
REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Very important (top 5%)

Reviewer #2: Highly important (top 20%)

Reviewer #3: Highly important (top 20%)

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2. Please indicate whether the results discussed justify publication as a Research Article

Reviewer #1: Publish as a Research Article

Reviewer #2: Publish as a Research Article

Reviewer #3: Publish as a Research Article

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3. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Superfluous

Reviewer #3: Insufficient

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4. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Too long

Reviewer #3: Concise

5. Please rate the verification of hypotheses and conclusions by the presented data

Reviewer #1: Fully consistent

Reviewer #2: Fully consistent

Reviewer #3: Fully consistent

6. Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

Reviewer #3: (No Response)

7. Please indicate whether you have included attachments

Reviewer #1: No

Reviewer #2: No

Reviewer #3: Yes, for the author

8. Please rate the quality of the Supporting Information

Reviewer #1: Satisfactory

Reviewer #2: Satisfactory

Reviewer #3: Satisfactory

COMMENTS TO AUTHOR:

Reviewer 1: It was a pleasure to receive this paper to review. This is an excellent work by Liu and a coworker presenting the chemistry of a monomeric N-aluminylene.
While several low-valent Al species have been reported over the decades, it is only very recently that Power et. Al. have successfully isolated the bottleable monomeric aluminylene, and disclosed its peculiar chemical behavior. There should be more to explore in this class of species.

The authors have wisely employed the carbazolyl group featuring π-donor stabilization effect, and succeeded in isolating the first monomeric N-aluminylene (2b), which is fully characterized by both experimental and computational methods. It has also been demonstrated that the Al center of (2b) may exhibit various coordination modes with metal and Lewis bases in those complexes (3-7). Very interestingly, the insertion of the Al (I) into a Cu-Cl bond gave rise to the Cu-alumanyl complex (9), indicating the potential utility of the aluminylene for the development of various alumanyl-metal complexes. Mechanistic study for the formation of (9) is also done completely.

This reviewer is wondering if a one-electron reduction of (9) will give a Cu(0) species supported by Al(I) and NHC. This is just by curiosity, will be their future work, and not a request to add any experiments in this nice paper.

Collectively, the present work is highly original, fundamentally very important, I really enjoyed reading this nice work. The unique electronic structure of the novel Al(I) species, demonstration of reactivity, and elucidation of diverse bonding modes will attract a great readership in the main group community. I strongly recommend the publication of the manuscript in Angewandte.
The minor points indicated below should be addressed before publication.

--- Regarding the reactivities of Al(I) species (ref10), the authors might wish to add P_4 activation by an Al anion (Organometallics 2020, 39, 4183 - 4186).

---Fig3. I would suggest that transparent mode (like Fig 5) should be used to depict the orbital lobes (instead of the current solid mode) so that the readers could identify the atom positions and readily follow the discussion.

---Fig8. The pictures could be improved so as to identify/view the key points readily. For instance, the key atoms such as Cu, Al, Cl in the pictures could be labeled, some parts of the molecules could be drawn using the wire depiction.

---SI. Scheme for formation of (a). To be consistent with other schemes, it would be better to add the solvents (dioxane/H2O) in the scheme.

Reviewer 2: This paper reports on the synthesis and reactivity of an Al(I) carbazole derivative. The Al atom is one-coordinate thereby making it a very rare molecular type of which only one previous example is known. I agree with most of the assertions and conclusions but I was disappointed by the organization and writing in the paper. There is no need for a general discussion of the possible applications of such compounds (there is no catalytic work in this paper after all). Much of the discussion about ligand types I, II, IIi and IV is unnecessary. Their ligand is of a fairly simple type that is related to compound E with a possibility of the interaction of the ligand nitrogen lone pair with the out-of-plane aluminium p-orbital. It can behave as a Lewis base as in 3 and the aluminium is sufficiently unsaturated to allow further Lewis base coordination as in 4,5,and 6. I do not think the rest of the compounds 7 and 9 add much to the paper and could be kept back for a full paper. In essence I recommend drastically cutting the introduction (they could begin at line 3 on page 2 which also means cutting most of the references up to about reference (7). Figure 5 would be better off in the SI. One flaw in the paper is the absence of any significant discussion of electronic spectral data for 2b. I assume the transitions involving Al or N are in the UV region but they do not appear to be given. The Al-N bonding discussion is also poor . How does the Al-N pi bonding overlap compare with those in R2Al-NR'2 compounds or (RAlNR')n (n=2 or 3) which also have 3-coordinate nitrogens? These data should be provided.

Reviewer 3: A Free Aluminylene with Diverse s-donating and doubly s/p-acceting ligand features for transition metals.
Angew. Chem. Int. Ed. 202111975
Liu and Zhang report the synthesis of a one-coordinate aluminylene along with its coordination to transition metal carbonyl fragments and oxidative reaction with a group 11 metal chloride. There is significant current interest in the chemistry of low-oxidation state aluminium complexes. This work describes only the second one-coordinate aluminylene compound (J. Am. Chem. Soc. 2020, 20554). A detailed experimental and computational study investigates the electronic structure of this compound in its role as a ligand.

The conclusions largely reflect those published in recent works on closely related aluminylene compounds (J. Am. Chem. Soc. 2020, 19874; Dalton Trans. 20212, 7810).

The case for publication in Angew. Chem. I think is borderline. While the results are remarkable, nearly every core point of novelty has been published on related systems in the last two years. That said, the intense interest in this field means that it is likely these results will find high impact. As such I believe a case can be made for publication. There are several minor points for the authors to consider.

(1) In terms of the discussion and characterisation of the products, it would be useful for the authors to briefly comment on how they have ruled out the assignment as 2b as a hydride complex (either through analysis of the IR spectrum or reactions with H2 to deliberately prepare the corresponding dihydride – see Nature 2018, 557, 92). For 3-6 it may also be useful to comment on whether the CO ligands demonstrate any semi-bridging character (Dalton Trans. 2015, 17007). Both points would clarify the authors arguments.

(2) Personally, I found the authors definitions and claims around σ- and π-accepting quite confusing.

- The π-accepting character refers to genuine M–Al interactions while σ-accepting is not within the M–Al bond rather the ability of Al to act as a Lewis acid for external ligands. I think the framing of these classifications could be clearer.
- In addition, the line-drawings in Figure 1 are confusing, presumably the boxes represent acceptor orbitals, why are these represented on Al but not on M?
- Furthermore, I believe that the key claims the authors make about the s-accepting character (i.e. Lewis-acidity) of aluminylene ligands are important for known catalytic systems. This type of interaction has been invoked in mechanistic studies using aluminylene ligands (Chem. Sci. 2018, 5435) and related gallylene systems (Nat. Chem., 2017, 1256–1262). The authors could perhaps highlight that they are characterising an interaction proposed to be important to existing catalytic processes.

(3) Prior literature. There is some additional literature that perhaps needs to be cited.

- Very recently related Cu–Al alumanyl systems have been published (Chem. Sci. 2021, doi.org/10.1039/D1SC04676D).
- In addition, the bridging mode referred to as rare for aluminylene systems has been observed in some related metal hydride complexes that have been proposed to have aluminylene character (Chem. Eur. J., 2014, 17624; Chem. Sci. 2015, 5617).

(4) Aspects of the presentation of the data can be improved.

- All bond lengths should be provided with esds
- Vibration data should be quoted to the nearest whole number not the first

decimal point

- The authors should be clearer when discussing energies. For EDA-NOCV the components of the energies should be clarified using the proper nomenclature. In addition, they should clarify the energies in Figure 8. Presumably these are Gibbs energies?