Referee 1

Recommendation: Publish after minor revisions.

The communication reported on carbon atom transfer from benzoannulated NHC to strained aluminum cyclopropene in the reaction of NHC-stabilized alumylene with bis(trimethylsilyl)acetylene. This transfer is quite unexpected and interesting. DFT calculation strongly support the formation of cycloprepenylidene intermediate. The experimental part is solid and new compounds have been well-characterized.

(1) For the carbon atom transfer reaction, if common NHCs are employed instead of benzoannulated NHCs such as in this case, similar carbon transfer could take place with the NHCs?

(2) IN4 in Figure 5 could be drawn as a zwitterionic species since the positive C3 ring is aromatic.

Additional Questions:
Significance: Above Average (suitable for Organometallics)
Novelty: Top 10% (suitable for Organometallics)
Broad Interest: Above Average (suitable for Organometallics)
Scholarly Presentation: Above Average (suitable for Organometallics)
Is a Communication the best format for the work?: Yes
Would it be preferable to expand the Communication to an Article?: No
Can the manuscript be shortened to two pages by moving some information to the Supporting Information? If so, please provide suggestions in your review.: No
Are the conclusions adequately supported by the data?: Yes
Are the literature references appropriate and correct?: Yes
Are any proposed reaction mechanisms reasonable and supported by data or literature precedent?: Yes
Is the Supporting Information of sufficient quality and completeness to evaluate the manuscript and enable reproduction of the work?: Yes
Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?: Yes
Is the writing clear and concise, and is the grammar and language (English) acceptable?: Yes

Referee 2

Recommendation: Publish after minor revisions.
This is a nice paper by Liu and co-workers reporting the synthesis of base-stabilized aluminacyclopropene and its isomerization to a cyclopropene.
The first part presents the reaction of an NHC-stabilized alumylene (1) with acetylene, giving rise to an NHC-coordinated aluminacyclopropene (2) via a formal [1+2] cycloaddition reaction.
While this part is similar to the previous report by Braunschweig et.al. (ref 9), the characterization of (2) is fully done both experimentally and computationally in high

quality, allowing a deep understanding of the fundamental bonding of the AlC2 moiety. The second part demonstrates thermal isomerization of (2) to a cyclopropenylalane (3). It is very interesting that this rearrangement involves an intramolecular carbene carbon extrusion process. The plausible reaction mechanism is investigated theoretically.
The reaction mode from (2) to (3) is still rare in the area, which should attract a readership in organometallics. I highly recommend the acceptance for publication after addressing the minor points shown below.

(i) Although the Al-C bonds in (2) show a strong ionic nature, structurally, it is concluded as an aluminacyclopropene, meaning that the interaction between the Al center and those two C atoms is not in a donor-acceptor manner in principle. Therefore, the description of “the coordinated C=C group” might not be proper in this case.

(ii) Experimentally, although it takes a longer time, the reaction proceeding at room temperature is confirmed to give (3). TS2 involved with 31.0 kcal/mol seems high for r.t. reaction. Is it reasonable?

(iii) Compound (3) involves two chiral centers (Al and sp3-C in the C3 ring), and according to the calculation (from IN4 to 3’ via TS5), the formation of the diastereomers may be possible. Nevertheless, it seems that only one diastereomer is obtained experimentally. It would be great if the authors could comment on this point.

(iv) If another NHC without iPr is employed, would it be possible to isolate IN4 and further use it as the C3(TMS)2 carbene source? This is not a requirement but just by curiosity and could be their future consideration.

Additional Questions:
Significance: Top 10% (suitable for Organometallics)
Novelty: Top 10% (suitable for Organometallics)
Broad Interest: Top 10% (suitable for Organometallics)
Scholarly Presentation: Top 10% (suitable for Organometallics)
Is a Communication the best format for the work?:
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Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?:

Is the writing clear and concise, and is the grammar and language (English) acceptable?: