

This paper was accepted in CCS Chem. upon addressing the concerns of referees from a previous JACS peer-review process.

Reviewer: 1

Recommendation: Publish in JACS after minor revisions.

Comments:

This is an excellent work by Liu and co-workers revealing the unprecedented nature of a monomeric N-aluminylene as a formal "Al+" transfer reagent.

While a variety of low-valent or zero-valent species of group 13-15 elements have been isolated to date, only a handful of compounds involving N, P, Si atoms are capable of transferring the respective atomic fragment to other substrates, as correctly exemplified in Fig 1. So far, the transfer of an Al atom to unsaturated hydrocarbons has never been achieved.

In the first part of the present study, the authors demonstrate the mono-valent carbazoly aluminylene (1) undergoes the cyclization reaction with dienes or two alkynes, giving rise to the AlC<sub>4</sub> five-membered ring species (2, 3, 4, 5). Although this part is reminiscent of the chemistry of NaCNaAl(I) species (ref 31, 33), the direct synthesis of alumole derivatives (4, 5) starting from simple alkynes has hitherto unknown and this protocol is fundamentally significant.

In the second half, the authors have wisely employed BnK to cleave the Al-N bond of compounds (4, 5) and succeeded in accomplishing the Al transfer.

Not only all products are fully characterized by the standard spectroscopy and x-ray diffractometry, but also the theoretical mechanistic study for the formation of (2, 3, 4) is comprehensively done.

Overall, the two-step reaction to completely transfer the Al atom from (1) to unsaturated hydrocarbon concomitant with the construction of alumole derivatives is highly original and very interesting. The technical parts are done in a high-standard quality and the manuscript is presented well scholarly. This study should attract a wide readership in JACS, and hence, I would recommend the acceptance for publication after the authors address the minor points indicated below.

---In Fig 1 and TOC. I understand the "Al+" transfer ability of (1), but descriptions like "equivalent" for compound (1) and "Al+" might not be scientifically accurate, as they are not equivalent precisely?

---Fig 7. An equilibrium is proposed. Have the authors experimentally

confirmed it (i.e. by VT-NMR or other methods)?

---Fig 1. The substituents on the N atoms in compound B are missing.

---Fig 1. "Z" in compound C should be specified.

---Fig 1. The substituent on Ge in compound F seems wrong, it is not 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> but 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Trip = 2,4,6-Triisopropylphenyl).

Additional Questions:

Significance: High (suitable for JACS)

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

Broad interest: High (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

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:

This paper is a follow-up to the recent report of their one-coordinate aluminum carbazole derivative. The products 2-5 indicate the formation of an alumole ring consistent with the ability of 1 to transfer a moiety containing a single Al atom. But there are many examples in the literature where an aluminyl species or its heavier Gp. 13 homologs (mostly ignored here) react with unsaturated hydrocarbons to give ring species e.g. *Angew. Chem. Int. Ed.* 2005,127, 10170. The distinction in this paper appears to be that the Al atom in the products 2,4 and 5 remains three-coordinate. In this case they should also cite related work incorporating three-coordinate Ga species (e.g. in *Chem Eur J* 2009, 15, 5263 and *Chem Commun* 2011, 47, 7506).

In a more general sense I do not understand their use of the term "atomically precise". The Al atom is transferred a part of a sterically hindered unit and not as an individual Al atom as implied by the title. It appears that it is the size of the Al substituent limits the no of Al moieties transferred as also seen in the work of Schnockel, Roesky and Power. Not to mention other problems---the use

of other Al or Ga species to transfer more than one Al or Ga atom can also be termed "atomically precise", but why bother? I suggest deleting the gimmicky and inaccurate phrase "atomically precise".

The discussion of the Al-N bonding appears to be simplistic. The three-coordinate Al atoms feature a p-orbital that can potentially participate in pi bonding. There have been several studies of this bonding possibility but these are not mentioned.

In summary the work in this paper may be publishable provided that the points raised above are addressed and the literature citations are properly modified.

Additional Questions:

Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

Are the conclusions adequately supported by the data?:

Are the literature references appropriate and correct?: In Part

Reviewer: 3

Recommendation: Publish elsewhere.

Comments:

This paper describes reaction of recently reported amido-substituted neutral Al(I) compound toward diene and alkynes, and photophysical property and reactivity of the resulting five-membered ring species. Considering that the formation of Al-containing five-membered ring from neutral or anionic Al(I) species and photophysical property and reactivity of alumole derivatives have already been reported, the reviewer considers the present manuscript would not provide significant advance in main group chemistry. Therefore, he suggests to forward this paper to more specialized journal such as Organometallics or ACS Organic & Inorganic Au. Please find the comments.

1) In the introduction (line 30-31), The authors mentioned "anionic alumanone". Is this name for the previously reported anionic Al=O compound right considering IUPAC nomenclature?

2) page 2, please mention about the stereochemistry of two phenyl group in 3 and its origin in the mechanistic point of view.

3) page 2, right, The authors mentioned "the syntheses of 2 and 3 represent the first examples of cycloadditions of a monocoordinate aluminylene with unsaturated hydrocarbons.<sup>29</sup>" The reviewer could not understand why the authors did not mention about the previously reported cycloaddition reaction of neutral and anionic Al(I) species.

4) page 3,

Why did the authors started the first paragraph with comment of carbazole-based materials even the present system exhibited absorption and emission based on alumole moiety?

Is there any previous report on the photophysical property of alumole derivatives? If such papers exist, they should be referred here.

Why did compound 5 show the dual emission? Are there two emissive states caused by the substituents?

5) page 3-4, Figure 5 and related text, Is this the first example for Al-N cleavage of (triorgano)(monoamido)aluminate species? If it is not, the reactivity pattern of the present compound is not surprising and appropriate papers should be cited here.

Additional Questions:

Significance: Moderate (not suitable for JACS)

Novelty: Lowest (not suitable for JACS)

Broad interest: Moderate (not suitable for JACS)

Scholarly presentation: Lowest (not suitable for JACS)

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

Are the literature references appropriate and correct?: No

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