Synthesis of Four-Membered BN₃ Heterocycles by Borylation of Triazenes

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Supporting Information Placeholder

ABSTRACT: Borylated triazenes were synthesized by dehydrocoupling of triazenes with 9-borabicyclo(3.3.1)nonane, by condensation of triazenes with BEt₃, or by reaction of sodium triazenides with dialkyl- or diarylboron halides. The structures of the products were found to depend on the size of the substituents. Sterically demanding mesityl groups at boron or nitrogen gave rise to open chain structures, whereas smaller substituents led to the formation of novel **BN₃** heterocycles.

Introduction

Four-membered heterocycles containing alternating boron and nitrogen atoms (**BNBN**) are known for more than 50 years,[1] and ring systems of this kind have been studied in the context of main group chemistry,[2] hydrogen economy,[3] polymer chemistry,[4] and photochemistry.[5] The chemistry of other four-membered B_xN_y rings is less developed. An isomeric B_2N_2 heterocycle was described in 1992 by Paetzold and coworkers.[6] A third member of this series, B_3N, was reported in 2001 by Nöth and co-workers (Figure 1).[7] To the best of our knowledge, isolated heterocycles containing three N-atoms and one B-atom have not been described so far,[8] even though there are examples of **BNCN** ring systems.[9] Striving to fill this gap, we have investigated the borylation of triazenes.
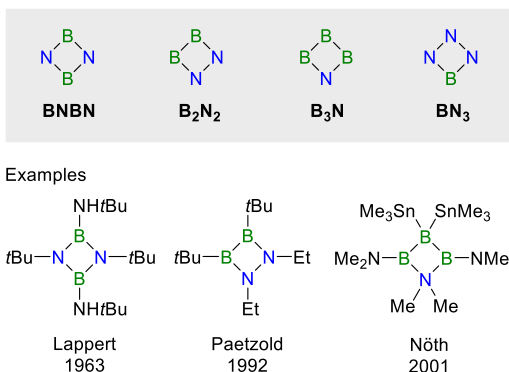
Figure 1. Four-membered boron-nitrogen heterocycles.

Selected examples of borylated triazenes were recently reported by Braunschweig and coworkers. Thermally unstable azaborinines of type **A** (Figure 2) were obtained by insertion of organic azides into the carbon-boron bond of boroles.[10] Organic azides were likewise used for the synthesis of diboryl-substituted triazenes of type **B** and **C** (Figure 2).[11]

Our interest in borylated triazenes was triggered by the following question: how do Lewis-acidic boron compounds bind to triazenes? This question is of relevance for the synthetic organic chemistry of triazenes,[12] because Lewis acids such as BF₃ can promote triazene substitution reactions.[13] At low temperature, we were able to crystallize adducts of tri-substituted triazenes and B(C₆F₅)₃, and crystallographic analyses revealed coordination to

the N1 atom of the triazene (Figure 2, **D**).[14] In the course of these studies, we realized that disubstituted triazenes can be used for the synthesis of novel **BN₃** ring systems (Figure 2, **E**), and details of these investigations are summarized below.
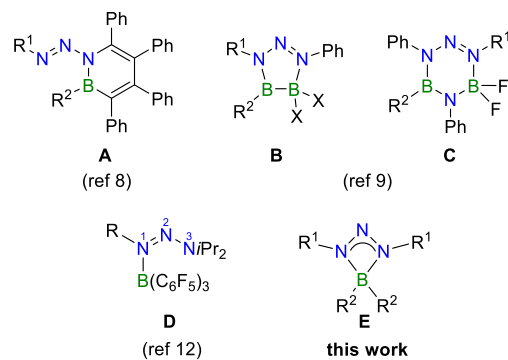
Figure 2. Examples of borylated triazenes.

Results and Discussion

Inspired by a recent study of Bertrand and co-workers on catalyst-free dehydrocoupling of 9-borabicyclo(3.3.1)nonane (9-BBN) with amines,[15] we investigated the reaction of readily available 1,3-dimesityltriazene[16] with 9-BBN (Scheme 1). The reaction was carried out in THF at room temperature and gave the B–N coupling product **1**, which could be isolated as a colorless solid in 38% yield after recrystallization.

