

RESEARCH ARTICLE

View Article Online
View Journal | View IssueCite this: *Org. Chem. Front.*, 2021, **8**,
6663

Wanzlick's equilibrium in tri- and tetraaminoolefins†

Julian Messelberger,^{‡a} Manoj Kumar,^{‡a} Stephen J. Goodner^{a,b} and
Dominik Munz^{ID} ^{*a,b}

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 (KOtBu 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.

Received 5th September 2021

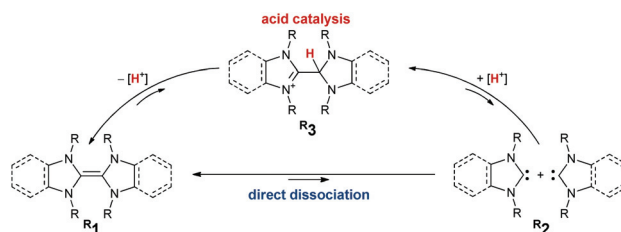
Accepted 13th October 2021

DOI: 10.1039/d1qo01320c

rsc.li/frontiers-organic

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.* **Me1**, R = Me and **Et1**, 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* ¹H 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**.

^aSaarland University, Inorganic Chemistry: Coordination Chemistry, Campus C4.1, D-66123 Saarbrücken, Germany. E-mail: dominik.munz@uni-saarland.de

^bFriedrich-Alexander Universität Erlangen-Nürnberg, Department of Chemistry and Pharmacy: Chair of Inorganic and General Chemistry, Egerlandstraße 1, D-91058 Erlangen, Germany

†Electronic supplementary information (ESI) available. See DOI: 10.1039/d1qo01320c

‡Both authors contributed equally.



Research Article

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 heterodimers⁴³ 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 **Me5** by KOtBu gives dimer **Me6** (Scheme 2, right).⁴⁵ To our surprise, when using KHMDS [KN(SiMe₃)₂] as a base in benzene at room temperature, we obtained instead a mixture of the dimer (44%, Fig. S1†) and the free carbene **Me4** (56%, Scheme 2, left). The latter, unambiguously identified through a signal in the ¹³C 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 **Me5** by KOtBu in C₆D₆, however, indeed corroborated the instantaneous and quantitative formation of **Me6**. These observations suggest that HOtBu (*pK*_a = 16.5)⁴⁶ catalyzes the dimerization, whereas less acidic HN(SiMe₃)₂ (*pK*_a = 25.8)⁴⁷ does not (or to a much lesser extent, respectively). Indeed, adding small amounts of HOtBu to the free carbene **Me4** led to the immediate and quantitative formation of **Me6**. In contrast, free carbene **Me4** could be obtained quantitatively by adding **Me5** 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 (*δ*^{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 heterodimers⁴⁸ with varying steric and electronic properties (Scheme 3, top). Following our previously reported route for the formation of **Me10** via **Me9**,⁴³ we obtained **Et9** (61%) and **Et10** (86%) ana-



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



Scheme 3 The CAAC-derived protonated heterodimer **Et9** and olefins **Et10**, **Me13** do not dissociate in solution at room temperature (top), whereas saNHC-derived **Me12** stands in equilibrium with the starting materials **Me4** and **Me11**.

lytically pure. Salts **R9** represent the triamino-equivalent of Lemal's transient intermediate **3**. Conversely, the synthesis of the saNHC=benzNHC tetraaminoolefins **R13** (Scheme 3, bottom) proved more challenging.

In the case of salt **Me12**, the *in situ* ¹H NMR spectroscopic analysis in DMSO indicated that the reaction leveled out at approximately 80% conversion after 1 h, with the concomitant presence of imidazolium- (**Me11**, 5%) and benzimidazolium (**Me8**, 15%) salt (Fig. S14†). In fact, after prolonged reaction time, we observed the slow formation of **Me13**. In case of **Et13**, we even did not manage to obtain useful conversion (>5%) to **Et12**. 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 **Me4** to **Me11** proceeds essentially isoergic, but equally the protonation of **Me13**. Still, treatment of the mixture with KHMDS afforded, after workup, olefin **Me13** in satisfactory purity (Fig. S16†).

