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# Wanzlick's equilibrium in tri- and tetraaminoolefins†

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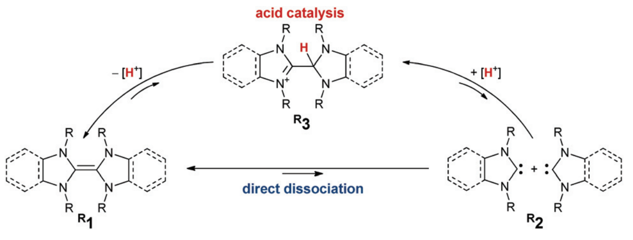
The dissociation mechanism of electron-rich olefins into their parent carbenes has been a controversial topic since Wanzlick's pioneering work. Herein, we present a combined synthetic and computational study on the formation (dissociation, respectively) of hetero- and homo-carbene dimers derived from benzimidazolin-2-ylidenes (benzNHCs), imidazolidin-2-ylidenes (saNHC), and cyclic (alkyl) (amino) carbenes (CAACs) through sublimation (*in vacuo*) as well as in condensed phase. We quantify the effect of proton catalysis and report that even triaminoolefins dissociate to their free carbenes, yet only under proton catalysis. Accordingly, we report how the judicious choice of the base (KO*t*Bu *vs.* KHMDS) and solvent (hexane/benzene *vs.* THF) allows *N*,*N*′-dimethylbenzimidazolin-2-ylidene to be obtained quantitatively as a metastable, kinetic product. This free carbene had been previously reported to dimerize directly to the olefin-dimer, which is the thermodynamic product.

Electron-rich olefins serve as valuable organic materials and reagents.[1] This is arguably due to the presence of three stable redox states.[2–4] Thereby, the radical cations[5,6] show peculiar photo-chemical and conductive properties.[7–10] In their neutral, reduced redox state, they are of use as organic redox agents.[11–15] Nitrogen-containing derivatives such as enetetramines (tetraaminoolefins, respectively) **1** are dimers of *N*-heterocyclic carbenes (NHCs) **2**.[16] While the dimerization is unfavorable for unsaturated ("conventional") NHCs,[17–19] more π-acidic carbenes dimerize.[20] On the contrary to carbene chemistry, where dimerization is undesired, it is required to control dissociation of their dimers in organic electronics. One approach, albeit synthetically tedious, is the installation of tethers.[21] Alternatively, steric and electronic effects may control the dissociation/association equilibrium. However, there has been a long debate on the mechanistic intricacies surrounding potential involvement of proton catalysis. Already in the 1960s, Wanzlick proposed that free carbenes form through direct dissociation of the enetetramine (Scheme 1).[22–24] Later, Lemal and Winberg reconsidered the suggested equilibrium and emphasized the importance of proton catalysis involving transient **3** due to the requirement for the addition of catalytic amounts of proton sources, such as mineral acids.[25,26] This was also observed by Arduengo for stable thiazol-2-ylidenes which only dimerized upon the presence of thiazolium salts.[27] Almost 40 years later, Alder showed that **3** is integral to the formation of **1**.[28,29] Murphy reported on tethered olefins, where dissociation occurred likely through proton catalysis.[30] Denk showed that NHCs dimerize slowly under aprotic conditions.[31] Further, he presented evidence for carbene metathesis ("crossover") between different enetetramines with small *N*-substituents (*e.g.* $^{\mathrm{Me}}\mathbf{1}$, R = Me and $^{\mathrm{Et}}\mathbf{1}$, R = Et) in solution under heating.[32,33] Hahn and Lemal revealed benzimidazolin-2-ylidene formation upon heating the respective dimers in solution using *in situ* $^{1}$H NMR spectroscopic studies.[34–37] These results were further corroborated by computations.[38–41] To the best of our knowledge, experimental



**Scheme 1** Acid catalysis in the equilibrium between tetraaminoolefins **1** and NHC monomers **2**.

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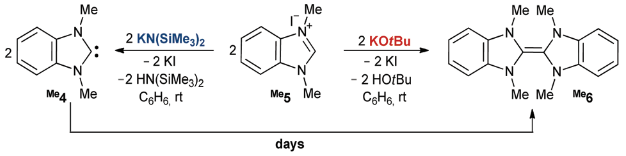
investigations during sublimation (*i.e.* gas phase), devoid of the serendipitous presence of protons as is the case in solution in glassware remain hitherto elusive.[42] Furthermore, studies on the dissociation of triaminoolefins remain to be reported. Thus, we communicate herein on the sublimation of heterodimers[43] derived from benzNHCs, saNHCs, and CAACs as well as their protonated derivatives equivalent to Lemal's intermediate **3**.[44] Complemented by computations, we quantify the effect of proton-catalysis and show how to avoid/slow down the undesired dimerization of transient carbenes (dissociation of electron-rich olefins, respectively).

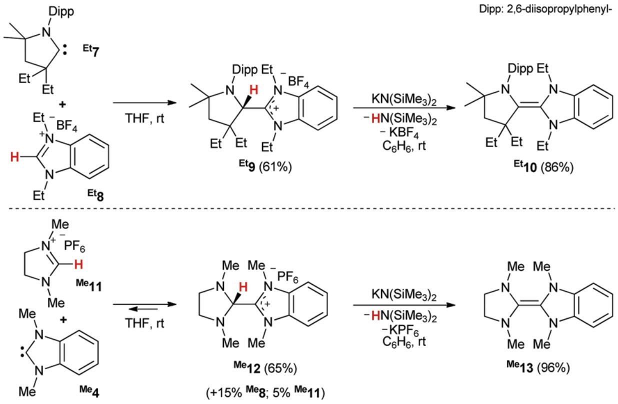
## Synthesis

It has been reported that deprotonation of benzimidazolium salt $^{\text{Me}}$**5** by KO*t*Bu gives dimer $^{\text{Me}}$**6** (Scheme 2, right).[45] To our surprise, when using KHMDS [KN(SiMe$_3$)$_2$] as a base in benzene at room temperature, we obtained instead a mixture of the dimer (44%, Fig. S1†) and the free carbene $^{\text{Me}}$**4** (56%, Scheme 2, left). The latter, unambiguously identified through a signal in the $^{13}$C NMR spectrum at 218 ppm, proved kinetically surprisingly stable with a half-life $t_{1/2}$ of more than one day ($c$ = 0.4 M) and consequently required several days to dimerize with a pseudo-second order rate law (Fig. S8†). Following the deprotonation of a suspension of $^{\text{Me}}$**5** by KO*t*Bu in C$_6$D$_6$, however, indeed corroborated the instantaneous and quantitative formation of $^{\text{Me}}$**6**. These observations suggest that HO*t*Bu (p$K_\text{a}$ = 16.5)[46] catalyzes the dimerization, whereas less acidic HN(SiMe$_3$)$_2$ (p$K_\text{a}$ = 25.8)[47] does not (or to a much lesser extent, respectively). Indeed, adding small amounts of HO*t*Bu to the free carbene $^{\text{Me}}$**4** led to the immediate and quantitative formation of $^{\text{Me}}$**6**. In contrast, free carbene $^{\text{Me}}$**4** could be obtained quantitatively by adding $^{\text{Me}}$**5** to KHMDS dissolved in a 1 : 1 mixture of benzene and hexane at 5 °C under moderately dilute conditions ($c$ = 0.04 M; ≈3% dimerization after one day at room temperature; Fig. S3 and S4†). Even removing the solvent, *i.e.* isolation of the free carbene, led to only ≈4% dimerization (Fig. S5†). The deprotonation by lithium diisopropylamide (LDA) in benzene formed quantitatively the lithium complex ($\delta^{\text{carbene}}$ = 207 ppm), which converted by ≈2% to the dimer within three days ($c$ = 0.4 M; Fig. S6 and S7†).

To further elucidate the dimerization (dissociation, respectively) mechanism, we synthesized a series of carbene heterodimers[48] with varying steric and electronic properties (Scheme 3, top). Following our previously reported route for the formation of $^{\text{Me}}$**10** *via* $^{\text{Me}}$**9**,[43] we obtained $^{\text{Et}}$**9** (61%) and $^{\text{Et}}$**10** (86%) analytically pure. Salts $^{\text{R}}$**9** represent the triamino-equivalent of Lemal's transient intermediate **3**. Conversely, the synthesis of the saNHC=benzNHC tetraaminoolefins $^{\text{R}}$**13** (Scheme 3, bottom) proved more challenging.



Scheme 2 The rate for the formation of **6** from **5** is dependent on the base.



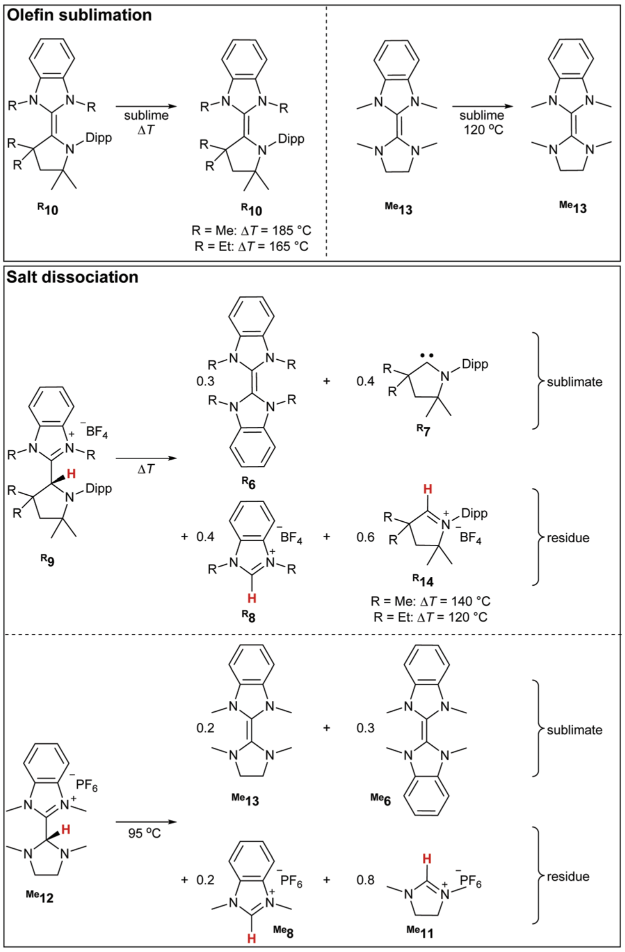
Scheme 3 The CAAC-derived protonated heterodimer $^{\text{Et}}$**9** and olefins $^{\text{Et}}$**10**, $^{\text{Me}}$**13** do not dissociate in solution at room temperature (top), whereas saNHC-derived $^{\text{Me}}$**12** stands in equilibrium with the starting materials $^{\text{Me}}$**4** and $^{\text{Me}}$**11**.

In the case of salt $^{\text{Me}}$**12**, the *in situ* $^1$H NMR spectroscopic analysis in DMSO indicated that the reaction leveled out at approximately 80% conversion after 1 h, with the concomitant presence of imidazolinium- ($^{\text{Me}}$**11**, 5%) and benzimidazolium ($^{\text{Me}}$**8**, 15%) salt (Fig. S14†). In fact, after prolonged reaction time, we observed the slow formation of $^{\text{Me}}$**13**. In case of $^{\text{Et}}$**13**, we even did not manage to obtain useful conversion (>5%) to $^{\text{Et}}$**12**. Overall, these results are consistent with the rare reports[28,49–51] of protonated enetetramines ("Lemal's intermediate") and suggest that not only the addition of $^{\text{Me}}$**4** to $^{\text{Me}}$**11** proceeds essentially isoergic, but equally the protonation of $^{\text{Me}}$**13**. Still, treatment of the mixture with KHMDS afforded, after workup, olefin $^{\text{Me}}$**13** in satisfactory purity (Fig. S16†).

## Sublimation experiments

Upon heating the triaminoolefins $^{\text{Me}}$**10** and $^{\text{Et}}$**10** *in vacuo* to 185 °C and 165 °C, respectively, yellow crystals formed at the walls of the sublimation flask (Scheme 4).

The $^1$H NMR spectroscopic analysis identified these crystals as the starting material without the concomitant formation of $^{\text{Me}}$**6** (Fig. S18†). In addition, no metathesis occurred when heating a mixture of $^{\text{Me}}$**10**, and $^{\text{Et}}$**10** (Fig. S22†). We conclude that such triaminoolefins do not dissociate at these temperatures in the absence of proton catalysis. This seems to be also the case for enetetramine $^{\text{Me}}$**13**, where only starting material was obtained in the sublimate after heating it to 120 °C. In case of the salts $^{\text{Me}}$**9**, $^{\text{Et}}$**9**, and $^{\text{Me}}$**12**, dissociation and subsequent sublimation of homo- and heterodimers occurred at considerably lower temperatures (140 °C, 120 °C, 95 °C) than found for the olefins (Scheme 4, bottom). Accordingly, the presence of free carbene, as well as homodimers, confirms dis-



**Scheme 4** Whereas sublimation was observed for the electron-rich olefins $^{\mathbf{R}}\mathbf{10}$ and $^{\mathbf{Me}}\mathbf{13}$ (top), dissociation and subsequent separation of volatile and non-volatile products were obtained for their protonated congeners $^{\mathbf{R}}\mathbf{9}$ and $^{\mathbf{Me}}\mathbf{12}$ (bottom). All experiments were conducted at 5 × $10^{-3}$ mbar.

sociation. For instance, in case of $^{\mathbf{Me}}\mathbf{9}$, the sublimed material consisted of the homodimers and the free CAAC, respectively ($^{\mathbf{Me}}\mathbf{6}$: 30%; $^{\mathbf{Me}}\mathbf{7}$: 40%), whereas the residue consisted of both benzimidazolium- ($^{\mathbf{Me}}\mathbf{8}$: 40%) as well as cyclic iminium ($^{\mathbf{Me}}\mathbf{14}$: 60%) salt. Overall, we conclude that both tetra- and triamino-olefins dissociate readily under proton catalysis on gentle heating.

## Computational analysis

Computational investigations at the DLPNO-CCSD(T)/def2-TZVPP//BLYP-D3BJ/def2-TZVPP level of theory were performed. Consistent with the experiment, where no dissociation was observed at temperatures as high as 185 °C, the dissociation of triaminoolefin $^{\mathbf{Me}}\mathbf{10}$ is predicted to occur with a high barrier of $\Delta G^{\neq}$ = +200 kJ $\mathrm{mol}^{-1}$ (Fig. 1, top) and considerably endergonic ($\Delta G$ = +76 kJ $\mathrm{mol}^{-1}$). The barrier for ethyl derivative $^{\mathbf{Et}}\mathbf{10}$ is significantly lower with $\Delta G^{\neq}$ = +172 kJ $\mathrm{mol}^{-1}$, yet still too high to form $^{\mathbf{Et}}\mathbf{4}$ and $^{\mathbf{Et}}\mathbf{7}$ ($\Delta G$ = +53 kJ $\mathrm{mol}^{-1}$) under mild conditions. Tetraaminoolefin $^{\mathbf{Me}}\mathbf{13}$ is expected to dissociate with $\Delta G^{\neq}$ = +146 kJ $\mathrm{mol}^{-1}$ ($\Delta G$ = +55 kJ $\mathrm{mol}^{-1}$), which seems consistent with dissociation starting at a (slightly) higher temperature than the sublimation temperature of 120 °C. Also here, the introduction of ethyl groups ($^{\mathbf{Et}}\mathbf{13}$) further facilitates dissociation ($\Delta G^{\neq}$ = +138 kJ $\mathrm{mol}^{-1}$; $\Delta G$ = +43 kJ $\mathrm{mol}^{-1}$).