Scheme 1. Synthesis (Top) and Crystal Structure (Bottom) of 1.[a]
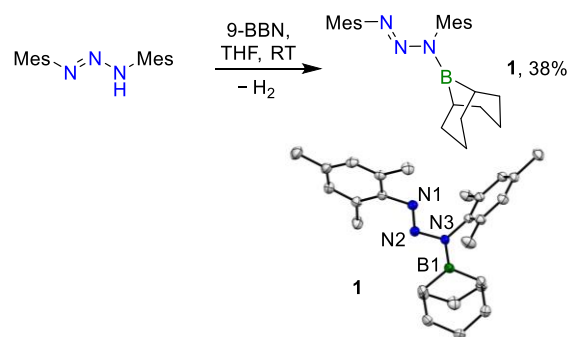
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **1**: B1–N3 = 1.4204(14), N2–N3 = 1.4006(11), N1–N2 = 1.2495(12); N1-N2-N3 = 112.71(8), N2-N3-B1 = 116.38(8).

A crystallographic analysis of **1** confirmed that the acidic hydrogen of 1,3-dimesityltriazene was replaced by a dialkylborane substituent. However, the targeted **BN₃** ring system had not formed. Instead, an open-chain structure with a three-coordinate boron center was observed. The N–B bond length of 1.4204(14) Å in **1** is

significantly shorter than what was observed for the dative N→B bonds in compounds of type **D** (~1.62 Å). The triazene groups shows the expected bond length alternation with a short N1–N2 bond of 1.2495(12) Å and a longer N2–N3 bond of 1.4006(11) Å.

A likely mechanism for the dehydrocoupling reaction leading to **1** involves an initial coordination of 9-BBN to the N1 atom of 1,3-dimesityltriazene (as observed for adducts of type **C**, Figure 2), followed by coupling of the hydridic B–H with the acidic N–H to give hydrogen. The formation of a gas was evidenced by bubbles, which formed during the reaction.

We hypothesized that the sterically demanding mesityl groups could prevent an intramolecular coordination of N1 to the Lewis-acidic boron center. Therefore, we examined the reaction of the less bulky 1,3-diphenyltriazene with 9-BBN (Scheme 2). As before, we observed the formation of bubbles, indicating dihydrogen formation. From the reaction mixture, we were able to isolate the borylated triazene **2** in 90% yield as a yellow crystalline solid.

Scheme 2. Synthesis of 2–4 (Top) and Crystal Structure (Bottom) of 2.[a]
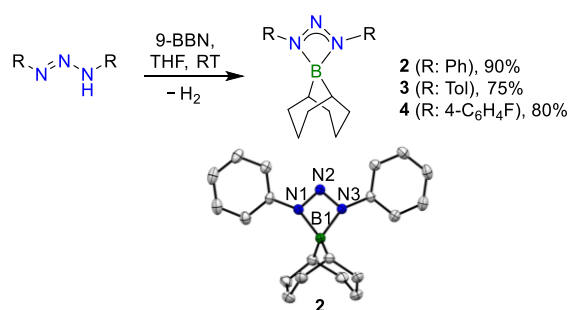
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **2**: B1–N1 = 1.6226(15), B1–N3 = 1.6259(15), N1–N2 = 1.3155(13), N2–N3 = 1.3161(13); N1-N2-N3 = 99.34(8), N2-N3-B1 = 92.10(8), N1-B1-N3 = 76.27(7).

A crystallographic analysis of **2** revealed that the reduced steric demand of the phenyl group did have the desired effect: a **BN₃** ring system had formed. The triazenyl group is bound to the borane in a symmetric fashion, with two nearly equally long N–B bonds of 1.6226(15) Å and 1.6259(15) Å. Accordingly, we observe two equidistant N–N bonds of 1.3155(13) Å and 1.3161(13) Å. The two phenyl groups and the N₃ unit are co-planar, allowing for electron delocalization over the triazenyl fragment. A similar co-planar arrangement is found for transition metal complexes containing the (PhN₃Ph)⁻ ligand.[17]

The results of NMR spectroscopic analyses showed that the **BN₃** ring system is maintained in C₆D₆ solution. Only one set of ^{1}H and ^{13}C NMR signals was observed for the two phenyl groups, which is in contrast to what was found for **1** (two sets of signals for the two mesityl groups). Furthermore, the tetracoordinate boron environment of **2** lead to a high field shift of the ^{11}B NMR signal when compared to what was found for the trigonal boron in **1** (**1**: 57 ppm, **2**: 28 ppm).

In order to expand the scope of the coupling, we have performed reactions between 9-BBN and triazenes containing *p*-tolyl and *p*-fluorophenyl substituents. The corresponding borylated triazenes **3** and **4** could be isolated in yields of 75% and 80%, respectively (Scheme 2). The NMR data were in line with the formation of **BN₃** rings, as evidenced by the high apparent symmetry and by ^{11}B NMR signals at 30 ppm (**3**) and 37 ppm (**4**). Compounds **3** and **4** were also analyzed by single crystal X-ray crystallography. The structures were found to be similar to that of **2**, and details are given in the Supporting Information (SI).

