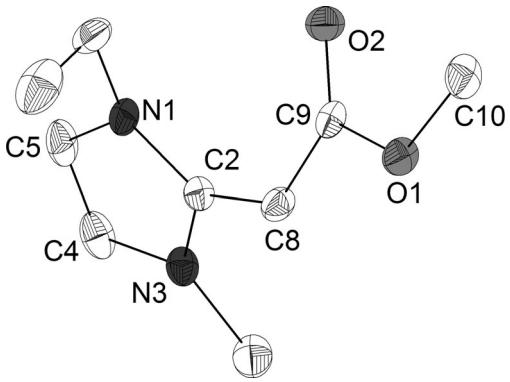
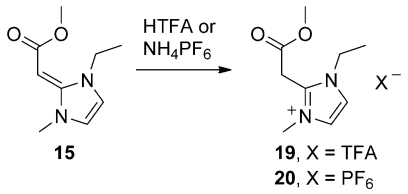


Figure 6. Molecular structure of methoxycarbonyl-stabilized NHO **15.** Hydrogen atoms and a second crystallographically independent molecule have been omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances [Å] and angles [°]: C2–N1 1.363(2), C2–N3 1.364(2), C2–C8 1.407(2), C8–C9 1.411(2), C9–O1 1.384(2), C9–O2 1.232(2), O1–C10 1.441(2), N1-C2-N3 106.1(1), O1-C9-O2 120.0(1), N1-C2-C8-C9 31.6(3).

The asymmetric unit consists of two crystallographically independent molecules that show almost identical bond lengths and angles. For simplicity, the discussion of the structure will detail only one of the molecules. In contrast to the carboxylate **4** and its literature-known congeners, the CO_2 moiety is not roughly perpendicular to the imidazolium ring but is rotated with an interplanar angle of merely 32°. This indicates partial but not perfect π conjugation of the sp^2 carbon at C8 with the two electron-withdrawing substituents, namely the 2-imidazolium cation and the methoxycarbonyl group. The two C–C bonds competing for carbon electron density, *d*(C2–C8) = 1.407(2) Å and *d*(C8–C9) = 1.411(2) Å, are within 2σ of the same length and show a bond order between a single and double bond. As expected, they are significantly shorter than the corresponding distances in the carboxylate **4** (*d*(C2–C8) = 1.474(2) Å, *d*(C8–C9) = 1.547(2) Å). The conjugate electron delocalization into the imidazolium cation of **15** leads to a shortening of both apical C–N bonds (*d*(N1–C2) = 1.363(2) Å, *d*(C2–N3) = 1.364(2) Å), an elongation of the other two, and shortening of the C4–C5 distance compared with undisturbed aromatic imidazolium cations such as in **4**. Owing to the methyl substituent the charge delocalization by the carboxylate moiety is asymmetric with *d*(C9–O1) = 1.384(2) Å and *d*(C9–O2) = 1.232(2) Å, which contrasts with the very symmetric zwitterion **4** (see the Supporting Information for further bond lengths of **4**). The bond distances and angles of **15** are in good agreement with the related *N*,*N*′-diorgano-2-ethoxycarbonylmethylenebenzimidazole structure.[34] In **15**, similarly to the reference structure, the olefinic hydrogen atom is oriented towards the smaller *N*-methyl group, whereas the alkoxycarbonyl group is oriented towards the larger *N*-ethyl substituent. The 2D H,H NOESY NMR spectra of **15** in [D_8]toluene at 25 and −50 °C show strong cross-peaks between the olefinic hydrogen atom and the *N*-methyl group as well as between the olefinic hydrogen atom and the *N*-methylene group on the opposite side of the imidazole moiety. This indicates that the double bond configuration is not fixed but prone to isomerization in solution. The presence of only one isomer in the crystalline state after sublimation is probably a result of energetically more favorable lattice packing.

In following experiments we investigated the reactions of **15** with acids. Compound **15** was protonated by trifluoroacetic acid and even by the weak acid NH_4PF_6 at C8 with highly selective formation of functionalized ILs (Scheme 11).



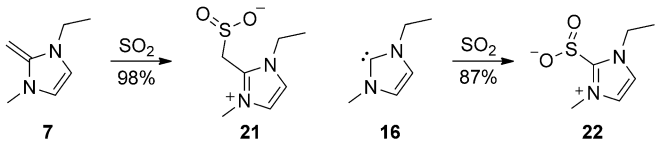
Scheme 11. Reaction of **15** with the acids HTFA and NH_4PF_6 to yield [NHO–CO_2Me][X].

