

REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Highly important (top 20%)

Reviewer #2: Very important (top 5%)

2. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Appropriate

3. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

4. Please rate the verification of hypotheses and conclusions by the presented data

Reviewer #1: Minor inconsistencies

Reviewer #2: Fully consistent

5. Please indicate which other journal you consider more appropriate

Reviewer #1:

Reviewer #2: (No Response)

6. Please indicate whether you have included attachments

Reviewer #1: No

Reviewer #2: No

7. Please rate the quality of the Supporting Information

Reviewer #1: Insufficient or incomplete

Reviewer #2: Satisfactory

Responses to referees' comments

Our responses to the referees' comments below are in the order R1-R2.

Referee 1 (R1)

Liu and coworkers describe the formation of a bulky (phosphino)diazomethyl anion $[R_2PC(N_2)]^-$, compound 1, and report facile N_2/CO exchange to yield the ketenyl anion derivative $[R_2PC=C=O]^-$. Of note, $[R_2PC(N_2)]^-$ species have been known for a few decades now, and used by Bertrand to access the first isolable carbene, JACS 1988, 110, 6463. In related studies, Hansmann showed N_2/CO exchange featuring

diazoolefins, $R_2C=C=N_2$ supported by mesoionic carbene units as the terminal R_2C group (see JACS 2021, 143, 12878); moreover, the mechanism computed in Figure 2 (Scheme?) is similar as that proposed by Hansmann and coworkers. Therefore, the initial part of this work, N_2/CO exchange is not entirely surprising. Fortunately, the reactivity studies involving the ketenyl anion, compound 2, found at the end of the paper showcase some really interesting transformations. What caught my attention the most was the formal imine metathesis (or $C=N$ bond cleavage) reaction between an imine and 2 to yield the addition product 9. I do have some points and corrections that need to be addressed before this work can appear in Angewandte Chemie.

- The authors "oversell" compound 1 as an N_2 -complex of anionic carbyne $[RC\leftarrow N_2]^-$; I see no evidence from computations or mechanistic studies that support the formation of such dative bonding (as the sole $C-N$ interaction). Likewise, I am not convinced that compound C in Figure 1 should be shown with a dominant contributor ($[h_3P\rightarrow N_2\leftarrow PPh_3]$), despite what Frenking and coworkers claim; note: one would need to access a very high energy excited state of N_2 to generate the bis-nitrene acceptor situation required at N_2 .

- The authors should look at the role of $C(lp)$ to $P-C$ σ^* hyperconjugation in both compounds 1 and the oxidized analogue 3. The shorter $P-C$ distance and high Wiberg bond index in 1 suggests that hyperconjugation could be an important bonding factor. In compound 3, I would expect even greater $C(lp)$ to $P-C$ σ^* hyperconjugation as now a formal $P(V)$ center is present. Does second order perturbation analysis via NBO give any added insight?

- The IR data for 2 is given but no comparison of the CO stretching frequency with those of related species by Hansmann or known $R_3P=C=C=O$ species is provided. This seems to be an important omission as this would provide insight into the impact of the phosphino ligand on ketenyl bonding.

- How thermally stable are compounds 1 and 2? This information should be provided, at least as a footnote somewhere in the paper.
- Elemental analysis data need to be provided as evidence of bulk purity for all new compounds.
- Page 2, column 2, line 8: replace "straight angle" with "linear geometry".
- Reference 1: delete volume numbers as they are not required for the journals cited here.
- ESI and main text: replace "¹³C" by "¹³{¹H}"
- ESI: While the ¹H NMR data are assigned fully, there are many resonances left unassigned in the ¹³C{¹H} NMR data provided; even general assignments, such as "ArC" would be of value to include for the reader.
- ESI: Please label all residual solvent, vacuum grease and impurity peaks on the NMR spectra provided.
- ESI: It is not clear how much solvent was used for some product washings and extractions. Please update as needed.
- ESI: The number of significant figures for the # mmoles and mass amounts of each reagent need to match. For example, on page 3, paragraph 2: "2 mg, 0.025 mmols" should be "2 mg, 0.03 mmols" and "15 mg, 0.02 mmols" should be "15 mg, 0.02x mmols" (x = appropriate number).
- ESI, Page 2: replace "PCN2K" by "compound 1" in the preparation of 2.

- ESI, Page 2: I am not sure how 2 atm of pressure would be obtained by bubbling CO through a reaction mixture, unless the authors set a bubbler at this high pressure. Can the authors explain more clearly how the 2 atm of pressure was maintained/achieved? Typically, this is done by cooling a solution that has been saturated with CO to -78 °C, and the warming the solution to room temperature under a closed system.

- ESI, 1H NMR data: List each multiplet resonance as a range.

- ESI, Page 6, paragraph 2, line 3: "8" should be in bold font.

Referee 2 (R2)

This work reports the synthesis and chemistry of ketyl anions. It is quite obvious that this work is a back-to-back study with Gessner's very recent publication (Science 2022, 378, 1331). In the present manuscript, Liu and coworkers prepared a (phosphino)ketyl anion via N₂/CO ligand exchange reaction at a phosphinocarbyne anion. The observed highly bent P-C-C angle in the solid-state structure corroborated with DFT calculations indicates its nature as a ketyl anion. Reactivity studies show that such ketyl anion can not only be used for the synthesis of ketenes through reactions with diverse electrophiles but also reveal new reactivity patterns to derivatives of enolate, acrylate and acrylimidate moieties. The results are of great importance and the manuscript is well written and readable. A number of interesting reactions are presented. The distinctions in this manuscript from Gessner's work appear to be the synthetic route (N₂/CO replacement), the behavior of the non-innocent phosphino substituent (can be functionalized) and the formation of 4 (first structurally characterized Ge-substituted ketene), 5 (first Cu-substituted ketene), 7 (acetylene C-H bond activation) and 9 (imine activation). Overall, this is a highly original work and an important addition to the area of ketene chemistry and warrants publication in Angewandte Chemie after minor revisions.

1. In figure 6(b), the nitrogen atom of CAAC is mislabeled as a carbon atom.
2. In the ESI, some high-resolution mass spectrometry (HRMS) results are missing. This information should be added and listed for all new compounds.
3. For synthesis of 4 and 5, how much n-pentane was used to extract the products?
4. In the Introduction, conventional ketene synthesis mostly involves stoichiometric reactions from derivatives of carboxylic acids or diazoketones, or via pyrolysis. This should be corrected.