

# Imidazol-2-and-4-ylidene by decarboxylation. Studies on the cross-conjugated mesomeric betaine-alkaloid norzooanemonine and its pseudo-cross-conjugated isomer

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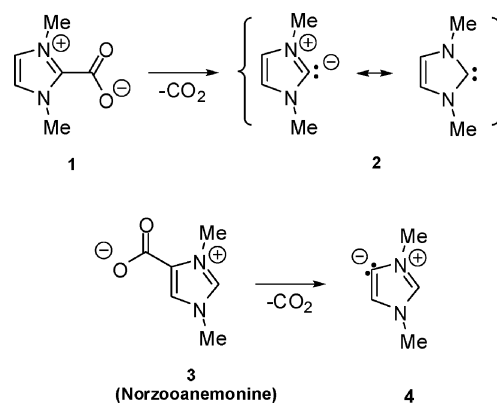
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1,3-Dimethylimidazolium-2-carboxylate and -4-carboxylate (norzooanemonine), which belong to two distinct classes of heterocyclic mesomeric betaines, undergo thermal decarboxylations to the *N*-heterocyclic carbenes imidazol-2-ylidene and imidazol-4-ylidene, respectively. These carbenes can be detected by ESI mass spectrometry and can be trapped by isocyanates to imidazolium-amidates, the structure of which was proved by independent syntheses. We performed calculations to characterize the different types of conjugation in the imidazolium-carboxylates.

## Introduction

Currently considerable interest is focussed on the chemistry of *N*-heterocyclic carbenes. They are utilized not only as ligands in metal-organic chemistry,<sup>1</sup> but also as organocatalysts in Stetter reactions,<sup>2</sup> benzoin condensations,<sup>3</sup> transesterifications,<sup>4</sup> enantioselective acylations of secondary alcohols,<sup>5</sup> hydroacylations of activated ketones,<sup>6</sup> trialkylsilylcyanations,<sup>7</sup> redox esterifications of aldehydes,<sup>8</sup> and many other reactions. With few exceptions, neither the structural nor the chemical relationship between *N*-heterocyclic carbenes (NHC) and heterocyclic mesomeric betaines (HMB) has been recognized to date. Representatives of the latter mentioned class of compounds are neutral conjugated molecules which can exclusively be represented by dipolar canonical formulae. They delocalize an even number of charges within a common  $\pi$ -electron system. A first classification (1985) by Ollis *et al.* divided HMB into four major groups, *i.e.* into conjugated mesomeric betaines (CMB), conjugated heterocyclic *N*-ylides, cross-conjugated mesomeric betaines (CCMB) and pseudo-cross-conjugated mesomeric betaines (PCCMB).<sup>9</sup> The characteristics of these distinct types of conjugation<sup>10</sup> and their occurrence among natural products<sup>11</sup>—insofar investigated to date—have been surveyed recently. Whereas conjugated mesomeric betaines, which also include mesoions such as sydnones, münchnones, isothiomünchnones, *N*-ylides, and cross-conjugated mesomeric betaines have been explored intensively as versatile key intermediates in heterocyclic<sup>9,12</sup> as well as natural product synthesis,<sup>13</sup> pseudo-cross-conjugated mesomeric betaines obviously still constitute an exceptional role among the different types of conjugated systems. Although originally classified somewhere between CMB and CCMB, recent results show that they in fact do have characteristic features which are not only of theoretical nature, but do also translate into chemistry.<sup>14,15</sup> *A priori*, cross-conjugated as well as pseudo-cross-conjugated heterocyclic

mesomeric betaines can be considered as precursors of *N*-heterocyclic carbenes. Related to the valence bond theory based classification of mesomeric betaines, at least three distinct types of *N*-heterocyclic carbenes can be seen. Wantzlick/Arduengo carbenes, which result in extrusion of heterocumulenes such as carbon dioxide from pseudo-cross-conjugated mesomeric betaines can be represented either by polar all-octet or by nonpolar non-octet canonical formula. An example is the decarboxylation of the PCCMB 1,2-dimethylimidazolium-2-carboxylate **1** to the NHC 1,2-dimethylimidazol-2-ylidene **2** (Scheme 1). By contrast, on decarboxylation of the cross-conjugated mesomeric betaine 1,2-dimethylimidazolium-4-carboxylate **3** the NHC 1,2-dimethylimidazol-4-ylidene **4** is formed which can exclusively be represented by a dipolar all-octet structure. The same is true for *r*NHC (*r* = remote heteroatom) which results from CCMB.<sup>16</sup> Molecule **4** is currently considered as “abnormal carbene” (aNHC) in its behaviour in coordination chemistry.<sup>17</sup>



Scheme 1

The mesomeric betaine **3** is known as norzooanemonine and was identified as alkaloid in marine sponges such as *Pseudoptero-gorgia americana*, *Cacospongia scalaris* and *Astrosclera willeyana* LISTER 1900.<sup>18</sup>

As part of an ongoing project dealing with *N*-heterocyclic carbenes as well as mesomeric betaines from nature,<sup>19</sup> we were

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interested in a detailed comparison of the PCCMB **1** and the CCMB **3**.

## Results and discussion

### Classifications and calculations

In the pseudo-cross-conjugated heterocyclic mesomeric betaine **1** the two parts of the molecule are combined by a “union bond”, which we calculated to be 153.6 pm. In the valence bond approach, the charges are “effectively, but not exclusively” (Ollis *et al.*<sup>9</sup>) restricted to separate parts of the molecule, as the dipolar canonical formula **I** exists in which the positive charge is localized in the carboxylate group (Fig. 1). This is an electron sextet structure without internal octet stabilization. Undoubtedly, this canonical formula is no more than a means to recognize pseudo-cross-conjugation, and to distinguish the three types of conjugation of mesomeric betaines by their canonical formulae. Furthermore, the dipole type **II** is characteristic of PCCMB. Similar to the CCMB norzooanemonine **3**, the anionic partial structure is joined through an unstarred position (**III**), *i.e.* through a nodal position of the HOMO (**IV**) to the cationic portion of the betaine. The torsion angle between imidazole and carboxylate group is 19.2° according to the calculation.

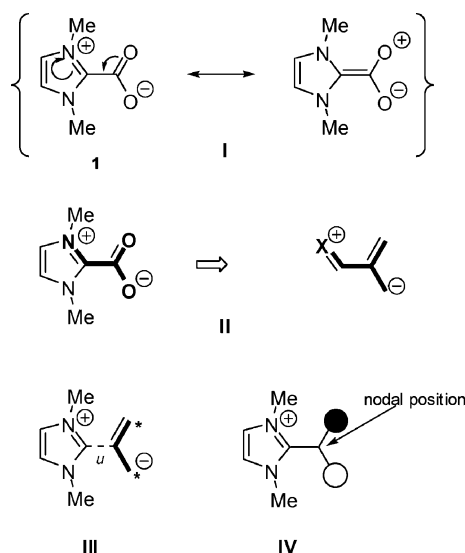


Fig. 1 Characteristics of pseudo-cross-conjugation.

