BN-Arynes

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BN-Phenanthryne: Cyclotetramerization of an 1,2-Azaborine Derivative**

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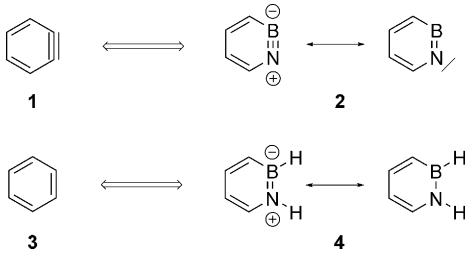
Abstract: *Thermolysis of 9-azido-9-borafluorene in heptane solution produces the tetramer of a BN-phenanthryne. The isolation of the self-trapping product provides evidence for the involvement of the BN-aryne in the thermolysis reaction. Its formation may be rationalized by denitrogenation of the azide and ring enlargement.*

After it was demonstrated that a symmetric intermediate, 1,2-didehydrobenzene (*ortho*-benzyne; **1**), is involved in nucleophilic aromatic substitution,[1] Wittig and Pohmer,[2] then in Tübingen, trapped **1** by a Diels–Alder reaction with furan. They generated **1** from fluorobenzene and butyllithium.[2] Since then, **1** has developed into a well-understood reactive intermediate that is highly valued for its usefulness in organic synthesis.[3]

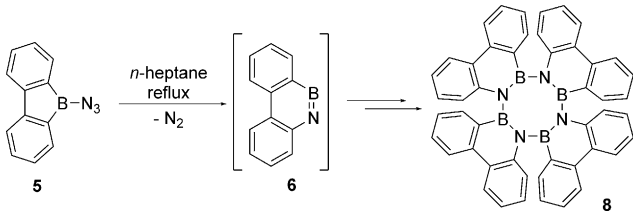
The isoelectronic substitution of the two dehydro carbon atoms by a BN unit relates **1** to 1,2-azaborine **2**, in much the same way as benzene **3** and 1,2-dihydro-1,2-azaborine **4** are related (Scheme 1). Compound **4** was first synthesized by Liu and co-workers in 2009.[4] In contrast to **1**, BN-aryne **2** has received very limited attention. A computational investigation of **2** by Fazen and Burke revealed a distorted planar structure for the singlet ground state and a singlet-triplet energy splitting of roughly 50 kcal mol^{-1} in favor of the singlet state.[5] Experimental investigations of **2** or its derivatives have not been carried out to the best of our knowledge.



Scheme 1. Isoelectronic relationship between 1,2-didehydrobenzene **1** and 1,2-azaborine **2**.

1,2-Didehydrobenzenes show reactivity akin to strained alkynes.[3] The BN analogues of alkynes, iminoboranes, do not show kinetic stability because of the polarity of the B–N bond.[6] Unless kinetically stabilized by bulky substituents, iminoboranes undergo oligomerization reactions mostly under formation of borazines.[6] Likewise, cyclic iminoboranes are very unstable and cyclotrimerize.[7] It may thus be inferred that 1,2-azaborines should be ferocious reactive intermediates in view of the chemistry of cyclic and acyclic iminoboranes.[6,7]

How could access to the 1,2-azaborine motif be achieved? We reasoned that 1,2-azaborines might be generated by N_2 elimination and ring enlargement of azidoboroles, as earlier reports by Paetzold et al. indicate that acyclic azidodiorganylboranes R_2BN_3 rearrange thermally to iminoboranes RBNR without intermediate formation of borylnitrenes R_2BN.[8,9] As azidoboroles are unknown and expected to be highly unstable,[10] we studied the thermal decomposition of the dibenzo derivative 9-azido-9-borafluorene **5**. This compound was synthesized earlier by our group and found to be rather labile.[11] Thermal decomposition of **5** should result in N_2 elimination and could yield the dibenzo derivative (**6**) of **2** (Scheme 2). Compound **6** is the BN analogue of 9,10-phenanthryne.[12] The known chemistry of acyclic and cyclic iminoboranes suggests that **6** might undergo cyclooligomerization to borazine **7**[13,14] or tetraazatetraborocine **8**,[14] polymerization, or be trapped by unreacted azide **5**.[15] However, the thermal decomposition of azidoboranes often gives complex mixtures of unidentified reaction products.[8] As a consequence of the facile decomposition of **5**,[11] we synthesized it in situ from the corresponding chloroborane and azidotrimethylsilane and heated the resulting mixture of **5** and trimethylchlorosilane in a number of solvents, including heptane, at reflux. This treatment produced insoluble colorless tetramer **8**, which could be separated in a yield of 8–10% by centrifugation from a dark brown solution of reaction



Scheme 2. Formation of tetramer **8** of BN-aryne **6** formed by the thermal decomposition of azide **5**.

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products. The insoluble compound **8** was identified by high-resolution mass spectrometry and by IR spectroscopy.

We first observed **8** as a by-product in the high-temperature (405 °C) synthesis of **7** from *N*,*N*′,*N*″-tri(biphenylyl)borazine **9**,[14] by following the procedure described by Köster et al.[13] We proposed a tetraazatetraborocine structure on the basis of solid-state ^{11}B NMR spectroscopy, IR spectroscopy, and computational data.[14] This proposal can now be confirmed by single-crystal X-ray diffraction of **8** (Figure 1), as suitable crystals were obtained from the melt (405 °C) of **9** (Scheme 3).

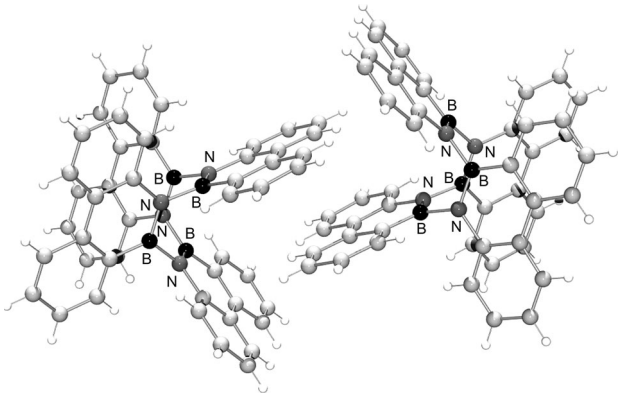
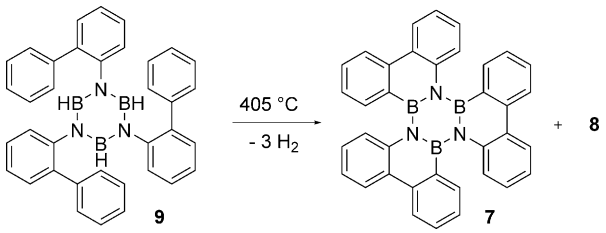


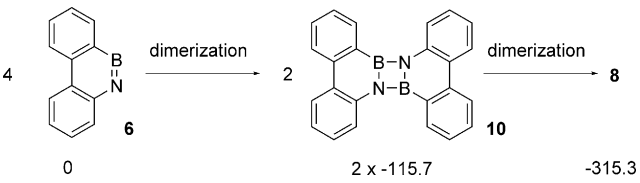
Figure 1. Two molecules of **8** in the solid state.



Scheme 3. Synthesis of **8** from **9** for obtaining X-ray quality crystals of **8**.

Compound **8** crystallized in the monoclinic space group *C*2/c with four molecules in the unit cell.[16] The molecules have the expected B_4N_4 ring in a boat conformation, but the boron and nitrogen atoms cannot be assigned unambiguously because of positional disorder. The biphenylyl groups are essentially planar and are oriented to avoid steric congestion. The packing of the molecules reveals both π-π stacking and CH-π interactions.