Sublimation experiments

Upon heating the triaminoolefins **Me10** and **Et10** *in vacuo* to 185 °C and 165 °C, respectively, yellow crystals formed at the walls of the sublimation flask (Scheme 4).

The ¹H NMR spectroscopic analysis identified these crystals as the starting material without the concomitant formation of **Me6** (Fig. S18†). In addition, no metathesis occurred when heating a mixture of **Me10**, and **Et10** (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 **Me13**, where only starting material was obtained in the sublimate after heating it to 120 °C. In case of the salts **Me9**, **Et9**, and **Me12**, 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 **R10** and **Me13** (top), dissociation and subsequent separation of volatile and non-volatile products were obtained for their protonated congeners **R9** and **Me12** (bottom). All experiments were conducted at 5×10^{-3} mbar.

sociation. For instance, in case of **Me9**, the sublimed material consisted of the homodimers and the free CAAC, respectively (**Me6**: 30%; **Me7**: 40%), whereas the residue consisted of both benzimidazolium- (**Me8**: 40%) as well as cyclic iminium (**Me14**: 60%) salt. Overall, we conclude that both tetra- and triaminoolefins 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 **Me10** is predicted to occur with a high barrier of $\Delta G^\ddagger = +200 \text{ kJ mol}^{-1}$ (Fig. 1, top) and considerably endergonic ($\Delta G = +76 \text{ kJ mol}^{-1}$). The barrier for ethyl derivative **Et10** is significantly lower with $\Delta G^\ddagger = +172 \text{ kJ mol}^{-1}$, yet still too high to