The HOMO/LUMO topology of **1** and the electrostatic potential surface are displayed in Figs. 2 and 3, respectively. As can be observed, all of them exhibit the  $C_{2v}$  point-group symmetry of this molecule.

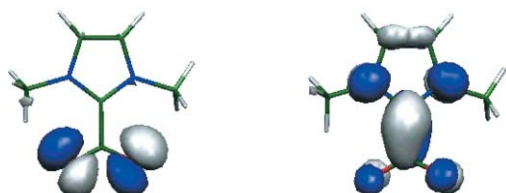


Fig. 2 HOMO (left) and LUMO (right) of 1,3-dimethylimidazoli-um-2-carboxylate **1**.

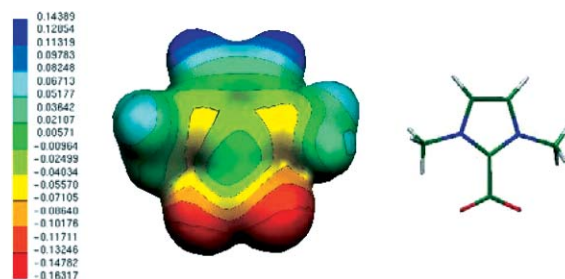


Fig. 3 Electrostatic potential surface of PCCMB **1**.

In norzooanemonine **3** the charges are delocalized in separate parts of the  $\pi$ -electron system, as exemplified by **V** in Fig. 4. The charges are strictly separated by a “union bond”—which in contrast to the rest of the molecule’s bonds has a single bond character. We calculated the bond length to be 152.4 pm. The torsion angle was determined to be 174.8°. Furthermore, there exist specific dipole increments for all types of conjugation in the betaines: This is **VI** for CCMBs in betaine **3**. The anionic part of the CCMB is isoconjugate to an odd, alternant hydrocarbon anion (**VII**) which is connected through a nodal position of the highest occupied molecular orbital (HOMO) *via* the “union bond” (*u*) to the cationic part of the molecule (**VIII**).

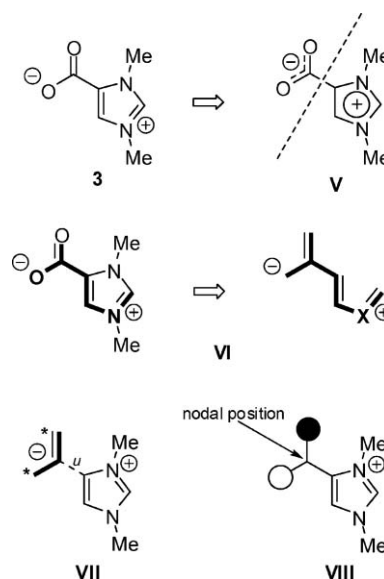


Fig. 4 Characteristics of cross-conjugation.

The frontier orbital topology of norzooanemonine **3** is presented in Fig. 5. The HOMO is located in the carboxylate group;

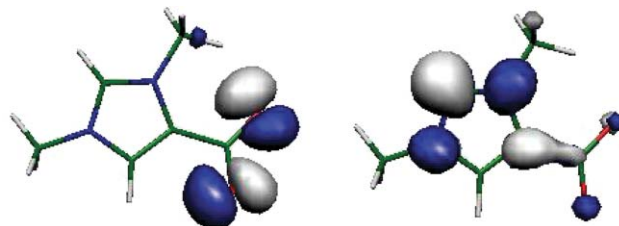
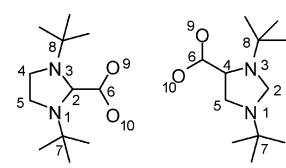


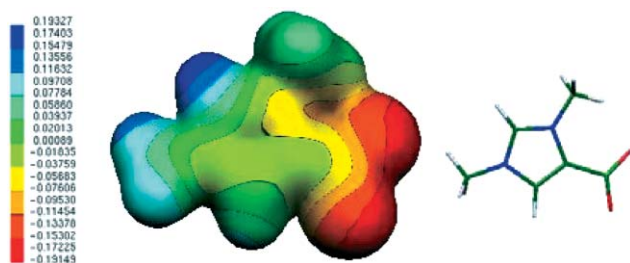
Fig. 5 HOMO (left) and LUMO (right) of norzooanemonine.

**Table 1** Selected calculated bond lengths of **1** and **3**


Bond (atom A–B)	Bond length/Å	
	<b>1</b>	<b>3</b>
N <sub>1</sub> –C <sub>2</sub>	1.349	1.336
N <sub>1</sub> –C <sub>5</sub>	1.375	1.374
N <sub>3</sub> –C <sub>2</sub>	1.350	1.333
N <sub>3</sub> –C <sub>4</sub>	1.373	1.391
C <sub>5</sub> –C <sub>4</sub>	1.360	1.368
C <sub>4</sub> –C <sub>6</sub> /C <sub>2</sub> –C <sub>6</sub> “union bonds”	1.536	1.524
C <sub>6</sub> –O <sub>9</sub>	1.247	1.254
C <sub>6</sub> –O <sub>10</sub>	1.250	1.251

the LUMO is essentially located in the imidazole ring as well as in the union bond.

We then calculated the electrostatic potential surface which is presented in Fig. 6.

**Fig. 6** Electrostatic surface of norzooanemonine **3**.

Calculated bond lengths are presented in Table 1. The CN bond distances within the 5-membered ring system are influenced by the substitution. The calculated natural bond orders (NBO) showed a good correlation with the corresponding bond lengths. They localized the double bonds within the imidazole ring between the C<sub>4</sub>–C<sub>5</sub> and the C<sub>2</sub>–N<sub>3</sub> bonds in both molecules. The obtained values for the imidazolium-2-carboxylate **1** were 1.90 and 1.93, respectively, while for norzooanemonine **3** they were 1.88 and 1.94. As expected, the union bonds clearly show single bond character (the NBO was 0.99 in both cases), which supports the two separate  $\pi$ -electron systems in either molecule with double bond character in the positive and negative fragment, respectively.

Selected calculated bond angles are presented in Table 2.