This reaction behavior demonstrates that despite containing one stabilizing methoxycarbonyl group, **15** still has the typical basicity of an NHO, which can be used in highly efficient IL syntheses.[21] In the light of the fact that NHO **7** and its COOR stabilized derivative **15** exhibits the same reactivity pattern towards electrophiles, and protons in particular, it is interesting to note that the introduction of a COOR substituent at a classical olefin leads to contrasting reactivity patterns, for example, ethylene and methyl acrylate, towards electrophiles and nucleophiles.

6. NHC– and NHO–SO_2 adducts: zwitterionic sulfinates

We have learned that NHO–CO_2 adducts are stable storage forms of N-heterocyclic olefins. They can be used for the synthesis of a wide range of 2-alkylimidazolium ionic liquids as well as for interesting C–C coupling reactions involving two of the most prominent electrophiles of green chemistry, CO_2 and dimethyl carbonate. The question arises as to whether NHO **7** forms a similar adduct with the Lewis acid SO_2 and whether a NHO–SO_2 adduct will show similar reactivity patterns to its CO_2 counterpart, for example, if treated with methanol. According to literature reports, aromatic NHCs such as **16** do not form stable adducts with SO_2.[35] Previous reports of an adamantyl-substituted aromatic NHC–SO_2 adduct in the form of a planar sulfene[36] have been doubted.[37] Our experiments showed, however, that NHO **7** as well as NHC **16** react selectively with SO_2 to form stable adducts. The NHO– and NHC–SO_2 adducts **21** and **22** precipitated as light-yellow solids and were isolated in yields of 98 and 87%, respectively, when SO_2 gas was passed into solutions of the Lewis bases in THF (Scheme 12).

The molecular structures of sulfinate zwitterions **21** and **22** were validated by single-crystal X-ray structure analysis (Figures 7 and 8). Crystals of **21** were grown in an acetonitrile solu-



Scheme 12. Synthesis of 1-ethyl-3-methylimidazolium-2-methylenesulfinate (NHO–SO_2, **21**) and 1-ethyl-3-methylimidazolium-2-sulfinate (NHC–SO_2, **22**).

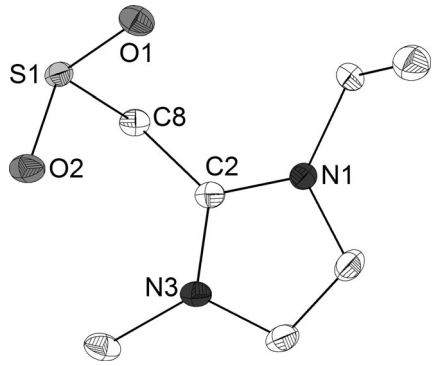


Figure 7. Molecular structure of NHO–SO_2 adduct **21**. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances [Å] and angles [°]: C2–N1 1.339(3), C2–N3 1.343(2), C2–C8 1.470(3), C8–S1 1.874(2), S1–O1 1.499(1), S1–O2 1.494(1), N1-C2-N3 107.4 (2), O1-S1-O2 111.1(1).

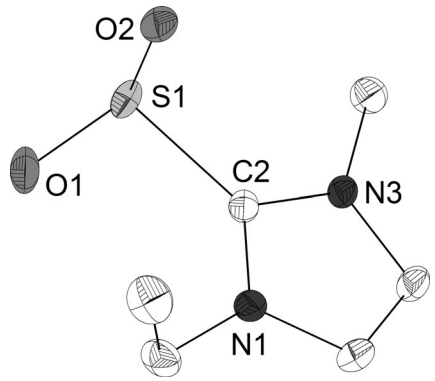
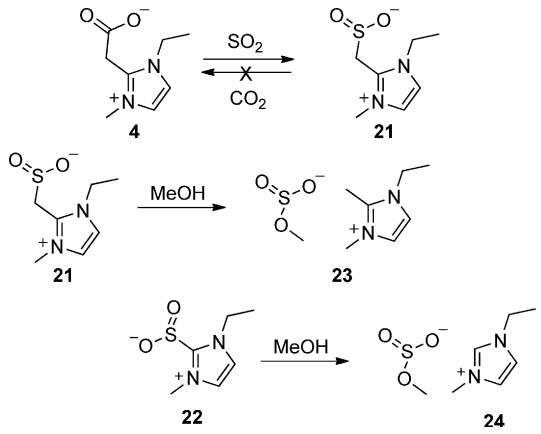


