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4,5-Bis(dialkylamino)-Substituted Imidazolium Systems: Facile Access to N-Heterocyclic Carbenes with Self-Umpolung Option

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Dedicated to Professor Robert West

Abstract: The first synthesis of 4,5-bis(dimethylamino)-substituted imidazolium compounds was developed, which is based on the reaction of a 1,2-diamino-1,2-bis(phosphonio)ethene with lithiated formamidines. This represents the first application of this class of ethene derivatives for the preparation of heterocycles. These N-heterocyclic carbene (NHC) precursors show a remarkably reduced basicity and nucleophilicity of their NMe_2 groups, which is due to the strong anomeric interactions of the latter with the imidazolium core. According to DFT calculations, these NHCs are capable of self-umpolung if sufficiently strong acceptor substituents are introduced at the carbene center. To test the self-umpolung capabilities of the NHCs, various substituents were attached to the carbene center and the obtained compounds were characterized by single-crystal X-ray analysis as well as quantum chemical computations. Strong acceptor substituents are required to induce self-umpolung, such as in the phosphonio-substituted derivative, for which partial self-umpolung was found. The *N*,*N'*-bis(4-dimethylaminophenyl)-substituted imidazolium compound represents a special case, as it incorporates as much as three two-step redox systems within the NHC framework. This will probably result in a high electronic flexibility of the corresponding nucleophilic carbenes, especially when they serve as ligands in transition metal complexes.

Keywords: carbenes · cyclization · heterocycles · ligand design · redox chemistry

Introduction

In previous work[1–5] a central focus of our research has been on the development of a novel type of nucleophilic carbenes, which incorporate the option of "self-umpolung". These systems should be able to adapt chameleon-like to the electronic demands of an organic or inorganic substituent attached to them.[3a,4] The formal conceptual basis for this is a "short-circuit-like" connection through π conjugation between a singlet carbene center **OX′** and a two-stage redox module in its **RED** form[6] according to Figure 1. Structure **A** is in resonance with the electronically complementary structure **B**, in which the "carbene" carbon center is formally reduced to a di-ide by the electron-rich π module (Figure 1).[3a,4,5]

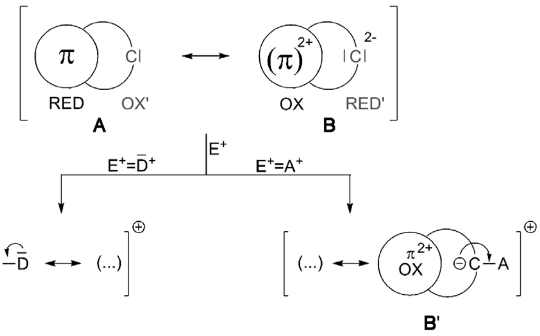

Figure 1. Schematic depiction of the general structural motif of a "self-umpolung" carbene (and its derivatives).

This "redox resonance" indicates an electronic flexibility of this type of carbenes, which in principle allows stabilizing π interactions with both electron-donating and electron-accepting partners, as shown by **A′** and **B′** (being the extreme cases, with intermediate electronic demands forming a continuous spectrum in-between **A′** and **B′**).

In the past we have conceived carbenes **1**–**3** (Scheme 1), which exemplify this concept. At the same time, the dinitroxide-carbene **4** and its radical anion **5** already represent a conceptual extension, as in these cases the carbene center is coupled with two two-stage redox systems through π conjugation (under avoidance of cyclic π conjugation).

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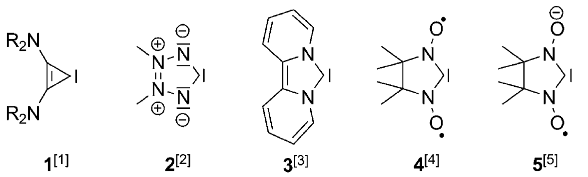
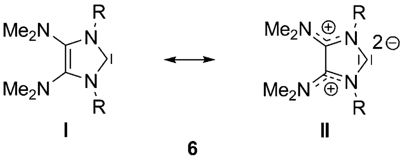


Scheme 1. Closed-shell and open-shell examples of nucleophilic carbenes with „self-umpolung“ option.

Considering the importance and prevalence of imidazole-based N-heterocyclic carbenes (NHCs) in various areas of modern chemistry,[7] we subsequently set out to develop a structurally variable and synthetically efficient synthesis of imidazolin-2-ylidenes with built-in π-redox modulation.

Prima facie, the 4,5-bis(dialkylamino)imidazolinylidene **6** (Scheme 2) fulfills the criteria for “NHC-chameleons”, as defined above. Electronic structure calculations confirm this view (see below).



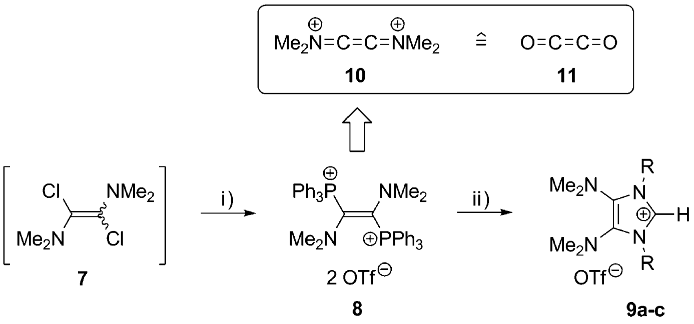
Scheme 2. Structural characteristics of 4,5-bis(dialkylamino)imidazolin-2-ylidene **6**.

