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June 22, 2017

Prof. Dr. Douglas Stephan
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RE: Journal of the American Chemical Society Manuscript Revision Request
Manuscript ID: ja-2017-05120j
Manuscript Type: Article
Title: "Single Electron Delivery to Lewis Pairs: An Avenue to Anions by Small Molecule Activation"
Author(s): Liu, Liu (Leo); Cao, Levy; Shao, Yue; Stephan, Douglas

Dear Prof. Stephan:

Your manuscript has been examined by 2 independent referees whose reviews are attached. Both of them are sufficiently enthusiastic that I conclude the manuscript is suitable for publication *in JACS*. However, some modification would be appropriate in response to the comments of the reviewers.

Please submit a revised manuscript to the Paragon website as indicated below, and include a letter indicating what revisions have been made.

We ask that you submit your revision by July 6, 2017.

To help me expedite processing, explicitly address the questions raised by the Editor and reviewers and clearly point out the changes made in the manuscript. Provide this information in the "Response to Decision Letter" text box provided for your use when you submit the revised manuscript. Alternatively, you may attach a file containing your detailed responses, including explanations for disagreeing with any of the suggestions that you have chosen not to follow. We encourage you to annotate a copy of the manuscript to show where changes were made. This marked manuscript should be uploaded electronically in the File Upload section as "Supporting Information for Review Only".

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Stephan Douglas ja-2017-05120j .

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We look forward to receiving your revised manuscript so that processing of your Article may proceed without further delay. Thank you for considering the *Journal of the American Chemical Society* as a forum for the publication of your work.

Sincerely,



William D. Jones
Associate Editor

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish in JACS after minor revisions.

Comments:

In this report Stephan et al. report reactions of $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ with weak Lewis base in the presence of Cp^*2Fe as a reductant. Reactions seemed to be initiated by single-electron transfer from Cp^*2Fe to $E(C_6F_5)_3$ to form the corresponding radical anion species. Subsequent reaction of $E(C_6F_5)_3$ radical anions with group 16-group 16 element bonds, tin hydride, DDQ, TEMPO, and elemental group 16 construct a systematic view to understand the reactivity of the radical anions. Therefore, the reviewer considers this work should be published in JACS after minor revision. Please find the following comments.

- 1) Throughout the paper, chemical yields of major products should be very important to consider the reaction mechanism. NMR yields of the major products in the crude mixture would be better to understand the complicated reaction.
- 2) page 2, right, the last sentence of the 1st paragraph, the authors stated "The Al-S bond lengths were found to be 2.358(2) Å and 2.339(2) Å", but this phrase should appear just after "the known anion, $[PhSB(C_6F_5)_3]^{2-}$ " in the same paragraph.
- 3) page 3, left, Figure 3, Why authors did not calculate TSs before&after IN1? If the TSs were higher in energy, we should consider other scenario for the mechanism. The same thing should also be considered for TSs before&after IN4 in Figure 5, page 4.
- 4) page 5, left, lines 26-29, the authors stated "DFT calculations reveal that the spin density of the radical adducts TEMPO- $E(C_6F_5)_3$ (E = B and Al) is predominantly distributed over the N [62.6 % and 61.6 %] and O [31.5 % and 31.6 %] centers, respectively.", however, the following discussion only focused about LUMO, not SOMO. The reviewer suggest to put the SOMO orbital into SI. (The reviewer guesses the authors referred SOMO as "LUMO" in the main text according to the following discussion.)
- 5) page 5, right, lines 17-18, the authors stated "indicating a very weak interaction between two Al centers.". If the authors claimed this point, they should provide direct evidence to support the interaction. The reviewer suggests to remove this phrase.

Additional Questions:

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

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

Broad interest: High (suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Do the contents justify the length of this manuscript?: Yes

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:

Continuing on the general theme of small molecule activation by Lewis pairs, this interesting contribution by Stephan and co-workers reports the use of single electron transfer (SET) reactions, enabled by Lewis pairs consisting of a strong Lewis acid $E(C_6F_5)_3$ ($E = B, Al$) and decamethylferrocene (Cp^*_2Fe), to activate several small molecules homolytically. The work was well done; with its nice coupling of the FLP chemistry with SET, the results are of fundamental interest to the FLP community. While recommending acceptance after minor revisions, this reviewer suggests the following points or corrections for the authors to consider.

1. We also looked at the reaction between decamethylferrocene and alane sometime ago and found that decamethylferrocene was not fully oxidized even after one day. The point is raised here about whether the radical anion $[Al(C_6F_5)_3]^-$ is involved in the reaction between decamethylferrocene, alane and disulfide reported herein. The latter reaction to give $[Cp^*_2Fe][(\mu-PhS)(Al(C_6F_5)_3)_2]$ is reported to be very fast (2 minutes), in contrast to the slow SET from decamethylferrocene to alane we observed. The current calculations showed the free energies for some key intermediates (Figure 3a), but without transition states. The authors also commented no adduct formation between alane and disulfide but didn't rule out the possibility for rapid exchange that favors the dissociation. This really makes me wonder if the transient $[Al(C_6F_5)_3]^-$ is actually involved in the generation of $[Cp^*_2Fe][(\mu-PhS)(Al(C_6F_5)_3)_2]$. The SET might be the second step or the whole process might be concerted.
2. Figure 1 and TOC graphic: "AE" should be changed to "EA".
3. P2, L14, right column: a superscript denoting the negative charge is missing.
4. The chemical formula for 12 and several other analogous compounds) are incorrect throughout the manuscript (the Abstract, main text, SI...); there should have two ferrocenium cations to balance the charge of the dianionic counterion.

Additional Questions:

Significance: High (suitable for JACS)
Novelty: High (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?: In Part
Are the literature references appropriate and correct?: Yes
Do the contents justify the length of this manuscript?: Yes

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