Figure 8. Molecular structure of NHC–SO_2 adduct **22**. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances [Å] and angles [°]: C2–N1 1.339(2), C2–N3 1.340(2), C2–S1 1.859(1), S1–O1 1.485(1), S1–O2 1.489(1), N1-C2-N3 107.4 (1), O1-S1-O2 111.3(1).

tion layered with diethyl ether, and **22** crystallized upon cooling a room-temperature saturated solution of **22** in THF to −20 °C.

In both structures the sulfur(IV) atom is coordinated in a pyramidal fashion due to the remaining electron lone pair. The C8–S1 bond in NHO–SO_2 **21** has a length of 1.874(2) Å, which is significantly longer than the sp^3(C)–SO_2 bond in *N*-[(1-phenylethyl)ammonio]propanesulfinate (1.807 Å)[38] as well as those in the metal complexes of, for example, *O*-ethyl- or *O*-methylsulfinato ligands (1.757–1.824 Å).[39] Only in a propynesulfinate ligand coordinated to tin through one of the oxygen atoms is a similar bond length (1.862 Å) observed.[40] The C2–S1 bond in NHC–SO_2 **22** has a length of 1.859(1) Å, which is significantly shorter than the C–S distance in a cyclic diaminocarbene–SO_2 adduct (2.030(2) Å).[35] It is, however, in perfect agreement with the C–S bond length in thiourea *S*,*S*-dioxide (1.859(1) Å).[41] In contrast to the diaminocarbene–SO_2 adduct, the sulfur atom in **22** is perfectly co-planar with the CN_2 unit of the NHC ring. The SO bonds in **21** (1.499(1) and 1.494(1) Å) and **22** (1.485(1) and 1.489(1) Å) indicate negative charge delocalization in the SO_2 moiety. The S–O bonds in the literature-known diaminocarbene–SO_2 adduct are significantly shorter (both 1.469(1) Å), which may be expected due to the equally longer C–S interaction. Nevertheless, the long C–S bonds in **21** and **22** suggest a weakened bond that may be cleaved by appropriate nucleophiles, thereby rendering these molecules suitable for further reactions. In a comparative experiment we elucidated the relative stability of NHO–CO_2 adduct **4** compared with NHO–SO_2 adduct **21**. While **21** appeared to be stable towards CO_2 at 50 °C, the NHO–CO_2 adduct reacted immediately with SO_2 at ambient temperature to form **21** (see the Supporting Information for details). However, both sulfinates **21** and **22** readily underwent cleavage in the presence of methanol at ambient temperature to form the methyl sulfite salts **23** and **24** (Scheme 13).



Scheme 13. Cleavage of **21** with methanol to yield [EMMIm][$MeOSO_2$] (**23**) and the corresponding reaction of **22** to give [EMIm][$MeOSO_2$] (**24**).

Up to now, imidazolium alkyl sulfites have been obtained in patented processes by the methylation of *N*-alkylimidazoles with dimethyl sulfite[42] or by the reaction of imidazolium halide or carboxylate salts with a symmetrically substituted dialkyl sulfite.[43] The potential of the zwitterionic sulfinates **21** and **22** to act as precursors for other sulfite salts and sulfonylation reactions related to the corresponding carboxylation reactions is under continued investigation.

Conclusions

We have carefully investigated the conditions of the highly selective and fully reversible formation of NHC–CO_2 and NHO–CO_2 adducts in methanol from their imidazolium methyl carbonate precursors. In highly concentrated MeOH solution, in particular in the absence of methanol during the isolation of [EMIm][OCO_2Me] or [EMMIm][OCO_2Me], the anion becomes

less efficiently solvated, and thus a stronger base, such that the fully reversible equilibria of these thermodynamically controlled carboxylations are shifted nearly quantitatively towards the NHC–CO_2 adduct **2** or partly towards the NHO–CO_2 adduct **4**, even at room temperature. Following this synthetic strategy the reaction patterns of the NHO–CO_2 adduct **4** were investigated and compared with the nowadays well-established chemistry of the NHC–CO_2 adduct **2**.