In the limiting case **I**, this type of molecule can be conceived as a cyclic π-conjugated complex between a (strongly reducing)[8] tetraaminoethene substructure and divalent carbon. In the redox-complementary resonance structure **II**, these compounds can be considered as special examples of bisonio-diides, which have been the subject of intense discussion lately.[9] The latter structure (**II**) points to a further interpretation of **6**, according to which this nucleophilic carbene could be viewed as a chelate complex between an oxalylic acid bisamidine and a ^{1}D carbon atom.[10]

Although several 4,5-bis(dialkylamino)-substituted, N-monosubstituted imidazoles are known,[11] selective alkylations at the N3 position would pose problems due to the presence of the two amino groups.[12] Herein, we report on the synthesis of the previously unknown 4,5-bis(dimethylamino)imidazolium system **9**, the deprotonation of which allows a general access to the desired class of compound **6**.

Results and Discussion

The decisive building block for the synthesis of **9** turned out to be the bis(phosphonio)diaminoethene **8**, which preparation we recently reported.[13] As an a^1,a^2-biselectrophile that is easy to handle and dose, ethene **8** can be conveniently converted to the desired imidazolium system **9** by a novel [3+2] cyclodisubstitution reaction with formamidine anions as d^0,d^2-bisnucleophiles (Scheme 3). The dicationic salt **8** serves as a reagent for the ethene-bis(dimethyliminium) synthon **10** and thus indirectly also for the elusive C_2O_2[14] (**11**). This synthetic route constitutes a novel and direct access to the imidazolium core, which does not involve a quaternization of an imidazole intermediate.

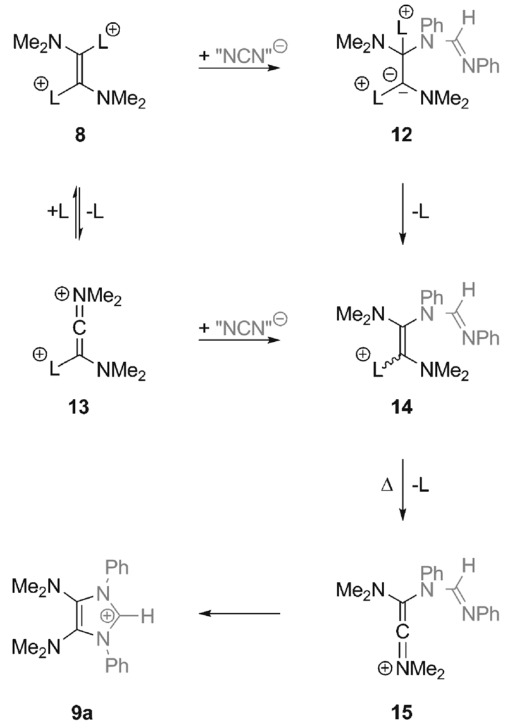


R	C_6H_5	C_6H_4-CH_3	C_6H_4-NMe_2
	9a (59%)	**9b** (66%)	**9c** (42%)

Scheme 3. Synthesis of 4,5-bis(dimethylamino)-substituted imidazolium systems. i) PPh_3 (2 equiv), trimethylsilyl trifluoromethanesulfonate (TMSOT, 2 equiv); ii) RN(Li)C(H)NR.

Interestingly, although **9a** was also detected by mass spectrometry when using the ethene derivative **7** instead of **8** as bis-electrophile in the reaction with the respective formamidine, the product seemed to have been formed in low yield only and could not be isolated. This might in part be due to the very reactive nature of **7**, which necessitates its preparation in situ and thus makes it difficult to add the formamidine anion in an exact 1:1 stoichiometry. In addition, the bis(phosphonio)derivative **8** might also offer an alternative mechanistic route to the product that is not feasible (or not as favorable) with ethene **7**. After addition of the formamidine and stirring for several hours at room temperature, intermediate **14** (Scheme 4) was detected by mass spectrometry, whereas substitution of the second phosphane ligand required thermal activation. Formation of intermediate **14** can be accomplished either by an elimination–addition route via the ketene iminium **13** or by an addition–elimination pathway via the phosphonium ylide **12**. Although we cannot rule out one of these alternatives based on the current experimental data, the ylidic stabilization of the negative charge in **12** renders this intermediate much more favorable than a hypothetical dichloro analogue (starting from **7**). The substitution of the second phosphane ligand should proceed via the ketene iminium intermediate **15**, as an addition–elimination pathway would require the localization of negative charge between two amine substituents at the ethene backbone.

Investigations by cyclic voltammetry yielded a reversible oxidation wave for **9a** at 0.95 V (vs. a saturated calomel electrode (SCE)) as well as an irreversible reduction wave at −0.86 V (vs. SCE). Compound **9c** includes two further, *p*-



Scheme 4. Possible mechanistic routes for the preparation of **9a–c**. Anions are omitted for clarity; L = PPh_3.

phenylenediamine-like, redox systems and is spontaneously oxidized in solution by aerial oxygen (although being reasonably stable as a solid). When treating a solution of **9b** or **9c** in CH_2Cl_2 with 1.5 equivalents of $SbCl_5$ at 0 °C, an instantaneous color change towards purple was observed, which is indicative for the formation of the respective dication radical species. However, rapid decoloration followed, and no defined product could be isolated.