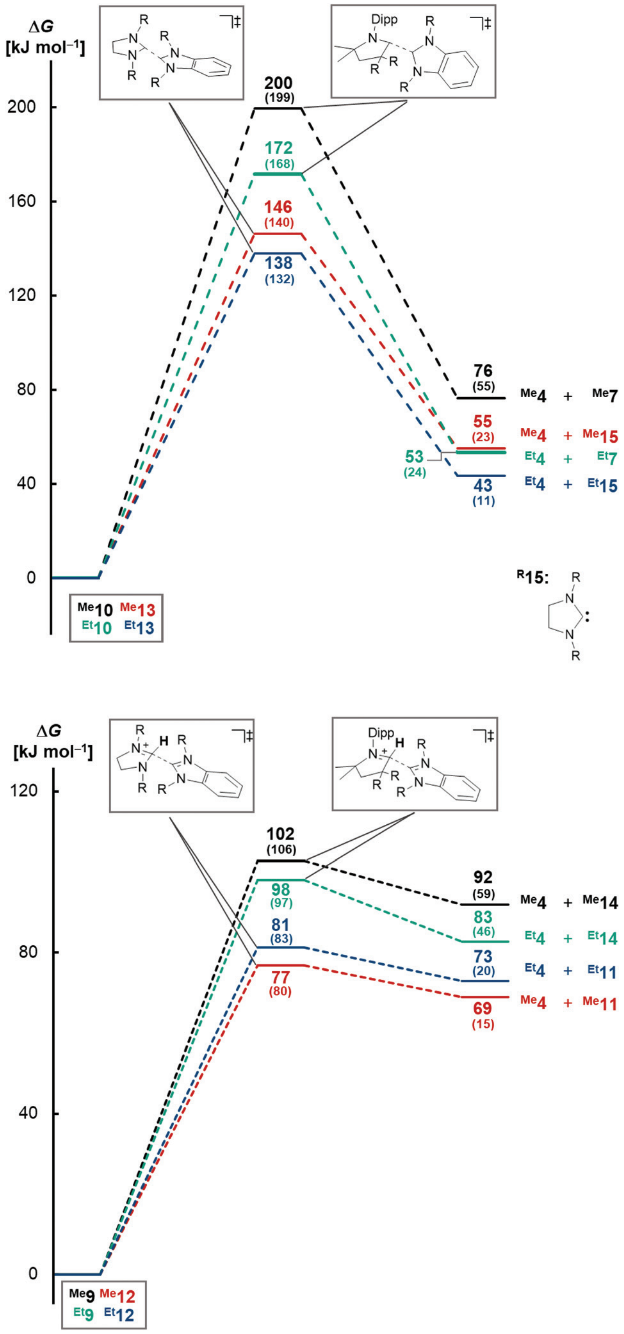


**Fig. 1** Calculations at the DLPNO-CCSD(T)/def2-TZVPP//BLYP-D3BJ/def2-TZVPP level of theory quantify acid catalysis for dissociation of tri- and tetraaminoolefins. Values in parentheses relate to implicit solvation in THF.