Upon protonation, the NHO–CO_2 adduct **4** can serve as a masked NHO precursor for the preparation of ionic liquids [EMMIm][X] based on 2-methylimidazolium cations. However, its decarboxylation in methanol or acetonitrile is much more dependent on the reaction conditions and partners than the NHC–CO_2 adducts: Its reaction with strong acids with weakly nucleophilic anions (X = TFA, TFSI) primarily leads to imidazolium salts [NHO–CO_2H][X] with 2-CH_2-COOH substituents at ambient temperature. Their decarboxylation to the corresponding 2-methylimidazolium salts [EMMIm][TFA] and [EMMIm][TFSI] occurs at elevated temperatures or is catalyzed by nucleophiles such as dimethylaminopyridine (DMAP). In contrast, the reaction of the NHO–CO_2 zwitterion **4** with the weak acid ammonium hexafluorophosphate, which provides a sufficiently nucleophilic conjugate base NH_3 as catalyst, leads to decarboxylation and the quantitative formation of [EMMIm][PF_6] at ambient temperature.

Furthermore, we have demonstrated that the NHO–CO_2 zwitterion **4** can act as an efficient carboxylating agent towards CH acids such as acetonitrile: The decarboxylation of **4** at elevated temperatures generates an N-heterocyclic olefin in situ. This base assists the deprotonation of the CH acidic positions of acetonitrile to form EMMIm cyanoacetate and $EMMIm_2$ cyanomalonate salts, thereby exemplifying the first C–C bond-forming carboxylations with NHO-activated CO_2. The reaction of the NHO–CO_2 zwitterion with dimethyl carbonate under kinetic control leads to methoxycarbonylation and the formation of the methoxycarbonyl-stabilized NHO **15**. NHO **15** is accessible with the highest selectivity from the corresponding NHO and dimethyl carbonate.

With a view to the future, we have presented the synthesis of the novel NHO–SO_2 adduct **21** and corresponding NHC–SO_2 **22**, which, by methanolysis, can be selectively transformed into the corresponding methyl sulfite ILs, thereby demonstrating their potential to access a variety of organic salts. We have shown that the CO_2 and SO_2 adducts of NHC and NHO are convenient storage forms of these carbon nucleophiles. The small deviations of their reactivity patterns compared with the NHC and NHO parent compounds can lead to undesired IL impurities, which are difficult to separate, in otherwise highly efficient IL syntheses with these synthons. The results presented herein allows these difficulties to be avoided in IL purification and opens up opportunities for interesting new CO_2 and SO_2 reactions mediated by NHCs and NHOs.

Experimental Section

Methods and devices

Unless stated otherwise, all the synthetic steps were conducted by using standard Schlenk techniques and freshly dried solvents. Elemental analyses (C, H, N, S) were carried out by the service department for routine analysis and mass spectra were recorded with a vario MICRO cube (Elementar). Samples of air- or moisture-sensitive compounds were weighed into tin capsules inside a nitrogen-filled glovebox. Melting points were determined with a Büchi Melting Point B540 apparatus. ^{1}H, proton-decoupled ^{13}C, and ^{19}F NMR spectra were recorded at 300 K in automation with a Bruker Avance II 300 spectrometer. ^{1}H and ^{13}C NMR spectra were calibrated against residual proton and solvent signals, respectively ([D_6]DMSO: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm).[44] ^{19}F NMR spectra were referenced externally against $CFCl_3$. ^{1}H,^{13}C HMBC and ^{29}Si NMR spectra were recorded with a Bruker Avance III 500 or Avance III HD 300 spectrometer. The latter spectra were calibrated externally against Me_4Si. IR spectra were recorded on a Bruker APLPHA FT-IR spectrometer with Platinum ATR sampling (diamond single crystal). High-resolution ESI mass spectra were acquired with a LTQ-FT Ultra mass spectrometer (Thermo Fischer Scientific). The resolution was set to 100 000. High-resolution EI mass spectra were acquired with a AccuTOF-GCv TOF mass spectrometer (JEOL). Single-crystal structure determinations were performed on a Bruker D8 QUEST diffractometer by the X-ray service department of the Fachbereich Chemie, University of Marburg. Bruker software (APEX2, SAINT) was used for data collection, cell refinement, and data reduction.[45] The structures were solved with SIR97,[46] SIR2011,[47] or SHELXS,[48] refined with SHELXL-2014,[49] and finally validated by using the PLATON[50] software, all within the WinGX[51] or ShelXle[52] software bundle. Absorption corrections were applied beforehand within the APEX2 software (multi-scan).[53] Graphic representations were created by using Diamond 4.[54] Hydrogen atoms were constrained to the parent sites and are not shown except when participating in hydrogen bonds.