The structures of the three products **9a–c** were confirmed by spectroscopic data and single-crystal X-ray analyses.

The crystals of **9a** and **9b**, grown at room temperature, undergo a phase transition at approximately −20 °C and could thus only be measured at −10 °C. As a consequence, the dimethylamino groups are disordered in both cases, but nevertheless a near-perpendicular orientation of the NMe_2 groups relative to the imidazolium ring is identifiable. In the case of (non-disordered) **9c**, both NMe_2 groups at the imidazolium core are also orientated perpendicularly to the ring system (with the methyl groups above and below the ring plane) and are considerably pyramidalized (Figure 2).

This spatial arrangement is characteristic for an anomeric donation of the NMe_2 lone pairs into the adjacent C–N σ* orbitals of the imidazolium core (Scheme 5). Accordingly, the N3–C4[15] and N1–C5 bond lengths of the imidazolium compounds **9a–c** are markedly elongated compared to suitable reference systems. More precisely, the N1–C5 bond lengths for **9a–c** lie in a range of 1.394–1.416 Å, whereas that of 1,3-bis(mesityl)imidazolium chloride is 1.383 Å[16] and that of its 4,5-dichloro derivative is 1.385 Å.[17]

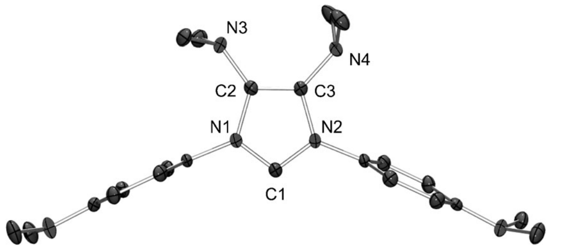
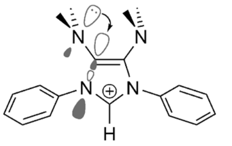


Figure 2. Molecular structure of **9c**.[36] The counteranion and hydrogen atoms are omitted for clarity. Selected bond lengths [A] and angles [°]: N1–C1 1.325, N1–C2 1.411, C2–C3 1.362, C2–N3 1.397, N1-C1-N2 109.6, N3-C2-C3 128.2.

This interaction is also confirmed by DFT calculations[18] on a model system (which bears methyl substituents on the imidazolium nitrogen atoms): a natural bond orbital (NBO) analysis[19] in combination with a second-order perturbation analysis reveals a stabilization of the molecule by about 11 kcal mol^{-1} due to anomeric interaction of the NMe_2 lone pairs with the C5–N1[15] and C4–N3 σ* orbitals. A further anomeric donation into the C4–C5 σ* orbital yields an additional stabilization by about 9 kcal mol^{-1}. Such an n→σ* charge transfer within the imidazolium σ framework has so far not been described. This effect is—at least partially—enforced by mutual steric hindrance of the two NMe_2 groups when co-planar with the ring system. This latter arrangement could only be approximated with the two donor groups as part of a rigid ring system.[20]

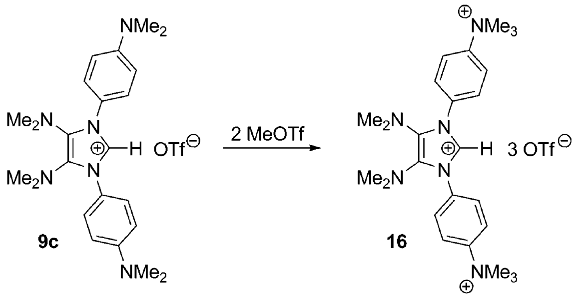


Scheme 5. Anomeric n→σ* interaction in the imidazolium system **9a**.

Because of the donation of the nitrogen lone pairs of the amino groups into the σ backbone of the imidazolium core, less electron density is available for external electrophiles. This has noticeable consequences on the reactivity of **9a** and **9b** towards electrophiles: for instance, **9a** can not be measurably protonated by either CF_3COOH or one equivalent of HOTf. Only by addition of a massive excess of HOTf could protonation be achieved, but this also leads to partial protonation of the second NMe_2 group. Addition of one equivalent of MeOTf to **9a** resulted in only about 20 % methylation, apparently because an equilibrium is in place.

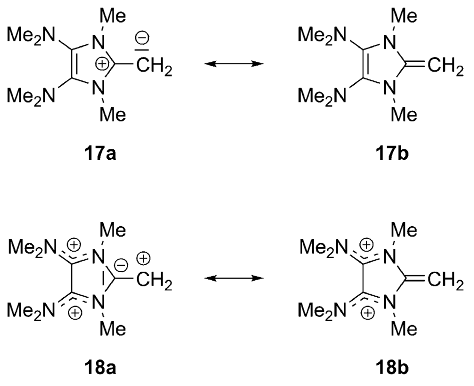
The unusually low reactivity of both dimethylamino groups at the C4 and C5 positions is also reflected in the methylation of **9c** with two equivalents of MeOTf (Scheme 6), which selectively occurs at both phenylic NMe_2 groups and thus yields the air-stable tricationic species **16** as the exclusive product in quantitative yield (for single-crystal X-ray analysis see the Supporting Information).

Having established the synthesis of the imidazolium compounds **9a–c**, our next goal was to introduce various substituents at the "carbene" position C2 to test the self-umpolung capabilities of these bis(amino)-substituted imidazolium systems. In advance, orientating DFT calculations[18] on a model system (bearing methyl substituents on the imidazo-



Scheme 6. Methylation of **9c**.

