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The intersection of allenylidenes and mesomeric betaines. 1-Methylpyridinium-2-acetylide and its palladium complexes

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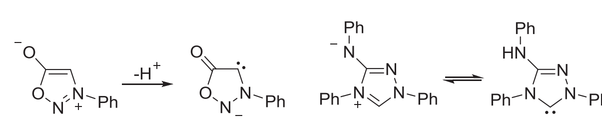
ABSTRACT

The anion of 2-ethynyl-1-methylpyridinium salts, which polymerized rapidly, can be represented as the mesomeric betaine 1-methylpyridinium-2-acetylide or as the cumulene-type structure 1-methylpyridin-2-allenylidene. Palladium complexes have been prepared starting from 2-ethynylpyridine and $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ followed by methylation of the resulting complexes to the title compounds. Results of calculations and spectroscopic measurements are discussed with respect to the zwitterionic or allenylidene resonance forms.

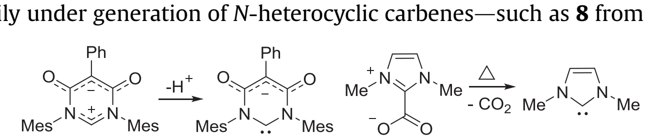
1. Introduction

Mesomeric betaines (MBs) are compounds which can exclusively be represented by dipolar resonance forms in which the positive and negative charges are delocalized within a common π-electron system.[1] In general, according to the rules of resonance not all canonical forms contribute equally to the true molecule.[2] Not surprisingly the adequate formulation of mesomeric betaines had been the matter of debate for a long period of time,[3] and this seems in particular to be true because their formulation contradicts one of the intuitions for finding the most adequate resonance forms, i.e. the rule that stability is decreased by an increase in charge separation.[2] Several classification systems had been proposed in the history of this class of compounds or of its subclasses,[1,4] and the last one has been suggested in 2013 by *Ramsden*[5] as an expansion of an earlier system.[1] Today, conjugated (CMB), cross-conjugated (CCMB), pseudo-cross-conjugated (PCCMB), semi-conjugated (SCMB), and pseudo-semi-conjugated heterocyclic mesomeric betaines (PSCMB) can be distinguished, and this classification has a sound theoretical background.[6] Interestingly, the classification of mesomeric betaines also translates into the chemistry of *N*-heterocyclic carbenes. A review summarizes results achieved so far.[7] As an example, conjugated mesomeric betaines such as sydnones **1** form anionic *N*-heterocyclic carbenes such as **2** on deprotonation[8] (Scheme 1). Other examples have also been reported.[9] Conjugated mesomeric betaines such as the reagent nitron **3/4**[10] and others[11] are in tautomeric equilibrium with their *N*-heterocyclic carbenes and undergo typical carbene trapping reactions.



Scheme 1. Examples of NHCs from MBs.

In the cross-conjugated mesomeric betaine **5** the charges are exclusively delocalized in separated parts of the common π-electron system (Scheme 2). As a consequence and in contrast to **2** the negative charge of its anionic *N*-heterocyclic carbene **6**[12] is π-electronically separated from the diamino carbene center. Members of the class of pseudo-cross-conjugated mesomeric betaines such as imidazolium-2-carboxylates **7**,[13] pyrazolium-3-carboxylates[14] or indazolium-3-carboxylates[15] decarboxylate easily under generation of *N*-heterocyclic carbenes—such as **8** from **7**.



Scheme 2. Examples of a cross-conjugated (**5**) and pseudo-cross-conjugated mesomeric betaine (**7**) and their conversion into mesomeric betaines **6** and **8**, respectively.

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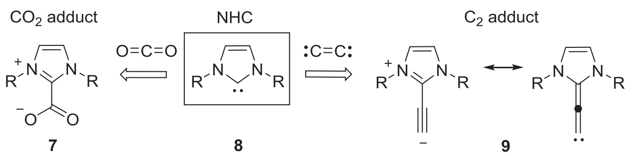
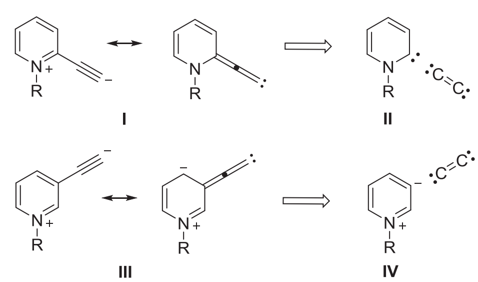
Pseudo-cross-conjugated precursors of *N*-heterocyclic carbenes can be regarded as heterocumulene adducts of normal *N*-heterocyclic carbenes. Formal replacement of CO_2 in **7** towards ethenediylidene (diatomic carbon, C_2) results in imidazolium-2-acetylides **9** which can be represented as mesomeric betaines or as allenylidenes (Scheme 3). Betaine/allenylidene **9** has been prepared as lithium adduct by deprotonation of 2-ethynyl-1,3-dimethylimidazolium triflate and has been subjected to several trapping reactions.[16]



Scheme 3. Dissection of imidazole-2-ylidene from imidazolium-2-carboxylate and imidazolium-2-acetylide/imidazol-2-allenylidene.