As expected, in either molecule the imidazolium ring including the methyl groups is planar. The same is true for the carboxylate group of norzooanemonine **3**, whereas that of 1,3-dimethylimidazolium-2-carboxylate adopts an angle of 19.2° with respect to the imidazolium ring. Torsion angles are given in Table 3. Fig. 7 presents the calculated permanent dipole moments of **1** (12.44 D) and **3** (17.12 D).

## Syntheses

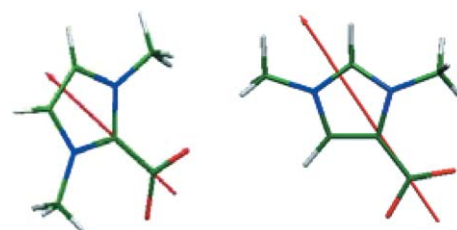
Some procedures have been described to date for the synthesis of 1,3-disubstituted imidazolium-2-carboxylates.<sup>20</sup> 1-Methyl-

**Table 2** Selected calculated bond angles of **1** and **3**

Atoms A–B–C	Bond angles/°	
	CCMB <b>3</b>	PCCMB <b>1</b>
C <sub>2</sub> –N <sub>3</sub> –C <sub>4</sub>	109.08	109.57
C <sub>2</sub> –N <sub>3</sub> –C <sub>8</sub>	123.74	126.92
C <sub>4</sub> –N <sub>3</sub> –C <sub>8</sub>	127.15	123.51
C <sub>2</sub> –N <sub>1</sub> –C <sub>5</sub>	108.50	109.65
C <sub>2</sub> –N <sub>1</sub> –C <sub>7</sub>	125.51	126.83
C <sub>5</sub> –N <sub>1</sub> –C <sub>7</sub>	125.98	123.47
C <sub>5</sub> –C <sub>4</sub> –N <sub>3</sub>	105.76	107.13
C <sub>5</sub> –C <sub>4</sub> –C <sub>6</sub>	126.65	N <sub>1</sub> –C <sub>2</sub> –C <sub>6</sub> 128.04
N <sub>3</sub> –C <sub>4</sub> –C <sub>6</sub>	127.57	N <sub>3</sub> –C <sub>2</sub> –C <sub>6</sub> 125.24
N <sub>3</sub> –C <sub>2</sub> –N <sub>1</sub>	108.71	106.72
O <sub>10</sub> –C <sub>6</sub> –O <sub>9</sub>	128.98	130.01
O <sub>10</sub> –C <sub>6</sub> –C <sub>4</sub>	113.48	O <sub>10</sub> –C <sub>6</sub> –C <sub>2</sub> 115.89
O <sub>9</sub> –C <sub>6</sub> –C <sub>4</sub>	117.54	O <sub>9</sub> –C <sub>6</sub> –C <sub>2</sub> 114.10

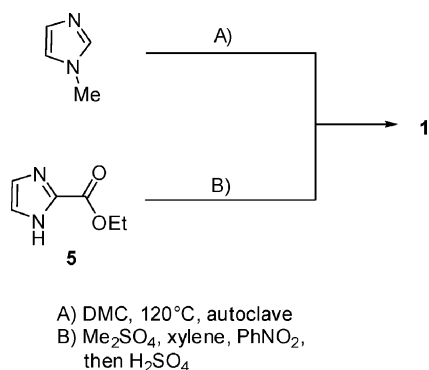
**Table 3** Torsion angles in the CCMB and PCCMB

Atom A–B–C–D	Torsion angles/°	
	CCMB <b>3</b>	PCCMB <b>1</b>
C <sub>2</sub> –N <sub>3</sub> –C <sub>4</sub> –C <sub>8</sub>	–178.2	177.8
C <sub>5</sub> –N <sub>1</sub> –C <sub>2</sub> –C <sub>7</sub>	–179.5	–179.4
C <sub>5</sub> –C <sub>4</sub> –N <sub>3</sub> –C <sub>6</sub>	178.8	N <sub>3</sub> –C <sub>2</sub> –N <sub>1</sub> –C <sub>6</sub> –0.1
C <sub>4</sub> –C <sub>6</sub> –O <sub>9</sub> –O <sub>10</sub>	–179.4	C <sub>2</sub> –C <sub>6</sub> –O <sub>9</sub> –O <sub>10</sub> 179.5
N <sub>3</sub> –C <sub>4</sub> –C <sub>6</sub> –O <sub>9</sub>	–3.7	N <sub>3</sub> –C <sub>2</sub> –C <sub>6</sub> –O <sub>9</sub> 19.2
C <sub>5</sub> –C <sub>4</sub> –C <sub>6</sub> –O <sub>10</sub>	–4.7	N <sub>3</sub> –C <sub>2</sub> –C <sub>6</sub> –O <sub>10</sub> –161.2
C <sub>5</sub> –C <sub>4</sub> –C <sub>6</sub> –O <sub>9</sub>	–3.6	C <sub>5</sub> –N <sub>1</sub> –C <sub>2</sub> –C <sub>6</sub> 179.9
N <sub>3</sub> –C <sub>4</sub> –C <sub>6</sub> –O <sub>10</sub>	176.8	C <sub>4</sub> –N <sub>3</sub> –C <sub>2</sub> –C <sub>6</sub> 179.8

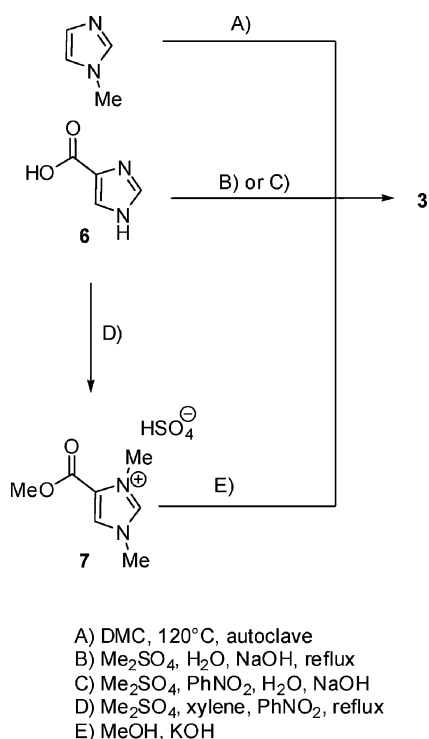
**Fig. 7** Permanent dipole moments of **1** (left) and **3** (right).

imidazole reacted with dimethylcarbonate in an autoclave over a period of 10 h at 120 °C to give imidazolium-2-carboxylate **1** or imidazolium-4-carboxylate **3** (Scheme 2, procedure A), depending on the reaction conditions.<sup>21</sup> Conducting the reaction of 1-methylimidazole with dimethylcarbonate at 120 °C yielded the target compound, betaine **1**. The <sup>13</sup>C NMR spectrum displays four signals, consistent with the assigned structure. As the yield of this procedure is low, we tested alternative approaches. Methylation of the ethyl imidazole-2-carboxylate with dimethylsulfate in the presence of catalytic amounts of nitrobenzene in xylene yielded a 1,3-dimethylimidazolium salt which was subjected to a saponification with diluted sulfuric acid. The isolated product proved to be identical with an authentic sample (Scheme 2, procedure B).

