Referee 1 (R1)

This study reports a very interesting compound and combines synthesis and computations in a synergistic manner. The carbyne species presented is of potential interest for a wide range of experimental investigations in the future.

The computational part is carried out quite satisfyingly throughout, but I have several remarks which need to be addressed

Major remarks:

- The EDA data have to be presented in detail to enable review of this important piece of information

- The analysis carried out for compound 6 (NLMO, partial charges, EDA-NOCV) has to be repeated for the previously reported (ref. 30) Au compound to enable the comparison of the claimed differences in bonding situation.

- The barrier heights presented in Figure 5 (up to 30 kcal/mol) are not in line with the experimental finding of rapid reaction at room temperature. The authors should ramp up their computational approach, provide optimization at the TZ level and energy calculations with more recent and more accurate functionals (e.g. R2SCAN-D3 or wB97 family) including consideration of BSSE effects (e.g. via gCP correction).
  If the discrepancy persists, it has to be discussed.

- The P-C-M bond angle is taken as criterion to distinguish Cu and Au complex. But in the latter the Dipp ligand has been replaced by Me in the computations. This should be made consistent as the size of the ligand could influence the bond angle as well.

Referee 2 (R2)

This is a beautiful piece of work, highly original, of general interest and paramount importance.

Metal carbyne anionic complexes capable of transferring the carbyne anionic fragment are remarkable both in terms of bonding and reactivity.

Compared to the related Au species, the reported Cu complexes display highly ionic Cu-C bonds, and their reactions with Si/Ge electrophiles to give stable phosphino-carbenes provide compelling and synthetically useful evidence for the transfer of the anionic phosphino-carbyne fragment.

I very much recommend the publication of this work in Nature Synthesis.

I noticed however a few minor points that may require consideration and would likely contribute to further increase the quality of the paper:

- The relative contributions of the orbital (covalent) and electrostatic (ionic) contributions in the Cu-C/Au-C bonding (EDA-NOCV analyses) should be provided and commented in order to further compare the Au and Cu complexes.

- The activation barrier predicted computationally for the reaction of 5 with Me3SiCN is quite large (about 31 kcal/mol for the silyl migration from IN2 to 9) with respect to the experimental observations (the reaction is over within 5 min at rt according to the SI). Is it possible that the cyanide is first isomerized into the corresponding isocyanide (eventually upon assistance of the carbyne complex) and then undergoes carbene/isocyanide coupling?

- Given the lack of precedent for related anionic carbyne complexes, it is somewhat exaggerated to state that « The 13C NMR spectra of 5 (99.9 ppm) and 6 (102.8 ppm) exhibited characteristic doublets attributable to the carbyne anion carbons… ». Should be balanced.

- A few anionic carbyne complexes have been reported. The corresponding references should be cited (see for example A F Hill, Chem. Commun., 2017, 53, 2032 and references therein)

- The recent work of Suero et al on diazomethyne radicals as carbyne equivalents (Nature 2018, 554, 86) is also worth citing.

<u>Referee 3 (R3)</u>

This interesting manuscript reports the synthesis and reactivity of two novel copper phosphinocarbyne complexes. By irradiation of Cu-substituted diazomethane precursors with a UV lamp, the authors have successfully isolated the unusual copper phosphinocarbyne complexes [(CH2)(NDipp)]2PCCu(IDipp) (5) and [(CH2)(NDipp)]2PCCu(IPent) (6). On the basis of computational studies, the authors conclude that the bonding between [(CH2)(NDipp)]2PC]- and Cu(I) in 5 and 6 is dominated by ionic interactions. The complexes show reactivity of carbyne anion when treated with reagents such as Me3SiCl, Ph3GeOTf and Me3SiCN, leading to interesting new compounds including an elusive germanyl-substituted free carbene. The new complexes have been well-characterized by NMR, MS, and in many cases, also by X-ray crystallography.

The followings are few issues for authors to consider or address in a revision.

(1) I am not sure if it is most appropriate to describe the complexes 5 and 6 as “carbyne anion complexes”. For example, a complex derived from a [RC≡C]- anion is usually not called an alkynyl anion complex.

(2) In Figure 1d, the authors presented a resonance structure for 5 and 6, showing a P-C single bond, a “…” bond between C and Cu, and a vacant orbital on C, apparently to emphasize the ionic nature of the carbon-copper bond, and the monoanionic carbyne formulism. The X-ray data as well as the computational work suggest that there are resonance structures more important than that presented in that Figure. (1) The X-ray data show that the P-C bond is shorter than a typical P-C single bond and has multiple bond character. The Cu-C distance (ca. 1.82 Å) is even shorter than that of Cu-C(NHC) bond (ca. 1.87 Å). The Cu-C distance of 1.82 Å is in fact similar to those of typical Cu=CR2 (R = H, or alkyl) bonds (1.82- 1.84 Å). (2) The computational results shown in Figure 3 suggest that the bond between P and C is more like a triple bond, and that there is no vacant orbital on the carbyne carbon. Thus, other Lewis structures (e.g., P≡C-Cu, P=C=Cu) may also contribute to the structure (perhaps, even more significantly), and should be considered in the discussion. Calculations on the electronic structure and bonding of species such as HC≡C-Cu-NHC, :P≡C-Cu-NHC, [H2C=C=Cu(NHC)]+ may help to understand the carbon-copper bonding in 5 and 6.

(3) Complexes of the types M≡CPR2 and MC≡P are known. Some comments could be added to compare the properties of these complexes and the complexes 5 and 6.

(4). It was stated in line 152 that “the anionic carbon of 5 and 6 formally contains two lone pairs of electrons and a vacant orbital”. The computational results indicate that “the anionic carbon” does not have a vacant valence orbital.

(5) For easily reading, the key structural parameters can be added to the captions of Figures 2 and 4.

(6) The copper complexes are regarded as carbyne anion complexes, whereas the analogous gold complexes are regarded as carbene complexes. Additional comments (apart from P-C-M bond angles, and electronegativity) could be added to more clearly indicate the difference (e.g. in terms of bonding, reactivity), and explain the cause for the difference.