Subsequently, we have explored different reaction pathways for the synthesis of triazene-derived **BN₃** heterocycles. It is known that BEt₃ can undergo catalyst-free condensation reactions with NH-acidic compounds.[18,19] A related reaction could be realized with 1,3-diphenyltriazene. Gentle heating of a solution of BEt₃ and 1,3-diphenyltriazene in hexane lead to the formation of the borylated triazene **5**, which was isolated in 60% yield (Scheme 3). The formation of a **BN₃** ring was evidenced by single crystal X-ray crystallography. The bond length and angles observed for **5** are similar to what was found for **2–4**. As in the case of **1**–**4**, we assume that the reaction is initiated by coordination of BEt₃ to the N1 atom of the triazenes. Proton transfer to the ethyl group could then occur via a six-membered transition state, as suggested for the reaction of BEt₃ with amidines[19] or with carboxylic acids.[20]

Scheme 3. Synthesis (Top) of and Crystal Structure (Bottom) of 5.[a]
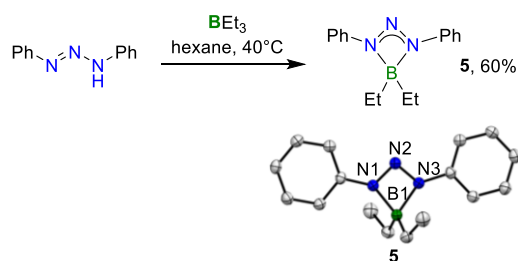
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **5**: B1–N1 = 1.6103(19), N1–N2 = 1.3177(15); N1-N2-N3 = 97.29(14), N1-N2-B1 = 93.46(9), N1-B1-N3 = 75.79(12).

Scheme 4. Synthesis (Top) and Crystal Structures (Bottom) of 6 and 7.[a]
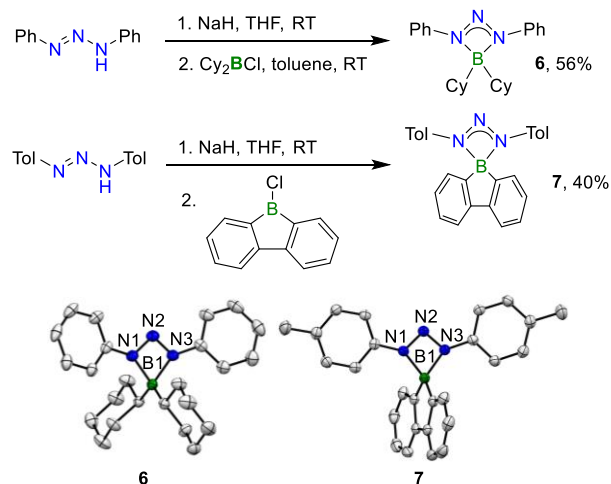
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **6**: B1–N1 = 1.6240(16), B1–N3 = 1.6128(15), N1–N2 = 1.3179(14), N2–N3 = 1.3161(14); N1-N2-N3 = 97.75(9), N2-N3-B1 = 93.60(8), N1-B1-N3 = 75.62(7). Compound **7**: B1–N1 = 1.5966(15), B1–N3 = 1.5945(16), N1–N2 = 1.3224(13), N2–N3 = 1.3142(13); N1-N2-N3 = 97.18(9), N2-N3-B1 = 93.32(8), N1-B1-N3 = 76.58(8).

Next, we have investigated if **BN₃** heterocycles can be prepared by reaction of triazenide salts with boron chlorides. Deprotonation of 1,3-diphenyltriazene with NaH in THF affords sodium triazenide (Ph₂N₃Na), which was used directly for the reaction with dicyclohexylboron chloride. From the reaction mixture, we were

able to isolate the borylated triazene **6** as an orange solid in 56% yield (Scheme 4). In a related fashion, we prepared the 9-borafluorenyl-containing compound **7** (isolated yield: 40%).

The presence of four-membered **BN₃** rings in **6** and **7** was established by single crystal X-ray crystallography. In terms of bond length and angles, compound **6** shows similar values as found for **2**–**5**. Compound **7**, on the other hand, shows slightly shorter B–N bonds (1.5966(15) Å and 1.5945(16) Å). The difference can be attributed to electron-withdrawing character of the aromatic groups attached to boron.