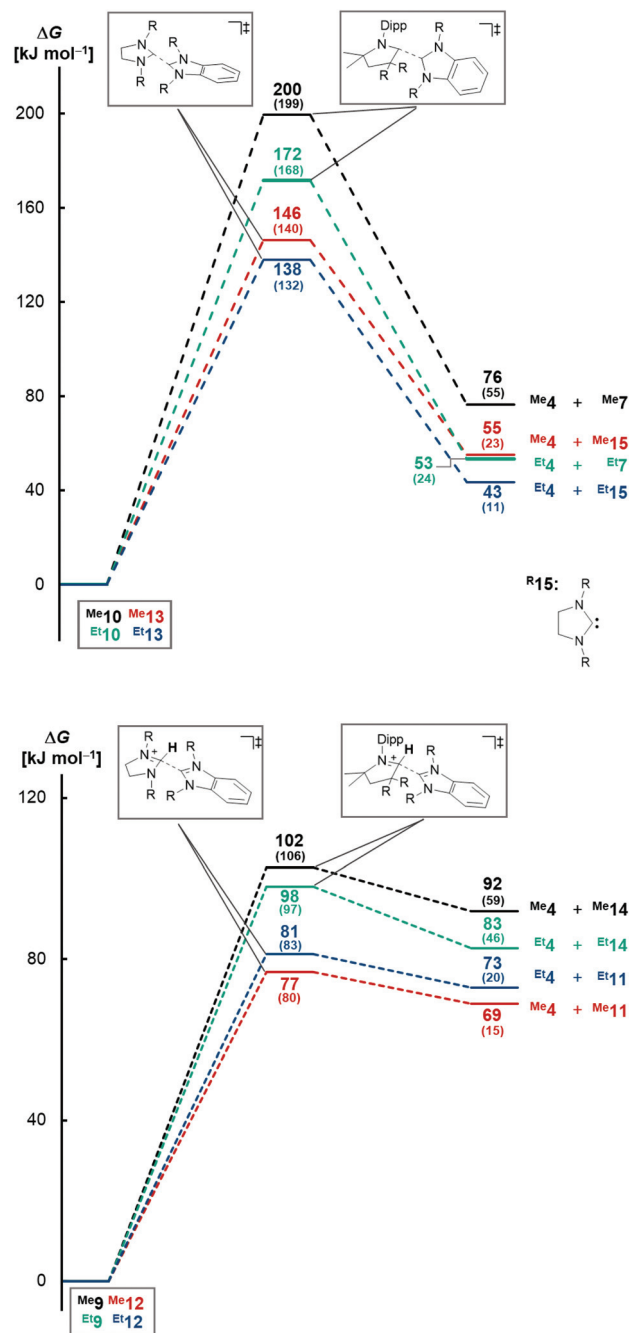


Fig. 1 Calculations at the DLPNO-CCSD(T)/def2-TZVPP//BLYP-D3BJ/def2-TZVPP level of theory quantify acid catalysis for dissociation of tri- and tetraaminoolefins. Values in parentheses relate to implicit solvation in THF.

form **Et4** and **Et7** ($\Delta G = +53 \text{ kJ mol}^{-1}$) under mild conditions. Tetraaminoolefin **Me13** is expected to dissociate with $\Delta G^\ddagger = +146 \text{ kJ mol}^{-1}$ ($\Delta G = +55 \text{ kJ mol}^{-1}$), 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 (**Et13**) further facilitates dissociation ($\Delta G^\ddagger = +138 \text{ kJ mol}^{-1}$; $\Delta G = +43 \text{ kJ mol}^{-1}$).



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 ($\Delta G^\ddagger = +102 \text{ kJ mol}^{-1}$) and ^{Et}9 ($\Delta G^\ddagger = +98 \text{ kJ mol}^{-1}$) suggests dissociation at elevated temperatures, the value of $\Delta G^\ddagger = +77 \text{ kJ mol}^{-1}$ ($\Delta G = +69 \text{ kJ mol}^{-1}$) found for saNHC–benzNHC salts ^{Me}12 and $\Delta G^\ddagger = +81 \text{ kJ mol}^{-1}$ ($\Delta G = +73 \text{ kJ mol}^{-1}$) 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 ($\Delta G = +15 \text{ kJ mol}^{-1}$) and ^{Et}12 ($\Delta G = +20 \text{ kJ mol}^{-1}$) proceeds almost isoergic in solution with low barriers (^{Me}12, $\Delta G^\ddagger = +80 \text{ kJ mol}^{-1}$; ^{Et}12, $\Delta G^\ddagger = +83 \text{ kJ mol}^{-1}$), consistent with a reaction occurring at room temperature. Salts ^{Me}9 and ^{Et}9 are kinetically (^{Me}9, $\Delta G^\ddagger = +106 \text{ kJ mol}^{-1}$; ^{Et}9, $\Delta G^\ddagger = +97 \text{ kJ mol}^{-1}$) and thermodynamically (^{Me}9, $\Delta G = +59 \text{ kJ mol}^{-1}$; ^{Et}9, $\Delta G = +46 \text{ kJ mol}^{-1}$) 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 $\Delta\Delta G^\ddagger = 146 \text{ kJ mol}^{-1} - 77 \text{ kJ mol}^{-1} = 69 \text{ kJ mol}^{-1}$ ($\Delta\Delta G = 138 \text{ kJ mol}^{-1} - 81 \text{ kJ mol}^{-1} = 57 \text{ kJ mol}^{-1}$ for the ethyl-substituted derivative) and in case of the methyl-functionalized triaminoolefin by $\Delta\Delta G = 200 \text{ kJ mol}^{-1} - 102 \text{ kJ mol}^{-1} = 98 \text{ kJ mol}^{-1}$ ($\Delta\Delta G = 172 \text{ kJ mol}^{-1} - 98 \text{ kJ mol}^{-1} = 74 \text{ kJ mol}^{-1}$ 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 $\text{KN}(\text{SiMe}_3)_2$ 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 $\text{KO}t\text{Bu}$ 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 compu-

tations, 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.

Acknowledgements

We thank the RRZ Erlangen for computational resources. We also thank K. Meyer for his support.