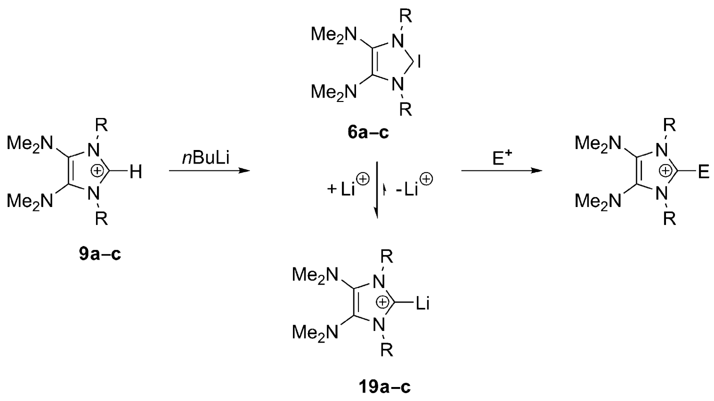
lium nitrogen atoms) were conducted with the prototypical donor $-CH_2^-$ and acceptor $-CH_2^+$ as substituents at the C2 position to investigate the structural effects of self-umpolung. Scheme 7 shows some relevant resonance structures for these derivatives **17** and **18**.



Scheme 7. Model systems **17** and **18** for computational self-umpolung investigations.

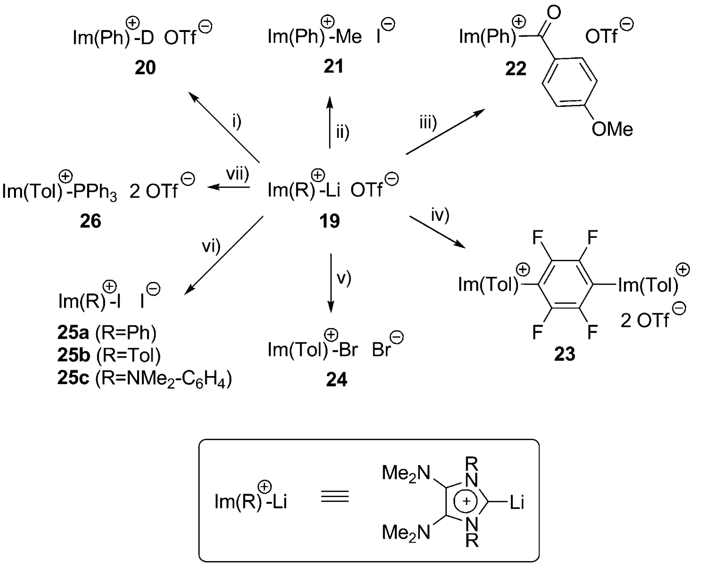
The most pronounced structural differences between those extreme cases are in accord with the resonance structures **17b** and **18b**. Thus, in a comparison of the "normal" electronic situation **17** to the self-umpoled case **18**, the C–NMe$_2$ and the C4–N3/C5–N1[15] bond lengths are shorter (1.400 vs. 1.328 and 1.416 vs. 1.345 Å), whereas the C4–C5 bond length increases markedly (1.362 vs. 1.505 Å). In addition, the orientation and geometry of the dimethylamino groups changes from pyramidalized NMe$_2$ groups that are perpendicular to the ring system (**17**) to planar NMe$_2$ groups that are as parallel to the π-ring system as (sterically) possible (**18**).

Derivatization with electrophiles: Derivatization of the imidazolium systems **9a–c** at the C2 position could be achieved by generation of their lithiated forms **19a–c** (serving as synthetic equivalents for carbenes **6a–c**) with *n*BuLi and in situ treatment with electrophiles (Scheme 8).



Scheme 8. Generation and exemplary derivatization of the electron-rich carbenes **6a–c** (or their lithiated forms **19a–c**). Counteranions are omitted for clarity. E = electrophile; R = Ph (**a**), 4-Me-C_6H_4 (**b**), 4-NMe$_2$-C_6H_4 (**c**) (see text).

Carbene **6b** could be generated by deprotonation of **9b** with KH in degassed THF at −20 °C. Its carbene carbon atom shows a ^{13}C NMR signal at $\delta = 190$ ppm, which is in the typical range for NHCs.[21] Lithiation of **9a–c** with *n*-butyllithium at −78 °C in THF generates **19a–c** in quantitative yield without any side products, as shown by ^{1}H NMR spectroscopy. Consequently, the lithiated species **19a–c** were chosen as starting materials for the subsequent derivatization with electrophiles. An overview of those electrophilic substitution reactions on **19a–c** is presented in Scheme 9.



Scheme 9. Electrophilic substitution reactions on **19a–c**. i) CF_3COOD, TMSOTf; ii) MeI; iii) MeO-C_6H_4-C(O)Cl; iv) C_6F_6; v) Br_2; vi) I_2; vii) $(PPh_3)_2(OTf)_2$. Im = 4,5-bis(dimethylamino)imidazolium; Tol = tolyl.