Methylation of imidazole-4-carboxylic acid **6** in aqueous sodium hydroxide with dimethylsulfate yielded norzooanemonine **3** (Scheme 3). Purification, however, met with difficulties, as inorganic materials could not be removed due to the water-solubility of norzooanemonine. The same was found to be true conducting the reaction in nitrobenzene or in a two-phase system consisting of nitrobenzene and aqueous sodium hydroxide. Conducting the



Scheme 2



Scheme 3

reaction in xylene with a small amount of nitrobenzene and using 3 eq of dimethylsulfate to methylate **6** lead to methyl imidazole-4-carboxylate **7** which was then subjected to saponification.

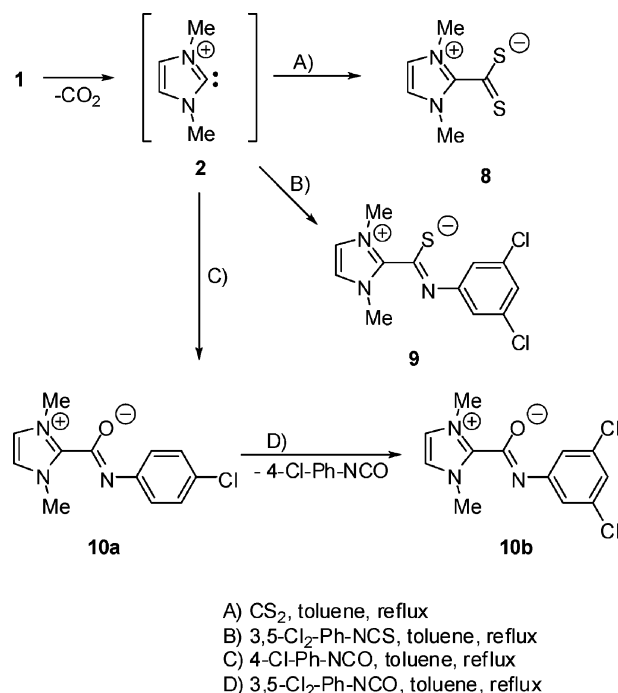
The two isomers **1** and **3** can readily be distinguished by their NMR spectra. Thus, in the <sup>13</sup>C NMR spectra of **3**, six signals were detectable, proving a non-symmetric substitution pattern. Application of HH-COSY, HSQC and HMBC techniques allowed the unambiguous peak assignment as presented in the Experimental. Accordingly, C5-*H* couples with C7-*H*<sub>3</sub>, and C7-*H*<sub>3</sub> with C2-*H* as well as C5-*H*. Finally, a NOESY NMR experiment proved the structure of 1,3-dimethylimidazolium-4-carboxylate, as C2-*H* couples with either methyl group (*cf.* Fig. 8, Experimental).

### Reactions of 1,3-dimethylimidazolium-2-carboxylate

1,3-Dimethylimidazolium-2-carboxylate **1** is known to be stable at room temperature towards decarboxylation in most organic solvents.<sup>22</sup> In methanol in the presence of NaBF<sub>4</sub> formation of

imidazolium salts was observed.<sup>23</sup> However, it decomposes in MeOD at reflux temperature within 2 h, as evidenced by NMR spectroscopy. Moreover, H/D-exchange took place for both C4-*H*, and C5-*H* in an NMR-sample measured in MeOD. The relation of the two aryl-*H*s to the two methyl groups was 2 : 46 instead of 2 : 6 as showed the NMR of the same sample measured in DMSO-*d*<sub>6</sub>.

Under ESIMS measurement conditions, the *N*-heterocyclic carbene **2** was identified as sodium adduct at *m/z* = 119.0606 on spraying a sample of **1** with MeOH in the range of 0 V to 20 V fragmentor voltage. On a preparative scale, heating in toluene produced **2** which was reacted *in-situ* with heterocumulenes. Examples of typical trapping reactions are presented in Scheme 4.

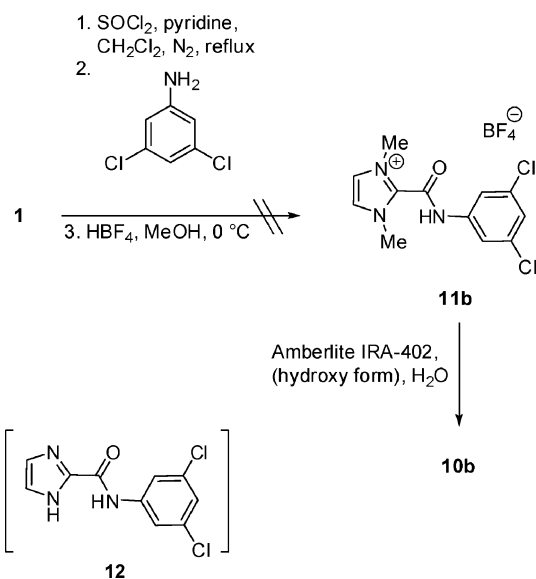


Scheme 4

Thus, CS<sub>2</sub> reacted to the dithiocarboxylate **8** in low yield, 3,5-dichloroisothiocyanate to the thioamide **9** in 89% yield, and 4-chlorophenylisocyanate to the amidate **10a** in 80% yield. The isocyanate moiety can also be exchanged *via* the NHC. As an example, we performed an exchange reaction of the 4-chlorophenylamidate in **10a** to a 3,5-dichlorophenylamidate in **10b**. The compounds **8**, **9**, and **10a,b** are representatives of the class of pseudo-cross-conjugated mesomeric betaines. Imidazol-2-ylidenes were prepared earlier by reduction of imidazole-2(3*H*)-thione with potassium as a pale yellow solid.<sup>23</sup> Their reactions with CO<sub>2</sub><sup>24</sup> or CS<sub>2</sub><sup>25</sup> to the PCCMBs imidazolium-2-carboxylate and -2-dithiocarboxylate and other reactions<sup>26</sup> have been studied intensively by Kuhn and co-workers.