Notes and references

- M. Bendikov, F. Wudl and D. F. Perepichka, Tetrathiafulvalenes, Oligoacenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics, *Chem. Rev.*, 2004, **104**, 4891–4946.
- R. W. Hoffmann, Reactions of Electron-Rich Olefins, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 754–765.
- J. Hocker and R. Merten, Reactions of Electron-Rich Olefins with Proton-Active Compounds, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 964–973.
- M. F. Lappert, The coordination chemistry of electron-rich alkenes (enetetramines), *J. Organomet. Chem.*, 1988, **358**, 185–213.
- J. Messelberger, A. Grünwald, S. J. Goodner, F. Zeilinger, P. Pinter, M. E. Miehlich, F. W. Heinemann, M. M. Hansmann and D. Munz, Aromaticity and sterics control whether a cationic olefin radical is resistant to disproportionation, *Chem. Sci.*, 2020, **11**, 4138–4149.
- Y. Kim and E. Lee, Stable Organic Radicals Derived from *N*-Heterocyclic Carbenes, *Chem. – Eur. J.*, 2018, **24**, 19110–19121.
- R. J. Mortimer, Electrochromic materials, *Chem. Soc. Rev.*, 1997, **26**, 147–156.
- N. Martin, Tetrathiafulvalene: the advent of organic metals, *Chem. Commun.*, 2013, **49**, 7025–7027.
- D. Canevet, M. Salle, G. Zhang, D. Zhang and D. Zhu, Tetrathiafulvalene (TTF) derivatives: key building-blocks for switchable processes, *Chem. Commun.*, 2009, 2245–2269.
- J. Messelberger, A. Grünwald, P. Pinter, M. M. Hansmann and D. Munz, Carbene derived diradicaloids-building blocks for singlet fission?, *Chem. Sci.*, 2018, **9**, 6107–6117.
- J. Broggi, T. Terme and P. Vanelle, Organic electron donors as powerful single-electron reducing agents in organic synthesis, *Angew. Chem., Int. Ed.*, 2014, **53**, 384–413.
- J. A. Murphy, Discovery and Development of Organic Super-Electron-Donors, *J. Org. Chem.*, 2014, **79**, 3731–3746.
- E. Doni and J. A. Murphy, Evolution of neutral organic super-electron-donors and their applications, *Chem. Commun.*, 2014, **50**, 6073–6087.