In contrast, the dissociation from the salts, representing the key elementary step of proton catalysis, requires lower activation energies (Fig. 1, bottom). Whereas the Gibbs free activation energy for $^{Me}$**9** ($\Delta G^{\neq}$ = +102 kJ mol$^{-1}$) and $^{Et}$**9** ($\Delta G^{\neq}$ = +98 kJ mol$^{-1}$) suggests dissociation at elevated temperatures, the value of $\Delta G^{\neq}$ = +77 kJ mol$^{-1}$ ($\Delta G$ = +69 kJ mol$^{-1}$) found for saNHC–benzNHC salts $^{Me}$**12** and $\Delta G^{\neq}$ = +81 kJ mol$^{-1}$ ($\Delta G$ = +73 kJ mol$^{-1}$) for $^{Et}$**12** is indicative for dissociation at milder temperatures. Modeling the dissociation in condensed phase using implicit solvation in THF confirms that the dissociation of $^{Me}$**12** ($\Delta G$ = +15 kJ mol$^{-1}$) and $^{Et}$**12** ($\Delta G$ = +20 kJ mol$^{-1}$) proceeds almost isoergic in solution with low barriers ($^{Me}$**12**, $\Delta G^{\neq}$ = +80 kJ mol$^{-1}$; $^{Et}$**12**, $\Delta G^{\neq}$ = +83 kJ mol$^{-1}$), consistent with a reaction occurring at room temperature. Salts $^{Me}$**9** and $^{Et}$**9** are kinetically ($^{Me}$**9**, $\Delta G^{\neq}$ = +106 kJ mol$^{-1}$; $^{Et}$**9**, $\Delta G^{\neq}$ = +97 kJ mol$^{-1}$) and thermodynamically ($^{Me}$**9**, $\Delta G$ = +59 kJ mol$^{-1}$; $^{Et}$**9**, $\Delta G$ = +46 kJ mol$^{-1}$) more stable. These results in agreement with the experimental difficulties to isolate $^{Me}$**12** in analytically pure form (*vide supra*). Overall, we conclude that proton catalysis lowers the activation energy for dissociation for the methyl-substituted enetetramine by $\Delta\Delta G^{\neq}$ = 146 kJ mol$^{-1}$–77 kJ mol$^{-1}$ = 69 kJ mol$^{-1}$ ($\Delta\Delta G$ = 138 kJ mol$^{-1}$–81 kJ mol$^{-1}$ = 57 kJ mol$^{-1}$ for the ethyl-substituted derivative) and in case of the methyl-functionalized triaminoolefin by $\Delta\Delta G$ = 200 kJ mol$^{-1}$–102 kJ mol$^{-1}$ = 98 kJ mol$^{-1}$ ($\Delta\Delta G$ = 172 kJ mol$^{-1}$–98 kJ mol$^{-1}$ = 74 kJ mol$^{-1}$ for the ethyl-substituted derivative).

## Conclusion

The dissociation of electron-rich olefins into carbenes was studied in the absence of serendipitous proton sources. To this goal, representatives of tri- and tetraaminoolefins composed of NHCs and CAACs, and their protonated congeners, alleged key intermediates in a proton-catalysis pathway, were synthesized. Based on sublimation at elevated temperatures as well as the computational analysis, we quantified proton-catalysis and showed that not only tetraaminoolefins, but as well triaminoolefins may dissociate. However, acid catalysis is crucial in case of the latter, whereas the former dissociate under heating potentially as well through a direct mechanism. Eventually, we outlined how *N*,*N*′-dimethylbenzimidazolin-2-ylidene, previously reported to dimerize instantaneously, can be isolated through deprotonation with $KN(SiMe_3)_2$ in a mixture of benzene and hexane. This free carbene turned out to be metastable over the course of days, whereas weaker bases such as KO*t*Bu lead to direct dimer formation. Thus, this work serves as a guideline on how to generate transient carbenes and engineer thermodynamically and kinetically stable electron rich olefins being of use in organic electronics.

## Author contributions

The project idea was conceived by D.M., who also directed all work and wrote the manuscript. J.M. performed the computations, contributed to the synthesis, and wrote the first draft. M. K. synthesized all compounds and performed the sublimation experiments. S.G. performed exploratory synthetic studies.

## Conflicts of interest

There are no conflicts to declare.

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