

Referee 1

This report by Liu and co-workers describes the synthesis and reactivity of a proposed free Stannyne, which has not been isolated previously. Due to the intriguing bonding situation between Sn and C, the compound exhibits ambiphilic reactivity. Reactivity of the lone pairs (i.e. carbene and stannylene) is highlighted on reaction with isocyanide and butadiene whereas alternate reactivity, more akin to anion/cation reactivity is shown with HCl and isocyanate. DFT studies are used to provide support for the nature of the bonding for the title compound. Examination of the frontier molecular orbitals shows the HOMO to consist of P=C multiple bond with Sn lone pair, whereas the HOMO-1 contains a 3c-2e bond across the P-C-Sn unit. Overall, I find this paper informative and concisely written. The work is novel and of interest to those within the main group community.

Comments/Suggestions:

1. I am not convinced that it is a free stannyne with a Sn-C triple bond, due to the observed reactivity and supporting theoretical studies. I do agree that there is multiple bond character in title compound, but more that it is a heterocumulene P-C-Sn species (3A) based on the HOMO or that a Stannylumylidene resonance form may also exist (with P-C triple and Sn cation). As the latter would account for the observed HCl reactivity.
2. Synthesis of compound 3 is reported on a small scale yielding 18mg (95%). The reactivity studies for compounds 5 & 6 are performed with >30mg each. Therefore, if the synthesis of 3 has been performed on a larger scale please can you also include short note to say can be performed on larger scales with a note of the yields (or average). Alternatively, if the synthesis can not be performed on a larger scale, and >30mg has come from combined batches then please also clarify.
3. Crystallisation of compound 3: slow evaporation of pentane at -30oC? Not +30? Can you include a time frame.
4. Have you tried a reacting compound 3 with acetylenes or ethene to see if Sn-C unit reacts as a multiple bond and not the individual lone pair?
5. For the computational studies, have you tried more than one basis set to model the title compound? Currently the model is slightly overestimated compared to the experimental structures.
6. Proposed mechanisms for reactivity (Figure S31 and S41) have these been investigated computationally? If so please include the energies for each step. Or include a statement to make clear that it is not computed.

7. As you have performed NBO, it would also be worthwhile considering the Natural Resonance Theory to assess the contributions of the proposed resonance structures 3A-C.

Referee 2

In the manuscript titled "A Free Stannyne" Liu and co-workers report the preparation of a structurally characterised R1-C≡Sn-R2 complex and report a range of reactivity studies of the title compound 3, which is an unusual linkage which has not been reported previously and is remarkably stable and "bottle able" and would be of interest to a broad audience. Overall the manuscript is well put together and the experimental data is presented well. The selection of data (primarily XRD and NMR) support the formulations and the selection of reagents help to elucidate the nature of the Sn-C bond. A few queries and comments for the authors:

1) The preparation of 3 is reported on a small scale (0.02mmol). Did the authors attempt to prepare the compound on a larger scale or is it limited to this NMR scale?

2) During text and on figure captions please include {1H} notation to avoid ambiguity when discussing 31P and 119Sn NMR data.

3) In the SI please double check that the NMR frequencies are correct for each data collection. E.g. for 2 the 1H (500 MHz) and 13C (126 MHz) correspond to a 500MHz spectrometer, while the 31P (243 MHz) and 119Sn (149 MHz) correspond to 600 MHz and 400 MHz respectively. This may be correct but please check carefully before publication.

4) Throughout the manuscript the uncertainties on the bond angles are missing. Please include these for completeness.

5) Were there any attempts to perform elemental analysis on the compounds reported?

6) I think there could be more discussion on the exact nature of 3. The authors draw three resonance forms 3A-3C, does the DFT and computational data suggest which resonance form is most valid?

