

Referee: 1 Recommendation: Minor Revision: suitable for publication after changes
Comments:

This manuscript by Liu et al. reports the synthesis, isolation, and complete characterization of a stannyl-substituted phosphino carbene. DFT methods were applied to further investigate the electronic structure of this new compound. Some reactivity studies with cyanide, isocyanides, and carbon monoxide – which all form ketenimines or ketenes by interaction with the carbene center – demonstrate the singlet carbene type chemistry of the title compound. If there is a critical remark to be made than that none of the species reported here nor the methods are truly original and new. My recommendation to publish this paper in Chem Commun would have been even more enthusiastic would the authors show that the stannyl phosphinocarbene shows some very specific chemistry (like an exchange of the stannyl group for another unit like – for example – a transition metal fragment). But even in the present form, I believe that this fine piece of work should be published in the targeted journal.

1. The writing of the article is at passages not to my personal liking. For example the starting sentences: “Carbenes, featuring a carbon atom in a divalent state adorned with two nonbonding electrons, manifest primarily in either a triplet or singlet ground state.[1] The isolation of reactive triplet carbenes has historically posed a significant challenge.[2] However, the introduction of π -donor substituents has facilitated a transition to a more stable singlet state, thereby unlocking their extensive chemical potential.” A divalent carbon center has by definition two unbound electrons and the challenge of isolating a carbene in its triplet state is not solved by the preparation of a carbene in a singlet state instead, which shows a completely different reactivity. I find also the expression “primarily” confusing as this may imply that carbenes may even have other electronic ground states. A better (in my opinion) formulation would be: “Carbenes contain a divalent carbon center and exist either in a triplet or singlet electronic ground state. The isolation of triplet carbenes is challenging[2] while there are many examples of stable singlet carbenes, which allowed to investigate these species in detail.” There are many passages like this throughout the text and I leave it to the editors and authors to carefully reedit this paper with the specific aim to make it much shorter and focused.

2. An example for a sentence with no specific meaning and which should be erased completely is: “Compound 2 demonstrates exceptional stability at ambient temperatures in solid form under a nitrogen atmosphere.” What is exceptional here? There 100thousands of compounds showing this property. I guess the authors simply want to say that the compound can be stored at ambient temperature under an inert atmosphere.

Referee: 2 Recommendation: Minor Revision: suitable for publication after changes
Comments:

R. Wei, X. Wang, C. Hu, L. L. Liu have synthesised an acyclic phosphino-stannyl

carbene that is crystalline and stable at room temperature. This is an extension to their previous work by substituting one side of the phosphino-carbene with a trialkyltin group. The free carbene was isolated and three reactions demonstrate the reactivity at the carbon center.

The manuscript is well-written and the results have been presented clearly. I recommend acceptance of this manuscript to Chemical Communications after addressing the following comments:

1. The word ambiphilic is used throughout the manuscript with little evidence of this reactivity except the postulated oxidative addition of TMSCN and the non-bonding lone pair on the carbon atom. Is there more evidence to this reactivity? The authors may also wish to extend their research on their compound by using one of the standard techniques for evaluating electronics of carbenes: H. V. Huynh, Chem. Rev. 2018, 118, 9457.

2. For the reaction with CO to form compound 5, the text says "bubbling CO through a benzene solution of 2..." whilst Figure 5 and the experimental section in the SI suggests the solution was put under 3 atm of CO. Please make sure this is consistent.

3. Here are also minor suggestions to improve the manuscript.

3.1. As these phosphino-carbenes now have several precedents in the literature, it will help to illustrate the difference by mentioning substrates the carbene is inert towards such as alkenes, CO₂ etc.

3.2. The carbon NMR is only partially assigned in the supporting information.

3.3. Details for the broad spectrum (352 nm) LED light is missing.