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Dear Executive Editor

Dr. Guy Richardson

Article No. 202517656

Enclosed please find our **revised** research article No. 202517656 entitled 'One Collision – Two Heteroatoms: Gas-Phase Preparation of Azasilabenzenes' for the journal of the German Chemical Society – *Angewandte Chemie International Edition*. All changes made to the text during revision were highlighted in yellow.

We sincerely thank the editor and reviewers for taking the time to review our manuscript and providing constructive feedback to improve our manuscript. We have revised the manuscript accordingly by following the reviewers' suggestions. Below are the original comments from the editor and reviewers and our point-by-point response (in blue):

Editor:

Furthermore, the editorial office requires that you make the following checks/changes before uploading your revision:

- Ensure the key responses to the referees are also reflected in the content of the main manuscript.
Response: Contents are modified according to the reviewers' suggestions, which are highlighted in the text. Necessary calculations are performed and included in the manuscript and supporting information.
- Manuscripts generally benefit from careful re-reading before submitting the revised version. In particular, check that the text and axis labels in all graphics are correct and are correctly spelled. Please define all acronyms when first mentioned and apply them thereafter (the title, abstract, and Table of Contents text must each be understandable as standalone texts). We also recommend running a spell check.
Response: The manuscript was carefully re-read before submitting the revised version.
- Check that all parts, insets, and footnotes of Figures and Schemes are mentioned in the caption.

Response: All the captions are checked, and necessary corrections are made.

- Please define error bars in all relevant graphic captions. Make sure that Figure/Table captions contain the information on sample size (n), error bars, probability (P) value, the specific statistical test for each experiment, data presentation, and the meaning of the significance symbol.

Response: Necessary information has been added to the figure captions.

- If the reviewers have suggested adding new references, please use your own judgment of their relevance to this manuscript when deciding whether to include them.

Response: Added as per requirement.

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Response: No copyright permission is required.

Reviewer 1

Kaiser and coworkers reported their combined experimental and computational study on the first gas-phase formation of two new six-membered, silicon-nitrogen heterocyclic azasilabenzenes (26 & 27) using uncommon approach (addition of silicon nitride radical to 1,3-butadiene via molecular collision conditions using the crossed molecular beams approach). Notably, no common organic synthetic approach was reported to form the two azasilabenzenes products. In a sharp contrast, the molecular collision conditions for isovalent CN radical with 1,3-butadiene led to form acyclic 1-cyano-1,3-butadiene product. To gain more mechanistic insight, a high-level computational study (using CCSD(T)-F12/TZP//B2PLYP-D3(BJ)/TZP) were performed to get energetic profiles for a few possible pathways. Their computational results can nicely explain the observed distribution of different products. Their computational results are reasonable and should be reliable. As synthesis of azasilabenzenes is synthetically challenging, this study should be of general interest for Angew readers, I would recommend this work after the authors address the following below issues.

1. Pages 2-3, the authors summarized a few interesting bonding features between carbon and isovalent silicon. The authors proposed that larger atomic size of Si partly renders different structures? I think bonding feature difference between 2p and 3p should be one key factor.

Response: We thank reviewers for pointing out this, and we also agree with the comments. We have modified the text as:

“...The primary reason for this divergence arises from the larger atomic radius of silicon (110 pm) compared to carbon (70 pm), its lower electronegativity (1.90 vs 2.55 on the Pauling scale), and the less effective s-p mixing between the 3s and 3p orbitals relative to the 2s and 2p orbitals....”

2. The authors used reactive scattering signals to determine the identity of the Azasilabenzenes. Could the authors use other spectroscopies (e.g. IR and/or UV-Vis) to characterize the Azasilabenzenes and give stronger evidence of the formation of 26 & 27.

Response: We would like to thank the reviewers for this suggestion. However, our primary objective in this study is to investigate the reaction dynamics of the silicon nitride (SiN) and 1,3-butadiene reaction in the gas phase, not in the matrix isolation experiments where FTIR and UV-Vis spectra can be obtained. We have identified the mechanistic pathways leading to the formation of cyclic products (Azasilabenzenes) from acyclic reactants. To achieve this, the crossed molecular beam technique was employed, as it provides a clean reaction environment free from secondary collisions or wall effects. This setup also enables the detection of molecules, atoms, or radicals with extremely low number densities.

In this particular reaction, product formation was challenging because one of the reactants, silicon nitride (SiN), was generated *in situ* within the molecular beam, resulting in a very low product number density. Such low densities are not suitable for conventional spectroscopic techniques like IR or UV-Vis spectroscopy. Although resonance-enhanced multiphoton ionization (REMPI) has been

successfully applied in other molecular beam studies for spectroscopic characterization, it is not feasible in our current setup due to instrumental design constraints. Nevertheless, the accurate fitting of the laboratory angular distribution and time-of-flight spectra provides strong evidence for product formation, as any deviation in the product's energy would not lead to a fit of the experimental data.

3. The authors stated that an isomerization pathway of p2 to p1 through a transition state of 200 kJ/mol. I am quite confused how the authors got a value of "200". Also, "a lose transition state" could be also confusing.

