
Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Reconsider after major revisions.

Comments:
This is an interesting work reporting the synthesis of an antiaromatic Os-substituted naphthalene. Metalla-benzenes are well known, in which a CH unit is substituted by a transition metal atom. However, metallabezene is aromatic. The boron-analog of a metallabenzene has also been reported recently, in which aromaticity remains (JACS 141, 17854, 2019).

What is surprising in this work is the antiaromaticity of the newly synthesized Os-naphthalene compound. Its antiaromaticity seems to be well established using different criteria. The electronic structure was analyzed to decipher the antiaromaticity. Seven pi orbitals (14 pi electrons) were identified, which seem to support an aromatic system according to the 4n+2 Huckel rule for aromaticity. Among the seven pi MOs, there are three Mobius type and four Huckel type. Hence, the authors conclude "Thus, the overall antiaromaticity of 3a' could be regarded as a combination of 6e Möbius antiaromaticity with 8e Hückel antiaromaticity."

In my opinion, the Os-substituted naphthalene is an interesting case of Mobius antiaromaticity. As the authors know well (Fig. 1a), Mobius aromaticity has an opposite electron counting rule as Huckel aromaticity. Thus, 14 pi electrons make a convincing case for Mobius antiaromaticity. I don't think the authors' separation of the seven pi MOs into a Mobius and Huckel set is valid. I believe the authors have found something more interesting than they have recognized. I should also point out that a simple and cyclic Mobius aromatic system has recently been reported in planar matallaborocycles (JACS 142, 3356, 2020). These systems contain two pi MOs (4 pi electrons), consistent with the 4n electron counting rule for Mobius aromaticity. I think the authors have found a 4n+2 Mobius antiaromatic system.

This work is definitely publishable in JACS. The authors should be congratulated for an interesting finding, but they should reconsider their discussion and conclusion.

A minor typo: line 4 in the abstract, delete "the".

Additional Questions:

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

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

Broad interest: High (suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

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

Are the literature references appropriate and correct?: In Part

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:
This interesting manuscript reports the unprecedented synthesis of metal-bridgehead naphthalenes featuring planar antiaromaticity. The results are important as well-defined antiaromatic organometallic compounds are exceedingly rare. The chemistry demonstrated is potentially useful for further development of chemistry of metalla-aromatics. The conclusions are supported by both experimental and computational evidences. The results are clearly presented. The manuscript could be accepted for publication after minor correction.
Minor comments:
The authors are suggested to provide a plausible mechanism for the formation of complexes 1 and 2, in the supporting information.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (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

Reviewer: 3

Recommendation: Publish in JACS after minor revisions.

Comments:
In this communication, the authors report an experimental and computational study of a metal-bridgedhead naphthalene. Although the existence of metallanaphthalenes was already reported some years ago, to my knowledge this is the first metallacycle derived from an aromatic polycyclic hydrocarbon like naphthalene in which the metal is located in a bridge position. In this sense, my opinion is that this finding is remarkable and deserves publication in J. Am. Chem. Soc. Still, I have several remarks that the authors should answer before the paper is accepted for publication:
1. Abstract. The sentence "…leading to the unprecedented synthesis of metalbridgehead naphthalene featuring planar antiaromaticity." is wrong. The authors did not synthesize a planar antiaromatic compound. This structure was a computational model.
2. Introduction. When referring to reviews of metalloaromaticity, the authors may add:F. Feixas et al. WIREs Comput. Mol. Sci., 3 (2013) 105-122.
3. Introduction. Al_4^{2-} results from the substitution of CH–CH by Al–Al in cyclobutadiene (not only carbon atoms).
4. The authors should indicate whether the 3-1', 3a', and 3b' are minima or transition states.
5. Figures 3c and 3d. The ring currents in the ACID plot cannot be seen. One can only see the arrows depicted by the authors but not the arrows of the ring currents.
6. In the following paper, D. W. Szczepanik and M. Solà, ChemistryOpen, 8 (2019) 219-227, the authors show that the metallacycles in many cases are Hückel-Möbius hybrids. This should be commented in the context of the discussion about the eightelectron Hückel and six-electron Möbius antiaromatic species.
7. Electron counting in metallacycles is disputable. For instance, in my opinion, contribution of the d orbitals of the metal in the HOMO-11 and HOMO-13 molecular orbitals (MOs) is not enough to include these MOs in the list of Möbius or Hückel MOs. For the HOMO-2 is the other way round. This is a MO with almost no contribution from the 2pz of the C atoms, so it is a MO that does not contribute to (anti)aromaticity. The authors should mention that electron counting in debatable. The authors provide their interpretation and this is what they should do, but they should warn the readers that other interpretations could be also acceptable.
8. Figure S26. There is a PH_2 that should be PH_3.
9. I suggest the authors to compute the triplet state of 3 to check if it becomes more planar and aromatic following the Baird rule.

Additional Questions:
Significance: High (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?: In Part