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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: Very important (top 5%)

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

Reviewer #1: Publish as a Communication

Reviewer #2: Publish as a Research Article

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3. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Appropriate

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4. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

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

Reviewer #1: Fully consistent

Reviewer #2: Fully consistent

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6. Please indicate which other journal you consider more appropriate

Reviewer #1: ----

Reviewer #2: ----

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7. Please indicate whether you have included attachments

Reviewer #1: No

Reviewer #2: No

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8. Please rate the quality of the Supporting Information

Reviewer #1: Satisfactory

Reviewer #2: Satisfactory

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COMMENTS TO AUTHOR:

Reviewer 1: This is a very interesting paper that redox property of a monocoordinated aluminylene and its NHC adduct making it isoelectronic at Al to an NHC. The reactivity of this species is demonstrated in [4+1] cycloaddition reaction of naphthalene and biphenylene.

The products of these reactions are fully characterized and the mechanisms of formation are clarified by DFT calculations. This work demonstrates the analog between these Al-NHC adducts and NHCs and illustrates very interesting reactivity. This work will be of broad interest to the chemical community I support publication and see no reason for revision. Congratulations to the authors on a very insightful and interesting study.

Reviewer 2: This manuscript develops the chemistry of a recently isolated class of aluminylene compound and demonstrates some fascinating and unique new reactivity for main group metals. The coordination of a carbene to the aluminum center significantly changes the electronic properties of the complex by reducing the HOMO-LUMO gap, as comprehensively characterized by the authors using spectroscopic (UV/vis) and computational methods. The consequences of this change when compared to the base-free analogue is profound in the reactivity, with the new species showing inter- and intramolecular activation of aromatic C-C bonds.

One minor point that needs clarification is the claim that the conversion between 2 and 3 is reversible. Heating 3 in C<sub>6</sub>D<sub>6</sub> does not show 2 (spectroscopically), so it is unclear to me how this claim is justified. Further explanation backing up this claim is needed.

The manuscript is very clearly written, and the references cover all of the relevant material, including a very comprehensive introduction putting this

work in context. The observed reactivity opens new avenues for the application of main group compounds in the modification of organic fragments, and as such will have a wide appeal to the readership of *Angewandte Chemie*.