As first simple derivatizations of **19a**, the deuterated (**20**) and methylated (**21**) compounds were prepared in 49 and 87 % yield, respectively. Deuteration was achieved by treatment with CF_3COOD and subsequent anion exchange with TMSOTf. The apparent incomplete nature of the exchange might explain the overall low yield of the product, which was isolated as the pure triflate salt. Methylation of **19a** was performed by using methyl iodide, which resulted in precipitation of the pure iodide salt **21** from the reaction mixture. Compound **21** was also characterized by single-crystal X-ray analysis (see the Supporting Information). As expected, the structural features of the imidazolium part of **21** are very similar to those of **9a**. The iodide counterion resides atop the π-ring system of the cation in the solid-phase structure.

An acyl substituent served as the first π acceptor that was introduced at the carbene position of the imidazolium systems. Accordingly, the lithiated species **19a** was treated with *p*-methoxybenzoylchloride at low temperatures (−50 °C) in THF. After subsequent anion exchange with TMSOTf, the triflate salt **22** was isolated in 67 % overall yield. Related carbonyl-substituted imidazolium systems are known[22] and have been used as acylation reagents.[23] The C=O stretch frequency of salt **22** occurs at $\tilde{\nu} = 1664\,\text{cm}^{-1}$ and thus denotes the imidazolium part as an electron donor towards the carbonyl group (compare C=O stretch frequencies of $\tilde{\nu} = 1692$ and $1650\,\text{cm}^{-1}$ for the corresponding aldehyde and amide, respectively).[24] A single-crystal X-ray analysis of **22** (see the Supporting Information), however, shows a near-perpendicular orientation of the acyl substituent relative to the π-ring system (torsion angle 73°) and furthermore "non-self-umpoled" structural characteristics of the imidazolium core. In addition, a bond length of 1.525 Å between the "carbene" C atom and the carbonyl C atom as well as a C=O bond length of 1.241 Å show no indication of π donation from the imidazolium part and are very similar to those of a related 1-acyl-4,5-bismethylated imidazolium compound.[25] Thus, the imidazolium part acts merely as a σ donor towards the acyl moiety. DFT calculations[18] show that the perpendicular orientation of the acyl part in **22** is mainly due to steric interactions and that the formyl group as a very small acyl substituent would orient itself almost co-planar with the ring system. Interestingly, however, even the formyl substituent is predicted by DFT to induce only a weak self-umpolung effect on the imidazolium backbone.

Accordingly, we turned our attention to stronger electron acceptors at the C2 position. Introduction of a pentafluorophenyl moiety, for instance, would generate a substrate for the SASAPOS-protocol[26] and would thus allow the introduction of a pentaoniobenzene substituent at the C2 position. Reaction of **19b** with one equivalent of hexafluorobenzene, though, led to formation of the bis(imidazolium)derivative **23**, which was isolated in 29 % yield (relative to hexafluorobenzene). No other products were detected by mass spectrometry. To the best of our knowledge, bis(imidazolium)-substituted derivatives of hexafluorobenzene were previously unknown. Although bis(imidazolio)benzenes have been reported,[27] they have not been characterized structurally. In contrast, salt **23** was studied by single-crystal X-ray analysis (see Figure 3; the crystal cell contains four independent dications of **23**, one of which is shown here).

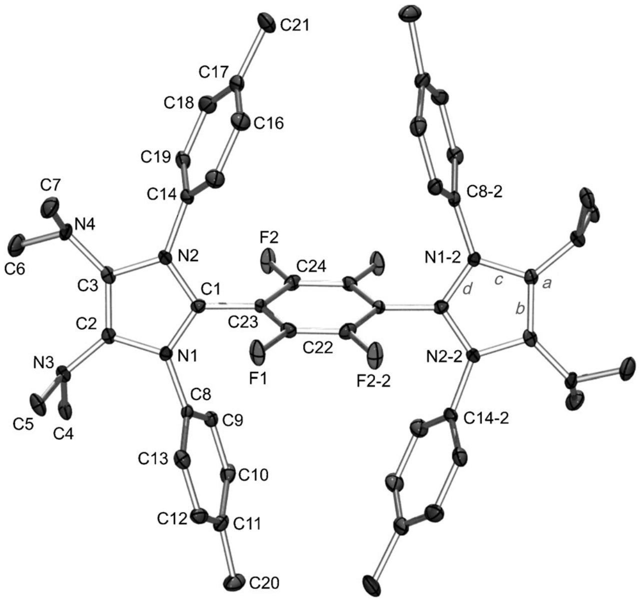


Figure 3. Cation of **23** (hydrogen atoms are omitted for clarity);[36] $a = 1.388$, $b = 1.364$, $c = 1.409$, and $d = 1.336$ Å, angle of torsion (N2-C1-C23-C24) = 70.2° (mean values over all four dications).

Structural data of the diamino-imidazolium core show no indications of self-umpolung. Apparently, the inductive electron withdrawal of the tetrafluorobenzene part is too weak to induce "self-umpolung by polarization". The anions of **23** are coordinated by weak hydrogen bonds at the periphery of the imidazolium ligands.

Subsequently, compound **23** was exposed to SASAPOS conditions[26] to substitute all fluorine substituents by 4-dimethylaminopyridinium ligands. Although indications for the formation of the hexacationic product were obtained (after six hours of heating to reflux in acetonitrile) by mass spectrometry and elemental analysis, the isolated red solid proved to be extremely labile to hydrolysis. Consequently, attempts to characterize the compound by NMR spectroscopy and single-crystal X-ray analysis failed.