- 14 S. Rohrbach, R. S. Shah, T. Tuttle and J. A. Murphy, Neutral Organic Super Electron Donors Made Catalytic, *Angew. Chem., Int. Ed.*, 2019, **58**, 11454–11458.
- 15 Y. Zhao, M. Rollet, L. Charles, G. Canard, D. Gimes, P. Vanelle and J. Broggi, Switching from single to simultaneous free radical and anionic polymerization with enamine-based organic electron donors, *Angew. Chem.*, 2021, **60**, 19389–19396.
- 16 For concise and recent reviews on carbenes and carbene ligands, see: (a) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, An overview of *N*-heterocyclic carbenes, *Nature*, 2014, **510**, 485–496; (b) R. S. Ghadwal, Carbon-based two electron σ -donor ligands beyond classical *N*-heterocyclic carbenes, *Dalton Trans.*, 2016, **45**, 16081–16095; (c) D. Munz, Pushing Electrons-Which Carbene Ligand for Which Application?, *Organometallics*, 2018, **37**, 275–289; (d) P. Bellotti, M. Koy, M. N. Hopkinson and F. Glorius, Recent advances in the chemistry and applications of *N*-heterocyclic carbenes, *Nat. Rev. Chem.*, 2021, **5**, 711–725; For a comprehensive review on carbenes in main group chemistry, see: (e) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, NHCs in Main Group Chemistry, *Chem. Rev.*, 2018, **118**, 9678–9842; For thematic issues and books on NHCs, see: (f) A. J. Arduengo III and G. Bertrand, Carbenes Introduction, *Chem. Rev.*, 2009, **109**, 3209–3210; (g) S. Díez González, *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, Royal Society of Chemistry, Cambridge, UK, 2010; (h) T. Rovis and S. P. Nolan, Stable Carbenes: From ‘Laboratory Curiosities’ to Catalysis Mainstays, *Synlett*, 2013, 1188–1189; (i) S. P. Nolan, *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*, Wiley-VCH, Weinheim, Germany, 2014; (j) H. V. Huynh, *The Organometallic Chemistry of N-heterocyclic Carbenes*, John Wiley & Sons, Hoboken, New Jersey, USA, 2017; (k) F. E. Hahn, Introduction: Carbene Chemistry, *Chem. Rev.*, 2018, **118**, 9455–9456. For a leading review with a focus on cyclic singlet carbenes, see: (l) M. Melaimi, M. Soleilhavoup and G. Bertrand, Stable Cyclic Carbenes and Related Species beyond Diaminocarbenes, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810–8849. For a visual tutorial on isolating free carbenes and heterodimers, see: (m) A. Grünwald, S. J. Goodner and D. Munz, Isolating Free Carbenes, their Mixed Dimers and Organic Radicals, *J. Visualized Exp.*, 2019, e59389.
- 17 A. J. Arduengo III, R. L. Harlow and M. Kline, A stable crystalline carbene, *J. Am. Chem. Soc.*, 1991, **113**, 361–363.
- 18 R. P. Thummel, V. Goulle and B. Chen, Bridged derivatives of 2,2'-biimidazole, *J. Org. Chem.*, 1989, **54**, 3057–3061.
- 19 Z. Shi and R. P. Thummel, Bridged bibenzimidazolium salts and their conversion to ureaphanes, *Tetrahedron Lett.*, 1994, **35**, 33–36.
- 20 A. J. Arduengo III, J. R. Goerlich and W. J. Marshall, A stable diaminocarbene, *J. Am. Chem. Soc.*, 1995, **117**, 11027–11028.
- 21 T. A. Taton and P. Chen, A stable tetraazafulvalene, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1011–1013.
- 22 H. W. Wanzlick and E. Schikora, Ein Neuer Zugang Zur Carben-Chemie, *Angew. Chem., Int. Ed. Engl.*, 1960, **72**, 494–494.
- 23 H. W. Wanzlick and E. Schikora, Ein Nucleophiles Carben, *Chem. Ber./Recl.*, 1961, **94**, 2389–2393.
- 24 H. W. Wanzlick, Aspects of Nucleophilic Carbene Chemistry, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 75–80.
- 25 D. M. Lemal, R. A. Lovald and K. I. Kawano, Tetraaminoethylenes. The Question of Dissociation, *J. Am. Chem. Soc.*, 1964, **86**, 2518–2519.
- 26 H. E. Winberg, J. E. Carnahan, D. D. Coffman and M. Brown, Tetraaminoethylenes, *J. Am. Chem. Soc.*, 1965, **87**, 2055–2056.
- 27 A. J. Arduengo III, J. R. Goerlich and W. J. Marshall, A Stable Thiazol-2-ylidene and Its Dimer, *Liebigs Ann.*, 1997, 365–374.
- 28 R. W. Alder, L. Chaker and F. P. V. Paolini, Bis(diethylamino)carbene and the mechanism of dimerisation for simple diaminocarbenes, *Chem. Commun.*, 2004, 2172–2173.
- 29 R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini and J. Schütz, When and How Do Diaminocarbenes Dimerize?, *Angew. Chem., Int. Ed.*, 2004, **43**, 5896–5911.
- 30 P. I. Jolly, S. Zhou, D. W. Thomson, J. Garnier, J. A. Parkinson, T. Tuttle and J. A. Murphy, Imidazole-derived carbenes and their elusive tetraazafulvalene dimers, *Chem. Sci.*, 2012, **3**, 1675–1679.
- 31 M. K. Denk, A. Thadani, K. Hatano and A. J. Lough, Steric Stabilization of Nucleophilic Carbenes, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2607–2609.
- 32 M. K. Denk, K. Hatano and M. Ma, Nucleophilic carbenes and the wanzlick equilibrium: A reinvestigation, *Tetrahedron Lett.*, 1999, **40**, 2057–2060.
- 33 Y. Liu and D. M. Lemal, Concerning the “Wanzlick equilibrium”, *Tetrahedron Lett.*, 2000, **41**, 599–602.
- 34 Y. Liu, P. E. Lindner and D. M. Lemal, Thermodynamics of a Diaminocarbene–Tetraaminoethylene Equilibrium, *J. Am. Chem. Soc.*, 1999, **121**, 10626–10627.
- 35 F. E. Hahn, L. Wittenbecher, D. Le Van and R. Fröhlich, Evidence for an Equilibrium between an *N*-heterocyclic Carbene and Its Dimer in Solution, *Angew. Chem., Int. Ed.*, 2000, **39**, 541–544.
- 36 V. P. W. Böhm and W. A. Herrmann, The “Wanzlick Equilibrium”, *Angew. Chem., Int. Ed.*, 2000, **39**, 4036–4038.
- 37 J. W. Kamplain and C. W. Bielawski, Dynamic covalent polymers based upon carbene dimerization, *Chem. Commun.*, 2006, 1727–1729.
- 38 K. Młodzikowska, A. A. Rajkiewicz, K. Grela and B. Trzaskowski, Boron–boron, carbon–carbon and nitrogen–nitrogen bonding in *N*-heterocyclic carbenes and their diazaboryl and triazole analogues: Wanzlick equilibrium revisited, *New J. Chem.*, 2018, **42**, 6183–6190.