CCDC 1485857 (**4**·DMSO), 1485858 (**5**·0.5 THF), 1485859 (**8**), 1485860 (**14a**), 1485861 (**15**), 1485862 (**21**), and 1485863 (**22**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Starting materials

All solvents were dried according to common procedures[55] and passed through columns of aluminium oxide, 3 Å molecular sieves, and R3-11G-catalyst (BASF) or stored over molecular sieves (3 or 4 Å) until use. 1-Ethyl-2-methylimidazole was prepared according to a published general procedure for the alkylation of imidazoles.[56] As the sodium salt of 2-methylimidazole reacted violently with ethyl bromide if following the original specifications, the sodium imidazolate was suspended in twice the recommended volume of THF and ethyl bromide was then added dropwise at 0 °C before warming to room temperature.

Representative synthetic procedures

The procedures used for the synthesis of all compounds described herein are supplied in the Supporting Information (S1–S56).

Reaction of NHO–CO_2 4 with ammonium hexafluorophosphate: NHO–CO_2 **4** (142 mg, 839 μmol, 1.00 equiv) was dissolved in methanol (5 mL) and NH_4PF_6 (139 mg, 853 μmol, 1.02 equiv) was added to the solution. The mixture was stirred at ambient temperature

for 24 h and then evaporated to dryness in vacuo. [EMMIm][PF_6] was isolated as a colorless solid in a yield of 201 mg (744 μmol, 89%). ^{1}H NMR (300.1 MHz, [D_6]DMSO): $\delta = 1.34$ (t, $^3J_{HH} = 7.3$ Hz, 3H; CH_2CH_3), 2.57 (s, 3H; CCH_3), 3.74 (s, 3H; NCH_3), 4.13 (q, $^3J_{HH} = 7.3$ Hz, 2H; CH_2CH_3), 7.59 (d, $^3J_{HH} = 2.1$ Hz, 1H; 4/5-H), 7.64 (d, $^3J_{HH} = 2.1$ Hz, 1H; 4/5-H) ppm; ^{13}C NMR (75.5 MHz, [D_6]DMSO): $\delta = 8.9$ (1C; CCH_3), 14.7 (1C; CH_2CH_3), 34.5 (1C; NCH_3), 42.7 (1C; CH_2CH_3), 120.2 (1C; C-4/5), 122.3 (1C; C-4/5), 144.0 (1C; C-2) ppm; ^{19}F NMR (282.4 MHz, [D_6]DMSO): $\delta = -71.1$ (d, $^1J_{FP} = 711$ Hz, 6F; PF_6) ppm.

Synthesis of [NHO–CO_2H][TFSI] (10): Bis(trifluoromethyl-sulfonyl)-imide (HTFSI; 175 mg, 0.62 mmol, 1.1 equiv) was dissolved in acetonitrile (5 mL) and added to NHO–CO_2 **4** (92 mg, 0.54 mmol, 1.0 equiv). The mixture was stirred at ambient temperature for 18 h and then evaporated to dryness in vacuo to leave a colorless oil. The resulting residue consisted primarily (<80%) of the protonated carboxylate salt [NHO–CO_2H][TFSI] (**10**). Analogous results were obtained on varying the reaction time between 2 h and 2 d and upon changing the solvent for methanol. IR (neat): $\tilde{\nu}_{max} =$ 3450–3000 (br, w), 3149 (w), 1728 (w), 1540 (w), 1345 (m), 1327 (sh, m), 1180 (vs), 1132 (s), 1050 (s), 825 (w), 792 (w), 762 (w), 740 (w), 608 (s), 569 (s), 510 (m) cm^{-1}; ^{1}H NMR (300.1 MHz, [D_6]DMSO): $\delta =$ 1.33 (t, $^3J_{HH} = 7.3$ Hz, 3H; CH_2CH_3), 3.79 (s, 3H; NCH_3), 4.19 (q, $^3J_{HH} =$ 7.3 Hz, 2H; CH_2CH_3), 4.37 (s, 2H; CH_2CO_2H), 7.73 (d, $^3J_{HH} = 1.7$ Hz, 1H; 4/5-H), 7.79 (d, $^3J_{HH} = 1.7$ Hz, 1H; 4/5-H), 13.20 (br s, 1H; CO_2H) ppm; ^{13}C NMR (75.5 MHz, [D_6]DMSO): $\delta = 15.0$ (1C; CH_2CH_3), 29.3 (1C; CCH_2CO_2H), 34.8 (1C; NCH_3), 43.1 (1C; CH_2CH_3), 119.4 (q, $^1J_{CF} = 322$ Hz, 1C; CF_3), 121.1 (1C; C-4/5), 123.3 (1C; C-4/5), 140.7 (1C; C-2), 167.5 (1C; CO_2H) ppm; ^{19}F NMR (282.4 MHz, [D_6]DMSO): $\delta = -79.5$ (3F; CF_3) ppm.