Because phosphonio ligands constitute particularly strongly electron-withdrawing substituents by virtue of ylidic charge stabilization, we also prepared the phosphonio-substituted derivative of **9b** by treating its lithiated form with $PPh_3(OTf)_2$ (prepared in situ from PPh_3O and Tf_2O).[28] To the best of our knowledge, no C2-phosphonio-substituted imidazolium compounds have been previously reported.[29] The overall yield of **26** was 22 %. Interestingly, the ^{13}C NMR peak of the C4/C5 carbon atom of the imidazolium ring occurs at $\delta = 143$ ppm, about 8 ppm downfield shifted compared to the parent compound **9b**. No such shift was observed for all previous derivatives of **9b**. This effect might be explained by a higher weight of the self-umpoled structure of type **II** (see Scheme 2). Although no suitable single crystals for X-ray analysis could be obtained, DFT calculations[18] on a model system (see Figure 4) point towards (at least partial) self-umpolung.

Hence, the amino groups are now almost planar (sum of angles: 354°) and are orientated at a 45° angle relative to the imidazolium ring. In addition, the elongated C4−C5

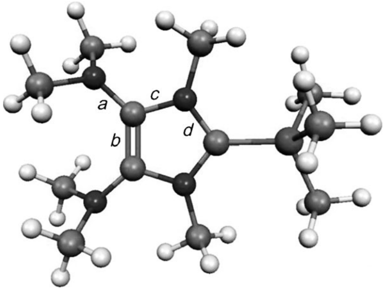


Figure 4. Model system for phosphonio derivative **26**, as obtained by DFT calculations; $a=1.367$, $b=1.406$, $c=1.391$, and $d=1.366$ Å.

bond length (1.406 Å) and the shortened C–NMe$_2$ bond length (1.367 Å) relative to the parent compound (compare Figure 2 and the Supporting Information) are visible proof of a partial self-umpolung according to Figure 1 (**B′**). An NBO analysis of the model system shown in Figure 4 further confirms this by the finding that the single most important interaction of the NMe$_2$ lone pairs with the imidazolium ring is found to be an n→π* donation. All these data indicate that the electronic structure of **9b** is at least partially of the self-umpoled variety.

In order to be able to introduce nucleophiles at the carbene center, halogenated derivatives of **9a–c** were also prepared. Thus, the lithiated species were treated with one equivalent of elemental bromine or iodine to give compounds **24** (R = Tol) and **25a–c** (R = Ph, Tol, 4-NMe$_2$-C$_6$H$_4$). The imidazolium bromo-bromide[30] **24** was isolated in 76 % yield and characterized by single-crystal X-ray analysis (see the Supporting Information). To the best of our knowledge, this represents the first structural data for such a system (although C2-bromo-substituted imidazolium derivatives with other anions have already been characterized).[31] The bromide counteranion forms a halogen bond with the cation (featuring a Br–Br distance of 3.283 Å) and also sits atop the imidazolium ring of a second cation (n→π* interaction).[32] The dimers thus formed might explain the unusual solvation behavior of compound **24**, which is only well soluble in CH$_2$Cl$_2$.

The iodo-iodides **25a–c** were obtained in good yields (**25a**: 52, **25b**: 57, **25c**: 59 %). Although **25b** is insoluble in all tested solvents, **25a** and **25c** are reasonable soluble in CH$_2$Cl$_2$ and CHCl$_3$ (similar to **24**). Compound **25a** could also be characterized by single-crystal X-ray crystallography (see Figure 5).

Similar to compound **24**, a strong halogen bond between the anion and the cation is found, with an I–I distance of 3.357 Å. This is in accord with structural data of already reported imidazolium iodo-iodides.[33] The fact that the halogen bond length is distinctly longer than for a C4,C5-unsubstituted iodo-iodide[33a] (3.26 Å) and more like that of a C4,C5-methylated system[33b] (3.35 Å) might be attributable to the anomeric donation of the NMe$_2$ lone pairs, which would render the C–I σ*orbital of the cation less susceptible to halogen bond formation with the anion. The further structural data of the imidazolium core are similar to that of the parent compound.

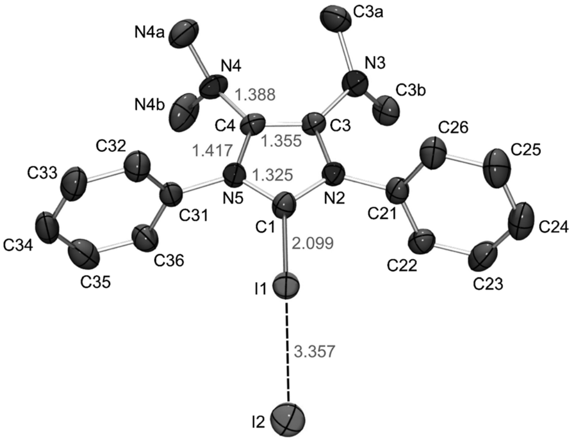


Figure 5. Crystal structure of compound **25a** (hydrogen atoms are omitted for clarity).[36]

Further crystals also formed in the mother liquor from which **25a** was precipitated. Here, the counteranions consist of a 1:1 mixture of iodide and tri-iodide (see Figure 6). The latter was apparently formed with a slight excess of iodine during the preparation of **25a**. In the crystal structure, the iodide is coordinated to two cations through nearly-orthogonal (98°) halogen bonds (with I–I distances of 3.303 and 3.306 Å). The tri-iodide, in contrast, is hydrogen bonded to a dimethylamino group. Thus, even when already coordinated to an imidazolium cation, the iodide is still a stronger Lewis base than the tri-iodide anion. This, in turn, means that molecular iodine is a stronger halogen bond donor (i.e., σ*-Lewis acid) than the cationic imidazolium system. The overall structural motive of **25a**, especially the perpendicular orientation of the C2–I2 and I1–C1 vectors at I3 (see Figure 6), is reminiscent of pentaiodide I$_5^-$.[34] This spatial arrangement of two iodocarbenium ions relative to a halide center is unprecedented, to the best of our knowledge.