Chlorination of the PCCMB **1** with SOCl<sub>2</sub> and subsequent reaction with 3,5-dichloroaniline to **11b** failed. As evidenced by mass spectrometry and <sup>1</sup>H NMR spectroscopy of the crude reaction mixture, we obtained the demethylated product **12** and yet unidentified by-products (Scheme 5). Thus, we were prevented from deprotonation with the anion exchange resin Amberlite IRA-402 in its hydroxy form.

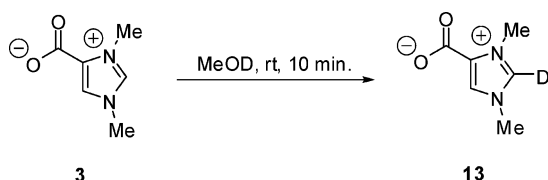




Scheme 5

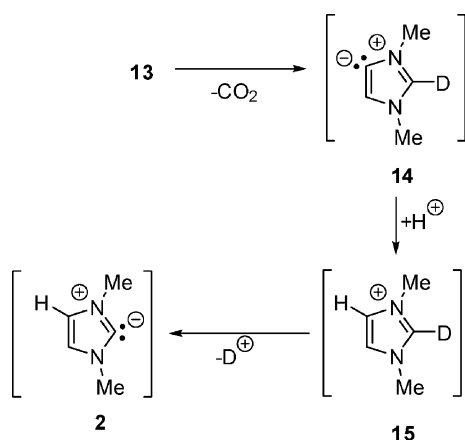
### Reactions of norzooanemonine 3

First, we studied H/D-exchange reactions. Norzooanemonine readily exchanged 2-*H* with MeOD at rt to **13** (Scheme 6).



Scheme 6

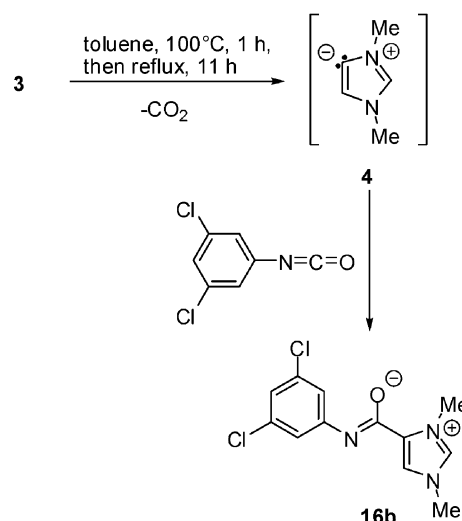
In high resolution electrospray ionization mass spectrometry of **3** at zero volt fragmentor voltage a mass was detected that is in accord to the *N*-heterocyclic carbene **4** as sodium adduct ( $m/z = 119.0595$ ; Calcd. for  $C_5H_8N_2Na$ : 119.0585) (Scheme 7). In addition, the protonated species, *i.e.* the imidazolium cation was found at  $m/z = 97.0765$  (Calcd for  $C_5H_9N_2$ : 97.0766). In order to gain some knowledge about this species, and to exclude the formation of carbene **2** from consideration, we sprayed the 2-deuterio-norzooanemonine **13**, dissolved in MeOD and



Scheme 7

sprayed from MeOH, under ESIMS conditions, and found the molecular peak at  $m/z = 164.1$ . At higher fragmentor voltages than approximately 30 V, a mass consistent to the 2-deuterio-imidazol-4-ylidene **14** as sodium adduct was indeed detected at  $m/z = 120.2$  (40% at 80 V). Obviously, this carbene is stable under these conditions. The corresponding monodeutero-imidazolium salt **15** was found at  $m/z = 98.1$  and only traces of **2** were detected. In our experiments, the ratio of non-deuterated to deuterated species in the peaks at  $m/z = 164.1 : 163.1$  and  $120.2 : 119.2$  was identical (1 : 0.45, respectively). Obviously, there are no exchange reactions during the electrospray ionization process.

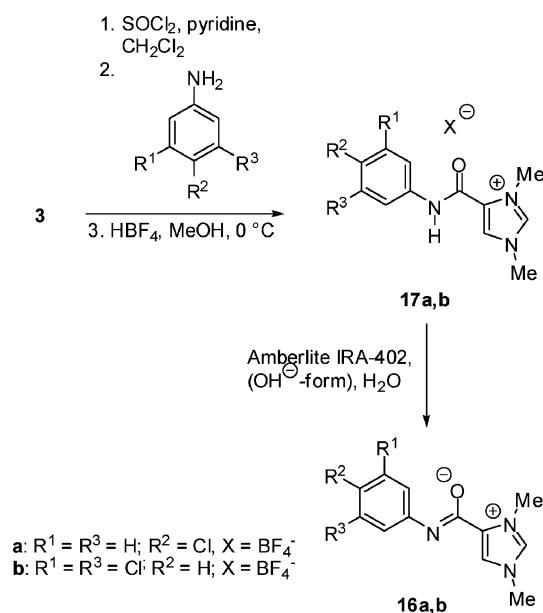
The formation of NHC **4** is also supported experimentally. Norzooanemonine **3** reacted with 3,5-dichlorophenylisocyanate in toluene at reflux temperature to the imidazolium-amide **16b**, which is hygroscopic and forms the corresponding amide with water (Scheme 8). Two methyl groups at 3.86 and 3.99 ppm in the  $^1H$  NMR spectra lend support to the structure of the 4-substituted imidazolium ring. This reaction can be interpreted as trapping reaction of the imidazol-4-ylidene **4**. Under analogous reaction conditions no reaction occurred, however, with 4-chlorophenylisocyanate which obviously gives a weaker union bond between negatively and positively charged partial structures. This is also reflected in the isocyanate exchange reaction depicted in Scheme 4.



Scheme 8

To prove the structure independently, we chlorinated norzooanemonine **3** with thionyl chloride and reacted the resulting chloride with anilines to the imidazolium salts **17a,b**. Deprotonation yielded the imidazolium-4-amides **16a,b** as new representatives of cross-conjugated mesomeric betaines (Scheme 9). All spectroscopic data of the sample thus obtained are identical to the trapping adduct of imidazol-4-ylidene **4**.

In summary, the distinct classes of heterocyclic mesomeric betaines display their own characteristic chemistry depending on the type of conjugation. Pseudo-cross-conjugated heterocyclic mesomeric betaines, including 1,3-dimethylimidazolium-2-carboxylate, undergo typical extrusion reactions of heterocumulenes to *N*-heterocyclic carbenes. To the best of our knowledge, however, we have also presented the first trapping reaction



Scheme 9

of the *N*-heterocyclic carbene 1,3-dimethylimidazolium-4-ylidene, formed on decarboxylation of the alkaloid norzooanemonine which belongs to the class of cross-conjugated heterocyclic mesomeric betaines.

