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N=N bond cleavage in diazirines by a cyclic diborane(4) compound†

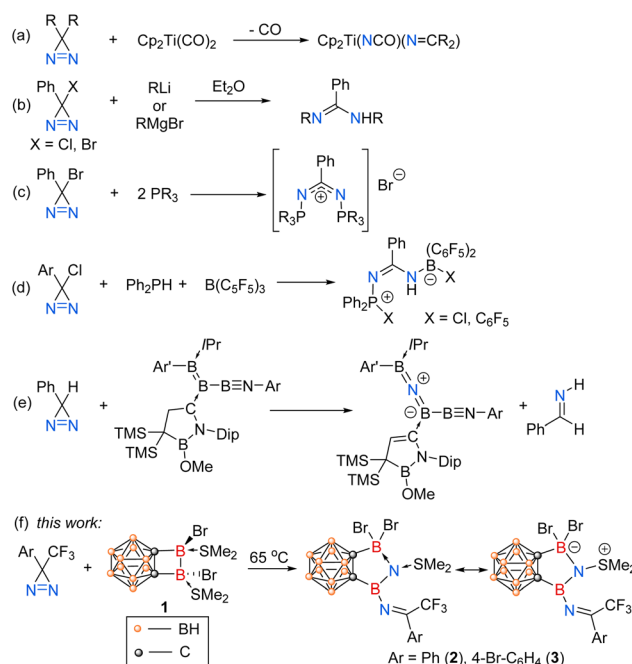Minling Zhong,[a] Jie Zhang [ID][b] and Zuowei Xie [ID] *[a]

Reactions of *o*-carborane-fused diborane(4) with 3*H*-diazirines led to the complete cleavage of the N=N bond, with one nitrogen atom being incorporated into the B–B bond. The molecular and electronic structures of the resultant borylnitrogen compounds were confirmed through single-crystal X-ray analyses and computational studies. The related reaction mechanism was investigated using DFT calculations.

Diaziridines are highly strained three-membered rings composed of one carbon and two nitrogen atoms, with a double bond between the nitrogen atoms.[1] Upon activation with light, heat,[2] or ultrasonication,[3] they can be transformed into carbenes by breaking the C–N bonds and liberating dinitrogen. Consequently, they have been extensively studied as carbene precursors in organic chemistry[4,5] and find wide applications in photoaffinity labelling (PAL)[6–9] and polymer crosslinkers.[10–12]

In striking contrast, the complete cleavage of the N=N bond in diazirines has rarely been reported. In 1987, the Kisch group showed that $Cp_2Ti(CO)_2$ had an unprecedented capability to activate diazo compounds, exposure of which to 3*H*-diazirines led to oxidative addition of the N=N double bond and the generation of $Cp_2Ti(NCO)(N=CR_2)$ (Scheme 1a).[13] Except for transition metals, certain main-group species such as Grignard reagents,[14] lithium reagents,[14,15] and phosphines[16,17] have also been reported to cleave the N=N double bonds of the halodiazirines through nucleophilic substitution processes (Scheme 1b and c). However, it is only in recent years that low-valent boron-containing species (*e.g.*, borylenes, boron radicals) have been employed to activate the enthalpically strong N=N or N≡N bonds.[18–21] In 2022, the Stephan group reported the reactions of phosphine/borane frustrated Lewis pairs with chlorodiazirines, resulting in the reduction of the N=N double bond (Scheme 1d).[22] In 2023, the Kinjo group demonstrated that triboraazabutenynes bearing an extremely polarized B=B bond reacted with phenyldiazirine, leading to the cleavage of the N=N bond and the incorporation of a single nitrogen atom into the B=B bond (Scheme 1e).[23]

We recently reported that *o*-carborane-fused diboracycle (**1**) can serve as a "strain-release" reagent for catalyst-free diboration of alkenes and alkynes.[24] During our reactivity studies of compound **1**, we serendipitously discovered that *o*-carborane-fused diborane(4) completely cleaved the strong N=N bond in 3*H*-diazirines, resulting in the incorporation of one nitrogen atom into the B–B bond and the subsequent formation of borylnitrogen compounds (Scheme 1f). These results are reported in this paper.

