
REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Highly important (top 20%)

Reviewer #2: Important

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2. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Insufficient

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3. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

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

Reviewer #1: Fully consistent

Reviewer #2: Minor inconsistencies

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5. Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

COMMENTS TO AUTHOR:

Reviewer 1: This manuscript highlights a series of coordination compounds with Cr, Mo, Co and Ni of a 6-electron, 4-member C2P2 cycle stabilized by N-heterocyclic carbenes. The ligands have recently been described in another Angew. Chem. communication. The described complexes are the first examples containing a neutral 4-member, 6-electron donor π ligand. The infrared characterization and DFT calculations suggest that these ligands are stronger donors than the anionic cyclopentadienyl. For these reasons, I think that the manuscript deserves to be published as a communication. The addition of a cyclic voltammetric study would be valuable to further confirm the superior electron donor ability. Another suggestions for the authors: rather than cooking the ligand with Cr(CO)6 or Mo(CO)6 for one month, why not using more labile precursors, such as M(CO)(η6-arene) or M(CO)(MeCN)3? The ligand exchange thermodynamics would also be of interest (does the C2P2 ligand replace an arene, or viceversa?).

I do not see wrong statements or important missing information. On the other hand, the quality of the manuscript can be significantly improved.

1. Page 1, lines 40-44 (left): A and B do not contain phosphinine and phospholes. The authors probably refer to C and D.
2. Page 1, line 47 (right): "more electrophilic but less π-electron donating". Why "but"?
3. Page 1, line 56 (right): "as a comparison of …": something is missing in this sentence.
4. Page 3, line 39 (left): a yield >93% is not quantitative.
5. Page 4, line 26 (left): "a deeper insight" (not inside)
6. Page 4, lines 56-57 (left): please specify that the calculated bonding energy concerns the interaction between [Co(CO)2]+ and benzene.
7. Page 4, line 32 (right): "may intrigue the synthesis": what does it mean? Perhaps "may inspire"?
8. In numerous places, sentences begin with "But". In other places, "which" is used without being preceded by a comma. These are grammatical mistakes. Proofreading by a native English speaker is required.

Reviewer 2: The authors present an interesting follow-up study on a di-NHC C-substituted C2P2 ring system on which they reported earlier in ACIE (ref. 8). The current study focusses on the

additional complexation of Cr(CO)3, $Mo(CO)_3$, and $NiBr_2$ to the C_2P_2 ring.

The introduction of the manuscript is quite inadequate. Most of first page sets an inappropriate tone, does not cite needed references, and gives incomplete comparisons with related systems.

The comparison between 1a' and J (Figure 2) is inappropriate. J is a diene. For proper comparison, the anti-aromatic version should be used in which all C-P bonds are equal. There is a tremendous amount of literature on the related cyclobutadiene and its far less stable anti-aromatic version. This comparison would seem relevant with appropriate citations.

The discussion on the synthesis of the cobalt $L_2C_2P_2$ complexes via the radical cations is interesting and includes characterization of the cationic complexes 5a,b and the related 6a,b (anion $[Co(CO)_4]^-$ is replaced for the $[BARF]^-$ anion). This reviewer wonders where the story and analysis is on the synthesis (and intermediates) of the corresponding molybdenum L2C2P2 complexes?

Page 4, Table 1: It is not clear to this reviewer why both 5a,b and 6a,b have to be presented in the main text. One set could be moved to the Supporting Information. It is neither clear why K and L are included in Table 1 as these two structures differ significantly from 2a,b, 3a,b, and 5a,b, having respectively η-C_6H_6 and η-C_5H_5 ligands instead of a four-membered one.

Page 4 under Table 1 and including Figure 4: this section is dry as a bone. Instead of providing a summation of computational data, a more useful analysis should be provided for the general reader. It is awkward to provide details on low lying molecular orbitals such HOMO-6 and HOMO-11. What is to be gained from it?

Page 4, Figure 4 and related text: To this reviewer it is not clear why the focus is on $[Co(CO)_2(L_2C_2P_2)]$+ [5a']+. Why not address 2a' (and/or 3a' and/or 7a')? An orbital analysis could then be giving as an extension to the one given in Figure 1 to reflect on the stabilization gained from the metal fragment $M(CO)_2$ or $NiBr_2$. It would also be appropriate to evaluate electron density differences for the C_2P_2 ring of these systems (improved J, 1a' and, e.g., 2a') to address the nature of the stabilization.

Some specific aspects:

Page 1, line 34: insert "to catalysts," in between "drugs" and "to materials".

Page 1, line 36: I object to the term "anti-aromatic" and suggest to change the sentence to "…complexes with rings having a formal 4n pi-electron…". The use of anti-aromatic is quite misleading if not simply wrong.

Page 1, lines 39-40: same issue. I would suggest replacing "aromatic and anti-aromatic" for "analogues".

Page 1, line 40: "…which soon also employed…" is not clear and seems to miss a reference.

Page 1, line 43: This sentence is awkward. Does it refer to A and B of Figure 1 or to all the compounds A-I shown in Figure 1? The sentence does not either connect properly with the next one ("Figure 1 shows …") directly under Figure 1.

Page 1, text under Figure 1 refers to the compounds A-I, but lacks all the required references to these compounds, making it impossible to verify, e.g., whether the listed CO stretching frequencies are in fact correct. It is mandatory to include these references. As to the phosphorus containing molecules, also related work of Regitz, Nixon, Lammertsma, and Le Floch needs to be cited.

Page 1, 2nd column, lines 48-49: do not use the term "anti-aromatic rings". The rings withdraw indeed electron density from the metal, but so do five-membered rings, which are, of course, not labeled as radical ligands.

Page 1, 2nd column, lines 50-52: the sentence "But …acceptor." is not evident to this reviewer and may need more thought in light of my previous remarks. Moreover, with such a statement, a reference is needed.

Page 1, 2nd column, line 53 (and Figure 1): Why is the known structure related to I, but with the two phosphorus atoms occupying the 1 and 3 positions of the C_2P_2 ring, not included? This would also make a more compelling difference with the key structures of the manuscript.

Page 1, 2nd column, lines 56-57: the sentence "…as a comparison…SiR'_3." Seems incomplete.

Page 2, line 49: J is not anti-aromatic. It is a diene.

Page 2, 2nd column, line 5: "In the present work…" should start at a new paragraph.

Page 3, lines 19-20: The sentence "The synthesis …reactions.[17]" is not clear. What is the different pathway? Different from what? Reference [17] deals with Hf complexes and not the Co atom. On page 2, 2nd column directly under Scheme 1, the authors state "Treatment ….$[M(CO)_6]$ (M = Cr, Mo) …". In short, the statement is confusing.

Page 3, lines 35-40: Why is this section on Ni-complexation of 1a,b dealt separately and in passing.

Page 3, Figure 3: I would recommend the use of colors in the molecular structures.

Finally, this reviewer wonders whether it would be feasible to form sandwich complex of 1a akin to the $Fe(C_2P_2)$ and $Co(C_2P_2)$ complexes of Wolf et al.?

In summary, this manuscript may become suitable for publication in Angewandte Chemie after significant modifications that should be reviewed again.