[20] Of 230 crystallographic space groups 65 are chiral, for example $P2_12_12_1$ or $P2_1$. Consequently, enantiomorphic crystals can grow from solutions of an achiral compound. For example, $NaClO_3$ has been intensively investigated recently, there are other compounds quoted in ref [1j], which have been known since the end of the 19th century. Since 1990 it has been known from the work of Kondepudi et al., that simply stirring during the crystallization process can lead to the formation of almost exclusively one sort from enantiomorphic crystals in the reaction, however, the chirality can not be controlled. a) D. K. Kondepudi, R. J. Kaufmann, N. Singh, *Science* **1990**, *250*, 975 – 976; b) J. M. McBride, R. L. Carter, *Angew. Chem.* **1991**, *103*, 298 – 300; *Angew. Chem. Int. Ed.* **1991**, *30*, 293-295; c) D. K. Kondepudi, K. L. Bullok, J. A. Digits, J. K. Hall, J. M. Miller, *J. Am. Chem. Soc.* **1993**, *115*, 10211 – 10216; d) D. K. Kondepudi, K. L. Bullok, J. A. Digits, P. D. Yarborough, *J. Am. Chem. Soc.* **1995**, *117*, 401 – 404. For spontaneous enantiomer separation in liquid crystalline phases or two-dimensional crystallites see Y. Takanishi, H. Takezoe, Y. Suzuki, I. Kobayashi, T. Yajima, M. Terada, K. Mikami, *Angew. Chem.* **1999**, *111*, 2502 – 2504; *Angew. Chem. Int. Ed.* **1999**, *38*, 2354 – 2356; or M. Lahav, L. Leiserowitz, *Angew. Chem.* **1999**, *111*, 2691 – 2694; *Angew. Chem. Int. Ed.* **1999**, *38*, 2533 – 2536.

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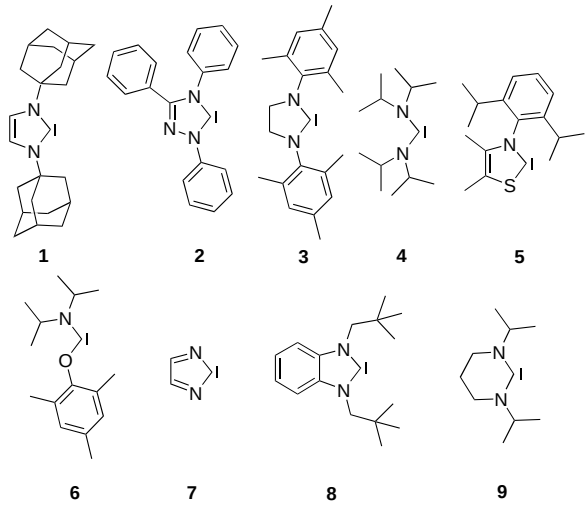
# The "Wanzlick Equilibrium"**

**Volker P. W. Böhm and Wolfgang A. Herrmann***

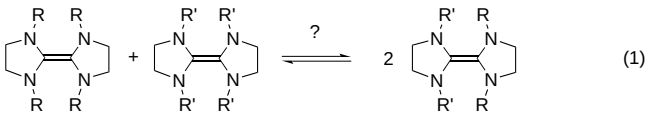
*Dedicated to Professor Manfred Regitz on the occasion of his 65th birthday*

Carbenes have attracted considerable attention in both organic and inorganic preparative literature due to their unique properties as reagents and reaction intermediates.[1] The isolation of a stable carbene was pursued for a long time until 1,3-bis(1'-adamantyl)imidazolin-2-ylidene (**1**) was prepared in 1991.[2] In the following years, related carbenes, such as **2** – **9**, were characterized.[3–9] Among these, imidazolidin-2-ylidenes like **3**,[2f, 10] had been postulated by H.-W. Wanzlick in 1960 as intermediates in the formation of electron-rich tetraaminoethylenes.[11] At that time, Wanzlick already suspected these carbenes to be rather stable, although they could only be identified by characteristic trapping reactions.[12] Wanzlick's assumption of an equilibrium between the carbene and the olefin [Eq. (1)] was based on simple molecular weight measurements.[11]



**1** **2** **3** **4** **5**

**6** **7** **8** **9**



**10a** **10b** **10c** (1)

Before their isolation, carbenes were seen stable only as ligands in metal complexes. The first two complexes of N-heterocyclic carbenes of type **1** were isolated independently by Wanzlick in Berlin and by Öfele in Munich in 1968.[13, 14] In the meantime, the coordination chemistry of these ligands has attracted attention: A broad scope of synthetic routes to their metal complexes was established.[15] N-heterocyclic carbenes (NHCs) were also used as ligands in the catalytic hydrosilylation.[16] It was shown that asymmetric induction is also possible with NHC ligands in catalysis.[17] However, major interest in catalysts that bear NHC ligands started when applications in ruthenium-catalyzed olefin metathesis[18–20]

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[**] V.P.W.B. wishes to thank the Fonds der Chemischen Industrie for a Kekulé fellowship.