Treatment of *o*-carborane-fused diboracycle **1** with 1.5 equiv. of 3-phenyl-3-(trifluoromethyl)-3*H*-diazirine in benzene at 65 °C overnight gave compound **2** as colourless crystals in 49% isolated yield (Scheme 2). Its ^{11}B NMR spectrum exhibited two

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Scheme 1 Examples of N=N bond cleavage of 3*H*-diazirines.
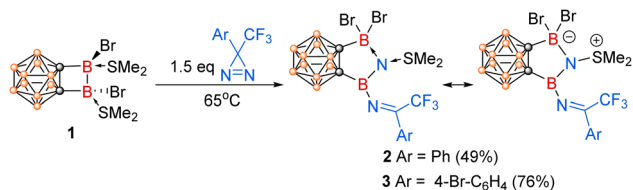
Scheme 2 N=N bond cleavage of 3*H*-diazirines by the cyclic diborane(4) compound **1**.
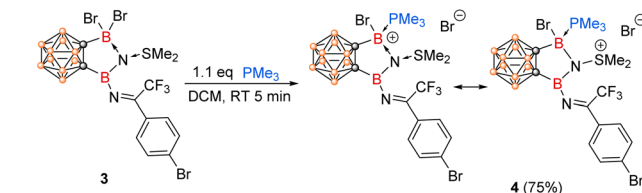
Scheme 3 Reaction of **3** with PMe₃.

singlets at 29.13 and −0.25 ppm for two *exo*-polyhedral boron atoms. The obvious down-field shift of one boron relative to the starting material **1** ($\delta = -3.04$ ppm)[24] indicated the formation of a three-coordinate boron center in **2**. The ^{19}F NMR spectrum displayed one singlet at −66.65 ppm attributable to the CF₃ group in **2**. In its ^{1}H NMR, the two methyl groups of SMe₂ showed two singlets at 2.99 and 2.92 ppm, which were magnetically inequivalent due probably to the restricted rotation caused by the adjacent bromide atoms.

In the same manner, reaction of **1** with 1.5 equiv. of 3-(4-bromophenyl)-3-(trifluoromethyl)-3*H*-diazirine in dichloromethane at 65 °C overnight afforded another analogous compound **3** in 76% yield. Its NMR spectra were very similar to those observed in **2**, suggesting that they may have very similar molecular structure.

The solid-state structure of **2** was unambiguously confirmed by single-crystal X-ray analyses, showing a coplanar five-membered C₂B₂N ring (Fig. 1). Both the N1 and B14 centers adopt a trigonal-planar geometry as evidenced by the sum of the bond angles around N1 (360.1(9))° and B14 (359.9(2))°, respectively. The B14–N1 distance of 1.434(6) Å is much shorter than that of 1.531(6) Å for B13–N1 bond. On the other hand, the B14–N2 bond length of 1.384(6) Å is significantly shorter than that of B14–N1 one, indicating the presence of electron donation from the lone pair on N2 to the empty p orbital of B14. The S1–N1 distance (1.653(3) Å) lies within the range of the reported S–N dative bonds in the sulfiimines (1.610–1.669 Å).[25–27]

On the other hand, reaction of **3** with 1.1 equiv. of PMe₃ resulted in the formation of boronium cation **4** in 75% yield *via* a nucleophilic displacement of Br⁻ by PMe₃ (Scheme 3). Treatment of excess PMe₃ did not result in the replacement of the coordinated SMe₂, suggesting very strong interactions between SMe₂ and N1 centre. Compound **4** was not thermally

stable under ambient conditions as evidenced by NMR spectra (see Fig. S1 in the ESI†). Its solid-state structure was confirmed by single-crystal X-ray analysis (Fig. 2), which also supports the formation of **3**. The structural parameters of the N1 centre in **4** parallel those in **2**, with the B14–N1, B13–N1, and S1–N1 bond lengths of 1.418(15) Å, 1.577(13) Å and 1.662(7) Å, respectively. The newly formed B13–P1 bond distance of 1.990(10) Å is comparable to those reported in phosphine-stabilized borenium or boronium species (1.89–1.97 Å).[28–30]

To gain further insight into the electronic structure of compound **2**, density functional theory (DFT) calculations were conducted at the B3LYP/6-311+G(d,p) level of theory. The molecular orbital analyses show that the LUMO corresponds to π* anti-bonding of the phenylimine moiety, whilst the HOMO primarily represents the lone pair orbital of the bromine groups (Fig. 3a). The natural bond orbital (NBO) analyses indicate that N1 has two lone pairs with the lone pair occupancy of LP(σ) and LP(π) is 1.74 and 1.68, respectively (see Table S2 in the ESI†). Second-order perturbation analyses show the donor–acceptor interactions from either lone pair orbital on N1 to the LP* orbitals of B13 or B14 atoms (Fig. 3b). The hyperconjugation donation from LP(σ) of N1 to LP*(σ) of B13 (175.45 kcal mol⁻¹) is significantly stronger than that from LP(π) of N1 to LP*(π) of B14 (52.80 kcal mol⁻¹) (see Table S3 in the ESI†).