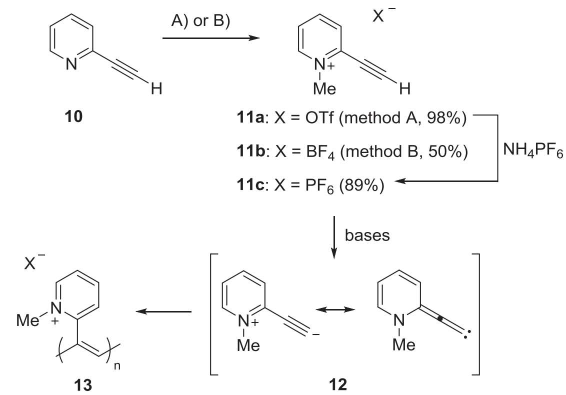
In continuation of our interest in mesomeric betaines, *N*-heterocyclic carbenes, the area of overlap between these two classes,[7,8,11] and in particular the chemistry of pyridines[17,18] we report here on pyridinium-2-acetylide/pyridin-2-allenylidene **I** (Scheme 4). This system differs from pyridinium-3-acetylide **III**[18] in such a way that only dipolar resonance forms of the latter can be drawn, as the type of conjugation is different. Whereas **I** is the formal C_2 adduct of the normal *N*-heterocyclic carbene pyridin-2-ylidene **II**, pyridinium-3-acetylide **III** is the formal C_2 adduct of the remote *N*-heterocyclic carbene **IV**.



Scheme 4. Resonance forms of the isomeric compounds pyridinium-2- and -3-acetylide.

2. Results and discussion

2-Ethynylpyridine **10** was prepared starting from 2-bromopyridine which was subjected to a Sonogashira–Hagihara coupling with ethynyltrimethylsilane (TMSE) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI, followed by protection group removal with sodium carbonate in methanol in 82% according to a literature procedure[19] (Scheme 5). The starting material was methylated by methyl triflate to give the pyridinium salt **11a** (method A, X=OTf), which was converted into its hexafluorophosphate **11c** in very good yields by anion exchange. The tetrafluoroborate **11b** was prepared by methylation of **10** with Meerwein's reagent (method B). The pyridinium salt **11a** has been prepared before by another procedure[20] and has been used for polymerisations to produce homopolymers,[21] to synthesize water soluble single-walled carbon nanotube graft ionic polyacetylene nanocomposites,[22] copolymers,[23] oligomers,[24] and as starting material for organic syntheses.[20] The ^{13}C NMR chemical shifts of the triple bond of **11b** are 98.1 ppm (C≡*C*–H) and 74.2 ppm (*C*≡C–H) and the $\nu_{C\equiv C}$ frequency was detected at 2123 cm^{-1}. It is literature-known that pyridine, pyridine derivatives and AIBN are able to induce polymerisations to form **13**.[25] Attempts to generate and isolate the betaine **12** by deprotonation of **11a–c** with nBuLi in hexane/THF at

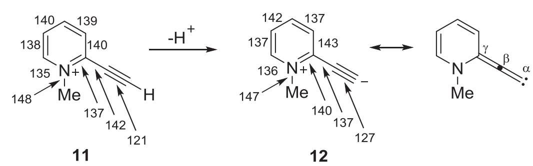


A) MeOTf, CH_2Cl_2, 0 °C, 1 h; B) Me_3OBF_4, CH_2Cl_2, -10 °C, 30 min.

Scheme 5. Synthesis of 2-ethynylpyridinium salts and deprotonations.

low temperatures (−78 °C, −40 °C) failed, because a rapid decomposition and/or polymerisation occurred. Similar results were obtained on deprotonations with NaOD in MeOD at rt, NaOD in D_2O at rt, or *n*BuLi in CD_3CN at −40 °C.

According to a DFT calculation the bond length of the $C_\alpha \equiv C_\beta$ triple bond of the pyridinium cation **11** considerably increases on deprotonation to the betaine **12** (121 pm→127 pm; Δ=+6 pm), whereas the $\equiv C_\beta - C_\gamma$ bond is considerably shortened (142 pm→137 pm; Δ=−5 pm), which supports contributions of an allenylidene resonance form to the overall structure (Scheme 6). These calculated bond lengths correspond to those of the aforementioned imidazole-2-allenylidene.[16] In the isomeric betaine, pyridinium-3-acetylide, which we examined earlier,[18] the allenylidene resonance form is slightly less dominant.



Scheme 6. Calculated bond lengths [pm].

In analogy to **9**,[16] the frontier orbital profile of **12** refers to those of a singlet carbene, as the HOMO and LUMO are σ lone pairs and π orbitals, respectively (Fig. 1). The calculated ^{13}C NMR spectrum (LACVP*/B3LYP, ADF2016.103, TZ2P, KT2, ZORA)[26–28] of **12** shifts the resonance frequency of the α carbon atom to approximately 310 ppm, whereas the chemical shift of the β carbon atom was predicted to be approximately 129 ppm. These values are more downfield than calculated for imidazol-2-allenylidene (δ_α=285 ppm/δ_β=99.8 ppm).[16] The theoretical values of the imidazole species have not been confirmed by experiments due to lithium adduct formation[16], which indicate a considerable contribution of the zwitterionic resonance form to the overall description of imidazol-2-allenylidene.

As a spectroscopic comparison we also prepared 1,2-di-[*N,N'*-dimethyl-(2,2'-pyridylium)]ethyne as triflate, the tetrafluoroborate of which is known[29] (Scheme 7). In this dication, the signals of the non-polarized triple bond were detected at δ=91.5 ppm.

Attempts to convert the in situ generated betaine **12** into the palladium complex **16** failed due to the immediate decomposition of the betaine. We therefore reacted the anion of 2-ethynylpyridine **10** with tetrakis(triphenylphosphine)palladium in THF and obtained the palladium complex **17** in very good yield (Scheme 8). Methylation then converted **17** into the target complex **16**, which