- 39 M.-J. Cheng, C.-L. Lai and C.-H. Hu, Theoretical study of the Wanzlick equilibrium, *Mol. Phys.*, 2004, **102**, 2617–2621.
- 40 A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan and L. Cavallo, Thermodynamics of *N*-Heterocyclic Carbene Dimerization: The Balance of Sterics and Electronics, *Organometallics*, 2008, **27**, 2679–2681.
- 41 D. C. Graham, K. J. Cavell and B. F. Yates, Dimerization mechanisms of heterocyclic carbenes, *J. Phys. Org. Chem.*, 2005, **18**, 298–309.
- 42 For a mass spectrometry and computational study that suggests Lemal's intermediate to be preferred over the hydrogen bonded dimer C–H⋯:C in case of saturated NHCs and almost isoergic for imidazolin-derived aromatic NHCs, see: (a) M. Paul, E. Detmar, M. Schlangen, M. Breugst, J.-M. Neudörfl, H. Schwarz, A. Berkessel and M. Schäfer, Intermediates of *N*-Heterocyclic Carbene (NHC) Dimerization Probed in the Gas Phase by Ion Mobility Mass Spectrometry: C–H⋯:C Hydrogen Bonding Versus Covalent Dimer Formation, *Chem. – Eur. J.*, 2019, **25**, 2511–2518. For the hydrogen bonded dimer C–H⋯:C, see: (b) A. J. Arduengo III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson and H. A. Craig, A Bis(carbene)-Proton Complex: Structure of a C–H–C Hydrogen Bond, *J. Am. Chem. Soc.*, 1995, **117**, 572–573.
- 43 D. Munz, J. Chu, M. Melaimi and G. Bertrand, NHC–CAAC Heterodimers with Three Stable Oxidation States, *Angew. Chem., Int. Ed.*, 2016, **55**, 12886–12890.
- 44 For the first report of a CAAC, see: (a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadiou and G. Bertrand, Stable Cyclic (Alkyl)(Amino)Carbenes as Rigid or Flexible, Bulky, Electron-Rich Ligands for Transition-Metal Catalysts: A Quaternary Carbon Atom Makes the Difference, *Angew. Chem., Int. Ed.*, 2005, **44**, 5705–5709. For reviews on CAACs, see: (b) M. Soleilhavoup and G. Bertrand, Cyclic (Alkyl)(Amino)Carbenes (CAACs): Stable Carbenes on the Rise, *Acc. Chem. Res.*, 2015, **48**, 256–266; (c) S. Roy, K. C. Mondal and H. W. Roesky, Cyclic Alkyl(amino) Carbene Stabilized Complexes with Low Coordinate Metals of Enduring Nature, *Acc. Chem. Res.*, 2016, **49**, 357–369; (d) M. Melaimi, R. Jazzar, M. Soleilhavoup and G. Bertrand, Cyclic (Alkyl)(amino)carbenes (CAACs): Recent Developments, *Angew. Chem., Int. Ed.*, 2017, **56**, 10046–10068; (e) U. S. D. Paul and U. Radius, What Wanzlick Did Not Dare To Dream: Cyclic (Alkyl)(amino)carbenes (CAACs) as New Key Players in Transition-Metal Chemistry, *Eur. J. Inorg. Chem.*, 2017, 3362–3375; (f) R. Jazzar, M. Soleilhavoup and G. Bertrand, Cyclic (Alkyl)- and (Aryl)-(amino)carbene Coinage Metal Complexes and Their Applications, *Chem. Rev.*, 2020, **120**, 4141–4168. For the synthesis of donor substituted CAACs, see: (g) J. Chu, D. Munz, R. Jazzar, M. Melaimi and G. Bertrand, Synthesis of Hemilabile Cyclic (Alkyl)(amino)carbenes (CAACs) and Applications in Organometallic Chemistry, *J. Am. Chem. Soc.*, 2016, **138**, 7884–7887.
- 45 This finding was reproduced in THF: (a) G. Tintori, A. Fall, N. Assani, Y. Zhao, D. Bergé-Lefranc, S. Redon, P. Vanelle and J. Broggi, Generation of powerful organic electron donors by water-assisted decarboxylation of benzimidazolium carboxylates, *Org. Chem. Front.*, 2021, **8**, 1197–1205.
- 46 W. Reeve, C. M. Erikson and P. F. Aluotto, A new method for the determination of the relative acidities of alcohols in alcoholic solutions. The nucleophilicities and competitive reactivities of alkoxides and phenoxides, *Can. J. Chem.*, 1979, **57**, 2747–2754.
- 47 R. R. Fraser, T. S. Mansour and S. Savard, Acidity measurements on pyridines in tetrahydrofuran using lithiated silylamines, *J. Org. Chem.*, 1985, **50**, 3232–3234.
- 48 For recent and leading examples on carbene derived heterodimers, see: (a) A. J. Arduengo III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, An Air Stable Carbene and Mixed Carbene “Dimers”, *J. Am. Chem. Soc.*, 1997, **119**, 12742–12749; (b) P. W. Antoni and M. M. Hansmann, Pyrylenes: A New Class of Tunable, Redox-Switchable, Photoexcitable Pyrylium–Carbene Hybrids with Three Stable Redox-States, *J. Am. Chem. Soc.*, 2018, **140**, 14823–14835; (c) P. W. Antoni, T. Bruckhoff and M. M. Hansmann, Organic Redox Systems Based on Pyridinium–Carbene Hybrids, *J. Am. Chem. Soc.*, 2019, **141**, 9701–9711; (d) D. Mandal, R. Dolai, N. Chrysochos, P. Kalita, R. Kumar, D. Dhara, A. Maiti, R. S. Narayanan, G. Rajaraman, C. Schulzke, V. Chandrasekhar and A. Jana, Stepwise Reversible Oxidation of *N*-Peralkyl-Substituted NHC–CAAC Derived Triazaalkenes: Isolation of Radical Cations and Dications, *Org. Lett.*, 2017, **19**, 5605–5608; (e) D. Mandal, R. Dolai, R. Kumar, S. Suhr, N. Chrysochos, P. Kalita, R. S. Narayanan, G. Rajaraman, C. Schulzke, B. Sarkar, V. Chandrasekhar and A. Jana, Influence of *N*-Substitution on the Formation and Oxidation of NHC–CAAC-Derived Triazaalkene, *J. Org. Chem.*, 2019, **84**, 8899–8909; (f) M. K. Nayak, S. Suhr, N. Chrysochos, H. Rawat, C. Schulzke, V. Chandrasekhar, B. Sarkar and A. Jana, Tethered CAAC–CAAC dimers: oxidation to persistent radical cations and bridging-unit dependent reactivity/stability of the dications, *Chem. Commun.*, 2021, **57**, 1210–1213; (g) J. Stubbe, S. Suhr, J. Beerhues, M. Nößler and B. Sarkar, The transformations of a methylene-bridged bis-triazolium salt: a mesoionic carbene based metallocage and analogues of TCNE and NacNac, *Chem. Sci.*, 2021, **12**, 3170–3178. For electrochemical studies on hetero- as well as homodimers, see: (h) J. R. Ames, M. A. Houghtaling, D. L. Terrian and T. P. Mitchell, Annulated derivatives of 2, 2'-biimidazole, 2-(2'-imidazolyl) benzimidazole, and 2, 2'-bibenzimidazole, *Can. J. Chem.*, 1997, **75**, 28–36. For a tethered heterodimer, see: (i) S. Simonovic, J.-C. Frison, H. Koyuncu, A. C. Whitwood and R. E. Douthwaite, Addition of *N*-Heterocyclic Carbenes to Imines: Phenoxide Assisted Deprotonation of an Imidazolium Moiety and Generation of Breslow Intermediates Derived from Imines, *Org. Lett.*, 2009, **11**, 245–247. For heterodimers derived



