Responses to referees' comments

REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

Please rate the importance compared to published work in this subject area

Reviewer #1: Outstanding (Top 5%)

Reviewer #2: High (Top 20%)

Reviewer #3: High (Top 20%)

Please rate the novelty compared to published work in this subject area

Reviewer #1: Outstanding (Top 5%)

Reviewer #2: High (Top 20%)

Reviewer #3: Outstanding (Top 5%)

Which aspects of scholarly presentation require improvement (if any)?

Reviewer #1: (No Response)

Reviewer #2:Clarity

Reviewer #3: (No Response)

Do the methods, data and analysis (including statistical analysis where applicable) adequately test the hypothesis and support the conclusions?

Reviewer #1: Yes

Reviewer #2: Yes

Reviewer #3: Yes

Are the methods, data and analysis described in sufficient detail to be reproduced?

Reviewer #1: Yes

Reviewer #2: Yes

Reviewer #3: Yes

Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

Reviewer #3: (No Response)

Please indicate whether you have included attachments

Reviewer #1:No

Reviewer #2:No

Reviewer #3:No

Referee 1

In this manuscript Zhang, Kong, and Liu report on the reactivity of a Lewis-base coordinated aluminylene 1, an Al(I) compound, with heavy chalcogens Se and Te to afford the unusual heterocycles featuring an AlSe2, AlSe3, AlTe2 or AlTe3 ring. Remarkably, the ring expansion of AlSe2- and AlTe2-compounds by one chalcogen atom has been shown to yield four-membered heterocycles, including compound 5 featuring an AlSe2Te ring. The rational and selective formation of these compounds seem to stem from a careful choice of reagents and reaction conditions. Compounds 2, 3, 4, 5, and 6 have been fully characterized with a high scientific standard including their solid state structures by sc-XRD. The electronic structures of the selected compounds have been analyzed by quantum chemical calculations, which are in line with their bonding descriptions (and corroborated by reactivity studies) presented by the authors. The nature of these compounds is showcased by the reactivity studies of 2/3 with different reagents to result in 7, 8, 9, and 10. A mechanistic proposal for the formation of 7 as outlined based on DFT calculations seems reasonable. Also, the use of 4 as a selenium atom transfer reagent as well as a selenium-centered Lewis base is shown in Figure 6.

In general, the work is highly original and the manuscript reads well. The results have been scholarly presented and would interest to a broad general chemistry readership. This reviewer recommends publication in Angewandte Chemie pending minor revisions:

(1) All compounds have been prepared in good yields. I suggest the authors to mention the yields of the compounds in Schemes.

(2) To prepare compound 6 from 3, the authors used CS2 as a (co)-solvent at 65 C with a reaction time of 10h. Cannot this reaction, like others, be performed in toluene? Please elaborate.

(3) I wonder whether these compounds can be used as chalcogen atom transfer reagents, like R3PTe. For instance, Is it possible to prepare acyclic Al-Te/Se compounds by reacting 2/3 with 1?

Referee 2

The manuscript reported the synthesis, structure and reactivity of N(D)AlSe2 and N(D)AlTe2 compounds, which have been obtained by the reaction of an NHC-supported Al(I) amide with selenium or Te=PR3. Al-Ch compounds are important class of compounds for Al-Ch materials. However, there are only a few of three-membered ring AlCh2 species that have been reported. The present work provided the novel strategy for the generation of these novel species and structural imformation on these interesting compounds. In addition, their chemsitry has been investiagted with a range of small molecules, leading to some unexpected reactions and formation of new ring expansion or opening products. The experimental wok is well-done and the materials were well-organized. This reviewer recommend to publish the work after some minor modifications.

(1) The ring expansion with polar unsaturated bonds give five-mmbered ring products, is it possible to remove one or two Ch atoms from these rings.

(2) In addition, the insertion of a single atom to Ch-Ch bond was also observed for the three-membered ring AlCh2, the transfer of one of the Ch atoms to some unsaturated substrates should be explored.

Referee 3

This manuscript reports on the synthesis and isolation of aluminiumdichalcogeniranes and aluminiumtrichalcogenetanes. The synthesis of the target heavy dioxiranes is achieved from the reaction of the NHC-stabilized aluminium(I) species with Se/Te=PnBu3. These can further be converted into heavy trioxetanes derivatives with additional corresponding chalcogens. The molecular structures of these compounds have been well elucidated, including XRD analysis. The electronic structures/bonding nature of 3 and 4 were also discussed with the DFT-derived results. It is of note that the authors isolated the mixed TeSe2Al cycle 5 as well. Moreover, the activity of 2 and 3 towards small molecules (Ar-N=C=O, PhN=O, Ph2CO, MeI) was also described together with the reaction mechanism obtained by DFT calculations. Interestingly, compound 2 can be regenerated by the reaction of 4 with PnBu3. This paper contains the synthesis and reactivity of the first examples of aluminiumdichalcogeniranes and aluminiumtrichalcogenetanes. The synthetic and theoretical parts are well described, and the manuscript is readable. Thus, the reviewer supports this manuscript for publication in ACIE, pending the following minor points:

(1) The Te2SeAl cycle can also be obtained from the reaction of 3 with Se?

(2) Thermodynamic stability between AlE2 vs AlE3 (E = Se, Te) can also be discussed.

(3) Some reported aluminium chalcogene cycles AlEn (E = S, Se, Te; n = 3,4,5…) can also be cited.