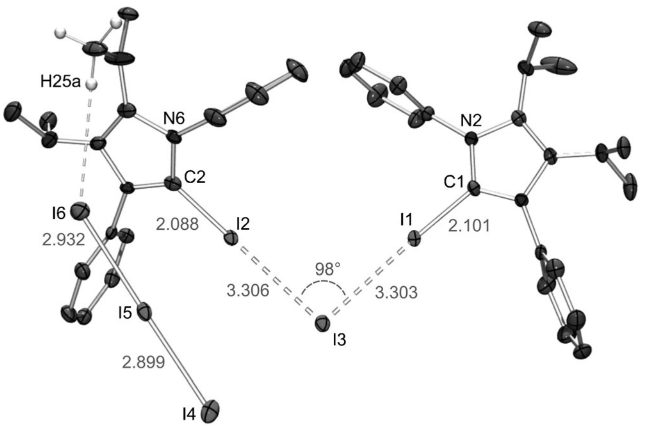
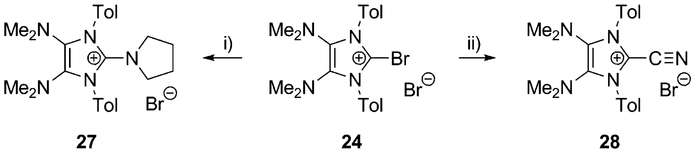


Figure 6. Crystal structure of the cation of **25a** with a 1:1 mixture of iodide and tri-iodide counteranions (most hydrogen atoms are omitted for clarity).[36]

Derivatization of compound 24 with nucleophiles: Bromo-bromide **24** proved to be a suitable starting material for the introduction of nucleophiles at the C2 position of the imidazolium backbone. In order to introduce prototypical π-donor and π-acceptor substituents, an amine (pyrrolidine) and cyanide were chosen as nucleophiles, respectively (Scheme 10).



Scheme 10. Nucleophilic substitution reactions on bromo-bromide **24**. i) 2 pyrrolidine; ii) NEt_4CN.

Thus, treatment of **24** with two equivalents of pyrrolidine (with one of them acting as a base) led to the isolation of the tris(amino)-substituted imidazolium compound **27** in 62 % yield. Orientating PM3 calculations showed that the newly-introduced amino group is orientated perpendicular to the imidazolium ring for steric reasons. Cyclic voltammetry measurements resulted in a reversible oxidation peak at 0.64 V (vs. SCE), about 0.31 V lower than that for the parent compound. This shift can easily be explained by the electron donation of the amino group. When we tried to grow crystals of **27** by diffusion of ether into a solution of **27** in CH_2Cl_2, crystal material was indeed obtained. The crystals, however, referred to a guanidine derivative **27***, as shown in Figure 7 (as every second molecule is protonated by HBr, the overall crystal structure represents a 1:1 co-crystal between protonated and unprotonated amidine).

Because compound **27** had been unambiguously characterized before, apparently a ring-cleavage reaction had taken place. We were able to reproduce this result by treating a solution of **27** in CH_2Cl_2 with concentrated HCl (and therefore we assume that the charge of CH_2Cl_2 that was used for crystallization was contaminated with acid). As for the mechanism of the ring cleavage, we assume that protonation of the pyrrolidino nitrogen leads to a further intensification of the anomeric donation of the NMe_2 lone pairs (because the cationic charge on the pyrrolidino substituent should lower the acceptor orbitals on the imidazolium ring). This apparently leads to cleavage of the C4−N3 (or C5−N1) bond of the ring system, through formation of a ketene iminium intermediate. Thus, the first step of the hydrolysis corresponds to the reversal of the formation of the imidazolium ring system (see Scheme 4) and further illustrates the importance of the anomeric interaction for the chemistry of these systems.

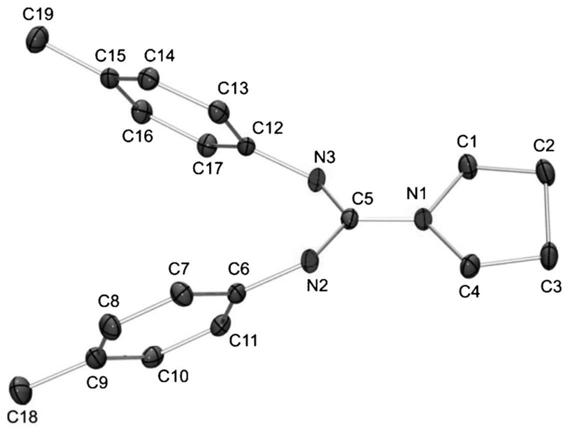


Figure 7. Crystal structure of **27*** after apparent hydrolysis of **27** (hydrogen atoms and the bromide counteranion are omitted for clarity).