The possibility to use diarylboron halides inspired us to use commercially available dimesitylboron fluoride (Mes₂BF) for the reaction with sodium diphenyl triazenide (Scheme 5). Work-up gave the borylated triazene **8** in 65% yield. NMR spectroscopy and X-ray crystallography showed that **8** adopts an open-chain structure. As in the case of **1**, the presence of sterically demanding mesityl substituents prevents the formation of a four-membered ring system. Furthermore, we employed the asymmetric 3-methyl-1-(p-tolyl)triazene in the reaction with Mes₂BF. Despite the reduced steric demand of this triazene, we again isolated an open-chain product, **9**. The structural and spectroscopic data of **9** are similar to those of **8**.

Scheme 5. Synthesis (Top) and Crystal Structure (Bottom) of 8.[a]
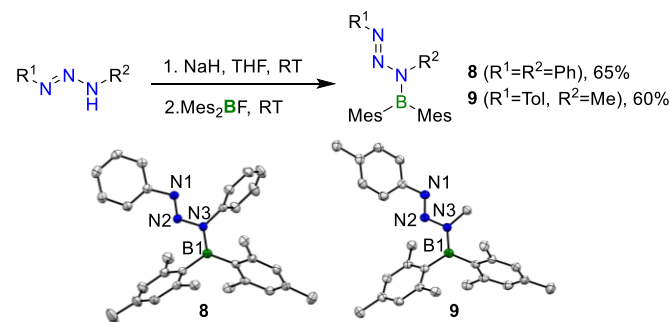
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **8**: B1–N3 = 1.4204(14), N3–N2 = 1.4006(11), N2–N1 = 1.2495(12); N1-N2-N3 = 112.71(8), N2-N3-B1 = 116.38(8). Compound **9**: B1–N3 = 1.4308(17), N3–N2 = 1.3836(14), N2–N1 = 1.2588(14); N1-N2-N3 = 112.55(10), N2-N3-B1 = 117.47(10).

Interestingly, the open-chain compound **1**, **8** and **9** show a different photophysical behavior than the cyclic compounds. The heterocycles **2**–**7** all display bright luminescence in the solid state (**2**–**6**: yellow-green emission; **7**: orange emission), whereas solid **1**, **8** and **9** are non-emissive. The luminescence of **2**–**7** is restricted to the solid state. In solution (THF, toluene, CH₃CN), the emission of **2** is very weak. This behavior can be linked to aggregation-induced emission (AIE), a phenomenon which has received substantial attention in recent years.[21] Since the borylated triazenes display a high susceptibility to hydrolysis, further photophysical investigations of the solids were not performed.

Borylated triazenes are structurally close to boron amidinates and guanidinates.[22] These compounds have been studied in the context of frustrated Lewis pair (FLP) chemistry, and they were found to undergo insertion reactions in the B–N bond.[9,19a] Preliminary studies show that **BN₃** heterocycles can display a related reactivity. For example, 2,6-dimethylphenyl isocyanide (Xyl-NC) readily reacts with **2** at room temperature in hexane. The insertion product **10** was isolated in 67% yield as an orange-red crystalline solid, and it was characterized by single crystal X-ray diffraction (Scheme 6). To the best of our knowledge, five-membered **BN₃C** rings like in compound **10** have not been reported before.

The insertion reaction was found to be reversible. In toluene-d_8, a dynamic equilibrium between **10** and the corresponding starting materials **2** and Xyl-NC was observed. At room temperature, the ¹¹B NMR spectrum showed two broad peaks corresponding to **10** (0 ppm) and **2** (26 ppm). Cooling the solution to – 50 °C led to full conversion into **10**, whereas heating to 80 °C led to complete dissociation into **2** (for details see SI).

We have also examined the reactivity of **2** towards different gases (CO₂, H₂, N₂O, and CO; RT, 1 atm, C₆D₆) and phenyl acetylene (RT, C₆D₆). In all cases, no conversion was observed when the mixture was analysed by NMR spectroscopy.

Scheme 6. Synthesis (Top) and Crystal Structure (Bottom) of 10.[a]
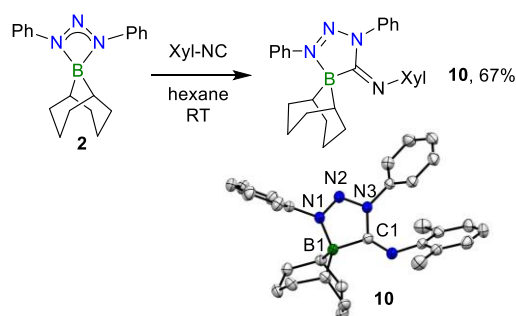
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **10**: B1–N1 = 1.6065(17), B1–C1 = 1.6221(17), N1–N2 = 1.2796(14), N2–N3 = 1.3309(14), C1–N3 = 1.4535(16); N1-N2-N3 = 111.13(10), N2-N1-B1 = 115.33(9), N2-N3-C1 = 113.14(10), N3-C1-B1 = 105.92(9).

