

Responses to referees' comments

Referee 1

This manuscript by Liu, Liang, and Kong et al. reports the synthesis, characterization, and reactivity study of a diboryl diazene.

Azo compounds with hydrocarbyl and p-block element substituents are widely known, whereas boryl-substituted derivatives are reported only as the polymeric form or transient species. By incorporating bulky Mes groups on the B atoms, the authors successfully synthesize a diboryl diazene in a monomeric form. This compound is thoroughly characterized by NMR, X-ray, UV, Raman, CV, and computational studies (MO analysis, NRT, TDDFT), revealing the cumulene character. Interestingly, this compound exhibits a robust thermal stability, while the reactions of the boryl diazene with an NHC and various carbonyl substrates demonstrate that this may serve as a surrogate of Mes₂B radical. Moreover, the N and B centers of the boryl diazene cooperatively activate ammonia to furnish an amine-borane Mes₂BNH₂, the mechanism is also investigated computationally.

I enjoyed reading this very nice work. This is not just an additional example of a diazo compound with another substituent. Although N₂ release concomitant with the R radical generation from R-N=N-R is well known, this study demonstrates such a process is applicable for the generation of boryl radical, which is outstanding because the B radical species are in general yielded by redox reactions (ref 26) and the carbene-derived formation of B radicals is still rare (JACS 2024, 146, 20945). Moreover, the reaction of diazenes with NH₃ is not common. The study is comprehensively done, highly original, and it should have a good readership not only from boron chemists but also inorganic and synthetic communities. I recommend the present manuscript for publication in JACS. Some minor comments are shown below for their revision.

(1) Fig 1(a). I am not sure what the 'CAr' here means.

(2) 176.4(6) ppm of BNNB core is not perfectly linear. To be accurate, 'nearly' might be added (in abstract, etc..)

(3) As confirmed by MO analysis and they concluded, this compound has the cumulenic B=N=N=B core. So, why are the B-N moieties still indicated with dash-bonds instead of double bonds?

(4) Fig 4, NHC reaction. If a catalytic amount of NHC is employed, Mes₂B radical without NHC would be yielded, which should further react with 2 continuously. Then, Mes₂B-BMes₂ is formed?

(5) Fig 4, reactivity with carbonyls. Chung reported diboron(4) shows radical-type reactivity when adding carbonyls (ref 30,31). I was wondering if those products 4-7 are actually not from the direct capture of Mes₂B radical but from Mes₂B-BMes₂, although sterically hindered but Shoji et al confirmed it exists (ACIE, 2022, 61, e202113549). Have the authors considered this possibility?

(6) The baseline of some NMR spectra (Fig S3, S12 etc..) should be adjusted properly

Referee 2

This manuscript by Huang et al. describes the synthesis, isolation, and reactivity studies of a diboryl diazene (compound 2) featuring a B–N=N–B unit. Compound 2 was obtained from the reaction of diboryl hydrazine with two equivalents of tBuLi. Its molecular structure was determined by X-ray diffraction, revealing a nearly linear central B–N=N–B unit. DFT calculations and spectroscopic analyses support the cumulenenic triene form as the dominant resonance contributor.

The authors further explored the reactivity of 2. Reaction with an NHC afforded an NHC-stabilized boron radical, while reactions with ketone/dione derivatives produced boron-containing products accompanied by N₂ elimination. Interestingly, treatment of 2 with NH₃ yielded Mes₂B–NH₂ and the corresponding bisboryl hydrazine (compound 1). The reaction mechanisms have been discussed on the basis of DFT results.

Overall, this is a well-executed and insightful study. The manuscript presents the isolation and structural characterization of a unique diboryl diazene, along with its intriguing reactivity profile. I therefore support publication of this work in JACS, provided the authors address the following points:

1. Thermal and photochemical stability: The authors should discuss the stability and potential reactivity of compound 2 under elevated temperature or photolysis conditions. Is compound 2 stable under such conditions, and does N₂ elimination occur?
2. Reactivity with small molecules: The reviewer is curious about the reactivity of 2 with amines (R₂NH or RNH₂) and H₂. How does it behave in the presence of these molecules?
3. Rotation barrier: Have the authors considered discussing the rotational barrier of the B–N=N–B unit? In particular, how do the planar/linear and perpendicular geometries compare energetically?

Referee 3

Liang, Liu and Kong reported a crystalline monomeric diboryl diazene, featuring a linear, cumulenenic B=N=N=B core. Coordination by Lewis bases can trigger N₂ extrusion to generate boryl radicals that participate in diverse B–C, B–O, and C–C bond-forming processes. In contrast, reaction with NH₃ proceeds via B,N-cooperative N–H activation to give dimesitylboryl amine and N₂H₂. As all these results are particularly interesting for the development of boron radical chemistry as well as main-group species for dinitrogen transformations, I strongly suggest a publication of this manuscript in this journal unless the minor issues listed below are fully addressed.

1. When the authors mentioned in the Introduction that recent efforts have moved beyond hydrocarbyl substitutions to main group analogues bearing E–N=N–E skeletons, the recent prediction of near-infrared absorbance of E and Z diazene could be discussed (J. Org. Chem. 2023, 88, 12183–12193).
2. The authors mentioned in the Introduction that a diboryl diazene species (VIII) was proposed computationally as a reactive intermediate in the boron-mediated N₂-to-NH₃ conversion via radical pathways (ref 18: Angew. Chem., Int. Ed., 2023, 62, e202209102). It should be pointed out that such a radical pathway was proposed earlier by Zhu group in 2022 (Inorg. Chem. 2022, 61, 2234–2241).

3. On Page 3, the authors stated that Natural population analysis (NPA) further indicates B–N bond polarization, with calculated charges of +0.68 a.u. on boron and –0.19 a.u. on nitrogen. Actually, such a charge polarization has been used to rationalize BN-heterocycle stability and BN-doped polyenes (Org. Biomol. Chem. 2025, 23, 4508-4518 and Chem. Asian J. 2017, 12, 605–614), which could be mentioned and compared.

4. In Figure S26 on page 28 of the SI, the authors show two distinct energies (+67.6 and -45.6 kcal/mol). The factor for such a significant difference should be probed. The B-N bond strength could be one of these factors, which can be examined by computing the B-N bond orders.

5. The N-H bond activation in NH₃ has been observed and computed in Figs 4 and 6. How about the other N-H bond in the primary and secondary amines, which should be checked both experimentally and computationally.

Referee 4

This manuscript reports the synthesis and reactivity of a monomeric diboryl diazene. The structure of 2 has been well investigated by experiment methods and computational studies. Compound 2 exhibits some interesting reactivity, especially generating the Mes₂B• radical in the presence of a carbene. The work is novel and well-executed, meeting the high standard for JACS. This reviewer recommends its publication after addressing the following points.

(1) Compound 2 exhibits a short N=N bond compared to hydrocarbyl-substituted azo compounds. This is consistent with its enhanced bond strength, as indicated by Raman spectroscopy. A discussion is necessary to explain why the boryl substituent strength the N=N bond.

(2) Given the only 43% yield of 3, does this reaction generate one or two equiv of Mes₂B• radical?

(3) Would the reaction of 2 with two equivalents of tetrachloro-1,2-benzoquinone yield a product analogous to 6?

Similarly, does the reaction of 2 with only one equiv of 9,10-phenanthrenequinone lead to the product like 5?

It is essential to discuss why the similar substrates result in different products.

(4) In SI, the shape of boron spectrum of 2 looks anomalous. Has phase correction been performed?