

Referee 1 (R1)

This paper reports on the synthesis and characterization of a Sn(II) complex with a bulky tris(carbene)borate ligand. Interestingly, despite the positive charge on the complex, it has nucleophilic character. This is supported by its reactivity, including as a ligand to coinage metals. The nucleophilicity is in contrast to all other examples of Sn(II) cation complexes.

Overall, the results are compelling, with the synthetic results supporting the electronic structure insights from DFT. The ability of the tris(carbene)borate ligand to induce umpolung is likely to inspire the use of other strong donor ligands in main group chemistry. I think the work is suited for publication in Inorg. Chem.

I have a few comments:

1. The formation of 2+ as a cation is attributed to the strong donor property of the ligand. This may well be true, but can the authors exclude sterics as a factor driving the ionization of triflate?
2. The low frequency shift of the ^{119}Sn resonance is noted. Can the authors make any conclusion from this observation?

The ^{119}Sn NMR signal is low-frequency shifted in comparison with those of three-coordinate Sn(II) cations supported by a bis(oxazoline) ligand (-389.2 and -377.1 ppm),^{6h} which implies the strong electron-releasing ability of [PhB(tBuIm)₃]-.

3. While the reactions of 2+ with o-chloroanil and S8 do support the authors' hypotheses, these are not the most obvious reagents to try. Where any other oxidants investigated, and if so, were tractable products obtained?
4. It is notable that the ^1H NMR spectra for most of the compounds have additional, albeit small, resonances in the aromatic region. Can the authors comment on this?
5. The authors have used a relatively small basis set (double zeta) for their calculations. At the very least, I suggest that they provide the results of single point calculations with larger basis set for the tin atom.

Some minor points:

1. p3, line 34, "behaving overall ambiphilicity" probably should be "having small ambiphilicity"?
2. p12, line 30 should be "hitherto unknown"

Reviewer: 2

Recommendation: Publish after minor revisions.

Comments:

The submitted article by Hu and Liu describes the use of a known tris(carbene)borate, TCB, ligand scaffold to generate a cationic tin complex. The crux of the paper is the retention of nucleophilic character in what

essentially is a cationic salt of Sn(II). Overall, this study is described clearly, and the supporting computational investigations are convincing. The reactivity of the title complex does highlight the impact of the strongly electron-donating TCB ligand on the reactivity of the Sn(II) center, with coordination to metals and oxidation to yield Sn(IV) products demonstrated. While this work might not be of tremendous interest to all working in synthetic inorganic chemistry, experts in main group chemistry will find this study of significant value. Thus, I recommend that this article appears in Inorg. Chem. after minor revisions:

- The title is rather vague and might not do enough to attract readers to the paper.

- It would be instructive to evaluate the Lewis acidity of $2[\text{OTf}]$ via the Gutmann-Beckett method.

- Abstract, line 1: update as "...that a tris(carbene)borate (TCB) ligand, ..."

- Abstract, line 6: "rare Sn(IV) cation salts" seems like an over-sell here. There are many cationic complexes with ligated Sn(IV) centers.

- Abstract, line 7: The use of "novel" here is, again, an over-sell.

- Abstract, 2nd last line: consider replacing "unravel" by "uncover"

- Page 2, paragraph 2, line 6: update as "...cations adopt singlet ground-states (Figure 1a)."

- Page 2, reference 4 should include the following papers: Chem. Eur. J. 2009, 15, 5263 and J. Am. Chem. Soc. 2020, 142, 20554.

- Page 2, line 9: "render such species", which species? $[\text{R-Sn}]^+$, Sn^{2+} or both?

- Page 4, paragraph 2, line 1: update as "...that a TCB ligand reported originally by Smith..."

- Figure 1: The use of "Cp" in I as a general abbreviation for all cyclopentadienyl derivatives is misleading since Cp is a dedicated abbreviation for C_5H_5^- .

- Figure 1 (This work): Please draw the full structure of the TCB ligand; as depicted, it is difficult to see that the title species features a tris(carbene)borate ligand.

- Page 6, line 1: replace "install" with "bind"
- Page 7, line 2 (and elsewhere): use the correct symbol for degree Celsius.
- Page 7 (and elsewhere): Please give estimated standard deviations (esds) for all metric parameters determined by X-ray crystallography (including for averaged values).
- Figure 2 caption: Please supply esds for all bond lengths and angles determined by X-ray crystallography.
- The subheading "Isolation of Sn(IV) Cation Salts" is too vague/uninformative.
- Page 14, heading: Insert "of a Cationic Sn(II) Center" after "Behavior".
- Page 15, paragraph 2: "The second [BF₄]⁻ anion is away from the cation 6". Can the authors be more specific here? "Away" in which sense?
- Page 16, line 2: Please provide the level of theory used for the calculation in question.
- Reference 3 (and elsewhere): Please include sub- and superscripts for numbers and charges as needed.
- References 8b and 11a: delete the volume numbers; not required for the Eur. J. Inorg. Chem.
- TOC graphic: Too much text is provided here.
- ESI: Please provide elemental analysis data as evidence of bulk purity.
- Page S4 (and elsewhere): How much toluene and hexane were used to wash the product? Was the crystallization conducted at room temperature? Replace "celite" by "Celite"
- Figure S7 (and elsewhere): The solvent label should be "CHCl₃" (CDCl₃ is ¹H NMR silent) and make sure to label all residual solvent peaks, such as those from hexane.
- Figure S26: The ¹H NMR spectrum provided seems to have considerable impurities. Likewise, the ¹H NMR spectrum of the Au complex (Figure S27) has quite a lot of THT contaminant.