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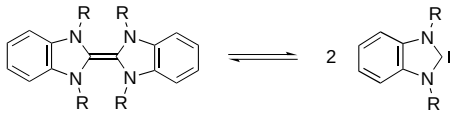
and in palladium-catalyzed cross-coupling reactions were discovered.[21–23] Meanwhile, materials science also took advantage of the strong metal–ligand bond.[24] The unique properties of the carbenes **1**–**9** and their metal complexes is documented by a variety of review articles about this class of compounds.[15, 25]

Electron-rich tetraaminoethylenes are prepared by dimerization of the corresponding carbenes.[26] Although these olefins can be used to prepare carbene complexes with electrophilic metal precursors,[15] the equilibrium of the carbene and the tetraaminoethylene has only been speculative.[11, 12] Early work excluded this equilibrium for NHCs of type **3**.[27] The crossed product **10c** of two different tetraaminoethylenes **10a** and **10b** was only observable in the presence of catalytic amounts of electrophiles [Eq. (1)].[27b, 28] Even in the absence of electrophiles, the reaction mechanism does not necessarily involve carbene intermediates, as the results could also be explained by a [2+2] cycloaddition/[2+2] cycloreversion mechanism.[29] In contrast for NHCs of type **1**, the corresponding tetraaminoethylene products become unstable[30] and can be observed only in bridged systems.[31]

The equilibrium of a tetraaminoethylene and its corresponding carbene would only be proved unequivocally if both compounds were detected as a mixture while starting from the analytically pure olefin in the absence of any catalytic electrophiles. This task was solved recently by Hahn et al. and Lemal et al. Both groups submitted their results in June[32] and July[33] of 1999, respectively. The essential change in regard to previous experiments is the use of dibenzotetraazafulvalenes **11** (Scheme 1). Sterically less demanding substituents like methyl (**a**) and ethyl (**b**) moieties favor the formation of the tetraaminoethylene **11**, whereas sterically demanding substituents like isobutyl (**c**) and neopentyl (**d**) groups shift the equilibrium towards the free carbene **12**.



**11** **12**

**a**: R = $CH_3$
**b**: R = $CH_2CH_3$
**c**: R = $CH_2CH(CH_3)_2$
**d**: R = $CH_2C(CH_3)_3$

Scheme 1. Compounds used to demonstrate the "Wanzlick equilibrium".

Recrystallized, electrophile-free samples of **11a**–**11c** were examined by $^1$H and $^{13}$C NMR spectroscopy. In the case of **11c**, an equilibrium mixture of **11c**:**12c** = 1:9 is obtained after 24 h even at room temperature (Figure 1).[32] In the case of **11a** and **11b**, characteristic signals of the carbenes **12a** and **12b** could be observed at 140 °C but not at room temperature.[33] The van't Hoff plot for the dissociation equilibria of **11b** and **12b** at different temperatures reveals the thermodynamic parameters for the dissociation: $\Delta H^\circ = 13.7 \pm 0.6$ kcal mol$^{-1}$ and $\Delta S^\circ = 30.4 \pm 1.7$ cal mol$^{-1}$ K$^{-1}$.[33]

Now, 40 years after the first experimental and theoretical treatment of "stable" *N*-heterocyclic carbenes by H.-W. Wanzlick, the last remaining important question is answered:

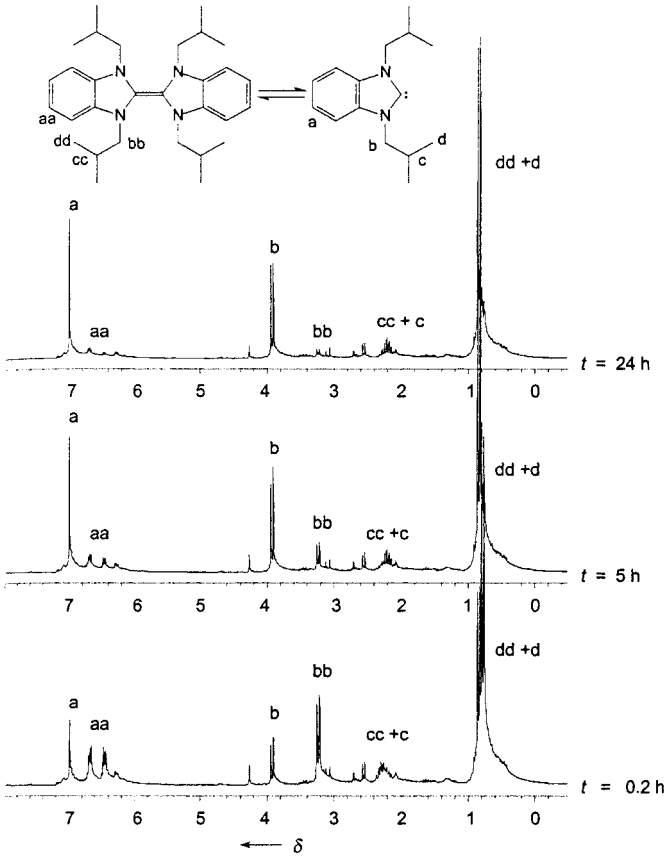



Figure 1. Equilibration of **11c** and **12c**, as observed by $^1$H NMR spectroscopy (200 MHz, [$D_8$]-toluene, 298 K).

The simultaneous spectroscopic identification of **11** and **12** in a solution originally containing pure **11** has proved that the "Wanzlick equilibrium" between a tetraaminoethylene and its corresponding carbene exists. Along with the isolation of various stable carbenes **1**–**9** in previous work, Wanzlick's ideas and reaction models have finally been proved to be reality. The "Wanzlick equilibrium" is likely to yield novel chemistry, especially in the light of recent successful results in homogeneous catalysis.[18–23]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