

Referee 1

Recommendation: Publish elsewhere.

Liu Leo Liu and co-workers report the synthesis of the first neutral isoelectronic Al analogues of carbonyl, containing Al = Ch (Ch = Se and Te) moiety. The scientific standard is high and most conclusions are supported by the experimental and computational evidence. However, the most interesting features of this work, for example, the shortest reported Al-Te and Al-Se bonds, are underemphasised and not well contextualized, so do not convince the reader of the novelty of this work. In addition, compounds with Al=Ch bonds have been reported as cited in the references, that is, I am afraid that the work lacks novelty. Improving the introduction and some of the discussion would make this article much more interesting. It is especially of important to relate this work to the grander theme of E-E' main group element bonds, specifically to what extent does Al form bonds with multiple bond character to other more electronegative elements, like chalcogens, and how might different bonding situations affect their reactivity or the products observed. In my opinion, this manuscript is unlikely to be of high interest to main group chemists, although there are already some examples of Al=Ch species reported. This work may be suitable for a more specialized journal after addressing the following points:

1) Introduction: it is not detailed or engaging enough

-The work from Aldridge and Coles etc is underplayed and the (Al-Ch)- species should also be shown in the figure, even though they are anionic species they are highly relevant to this work

-This would then enable some comparison between compounds 2 and 3 with their anionic counterparts

-Some mention of the discussion around the nature of Al-Ch bonds in literature is important i.e. Al=O is as for all other species an ylide-type of compound and this doesn't change for the heavy chalcogens

- why should one be interested in the neutral tricoordinate Al-Ch species when there are already anionic tricoordinate Al-Ch and neutral tetracoordinate Al-Ch species? Some justification is needed and explanation of the subtleties of this work.

-The authors can also relate this to the greater study of trying to understand main group multiple bonds (which is the main aim of this work I presume) and in the case of Al, many Al-X species have been developed too (eg. N,P etc) and this is also relevant to this discussion

2) It is stated that these are the shortest Al-Te and Al-Se bonds reported, does this mean that they have more multiple bond character than other similar compounds? This should be discussed more explicitly

The authors should relate the findings of these quantum chemical calculations with other literature compounds, how does the bonding situation compare?

3) Figure 1: Dipp = 2,6-iPrC₆H₃ should be Dipp = 2,6-iPr₂C₆H₃

4) Figure 5 is too large and should be resized to fit on the previous page

5) Figure 5, compound 9 should be Se not Te

6) Reference format should be carefully checked, for example the subscripts in References 5, 11,12, 14,15,20,21.

Additional Questions:

Significance: Moderate (not suitable for JACS)

Novelty: Moderate (not suitable for JACS)

Broad interest: Moderate (not suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

Are the conclusions adequately supported by the data?: In Part

Are the literature references appropriate and correct?: Yes

Referee 2

Recommendation: Publish in JACS after minor revisions.

This manuscript by Liu et al. reports the isolation of neutral aluminum chalcogenides and their reactivity chemistry. I thoroughly enjoyed reading this nice work.

While several anionic compounds bearing an Al–Ch multiple bond character have been isolated, neutral species remain limited and all reported compounds (A/B/C in Fig 1b) involve the tetracoordinate Al center. In this study, the authors successfully synthesized aluminum selenide (2) and telluride (3) bearing a tricoordinate Al, being formally isoelectronic with carbonyl, which are characterized well both experimentally and computationally, and the chemical behavior has been examined by the reactions with an alkyne, nitrile, azide, MeI, silane, and C₆F₆. These detailed investigations disclose the essential nature of the Al–Se and Al–Te bonding in those species, fundamentally very important.

Overall, the present work is highly original and technically well done. The elucidation of the electronic structure and reactivity of the hitherto unprecedented Al–Se/Te bonds will attract a wide readership. I would recommend the acceptance of the present manuscript for publication in JACS after the minor revision on the points indicated below.

1. Since only Al–Se and Al–Te species are gained in this study, the title of the manuscript “Aluminum Chalcogenides” sounds a bit broad and would be better to be specified to Al–Se/Te to be accurately presented. I am curious what happens if compound 1 is oxidized (by the reaction with O₂, or R₃PO, etc), the corresponding Al–O species is formed?