## Experimental

### General remarks

The  $^1\text{H}$  (200 and 400 MHz) and  $^{13}\text{C}$  NMR spectra (50 and 100 MHz) were recorded on Bruker Digital FT-NMR Avance 400 and Avance DPX 200 spectrometers. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, m = multiplet. The numbering is defined in Fig. 8. FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to  $4000\text{ cm}^{-1}$  (2.5% pellets in KBr). The electrospray ionisation mass spectra (ESIMS) were measured with an Agilent LCMSD Series HP1100 with APIES, and EI mass spectra on a Hewlett Packard HP 5989. Melting points are uncorrected. Quantum chemical calculations were performed using the GAUSSIAN-03 package of programs.<sup>27</sup> We always used the split-valence 6-31G\*\* basis set,<sup>28,29</sup> which includes six s-type and three p-type polarization functions on all the atoms. Electron correlation energy was introduced using the hybrid functional B3PW91, within the density functional theory.<sup>30,31</sup> The minimal energy geometry, the topology of the frontier orbitals, the natural bond orders (NBO) and the electrostatic surface potential were computed by simulating a polar environment by means of a polarizable continuum model.<sup>32,33</sup> In

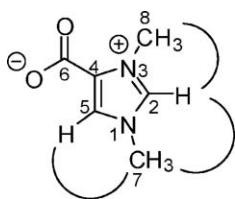


Fig. 8 Results of an HH-COSY experiment.

this model the solute molecule is placed into a size-adapted cavity formed from overlapping atom-centred van der Waals spheres, while the solvent is assimilated to a continuum characterized by its dielectric constant (78.4 for water). CAUTION: Dimethyl sulfate is *inter alia* highly toxic, mutagenic, carcinogenic, and corrosive; nitrobenzene and carbon disulfide are poisonous.

### 1,3-Dimethylimidazolium-2-carboxylate 1

**Method A<sup>21</sup>.** 30 mL (0.376 mol, 1 eq) of *N*-methylimidazole and 44.4 mL (0.527 mol, 1.4 eq) of dimethyl carbonate were given into an autoclave. The resulting clear solution was heated under stirring at  $120^\circ\text{C}$  for 50 h. Then, the solid was filtered off and dried *in vacuo*, giving 2.4 g (5%) of 1,3-dimethylimidazolium-2-carboxylate 1. All spectroscopic data are consistent to those reported in the literature.<sup>21</sup>

**Method B (two-step procedure).** A sample of 0.4 g (2.854 mmol, 1 eq) of ethyl 1*H*-imidazole-2-carboxylate was suspended in 12 mL of xylene. After addition of 0.35 mL (3.4 mmol, 1.19 eq) of nitrobenzene a yellow solution resulted which was heated to reflux temperature for 30 min. Then, 0.59 mL (6.279 mmol, 2.2 eq) of dimethyl sulfate were added. The mixture was then heated to reflux for 5 h. After cooling the resulting oil was separated, dried *in vacuo*, and purified by flash chromatography (silica gel; MeOH) to give 2-ethoxycarbonyl-1,3-dimethylimidazolium hydrogensulfate, yield 0.184 g (24%), mp  $> 245^\circ\text{C}$ ;  $\delta_{\text{H}}$  ( $\text{DMSO}-d_6$ ) 7.94 (2H, s, C4-*H*, C5-*H*), 4.45 (2H, q,  $J = 7.2\text{ Hz}$ ), 4.04 (6H, s; N-Me), 1.38 (3H, t,  $J = 7.2\text{ Hz}$ );  $\delta_{\text{C}}$  ( $\text{DMSO}-d_6$ ) 153.9, 132.9, 125.8, 63.5, 38.6, 13.7;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3440, 1742, 1638, 1533, 1448, 1095, 787, 643; MS:  $m/z = 169$  (18%) [M], 141 (11%) [ $\text{M}-\text{CH}_2-\text{CH}_3 + 1$ ].

A sample of 138 mg (0.518 mmol, 1 eq) of 2-ethoxycarbonyl-1,3-dimethylimidazolium hydrogensulfate was dissolved in 10 mL of 50%  $\text{H}_2\text{SO}_4$  and heated to reflux temperature for 5 h. After neutralization with NaOH, the solvent was evaporated. The resulting solid was recrystallized from ethanol and dried *in vacuo* to give 1 (0.065 g; 90% yield).

### Norzooanemonine 3

**Method A<sup>21</sup>.** 1-Methylimidazole (50 mL, 0.63 mol) and dimethyl carbonate (75 mL, 0.89 mol) were placed in an autoclave. The mixture was then heated under stirring to  $120^\circ\text{C}$ . After 7 h, the autoclave was allowed to cool to rt, the precipitate was filtered off, washed with diethyl ether, and recrystallized from ethanol : methanol (1 : 1). Yield: 19%.

**Method B.** A sample of 1.9 g (0.017 mol, 1 eq) of imidazole-4-carboxylic acid was suspended in 40 mL  $\text{H}_2\text{O}$ . Then, 7.5 mL of 20% NaOH and subsequently 5 mL (0.051 mol, 3 eq) of dimethyl sulfate were added. The mixture was heated for 5 h at reflux temperature. After cooling, diluted  $\text{NH}_3$  solution was added and the mixture was then neutralized with diluted HCl, and extracted twice with 150 mL of dichloromethane. The aqueous layer was evaporated to dryness under Dean–Stark conditions with toluene. The resulting solid was subsequently washed with diethyl ether and ethanol. Norzooanemonine was obtained as a white solid in 68% yield.

**Method C.** A sample of 1.25 g (0.0112 mol) of imidazole-4-carboxylic acid was suspended in a mixture of 18 mL of nitrobenzene, 3 mL of 20% aqueous NaOH, and 15 mL of water.

Then, 3.5 mL (0.037 mol) of dimethyl sulfate were added to the two-phase system, which was heated at 160–170 °C for 20 h. After cooling the reaction mixture was extracted with dichloromethane. The aqueous layer was evaporated to dryness, and the resulting precipitate was washed with ethanol to give norzooanemonine **3** as a colourless solid in 73% yield.