Scheme 7. Synthesis (Top) and Crystal Structure (Bottom) of 11.[a]
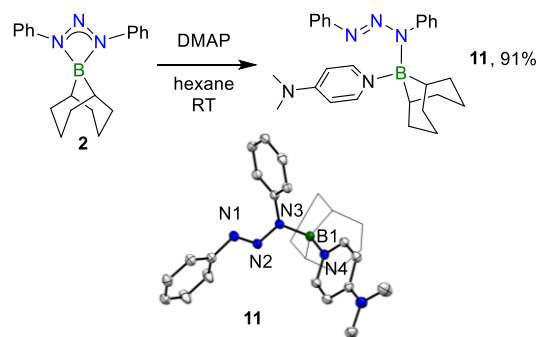
[a] Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) of **11**: B1–N3 = 1.570(2), N3–N2 = 1.333(2), N2–N1 = 1.279(2), B1–N4 = 1.635(2); N1-N2-N3 = 116.42(14), N2-N3-B1 = 115.55(13).

We have also examined ring-opening reactions of **2** with Lewis bases (Scheme 7). While compound **2** was unreactive towards pyridine and acetonitrile, the utilization of 4-dimethylaminopyridine (DMAP) gave adduct **11** in almost quantitative yield. The structure of **11** was confirmed by single-crystal X-ray crystallography. A noteworthy structural feature of **11** is the significantly longer B1–N3 bond (1.570(2) Å) when compared to what was found for the open-chain triazenides **1** (1.4204(14)), **8** (1.4204(14) Å), and **9** (1.4308(17) Å). The bond length extension can be ascribed to the reduced Lewis acidity of the boron center. Similar to what was observed for **1**, **8** and **9**, compound **11** is non-emissive when excited by UV light.

3

Conclusions

The borylation of disubstituted triazenes was achieved via three distinct routes: a) by dehydrocoupling of triazenes with 9-BBN, b) by condensation of triazenes with BEt_3, and c) by reaction of sodium triazenides with dialkyl- or diarylboron halides. The structures of the products was found to depend on the steric demand of the substituents. In the presence of bulky mesityl groups at nitrogen or boron, open chain structures were obtained. For smaller substituents, **BN₃** rings were formed. The **BN₃** heterocycles complete the series of four-membered **B$_x$N$_y$** ring systems, for which all possible combinations are now described. Preliminary reactivity studies show that the **BN₃** heterocycles can undergo ring-opening reaction with DMAP and insertion reaction, as evidenced by the formation of a five-membered **BN₃C** ring in a reaction with an isocyanide. Notably, the **BN₃** heterocycles exhibit solid state luminescence with green to orange emission.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publications …..

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) (a) Geymayer, P.; Rochow, E. G.; Wannagat, U. Bis-(trimethylsilyl)-amino-halogenoborane. *Angew. Chem.* **1964**, *76*, 499–500; (b) Russ, C. R.; MacDiarmid, A. G. Verbindungen mit Si–N–B–Bindungen. *Angew. Chem.* **1964**, *76*, 500–501; (c) Lappert, M. F.; Majumdar, M. K. The Three-coordinate Boron-Nitrogen Four-membered Ring System (1,3-Diaza-2,4-boretane). *Proc. Chem. Soc.* **1963**, 88.

(2) (a) He, G; Shynkaruk, O.; Lui, M. W.; Rivard, E. Small Inorganic Rings in the 21st Century: From Fleeting Intermediates to Novel Isolable Entities. *Chem. Rev.* **2014**, *114*, 7815–7880; (b) Paetzold, P. Boron-Nitrogen Analogues of Cyclobutadiene, Benzene and Cyclooctatetraene. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93*, 39–50.

(3) (a) Lau, S.; Gasperini, D.; Webster, R. L. Amine–Boranes as Transfer Hydrogenation and Hydrogenation Reagents: A Mechanistic Perspective. *Angew. Chem. Int. Ed.* **2021**, *60*, 14272; (b) Staubitz, A.; Robertson, A. P. M.; Manners, I. Ammonia-Borane and Related Compounds as Dihydrogen Sources. *Chem. Rev.* **2010**, *110*, 4079–4124.

(4) (a) Jäkle, F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Appliocations. *Chem. Rev.* **2010**, *110*, 3985–4022; (b) Matsumoto, F.; Chujo, Y. Poly(cyclodiborazane)s. *J. Organomet. Chem.* **2003**, *680*, 27–30.