For the most part the XRD data is good quality and the data-sets are well refined and support the author's claims in the manuscript, but there are a number of technical issues that should be addressed before publication:

1) In 2 the Sn is disordered over two positions, with wildly varying Sn-C distances. Is there an explanation for this? Why would a minor component have much shorter Sn-

C distances? Is it possible this is an artefact of absorption rather than the Sn being over two positions?

2) Solvent has been suppressed in several of the datasets. Please consider modelling the lattice solvent rather than using a solvent mask, especially for 3 where the lattice pentane is clearly seen and can be modelled fairly easily, as can the toluene in 7. Where solvent masks are required due to extensive disorder please include information in the cif special details.

3) Several cifs are missing information on software used or absorption details, Please include these fields (e.g. `_exptl_absorpt_process_details`, `_computing_cell_refinement`, `_computing_data_collection`, `computing_data_reduction`)

4) In 4, the Methyls C01V and C01U are clearly disordered and the isopropyl groups should be modelled over the two orientations.

5) In 6 the two hydrogens bonded to C1 are refined freely, was this deliberate? I think using AFIX 23 and refined as a standard CH₂ group would be more suitable. If the authors want to keep as freely refining these, then the atomic displacement needs tweaking. The two hydrogens need to be sorted in the atom list following the parent carbon atom (C1) for the -1.2x atomic displacement for the hydrogens to follow the parent carbon.

Referee 3

Liu and co-workers present the synthesis and reactivity of the first room-temperature-stable stannyne (3), obtained by irradiating an arylstannylenyldiazo(phosphino)methane precursor with release of N₂. X-ray crystallographic data reveal a trans-bent structure with a C–Sn bond length in the range between a single and double bond. DFT calculations show that the HOMO of 3 consists of the lone pair at the Sn center and the P=C π bond, while the HOMO-1 and HOMO-2 show delocalized P–C–Sn π bonding. The C–Sn bond is ionic in nature and the adjacent carbon and tin centers display carbene- and stannylene-type reactivity. Thus 1-adamantyl isocyanide reacts with the carbon centre to yield a stannylketenimine, whereas 2,3-dimethyl-1,3-butadiene reacts in a [4+1] cycloaddition at the tin centre. C≡Sn triple bond reactivity is observed with HCl, which adds twice across the C–Sn bond, yielding the first example of a phosphino(stannyl)carbene. Finally, the reaction with isopropylisocyanate resulted in the insertion and coupling of two iPrNCO molecules between the tin and carbon centres, concomitant with migration of one oxygen to the phosphine centre.

The experimental work is well done and the manuscript very well written and referenced. While the isolation of compound 3 is a very nice achievement indeed, I do

not think that it bears enough novelty or interest to the wider Chemistry community to warrant publication in Nature Chemistry. The DFT calculations speak for an electronic structure with a typical stannylene centre and a conjugated P=C=Sn framework, which also fits with the observed reactivity. Even the HCl addition is rationalised in terms of stannylene and carbene chemistry, rather than proper C≡Sn triple bond chemistry. I believe the study would be excellent material for high-profile chemistry journals such as JACS, Angewandte Chemie or Chemical Science.

Before the authors submit their work elsewhere, however, I would recommend checking their X-ray data again. I noticed that in 4 out of the 6 structures the Platon program Squeeze was applied to remove solvent electron density, without any mention of it in the cif files. Applying Squeeze is a non-trivial intervention in the reflection data, which must be mentioned explicitly. The cif file should contain the details of the .sqz file generated by Platon, the type of solvent and the number of solvent molecules squeezed (which should correspond to the number of electrons removed, as mentioned in the .sqz file). These details can be reported in the cif file under the heading `_refine_special_details` or at the end of the cif file. Furthermore, several structures show significant ellipsoid elongation in some of their substituents (isopropyl, adamantyl, terphenyl), which should probably be refined as disorders. Finally, the structure of 2 was modeled with a disordered Sn atom, which leads to nonsensical bond lengths for Sn2–C1 and Sn2–C2. Looking at the elongated ellipsoids of the rest of the molecule, it is very likely that the whole molecule must be modeled as twofold disordered – or perhaps the data contains twinning that hasn't been taken into account.

