

## Responses to referees' comments

### Referee 1

#### **Recommendation: Excellent; publish after minor revisions.**

This account summarizes the efforts of the Liu group in the area of mono-substituted carbon over the last years. These contributions have been exciting, and this summary puts them well into context with each other. I have a couple of suggestions which could strengthen the manuscript:

- 1.) The chapter on ligand design highlights hyperconjugation with the P–N  $\sigma^*$  as well as P: conjugation (Fig. 3). Of course, these interactions are important, and therefore of course, none of the presented molecules achieves effective P–C “pi-decoupling” in sight of significant multiple-bond character. I hence suggest adding and discussing canonical forms of the formally mono-valent species presented in more detail than superficial Fig. 1c (note, e.g., the pi-bond present in Fig. 6.). A more balanced discussion could take inspiration from pertinent NHC reviews, where the significant N–C double bond character is typically discussed right in the beginning.
- 2.) Along that line: What is the alleged C–C multiple bond character in phenyl carbyne (phenyl nitrenes, respectively)? Generally, I would find it useful to learn (a bit) more about this molecule in this account.
- 3.) It seems appropriate to reiterate/define valency in the introduction (and, in case, contextualize with oxidation state, # of lone pairs, etc.)
- 4.) Fig. 3: “idealized” D<sub>3h</sub>, C<sub>2v</sub> (also: subscripts are usually not put in italics).
- 5.) I find the arrow depiction of the NHC in the coinage metal complexes not ideal, particularly in combination with a “dashed” bond indicating an ionic interaction in Scheme 3... The ELF & MO-plots suggest similar covalency for PC–Au & NHC–Au...
- 6.) One could consider adding Nature 2023, 623, 66 to the introduction as an example of a formal C-dication.
- 7.) Typos: flexile, but also reduce, plumyne
- 8.) Fig. 7 is too large

### **Reviewer: 2**

#### **Recommendation: Above average; publish after minor revisions.**

The present Accounts submitted by Prof Liu describe the achievements of the author's group on the design, stabilization, synthesis, characterization, and reactivity studies of novel low-valent carbon species, by means of bulky cyclic phosphino substituents. The manuscript highlights the results of four high impact factor papers spanning from 2022 to 2024, which coincide with the four main sections of the article. This, in my opinion, is somewhat a short research journey to be published in ACR. Nevertheless, the research described is innovative and might deserve publication. The main criticism is on the scholarly presentation, and the language employed which is extremely wordy in some instances. A more composed and concise language would be desirable.

Points to revise:

1.) •The title is misleading! In only one section a copper carbyne is isolated. As the authors suggest in the conclusion section of the paper: "In this Account, we detail our recent endeavors in the design, stabilization, synthesis, characterization, and reactivity studies of novel low-valent carbon species, achieved through the employment of bulky cyclic phosphino substituents." I suggest the title being a variation of such a sentence.

2.) •There are two "#3" sections! Please modify section numbering accordingly.

3.) • None of the schemes show reaction conditions (solvent, time, temperature). It should be included in all of them, like in the original articles.

4.) Page 1, Line 47: Remove the word "endowed".

5.) Page 3, Line 12: Change "the close of the 19th century" for "the end of the 19th century".

6.) Page 3, Line 37: "Botteable" sounds too informal.

7.) Page 3, Line 43: Reference 10 is a review; the original work in which the rare monovalent carbene is described should be referenced as well.

8.) Page 3, Line 55: Change "the transition to" for "the transition towards".

9.) Page 3, Line 57: The second part of the following sentence does not add any relevant information. Please change: "Carbyne anions, characterized by a monovalent anionic carbon atom that contains four nonbonding electrons (Figure 1b), stand isoelectric with nitrenes" For "Carbyne anions are monovalent anionic carbon atoms that contain four nonbonding electrons (Figure 1b)."

