

REVIEWER REPORTS

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: Outstanding (Top 5%)

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: (No Response)

Reviewer #3: Other

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

Responses to referees' comments

Our responses to the referees' comments below are in the order R1-R2-R3.

Referee 1 (R1)

Comments:

Liu and coworkers report the reaction of a monomeric Aluminylene with boron Lewis bases, observing both B-O bond activation and adduct formation. This is an interesting paper and a well-executed study. I am supportive of publication and have a couple of minor comments that the authors may wish to address before they publish the work.

[Response:](#) We appreciate these positive comments and constructive suggestions from R1.

1. The calculated activation barrier of reaction of **1**' with Ph₂BOBPh₂ of 29 kcal mol⁻¹ is beyond that expected for a room temperature process. Can the authors comment on why this is the case, is it possible dispersion interactions stabilise this TS and hence our model replacing tBu for Me is a poor one.

[Response:](#) Thank you for this suggestion. Accordingly, we have re-calculated the mechanism at the SMD-BP86(D3BJ)/def2-TZVP//BP86(D3BJ)/def2-SVP level of theory using the real molecules **1** and Ph₂BOBPh₂. The activation energy of **TS** is 15.7 kcal mol⁻¹ which is in line with the reaction at room temperature. The text, Figure 3 and SI have been updated.

2. ¹⁹F NMR data on **3** is inconsistent with the static structure by XRD, but imply facile exchange of the C₆F₅ groups, have the authors conducted VT NMR experiments to try and slow down this exchange?

[Response:](#) Yes, we have done VT NMR experiments of **3**. Indeed, upon cooling a toluene solution of **3** to -80 °C, the ¹⁹F NMR spectrum of **3** exhibits six partly

overlapping signals (Figure S2). This observation indicates a fast exchange of the Al-F interaction in **3** at room temperature.

3. The temperature at which the NMR data was collected should be given in the manuscript itself for clarity.

Response: We thank R1 for this suggestion. This has been given in the 'Experimental Section' in the manuscript ("NMR spectra were acquired on a Bruker Avance 400 (¹H: 400 MHz, ¹³C: 101 MHz, ²⁷Al: 104 MHz, ¹¹B: 128 MHz, ¹⁹F: 376 MHz) or 600 (¹H: 400 MHz, ¹¹B: 193 MHz, ¹³C: 151 MHz, ¹⁹F: 565 MHz) NMR spectrometer at 298 K").

4. There is probably no need to list the ²⁷Al NMR data for each compound as in no case is a resonance reported.

Response: The ²⁷Al NMR data have been removed and we have added the sentence "In all cases, the ²⁷Al NMR resonances have not been observed." in the Experimental Section.

Referee 2 (R2)

Comments:

This paper reports the reactivity of the recently reported alumynylene by the same authors toward boron-containing compounds. Oxidative addition of B-O bond was observed to form Al-B bonded alumaborane compound, while simple coordination of Al(I) center to the boron center of B(C₆F₅)₃ and HB(C₆F₅)₂. These findings are interesting enough to be published. However, the observed HRMS data of **4** and **5** are identical. This would be caused by copying/pasting or inventions. Therefore, the reviewer recommends a minor revision before the final acceptance. Please find the following comments.

Response: We appreciate these positive comments and constructive suggestions from R2.

1) page 2, lines 16-18, Although the authors claimed "This suggests the existence of the overlapped vacant p orbitals at Al(1) and B(1), which is consistent with the calculated LUMO of 2 (Figure S17).", the aluminum atoms seems to have a small contribution in Figure S17.

Furthermore, the aluminum center has a small contribution of orbital which has an opposite phase to the orbital at the boron atom. How do the authors explain this?

Response: I would like to draw your attention to the LUMO of **2**, which can be seen in Figure S19. The LUMO is primarily composed of the overlapping 2p orbital at B and the 3p orbital at Al. It's worth noting that the "small contribution and opposite phase" mentioned earlier is from the 2p orbital and not the 3p orbital at Al. When considering a 3p orbital, the value of l (the angular momentum quantum number) is equal to 1. This means that the number of angular nodes is also 1, and the number of radial nodes is equal to $n-l-1$, which in this case is $3-1-1 = 1$.

2) Figure 3 and related discussion, The activation energy of 29.1 kcal/mol is too large to consider the reaction at room temperature. The reviewer guesses removal of tBu groups would cause this problem because it would lose the contribution of the London dispersion force. So he recommends to re-calculate the real system to evaluate the activation energy.

Response: Thank you for this suggestion. Accordingly, we have re-calculated the mechanism at the SMD-BP86(D3BJ)/def2-TZVP//BP86(D3BJ)/def2-SVP level of theory using the real molecules **1** and Ph₂BOBPh₂. The activation energy of **TS** is 15.7 kcal mol⁻¹ which is in line with the reaction at room temperature. The text, Figure 3 and SI have been updated.

3) pages 2-3, The crystal structure of **3** has F-Al coordination but the ¹⁹F NMR spectrum showed three C₆F₅ rings are magnetically equivalent at room temperature. These two results are inconsistent with each other. The reviewer considers the coordination of F to Al would be reversible and rapidly takes place in a solution at room

temperature. Therefore, he recommends measuring the ^{19}F NMR spectrum of **3** at a lower temperature. Similarly, the ^{19}F NMR spectrum of **4** at lower temperatures should also be recorded, because **4** should be less sterically congested than **3** to induce F-Al interaction.

[Response:](#) We have done VT NMR experiments of **3**. Indeed, upon cooling a toluene solution of **3** to $-80\text{ }^\circ\text{C}$, the ^{19}F NMR spectrum of **3** exhibits six partly overlapping signals (Figure S2). This observation indicates a fast exchange of the Al-F interaction in **3** at room temperature.

4) As mentioned above, the observed HRMS data of **4** and **5** are identical. It MUST BE DONE again. If this would take place many times in the future, other chemists can not believe the quality of the data from the Liu group. Take care.

[Response:](#) We regret the oversight that occurred during the copying and pasting process. We have taken immediate action to correct the HRMS data of **4**.

Referee 3 (R3)

Comments:

Liu and Zhang report on reactions between their recently developed aluminylene towards a diboroxane and several boron centred Lewis acids. In the first instance, oxidative insertion of the Al(I) centre of the aluminylene into a B-O bond occurs to give a rare example of an alumaborane. Reactions with mononuclear Lewis acids give adduct complexes. DFT calculations are used to examine reaction mechanisms. This is an interesting study which builds on the small, but growing, amount of chemistry derived from the authors 1-coordinate aluminylene. The work certainly adds to the field of Al Lewis base adducts of B Lewis acids, and will appeal to a broad audience of inorganic chemists. The work is thoroughly carried out, well written, and new compounds adequately characterised. This will make a fine addition to EJC and I recommend publication. The only change I suggest is to use compound formulae in addition to numbers in the abstract. This will help chemists searching databases, who only have access to the abstract in the first instance.

[Response:](#) We appreciate these positive comments and constructive suggestions from R3. Compound formulae have been added in the abstract.