The formation of the formal tetramer **8** is a strong indication for involvement of monomeric **6** as a reactive intermediate. A computational investigation (LPNO-CEPA/cc-pVTZ//B3LYP/6-311 + G** + ZPVE)[17] gives an energy barrier of 29.4 kcal mol^{-1} for the exothermic (−21.7 kcal mol^{-1}) loss of N_2 from **5**. At this level of theory, the N_2 elimination and ring enlargement to **6** proceed in a concerted manner. Computations indicate that the dimerization of **6** to diazadiboretidine (**10**) is very favorable (2 **6** → **10**, −115.7 kcal mol^{-1}). Tetramer **8** is possibly formed by dimerization of **10**, a known process in the chemistry of acyclic iminoboranes

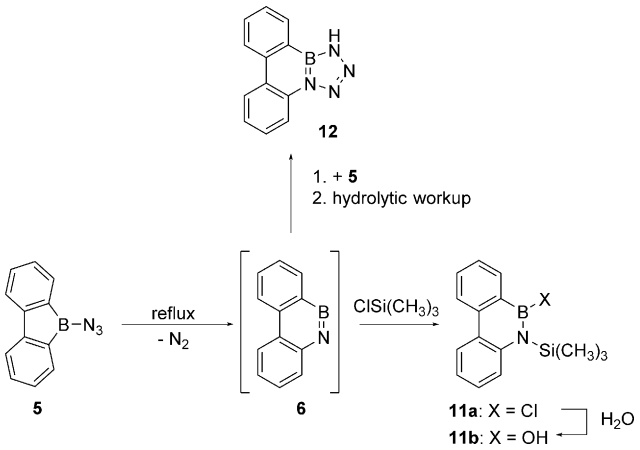


Scheme 4. Possible pathway for the formation **8** from **6**. Relative energies (in kcal mol^{-1}, LPNO-CEPA/cc-pVTZ//B3LYP/6-311 + G** + ZPVE) are given with respect to four molecules of **6**.

(Scheme 4).[7,18,19] The dimerization of **10** is exothermic by −83.9 kcal mol^{-1}, and hence the cyclotetramerization (4 **6** → **8**) is an extremely exothermic process (−315.3 kcal mol^{-1}) which indicates the high energy nature of **6**. The trimer **7** of BN-aryne **6** could be detected in the reaction mixture by mass spectrometry, but was formed in such low amounts that it could not be isolated in addition to **8**.[20] Control experiments showed that **7** did not decompose appreciably into **8** in heptane at reflux.

Hydrolysis or methanolysis of the dark solution obtained from the thermolysis of **5** followed by GC-MS analysis revealed formation of a complex mixture consisting of more than 20 products. Such an observation is not uncommon for the thermolysis of azidoboranes,[8] and also for some organic azides such as phenylazide.[21]

Only a few of the compounds that could be separated by GC could be tentatively assigned on the basis of mass spectrometry and derivatization with trifluoroacetic anhydride (TFAA) and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). These compounds include biphenyl, silyl derivative **11b**, and tetrazaboroline **12**. While **11b** is indicative of the trapping of **6** with trimethylchlorosilane, **12** can reasonably be explained by the trapping of **6** with unreacted azide **5** followed by hydrolysis (Scheme 5).[15] In addition, compounds with masses of biphenyl + **6** and biphenyl + 2 × **6** are detected, but the fragmentation patterns did not allow the constitution to be derived. Products arising from the hydrolysis of **5** were also observed, as confirmed by independently analyzing the hydrolysis products of **5**.



Scheme 5. Trapping of **6** generated from **5** with trimethylchlorosilane and **5** followed by hydrolytic workup. The most plausible isomers of **11** and **12** are displayed.

How similar are the dibenzo derivative **6** and parent 1,2-azaborine **2**? The geometries obtained for **6** and **2** by computational techniques are qualitatively similar, but reveal distinct differences (Figure 2). The large distortion of

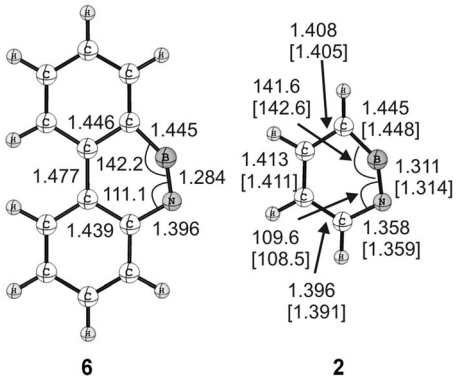


Figure 2. Comparison of the geometries of **6** and **2** computed at the B3LYP/6-311+G** level of theory. B3LYP data for **2** agree well with the higher level CCSD(T)/cc-pVTZ results (data in brackets). Bond lengths are given in Å, bond angles in degrees.

