

Referee 1

The isolation of the stable CAASn is very interesting and highly original. Experimental and theoretical characterizations are thoroughly done in a high-standard quality, and mechanistic study is achieved by the DFT method. Given the fact that the authors have recently isolated the stannyne (ref 49), the proposed intermediate of the transient stannyne is unquestionable. I enjoyed reading this nice manuscript, the work should attract a wide readership, and hence, I highly recommend the acceptance for publication.

Below are the minor points the authors might consider during a slight revision.

1. In Fig 1e, the transient stannyne is depicted as the allenic structure. For the isolable stannyne (ref 49), I understand that based on the X-ray and FMO/IBO analysis, the allenic structure ($>P=C=Sn-Ar$) is found to be the best described. However, because the substituent attached to the Sn in this study is N-based (isoindoline), which could have better interaction with the Sn center (such as $Sn=N<$), I was wondering if the allenic structure is still the best in this case or not.
2. Related to the comment above, the structure of the transient stannyne in Fig 1e differs from those in Figs 2/6 and TOC, those might be better to draw consistently.
3. “the carbene-like reactivity of **5a**”: As **5a** in Fig 5 involves the carbene center, ‘carbene-like’ reactivity here sounds a bit weird.
4. Fig 3, caption. (a)/(b)/(c) are missing.

Reviewer: 2

Liu and co-workers report on the fascinating synthesis of a phosphine-stabilized cyclic (alkyl)(amino)stannylene (CAASn) via transient stannyne. Considering the current impact of cyclic and particularly alkyl-substituted carbenes and their heavier analogues toward synthetic chemistry, the realization of a synthetic route to CAASns should be of great impact to a broad audience of chemistry. The structure and electronic properties of the stannylene was elucidated without any question. Furthermore, (although transient) the manuscript herein introduces buchner-ring expansion as another interesting reactivity mode of stannynes, which the authors clarify by DFT calculations, allowing to deepen the fundamental understanding of the properties of heavier triple bonds in general. Therefore, the present manuscript should be well suited for the broad audience in SCIENCE CHINA Chemistry, thus recommend publication after addressing few minor comments stated below.

1. p.3 left line 16: “5 displayed a chemical shift at 119.8 ppm” should be revised to “5

displayed a signal at a chemical shift of 119.8 ppm". Chemical shift and signal should be distinguished. Please revise other discussion regarding NMR spectra, accordingly.

2. p.3 right line 19: It would be nice if the sum of bond angles around Sn(1) and N(1) atoms are included in the discussion for clarity of the pyramidalization.

3. p.4, 2.2 Computational Studies: The authors discuss the electronic properties of the CAASn without any doubt. However, the electronic properties of the transient stannyne 5a should also be of interest. The authors state that the Ph groups in close proximity facilitate the ring expansion, but how about electronic effects? Are there remarkable differences, for example in the HOMO-LUMO energies between 5a and the stable stannyne B, which might be contributing to the reactivity differences? Maybe it is nice if the authors could briefly elaborate on this, if possible.

4. just out of curiosity. Bertrand and co-workers reported on the stable monosubstituted carbene in ref. 55 utilizing similar bulky isoindolinyll substituents but with 3,5-bis(trifluoromethyl)phenyl groups. Have the authors tried using this to prevent the buchner ring expansion?

4. p.7 ref. 48: Delete "43".