

Referee: 1

Recommendation: Minor Revision: suitable for publication after changes

Comments:

This paper records the synthesis, full characterisation, preliminary reactivity studies, and theoretical calculations of the diarylaluminum hydride $[\text{HAl}(\text{C}_6\text{F}_5)_2]_3$. The principal viewpoint of the paper is from the comparison and (mostly) contrasts of this neutral organoaluminum hydride with the borane analog $[\text{HB}(\text{C}_6\text{F}_5)_2]$, which is a popular reagent. Therefore, having a pure form of $[\text{HAl}(\text{C}_6\text{F}_5)_2]_3$ readily available (it was made impure in 2006), of potential use in a wide variety of reactions will undoubtedly be of interest to a broad section of ChemComm readers who have interests in synthesis and catalysis, especially in the main group arena, which is attracting larger and larger audiences these days. The synthesis, experimental NMR and X-ray data, combined with the DFT calculations which probe the energetics of forming trimeric **1** as well as the bonding via a combination of intrinsic bond orbital (IBO) calculations and QTAIM analysis, all appear sound as do the interpretations of them. The paper ends with some reactivity studies.

Therefore, I think the chemistry in the paper is of the high standard expected for a Chem Comm and although the technical side of the paper is not as good, I am pleased to recommend acceptance.

Chemistry points:

The title of the submission "The aluminum analogue of Piers' borane", might not mean much to a lot of ChemCommun readers, since it does not inform readers what the compound is nor what has been done with it. "Structural characterisation and reactivity studies of $[\text{HAl}(\text{C}_6\text{F}_5)_2]_3$, the aluminum analogue of Piers' borane", would be better.

Little effort has been made in the paper to compare it with other diorganoaluminium hydride compounds. Probably the best known one from a synthetic perspective is DIBAL, diisobutylaluminium hydride, which has been noted to be a trimer in solution by DOSY NMR studies (Angew. Chem. Int. Ed. 2018, 57, 10651 –10655). This is worth noting in the paper and begs the question what is the aggregation state of $[\text{HAl}(\text{C}_6\text{F}_5)_2]_3$ in solution? The fact that **1B**, a polymeric zig-zag variant of **1** has been found, the solution chemistry of **1** could be interesting.

"The notion of a dynamic aggregation via bridging hydrides was evidenced by dissolving **1** in different solvent". More experimental elaboration of this aspect is required in the text of the paper.

Reaction 4 is described as a dehydrogenative coupling as if it is distinct from that of reaction 3, but both could alternatively be interpreted as simple metalation (deprotonation) reactions.

Perhaps this is worth mentioning.

Technical points:

Scheme 2 preparation is not consistent with that written in the text nor S.I., as two equivalents of lithium aluminum hydride were used. Also, the amount of trimer produced should be 1/3 equivalents.

Figure 1 legend mentions blue N atoms and red Br atoms, but there are no N or Br atoms in the structure.

Scheme 2. M-H should read μ -H

"The Al- H distances averaged 1.69(2) Å", average bond lengths should not have an esd.

by storage "of" a chlorobenzene

The 4-dimethylaminopyridine (DMAP) reaction is incorrectly assigned to Scheme 2. Should be scheme 3.

The formulae of 2, 3, 4, and 5 should all be explicitly given in the text when first mentioned.

p-(Br(C₆H₄))C≡CH bracket missing in this formula.

In Parks, 1995 #89, what does #89 refer to?

In Scheme 3, the product 5 should have a stoichiometry of 1/2.

Reference 51 has a missing page number 5549

Additional Questions:

Author Information:

How significant is this article?: Significant to a general audience (top 20% of the field - suitable for publication in ChemComm)

Is this work urgent enough for publication as a communication?: Yes

Have authors provided fully convincing evidence for the homogeneity, purity and identity of all compounds they claim as new?: Yes

Are the references appropriate and balanced?: No – please suggest necessary changes in comments to author

Referee: 2

Recommendation: Minor Revision: suitable for publication after changes

Comments:

In this manuscript by Tan, Wu, Lui, Stephan and coworkers, the gram-scale synthesis and isolation of the aluminum analog of Piers' borane and its reactivities are described. Given the importance of the original "Piers borane" for synthesizing numerous boron Lewis acidic compounds, I am sure this work will likewise represent a vital contribution to the advancement of corresponding aluminum chemistry. The manuscript is well-written, and the compounds are sufficiently characterized. In some cases, impurities occurring in the NMR spectra were not fully assigned, and it remains open if isolation in a more pure fashion would be possible. However, this does not affect this work's outcome, and I recommend the manuscript for publication in Chem. Comm. The following minor point could be considered:

1) On page 1, right, discussion of the IR spectrum of 1, a comparison of the Al-H bond stretching with other alanes might be interesting to judge the nature of the Al-H bond.

2) The sentence on page 2, left, top: "Despite the poor..." sounds a bit odd, but might be reformulated to something like: "Despite the poor ...data, the connectivity of a zigzag aggregate isomer 1B was confirmed by scXRD.

3) In the computational section, page 2, left, bottom: a) it would be interesting to also have the dimerization energies for B and Al analogs. Why trimerization? b) In the computation of FIA, has the free compound or the trimer been used as the reference? Also, isodesmic FIA computations are more robust in terms of absolute values. Note that the Al compound appears to be a Lewis superacid.

4) Page 2, right, middle: The reference to Scheme 2 should be Scheme 3

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Have authors provided fully convincing evidence for the homogeneity, purity and identity of all compounds they claim as new?: Yes

Are the references appropriate and balanced?: Yes