the C_4BN ring[5] from a hexagonal structure remains after dibenzo annulation, as evident by the NBC and BNC angles in **6** (142.2° and 111.1°) being similar to that in **2** (141.6° and 109.6°). As expected, dibenzo annulation causes significant differences in the C–C bond lengths of the C_4BN ring of **6**, while the corresponding bonds have a very similar length in **2**. As a consequence of bond localization, the C–B and C–N distances increase, while the B–N distance decreases in **6** compared to that in **2**. The molecular orbitals remain similar in character: the HOMO is a π orbital and the LUMO is an empty in-plane orbital at the boron atom (see Figure S25 in the Supporting Information). The heats of hydrogenation of **6** and **2** to form BN-phenanthrene or BN-benzene **4** are similar: −64.7 and −59.7 kcal mol^{-1}, respectively. Considering that benzyne **1** behaves, by and large, like a strained alkyne[3c] and that the π system is orthogonal to the orbitals that determine aryne reactivity, the extent of aromaticity in the central six-membered ring is not of crucial importance and consequently phenanthryne shows chemistry similar to **1**. Likewise, the chemistry of BN-phenanthryne **6** is expected to closely resemble that of the as-yet unknown **2**.

In summary, we found that the thermolysis of 9-azido-9-borafluorene **5** produces the tetramer (**8**) of BN-aryne **6**. According to computations, loss of nitrogen and ring enlargement proceeds in a concerted reaction, with the cyclotetramerization of **6** being an exceedingly exothermic process. As a result of the high energy nature of **6**, a plethora of products are formed in addition to tetramer **8**. The formation of a few of them and of the tetramer can easily be rationalized by (self-) trapping of **6**.

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[1] a) G. Wittig, *Naturwissenschaften* **1942**, *30*, 696; b) J. D. Roberts, H. E. Simmons, L. A. Carlsmith, C. W. Vaughan, *J. Am. Chem. Soc.* **1953**, *75*, 3290; c) R. Huisgen, H. Rist, *Naturwissenschaften* **1954**, *41*, 358; d) R. Huisgen, H. Rist, *Justus Liebigs Ann. Chem.* **1955**, *594*, 137; e) J. D. Roberts, D. A. Semenow, H. E. Simmons, L. A. Carlsmith, *J. Am. Chem. Soc.* **1956**, *78*, 601.

[2] a) G. Wittig, L. Pohmer, *Angew. Chem.* **1955**, *67*, 348; b) G. Wittig, L. Pohmer, *Chem. Ber.* **1956**, *89*, 1334.

[3] For selected reviews on arynes, see a) P. M. Tadross, B. M. Stoltz, *Chem. Rev.* **2012**, *112*, 3550; b) C. M. Gampe, E. M. Carreira, *Angew. Chem. Int. Ed.* **2012**, *51*, 3766; *Angew. Chem.* **2012**, *124*, 3829; c) A. Bhunia, S. R. Yetra, A. T. Biju, *Chem. Soc. Rev.* **2012**, *41*, 3140; d) C. Wentrup, *Aust. J. Chem.* **2010**, *63*, 979; e) T. Kitamura, *Aust. J. Chem.* **2010**, *63*, 987; f) M. Winkler, W. Sander, *Aust. J. Chem.* **2010**, *63*, 1013; g) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem. Int. Ed.* **2003**, *42*, 502; *Angew. Chem.* **2003**, *115*, 518; h) H. Pellissier, M. Santelli, *Tetrahedron* **2003**, *59*, 701.