(5) (a) Shoji, Y.; Ikabata, Y.; Ryzhii, I.; Ayub, R.; El Bakouri, O.; Sato, T.; Wang, Q.; Miura, T.; Karunathilaka, B. S. B.; Tsuchiya, Y.; Adachi, C.; Ottosson, H.; Nakai, H.; Ikoma, T.; Fukushima, T. An Element-Substituted Cyclobutadiene Exhibiting High-Energy Blue Phosphorescence. *Angew. Chem. Int. Ed.* **2021**, *60*, 21817–21823; (b) Hayek, A.; Nicoud, J.-F.; Bolze, F.; Bourgogne, C.; Baldeck, P. L. Boron-Containing Two-Photon-Absorbing Chromophores: Electronic Interaction through the Cyclodiborazane Core. *Angew. Chem. Int. Ed.* **2006**, *45*, 6466–6469.

(6) Thiele, B.; Paetzold, P.; Englert, U. 1,2,3,4-Diazadiboretidine: Reaktionen einer neuen Klasse ungesättigter Bor-Stickstoff-Vierringe. *Chem. Ber.* **1992**, *125*, 2681–2686.

(7) (a) Habereder, T.; Nöth, H.; Wagner, M. Two Isomers of a Tris(dimethylamino)bis(trimethylstannyl) Triborane(5) and the Reaction of $(Me_3Sn)_2B_2(NMe_2)_2$ with $(Ph_3P)_2Pt(\eta^2-C_2H_4)$. *Eur. J. Inorg. Chem.* **2001**, 1665–1669. For examples of B_3N rings within clusters: (b) Dörfler, U.; Clegg, W.; Kennedy, J. D.; Thornton-Pett, M. Polyhedral azaborane chemistry. Nitrogen-vertex incorporation in metallaazaborane formation from 4-(NHEt$_2$)B$_9$H$_{13}$. Two isomers of $[(\eta^5-C_5Me_5)RhB_9H_{12}(NEt_2)]$. *J. Chem. Soc., Dalton Trans.* **1998**, 2353–2358; (c) Gaines, D. F.; McGaff, R. W.; Powell, D. R. Synthesis and structure of new aminopentaborane derivatives. *Inorg. Chem.* **1993**, *32*, 2612–2613; (d) Paetzold, P.; Redenz-Stormanns, B.; Boese, R.; Bühl, M.; von Ragué Schleyer, P. Azadiboriridine-Borane: a Non-Classical Acid-Base Adduct. *Angew. Chem. Int. Ed.* **1990**, *29*, 1059–1060.

(8) A bicyclic system containing a **BNBN** ring fused to a **BN₃** ring was desribed by Paetzold and co-workers. The structure of this compound was deduced by NMR spectroscopy. See: Schreyer, P.; Paetzold, P.; Boese, R. Reaktionen der Cyclobutadien-homologen Diazadiboretidine. *Chem. Ber.* **1988**, *121*, 195–205.

(9) (a) Ramos, A.; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R.; Garcia-Vivó, D. 9-Borabicyclo[3.3.1]nonane: a metal-free catalyst for the hydroboration of carbodiimides. *Chem. Commun.* **2019**, *55*, 3073–3076. (b) Moreno, S.; Ramos, A.; Carrillo-Hermosilla, F.; Rodríguez-Diéguez, A.; García-Vivó, D.; Fernández-Galán, R.; Antiñolo, A. Selective Three-component Coupling for CO2 Chemical Fixation to Boron Guanidinato Compounds, *Inorg. Chem.* **2018**, *57*, 8404–8413; (c) Ramos, A; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R.; Montero-Rama, M. D. P.; Villaseñor, E.; Rodríguez-Diéguez, A.; García-Vivó, D. Insertion reactions of small unsaturated molecules in the N–B bonds of boron guanidinates. *Dalton Trans.* **2017**, *46*, 10281–10299; (d) Cabrera, A. R.; Rojas, R. S.; Valderrama, M.; Plüss, P.; Berke, H.; Daniliuc, C. G.; Kehr, G.; Erker, G. Synthesis of new asymmetric substituted boron amidines – reactions with CO and transfer hydrogenations of phenylacetylene. *Dalton Trans.* **2015**, *44*, 19606–19614; (e) Dureen, M. A.; Stephan, D. W. Reactions of Boron Amidinates with CO2 and CO and Other Small Molecules. *J. Am. Chem. Soc.* **2010**, *132*, 13559–13568.