Finally, we introduced a cyano substituent at the former carbene position by addition of NEt_4CN to a solution of **24** in CH_3CN. The product **28** was isolated in 69 % yield. Structural data obtained by a single-crystal X-ray analysis (see the Supporting Information) shows no apparent signs of self-umpolung of the imidazolium system and thus indicates that the cyano substituent is not a very strong π acceptor, in accord with literature reports.[35] To the best of our knowledge, these data also represent the first structural characterization of a C2-cyano-substituted imidazolium system.

Summary on self-umpolung investigations: For all (acceptor-substituted) derivatives of **9a** and **9b** that could be characterized by single-crystal X-ray analysis, no indications of self-umpolung of the former carbene center could be found. However, DFT calculations indicate that the C2-phosphonio-substituted derivative **26** might show at least partial self-umpolung (see above). In order to determine, which kind of acceptor substituents at the C2 position would be needed to induce self-umpolung of the imidazolium ring, further DFT investigations,[18] coupled with NBO analyses, were undertaken. Table 1 shows the internal stabilization energies that arise from n→σ* versus n→π* donation of the NMe_2 lone pairs into the respective acceptor orbitals of the imidazolium ring (as computed by second-order perturbation theory analysis within the NBO routine) for various substituents at the C2 position. Again, a simplified model system was used (see Scheme 11).

Table 1. Internal stabilization energies [kcal mol^{-1}] for both types of lone pair donation (see Scheme 11) for various substituted systems.

R	$-CH_2^-$	$-NH_2$	$-H$	$-PMe_3^+$	$-N_2^+$	$-CH_2^+$
n→σ*	18.2	21.0	20.4	18.9	6.1	–[a]
n→π*	3.6	5.2	7.7	15.8	84.7	–[a]

[a] According to the NBO analysis, the NMe_2 lone pairs form double bonds with the imidazolium core.

Scheme 11. n→σ* versus n→π* donation of the NMe_2 lone pairs (compare Table 1).

As can be seen from Table 1, strong (cationic) acceptor substituents like the diazonium group are necessary to induce (almost) full self-umpolung and "switch on" the amino groups for π donation into the imidazolium ring. Unfortunately, all efforts to introduce either $-N_2^+$ or $-CH_2^+$ have not been successful. For other substituents, especially donors, the NMe_2 lone pairs are "locked" in the anomeric interaction with the σ^* orbitals of the ring.

It is also evident from the calculations that steric hindrance of the NMe_2 groups among each other prevents a completely planar orientation of the amino groups in the case of the self-umpoled structures. This issue might be resolved by connecting two of the methyl groups of adjacent amino functions and thus forming a second ring system.

Transition metals represent another class of potentially strong π-acceptor substituents. As the synthesis of such complexes did not represent an immediate goal of our investigations, we only undertook some preliminary test reactions. Thus, although we were able to confirm the formation of a transition metal complex in the reaction of lithiated **9b** with $PdCl_2$ and two equivalents of PBu_3 (and in the reaction of **16** with 0.5 equivalents of Ag_2O) by means of mass spectrometry, no clean product could be isolated in both cases.

Conclusion

The first synthesis of 4,5-bis(dimethylamino)-substituted imidazolium compounds also constitutes the first application of the dication **8** for the preparation of heterocycles. As a potent a^1,a^2-biselectrophile, the ethene derivative **8** should also be applicable for the synthesis of further electron-rich precursors of heterocyclic carbenes. Beyond these applications, compounds **8** possess a fascinating potential as synthetic equivalent of C_2O_2.

The novel NHC precursors presented in this paper show a remarkably reduced basicity and nucleophilicity of their NMe_2 groups, which is due to the strong anomeric interactions of the latter with the imidazolium core. On the one hand, this electron donation creates a predetermined breaking point of the ring system in form of the acceptor C–N bonds, whereas on the other hand the ring strain of the imidazolium core is somewhat released by elongation of the said bonds.

According to DFT calculations, these NHCs should, in principle, be capable of self-umpolung. However, our investigations have shown that typical acceptor substituents at the C2 position are not capable of inducing this effect. For this electronic re-organization, very strong (cationic) acceptor substituents are necessary, and consequently partial self-umpolung was found in the case of the phosphonio-substituted derivative.

Imidazolium compound **9c** represents a special case, as it incorporates as much as *three* two-step redox systems within the NHC framework. This will probably result in a high electronic flexibility of the corresponding nucleophilic carbenes, especially when they serve as ligands in transition metal complexes. Thus, manipulation of the spin states and electron richness of these systems by redox processes should be feasible. These considerations, however, lead well beyond the scope of our present investigations.

Experimental Section

Exemplary synthesis of 9a: A solution of *N,N'*-diphenylformamidine (1.061 g, 5.40 mmol) in THF (25 mL) was cooled to −78 °C, treated with a solution of *n*-butyllithium in hexane (3.4 mL, 1.6 M) and slowly warmed to room temperature. The resulting clear, yellowish solution was added to a suspension of compound **7** (5.052 g, 5.40 mmol) in THF (50 mL) and the mixture was stirred for 20 h at room temperature. After heating to reflux for 5 h a clear red solution was obtained. The solvent was evaporated and the residue was twice recrystallized from CH_2Cl_2 with an about 5-fold amount of Et_2O, filtered off, washed with Et_2O, and dried in high vacuo (yield 59 %).

For spectroscopic data and further experimental procedures see the Supporting Information.

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