

## REVIEWER REPORT

### EVALUATION:

Reviewer's Responses to Questions

Please rate the importance compared to published work in this subject area

Reviewer #1: Outstanding (Top 5%)

Reviewer #2: Outstanding (Top 5%)

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Please rate the novelty compared to published work in this subject area

Reviewer #1: Outstanding (Top 5%)

Reviewer #2: High (Top 20%)

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Which aspects of scholarly presentation require improvement (if any)?

Reviewer #1: (No Response)

Reviewer #2:

Clarity

Language

Supporting Information

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Do the methods, data and analysis (including statistical analysis where applicable) adequately test the hypothesis and support the conclusions?

Reviewer #1: (No Response)

Reviewer #2: Mostly

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Are the methods, data and analysis described in sufficient detail to be reproduced?

Reviewer #1: Yes

Reviewer #2: Yes

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Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

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Please indicate whether you have included attachments

Reviewer #1:

No

Reviewer #2:

No

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## **Responses to reviewer's comments**

### **Reviewer 1**

In this manuscript, entitled "Crystalline Silagermenides as Powerful Synthons: Unraveling  $\pi$ -Bonding and Lone Pair Effects in the Multiple Bonds of Heavier Vinyl Anion Analogs," Liu and colleagues report the synthesis of two silagermenide compounds (2 and 5) featuring a polarized Si=Ge double bond. The results and discussion begin with an electronic structural analysis of the parent species  $\text{H}_2\text{SiGeH}^-$ , providing valuable insight into the potential stability and reactivity of this class of compounds.

The vinyl group is a key substituent in organic chemistry and has also played a crucial role in advancing low-valent main group chemistry (Ref. 9). While heavier vinyl compounds are known in main group chemistry, acyclic compounds featuring a Si=Ge bond have remained elusive—an important gap that this manuscript successfully addresses. The study offers a comprehensive exploration of the bonding and structure of these rare low-valent main group compounds.

In addition to structural elucidation through spectroscopic techniques and single-crystal X-ray diffraction (sc-XRD), computational calculations provide further insight into their electronic structures. The authors also investigate the reactivity of compounds 2 and 5 with different substrates, and their findings align well with the structural descriptions. Furthermore, the reaction products are thoroughly characterized and thoughtfully discussed.

The manuscript is well written, and I thoroughly enjoyed reading it. The supporting information (SI) is excellent—particularly the comparative analysis in Table S1. The study is conducted to

a high scientific standard, representing a significant contribution to fundamental main group chemistry. I strongly recommend its publication in *Angewandte Chemie*.

1. The authors emphasize the highly polarized nature of the Si=Ge bond in 2 and 5, which is expected given the higher electronegativity of Si compared to Ge, the weak  $\pi$ -bond, and the greater metallylene character of Ge. I suggest including a relevant resonance structure (as shown for R<sub>2</sub>SiGeR, on far right top) in Figure 1c (for the yellow-highlighted part) and in the TOC.

2. The intriguing structure of 2 and 5, featuring adjacent electrophilic and nucleophilic sites within the same molecule, suggests their potential for cooperative activation of small molecules (e.g., H<sub>2</sub>, CO). As a possible avenue for future work, I wonder if the authors have explored this aspect.

3. Page 1, Introduction, line 45: Replace "heavier elements" with "heavier main group elements."

4. Some related works by Filippou should be cited, e.g., 10.1002/anie.201504494 and 10.1002/anie.202400227.

5. Page 3, line 12, right column: Replace "noncyclic" with "acyclic."

6. Figure 3: Is R (= Me<sub>3</sub>Si) the same for (a) and (b)? Please verify and ensure consistency.

7. Page 4, line 4, left column: "via desilylation." Please specify the reagent (KOtBu?).

## **Reviewer 2**

The paper *Crystalline Silagermenides as Powerful Synthons: Unraveling  $\pi$ -Bonding and Lone Pair Effects in the Multiple Bonds of Heavier Vinyl Anion Analogs* by Xue-Yi He, Qiuming Liang, Yanbo Mei, and Liu Leo Liu describes the synthesis and reactivity chemistry of silagermenides,

synthesized through desilylation of suitable precursors. The compounds are, to my knowledge, the first of their kind and therefore of great interest to main group chemistry community. The research appears to be well executed and the methods, data and analysis support the conclusions for the most part.

Some specific comments:

1. The manuscript text could easily be shorted and its clarity/language improved.
2. Computational evidence presented for the reaction of  $K^+5^-$  with one equivalent of  $Et_3GeCl$  does not rule out the possibility of forming 7 which then undergoes intramolecular transformations to give 8. The best, albeit indirect, evidence to support the proposed mechanism is compound 15, which is discussed only in the ESI. However, even in that case it is not certain how the initial reaction step takes place, that is, if the Si or the Ge atom is the nucleophile. The authors should revise this section accordingly.
3. In double auration of  $K^+5^-$ , the authors seem to imply that one can describe complex 14 as  $[(NHB)Si=Ge(Ar^*)]_2^{2+}$  and two  $[Me_2IPrAu]^-$  units. This is pure speculation given at the final paragraph of the paper and should, in my opinion, be removed. The authors can still state that they are looking into the reactivity of 14 from the perspective of nucleophilic gold compounds without invoking the (at the time) completely unsupported bonding situation.
- 4 The clarity in the ESI could be easily improved.
  - 4a) For example, there are no subheadings in the section Experimental Details.
  - 4b) And the optimized structures could be given in a separate coordinate (xyz) file for easy viewing.
  - 4c) Computational section gives energies but it not always clear if the energies are Gibbs energies or electronic energies.

4d) There are no elemental analysis data available to prove the purity of the compounds. Any comments?