(10) (a) Lindl, F.; Lin, S.; Krummenacher, I.; Lenczyk, C.; Stoy, A.; Mgller, M.; Lin, Z.; Braunschweig, H. 1,2,3-Diazaborinine: A BN Analogue of Pyridine Obtained by Ring Expansion of a Borole with an Organic Azide. *Angew. Chem. Int. Ed.* **2019**, *58*, 338–342; (b) Braunschweig, H.; Celik, M. A.; Hupp, F.; Krummenacher, I.; Mailander, L. Formation of BN Isosteres of Azo Dyes by Ring Expansion of Boroles with Azides. *Angew. Chem. Int. Ed.* **2015**, *54*, 6347–6351.

(11) Prieschl, D.; Bélanger-Chabot, G.; Guo, X.; Dietz, M.; Müller, M.; Krummenacher, I.; Lin, Z.; Braunschweig, H. Synthesis of Complex Boron–Nitrogen Heterocycles Comprising Borylated Triazenes and Tetrazenes Under Mild Conditions. *J. Am. Chem. Soc.* **2020**, *142*, 1065−1076.

(12) (a) Suleymanov, A. A.; Severin, K. Vinyl and Alkynyl Triazenes: Synthesis, Reactivity, and Applications. *Angew. Chem. Int. Ed.* **2021**, *60*, 6879–6889; (b) Dong, W.; Chen, Z.; Xu, J.; Miao, M.; Ren, H. Synthesis of Benzo-Fused Cyclic Compounds via Intramolecular Cyclization of Aryltriazenes. *Synlett* **2016**, *27*, 1318–1334; (c) Kimball, D. B.; Haley, M. M. Triazenes: A Versatile Tool in Organic Synthesis. *Angew. Chem. Int. Ed.* **2002**, *41*, 3338–3351.

(13) For examples, see: (a) Mao, S.; Chen, Z.; Wang, L.; Khadka, D. B.; Xin, M.; Li, P.; Zhang, S.-Q. Synthesis of Aryl Trimethylstannane via $BF_3 \cdot OEt_2$-Mediated Cross-Coupling of Hexaalkyl Distannane Reagent with Aryl Triazene at Room Temperature. *J. Org. Chem.* **2019**, *84*, 463–471; (b) Kovac, M.; Anderluh, M.; Vercouillie, J.; Guilloteau, D.; Emond, P.; Mavel, S. Aromatic fluoro-de-triazenation with boron trifluoride diethyl etherate under non-protic acid conditions. *J. Fluor. Chem.* **2013**, *147*, 5–9; (c) Zhu, C.; Yamane, M. Transition-Metal-Free Borylation of Aryltriazene Mediated by BF$_3$ OEt$_2$. *Org. Lett.* **2012**, *14*, 4560–4563; (d) Liu, C.-Y.; Knochel, P. Preparation of Polyfunctional Aryl Azides from Aryl Triazenes. A New Synthesis of Ellipticine, 9-Methoxyellipticine, Isoellipticine, and 7-Carbethoxyisoellipticine. *J. Org. Chem.* **2007**, *72*,

7106–7115; (e) Saeki, T.; Son, E.-C.; Tamao K. Boron Trifluoride Induced Palladium-Catalyzed Cross-Coupling Reaction of 1-Aryltriazenes with Areneboronic Acids. *Org. Lett.* **2004**, *6*, 617–619; (f) Zhang, Y.; Li, Y.; Zhang, X.; Jiang, X. Sulfide synthesis through copper-catalyzed C–S bond formation under biomolecule-compatible conditions. *Chem. Commun.* **2015**, *51*, 941–944.

(14) Landman, I. R.; Suleymanov, A. A.; Fadaei-Tirani, F.; Scopelliti, R.; Chadwick, F. M.; Severin, K. Brønsted and Lewis Acid Adducts of Triazenes. *Dalton Trans.* **2020**, *49*, 2317–2322.

(15) Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. Catalyst-free dehydrocoupling of amines, alcohols, and thiols with pinacol borane and 9-borabicyclononane (9-BBN). *Chem. Commun.* **2016**, *52*, 10563–10565

(16) (a) Kalden, D.; Krieck, S.; Görlsa, H.; Westerhausen, M. 1,3-Bis(2,4,6-trimethylphenyl)triazenides of potassium, magnesium, calcium, and strontium. *Dalton Trans.* **2015**, *44*, 8089–8099; (b) Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G. Synthesis of Highly Stable 1,3-Diaryl-1H-1,2,3-triazol-5-ylidenes and Their Applications in Ruthenium-Catalyzed Olefin Metathesis. *Organometallics* **2011**, *30*, 2617–2627.