The calculated natural population analyses (NPA) show that the N1 carries a considerably large negative charge (−1.18), while the N1-bonded boron and sulfur atoms carry positive charges (B13: 0.51; B14: 1.12; S1: 1.12) (Fig. 4). The calculated Wiberg bond indices (WBI) provide further insights into the bonding situation, indicating a B14–N1 covalent bond (WBI = 0.834), a rather strong S1–N1 dative bond (WBI = 0.741), and a weak N1–B13 dative bond (WBI = 0.583). The electronic structure and bonding analyses support **2** as a stabilized
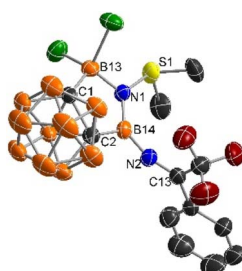

Fig. 1 Molecular structure of **2** (thermal ellipsoids are set at the 50% probability level, and all hydrogen atoms are omitted for clarity).
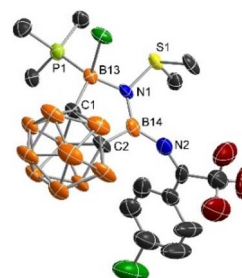

Fig. 2 Molecular structure of the cation in **4** (thermal ellipsoids are set at the 35% probability level, all hydrogen atoms are omitted for clarity).
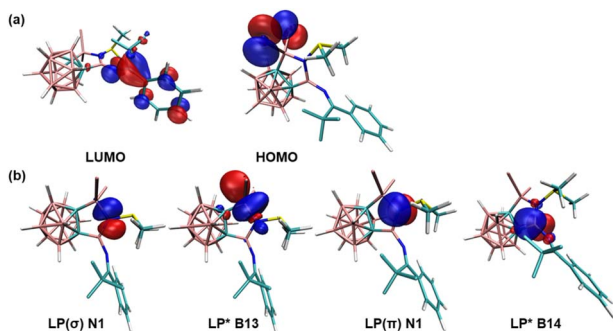
Fig. 3 Plots of selected (a) MOs and (b) NBOs of **2** calculated at the B3LYP-D3/6-311+G(d,p) level of theory (isovalue 0.04 a.u.).
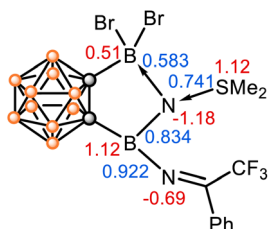

Fig. 4 Natural population analysis (NPA) charge distribution of selected atoms (in red) and Wiberg bond indices (WBI) values of selected bonds in **2** (in blue).

borylnitrogen compound, where the N donates its lone pairs to the neighboring boron centres and accepts electrons from the SMe$_2$ ligand. It is salient to highlight that the Lewis acid–base interactions play a key role in the stabilization of this borylnitrogen species. Noted that matrix-free nonmetallic nitrenes have been rarely reported thus far.[31–34]

To understand the reaction mechanism for the formation of compound **2**, DFT calculations were undertaken at the M06-2X/6-311G(d,p) level of theory in C$_6$H$_6$ solution (Scheme 4). The proposed mechanism involves several key steps. Initially, one SMe$_2$ group is dissociated, followed by the migration of bromide, resulting in the formation of an unsymmetric intermediate **B** *via* **TS1** with an energy barrier of 23.5 kcal mol^{-1}, which is the rate-determining step. Upon coordination of 3*H*-diazirine to the electron-deficient boron center, the B–B bond in **C** undergoes facile heterolytic cleavage, leading to the formation of a borylene intermediate **D** *via* **TS2**. The coordination of 3*H*-diazirine moiety to the other boron center results in the formation of a six-membered intermediate **E**. Subsequent insertion of the borylene into the N=N bond gives rise to the ring-contracted intermediate **F** *via* **TS3**. Following the liberation of SMe$_2$ from boron, and a nucleophilic attack of SMe$_2$ on the nitrogen occurs, leading to N–N bond cleavage and the formation of intermediate **I** *via* **TS4**. Finally, electron redistribution within the four-membered BN$_2$C ring occurs, resulting in the formation of compound **2**. The large energy gain in this step ($\Delta G_{I-2} = -99.1$ kcal mol^{-1}) may be attributed to the release of the ring strain.