2. After the detailed analysis, although the NBO analysis shows the WBI values more than 1, there is little Al–Se/Te π bonding character and the short Al–Se/Te bonds are predominantly due to the electrostatic attraction between Al⁺ and Ch⁻. Upon this conclusion, the drawing of compounds (2 and 3) with Al=Se/Al=Te double bond throughout the manuscript, TOC, and ESI seems not correct. Rather, the ambiphilic description (right drawing in Fig 1c) must be precise. Since this conclusion reflects the essential bonding nature of these beautiful molecules, I feel it is not necessary to over-emphasize the inaccurate double bond description in the drawing.

3. Related to the above comment, the dashed bond between Al and Ch atoms shown in TS1/TS2 (Fig 5) should be deleted considering there is no double bond in 2 and 3. The purely concerted [2+2] cycloaddition between two π bonds is a forbidden process?

4. The NBO charges at the N are negative like chalcogens. Since the N-Al bonds are shorter than Al-Ch bonds, I assume the lone pair of electrons on the N may interact with the Al more effectively compared with chalcogens. Thus, I am interested in the WBI value of the Al-N bond, and the IBO of the Al-N pair bonding.

5. The TS1 (24.2 kcal/mol) seems a bit high as the reaction completes within 3h at r.t. Any comments would be appreciated.

6. For the reaction with AdN3, the initial step could be [2+3] cycloaddition, which is followed by the elimination of N₂. Did the authors observe any intermediate such as AlSeN₃ five-membered ring species? Regarding the AlNSe three-membered ring product, the authors might wish to cite the recent perspective (10.1021/jacs.3c03152).

Additional Questions:

Significance: Highest (top 5%, suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS)

Broad interest: Highest (top 5%, suitable for JACS)

Scholarly presentation: Highest (top 5%, suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Referee 3

Recommendation: Publish in JACS after minor revisions.

In this contribution, Zhang and Liu outline the synthesis and isolation of novel neutral three coordinate aluminum chalcogenides and their reactivity towards various small molecules such. They utilized the N-heterocyclic carbene-stabilized aluminylene (1) as an excellent precursor for crafting the Al-Ch multiple bond species (Ch = Se, Te). X-ray crystallographic analysis revealed the short Al-Ch bonds and bonding nature was also examined by DFT calculations. Remarkably, these multiple bonds react with unsaturated organic compounds affording cycloaddition products.

Authors present a nice description of their experimental and theoretical results in a clear and concise manner. The chemistry is well done with a straightforward synthetic method to the target compounds and novel compounds are well characterized. The discussion of structure and bonding nature of neutral three coordinate aluminum chalcogenides with double bonding character is also described combined with obtained DFT calculations results. Thus, this work would be an important additional contribution and give further insight into this field. Therefore, referee would recommend publication of this paper in JACS,

however, following scientific issues should be corrected/fixed before the acceptance:

1. Authors discussed the bonding situation of compounds 2 and 3 according to bond lengths, WBI, NBO, IBO, etc. However, no description about the pi-donor stabilization from the lone pair electrons at N atom to the electrophilic aluminium center. Have authors observed it computationally? This should be checked and commented.
2. How reliable the DFT calculations for the reaction mechanisms in Figure 5? The estimated activation barrier with 24.2 kcal/mol at R.T. and 30.1 kcal/mol at 70 °C for the cycloaddition reactions are at first glance a bit weird. These values are not well fit with experimentally conducted reaction conditions in order to overcome these activation barriers with temperatures. For a first order reaction with a barrier of 30.1 kcal mol⁻¹ the half-life would be 16.6 days at 70°C. Thus, it would take around 83 days to reach >95% conversion. In the case of the activation barrier of 24.2 kcal mol⁻¹ half-life for a first order reaction would be 17.0 hours at 25°C. So it would take ~3.5 days to reach >95% conversion. These issues should be clarified and solved.

Additional Questions:

Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: In Part

Are the literature references appropriate and correct?: Yes