[4] a) A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973; *Angew. Chem.* **2009**, *121*, 991; b) A. M. Daly, C. Tanjaroon, A. J. V. Marwitz, S.-Y. Liu, S. G. Kukolich, *J. Am. Chem. Soc.* **2010**, *132*, 5501; c) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074; *Angew. Chem.* **2012**, *124*, 6178; d) A. N. Lamm, E. B. Garner, D. A. Dixon, S.-Y. Liu, *Angew. Chem.* **2011**, *123*, 8307; *Angew. Chem. Int. Ed.* **2011**, *50*, 8157. Hantzsch–Widman nomenclature uses the -inine ending.

[5] P. J. Fazen, L. A. Burke, *Inorg. Chem.* **2006**, *45*, 2494.

[6] For reviews, see a) P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123; b) P. Paetzold, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93–94*, 39.

[7] J. Münster, P. Paetzold, E. Schröder, H. Schwan, T. von Bennigsen-Mackiewicz, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2641.

[8] a) P. I. Paetzold, *Z. Anorg. Allg. Chem.* **1963**, *326*, 53; b) P. I. Paetzold, P. P. Habereder, R. Müllbauer, *J. Organomet. Chem.* **1967**, *7*, 51; c) P. Paetzold, R. Truppat, *Chem. Ber.* **1983**, *116*, 1531; d) P. Paetzold, E. Eleftheriadis, R. Minkwitz, V. Wölfel, R. Gleiter, P. Bischof, G. Friedrich, *Chem. Ber.* **1988**, *121*, 61.

[9] Borafluorenes are known to readily undergo ring-expansion reactions, for example: a) A. Hübner, Z.-W. Qu, U. Englert, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 4596; b) A. Hübner, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2012**, *51*, 12514; *Angew. Chem.* **2012**, *124*, 12682; c) S. Biswas, C. Maichle-Mössmer, H. F. Bettinger, *Chem. Commun.* **2012**, *48*, 4564.

[10] For reviews on boroles, see a) H. Braunschweig, T. Kupfer, *Chem. Commun.* **2011**, *47*, 10903; b) K. Nozaki, *Nature* **2010**, *464*, 1136; c) A. Steffen, R. M. Ward, W. D. Jones, T. B. Marder, *Coord. Chem. Rev.* **2010**, *254*, 1950.

[11] S. Biswas, I. M. Oppel, H. F. Bettinger, *Inorg. Chem.* **2010**, *49*, 4499.

[12] a) R. Huisgen, W. Mack, L. Möbius, *Tetrahedron* **1960**, *9*, 29; b) G. Wittig, W. Uhlenbrock, P. Weinhold, *Chem. Ber.* **1962**, *95*, 1692; c) H.-F. Grützmacher, U. Strabtmans, *Tetrahedron* **1980**, *36*, 807; d) H. Tomioka, A. Okuno, T. Sugiyama, S. Murata, *J. Org. Chem.* **1995**, *60*, 2344; e) R. Zahradník, P. Hobza, R. Burcl, B. A. Hess, Jr., J. G. Radziszewski, *J. Mol. Struct. THEOCHEM* **1994**, *313*, 335; f) J. Cioslowski, P. Piskorz, D. Moncrieff, *J. Am. Chem. Soc.* **1998**, *120*, 1695; g) J. Poater, F. M. Bickelhaupt, M. Sola, *J. Phys. Chem. A* **2007**, *111*, 5063.

[13] a) R. Köster, G. Benedikt, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 323; *Angew. Chem.* **1963**, *75*, 419; b) R. Köster, K. Iwasaki, S. Hattori, Y. Morita, *Liebigs Ann. Chem.* **1968**, *720*, 23.

[14] a) S. Biswas, M. Müller, C. Tönshoff, K. Eichele, C. Maichle-Mössmer, A. Ruff, B. Speiser, H. F. Bettinger, *Eur. J. Org. Chem.* **2012**, 4634; b) M. Müller, C. Maichle-Mössmer, P. Sirsch, H. F. Bettinger, *ChemPlusChem* **2013**, *78*, 988.

