

Responses to referees' comments

Referee 1

Reviewer #1: Liu Leo Liu and co-workers describe a new anion, the keteniminyl anion. This is a significant step forward in the fashionable push for new C/N cumulants and their ions. The study was carried out to an excellent standard. I have only minor comments and would mainly suggest that the authors revise the introduction and the beginning of the discussion to emphasise the novelty of this study, which is primarily the isolation of the first uncoordinated keteniminyl. I miss a definition of the position of the charge in the chosen nomenclature. A keteniminyl could also be $R_1R_2CCN^-$. A keteniminyl carbanion, a ketenimin-X-yl or an -ide nomenclature might help. I would like to see the revised study published in Chem with an improved discussion and clarification of the novelty.

The authors seem to have overlooked some nomenclature that can be found on Google and Reaxys using the term keteniminate, which should be considered in the revised introduction. Some of these papers show that alkali metal keteniminate are not necessarily very exotic in synthesis. Some examples are

<https://pubs.acs.org/doi/10.1021/om200404p>

<https://onlinelibrary.wiley.com/doi/10.1002/anie.201904530>

<https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.201406219>

Title:

- While I appreciate the homage to some known from the field (which could be stressed by adding "A stable"), a structural description $[R_1C=C=NR_2]^-$ as given in the abstract could avoid ambiguity in the name (see discussion also above)

Abstract:

- The abstract does not describe the substitution pattern, so "the PCCN chain" is not defined.

- I am not sure which substituent in which position is meant here: "In addition, the phosphino substituent in keteniminyl anions".

- R1 and R2 in the online version of the abstract are ambiguous because the super-/subscript is not defined. I am not sure if this is a problem. Perhaps use R and R prime instead?

Introduction:

- Please rephrase, of course resonance forms are not different isolable species. The distinction may still be useful here to say that species leaning one way or the other have not been isolated. "However, the challenge in isolating the keteniminyl anion $[R_1C=C=NR_2]^-$ I (Figure 1a), as well as its resonance counterpart, the ynamide anion $[R_1C\equiv C-NR_2]^-$ II,"

- I am not sure why the Lappert ynamide has been singled out when there seem to be many comparable transition metal compounds. Please explain.

- Would the novelty not be better highlighted by discussing that the anion is uncoordinated? The ynamide B is similar but not a free compound (like the transition metal ones). "Despite these advances, the search for mild, general routes for the isolation of keteniminyl anions remains a significant scientific challenge, with the full potential of their reactivity yet to be realised".

- I am confused as to why we jump back to 1962 and ketenimines, which were mentioned a page earlier. I do not think the paragraph after "In 1969" is necessary or would be better merged with the first introduction of ketenimines.

Results and discussion:

- I think it would be beneficial to emphasise (in the figure) that some of the isolated keteniminyl anions have no conceivable coordination to the counterions. This distinguishes this work from Lappert 1999.

- Please also discuss (and possibly provide data) for metal coordination in solution and compare with Lappert's compounds.

- NBO, NPA and WBI should be cited.

- Figure 4: It would be useful to show the LUMO to illustrate the discussion in panel a (possibly in the SI).

- If no further discussion is needed, I think a smaller representation of the SCXRD structures in Figure 6 could be included in Figure 5.

References:

- The title of ref 24 is incorrect.

Supporting information:

- The authors have calculated the mechanism of methanolysis of the copper complex. Have you tried to calculate the transition state of the direct reaction with methanol?

Reviewer #2: Liu and colleagues report keteniminyl anions stabilized by bulky P(III) and P(V) substituents. This study follows on the heels of isoelectronic ketenyl anions with the same P-substituents (Angew. Chem. Int. Ed. 2023, 62, e202219211), and stands in the context of the studies by the Gessner, Severin and Hansmann groups on ketenyl anions / diazoolefins (refs. 1-9). The presented synthesis is clever, the reactivity has been studied in detail, and the experimental details are well documented. Whereas the tailored P-ligands somewhat compromise the beauty of this study, and whereas corresponding p-, d- and f-block metal-coordinating species are known (refs 16-24), the novelty is high considering that corresponding alkali-derivatives remain

unknown beyond compound B (in 2c, K is encapsulated within the crypt). As such, I consider this manuscript suitable for publication with Chem.

- I suggest adding (and discussing in the context of the literature values) $1J(\text{CH})$ for compounds 1, as it is directly related with the acidity of 1 (basicity, respectively, of compounds 2 and 4)

- What is the difference in basicity/reactivity/stability, etc., between compounds 2 and 4 ? Ideally also add to Fig. 4. Fig. 4a seems a bit trivial and could be potentially omitted?

- As most compounds still coordinate the alkali ions, they should be also depicted as such in Fig. 2

- Table 1 seems too detailed for a high-profile manuscript

- The IR stretches should be assigned based on the computations (note, C-C-N would typically refer to the bending mode, yet the authors mean the C-C or (which one is it?) C-N stretching mode. And/or how are they coupled? To which extent do these two solid-state ATR stretches follow the expected trend based on the (weakly) coordinating alkali ions & the experimental bond lengths? Difference 2 vs. 4 ?

- The GGA BP86 (which might be a good choice for modeling IR) is a poor choice for MOs & delocalization of/within colorless main-group/organic molecules. These calculations (Fig. 4 and text) should be done at least with a hybrid single point (such as M06-2X used in the SI for the energy profile, or PBE0, etc.).

Reviewer #3: Liu et al. report a study exploring the synthesis, characterization, and reactivity of previously uncharted keteniminyl anions $[\text{R}_1\text{C}=\text{C}=\text{NR}_2]^-$, revealing their unique electronic properties through comprehensive analyses including NMR spectroscopy, X-ray crystallography, and density functional theory calculations. These anions demonstrate diverse reactivity, undergoing protonation, alkylation, silylation, and metalation, while the phosphino substituent acts as a weak π -electron acceptor, stabilizing the electron-rich anionic carbon and opening avenues for future exploration of novel electron-rich phosphino-substituted species.

The work is particularly intriguing due to the discovery of new reactivities of isolated keteniminyl anions, which will undoubtedly appeal to scientists in the field. I would recommend publication of this work in Chem, though I am curious about further potential investigations, specifically whether the authors can demonstrate one-electron redox reactivity to generate corresponding radical species, which cyclic voltammetry (CV) data may help elucidate the feasibility.