Conclusions

In conclusion, this work demonstrated the first example of N=N bond cleavage of 3*H*-diazirines by *o*-carborane-fused diborane(4) species **1**. The electronic structure and bonding analyses of the resulted compounds **2** & **3** revealed that the nitrogen centre N1 bears two lone pairs of electrons, which was stabilized through Lewis acid/base interactions. DFT calculations indicated that the reaction proceeded through a key intermediate, borylene **D**, followed by its insertion into the N=N double bond. Upon the treatment with strong Lewis base PMe$_3$, compound **3** undergoes nucleophilic attack on boron to
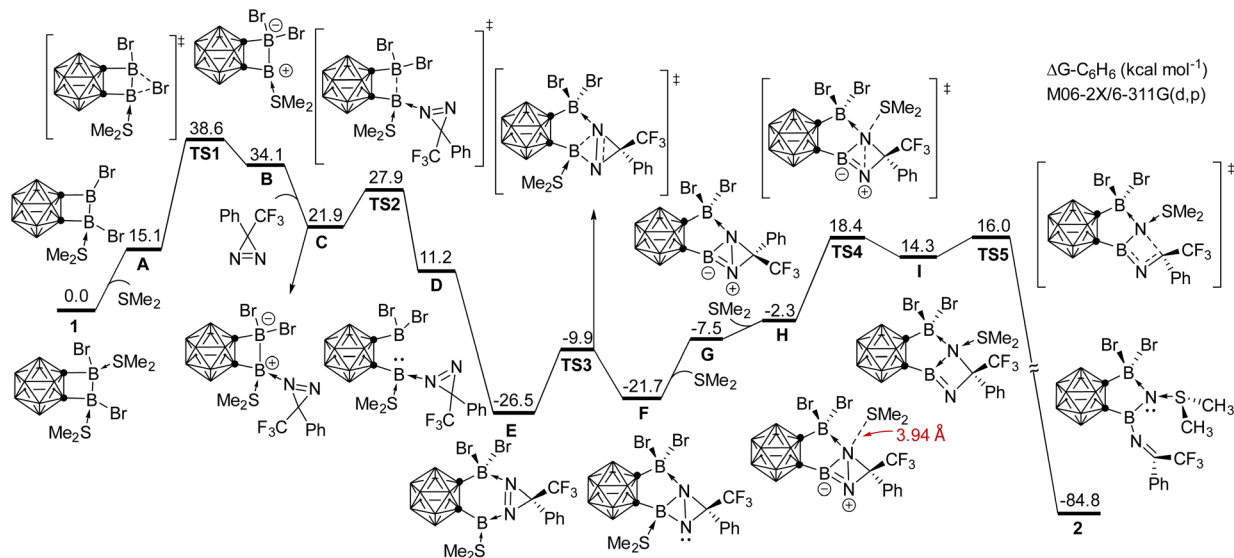
Scheme 4 Energy profile for the DFT-based mechanism for the reaction of **1** with 3*H*-diazirine calculated at the M06-2X/6-311G(d,p) level of theory. The relative Gibbs free energies are given in kcal mol^{-1}.

produce a boronium cation **4**. This finding provides some hints for the activation of enthalpically strong bonds by using diboranes.

Data availability

All data are available in the ESI† of this article.

Author contributions

Z. X. directed and conceived this project. M. Z. conducted the experiments. J. Z. did the theoretical work. All authors discussed the results and wrote the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Notes and references

1 R. A. Moss, *Acc. Chem. Res.*, 2006, **39**, 267–272.

2 M. T. Liu, *Chem. Soc. Rev.*, 1982, **11**, 127–140.

3 A. Blencowe and W. Hayes, *Soft Matter*, 2005, **1**, 178–205.

4 R. A. Moss, J.-M. Fedé and S. Yan, *J. Am. Chem. Soc.*, 2000, **122**, 9878–9879.

5 N. J. Porter, E. Danelius, T. Gonen and F. H. Arnold, *J. Am. Chem. Soc.*, 2022, **144**, 8892–8896.

6 J. Das, *Chem. Rev.*, 2011, **111**, 4405–4417.

7 L. Dubinsky, B. P. Krom and M. M. Meijler, *Bioorg. Med. Chem.*, 2012, **20**, 554–570.

8 M. Hashimoto and Y. Hatanaka, *Eur. J. Org Chem.*, 2008, **2008**, 2513–2523.

9 J. R. Hill and A. A. Robertson, *J. Med. Chem.*, 2018, **61**, 6945–6963.

10 K. Dey, S. R. Chowdhury, E. Dykstra, A. Koronatov, H. P. Lu, R. Shinar, J. Shinar and P. Anzenbacher, *J. Mater. Chem. C*, 2020, **8**, 11988–11996.