- 10.) Page 4, Line 8: After “singlet state”, “(Figure 1b)” should be included.
- 11.) Page 5, Figure 2: In the same manner as they are earlier mentioned in the text, Arduengo carbenes should be included in Figure 2.
- 12.) Page 6 Figure 3: The figure is not self-explanatory; it is too abstract! The angle degrees should be included in the x-axis, and more information to guide the reader.
- 13.) Page 7, Scheme 1: The intermediate phosphinodiazomethylide salt intermediate between compounds **1** and **2/3** should be drawn within brackets. This is a key synthon that should be visible for the readers.
- 14.) Page 7, Line 40: The verb “lay” should be in 3rd person singular, “lays”.
- 15.) Page 8, line 59: Please write  $\text{BH}_3 \cdot \text{THF}$  instead, also, in Scheme 2.
- 16.) Page 8, Line 60: Change “yielding a zwitterionic” for “yielding the zwitterionic”.
- 17.) Page 9, line 34: Remove “In view of the disparity in electronegativity”. This is redundant.
- 18.) Page 9, Line 49: A reference should be included at the end of the statement: “is to a linear alignment. ref”.
- 19.) Page 12, Line 38: The verb “indicate” should be in past tense, “indicated”.
- 20.) Page 12, Line 54: “Salts” should be singular, “salt”.
- 21.) Page 13, Line 24: A reference should be included at the end of the statement: “ketene, enolate acrylate, and acrylimidate moieties.ref”
- 22.) Page 16, Line 47: A reference should be included at the end of the statement: “their heteronuclear counterparts remain exceedingly rare.”
- 23.) Page 18, Line 48: A space should be included after “products **28** and **29**”.
- 24.) Page 18, Line 61: “ $\text{Et}_3\text{NHCl}$ ” should be changed to “ $\text{Et}_3\text{N} \cdot \text{HCl}$ ”.

25.) Page 19, Line 44: The following sentence should be removed; it is not a conclusion of the review. New work that has not been previously explained during the review cannot be included in the conclusions. "Further extending our research, the meticulous use of a diphosphino diazomethane precursor has enabled the isolation of a singlet carbene with an inverted electronic configuration." If the authors want to cite their recent "Science" paper, they should find another spot in the article.

26.) The following references present some mistakes:

- o Some characters or numbers should be subscripted or superscripted in references 14, 32, 34, 35, 41, 46, 61 and 63.

- o Ref 9: Remove "Review" after the page numbers.

- o Ref 27: Remove "Article" after the pages.

- o Ref 32: DOI should be removed.

- o Ref 60: DOI should be removed.

As I earlier mentioned, the language is often wordy and pompous. See some examples of this that I suggest should be rewritten in a more concise and scientific manner.

27.) Page 1, Line 60 "A further extension of this work".

28.) Page 2, Line 16: "thereby potentially establishing"

29.) Page 3, Line 61: "In the realm of chemistry"

30.) Page 2, Line 22: "As we continue to delve deeper and expand upon this foundational research, we are afforded not just a more profound understanding of reactive carbon species, but also an expansion of the synthetic chemist's toolkit".

31.) Page 4, Line 8: "This electronic feature renders them exceedingly reactive, yet intriguing, due to the high degree of unsaturation at the carbon center which facilitates flexible chemical elaboration."

32.) Page 8, line 40: "complexes **4** and **5** emerge as the inaugural instances of stable monometal substituted free carbenes"

33.) Page 13, Line 4: "This reaction provided rare instances of stable ketenyl anions 19."

34.) Page 7, Line 4: The transition between the previous section and this new one is too abrupt; it is awkward to start a new section cannot with "*It should be noted that...*". The paragraph should be rephrased; it is not clear what the author wants to prove. The comparison with BuLi seems somewhat farfetched..."*It should be noted that n-butyllithium is commonly used as a surrogate for the "n-butyl anion". Available commercially in pentane and hexane solutions, n-butyllithium does not exist as free n-butyl anions but forms clusters, polymers, or complexes instead. Therefore, if our objective was to synthesize a phosphinocarbyne anion, initiating the synthesis of its metal complex was a reasoned approach (Scheme 1).*"

35.) Page 16, Lines 3 to 16: This whole paragraph is not suitable to start this section. Some concepts/ideas like that "*phosphinodiazomethylide salts are versatile synthons*" are new and should be moved either to the introduction or to the initial gold carbene section, while others, like "*cyclic phosphino substituents have demonstrated superior efficacy in stabilizing low-valent carbon species compared to their noncyclic counterparts.*<sup>28, 29</sup> *This was inspired us to delve deeper into previously uncharted territories of low-valent carbon chemistry.*" are somewhat repetitive and might be eliminated.