Reviewer: 3

Recommendation: Reconsider after major revisions.

Comments:

Liu and co-worker present interesting chemistry of a tris(carbene)borate stabilized tin cation, which should be published in *Inorg. Chem* after consideration of the comments.

In the introduction page 3 line 12-15, the authors make a statement on the hitherto unknown nucleophilicity of tin cations. The terphenyl cation $[\text{Ar}^*-\text{Sn}]^+$ was shown to react as a nucleophile with $[(\text{Me}_3\text{P})_4\text{IrH}]$ and substitutes a PMe_3 ligand, Scheme 4 in the publication by Sindlinger, Wesemann et al., *Chem Sci.* 2022, doi.org/10.1039/D2SC05620H. Please change the text taking into account these results.

The authors present data of mass spectrometry to check the purity. To this referee elemental analyses are a necessary tool for the characterization of new compounds. The authors should at least give a comment on why they did not record these data.

Reviewer: 4

Recommendation: Publish after minor revisions.

Comments:

The Authors Chaopeng Hu and Liu Leo Liu present work titled a nucleophilic tin(ii) cation salt, in which they describe the synthesis of a tris-carbene borato ligand stabilized Sn(ii) salt, using comparable deprotonation strategies with LDA which have been successful for similarly designed complexes. Despite the formal Sn(II) oxidation state and dicationic nature, the species demonstrates uncharacteristic nucleophilic character via oxidation with sulfur and *o*-chloroanil, as well as coordination with AuCl, AgBF₄, and AgOTf. Crystal structures were obtained for each set of reported reactions, and bond-lengths and close contacts were discussed extensively with appropriate comparisons to notable literature examples. Structure 6[BF₄] was shown to contain close Ag-F contacts of one of the counter-anions, and NMR experiments reveal two inequivalent boron and fluorine environments. Structure 7 was found to crystallize as a dimeric Sn(ii) species flanking a central Ag₂S₂O₄ 8-membered ring. Interspersed, the authors described calculations performed with M06-2X/def2-SVP theory. Frontier molecular orbital energies, natural bond orbital calculations, intrinsic bond orbitals, dual descriptor, energy decomposition analysis with natural orbitals for chemical valence and principal interacting orbital analysis were used to probe the nucleophilic character and unusual directionality of the 5s orbital which shows pz character.

The authors explained the premise for the umpolung characters of their Sn(II) species and provided quality references of other Sn(II) complexes exhibiting electrophilic character, while noting the failed attempts made by other researchers to prepare coinage metal complexes with Sn. I think that calculations supporting nucleophilic character of their complex may be best suited to being presented together, rather than at two points during the paper. Similarly, while the level of theory was mentioned in the paper, the software used was not. I am unclear what structures were calculated on page 16.

Would like to see cif file – the figure of the 8 membered ring looks like the bonds are longer than they are reported, but this may just be a perspective issue and nothing to worry about. Could not validate bond lengths via cif file, but the 2nd orientation for compound 8 contained in the SI helped to dissuade some of my scepticism.

Overall, this is a solid manuscript and should be accepted for publication in Inorg. Chem.

Reviewer: 5

Recommendation: Reconsider after major revisions.

Comments:

In this manuscript, the authors report the synthesis of a tin(II) compound 2(OTf) bearing an anionic tris-NHC ligand. This compound has been characterized in solution (NMR) as well as in the solid-state (sc-XRD) and investigated by computational calculations. The results may be interesting to inorganic chemistry, in particular to main-group, readers but I cannot recommend this manuscript in the current form:

The presentation is misleading, the compound is described as a nucleophile, which is correct, but why do the authors intend to describe it as a Sn(II) cation (an electrophile?) throughout the manuscript? No data (structural, ^{119}Sn NMR) support this description for the reported compound.

The most appropriate picture would be to put a formal negative charge on the tin, while each 1,3-imidazole unit is formally positively charged, leaving the net charge on the cationic species +1. So all pictures shown with arrows should be updated using just a line instead of an arrow. Otherwise, why not use arrows for B-N or perhaps B-CPh bonds?

In fact, many such (isostructural) compounds with Group 14 elements (in particular, contributions by the Breher group) are literature known. just a few: Inorg. Chem. 1995, 34, 4846–4853; Dalton Trans., 2009, 5335-5347, <https://doi.org/10.1002/anie.200460910> etc...)

The introduction and discussion as well as SI should be updated accordingly in a revised manuscript.