



UNIVERSITY
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MĀNOA

Department of Chemistry

August 11, 2025

Dear Editors:

Please find attached our manuscript “One Collision – Two Heteroatoms: Gas Phase Preparation of Azasilabenzenes” by Surajit Metya, Iakov Medvedkov, Shane J. Goettl, Tosaporn Sattasathuchana, Mateus X. Silva, Breno R. L. Galvão, and Ralf I. Kaiser submitted for publication as an article in *Angewandte Chemie International Edition*.

Nature has long favored cyclic, particularly heterocyclic, molecules in the synthesis of key biomolecules. Silicon-substituted hydrocarbons have gained increasing attention due to their unique chemical bonding and electronic structure compared to their isovalent carbon counterparts. However, the synthesis of silicon-containing heterocyclic molecules remains a significant challenge. In this work, we investigate the reaction mechanism leading to a sparsely explored class of silicon- and nitrogen-containing aromatic heterocycles, in which silicon and nitrogen atoms are positioned adjacently within an aromatic, six-membered ring: azasilabenzenes. This is achieved through the reaction of the silicon nitride (SiN) radical with 1,3-butadiene (C_4H_6) via single collision conditions exploiting a crossed molecular beam experiment combined with electronic structure calculations and statistical analysis. Our results reveal the formation of two novel cyclic products: 1-aza-2-silacyclohexa-3,5-dien-2-ylidene and 1-aza-2-silabenzene. Interestingly, this reaction contrasts with the isovalent system involving the cyano radical (CN) and 1,3-butadiene (C_4H_6), which predominantly yields an acyclic product (1-cyano-1,3-butadiene) via a simple addition–elimination pathway. In addition to elucidating the reaction pathways, this study also provides insights into the nature of bonding and atomic interactions in the resulting products, offering a deeper understanding of structure–stability relationships in silicon–nitrogen heterocycles and the counterintuitive concept of isovalency.

We would also like to state that this manuscript is not under consideration for publication elsewhere.

As demonstrated by the selected references [1–6], the synthesis of organosilicon compounds and the elucidation of their underlying reaction mechanisms and dynamics are topics of considerable interest to the readership of *Angewandte Chemie International Edition*.

1. X. Lan, H. Wang, Q. Liang, L. L. Liu, "A Crystalline Mesoionic Diazasilole Featuring Low-Valent Silicon". *Angew. Chem. Int. Ed.* **2025**, *64*, e202415246.
2. B. Wang, J. Zhao, J. Ying, B. Cheng, Z. Lu, "Asymmetric Heck Silylation of Unactivated Alkenes". *Angew. Chem. Int. Ed.* **2025**, *64*, e202421500.
3. B. Neil, T. Deis, L. Fensterbank, C. Chauvier, "Reductive C(sp²)–Si Cross-Couplings by Catalytic Sodium-Bromine Exchange". *Angew. Chem. Int. Ed.* **2025**, *64*, e202419496.
4. P. Garg, A. Carpentier, I. Douair, D. Dange, Y. Jiang, K. Yuvaraj, L. Maron, C. Jones, "Activation of CO Using a 1,2-Disilylene: Facile Synthesis of an Abnormal N-Heterocyclic Silylene". *Angew. Chem. Int. Ed.* **2022**, *61*, e202201705.
5. T. Yang, B. B. Dangi, A. M. Thomas, B. J. Sun, T. J. Chou, A. H. Chang, R. I. Kaiser, "Gas-Phase Synthesis of 1-Silacyclopenta-2, 4-diene". *Angew. Chem.* **2016**, *128*, 8115-8119.
6. S. Park, S. Chang, "Catalytic Dearomatization of N-Heteroarenes with Silicon and Boron Compounds". *Angew. Chem. Int. Ed.* **2017**, *56*, 7720-7738.

We would like to suggest the following reviewers:

- 1) Prof. Robert J. McMahon, University of Wisconsin-Madison, e-mail: robert.mcmahon@wisc.edu
- 2) Prof. Arthur Suits, University of Missouri, e-mail: suitsa@missouri.edu
- 3) Dr. Nils Hansen, Sandia National Laboratories, e-mail: nhansen@sandia.gov
- 4) Prof. Wolfram Sander, Ruhr-Universität Bochum, e-mail: oc2@ruhr-uni-bochum.de

- 5) Prof. Christian Ochsenfeld, Ludwig Maximilians Universität München, e-mail:
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We would like to exclude the following reviewers due to conflict of interest:

- 1) Prof. Barney Ellison, University of Colorado Boulder
- 2) Prof. Piergiorgio Casavecchia, University of Perugia
- 3) Dr. David L. Osborn, Sandia National Laboratory
- 4) Dr. Craig Taatjes, Sandia National Laboratory
- 5) Prof. Hope Michelsen, University of Colorado Boulder

Thank you very much for your consideration.

With best regards,

Ralf

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