[15] For the reaction of isolated and transient iminoboranes with azides, see a) J. B. Leach, J. H. Morris, *J. Organomet. Chem.* **1968**, *13*, 313; b) P. I. Paetzold, G. Stohr, *Chem. Ber.* **1968**, *101*, 2874; c) P. Paetzold, C. von Plotho, *Chem. Ber.* **1982**, *115*, 2819; d) P. Paetzold, C. von Plotho, G. Schmid, R. Boese, B. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter, W. Schäfer, *Chem. Ber.* **1984**, *117*, 1089; e) H.-U. Meier, P. Paetzold, E. Schröder, *Chem. Ber.* **1984**, *117*, 1954; f) F. Truchet, B. Carboni, M. Vaultier, R. Carrié, *J. Organomet. Chem.* **1987**, *327*, 1.

[16] Crystallographic details for **8**: $C_{48}H_{32}B_4N_4$, $M_r = 708.02$, crystal size $0.45 \times 0.20 \times 0.15$ mm^3, monoclinic, *C*2/c, $a = 13.9427(8)$, $b = 13.8894(9)$, $c = 17.7368(12)$ Å, $\beta = 96.134(2)°$, $V = 3415.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.377$ mg m^{-3}, $\mu = 0.608$ mm^{-1}, F(000) = 1472, $Cu_{K\alpha}$ $\lambda = 1.54178$ Å, $T = 100(2)$ K, $2\Theta_{max} = 133.248$, 29619 reflections measured, 2835 reflections observed, 254 parameters refined, $R_1 = 0.0340$, $wR_2 = 0.0951$, and GOF = 1.051 for all data, $R_1 = 0.0333$, $wR_2 = 0.0943$, and GOF = 1.051 for reflections with $I > 2\sigma(I)$, max/min residual electron density $+0.189/-0.179$ e Å^{-3}. CCDC 990433 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] The geometry was computed using the B3LYP hybrid density functional [a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623] in conjunction with the 6-311 + G** [d) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213] basis set. Single energy points were computed using the local pair natural orbital coupled electron pair approximation LPNO-CEPA/1 [e) A. Hansen, D. G. Liakos, F. Neese, *J. Chem. Phys.* **2011**, *135*, 214102; f) D. G. Liakos, A. Hansen, F. Neese, *J. Chem. Theory Comput.* **2011**, *7*, 76; g) F. Neese, F. Wennmohs, A. Hansen, *J. Chem. Phys.* **2009**, *130*, 114108; h) F. Neese, A. Hansen, F. Wennmohs, S. Grimme, *Acc. Chem. Res.* **2009**, *42*, 641] in conjunction with Dunning's [i) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007] correlation consistent triple-ζ basis set, cc-pVTZ. Energies given in the text are corrected for zero-point vibrational energies (ZPVE). The geometry of **2** was also optimized at the coupled cluster level of theory, CCSD(T)/cc-pVTZ [j) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; k) G. E. Scuseria, *J. Chem. Phys.* **1991**, *94*, 442] level of theory. See the Supporting Information for further details and references.

[18] a) K. Delpy, H.-U. Meier, P. Paetzold, C. von Plotho, *Z. Naturforsch. B* **1984**, *39*, 1696; b) T. Franz, E. Hanecker, H. Nöth, W. Stöcker, W. Storch, G. Winter, *Chem. Ber.* **1986**, *119*, 900; c) P. Paetzold, K. Delpy, R. Boese, *Z. Naturforsch. B* **1988**, *43*, 839.

[19] For theoretical investigations of iminoborane and 1,3-diaza-2,4-diboretidine dimerization, see a) T. M. Gilbert, *Organometallics* **2003**, *22*, 2298; b) T. M. Gilbert, B. D. Gailbreath, *Organometallics* **2001**, *20*, 4727.

[20] The trimer **7** is the major product of the base-induced dehydrochlorination of 10-chloro-10,9-borazarophenanthrene, see Ref. [14a].

[21] P. A. S. Smith in *Azides and Nitrenes* (Ed.: E. F. V. Scriven), Academic Press, Orlando, **1984**, p. 95.