(17) (a) Beweries, T.; Reiß, F.; Rothe, J.; Schulz, A.; Villinger, A. Triazenido Complexes of Titanocene(III). *Eur. J. Inorg. Chem.* **2019**, 1993–1998; (b) Lee, W.-T.; Zeller, M.; Lugosan, A. Bis(triazenide), tris(triazenide), and lantern-type of triazenide ion complexes: Synthesis and structural characterization. *Inorg. Chim. Acta* **2018**, *477*, 109–113; (c) Albertin, G.; Antoniutti, S.; Bedin, M.; Castro, J.; Garcia-Fontán, S. Synthesis and Characterization of Triazenide and Triazene Complexes of Ruthenium and Osmium. *Inorg. Chem.* **2006**, *45*, 3816–3825; (d) Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L.; Winter, C. H. Synthesis and characterization of titanium and zirconium complexes bearing diphenyltriazenido ligands. *Polyhedron* **1997**, *16*, 4017–4022.

(18) (a) Iwanek, W.; Iwanek, A.; Woźniak, K.; Malińska, M. A simple and efficient synthesis of boron-imidazole macrocycles and their crystal structures. *Tetrahderon Lett.* **2012**, *53*, 4526–4528; (b) Vidjayacoumar, B.; Emslie, D. J. H.; Blackwell, J. M.; Clendenning, S. B.; Britten, J. F. Solution Reactions of a Bis(pyrrolylaldiminate)copper(II) Complex with Peralkyl Zinc, Aluminum, and Boron Reagents: Investigation of the Pathways Responsible for Copper Metal Deposition. *Chem. Mater.* **2010**, *22*, 4854–4866; (c) Cortes-Llamas, S. A.; Hernández-Pérez, J. M.; Hô, M.; Muñoz-Hernández, M.-A. Indazolato Derivatives of Boron, Aluminum, and Gallium: Cheracterization and Solvent-Dependent Regioisomeric Structures through π—π Interactions in the Solid State. *Organometallics* **2006**, *25*, 588–595; (d) Yalpani, M.; Köster, R.; Boese, R. Thermal C–Borylation in Crowded Pyrazolylboranes. *Chem. Ber.* **1991**, *124*, 1699–1704; (e) Niedenzu, K.; Woodrum, K. R. Triazaboles and Related Triazole Derivatives of Boron. *Inorg. Chem.* **1989**, *28*, 4022–4026.

(19) (a) Mikhailov, B. M.; Dorokhov, V. A.; Lavrinovich, L. I. N-Dialkylborylamidines from N,N'-Disubstituted Amidines. *Bull. Acad. Sci. USSR, Division of Chemical Science* **1977**, *27(11)*, 2304–2310 (https://doi.org/10.1007/BF00946682); (b) Trofimenko, S. N,N'-Diboryloxamidines. *J. Am. Chem. Soc.* **1967**, *89*, 7014–7106.

(20) (a) Brown, H. C.; Hébert, N. C. Organoboranes XXXIII. Protonolysis of Triethylborane with Carboxylic Acids. *J. Organomet. Chem.* **1983**, *255*, 135–141; (b) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. A Kinetic and Mechanistic Study on the Cleavage of the Carbon–Boron Bond. The Importance of Coordination. *J. Am. Chem. Soc.* **1965**, *87*, 1236–1240.

(21) (a) Zhao, Z.; Zhang, H.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: New Vistas at the Aggregate Level. *Angew. Chem. Int. Ed.* **2020**, *59*, 9888–9907; (b) Würthner, F. Aggregation-Induced Emission (AIE): A Historical Perspective. *Angew. Chem. Int. Ed.* **2020**, *59*, 14192–14196; (c) Shen, P.; Zhuang, Z.; Zhao, Z.; Tang, B. Z. AIEgens based on main group heterocycles. *J. Mater. Chem. C* **2018**, *6*, 11835–11852.

(22) Gyton, M. R.; Leverett, A. R.; Cole, M. L.; McKay, A. I. Bulky bis(aryl)triazenides: just aspiring amidinates? A structural and spectroscopic study. *Dalton Trans.* **2020**, *49*, 5653–5661.

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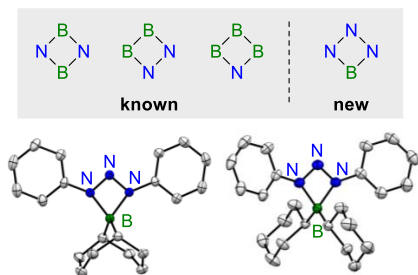
Synopsis: The borylation of 1,3-disubstituted triazenes leads to the formation of four-membered BN_3 heterocycles.