Referee 4

Liu and co-workers present the synthesis and reactivity of the first room-temperature-stable stannylene. In this article, Liu et al report the synthesis of the first base-free stable stannylene. The stable stannylene was characterized by various methods such as NMR, X-ray structural analysis and DFT calculations. The doubly ambiphilic nature of stannylene at Sn and C was also successfully demonstrated by its reactivity with various reagents. All compounds were appropriately isolated (clean NMR) and well characterized. Structural and theoretical analysis of stannylene clearly indicates that the pi-donor/acceptor effect of the phosphino substituent on the stannylene carbon atom is the key effect of stannylene stabilization and, consequently, the C-Sn moiety exhibits few multiple bonds and a (phosphino)carbene-stannylene type structure, as was also concluded for the previously reported phosphine-stabilized germylene, in contrast to the silylene compounds. However, the authors did not clearly mention these important elements in the abstract and conclusion. In addition, the results of the structural and theoretical analysis seem to me to be somewhat misinterpreted and incomplete. Nevertheless, in view of the novelty of the results and the great success, the reviewer feels that this article by Lieu et al. deserves to be published in Nature Chem, but only after substantial revisions taking into account all the reviewer's comments.

1 - The title "A free stannylene" is not clear at all. It should be "A base-free stannylene".

2 - The structure of stannyne 2 is somewhat unusual, as it shows that the planes of the phosphine and P-C-Sn fragments are almost perpendicular instead of the usual coplanar arrangement, due to the pi-interaction between the phosphine lone pair and the p-vacant orbital (or pi*(C-Sn) orbital) on the C atom. However, the authors did not mention and argue this particular structural property of 2 in the article. I believe that this point is the origin that makes the interpretation of the electronic state of stannyne 2 complex and difficult, and that it is therefore important to clarify it. A similar structure has also been observed for a carbocation stabilized by a diamminophosphine substituent (J. Am. Chem. Soc. 1989, 111, 6853-6854. J.Am.Chem.Soc.1991,113,3701-3704.). Such a twisted structure is not observed in phosphino-stannyl carbene 5. The authors must also argue and clarify this point.

3 - Page 6, last sentence: The author mentioned "The Wiberg bond indices (WBI) of P(1)-C(1), C(1)-Sn(1) and Sn(1)-C(2) are 2.10, 0.79 and 0.60 respectively, suggesting the multiple bonding character of P(1)-C(1) and stronger bonding between C(1) and Sn(1) than between Sn(1) and C(2). However, we note that WBIs may not accurately reflect multiple bonds with high ionic character, as shown by the small WBI of an Al-N triple bond in an iminoalane (0.89)." However, this statement is highly speculative and unconvincing. The author should compare the WIB value of stannyne 2 with those of other compounds such as 5 (phosphine-stanyl-carbene) and the C-protonated form of stannyne 2. I believe that, in 2, the lone pair of the carbon atom delocalizes to the P and Sn atoms (or interacts with the sigma* orbital of P and the p-vacant orbital of Sn), resulting in a small increase in the multiple-bonding character of the P-C and C-Sn fragments. Such a comparison of the WBIs of these compounds may help to understand better the situation.

4 - On page 5, figure 2, resonance structure B is misleading (no Sn-C triple bond character). It should be replaced by a resonance structure with PC triple bond character.

5 - The structure of 2 shows a bent structure at the C atom, and the P-C-Sn angle is even more acute than that of diazo precursor 1. This result suggests the presence of a lone pair on the C atom. But the author has not argued this question, although the presence of a lone pair on the Sn atom is clearly demonstrated. The author should comment on this point.

6 - In view of the further analysis and interpretation of the electronic properties of stannyne, the authors should improve the summary and conclusion.