11 S. F. Musolino, M. Mahbod, R. Nazir, L. Bi, H. A. Graham, A. S. Milani and J. E. Wulff, *Polym. Chem.*, 2022, **13**, 3833–3839.

12 C. Wu, C. Li, X. Yu, L. Chen, C. Gao, X. Zhang, G. Zhang and D. Zhang, *Angew. Chem., Int. Ed.*, 2021, **60**, 21521–21528.

13 G. Avar, W. Rüsseler and H. Kisch, *Z. Naturforsch. B Chem. Sci.*, 1987, **42b**, 1441–1446.

14 P. Kolářová, V. Čmolík, I. Linhart, I. Á. Martínez and T. Martinů, *Tetrahedron Lett.*, 2013, **54**, 6764–6767.

15 R. Navrátil, J. Tarábek, I. Linhart and T. Martinů, *Org. Lett.*, 2016, **18**, 3734–3737.

16 G. Alcaraz, A. Baceiredo, M. Nieger and G. Bertrand, *J. Am. Chem. Soc.*, 1994, **116**, 2159–2160.

17 G. Alcaraz, V. Piquet, A. Baceiredo, F. Dahan, W. W. Schoeller and G. Bertrand, *J. Am. Chem. Soc.*, 1996, **118**, 1060–1065.

18 S. Bennaamane, B. Rialland, L. Khrouz, M. Fustier-Boutignon, C. Bucher, E. Clot and N. Mézailles, *Angew. Chem., Int. Ed.*, 2023, **62**, e202209102.

19 (*a*) M.-A. Légaré, M. Rang, G. Bélanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. C. Holthausen and H. Braunschweig, *Science*, 2019, **363**, 1329–1332; (*b*) L. C. Haufe, L. Endres, M. Arrowsmith, R. Bertermann, M. Dietz, F. Fantuzzi, M. Finze and H. Braunschweig, *J. Am. Chem. Soc.*, 2023, **145**, 23986–23993.

20 M. A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels and H. Braunschweig, *Science*, 2018, **359**, 896–900.

21 B. Xu, H. Beckers, H. Ye, Y. Lu, J. Cheng, X. Wang and S. Riedel, *Angew. Chem., Int. Ed.*, 2021, **60**, 17205–17210.

22 D. Mandal, T. Chen, Z. W. Qu, S. Grimme and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209241.

23 L. Zhu and R. Kinjo, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306519.

24 M. Zhong, J. Zhang, Z. Lu and Z. Xie, *Dalton Trans.*, 2021, **50**, 17150–17155.

25 H. Lebel, H. Piras and J. Bartholoméüs, *Angew. Chem., Int. Ed.*, 2014, **53**, 7300–7304.

26 F. Pichierri, *Chem. Phys. Lett.*, 2010, **487**, 315–319.

27 X. Xiao, S. Huang, S. Tang, G. Jia, G. Ou and Y. Li, *J. Org. Chem.*, 2019, **84**, 7618–7629.

28 M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.*, 2008, 4303–4305.

29 A. J. V. Marwitz, J. T. Jenkins, L. N. Zakharov and S.-Y. Liu, *Organometallics*, 2011, **30**, 52–54.

30 S. R. Wang, M. Arrowsmith, H. Braunschweig, R. D. Dewhurst, V. Paprocki and L. Winner, *Chem. Commun.*, 2017, **53**, 11945–11947.

31 F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking and G. Bertrand, *Science*, 2012, **337**, 1526–1528.

32 F. Dielmann and G. Bertrand, *Chem.–Eur. J.*, 2015, **21**, 191–198.

33 M. Janssen, T. Frederichs, M. Olaru, E. Lork, E. Hupf and J. Beck-mann, *Science*, 2024, **385**, 318–321.

34 Y. Ding, S. K. Sarkar, M. Nazish, S. Muhammed, D. Luert, P. N. Ruth, C. M. Legendre, R. Herbst-Irmer, P. Parameswaran, D. Stalke, Z. Yang and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2021, **60**, 27206–27211.