Response: The relative energies of products **p1** and **p2** are -157 kJ mol^{-1} and -132 kJ mol^{-1} , respectively. Comparable stability of these product isomers was also reported in a previous study by **Veszprémi and co-workers**,¹ they identified a pathway for the isomerization of **p2 to p1** via a transition state with a barrier of 200 kJ mol^{-1} . We have not performed this calculation.

In our experiment, the reaction was investigated under **single-collision conditions** with a collision energy of $24.0 \pm 0.5 \text{ kJ mol}^{-1}$. In this reaction condition, interconversion between the two products is not feasible. According to our calculated PES, **p1** can only be formed from the **i6** intermediate through a barrierless exit channel.

For clarity, we have revised the text as follows:

“The relative stability of the products **p1** and **p2** agrees well with a previous study by Veszprémi and coworkers, where they also identified an isomerization pathway of **p2 to p1** through a transition state of 200 kJ mol^{-1} ”

The phrase “lose transition state” was a typographical error; it has been corrected to “loose transition state.”

¹ T. Veszprémi, L. Nyulászi, T. Kárpáti, "Toward stable silylenes". *J. Phys. Chem.* **1996**, *100*, 6262-6265.

4. The stronger N-H bond than Si-H bond was proposed to a greater stability of the non-aromatic product 27 compared to the aromatic products 26. Could the authors use 1-2 common computational methods (e.g. NICS) to evaluate aromaticity of the products 26-27.

Response: We added NICS (0) and NICS (1) results. The NICS values of product 26 are more negative than product 27, indicating that product 26 exhibits a stronger aromatic character than the latter.

5. The reaction with CN radical (instead of SiN radical) led to acyclic product(s). It might be very interesting for the authors to use the same computational approach to get energetic profiles of possible pathways for this reaction and understand the origin of such different reaction outcome.

Response: In addition to the experimental studies, detailed computational investigations on the reaction between the CN radical and 1,3-butadiene have already been performed previously. Morales et al. carried out calculations at the CCSD(T)/CBS//B3LYP/cc-pVTZ + ZPE (B3LYP/cc-pVTZ) level, and their results indicated that the major product formed is the acyclic 1-cyano-1,3-butadiene.¹ Subsequently, Sun et al. also explored all possible mechanistic pathways for the same reaction using CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ + ZPE (B3LYP/cc-pVTZ),² obtaining results consistent with those of Morales et al.

In our study, the calculations were performed at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3(BJ)/def2-TZVPP + ZPE (B2PLYP-D3(BJ)/def2-TZVPP) level, which is even better in accuracy to the methods used in the previous works. Therefore, we do not expect any deviation in the predicted product distribution.

¹ S. B. Morales, C. J. Bennett, S. D. Le Picard, A. Canosa, I. R. Sims, B. Sun, P. Chen, A. H. Chang, V. V. Kislov, A. M. Mebel, "A crossed molecular beam, low-temperature kinetics, and theoretical investigation of the reaction of the cyano radical (CN) with 1, 3-butadiene (C₄H₆). A route to complex nitrogen-bearing molecules in low-temperature extraterrestrial environments". *Astrophys. J.* **2011**, 742, 26.

² B. Sun, C. Huang, S. Chen, S. Chen, R. Kaiser, A. Chang, "Theoretical study on reaction mechanism of ground-state cyano radical with 1, 3-butadiene: prospect of pyridine formation". *J. Phys. Chem. A* **2014**, 118, 7715-7724.

6. Reference formats (e.g. journal abbreviation or missing page no.) should be fixed, e.g. refs. 6-7, 12-13, 16, 20, 23, 25, 30-34, 47, 53, 56-57, 60, 63, 65, 70.

Response: References are fixed.

7. All computed absolute energies for Fig. 2 should be given in SI.

Response: We have included that information in the Supporting Information.

Reviewer 2

The manuscript presents interesting and original findings in physical organic chemistry, specifically the preparation and characterization of azasilabenzenes. These results provide valuable new insight into fundamental aspects of chemical bonding, aromaticity, and heteroatom stabilization, and in my view, they warrant publication in this journal. The authors provide convincing experimental evidence for the formation of the azasilabenzene derivatives in the gas phase. These observations are further supported by DFT calculations, which elucidate the mechanism of formation and rationalize the relative stability of the two compounds investigated.

The authors propose that 1-aza-2-silabenzene is more aromatic than 1-aza-2-silicacyclohexa-3,5-dien-2-ylidene, in line with their mechanistic interpretation and stability arguments. To strengthen the manuscript further, it would be valuable to include quantitative aromaticity analyses, such as NICS(1)zz calculations, and either ACID or GIMIC ring current maps, to compare these results with benchmark systems such as benzene and 1,2-diazine. Such analyses would provide a more objective basis for their claim regarding relative aromaticity and place these findings into the broader framework of aromaticity in heteroaromatic systems.

Overall, the study is well articulated, well executed, and clearly presented. Incorporating a direct aromaticity comparison would further enhance the scientific impact and clarity of the conclusions.

Response: The NICS(0) and NICS(1) calculations, benchmarked with benzene, were added. The results are also in good agreement with our QUAO analysis, which shows that the degree of delocalization of product 26 is greater than that of product 27. There is a demonstration of using QUAO method to study the aromaticity of other systems:

<https://pubs.rsc.org/en/content/articlelanding/2024/cp/d4cp01802h>

We hope that the revised version is acceptable for publication.

Thank you

Ralf

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