from NHCs and aldehydes (Breslow intermediates), see: (j) A. Berkessel, S. Elfert, V. R. Yatham, J.-M. Neudörfl, N. E. Schlörer and J. H. Teles, Umpolung by *N*-heterocyclic carbenes: generation and reactivity of the elusive 2,2-diamino enols (Breslow intermediates), *Angew. Chem., Int. Ed.*, 2012, **51**, 12370–12374; (k) A. Berkessel, V. R. Yatham, S. Elfert and J.-M. Neudörfl, Characterization of the Key Intermediates of Carbene-Catalyzed Umpolung by NMR Spectroscopy and X-Ray Diffraction: Breslow Intermediates, Homo-enolates, and Azolium Enolates, *Angew. Chem., Int. Ed.*, 2013, **52**, 11158–11162; (l) J. Rehbein, S. M. Ruser and J. Phan, NHC-catalysed benzoin condensation - is it all down to the Breslow intermediate?, *Chem. Sci.*, 2015, **6**, 6013–6018. For carbene dimers separated by arene spacers, see: (m) M. M. Hansmann, M. Melaimi, D. Munz and G. Bertrand, Organic Mixed Valence Compounds Derived from Cyclic (Alkyl)(amino)carbenes, *J. Am. Chem. Soc.*, 2018, **140**, 2546–2554; (n) G. Kundu, S. De, S. Tothadi, A. Das, D. Koley and S. S. Sen, Saturated *N*-Heterocyclic Carbene Based Thiele's Hydrocarbon with a