**Method D/E.** A sample of 1 g (8.92 mmol, 1 eq) of imidazole-4-carboxylic acid was suspended in 20 mL of xylene. Then, 0.2 mL (1.943 mmol, 0.22 eq) of nitrobenzene and subsequently 2.8 mL (0.03 mol, 3.3 eq) of dimethyl sulfate were added, whereupon all solids dissolved. The mixture was then refluxed for 3 h, evaporated to dryness, and treated with 3 g (0.0535 mol) of methanolic KOH. Stirring was continued for 24 h, and then the solution was neutralized with diluted aqueous HCl. The solvent was then evaporated to give a brownish solid which was partially dissolved in ethanol. Evaporation to dryness followed by column chromatography [silica gel; methanol/ethyl acetate = 1/1] yielded a sample of norzooanemonine. All spectroscopic data are consistent to those reported in literature.<sup>21</sup>

### 1,3-Dimethylimidazolium-2-dithiolate **8**

A 25 mL flask was subsequently filled with 0.070 g of 1,3-dimethyl-1*H*-imidazolium-2-carboxylate **1**, 10 mL of toluene and 1 mL of CS<sub>2</sub>. The resulting orange coloured suspension was heated to 100 °C under vigorous stirring. After 3.5 h the mixture was cooled to rt, and the solvent was distilled off *in vacuo*. The resulting residue was then chromatographed (silica gel, MeOH) to give 1,3-dimethylimidazolium-2-dithiolate, yield 11 mg (16%), and recovered starting material (13 mg; 18.6%), mp 227 °C (found: 173.0210. C<sub>6</sub>H<sub>9</sub>N<sub>2</sub>S<sub>2</sub> requires 173.0207).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 6.86 (s, 2 H), 3.81 (s, 6 H) ppm;  $\delta_{\text{C}}$  (CDCl<sub>3</sub>): 224.0, 149.9, 119.0, 35.1 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3107, 1512, 1242, 1060 (CS<sub>2</sub>), 705; MS (70 eV):  $m/z$  = 172 (M<sup>+</sup>, 100%), 95 (M-CS<sub>2</sub>, 49%).

### 1,3-Dimethylimidazolium-2-*N*-(3,5-dichlorophenyl)thioamidate **9**

Under inert conditions 0.15 g (1.070 mmol, 1 eq) of 1,3-dimethylimidazolium-2-carboxylate were suspended in 4 mL of toluene, stirred for a short period of time, and treated with 0.22 g (1.070 mmol, 1 eq) of 3,5-dichlorophenylisothiocyanate and another 4 mL of toluene. The resulting yellow suspension was heated to reflux for 4.5 h. After cooling, the slightly brownish solid was filtered off and dried *in vacuo*, yield 0.2844 g (89%), mp 193–194 °C.  $\delta_{\text{H}}$  (MeOD) 7.41 (2H, s; C4-*H*, C5-*H*), 7.25 (2H, d,  $J$  = 1.9 Hz; H<sub>ar</sub>), 7.12 (1H, t,  $J$  = 1.9 Hz; H<sub>ar</sub>), 3.89 (6H, s, N-Me);  $\delta_{\text{C}}$  (MeOD) 172.2, 154.1, 147.1, 135.7, 124.2, 122.2, 122.1, 35.5 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3424, 3113, 1626, 1573, 1557, 1534, 1422, 1245, 1206, 1100, 1046, 994, 975, 899, 871; MS (70 eV):  $m/z$  = 300 (66%) [M], 203 (54%) [Cl<sub>2</sub>-Ph-N=C-S].

### 1,3-Dimethylimidazolium-2-*N*-(*p*-chlorophenyl)amidate **10a**

0.3 g (2.141 mmol, 1 eq) of 1,3-dimethylimidazolium-2-carboxylate **1** were suspended in 10 mL of toluene and treated with 0.33 g (2.141 mmol, 1 eq) of 4-chlorophenylisocyanate. After stirring for 10 min at rt the suspension was heated to reflux temperature. After stirring at reflux temperature for 3 h, the solution was cooled, the resulting slightly yellowish solid was

filtered off and dried *in vacuo*, yield 0.43 g (80%), mp 121 °C (found: C, 53.51; H, 4.41; N, 15.96. C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>OCl. H<sub>2</sub>O requires: C, 53.84; H, 5.27; N, 15.70).  $\delta_{\text{H}}$  (MeOD) 7.46 (2H, s; C4-*H*, C5-*H*), 7.42–7.35 (2H, m, H<sub>ar</sub>), 7.27–7.20 (2H, m, H<sub>ar</sub>), 3.98 (6H, s, N-Me);  $\delta_{\text{C}}$  (MeOD) 155.2, 148.0, 129.3, 128.6, 126.5, 123.1, 107.2, 36.4 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3424, 3109, 2960, 2215, 1596, 1561, 1513, 1482, 1453, 1398, 1341, 1249, 1235, 1097, 1010, 935, 897 cm<sup>-1</sup>; MS:  $m/z$  = 249 (31%) [M], 153 (100%) [Cl-C<sub>6</sub>H<sub>4</sub>-N=C-O].

### 1,3-Dimethylimidazolium-2-*N*-(3,5'-dichlorophenyl)amidate **10b**

A sample of 0.085 g (0.34 mmol, 1 eq) of 1,3-dimethylimidazolium-2-*N*-(*p*-chlorophenyl)amidate **10a** was suspended under inert conditions in 8 mL of toluene. Then, 0.064 g (0.34 mmol, 1 eq) of 3,5-dichlorophenylisocyanate were added. The mixture was stirred for 20 min at rt, and then for 3 h at reflux temperature. After evaporation of the solvent, a brown oil was obtained, yield 0.046 g (46%) (found: 284.0361. C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>OCl<sub>2</sub> requires 284.0357).  $\delta_{\text{H}}$  (MeOD) 7.55 (2H, s, C4-*H*, C5-*H*), 7.41–7.40 (3H, m, H<sub>ar</sub>), 3.91 (6H, s, N-Me);  $\delta_{\text{C}}$  (MeOD) 173.3, 172.4, 163.6, 134.1, 129.8, 123.7, 123.3, 36.6 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3333, 3216, 2961, 2361, 1598, 1563, 1512, 1494, 1430, 1342, 1306, 1241, 1173, 1092, 1009, 990, 941, 916, 892; ESI-MS: 308 (13%) [M + H<sup>+</sup> + Na<sup>+</sup>].

### 2-Deuterio-1,3-dimethylimidazolium-4-carboxylate **13**

Under nitrogen 0.020 g (0.143 mmol, 1 eq) of norzooanemonine **3** were dissolved in 1 mL of anhydrous MeOD and stirred for 1 h. The sample was directly analyzed by NMR-spectroscopy.  $\delta_{\text{H}}$  (MeOD) 7.70 (1H, s, C5-*H*), 4.08 (3H, s, C8-*H*), 3.89 (3H, s, C7-*H*) ppm;  $\delta_{\text{C}}$  (MeOD) = 162.9, 133.6, C2 not detectable, 126.9, 36.5, 36.3 ppm; ESI-MS:  $m/z$  = 164.1 (100%) [M + Na<sup>+</sup>], 120.2 (55%).