If the isolated substance was redissolved in acetonitrile or methanol and heated at 60–80 °C (30 min), or if the NMR sample in [D_6]DMSO was heated at 80 °C the substance quantitatively transformed into [EMMIm][TFSI] (**11**). IR (neat): $\tilde{\nu}_{max} = 3152$ (w), 1591 (w), 1541 (w), 1346 (m), 1330 (sh, m), 1174 (vs), 1132 (s), 1051 (s), 789 (w), 739 (w), 612 (m), 600 (m), 569 (m), 509 (m) cm^{-1}; ^{1}H NMR (300.1 MHz, [D_6]DMSO): $\delta = 1.33$ (t, $^3J_{HH} = 7.3$ Hz, 3H; CH_2CH_3), 2.58 (s, 3H; CCH_3), 3.74 (s, 3H; NCH_3), 4.13 (q, $^3J_{HH} = 7.3$ Hz, 2H; CH_2CH_3), 7.61 (d, $^3J_{HH} = 1.9$ Hz, 1H; 4/5-H), 7.65 (d, $^3J_{HH} = 1.9$ Hz, 1H; 4/5-H) ppm; ^{13}C NMR (75.5 MHz, [D_6]DMSO): $\delta = 8.9$ (1C; CCH_3), 14.7 (1C; CH_2CH_3), 34.5 (1C; NCH_3), 42.7 (1C; CH_2CH_3), 119.4 (q, $^1J_{CF} =$ 322 Hz, 1C; CF_3), 120.2 (1C; C-4/5), 122.3 (1C; C-4/5), 144.0 (1C; C-2) ppm; ^{19}F NMR (282.4 MHz, [D_6]DMSO): $\delta = -78.9$ (3F; CF_3) ppm.

Synthesis of methyl (*Z*)-2-(1-ethyl-3-methyl-1,3-dihydro-2*H*-imidazol-2-ylidene)acetate (15): 1-Ethyl-2,3-dimethylimidazolium bromide (935 mg, 4.56 mmol, 1.00 equiv), potassium hydride (219 mg, 5.46 mmol, 1.20 equiv), and potassium *tert*-butanolate (9 mg, 0.08 mmol, 2 mol%) were combined with THF (25 mL). The suspension was stirred for 24 h and then filtered through Celite to remove all solid components and the filter cake was washed with THF (10 mL). Dimethyl carbonate (0.42 mL, 0.45 g, 5.0 mmol, 1.1 equiv) was added to the solution at −20 °C, whereupon the mixture turned light yellow. The solution was stirred at −20 °C for 20 min and at ambient temperature for 1 h before all volatile components were removed in vacuo. Compound **15** was obtained as an off-white powder in a yield of 763 mg (4.19 mmol, 92%). The NMR signals were assigned on the basis of HMQC and HMBC 2D spectra. IR (neat): $\tilde{\nu}_{max} = 3163$ (w), 3122 (w), 2970 (w), 1629 (s), 1547 (vs), 1487 (m), 1434 (s), 1382 (m), 1326 (w), 1232 (m), 1147 (vs), 1056 (s), 1039 (s), 913 (s), 827 (m), 796 (w), 741 (s), 712 (m), 677 (m), 623 (s), 585 (s), 491 (w), 424 (w) cm^{-1}; ^{1}H NMR (300.1 MHz, [D_6]DMSO): $\delta = 1.18$ (t, $^3J_{HH} = 7.2$ Hz, 3H; CH_2CH_3), 3.36 (s, 3H; OCH_3), 3.37 (s, 3H; NCH_3), 3.72 (s, 1H; $CHCO_2Me$), 3.88 (q, $^3J_{HH} =$ 7.2 Hz, 2H; CH_2CH_3), 6.91 (m, 2H; 4/5-H) ppm; ^{13}C NMR (75.5 MHz, [D_6]DMSO): $\delta = 13.9$ (1C; CH_2CH_3), 34.9 (1C; NCH_3), 41.8 (1C; CH_2CH_3), 48.4 (1C; OCH_3), 52.6 (1C; $CHCO_2Me$), 115.9 (1C; C-5), 118.1 (1C; C-4), 150.3 (1C; C-2), 165.8 (1C; CO_2Me) ppm; HRMS (EI-TOF): *m/z*: calcd for $C_9H_{14}N_2O_2$: 182.10553 [M]$^+$; found: 182.10550; elemental analysis calcd (%) for $C_9H_{14}N_2O_2$ (182.22 g mol^{-1}): C 59.3, H 7.7, N 15.4; found: C 59.35, H 7.8, N 15.6.