Tetrafluorophenylene Linker, *Chem. – Eur. J.*, 2019, **25**, 16533–16537; (o) A. Maiti, J. Stubbe, N. I. Neuman, P. Kalita, P. Duari, C. Schulzke, V. Chandrasekhar, B. Sarkar and A. Jana, CAAC-Based Thiele and Schlenk Hydrocarbons, *Angew. Chem.*, 2020, **59**, 6729–6734; (p) A. Maiti, S. Chandra, B. Sarkar and A. Jana, Acyclic diaminocarbene-based Thiele, Chichibabin, and Müller hydrocarbons, *Chem. Sci.*, 2020, **11**, 11827–11833.

49 M. F. Lappert, S. Álvarez, G. Aullón, R. Fandos, A. Otero, A. Rodríguez, S. Rojas and P. Terreros, Reactivity of a super-electron-rich olefin derived from cyclam, *Eur. J. Inorg. Chem.*, 2009, 1851–1860.

50 U. S. D. Paul and U. Radius, Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino)Carbene, *Chem. – Eur. J.*, 2017, **23**, 3993–4009.

51 Y. T. Chen and F. Jordan, Reactivity of the thiazolium C2 ylide in aprotic solvents: novel experimental evidence for addition rather than insertion reactivity, *J. Org. Chem.*, 1991, **56**, 5029–5038.