### 1,3-Dimethylimidazolium-4-*N*-(3,5'-dichlorophenyl)amidate **16b**

A sample of 0.5 g (3.56 mmol) of norzooanemonine **3** was suspended in 10 mL of toluene. Then, 0.67 g (3.56 mmol) of 3,5-dichlorophenyl isocyanate were added, the mixture was heated to 100 °C for 1 h and then to reflux temperature for 10.5 h. After cooling, the white solid was filtered off and dried *in vacuo*, yield 0.13 g (13%), mp 230–240 °C (dec) (found: 284.0363. C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>OCl<sub>2</sub> requires 284.0357);  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>) 9.23 (1H, s, C2-*H*), 8.35 (1H, s, H<sub>ar</sub>), 7.56 (2H, s, H<sub>ar</sub>), 7.18 (1H, s, C5-*H*), 3.99 (3H, s, C8-*H*), 3.85 (3H, s, C7-*H*);  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>) 159.1, 152.0, 140.4, 134.1, 129.0, 125.0, 121.3, 116.5, 36.1, 36.0 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3444, 3304, 3157, 3129, 3096, 3050, 2695, 2522, 2435, 1727, 1650, 1587, 1549, 1483, 1418, 1223, 1165, 1060, 848; ESI-MS:  $m/z$  = 283 (10%)/285 (15%) [M].

### General procedure for the amide tetrafluoroborates **17a,b**

Under an inert atmosphere, 1 eq of 1,3-dimethylimidazolium-2-carboxylate **1** (0.15 g; 1.07 mmol) and norzooanemonine **3** (0.15 g, 1.07 mmol), respectively, was suspended in anhydrous dichloromethane. Then, 9 eq of SOCl<sub>2</sub> (1.15 g; 0.7 mL, 9.63 mmol) as well as 1 eq of anhydrous pyridine (0.09 g, 0.09 mL 1.07 mmol) were added, whereupon the mixture was stirred at reflux temperature for 30–60 min. Then 3 eq of the corresponding aniline were added carefully. After reflux for 3–6 h, the mixture was allowed to cool, the solvent was evaporated and water was added. The

resulting solid was dissolved in methanol and cooled to 0 °C. Then a 50% HBF<sub>4</sub>-solution was added and the mixture was stirred at 0 °C for 30 min. The resulting tetrafluoroborate was filtered off and dried *in vacuo*.

### 1,3-Dimethylimidazolium-4-*N*-(4-chlorophenyl)amide tetrafluoroborate 17a

The procedure described above yielded 412 mg (20%) of a brownish solid, mp 175–176 °C (found: C, 42.51%, H, 3.42%, N, 12.61%. C<sub>12</sub>H<sub>13</sub>BClF<sub>4</sub>N<sub>3</sub>O requires: C, 42.70%, H, 3.88%, N, 12.45%).  $\delta_{\text{H}}$  (MeOD) 8.90 (1H, s, C2-*H*, H/D exchangeable), 8.06 (1H, s, C5-*H*), 7.58 (2H, m, H<sub>ar</sub>), 7.27 (2H, m, H<sub>ar</sub>), 4.02 (3H, s, N-Me), 3.88 (3H, s, N-Me);  $\delta_{\text{C}}$  (MeOD) = 156.9, 137.7, 131.1, 130.0, 130.1, 129.0, 126.5, 123.2, 36.8, 36.7 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3349, 1684; ESI-MS (0V):  $m/z$  = 250 (100%) [M].

### 1,3-Dimethylimidazolium-4-*N*-(3,5-dichlorophenyl)amide tetrafluoroborate 17b

The procedure described above gave 188 mg (25%) of a colourless solid, mp 170 °C (found: 284.0366. C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>OCl<sub>2</sub> requires 284.0357).  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>) 10.93 (1H, bs; N-*H*), 9.26 (1H, s; C2-*H*), 8.36 (1H, s; H<sub>ar</sub>), 7.77 (2H, s; H<sub>ar</sub>), 7.41 (1H, s; C5-*H*), 4.02 (3H, s; C8-*H*), 3.93 (3H, s, C7-*H*);  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>) 156.0, 140.4, 140.3, 134.3, 126.1, 123.8, 118.4 (two overlapped signals), 36.3 (C-8), 36.1 (C-7) ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3129, 1697, 1594, 1541, 1444, 1271, 1084, 1003, 861 cm<sup>-1</sup>; ESI-MS:  $m/z$  = 284 (100%) [M].

### General procedure for the conversion of the amides 17a,b into the amidates 16a,b

An ion exchange resin, Amberlite IRA-402 was activated first with conc. HCl in a chromatography column to fully achieve the chloride form, then washed with water to pH 7. Conc. NaOH was then left on the column to exchange the anion to hydroxide. Then the resin was washed with water to pH 7–8. The amides (0.505 mmol, respectively) were applied in a mixture of MeOH/H<sub>2</sub>O (1/1) or EtOH/H<sub>2</sub>O (1/1) to the amberlite and rinsed through the ion exchange resin with the same solvent to give the corresponding amidates.

### 1,3-Dimethylimidazolium-4-*N*-(4-chlorophenyl)amidate 16a

Yield: 390 mg (99%) of a white solid, mp 263–264 °C (found: 250.0744. C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>OCl requires: 250.0747).  $\delta_{\text{H}}$  (MeOD) 8.86 (1H, s, C2-*H*, exchangeable), 8.06 (1H, s, C5-*H*), 7.49 (2H, m, H<sub>ar</sub>), 7.13 (2H, m, H<sub>ar</sub>), 3.90 (3H, s, C8-*H*), 3.77 (3H, s, C7-*H*);  $\delta_{\text{C}}$  (MeOD) = 157.0, 137.8, 131.0, 129.9, 128.9, 126.7, 123.2 (two overlapped signals), 37.0, 36.9 ppm;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3359, 1679 cm<sup>-1</sup>; MS:  $m/z$  = 249 (12%) [M], 153 (50%) [Cl-Ph-N=C-O], 127 (100%) [Cl-Ph-NH<sub>2</sub>].

### 1,3-Dimethylimidazolium-4-*N*-(3,5-dichlorophenyl)amidate 16b

Yield: 123 mg (86%) of a yellow solid. All spectroscopic data are identical to those described as the trapping experiment for NHC 4.

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