Synthesis of 1-ethyl-3-methylimidazolium-2-methylenesulfinate inner salt (NHO–SO_2, 21): 1-Ethyl-3-methyl-2-methylene-imidazoline (**7**; 2.30 g, 18.5 mmol, prepared and isolated in analogy to a literature procedure)[21] was dissolved in THF (50 mL) and the solution cooled to 0 °C. SO_2 was introduced into the solution whereupon a light-yellow solid precipitated immediately. The gas stream was stopped after 1 min and the suspension was filtered. The filter cake was washed with diethyl ether (20 mL) and dried under a fine vacuum. NHO–SO_2 (**21**) was isolated as a light-yellow powder in a yield of 3.40 g (18.1 mmol, 98%). IR (neat): $\tilde{\nu}_{max} = 3072$ (w), 1578 (w), 1526 (m), 1452 (w), 1298 (w), 1256 (w), 1166 (m), 1068 (vs), 1019 (m), 990 (vs), 855 (w), 794 (m), 714 (m), 594 (w), 549 (w), 504 (s), 449 (s) cm^{-1}; ^{1}H NMR (300.1 MHz, [D_6]DMSO): $\delta = 1.34$ (t, $^3J_{HH} =$ 7.3 Hz, 3H; CH_2CH_3), 3.71 (s, 2H; CH_2SO_2), 3.79 (s, 3H; NCH_3), 4.15 (q, $^3J_{HH} = 7.3$ Hz, 2H; CH_2CH_3), 7.56 (d, $^3J_{HH} = 2.1$ Hz, 1H; 4/5-H), 7.62 (d, $^3J_{HH} = 2.1$ Hz, 1H; 4/5-H) ppm; ^{13}C NMR (75.5 MHz, [D_6]DMSO): $\delta = 15.2$ (1C; CH_2CH_3), 35.1 (1C; NCH_3), 42.8 (1C; CH_2CH_3), 54.9 (1C; CH_2SO_2), 119.7 (1C; C-4/5), 122.1 (1C; C-4/5), 142.6 (1C; C-2) ppm; elemental analysis calcd (%) for $C_7H_{12}N_2O_2S_1$ (188.25 g mol^{-1}): C 44.7, H 6.4, N 14.9, S 17.0; found: C 44.8, H 6.5, N 15.3, S 16.7.

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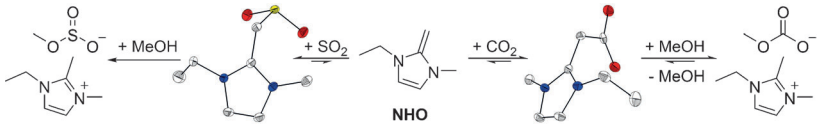

Heterocyclic stores: CO_2 and SO_2 adducts of N-heterocyclic carbenes (NHCs) and N-heterocyclic olefins (NHOs) are convenient storage forms of these carbon nucleophiles (see figure). The small deviations in their reactivity patterns compared with the NHC and NHO parent compounds open up opportunities for interesting new CO_2 and SO_2 reactions mediated by NHCs and NHOs.

Ionic Liquids

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N-Heterocyclic Olefin–Carbon Dioxide and –Sulfur Dioxide Adducts: Structures and Interesting Reactivity Patterns